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STEADY STATE ANALYSIS OF TROPOSPHERIC CHEMISTRY

by

WEN HSIUNG PAN


A dissertation submitted in partial
fulfillment of the requirements
for the degree of

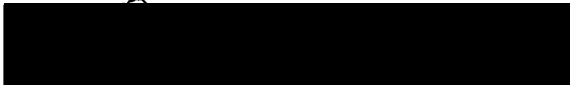
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in
ENVIRONMENTAL SCIENCES AND RESOURCES:
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1991


TO THE OFFICE OF GRADUATE STUDIES:

The members of the committee approve the dissertation of
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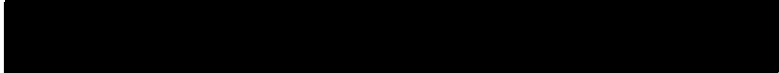

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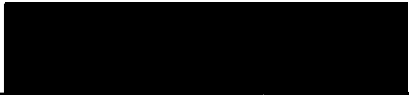

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AN ABSTRACT OF THE DISSERTATION OF Wen Hsiung Pan for the
Doctor of Philosophy in Environmental Sciences and
Resources: Chemistry presented March 9, 1990.

Title: Steady State Analysis of Tropospheric Chemistry


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Hydroxyl radical HO plays a central role in controlling chemical processes in the troposphere. Current mechanisms are believed to accurately describe its formation, destruction and interaction with other atmospheric trace gases in clean air. Hydroperoxyl radical HO₂ is linked to HO in several chain

processes and serves among other roles as a reservoir for HO. The relative concentration (HO_2/HO) in clean air is believed to be the order of 10^2 . We here examine the conditions under which steady-state kinetics apply to HO_x chemistry and derive simple relationships which can be used to predict HO and HO_2 concentration from measurable concentrations of the more stable trace gases. The equations assume a simple form for conditions where the ambient nitrogen oxide concentration is less than 1 ppb. These equations allow closed-form evaluation of the sensitivity of $[\text{HO}]$ and $[\text{HO}_2]$ to changes in the concentrations of the controlling species and allow assignment of uncertainty limits to the predictions of current tropospheric chemical models. Although most current efforts to test fast tropospheric photochemistry center upon measurements of ambient $[\text{HO}]$, our equations indicate that tropospheric $[\text{HO}_2]$ determinations may provide a more direct and accurate initial test of our knowledge of HO_x chemistry in the unpolluted lower atmosphere. Overall the goal of this study is to benefit the experimenter by providing the information of insight and simple but reliable equations and to understand the conditions under which these measurements should be made and how best to interpret their results.

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CHAPTER I

INTRODUCTION OF TROPOSPHERIC CHEMISTRY

The whole of atmospheric chemistry can be considered as a combination of different cycles, each with its own key species or catalyst. Then, the easiest way to understand the atmosphere is to study the individual cycles and seek the interplay among them. The most important thing is to find competitive reactions which produce atmospheric changes. This can be difficult because some reactions which dominate the system under certain conditions may disappear in importance if a perturbation takes place.

Prior to the study of the impact of human activities on the troposphere, it is essential to understand the chemistry of the natural, or unpolluted troposphere. The fundamental knowledge gained is a baseline for assessing the extent of man's influence (1).

Knowing the rates of formation and removal of key species is the key to perceiving the complex system. For example, NO_x is well known to control photochemical oxidants (e.g., ozone) in the troposphere. It is not so easy to reveal the processes (rate-determining steps or dominant reactions), especially for a complex reaction system, just by visualization. It would be a painful, error-prone and time-consuming procedure to solve

by hand.

Most radical-chain processes in the troposphere are photochemically driven and determine its oxidizing capability (2). In the troposphere, the concentrations of NO_x along with nonmethane hydrocarbons (NMHC) have been used as an index of cleanliness (3). Usually, the atmosphere over marine or remote continental areas with low $[\text{NO}_x]$ has been treated as clean air. But higher NO_x concentrations produced by man's activities can play a key role in perturbing the chemical processes in the troposphere. Since HO reacts with virtually all trace atmospheric species and is the primary scavenger in tropospheric chemical systems, there are growing concerns of the influence on HO concentrations by increasing methane or carbon monoxide. This has resulted in the investigation of the $\text{CO-CH}_4\text{-OH}$ chemical system. Study of the clean troposphere, at least, embodies HO_x , NO_x , O_3 and CO/CH_4 chemical systems. Although there is complex interlinking among these systems, we still try to segregate each from the others and introduce each individually. Note that pollutants are, traditionally, grouped into two categories: primary and secondary. Primary pollutants are the chemical species emitted directly from identifiable sources. Secondary pollutants, on the other hand, are species formed from the primary pollutants by chemical transformation. Adverse effects of pollutants are often associated more with the secondary than with the primary pollutants. There are a number of references and books which give the details

(1,2,3,4).

TABLE I
PHOTOCHEMICAL REACTIONS IN CLEAN TROPOSPHERE

| No. Reaction | | | | Rate Constant | | |
|--------------|--------|---|-----------|---------------|----------------|---------|
| 1. | O3 | + | hν | ----> | O(1D) + O2 | 8.8E-06 |
| 2 | O(1D) | + | N2 | ----> | O(3P) + N2 | 2.9E-11 |
| 3 | O(1D) | + | O2 | ----> | O(3P) + O2 | 3.6E-11 |
| 4. | O(1D) | + | H2O | ----> | HO + HO | 2.3E-10 |
| 5. | HO | + | CO + O2 | ----> | HO2 + CO2 | 2.7E-13 |
| 6. | HO | + | CH4 + O2 | ----> | H2O + CH3O2 | 8.0E-15 |
| 7. | H2O2 | + | hν | ----> | HO + HO | 7.6E-06 |
| 8. | HO2 | + | O3 | ----> | HO + 2 O2 | 1.6E-15 |
| 9. | HO2 | + | NO | ----> | HO + NO2 | 8.4E-12 |
| 10. | HO2 | + | HO2 | ----> | H2O2 + O2 | 4.1E-12 |
| 11. | HO | + | O3 | ----> | HO2 + O2 | 7.0E-14 |
| 12. | HO | + | H2O2 | ----> | H2O + HO2 | 1.7E-12 |
| 13. | H2O2 | | | ----> | RAINOUT | 1.2E-05 |
| 14. | HO | + | H2 + O2 | ----> | HO2 + H2O | 7.8E-15 |
| 15. | HO | + | H2CO + O2 | ----> | H2O + HO2 + CO | 1.0E-11 |
| 16. | CH3O2 | + | HO2 | ----> | CH3O2H + O2 | 6.0E-12 |
| 17. | CH3O2H | + | HO | ----> | CH3O2 + H2O | 1.6E-12 |
| 18. | CH3O2H | + | hν | ----> | CH3O + HO | 5.0E-06 |
| 19. | CH3O2 | + | CH3O2 | ----> | 2 CH3O + O2 | 4.6E-13 |
| 20. | CH3O2H | | | ----> | RAINOUT | 1.2E-05 |
| 21. | CH3O2 | + | NO | ----> | CH3O + NO2 | 7.0E-12 |
| 22. | CH3O | + | O2 | ----> | H2CO + HO2 | 6.4E-16 |
| 23. | H2CO | + | hν + 2O2 | ----> | 2 HO2 + CO | 2.2E-05 |
| 24. | H2CO | + | hν | ----> | H2 + CO | 2.9E-05 |
| 25. | H2CO | | | ----> | RAINOUT | 1.2E-06 |
| 26. | HO2 | + | NO2 | ----> | HNO2 + O2 | 3.0E-15 |
| 27. | O3 | + | NO | ----> | NO2 + O2 | 1.8E-14 |
| 28. | O3 | + | NO2 | ----> | NO3 + O2 | 3.4E-17 |
| 29. | NO | + | NO3 | ----> | 2 NO2 | 2.0E-11 |
| 30. | HO | + | HNO3 | ----> | NO3 + H2O | 8.5E-14 |
| 31. | HO | + | HNO2 | ----> | H2O + NO2 | 6.6E-12 |
| 32. | HO | + | HNO4 | ----> | NO2 + O2 + H2O | 5.0E-13 |
| 33. | HNO4 | | | ----> | HO2 + NO2 | 1.3E-01 |
| 34. | N2O5 | | | ----> | NO2 + NO3 | 4.2E-02 |
| 35. | HO | + | NO | ----> | HNO2 | 6.6E-12 |
| 36. | HO | + | NO2 | ----> | HNO3 | 1.1E-11 |
| 37. | HO2 | + | NO2 | ----> | HNO4 | 1.7E-12 |

TABLE I
PHOTOCHEMICAL REACTIONS IN CLEAN TROPOSPHERE
(continued)

| | | | | | | | |
|-----|-------------------------------|---|---------------------------------|-------|-------------------------------|---|--|
| 38. | NO ₂ | + | NO ₃ | ----> | N ₂ O ₅ | | 7.6E-13 |
| 39. | NO ₂ | + | hν | ----> | NO | + | O(3P) 7.6E-03 |
| 40. | NO ₃ | + | hν | ----> | NO | + | O ₂ 1.6E-02 |
| 41. | NO ₃ | + | hν | ----> | NO ₂ | + | O(3P) 3.3E-02 |
| 42. | N ₂ O ₅ | + | hν | ----> | NO ₂ | + | NO ₃ 1.6E-01 |
| 43. | HNO ₂ | + | hν | ----> | HO | + | NO 1.3E-03 |
| 44. | HNO ₃ | + | hν | ----> | HO | + | NO ₂ 9.8E-06 |
| 45. | HNO ₄ | + | hν | ----> | HO | + | NO ₃ 1.5E-01 |
| 46. | HNO ₂ | | | ----> | RAINOUT | | 1.2E-05 |
| 47. | HNO ₃ | | | ----> | RAINOUT | | 1.2E-05 |
| 48. | HNO ₄ | | | ----> | RAINOUT | | 1.2E-05 |
| 49. | O(3P) | + | O ₂ | ----> | O ₃ | | 1.5E-14 |
| 50. | O(1D) | + | CH ₄ +O ₂ | ----> | HO | + | CH ₃ O ₂ 1.3E-10 |
| 51. | O(1D) | + | CH ₄ | ----> | H ₂ | + | H ₂ CO 1.4E-11 |
| 52. | O(1D) | + | H ₂ +O ₂ | ----> | HO | + | HO ₂ 1.0E-11 |
| 53. | O ₃ | + | hν | ----> | O(3P) | + | O ₂ 5.8E-04 |

Note: All rate constants of reaction correspond to 45°NH at ground level during equinox.
The units of rate constants depend on the order of the reaction.
The unit of rate constants for reaction 13, 20, 25, 46, 47 & 48 is second⁻¹ (first order).
The unit of rate constants for the rest of reactions is cm³ molecule⁻¹ second⁻¹ (second order).
Any of reactions which contain three reactants (reactions 5, 6, 14, 15, 23, 50, 52) are treated as pseudo second order reaction.

NO₁ CHEMISTRY

Concentrations of HO_2 are particularly important in calculating the rate of tropospheric scavenging of man-made pollutants in the atmosphere. Hydroxyl radical HO and hydroperoxyl radical HO_2 (collectively HO_x) play central roles in controlling chemical processes in the troposphere. Current mechanisms are believed to accurately describe their

formation, destruction and interaction with other atmospheric trace gases in clean air (Table I). Hydroperoxyl radical HO_2 is linked to HO in several chain processes and serves among other roles as a reservoir for HO (5). In addition, HO_2 plays an important role in destruction or formation of ozone, depending on the NO concentration (1). Figure 1 summarizes our current understanding of HO_2 and other trace gases in the clean troposphere (6).

NO_x CHEMISTRY

Nitrogen-containing compounds, both inorganic and organic, play extremely important roles in the chemistry of both polluted and clean atmospheres. Sources of NO_x ($\text{NO} + \text{NO}_2$) in the remote troposphere include lightning, microbial activity in soils, injection from the stratosphere, and the burning of fossil fuels and biomass. The ratio NO/NO_2 depends on the rate of photolysis of NO_2 and the rate of NO oxidation in processes $\text{NO} + \text{HO}_2$, $\text{NO} + \text{CH}_3\text{O}_2$ and $\text{RO}_2 + \text{NO}$, together with the dominant reaction $\text{NO} + \text{O}_3$ (2). The sink for NO_x is assumed to be washout by precipitation in the troposphere or dry deposition at the surface and requires HNO_3 formation i.e., $\text{NO}_2 + \text{HO} \rightarrow \text{HNO}_3$. HNO_3 is a stable terminal product of NO_2 oxidation.

NO is a crucial species whose concentration is required to calculate ozone production rates in clean tropospheric air (7). The equilibrium existing among HO_2 , O_3 , NO and NO_2 (R27, R39, R49 in Table I) is known as the photostationary state

(PSS). Based on PSS, if either $[NO]$ or $[NO_2]$ is measured, then $[NO_x]$ can be calculated via

$$[NO_x] = [NO] \left(1 + \frac{k[O_3]}{J_{NO_2}} \right)$$

$$[NO_x] = [NO_2] \left(1 + \frac{J_{NO_2}}{k[O_3]} \right)$$

Here J_{NO_2} is the photolysis rate of NO_2 (R39 in Table I) and k is the rate constant for ozone reaction with NO (R27 in Table I). However, at nighttime J_{NO_2} becomes zero, then if $O_3 > NO$, $[NO_x] = [NO_2]$. The calculation of how HO depends on NO_x will be modeled in a later chapter.

O_3 CHEMISTRY

Ozone is well known as a primary source for the most reactive species HO in the troposphere. Study of the origin, transformation, transport and sink of ozone, either in the troposphere or stratosphere, has resulted in extended understanding of ozone and its relation with other reactive species. The two known sources of ozone in the troposphere are NO_2 photolysis and transport from the stratosphere, and the primary destruction of ozone is by deposition at the earth's surface or photolysis via R1 & R4 to produce HO . According to model calculation (1,8), one third of the ozone source is due to local photochemical production. i.e., photolysis of NO_2 , two thirds originates from the stratosphere; two thirds of the

destruction of ozone is due to photochemical reaction and one third is lost via ground deposition.

The HO-CO reaction can cause ozone destruction, as well as formation (72). Three cases are described, based on the dominance of HO₂ reacting with itself, NO or O₃. If the reaction of HO₂ + NO dominates, then ozone production occurs via the reactions of CO+HO+O₂ --> HO₂+CO₂ (R5), HO₂+NO --> NO₂ (R9), NO₂+hν --> NO+O(³P) (R39), O(³P)+O₂ --> O₃ (R49), and leads to net reaction of CO+2O₂ --> CO₂+O₃. If the reaction of HO₂ +O₃ dominates, then ozone will be lost via the reactions of CO+HO --> HO₂ (R5) and HO₂ +O₃ --> HO+2O₂, which leads to net reaction of CO+O₃ --> CO₂+O₂. If HO₂ + HO₂ dominates, there is no effect on ozone at all.

CH₄/CO CHEMISTRY

CH₄ is produced by bacterial fermentation processes in anaerobic environments which contain substantial organic matter, such as swamps, marshes, rice fields, and lakes. In addition, CH₄ is produced by enteric fermentation in mammals as well as by termites. Also, smaller amounts are emitted into the air via seepage of natural gas from the earth. Forest fires and other forms of combustion also produce methane. CO is produced from natural and man-caused combustion processes as well as generated in the atmosphere from methane and NMHC photooxidation as the primary source.

There is a feedback effect on the concentration of CH₄,

Khalil (9,10) estimates that 70% of the increase in CH_4 over the last 200 years is probably due to an increase in primary emission, with the remaining 30% due to a decrease in global HO concentration. It should be pointed out that, traditionally, the chemistry of CH_4 has been discussed separately from the other organic hydrocarbons (NMHC), which have considerably shorter atmospheric lifetimes.

GOAL OF RESEARCH

It is obvious that civilization will continue to require increasing amounts of fuel, transportation, industrial chemicals, fertilizers, pesticides and countless other products; and that it will continue to produce waste products of all descriptions. Many of these wastes will be released into the troposphere. Our objective is to analyze tropospheric chemistry and develop computer programs to assist in understanding the troposphere.

Numerous tropospheric models have been applied to the study of atmospheric chemical processes (6,11,12), but most use essentially the same set of dominant reactions. A typical set of such reactions is given in Table I. The traditional approach is to numerically integrate the resultant system of differential equations. Numerical solutions are obtained with modern high-speed computers but a complete three-dimensional analysis of tropospheric chemistry with a sufficiently fine grid may test the capabilities of even the most sophisticated

computer. Numerical approaches properly applied are of undisputed accuracy. However, they may offer little insight themselves into the dominant chemical processes. Since chemical processes in the "unpolluted" troposphere can be rather thoroughly described with approximately 50 chemical reactions, a traditional chemical kinetic application of so-called "steady-state" procedures should be capable not only of providing significant insight into the dominant processes, but of quantitatively establishing concentration dependence. The resultant equations then allow establishment of the uncertainty limits which models impose--very useful in interpreting ambient tropospheric measurements of HO_2 concentrations. Further, they allow straightforward predictions of changes in tropospheric HO and HO_2 resulting from past or future changes in concentrations of dominant trace gases.

CHAPTER II

STEADY STATE ASSUMPTION

The steady state approximation (SSA) was the mainstay of chemical kineticists for many decades, and has allowed accurate mathematical representation of innumerable chemical mechanisms (13,14,15,16,17,18,19,20,21,22,23,24,25,26,27). However, with the advent of fast computers and efficient integration algorithms, the necessity of using the steady-state approach has passed. Furthermore, situations wherein the SSA may be of doubtful validity can occur (28,29,30).

Traditionally, the steady state assumption is interpreted as the concentration of a species in a dynamic system changing insignificantly. In other words, from a kinetic viewpoint, the steady state assumption applied for a specific species means that the production term is equal (or approximately equal) to the loss term of that species, which is distinguished from a constant species in which both production and loss terms should be zero. The concept of steady state can be described mathematically as the derivative of species' concentration with respect to time being equal to zero. i.e.,

$$\frac{d[C]}{dt} = \text{Production} - \text{Loss} = 0 ;$$

where $[C]$ indicates the concentration of species C.

TREATMENTS OF SSA

Numerous papers related to the steady state assumption have used different designations for the same concept. These include quasi-steady state assumption (20,31), quasi-steady state approximation (17), generalized steady state method (23,25), pseudo steady state approximation (18,26,32), pseudo steady state hypothesis (21), steady state approximation (18,32), steady state hypothesis (22), singular perturbation theory (20,21,33), and extended steady state approximation (31). Although differences exist among the different approaches, the goal of seeking the applicability and validity of SSA is maintained.

Arguments against the QSSA are classified into several categories:

1. QSSA is not valid during the induction (transient) period in which free radicals increase from their initial concentration, usually zero, to their steady state values (18,26,34).

2. It is hard to predict when and for what species the QSSA will be correct (35).

3. The QSSA analysis gives no indication of the extent of the applicable time regime (29).

4. The errors (deviation) in the concentrations of intermediate radicals will affect critical rates in the

reaction model (19,28,30).

5. The partition between intermediates and other species is not always clear (34).

6. Since not all intermediates reach steady state at the same time, a numerical test for SS would have to be performed on each species at each time increment. (34).

7. The SSA induces instability (30).

On the contrary, the pro-QSSA arguments include

1. It can be used to solve the problem of stiffness in the numerical method (17,24). Here, in a chemical system, the stiffness of system results when time constants are widely different in magnitude or one of the time constants is quite small relative to the reaction range.

2. It is allowable to apply QSSA except during the induction period (18).

3. Allow the QSSA to be used for those species that have low concentration and small relaxation time (20). In other word, those species with high reaction rate can be treated as steady state species.

4. QSSA helps toward an understanding of the system (23).

5. If QSSA is applicable, accurate rate equations can rapidly be obtained using linear algebraic manipulation (27,36).

6. Singular perturbation can be used to refine the QSSA (20).

7. The instability of QSSA can be avoided (22,24).

In fact, the steady state assumption and related method have been used broadly covering atmospheric chemistry (13,37), combustion (31,38), biological and enzyme kinetics (20,21,39,40), nuclear reactor kinetics (25), etc.

Farrow et al. (30) criticized the adoption of QSSA in their example of an 81-reaction model where QSSA introduced a discrepancy and they suggested abandoning the use of QSSA. However, Hesstvedt et al. (13) stated that the large deviations demonstrated by Farrow and Edelson (30) are caused by their a priori assumption of the steady state for transitory species (free radicals) in an integration procedure with automatic step control, i.e., Farrow ignored that changeable lifetime of SS species may conflict with step size during the period of numerical integration. Hesstvedt et al. concluded contrarily that the QSSA method provides adequate solutions to certain problems in atmospheric chemistry and the application of this QSSA method represents a considerable savings compared to an automatic method like Gear's method, and it is therefore a useful tool when the calculations have to be repeated many times. Carter et al. (41), in response to the Farrow and Edelson conclusion (30), mentioned that the use of QSSA for reactive intermediates did not cause significant difference from results calculated without the QSSA and stated that the advantage of using QSSA is greatly reduced computational times. But Carter et al. never employed QSSA on

any species which has self-reaction such as HO_2 . Blakemore and Corcoran (18) tested the validity of QSSA by using a pyrolysis mechanism for n-butane at 519°C . It is apparent that this steady state assumption is not applicable to the induction period in which the free radicals increase from their initial concentration, usually zero, to their steady state values. However, the credibility of QSSA will be increased if the data created during the induction period are of less concern and QSSA-induced errors have been carefully controlled. The SSA is said to be valid if the duration of the induction period is much smaller than the overall reaction time. Qualitatively, if the rates of the destruction of the intermediate species are large compared with the overall reaction rates, then the intermediate species are present in the reaction mixture in relatively low concentrations, and so the assumption of QSSA is generally good. It turned out that the average deviation of the free-radical concentrations computed with the assumption of steady state from the values obtained without that assumption is 6% (18).

VALIDITY OF SSA

Hirschfelder (26) derived a formula to show the relationship between the zeroth approximation B_0 (PSSA concentration) and higher approximation B_1 and tested the validity of PSSA by comparing B_1 with B_0 . Start with the differential equation :

$$\frac{dB}{dt} = P - LB ;$$

apply zero order approximation to obtain B_0 . i.e.,

$$\frac{dB}{dt} = P - LB_0 = 0 \quad \text{imply} \quad B_0 = \frac{P}{L}$$

Then, solve first-order approximation B_1 ,

$$\frac{dB}{dt} = P - LB_1 ,$$

by substituting $B_0 = P/L$ and

$$B_1 = B_0 - \frac{1}{L} \frac{dB}{dt}$$

will be obtained.

Here B_0 is the zero order approximation solution for PSSA species, and B_1 is the first-order approximation solution, which is always more accurate than B_0 , and L is the sum of removal rate constant of species B .

Aiken (32,42) also illustrated the concept of stiffness and showed the advantages of applying QSSA to chemical kinetic problems. The final conclusion can be made that the stiffer the system, the smaller will be the contribution from the stiff eigenvalue and the better the application of QSSA. The eigenvalue (λ) here is defined as a scalar value of an eigenvector-eigenvalue equation such as

$$AV = \lambda V$$

where A is the matrix. An example is shown in Appendix D.

Hiestand (23) adopted an approach similar to Hirschfelder to analyze the steady state assumption and suggested two precautions (a). no GSSA (generalized steady state assumption) during transient period; (b). the appropriate choice of the number of SS intermediates is necessary. Shampine (24) derived a formula that shows the deviation of a solution induced by QSSA.

Shampine starts with the differential form of the rate expression for the concentration Y_i of species i :

$$Y_i' = P_i - Q_i Y_i$$

where P_i = total production rate and

Q_i = total first-order loss rate coefficient.

When P_i , Q_i are constant, and $Q_i \neq 0$, the solution of this differential equation is given by

$$Y_i(t) = S_i + [Y_{i,n} - S_i] \exp(-Q_i(t - t_n)) ; t > t_n$$

Where t_n is the integration time step.

While $Q_i \gg 1$ then $\exp(-Q_i(t - t_n))$ approaches zero. Consequently, $Y_i(t) = S_i$ = steady state solution.

Unfortunately, for the steady state solution to be valid, the rate of production P_i and the rate of loss Q_i are limited to be independent of t (time) and P_i can not depend on Y_i either. This is not the case in which the concentration of species changes dynamically.

DERIVATION OF STEADY STATE RATIO (SSR)

Although steady-state models have been sometimes criticized, it is a simple matter to explicitly describe the conditions under which the SSA has acceptable accuracy and to place quantitative limits upon errors introduced by its use. For a situation where transport can be ignored, the change in concentration of a species is described by an equation of the form

$$\text{Rate} = \text{Production} - \text{Loss} \quad \text{or}$$

$$\frac{d[C_i]}{dt} = R_i = \Sigma P_i - [C_i] \Sigma k_{ij} [C_j] \quad (2-1)$$

Here, $[C_i]$ represents the concentration of the i^{th} species and k_{ij} its chemical rate constants. C_j includes the same and other species concentrations as well as solar intensity. ΣP_i represents the production terms for the species, which can include emissions into the atmosphere as well as chemical reactions. Equations analogous to Eq. 2-1 may be obtained for situations where transport is not ignored. Eq. 2-1 may be rearranged to a form which directly determines the accuracy of the SSA:

$$[C_i] = \frac{\Sigma P_i}{\Sigma k_{ij} [C_j]} \left(1 - \frac{R_i}{\Sigma P_i}\right) = \frac{\Sigma P_i}{\Sigma k_{ij} [C_j]} (1 - \text{SSR}) \quad (2-2)$$

The error introduced by the SSA is contained in the parenthetical term in Eq. 2-2. If the net rate is much less

than the total production (steady state ratio = $SSR \approx R_i/\Sigma P_i \ll 1$), then the SSA is valid. For cases where R_i approaches ΣP_i , the error introduced by the SSA can be determined by the ratio SSR. If we compare Eq. 2-2 with the equation derived by Hirschfelder (26),

$$\begin{aligned} B_1 &= B_o - \frac{1}{L} \frac{dB}{dt} = \frac{P}{L} - \frac{R}{L} = \frac{1}{L} (P - R) \\ &= \frac{P}{L} \left(1 - \frac{R}{P}\right) \approx B_o (1 - SSR) ; \end{aligned}$$

and the ratio of R to P is exactly the same as our SSR.

CALCULATION OF SSA CONCENTRATION

In general, iterative methods (for instance, the Newton-Raphson method) have been used to calculate the SS concentration. DeTar et al. (43) suggested more than one method to implement the computation. The first method (regular) treats the SS concentration such that $S_n = P/L$. The subscript n represents the reactant n. Since S_n is approximate only, DeTar choose R_n as an index to truncate an iterative procedure of substituting the value of S_n found in the previous iteration. The procedure is described briefly :

The first step is to set $R_n = P/(LS_n)$, then $S_{n(\text{new})} = R_n S_{n(\text{old})}$; if S_n has its correct value, then $R_n = 1$; if $R_n > 1$ then S_n is too small and if $R_n < 1$ then S_n is too large.

Here we compare R_n with the ratio SSR and illustrate the relationship between the two.

$$R_n = \frac{P}{LS_n} \implies \frac{1}{R_n} = \frac{LS_n}{P}$$

$$\frac{1}{R_n} - 1 = \frac{LS_n}{P} - 1$$

Evaluating the right-hand side :

$$\frac{LS_n}{P} - 1 = - \frac{P - LS_n}{P} = \frac{\text{rate}}{P}$$

so the equation becomes

$$\frac{1}{R_n} - 1 = - \frac{\text{rate}}{P} \implies SSR = \frac{\text{rate}}{P} = 1 - \frac{1}{R_n}$$

it turns out that

$$R_n = \frac{1}{1 - SSR} .$$

Thus, if the ratio SSR is small compared to 1, then R_n equals 1. i.e., QSSA is valid.

A damping factor (DF) was introduced (43) into the calculation of the SS concentration in order to reduce the tendency toward over-compensation and hence oscillation.

$$S_{n(\text{new})} = (DF \times R_n + 1 - DF) S_{n(\text{old})} \quad (\text{for } R_n < 1)$$

$$S_{n(\text{new})} = \frac{S_{n(\text{old})}}{\frac{DF}{R_n} + 1 - DF} \quad (\text{for } R_n > 1)$$

Through this kind of iteration, DeTar claimed to

generate S_n accurate to within 0.2%, i.e., iterate until $R=1.000 \pm 0.002$ for each R.

DeTar's second method (perturbation) introduced a decrement D_n defined as

$$D_n = k_n S_{n1} S_{n2} \cdots X_{n1} X_{n2} \cdots \Delta t \quad (2-3)$$

where S_{n1} is the first steady state intermediate in reactant n, S_{n2} is the second steady state intermediate in reactant n, and X_{n1} is the first steady state of other type of reactant. If a perturbation term δS_{n1} is introduced, then

$$S_{n1} = S'_{n1} + \delta S_{n1} = S'_{n1} \left(1 + \frac{\delta S_{n1}}{S'_{n1}}\right) \quad (2-4)$$

where S_{n1}' is a preliminary estimate which is reasonably good and δS_{n1} is correction term.

After substitution of equation (2-4) into (2-3), the decrement D_n becomes

$$\begin{aligned} D_n &= k_n S'_{n1} \left(1 + \frac{\delta S_{n1}}{S'_{n1}}\right) S'_{n2} \left(1 + \frac{\delta S_{n2}}{S'_{n2}}\right) \cdots X_{n1} X_{n2} \cdots \Delta t \\ D_n &= k_n S'_{n1} S'_{n2} \cdots X_{n1} X_{n2} \cdots \left(1 + \frac{\delta S_{n1}}{S'_{n1}}\right) \left(1 + \frac{\delta S_{n2}}{S'_{n2}}\right) \cdots \Delta t \\ D_n &= D'_n \left(1 + \frac{\delta S_{n1}}{S'_{n1}}\right) \left(1 + \frac{\delta S_{n2}}{S'_{n2}}\right) \cdots \Delta t \end{aligned} \quad (2-5)$$

where $D_n' = k_n S_{n1}' S_{n2}' \cdots X_{n1} X_{n2} \cdots$

Checking the products of $(1 + \delta S_{n1}/S_{n1}')(1 + \delta S_{n2}/S_{n2}')$, we obtain an approximation by discarding the high order correction terms. i.e.,

$$\begin{aligned}
 \left(1 + \frac{\delta S_{n1}}{S'_{n1}}\right) \left(1 + \frac{\delta S_{n2}}{S'_{n2}}\right) &= 1 + \frac{\delta S_{n1}}{S'_{n1}} + \frac{\delta S_{n2}}{S'_{n2}} + \frac{\delta S_{n1} \delta S_{n2}}{S'_{n1} S'_{n2}} \\
 &\approx 1 + \frac{\delta S_{n1}}{S'_{n1}} + \frac{\delta S_{n2}}{S'_{n2}} = 1 + \sum_{k=1}^2 \left(\frac{\delta S_{nk}}{S'_{nk}}\right)
 \end{aligned}$$

Consequently, considering the k^{th} steady state species, the decrement D_n in reaction n will become

$$D_n = D'_n \left(1 + \sum_{k=1}^{g_n} \left(\frac{\delta S_{nk}}{S'_{nk}} \right) \right) \Delta t \quad (2-6)$$

g_n is the number of SS intermediates in reaction n .

From equation (2-6), it is clear that D_n approaches to D'_n if the deviation δS_{nk} is insignificant.

With an initial goal of keeping all intermediates in the system as possible steady state species, we adopted the form of $[C_{ss}] = \text{production rate} \times \text{lifetime}$ (lifetime has been defined as the reciprocal of the partial derivative of the rate with respect to the concentration of the species i of interest. i.e., $\text{lifetime}_i = |1/[\partial(\text{rate})/\partial C_i]|$). Alternatively, it can be defined as the reciprocal of the summation of first order sink terms for species i). This form is used to compute each SS concentration.

The first step is to calculate the $[C_{ss}]$ based on the existing data in the system as well as the error ratio. In steady state solution for self-reacting species, a quadratic solution must be used, for example, HO_2 & CH_3O_2 .

Several advantages will be pointed out for this simple

calculation :

1. The value of L is a criterion to predict the stiffness.
2. Since automatic adjustment of SS is an initial goal, this simple approach allows $QSSA$ to be switched on and off during computation without causing much trouble.
3. No iteration is required while the SS concentrations are calculated, and the error is detected based on the ratio SSR in Eq. 2-2.

In order to maintain flexibility in the computer program, whenever $L=0$, at which the formula is no longer valid due to the denominator is zero, the calculation will automatically switch to numerical integration. The validity of SSA can be treated by comparing the results from the SSA -free numerical integration approach with that from the SSA approach.

The mixed differential-algebraic equations (DAE) for numerical solutions have been discussed in several published papers (44,45,46). All claimed that it is an alternative way to solve stiff systems of ordinary differential equations. Datta (46) stated that the final steady state solution for a chemical system that approaches equilibrium is exact analytically, and that in the transient stage the error can be kept below the tolerable limit by appropriately choosing the step size. The numerical integration as well as the error will be described in the next chapter.

CHAPTER III

MATHEMATICAL APPROACH FOR SOLVING ODE AND ERROR ANALYSIS

ORDINARY DIFFERENTIAL EQUATIONS

The behavior of chemical and physical dynamic systems can be described by ordinary differential equations. Thus, the understanding and the seeking of methods of solution for differential equations are important to scientists. From an air pollution point of view, in study of the troposphere, it is important to monitor the concentration of pollutants or other species of interest and seek methods to predict the behavior of pollutants for control. Due to the complexity of the troposphere, it is difficult to simulate the entire chemical reaction set in a real tropospheric environment experimentally. Alternately, two approaches can be made to enhance knowledge of the troposphere, in order that some prior actions can be performed to moderate the pollution. The first is to simulate a subset of chemical reactions which focus on a specific problem (e.g., smog chamber experiment). The second is using the computer to model the troposphere.

In order to model the troposphere, we must consider:

1. How to code the tropospheric problem into mathematical formulation ?

2. How to choose the chemical mechanism which will cover the range of modelling ?
3. How to solve the problem ?
4. How to validate the approximate value ?
5. How to interpret the results & compare with observation ?
6. How to abstract useful information from modelling ?

A number of good books describe the numerical integration in detail (47,48,49,50,51,52). Here, we just quote briefly. A differential equation is an equation involving a function and its derivatives. If $f(x)$ is a function continuous on an interval $[a,b]$, then the differential equation of y with respect to x is given as

$$dy/dx = f(x,y) = y'(x)$$

and has a solution given by the fundamental theorem of calculus

$$Y(x) = B + \int_a^x f(t) dt$$

This represents a general solution for any value of the constant B ; the equation alone is not enough to specify a particular solution. In order to get a particular solution, more information should be given; one must either restrict the initial condition or give two boundary conditions.

The two types of ODE are classified as an initial value problem (IVP) or a boundary value problem (BVP). Ground level tropospheric chemistry using a zero-dimensional model is considered as an initial-value problem.

We take the simplest IVP ODE as an example :

$$dy/dx = y'(x) = f(x,y); \quad y(x_0)=y_0$$

where $f(x,y)$ indicates any explicit function,

y_0 is the initial value of $y(x)$ at $x=x_0$

This simple ODE can be solved analytically or numerically. But since a number of chemical reactions take place simultaneously in the troposphere, analytical solutions are usually impossible. In fact, computer modelling of atmospheric problems can be said to be equivalent to numerical solution of coupled nonlinear and/or linear ordinary differential equations.

$$dy_i/dx = y'_i(x) = f_i(x, y_1, y_2, y_3, \dots, y_n)$$

$$i=1,2,3,4,\dots, m \quad \& \quad y_i(x_0)=y_{0i}$$

In atmospheric modelling, x is usually treated as time (t), and y represents species as well as light intensity. This approach answers the first question mentioned at the beginning of this chapter.

Next, how do we solve a set of differential equations $y(t)$? As just mentioned, the set of differential equations cannot be solved exactly and a continuous approximation to the solution $y(t)$ will not be obtained; instead an approximation to $y(t)$ will be calculated at various points in the interval of interest. Namely, a number of discrete points are generated rather than a continuous curve. Hence, the differential equations become difference equations associated with certain types of numerical methods.

SINGLE STEP - EULER'S METHOD

The best choice of method concerns not only accuracy but also amount of computer time used. We start with Euler's method because it is easy to analyze and understand. In Euler's method, the value of the dependent variable at one point is calculated by a straight line extrapolation from a previous point. (Figure 2)

The derivation of Euler's method starts with Taylor's series. It is known that any function can be written in the following form in terms of Taylor's series:

$$y(t+h) = y'(t) + hy'(t) + \left(\frac{h^2}{2!}\right)y''(t) + \dots + \left(\frac{h^n}{n!}\right)y^n(t) \quad (3-1)$$

By using the first terms of Taylor's series and ignoring higher terms, we can calculate an approximation of $y(h)$ in linear form:

$$y(t+h) \approx y(t) + hy'(t) = y(t) + hf(y(t), t) \quad (3-2)$$

$$\text{and } f(y(t), t) = y'(t)$$

where h = step size

A graphical display is shown as Figure 3, in which $t=t_1$ and $h=t_2-t_1$. Once the concept of step size is introduced, the question of how to choose the step size while keeping the solution both accurate and efficient comes to the mind. Balancing the conflicting requirements of accuracy and efficiency is always a challenge to the numerical scientist. A number of numerical methods have been studied, discussed and

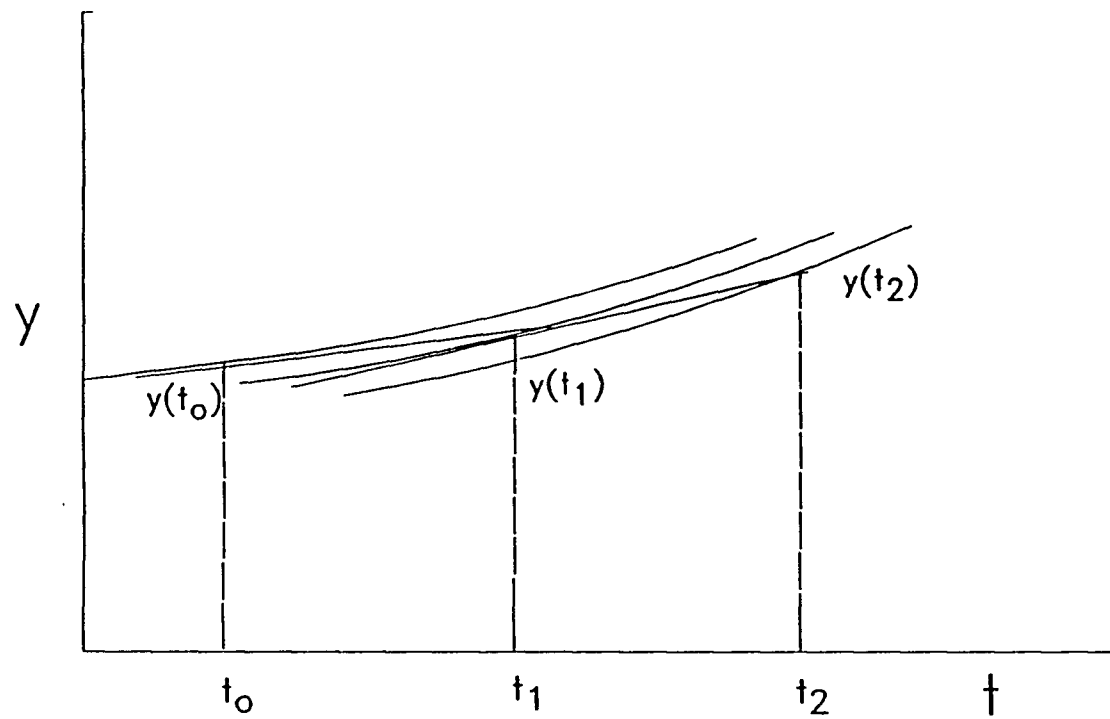


Figure 2. Graphic Euler's method. Starting with $y(t_0)$, $y(t_1)$ is augmented linearly by increasing t_0 to t_1 and so on.

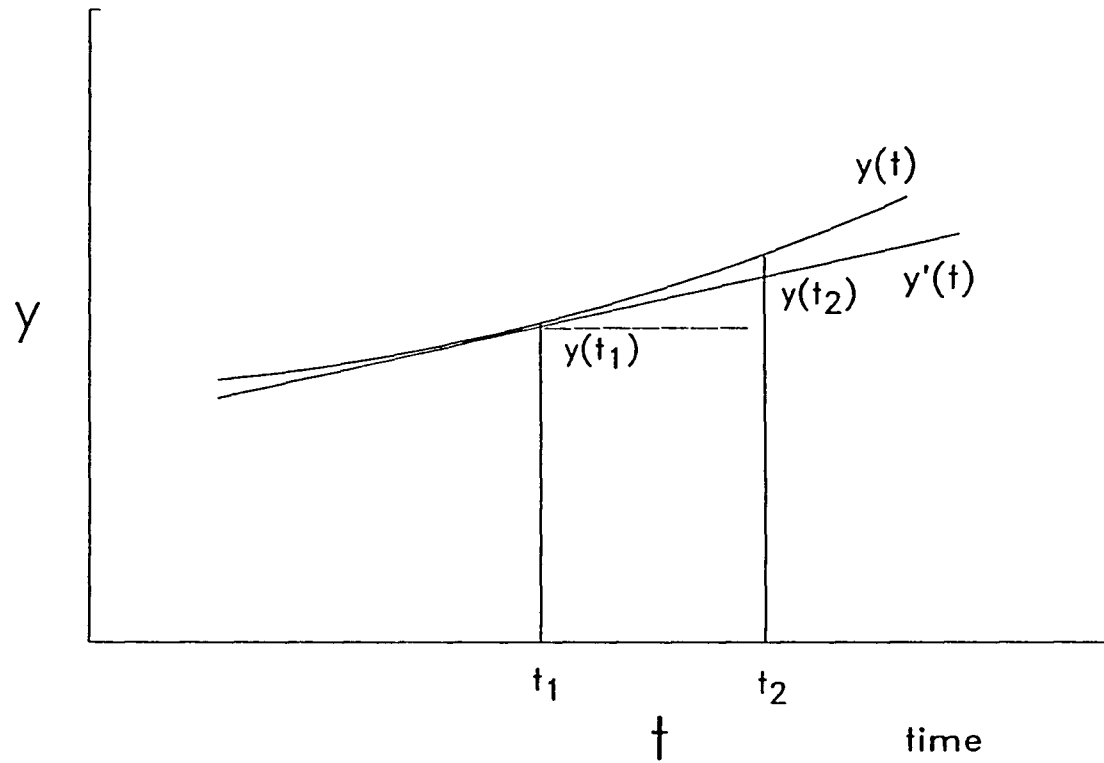


Figure 3. First order approximation of Taylor's series. The Euler's method for numerical integration is exactly equivalent to first order of Taylor's Series.

published. Fundamentally, several factors should always be kept in mind while dealing with numerical modelling :

1. step size selection. (any good criteria ?)
2. accuracy. (error estimation, how to control ?).
3. efficiency (time-consuming ?)
4. real-time type of modelling ?
5. comparison with experimental observation. (feedback to modify the modeling parameters).

Theoretically, the optimal step size obeys the following criterion : (51 and figure 4)

$$h = \sqrt{\frac{2\delta}{M}}$$

where δ = round off error and M = truncation error. In Euler's method, M is equal to or greater than the second derivative of the function y . In the case of a set of differential equations, M is the highest value of the second derivatives of all functions of y_i . Based on the step size formula, it is obvious that decreasing the step size (h) beyond this optimum would tend to increase the total error in the approximation. Normally, however, the value of δ is sufficiently small that this lower bound for h will not affect the accuracy of Euler's method. Thus the choice of lower bound must be based upon computational time.

All numerical values obtained by numerical integration are approximate, and error exists inherently (Figure 5 & text). (i.e., error=approx.-exact) Errors involved in

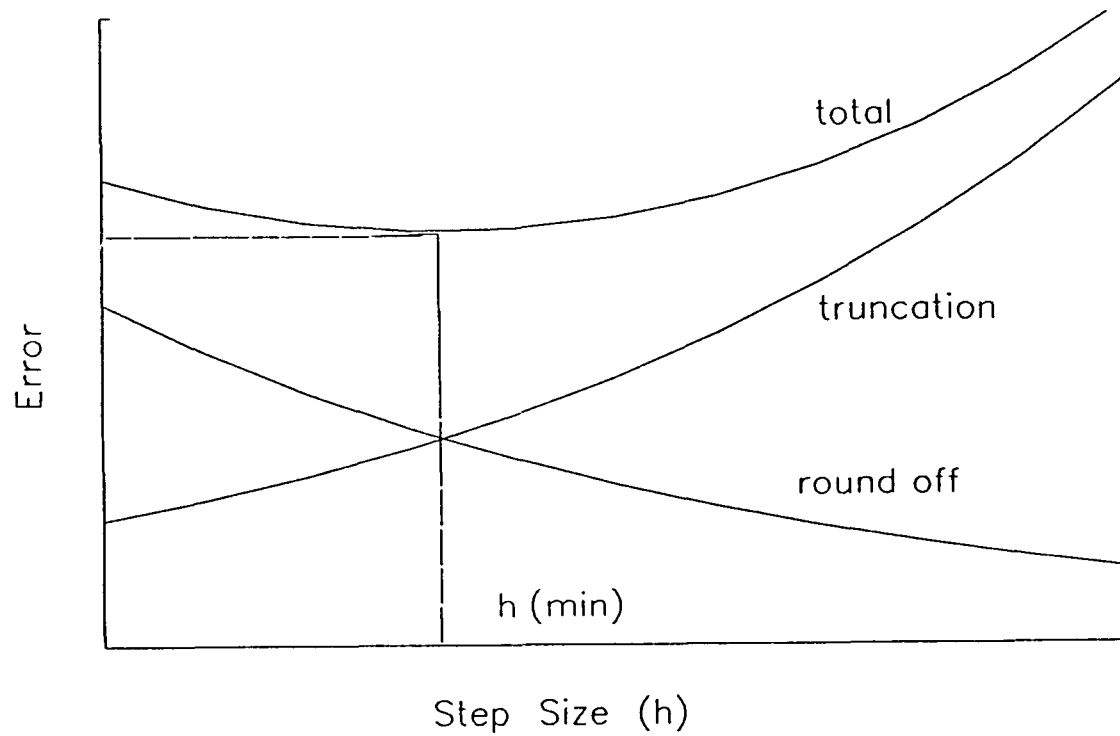


Figure 4. Optimization of step size. Truncation error is proportional to the magnitude of step size while the cumulative roundoff error is inversely proportional to step size. The choice of optimum step size is exactly equal to the lowest point of the curve of total error.

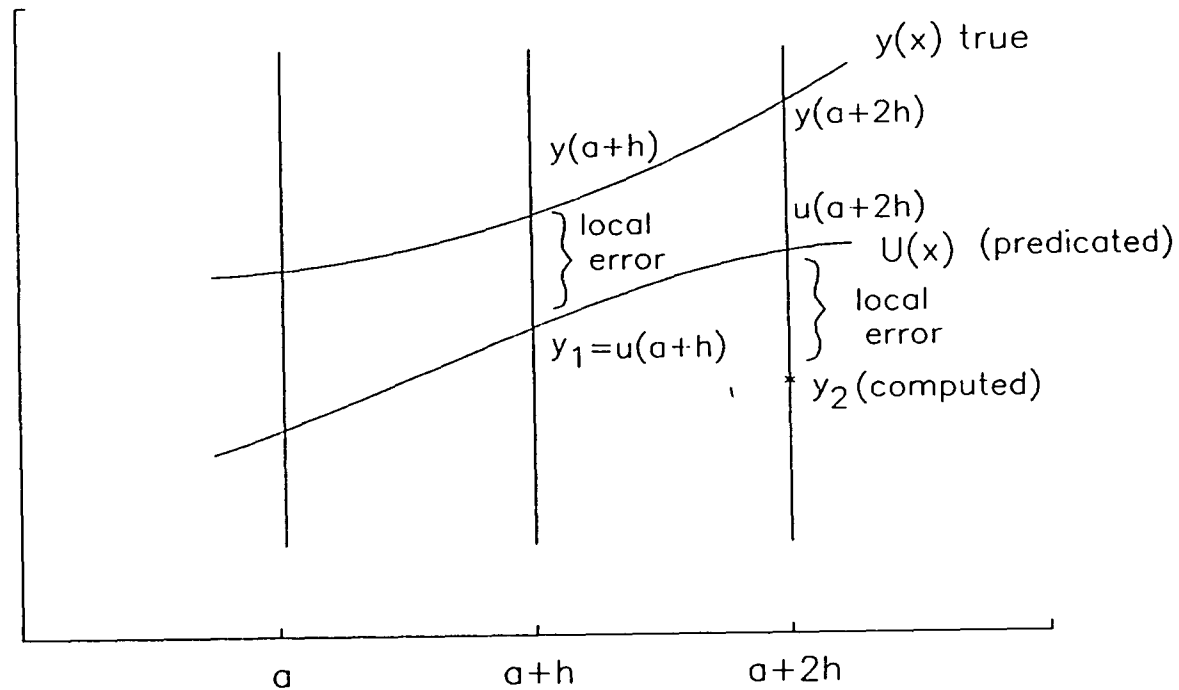


Figure 5. Relationship of local error and global error. Assuming no global error at time $a+h$, then, the difference between true value, $y(a+h)$, and approximation value, y_1 or $u(a+h)$, is local error (global error=local error). After an increment of step size h , the value of y_2 has been computed, the new local error is calculated as the difference between y_2 and $u(a+2h)$ which is a predicated value based on the $u(a+h)$. The global error becomes the divergence between $y(a+h)$ and y_2 , or approximately the sum of local errors. Here, there is assumed no propagation error.

computer modelling are classified into three different types. First is roundoff error, truncation error is next, followed by global error. In any numerical integration, the first two errors have been discussed above. Figure 4 shows the relationship between these two. Here, the description of errors will be focused on Euler's method (single step). Details in error induced by other methods (multiple step etc.) can be found in references 50,53,54 & 55.

ERROR ANALYSIS

Roundoff Error

Roundoff error originates in the computer and its architecture. Roundoff error arises because any real number x is represented with a fixed number of decimal or binary digits (56,57). In scientific calculation, a floating-point representation of a number is adopted, in which any number is represented by two (signed) sets of digits, known as mantissa (m) and a (signed) integer exponent (E). Thus the number n being represented has the value

$$n = m b^E \quad (3-3)$$

b is base or radix of the number system in use and b is equal to 10 in decimal system, 2 in binary system. The representation equation (3-3) is not unique, for instance, in the decimal system, the number 3.5 could be written as 0.35×10^1 , 3.5×10^0 , 35×10^{-1} , .. and so on. In order to avoid this

inconvenience, one common method of normalization is restricted on m , i.e., $1 > |m| \geq b^{-1}$, so that, $3.5 = 0.35 \times 10^1$, that is, with $m=0.35$ and $E=1$. Similarly, in binary system, m is written as equal to

$$m = A_k 2^{-1} + A_{k-1} 2^{-2} + A_{k-2} 2^{-3} + \dots$$

m is always smaller than 1 and greater than or equal to $\frac{1}{2}$. However, the computer must use a finite number of digits to represent a numeric value. Hence, a certain amount of error will be generated for each representation of numerical value in floating-point format. Assume N is an exact datum requiring more than k binary digits for its representation and n is the rounded k -bit approximation. Both have same sign and exponents, for instance, the binary number 110011101.11 can be represented as

$$N = 0.11001110111 \times 2^9 = (y)2^9$$

but after rounding to 10 bits (k) for mantissa, then

$$n = 0.1100111011 \times 2^9 = (q)2^9$$

Considering the mantissa parts ($1 > y \geq \frac{1}{2}$), the error is written

$$\delta = y - q = 0.0000000001 = 1 \times 2^{-11} < (\frac{1}{2}) \times 2^{-10} = (\frac{1}{2}) \times 2^{-k}$$

define the maximum absolute error by

$$|\delta| \leq (\frac{1}{2}) \times 2^{-k} = 2^{-(k+1)}$$

and relative roundoff error = $(y-q)/y = \delta/y = 2^{-k}$

where k is the maximum number of bits that the computer uses for representing the mantissa and $y(\min) = \frac{1}{2}$ (y is true value of m in Eq. 3-3).

For instance, in a typical 16-bit computer with 2 words (1 word \equiv 16 bits \equiv 2 bytes) for single precision in which 1 bit is reserved for sign and 7 bits for exponent, there are 24 bits (the value of each bit is either 1 or 0) available for the mantissa. Thus, the error will be around $2^{-24} = 6 \times 10^{-8} < 1 \times 10^{-7}$. i.e., the number is accurate to about seven decimal digits. If one uses double precision instead, then 56 bits are available for mantissa (if 7 bits are still reserved for the exponent too) giving 17 decimal digits of accuracy. ($2^{-56} = 1.388 \times 10^{-17}$)

The roundoff unit (or machine unit, epsilon, ϵ) of the floating-point representation is defined as

$$\epsilon = 2^{-k}$$

where k = number of mantissa bits (56 for double precision)

Two methods can diminish the round off error: the first is to use double precision, and second, to choose the computer with as many bits as possible since each type of computer has its own roundoff unit (ϵ) which is defined as the smallest positive value such that $1+\epsilon$ is greater than 1.

Truncation Error

This error is of most concern to the modeler. In Euler's method, truncation error at one step (58), by virtue of Taylor's formula, is given by

$$\text{True - Approximation} = \frac{h^2}{2} y''(t) \quad (3-4)$$

i.e., the difference between the Eqs. 3-1 and 3-2, if we ignore the higher terms.

In order to calculate the truncation error, the second derivative $y''(t)$ should be computed first. The practical evaluation of second derivatives make use of the following correlation (60):

$$\begin{aligned} \text{since } y'(t+h) &= f(y(t+h), t+h) \text{ (similar to Eq. 3-2) and} \\ f(y(t+h), t+h) &= f(y(t), t) + hf'(y(t), t) + (h^2/2!)f''(y(t), t) \dots \\ &= f(y(t), t) + hy'' \text{ (ignoring higher order terms)} \\ &\text{(recall } y' = f(y(t), t), y'' = f'(y(t), t)) \end{aligned}$$

therefore, $f(y(t+h), t+h) - f(y(t), t) = hy''$ or

$$y'' = \{ f(y(t+h), t+h) - f(y(t), t) \} / h = \{ y'(t+h) - y'(t) \} / h$$

Substitution into equation 3-4,

$$\begin{aligned} \text{True - Approximation} &= \frac{h^2}{2} y''(t) = \frac{h^2}{2} \frac{(y'(t+h) - y'(t))}{h} \\ &= \frac{h}{2} (y'(t+h) - y'(t)) \end{aligned} \quad (3-5)$$

i.e., the evaluation of the error of $y(t)$ needs one more further calculation of $y(t+h)$ to get the difference between the slopes y' and compute the truncation error. This is the method used in the program described below to calculate truncation error.

Global Error

The global error of a species is a summation of local error over the total integration time, which is a sum of local truncation error and round off error. However, the roundoff

error is usually insignificant, therefore, the local error is approximated as local truncation error. Consequently, the global error is treated as a summation of all truncation error.

As mentioned above, the truncation error of Euler's method is equal to the second derivative of the function multiplied by a constant, which is one half of the chosen step size. Gear's book (50) states that convergence assures that the true solution can be approximated arbitrarily closely by making h smaller and using greater precision. The truncation error can be reduced by reducing the step size (59). However, in reducing per-step truncation error by decreasing the step size, a limit is reached at which further reduction in step size increases the total number of integration steps to a point where roundoff error becomes dominant, and the total error will increase with further reduction in step size.

The relationship between the local error and the global error can be depicted as follows (Figure 5):

At time $a+h$, a local error exists between the true values $y(a+h)$ and a computed solution y_1 , and $u(a+h)$ represents a local solution of the differential equation having initial value $y(a)$ at time a . Initially, assume $y_1 = u(a+h)$. Then, calculate the global error (at time $a+2h$)

$$\begin{aligned} \text{global error} &= \text{Computed} - \text{True} = y_2 - y(a+2h) \\ &= \{y_2 - u(a+2h)\} + \{u(a+2h) - y(a+2h)\} \end{aligned}$$

The first term in brace $\{y_2 - u(a+2h)\}$ is the local error and the second term $\{u(a+2h) - y(a+2h)\}$ depends on the stability of the differential equation. Alternatively, the second term is approximately (small step size) equal to

$$\{1 + h \times J(h)\} \times \{\text{global error at } a+h\}$$

where h = step size and $J(h)$ is the Jacobian (51) of the differential equation at $[(a+h), y(a+h)]$. The eigenvalue of $J(h)$ determines the stability of the differential equation. This term measures the sensitivity of the problem itself. The most common procedure used in selecting the step size is to keep the local per step error below a predetermined, allowable value.

In general, for a method of order n the local error will be on the order of a constant times the step size raised to the power $n+1$. This may be expressed as

$$Ch^{(n+1)},$$

Assume $y(\text{true})$ is the true value at the point of $x(t)$ and $y(t)$ is the computed value at the point of time t .

TABLE II
ESTIMATED ERROR USING DIFFERENT STEP SIZE

| Step size | Predicted value | Estimated error |
|-----------|----------------------|--|
| h | $y(t)$ | $y(\text{true}) - y(t) = Ch^{(n+1)}$ |
| $h/2$ | $y_{\frac{1}{2}}(t)$ | $y(\text{true}) - y_{\frac{1}{2}}(t) = C(h/2)^{(n+1)}$ |

Table II shows the comparison of the two computed values generated by use of different step sizes, the difference is

$$\begin{aligned}
 y(t) - y_{\frac{1}{2}}(t) &= -Ch^{(n+1)} + C(h/2)^{(n+1)} \\
 &= Ch^{(n+1)} [(1/2)^{(n+1)} - 1]
 \end{aligned}$$

This can be solved to estimate the local error :

$$Ch^{n+1} = [y^{1/2}(t) - y(t)] \frac{2^{n+1}}{2^{n+1} - 1} \quad (3-6)$$

This approach has a disadvantage that requires the user to compute the value more than twice (i.e., $y(t)$, $y_{\frac{1}{2}}(t)$ & $Ch^{(n+1)}$). Nevertheless, this procedure is often included in the computational algorithm to make automatic adjustment in the step size as the computational process take place.

The easy way to estimate the global error is based on the rough idea that after N integration steps, the error is (60):
 $\epsilon_{\text{global}} = N(h) \times h^n$; n = order of the method used, assuming that the local error is of order h^n (see Eq. 3-4). Since, for a total integration time (δt),

$$\begin{aligned}
 N(h) &\sim \delta t/h, \\
 \epsilon_{\text{global}} &= \delta t/h \times h^n, \\
 \text{This results in } \epsilon_{\text{global}} &\sim h^{n-1}.
 \end{aligned}$$

From equation 2-2 (p.18), it reveals obviously that the QSSA error is calculated based on the SSR ratio for species of interest.

$$[C_i] = [C_{ss}] (1 - SSR_i) = [C_{ss}] - SSR_i [C_{ss}]$$

$$\Delta[C] = [C_i] - [C_{ss}] = -SSR_i [C_{ss}]$$

$$\text{where } [C_{ss}] = \frac{\sum P_i}{\sum k_{ij} [C_j]}$$

In other words, $QSSA_{\text{error}(i)} = |SSR_i| [C_{ss}]$.

CHAPTER IV

DEVELOPMENT OF SOFTWARE

INTRODUCTION

The application of modelling techniques to problems which may be inaccessible to direct experimental study or too complex for explicit theoretical analysis has given a new insight into the nature of science. Modelling frequently has been used to forecast the behavior of atmospheric chemistry (e.g., stratospheric ozone depletion or urban and rural ozone formation). The flow chart in Figure 6 denotes the correlation of components for computer modelling. There are at least two goals of modelling. The first is to predict the behavior of simulated systems based on the input initial conditions by solving appropriate mathematical equations. The second is to interpret experimental observations so that useful information can be abstracted about the underlying physical driving forces.

Development of software packages is motivated by the plain ideal to abstract simplicity from complexity and seek a deeper understanding of atmospheric chemical phenomena. In order to implement the goal, in a complex system, several questions arise, such as, are there any fundamental correlations which are capable of describing the system

closely or pointing out the pivotal forces concealed inside? If the answer is yes, mostly because simplicity is a rule in nature, then how to reveal this underlying relationship through modelling?

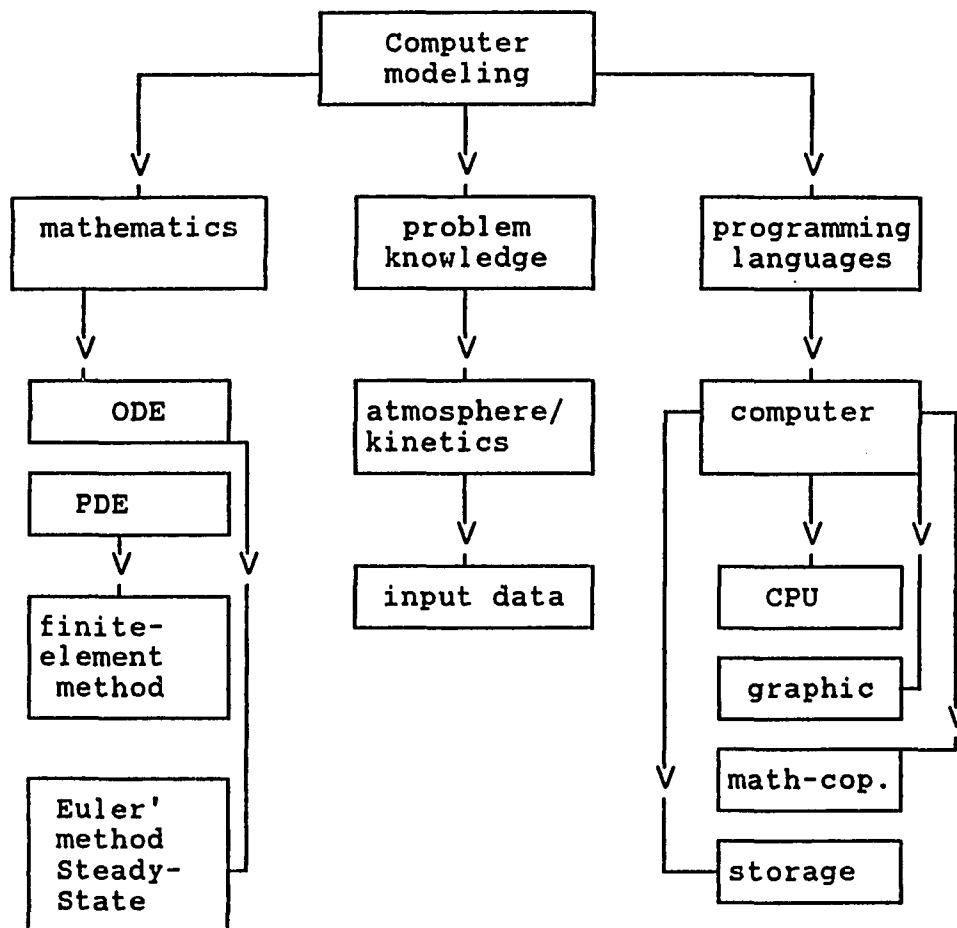


Figure 6. The components of computer modelling.

Although there is existing software which can be used to carry out the simulation of complex chemical reactions (61,62,63,64,65), not many are designed for the personal

computer (66) and those software programs do not always fit the needs. For example, does the software deal with chemical reactions initialized by a pulse or variation of light intensity? Does the software deal with an open-system chemical reaction in which species or conditions are permitted to change while the reaction takes place? Does the software recognize the distinction between purely numerical integration and application of steady-state hypotheses to the system? Does the software provide the capacity for real-time graphical data display? Does the software have a variety of options to store data? Does the software display data in a variety of formats? Does the software provide the option of treating experimental data as input data? Does the software manipulate all possible combinations of different species? Does the software have the capability to search for and build useful relationships among different species in a complex chemical system? Does the software have the capability to do a sensitivity analysis for a given set of relations? Does the software have a variable step size?

Facing these challenges, the integrated software package shown as Figure 7 was developed. The programming languages used for this software are Microsoft C and True Basic. The model employed is a so-called zero dimension model, meaning that it does not describe transport other than emissions and dilution. The program is designed to formulate and solve the system of differential equations describing the temporal

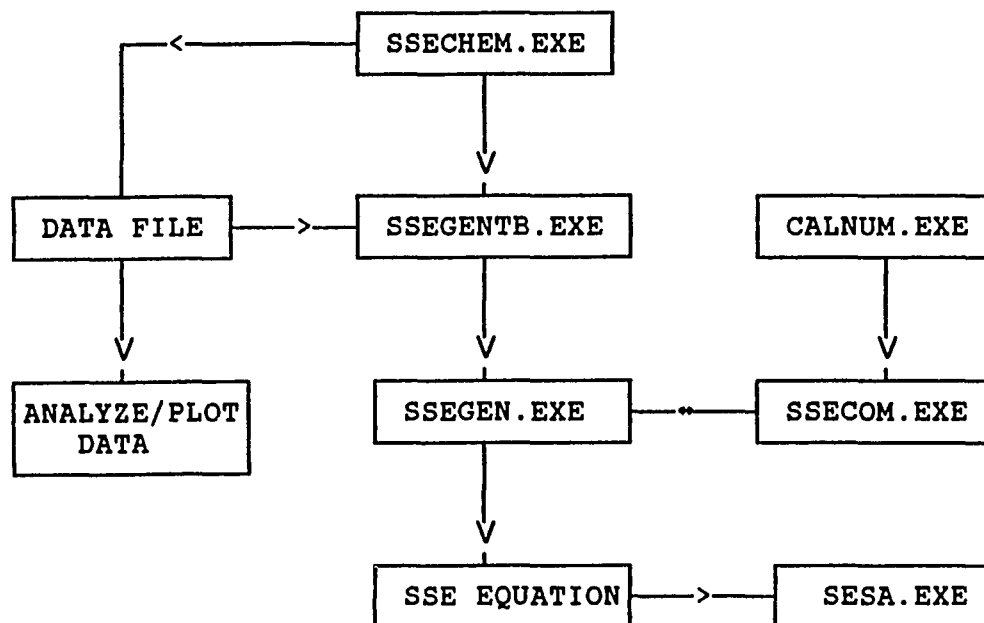


Figure 7. The SSE series of programs

DEVELOPMENT OF SSE PROGRAMS

The purposes for developing these programs are summarized below :

1. Learn how to apply numerical modelling for complex chemical systems.
2. Allow theoretical modelling of experimental data.
3. Employ the steady-state assumption in the numerical modelling.
4. Generate the steady-state equation for the species of interest.

5. Perform sensitivity analysis of generated steady-state equations.
6. Vary activation energies and temperatures to analyze different isothermal, spatially homogenous, multicomponent chemical reaction systems.

General Procedures

1. The integrated software of programs and their correlations are shown in Figure 7.
2. Edit the free-format input mechanism (SSECHEM).
3. Convert the free-format file into the formatted file (SSECHEM).
4. Run mechanism through SSECHEM.
5. Store data via SSECHEM.
6. Use plot program to plot or view the stored data. This can be either invoked from SSECHEM or run separately.
7. Run SSECOM to obtain the number of terms or rates left after manipulating the combinations.
8. Run SSEGENTB to regenerate data table from existing data file in step 5.
9. Run SSEGEN to create the steady state equations by judging the information based on the results from steps 7 & 8.
10. Run SSESAs to analyze the sensitivity of the equations resulting from step 9.

The primary goal of the software is to create an

environment in which the user can edit the input file, view all information and data, simulate the chemical reaction and display data in a variety of formats. The software permits changing the conditions while the reaction is taking place, interrupting the execution with no loss of the data, storing and plotting the data in linear or logarithmic scale and data plotting with the ability to calculate the maxima, average and integrated species concentrations. Graphical output includes screen dump to dot-matrix printer, color ink jet printer, or plotter, open self-debug window optionally and in addition, access on-line help easily and quickly.

The first program SSECHEM is designed to contain all features mentioned above and more details as depicted below. This file is an essential one of the series programs. The file is designed for handling a complex chemical reaction system. The change in concentration of chemical species with time can be treated as a set of ordinary differential equations. The numerical method used to solve the system of differential equations is Euler's method. The mixed differential and algebraic equations are adopted in this program. In chapter III, Euler's method has been discussed.

The traditional way to sort species into constant, numerical integral or steady state is based on the lifetime (τ_i) and/or time step adopted in the system (13). In the SSECHEM program, the index chosen to determine the validity for constant species is based on lifetime; however, for steady

state species it is based on the ratio SSR (Eq. 2-2). The time step chosen for numerical integration of the remaining species is fixed, changed manually, or computed based on the next potential steady state species candidate. Instead of the next potential SS candidate, it may be necessary to use the τ of the least stable species among those already determined to be in steady state.

Consequently, all species then can be categorized into three groups:

- (a) constant for those species which have long lifetime.
- (b) numerical integration with different approaches
(Euler's method, for instance) for those species with moderate lifetime.
- (c) applying steady state assumption to those species which meet the criteria (i.e., SSR is sufficiently small). Regarding error, it is easy to show the relationship

$$\text{error}_{(\text{total})} = \text{error}_{(\text{ni})} + \Sigma \text{error}_{(\text{ss})}$$

Where the numerical integration error_(ni) is proportional to step size (h) and the steady state error_(ss) is equivalent to SSA error, whose details are described in chapter III.

Methods used in numerical program

1. Euler's method (single-step method)

$$R(i) = dY(i)/dt = P(i) - L(i)Y(i) \text{ (differential form)}$$

can be represented numerically as

$$Y(i+1) = Y(i) + R(i)h ; \quad h = \text{step size}$$

Euler's method is equivalent to the first order part of Taylor's series, the local error is $O(h^2)$ and the global error is $O(h)$. $O(h)$ means an order of magnitude of h

Methods to calculate steady state equation

There are two approaches for two different possible cases. First, for a species which does not react with itself, the SS equation is equal to the production/loss term.

$$ax + b = 0$$

Second, for a species which reacts with itself, a quadratic equation should be used to represent the SS equation. Through the rationalizing the numerator, the form of the quadratic formula become:

$$ax^2 + bx + c = 0$$

$$x = \frac{-2c}{b + \sqrt{b^2 - 4ac}}$$

Species whose changes are known to be negligible during the entire integration time are treated as constants, and the sum of the rates affecting them are set to zero.

Options of diurnal & pulsed variation

Three different formulas are available for simulating any variation of light intensity or species injection rates. In general, the variation of light intensity will be reflected in the variation of rate constants. For instance, photolysis rate

constants vary with light intensity during daytime and are zero after sunset.

Sinusoidal Formula.

$$J_t = J_{\text{noon}} \sin \frac{(t - t_s) \pi}{L}$$

where J_t = variation of rate constant.

J_{noon} = noon value of rate constant. (max.)

t = variable time.

t_s = starting time (sunrise)

t_e = ending time (sunset)

L = duration = $t_e - t_s$.

Example : sunrise at 6 am and sunset at 6 pm gives

$$L=12.$$

the duration of daytime is 12 hours.

Then calculation of the value for rate constant at 8 am is done as follows :

$$\begin{aligned} J_8 &= J_{\text{noon}} \sin \{ (8 - 6) \pi / 12 \} \\ &= 0.5 J_{\text{noon}} \end{aligned}$$

The value of a photolysis rate coefficient at 8 am is equivalent to half that at noon.

Gaussian Formula.

The gaussian function is useful in simulating laser pulses. We know that three standard deviations are equivalent to 99.7% of probability density of the curve, therefore, three standard deviations = half of duration = $L / 2$.

Consequently, the formula resulted as

$$J_i = J_{\text{noon}} \exp \{-(t - t_0)^2/2\sigma^2\}$$

where σ = standard deviation = $L/6$

and t_0 is gaussian centroid.

Square Formula.

if $t > t_g$ or $t < t_g$ then $J_i = 0$

if $t_g \leq t \leq t_e$ then $J_i = 1$

LINEAR ALGEBRAIC MANIPULATION

In the previous section, we described the development of the main program SSECHEM handling numerical integration with numerous features. That time-dependent analysis of data is followed here by using linear algebraic manipulation. All steady state equations are set to zero by definition. Therefore, addition /subtraction or constant multiplication of individual steady state equations yields resultant equations with cancellation of terms. This can often simplify the form of the net equation. The program CALNUM will calculate the possible combinations contained in a given mechanism. The program SSECOM will handle the manipulation to obtain simplified relationships from combined reactions. The purpose of the program SSEGENTB is to reorganize the useful data from files generated by SSECHEM program into a table used by the program SSEGEN. Using the new resultant equations generated by SSEGEN, the program SSESA performs sensitivity analysis without any manual calculation. The output of these

programs is often a much simpler and more meaningful equation set. The concept of steady state assumption has been applied to individual species while integrating numerically. But steady state equations result from the combination of more than one species and may depict new correlations or information which exist inherently in the system. It is a way to simplify the complex system. The program SSEGEN was written to perform this task along with the program SSECOM. The details of individual program as well as the procedures and computational results are described in Appendix C.

CHAPTER V

COMPUTER MODELING

OVERVIEW

Using a computer as a tool to model a given system in which the physical or chemical reactions have been coded as mathematical equations or formulas has become popular. The name of computer experiment has been used to distinguish this effort from laboratory or field experiment. Here we attempt to model the chemical system of the troposphere to observe its behavior, abstract useful information to examine cause-and-effect relationships and build steady state equations for species of interest. The question arises about the reliability of results from modeling. In his paper (67), Ellsaesser concluded the result of observation is more trustworthy than that of modeling. Still computer modeling is one of the complementary methods for experimental measurement. Eventually, observations must be made for model improvement as well as validation. Here, we adopted an analytical approach for atmospheric modeling in order to seek an understanding of the chemical-physical process, attempt to establish cause-to-effect chains and develop equations to analyze experimental data.

All calculations were performed on an IBM compatible AT-Turbo 286 which uses the Intel 80286, a 16-bit microprocessor (10 MHz). A 80287 mathematical coprocessor was added to enhance floating point manipulations.

DESCRIPTION OF TROPOSPHERIC MODEL

The zero-dimension tropospheric photochemical model used in this study is taken from Logan (6). Simulation of diurnal light intensity is taken from Calvert (69). The model conditions and initial reactant concentrations for the clean troposphere are summarized in Table III. Noon values of non-constant species concentration given in Table IV & Figure 19.

TABLE III
SUMMARY OF CLEAN TROPOSPHERIC MODEL

| Conditions | |
|-----------------------|---|
| mechanism | Table I |
| latitude | 45° |
| hemisphere | Northern |
| season | Equinox |
| altitude | Ground level |
| constant species | concentration (molecules cm ⁻³) |
| H ₂ O | 2.62x10 ¹⁷ (1.05%) |
| H ₂ | 1.35x10 ¹³ (0.54 ppm) |
| CO | 4.9x10 ¹² (196 ppb) |
| CH ₄ | 4.16x10 ¹³ (1.4 ppm) |
| M | 2.5x10 ¹⁹ |
| N ₂ | 1.9x10 ¹⁹ |
| O ₂ | 5.15x10 ¹⁸ |
| hν | 1 (noon) |
| diurnal light | Sine curve |
| initial steady state | O(¹ D), O(³ P), CH ₃ O |
| variable NO | |
| fixed deposition rate | 1.2e-5 sec ⁻¹ (1 days) |

TABLE IV
SSR RATIO OF SPECIES IN CLEAN AIR

| species | noon concentration | SSR ratio ^a |
|----------------------------------|--------------------|------------------------|
| O(¹ D) | < 1 | -2.122e-6 |
| O(³ P) | < 1 | -2.122e-6 |
| HO | 1.0e6 | 4.127e-6 |
| NO | 1.6e8 | 1.494e-5 |
| NO ₂ | 3.1e8 | 1.512e-5 |
| NO ₃ | 1.8e6 | 1.917e-5 |
| HNO ₂ | 1.1e6 | 1.936e-5 |
| HNO ₄ | 6.0e5 | 1.963e-5 |
| CH ₃ O | < 1e2 | 3.294e-5 |
| N ₂ O ₅ | < 3e3 | 3.406e-5 |
| HO ₂ | 3.2e8 | 7.321e-4 |
| CH ₃ O ₂ | 1.2e8 | 9.491e-4 |
| O ₃ | 6.0e11 | -1.813e-3 |
| H ₂ CO | 3.1e9 | 2.207e-1 |
| H ₂ O ₂ | 1.5e10 | 5.416e-1 |
| CH ₃ O ₂ H | 1.4e10 | 5.847e-1 |
| HNO ₃ | 5.6e8 | -1.345 |

- a. SSR Ratio = rate / production.
b. All data of ratio are noon values of 30th day from 30 day run and the lifetime of rainout is 1 day. The unit of concentration is cm⁻³.
c. Conditions: 45°N latitude, equinox, clean air, ground level, noon time.

Constant species differ from steady state species although they may be considered a special case of steady state, in which both production and loss terms are exactly zero. i.e.,

$$\text{general form: } d[C]/dt = P - L [C]$$

$$\text{steady state } d[C]/dt = 0$$

$$\text{this implies (1) } P = L[C] \quad \text{steady state}$$

$$\text{or (2) } P = 0 = L \quad \text{constant concentration}$$

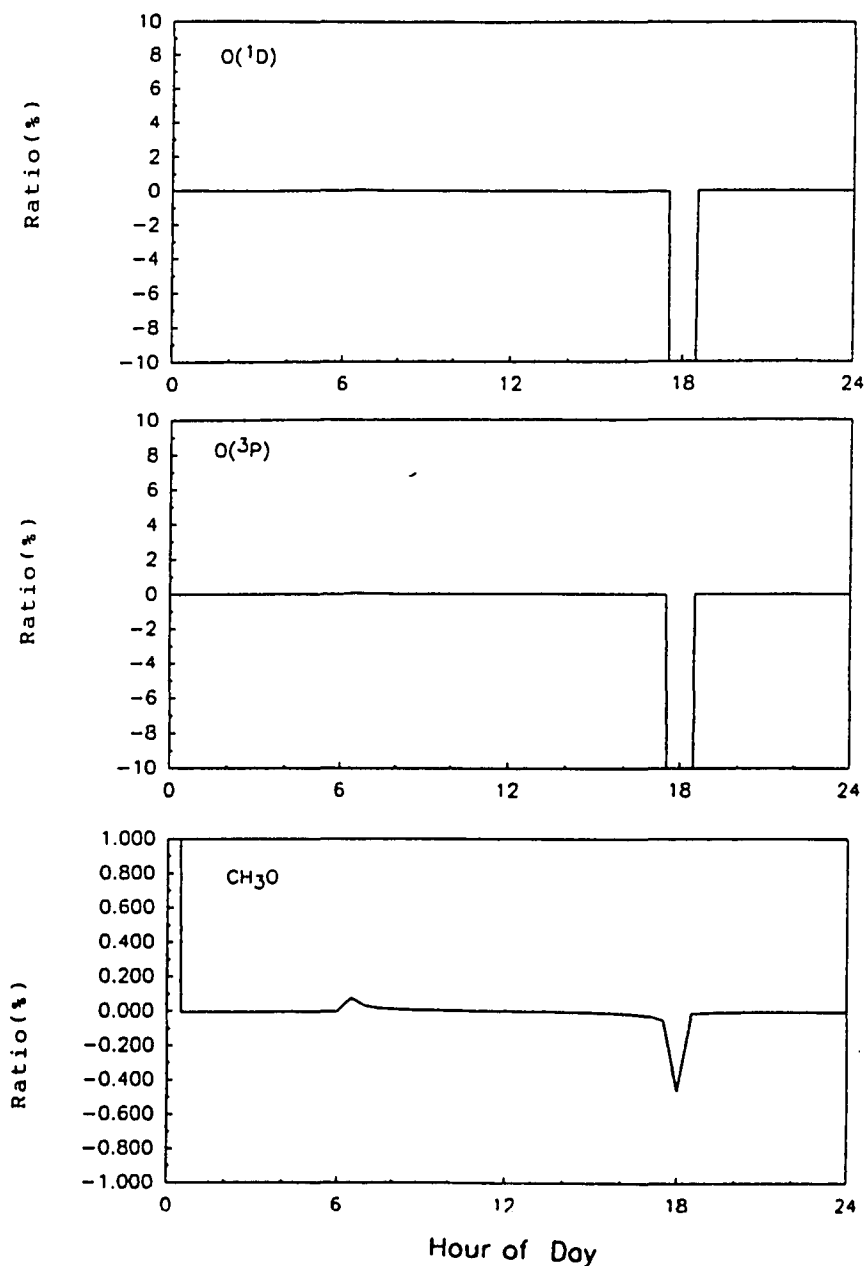


Figure 8. Application of SSA to diurnal variation of O(¹D), O(³P) and CH₃O. According to Equation 2-2, ratio (SSR) is defined as the net rate divided by the sum of the production rates for a species, if $SSR \ll 1$, then SSA is valid. This is seen to be the case for clean air species with short lifetimes except at sunrise and sunset. The data is the last day from 30 day run, $[NO_x]=50$ ppt and the lifetime of rainout is 1 day. The mechanism is shown on Table I.

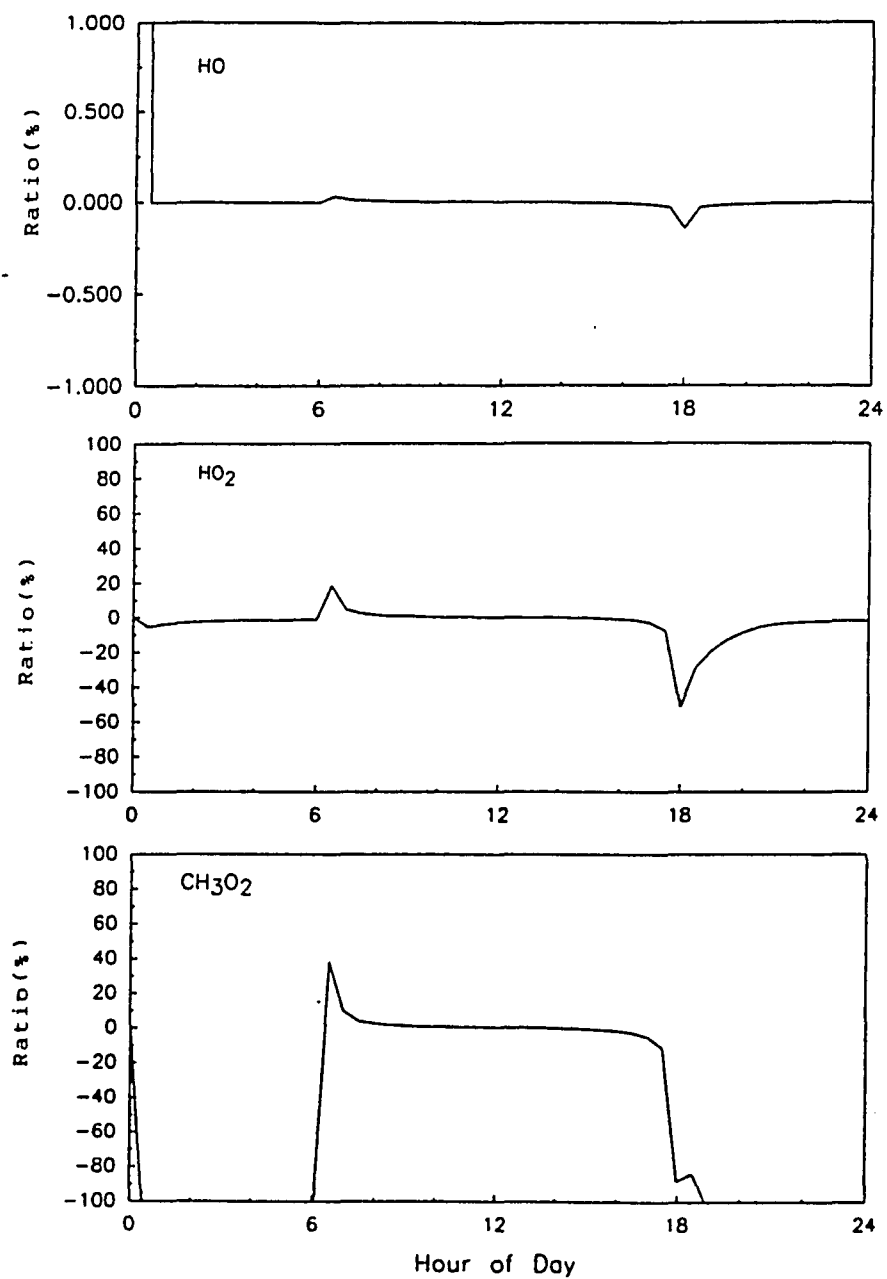


Figure 9. Application of SSA to diurnal variation of HO, HO₂ and CH₃O₂. See Figure 8 and text for details.

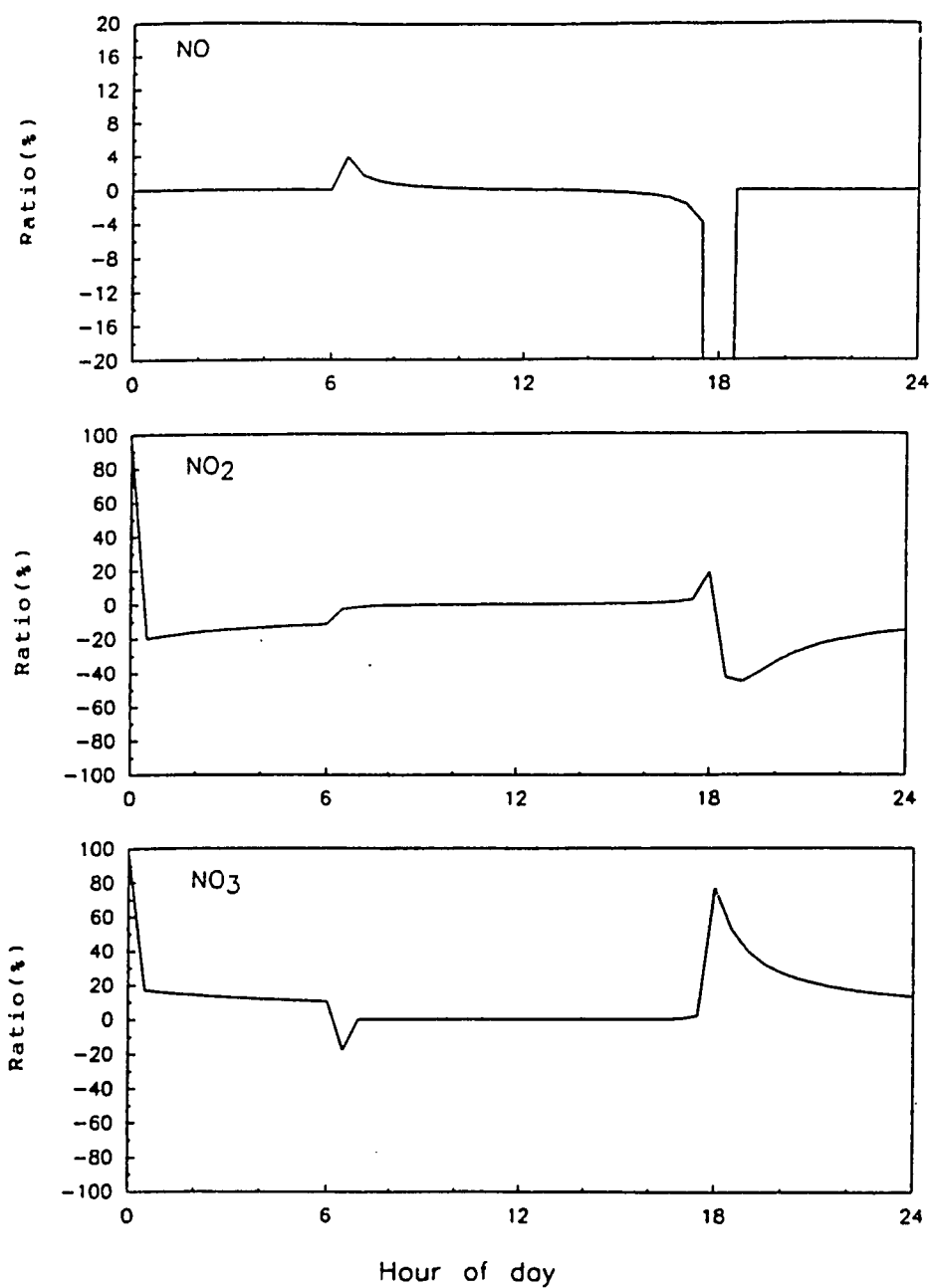


Figure 10. Application of SSA to diurnal variation of NO, NO₂ and NO₃. See Figure 8 and text for details.

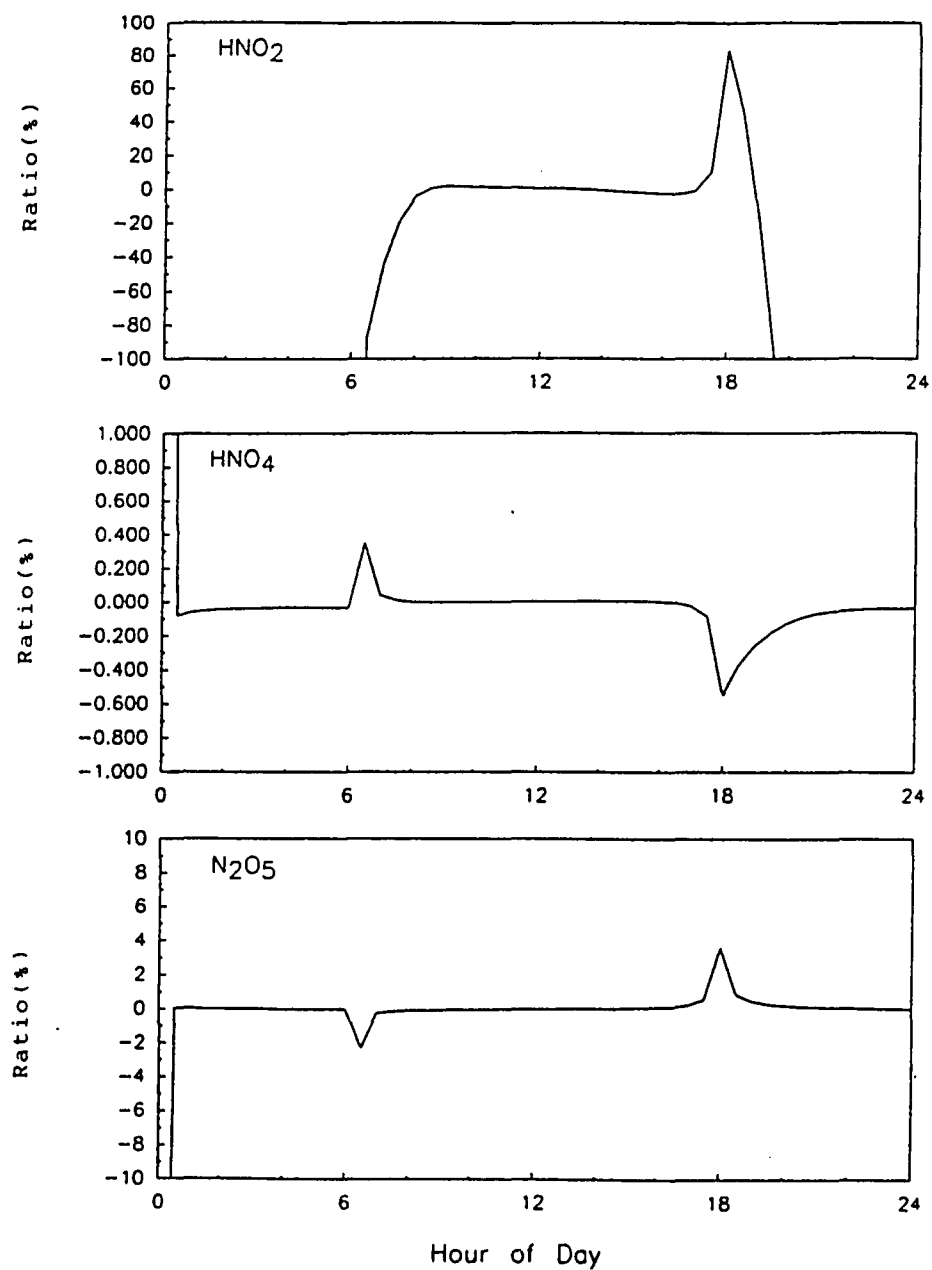


Figure 11. Application of SSA to diurnal variation of HNO_2 , HNO_4 and N_2O_5 . See Figure 8 and text for details.

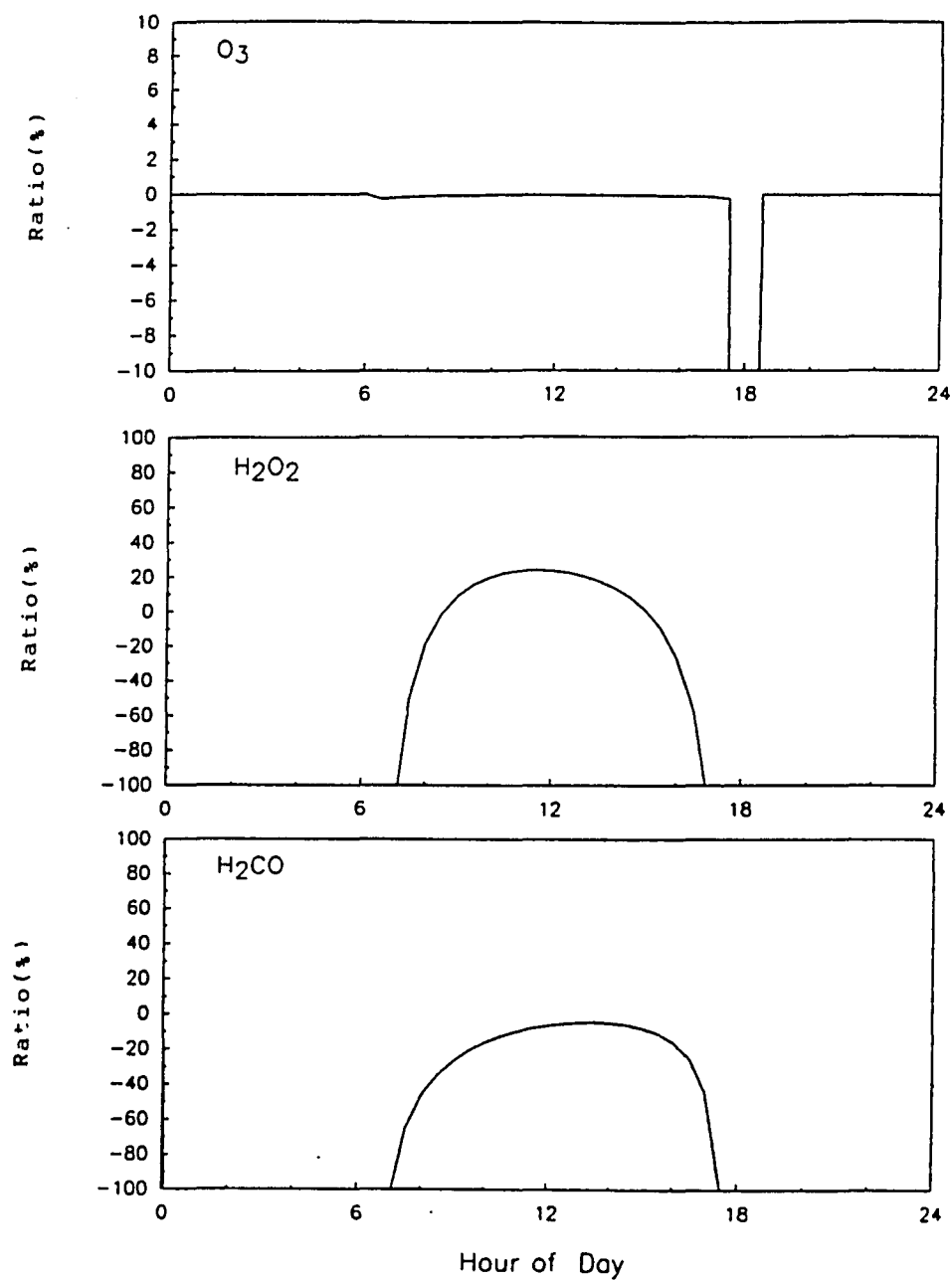


Figure 12. Application of SSA to diurnal variation of O₃, H₂O₂ and H₂CO. See Figure 8 and text for details

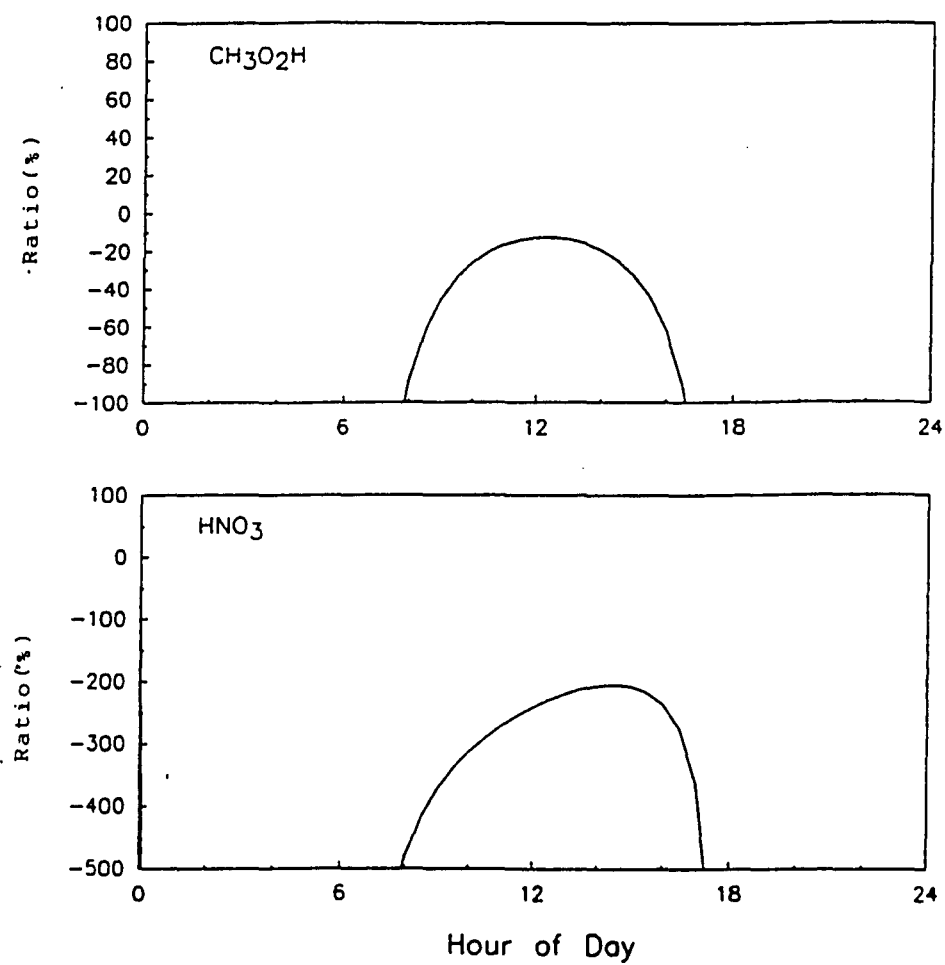


Figure 13. Application of SSA to diurnal variation of $\text{CH}_3\text{O}_2\text{H}$ and HNO_3 . See Figure 8 and text for details.

Simulation of the clean troposphere was carried out initially using conditions from Logan (6). SSECHEM (see Chapter IV and Appendix B,C) generated all data for analysis. Implementation of a tropospheric model was done in two steps. We first used Euler's method to integrate the mechanism with the SSA made only for $O(^3P)$, $O(^1D)$ and CH_3O . This result was compared with an SSA-free integration using the routine of Gear (68) to check both for numerical accuracy and for errors in entering reactions, rate constants, boundary conditions, etc. The two approaches were in good agreement. In the next step, we evaluated the quantity $R_i/\Sigma P_i$ in equation 2-2 for all species diurnally under clean air condition (i.e., $NO=15$ ppt). Results for the most important species are shown in Figure 8 to 13. Except for deviations associated with sunrise and sunset, most species obey the SSA requirements quite well during the day and can be set as steady state for continuous run. However, the profiles of ratios for long-lived species, such as H_2O_2 , CH_3O_2H , HNO_3 & H_2CO , are quite different from other species. The negative diurnal SSRs for these species indicate non-equilibrium. Without a constant source for NO_x , all species have been washed out at night and never recovered during daytime. In contrast, when a constant NO_x source is included, H_2O_2 , CH_3O_2H , HNO_3 & H_2CO show a positive SSRs during daytime. Figure 14 shows the last three days' ratio data after 10 days' run. These species may be classified together due to similar precursors of sources based on their ratio profiles.

For instance, HO_2 is a primary source for H_2O_2 while CH_3O_2 is a primary source for $\text{CH}_3\text{O}_2\text{H}$ & H_2CO . However, the diurnal ratio for HNO_3 is quite different from other species. The investigation explored this difference due to strong dependence of HNO_3 on NO_2 which has an sharp increase at sunrise due to the immediate photolysis of NO_3 . An eleven-day diurnal run with different rainout constants (i.e., zero, lifetime 1 day, lifetime 10 days) demonstrated the influence of rainout on these long-lived species in the troposphere. Figure 15 shows that the ratio curve of the 10-day lifetime case of HNO_3 moved up and, eventually, reached equilibrium with the ratio at noon with zero rainout. The ratio curves of H_2O_2 , $\text{CH}_3\text{O}_2\text{H}$ & H_2CO also approached zero ratio but from above, not below (Figure 16,17,18, respectively). For all species, the curves with zero rainout are more like the curves of their precursors which deviate from zero only at sunrise & sunset. To examine this difference, we investigate how the change in rainout reflects on the net rates of HNO_3 . It is conceivable that the decrease in removal of HNO_3 by rainout will make the net rate less negative, consequently, the SSR (=rate/prod.) will be shifted to near zero. Contradictorily, the decrease in rainout constant for H_2O_2 , $\text{CH}_3\text{O}_2\text{H}$ & H_2CO caused the net rates of species to decline so that their SSRs approach to zero. From this contradiction, it is obvious that the ratio table not only tells one the validity of the SSA on the basis of magnitude of SSR, but also may reveal information on inherent

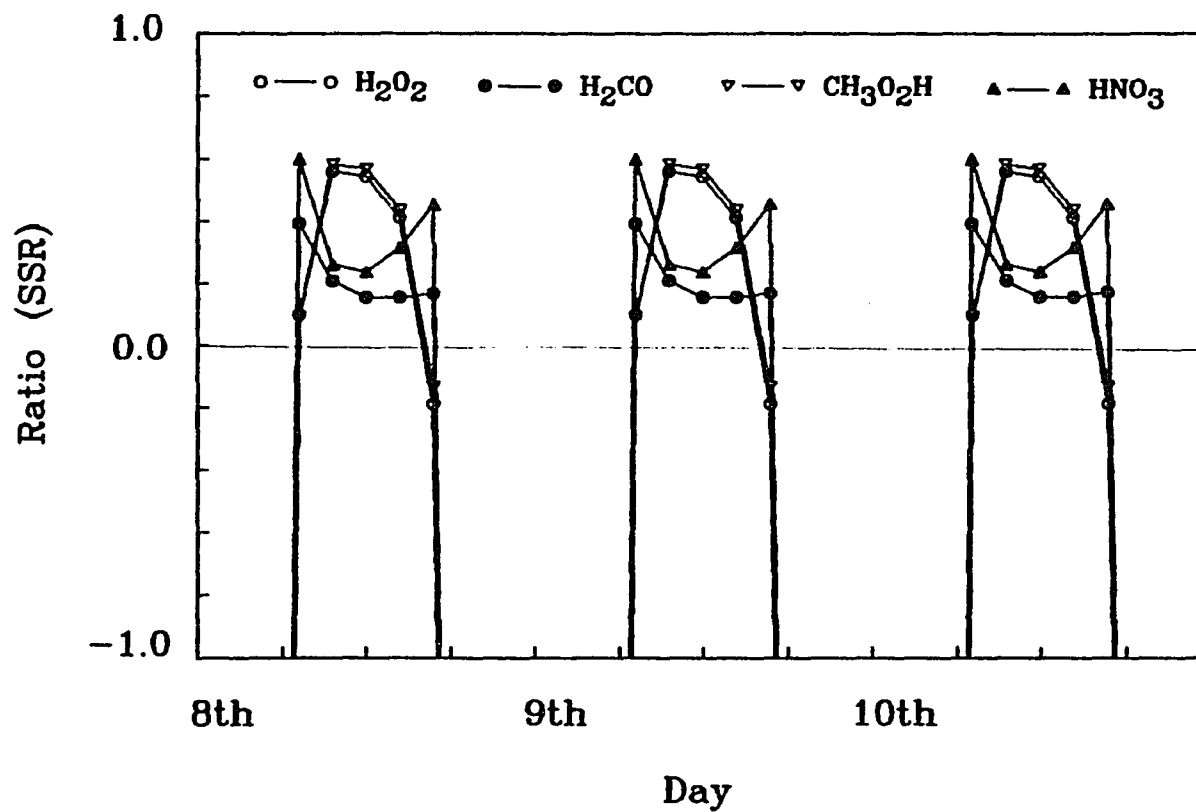


Figure 14. The last three days data from a 10 day run for species H_2O_2 , HNO_3 , $\text{CH}_3\text{O}_2\text{H}$ and H_2CO . Conditions are same as Figure 8 except the inclusion of constant NO_x source ($1 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$).

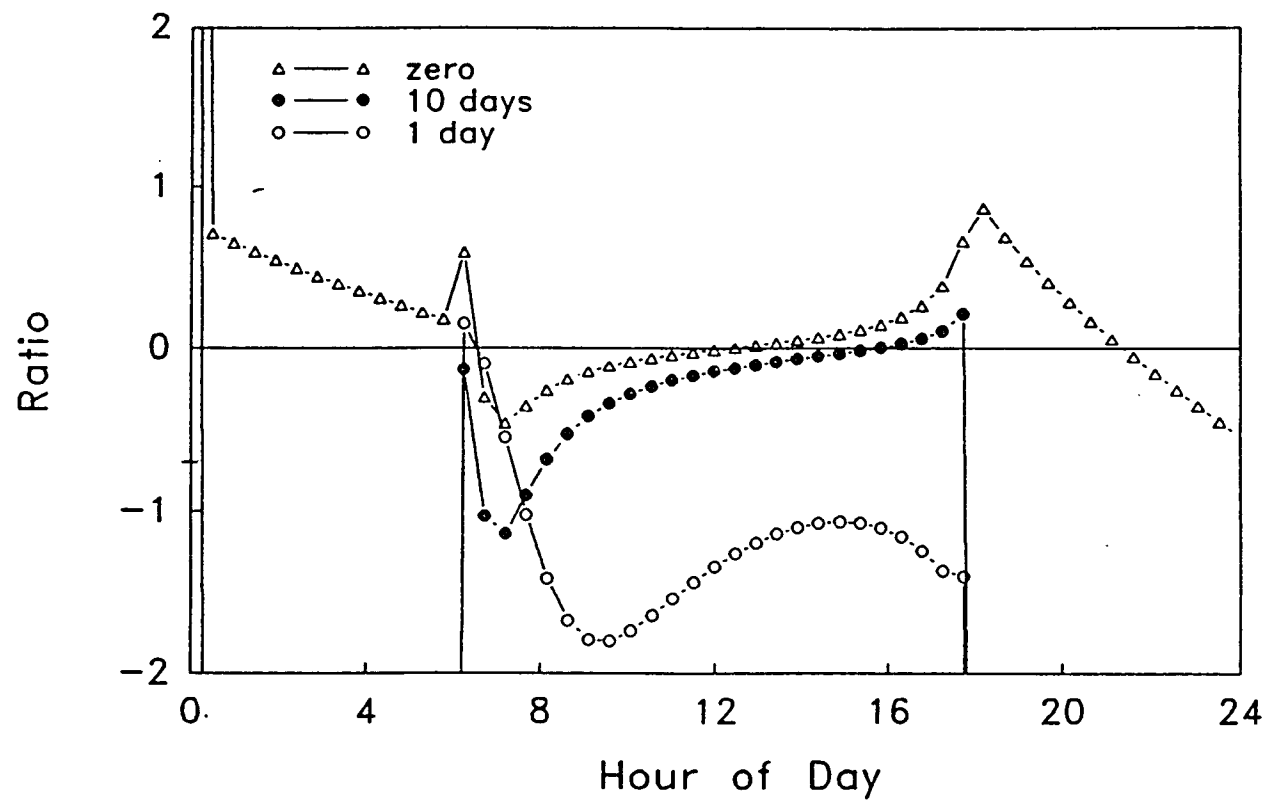


Figure 15. Diurnal SSR of HNO_3 . Conditions are same as Figure 8 except the inclusion of different rainout lifetime 1 day, 10 days and zero. The data given here are 30th day of 30-day run.

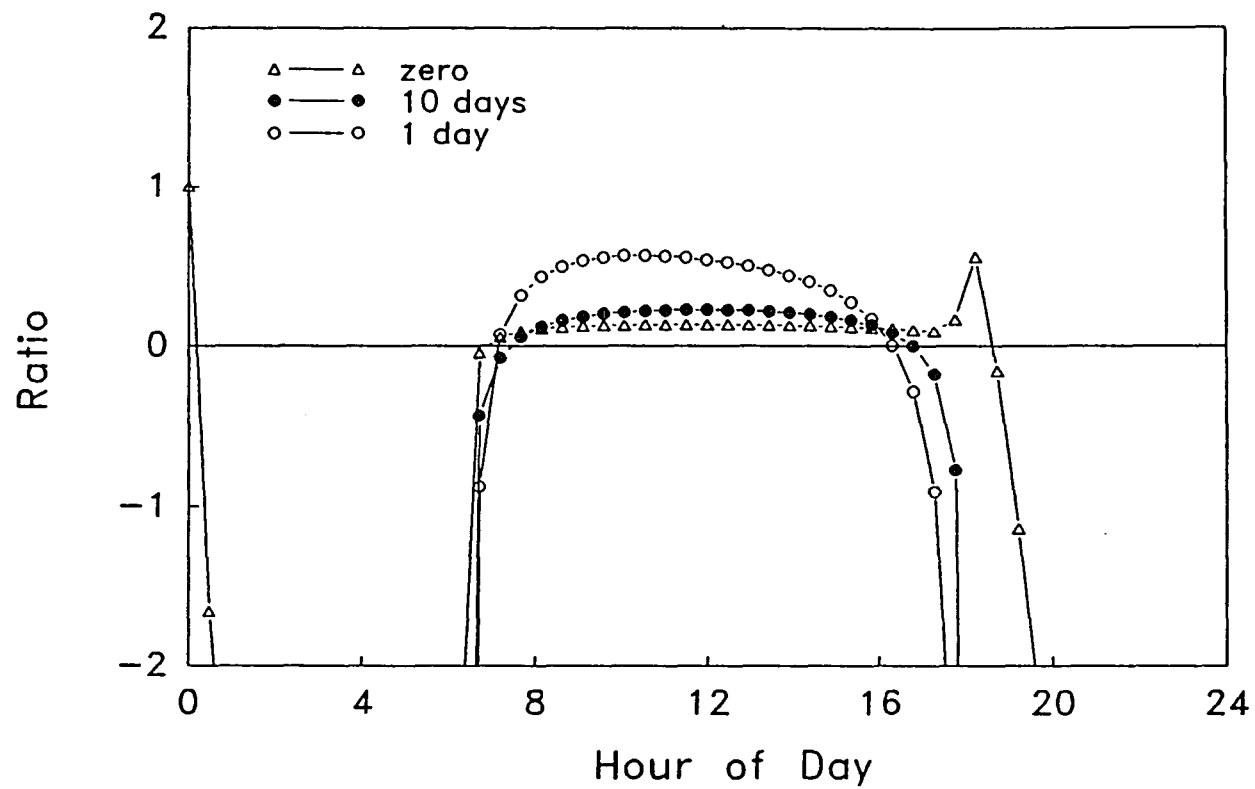


Figure 16. Diurnal SSR of H_2O_2 . Conditions are same as Figure 15.

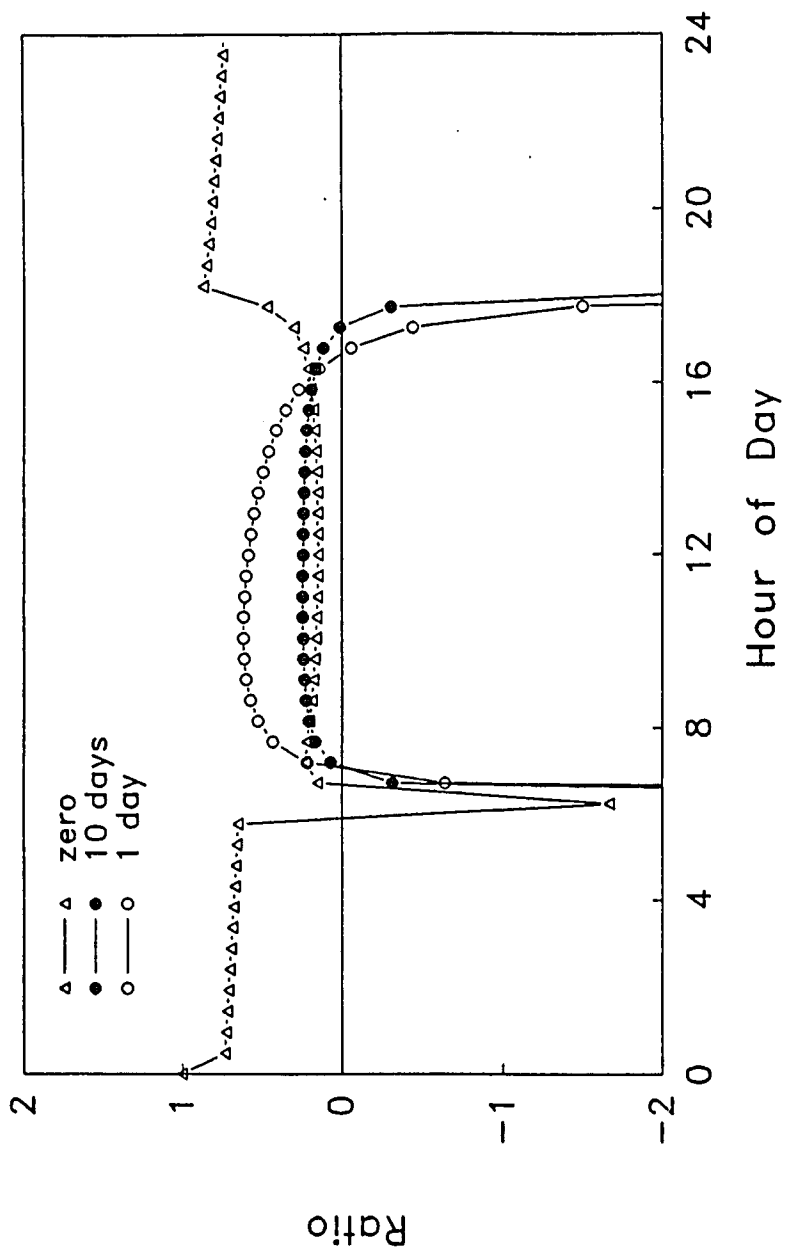


Figure 17. Diurnal SSR of $\text{CH}_3\text{O}_2\text{H}$. Conditions are same as Figure 15.

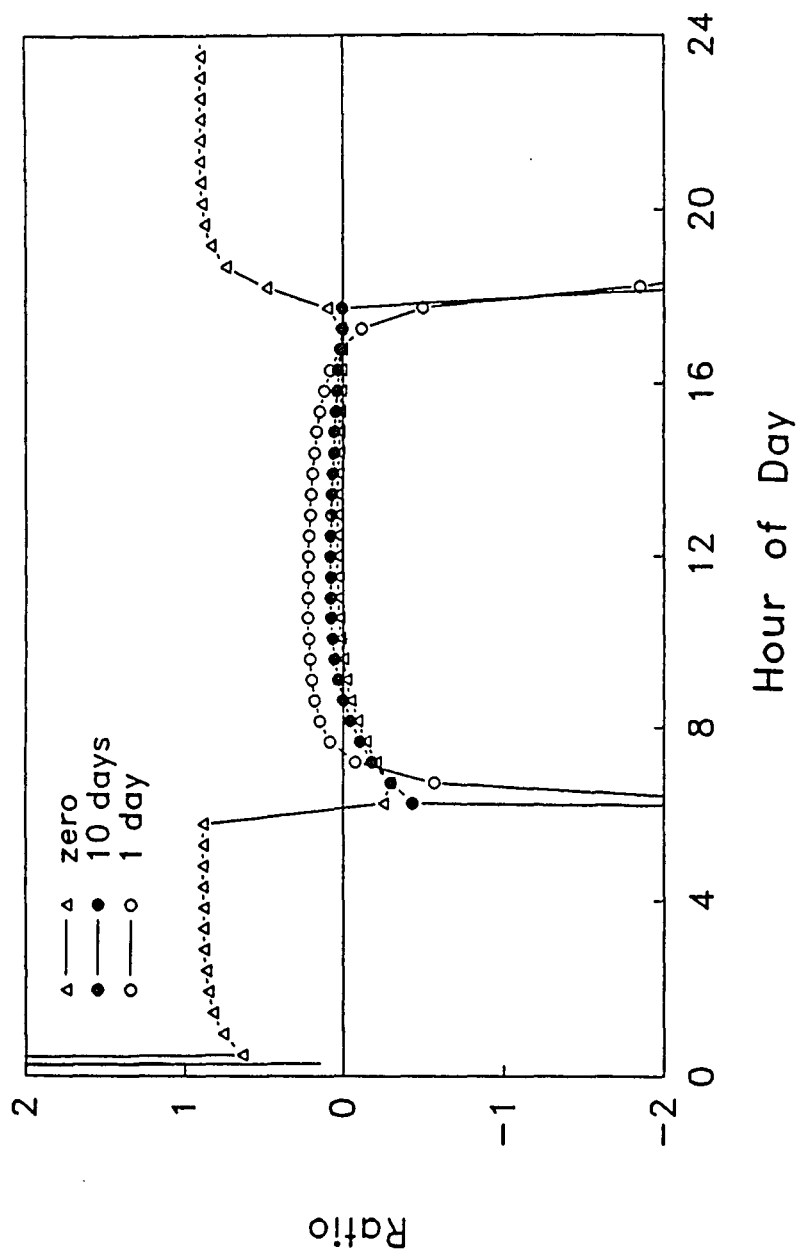


Figure 18. Diurnal SSR of CH_2O . Conditions are same as Figure 15.

positive or negative feedback existing in the troposphere. The importance of rainout process, which is shown by the variation of SSR, suggests deserts or areas that have been dried for a while are good choices for measuring the trace species in the troposphere. A summary of SSRs of species in clean air at noon is given in Table IV. Figure 19 shows the diurnal variation of species at ground level at equinox and noon for the clean troposphere.

MODELING OF CLEAN TROPOSPHERE BY PERTURBING $[\text{NO}_x]$

The study of perturbation from NO and investigation of the interplay between odd hydrogen and odd nitrogen chemistry are important in tropospheric chemistry. Modeling of the troposphere with varying NO_x concentration is accomplished by fixing different $[\text{NO}]$ and performing integration until the steady state is reached. The results are shown in Figure 20 & 21.

There are several interesting things that should be addressed here. First of all, we must understand the correlation existing among species and explore the information about HO_x . Secondly, we must figure out the unique nonlinearity of individual species vs. NO_x , especially at the inflection point.

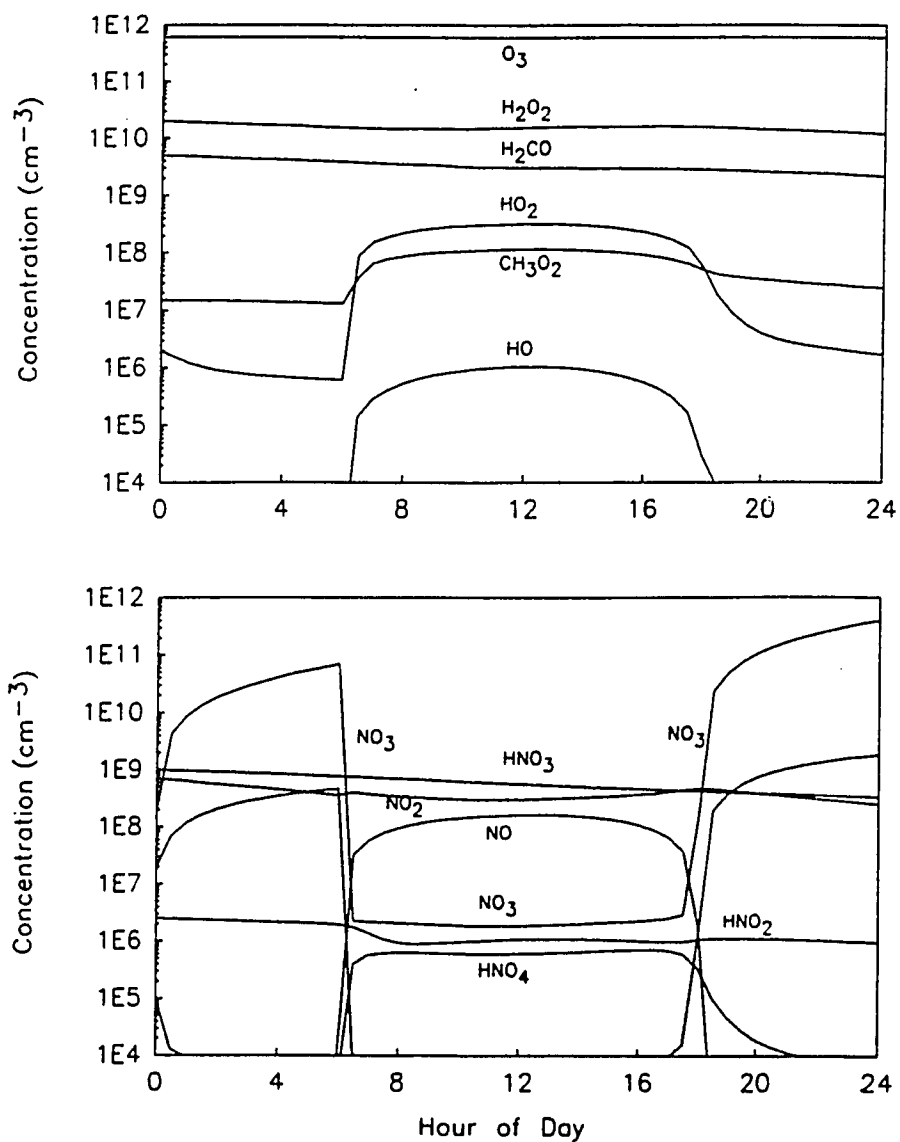


Figure 19. Diurnal variation of selected species. See Table I for mechanism. A sine wave is used for simulating light intensity. The lifetime of rainout is 1 day. Ozone deposition is zero and total $[\text{NO}_x]=50$ ppt. All data given here are 30th day of 30-day run. Conditions: clean air, 45°N latitude, equinox, ground level and variable ozone.

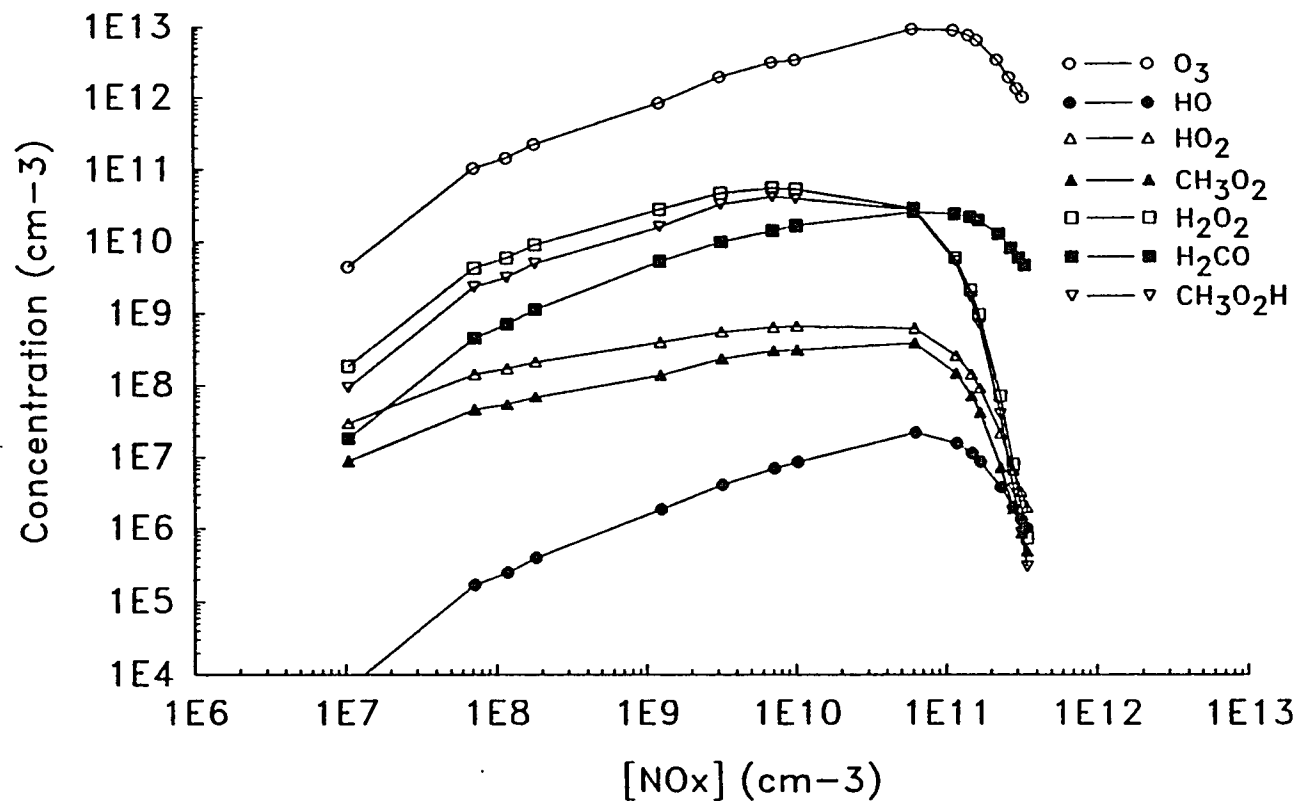


Figure 20. Variation of odd oxygen species concentration with [NO_x]. All data are noon values. Conditions are same as Figure 19. Each set of data at specific [NO_x] was obtained after 30 day run while NO was held constant. [NO_x] = [NO₂] + [NO].

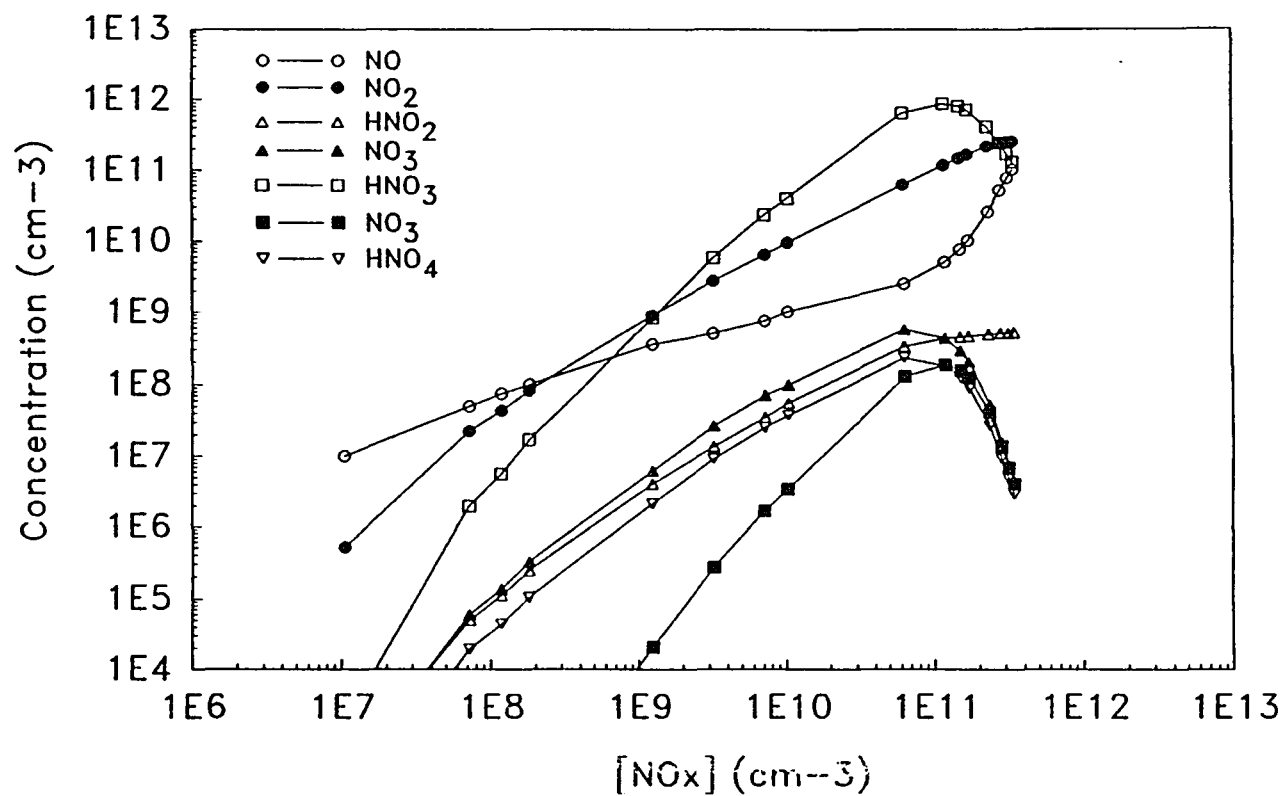
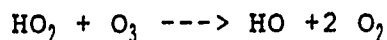
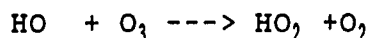


Figure 21. Variation of odd nitrogen species concentration with $[NO_x]$. All data are noon values. Conditions are same as Figure 19. Each set of data at specific $[NO_x]$ was obtained after 30 day run while NO was held constant. $[NO_x] = [NO_2] + [NO]$.

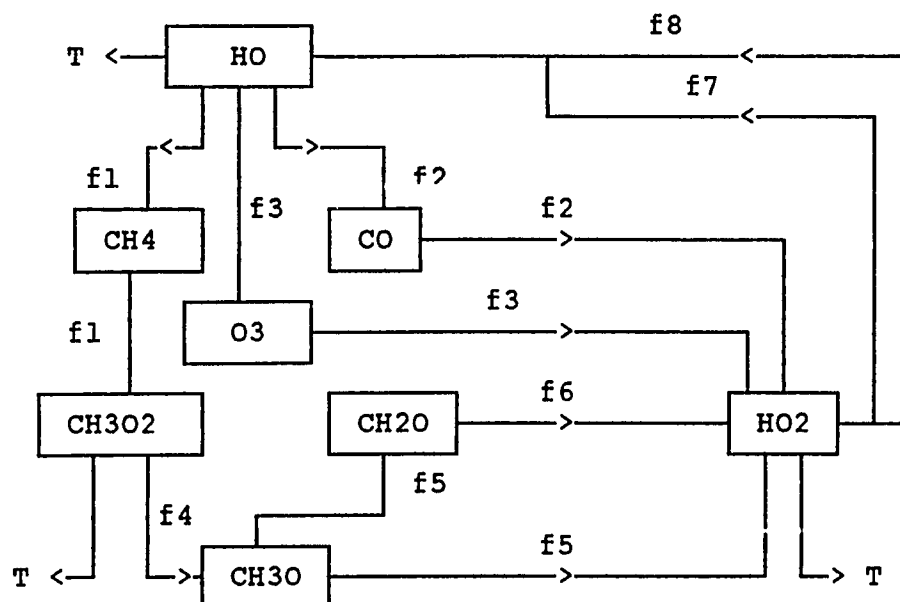
The study of HO_x interconversion will reveal the important reactions controlling HO_x chemistry.

In terms of loss of ozone, the reactions with HO_x are :



The second of these is more important than the first, since the conversion of HO to HO_2 is mainly by HO's reaction with CO and CH_4 rather than with ozone.

The recycling of HO_2 back to HO has been mentioned in various papers (4,5). Here, we followed Warneck's calculation (4); the paths of conversion between HO_x can be described as Figure 22, and it turns out that one molecule of HO consumed by reacting with CH_4 or CO will compensate for the loss of 0.37 molecules HO via the reactions of $\text{HO}_2 + \text{NO}$ and $\text{HO}_2 + \text{O}_3$, at $[\text{NO}_x]$ about 50 ppt (1×10^9 molecules cm^{-3}). Thus the net loss of HO is only 63%. Also, Ehhalt (70) claimed that the interconversion of HO_x is about 5 times greater than the destruction based on the removal of HO_x via reaction of HO with NO_2 . Figure 23 shows the regeneration percentage of HO. The peak is equivalent to $\text{NO}_x \approx 1.2 \times 10^9$ molecules cm^{-3} and the minimum occurs at $\text{NO}_x \approx 1.5 \times 10^{11}$. All relevant data are given in Table V & VI.



$f_5 = f_4 \times f_1$. $f_6 = 2 \times f_5 \times \%$ of $\text{H}_2\text{CO} + 2\text{O}_2 \rightarrow 2\text{HO}_2 + \text{CO}$ in total loss of H_2CO . $f_7 = (f_2 + f_3 + f_5 + f_6) \times \%$ of $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ in total loss of HO_2 . $f_8 = (f_2 + f_3 + f_5 + f_6) \times \%$ of $\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$ in total loss of HO_2 . T represents the termination reaction. f denotes the contribution of the specific reaction among the sink reactions for the species of interest.

This figure illustrates the reactions for HO_2 interconversion and calculate HO compensation via its loss and HO_2 reactions. Total compensation of HO (%) = $f_7 + f_8$. For example, at $[\text{NO}_2] = 1.052 \times 10^7$, the loss of HO due to $\text{HO} + \text{CH}_4$ reaction is about 19%, the contribution is $f_1 = 19\%$. Then, about 33.4% (f_4) CH_3O_2 loss produce CH_3O which generates one HO_2 and CH_2O . The 34.66% (f_6') CH_2O loss reproduce HO_2 . Therefore, the total HO_2 produced via the loss of $\text{HO} + \text{CH}_4$ is equal to the sum of $f_1 \times f_4 + f_1 \times f_4 \times f_6'$ or $f_5 + f_6$. Two other paths are f_2 & f_3 . From HO_2 to HO, two reactions dominate the conversion, i.e. $f_7 = (f_2 + f_3 + f_5 + f_6) \times f_7'$ and $f_8 = (f_2 + f_3 + f_5 + f_6) \times f_8'$.

$$f_5 = f_1 \times f_4 = 19 \times 0.334 = 6.34$$

$$f_6 = 2 \times f_5 \times f_6' = 2 \times 6.34 \times 0.3466 = 4.39$$

$$f_7 = (f_2 + f_3 + f_5 + f_6) \times f_7' = (75 + 0.02 + 6.34 + 4.39) \times 0.2155 = 18.50$$

$$f_8 = (f_2 + f_3 + f_5 + f_6) \times f_8' = (75 + 0.02 + 6.34 + 4.39) \times 0.018 = 1.54$$

$$\text{HO} = f_7 + f_8 = 18.5 + 1.54 = 20.04$$

All fraction reactions is shown in Table VI and data in Table V.

Figure 22. The paths of interconversion between HO_2 .

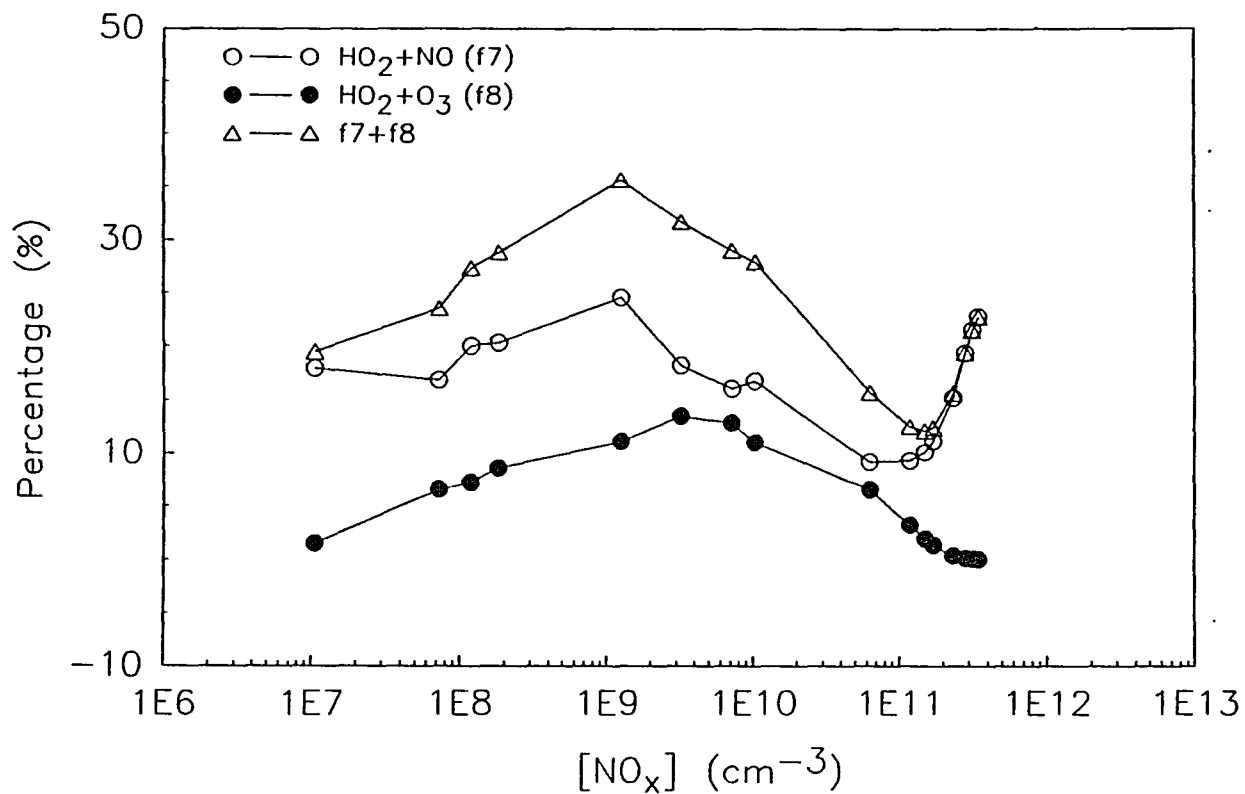


Figure 23. Variation of percentage of interconversion for HO₂ with [NO_x]. Conditions are same as Figure 20. The paths and reactions involved in the calculation can be found in Figure 22 and Table V & VI. Here the percentage (%) of f7 (f8) indicates the contribution of regeneration of HO from the reaction HO₂+NO (HO₂+O₃) and the percentage of the sum of f7+f8 indicates total compensation HO relative to its loss.

TABLE V
FRACTIONAL DATA FOR REGENERATING HO FROM HO₂
VARIES WITH NO_x (%)

| NO _x | f1 | f2 | f3 | f4 | f5 | f6' |
|-----------------|-------|-------|-------|-------|------|-------|
| 1.052e7 | 19.00 | 75.00 | 0.02 | 33.40 | 6.34 | 34.66 |
| 7.235e7 | 18.70 | 74.10 | 0.40 | 34.70 | 6.49 | 33.79 |
| 1.183e8 | 18.60 | 73.70 | 0.56 | 39.20 | 7.29 | 33.38 |
| 1.825e8 | 18.40 | 72.90 | 0.86 | 40.70 | 7.50 | 32.63 |
| 1.244e9 | 17.10 | 67.60 | 2.98 | 54.50 | 9.30 | 26.82 |
| 3.230e9 | 15.40 | 61.20 | 6.29 | 55.80 | 8.62 | 20.97 |
| 7.152e9 | 14.20 | 56.00 | 9.33 | 61.60 | 8.71 | 16.41 |
| 1.032e10 | 13.70 | 54.40 | 9.90 | 67.20 | 9.22 | 14.73 |
| 6.325e10 | 9.49 | 37.60 | 18.64 | 84.30 | 8.01 | 7.83 |
| 1.194e11 | 8.26 | 32.70 | 15.60 | 96.20 | 7.94 | 10.16 |
| 1.507e11 | 7.86 | 31.10 | 12.52 | 98.60 | 7.75 | 12.64 |
| 1.718e11 | 7.65 | 30.30 | 10.38 | 100.0 | 7.75 | 14.68 |
| 2.343e11 | 7.12 | 28.20 | 5.08 | 99.90 | 7.11 | 21.77 |
| 2.824e11 | 6.74 | 26.70 | 2.69 | 100.0 | 6.74 | 26.51 |
| 3.163e11 | 6.49 | 25.70 | 1.80 | 100.0 | 6.49 | 28.70 |
| 3.462e11 | 6.26 | 24.80 | 1.33 | 100.0 | 6.27 | 29.97 |

| NO _x | f6 | f7' | f7 | f8' | f8 | HO |
|-----------------|------|-------|-------|-------|-------|-------|
| 1.052e7 | 4.39 | 21.55 | 18.50 | 1.80 | 1.54 | 20.00 |
| 7.235e7 | 4.39 | 20.28 | 17.30 | 7.94 | 6.78 | 24.10 |
| 1.183e8 | 4.86 | 23.85 | 20.60 | 8.62 | 7.45 | 28.00 |
| 1.825e8 | 4.89 | 24.22 | 20.90 | 10.22 | 8.81 | 29.70 |
| 1.244e9 | 4.99 | 29.76 | 25.20 | 13.50 | 11.50 | 36.70 |
| 3.230e9 | 3.62 | 23.39 | 18.60 | 17.32 | 13.80 | 32.40 |
| 7.152e9 | 2.86 | 21.32 | 16.40 | 17.03 | 13.10 | 29.50 |
| 1.032e10 | 2.72 | 22.49 | 17.10 | 14.75 | 11.20 | 28.40 |
| 6.325e10 | 1.25 | 14.10 | 9.24 | 10.07 | 6.60 | 15.80 |
| 1.194e11 | 1.61 | 16.27 | 9.41 | 5.59 | 3.23 | 12.60 |
| 1.507e11 | 1.96 | 19.35 | 10.30 | 3.74 | 1.99 | 12.30 |
| 1.718e11 | 2.27 | 22.31 | 11.30 | 2.76 | 1.40 | 12.70 |
| 2.343e11 | 3.10 | 36.26 | 15.80 | 0.94 | 0.41 | 16.20 |
| 2.824e11 | 3.58 | 50.80 | 20.20 | 0.37 | 0.15 | 20.30 |
| 3.163e11 | 3.72 | 59.93 | 22.60 | 0.20 | 0.08 | 22.70 |
| 3.462e11 | 3.76 | 66.18 | 23.90 | 0.13 | 0.05 | 24.00 |

See notes of Figure 22.

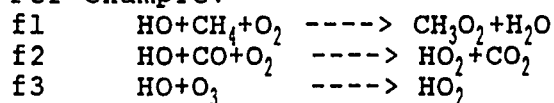
TABLE VI
FRACTIONAL REACTIONS

| code | reaction |
|----------|---|
| f1 | HO + CH ₄ |
| f2 | HO + CO |
| f3 | HO + O ₃ |
| f4 (sum) | CH ₃ O ₂ + NO |
| | CH ₃ O ₂ + CH ₃ O ₂ |
| f5 | CH ₃ O + O ₂ |
| f6 | CH ₂ O + hν |
| f7 | HO ₂ + NO |
| f8 | HO ₂ + O ₃ |

Refer to Table I for chemical mechanism.

Refer to Figure 22 for the detail of reaction path.

For example:



The data of production and removal rates for HO₂ & HO have been graphed as Figure 24 to 27. Figure 25 indicates the important removal steps via HO₂ reactions. Based on our analysis, the peak of HO₂ conversion corresponds to the point at which the reactions of HO₂ + O₃ and HO₂ + NO₂ meet. This can be interpreted that the important conversion reaction from HO₂ to HO (R8) is overcome by the non-HO-productive reaction of HO₂ (R37), resulting in the decline of HO₂ interconversion. Also, from the Figure 27, the apparent evidence for the

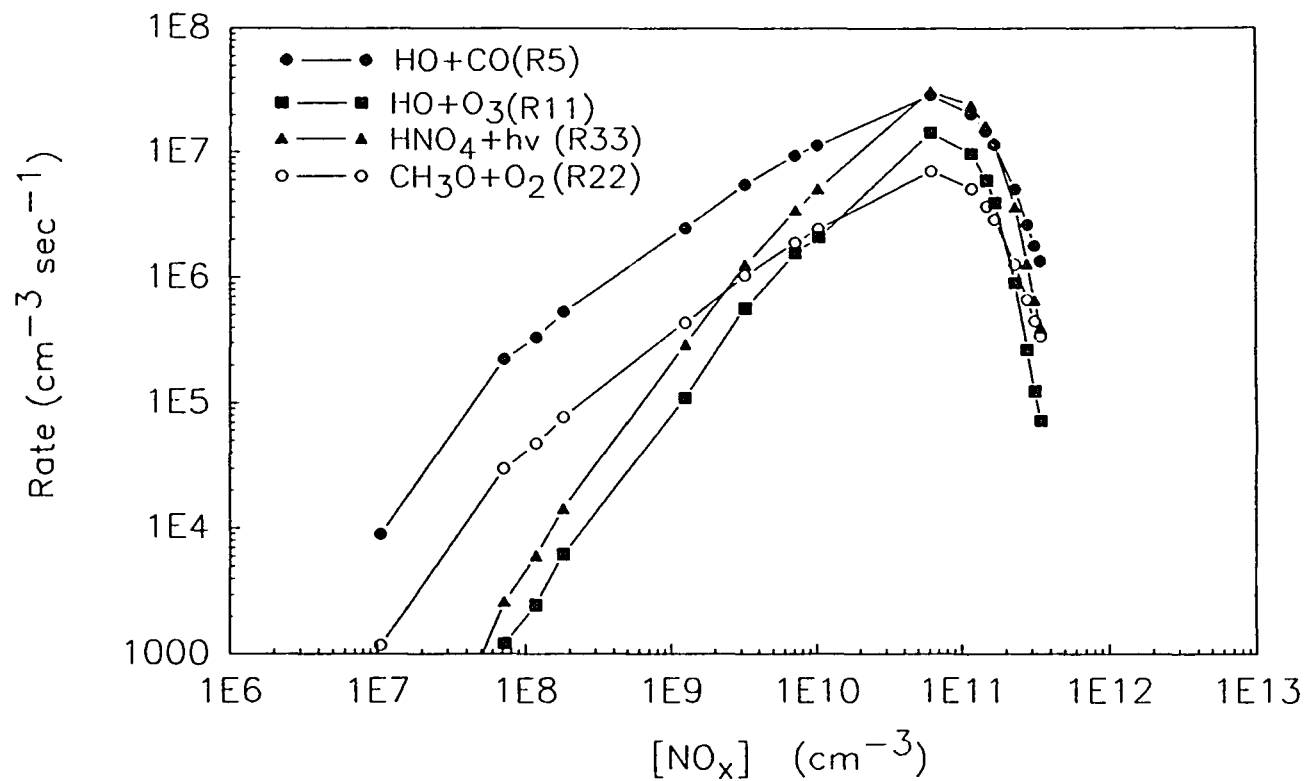


Figure 24. Variation of selected source rates for $[\text{HO}_2]$ with $[\text{NO}_x]$. Conditions are same as Figure 19.

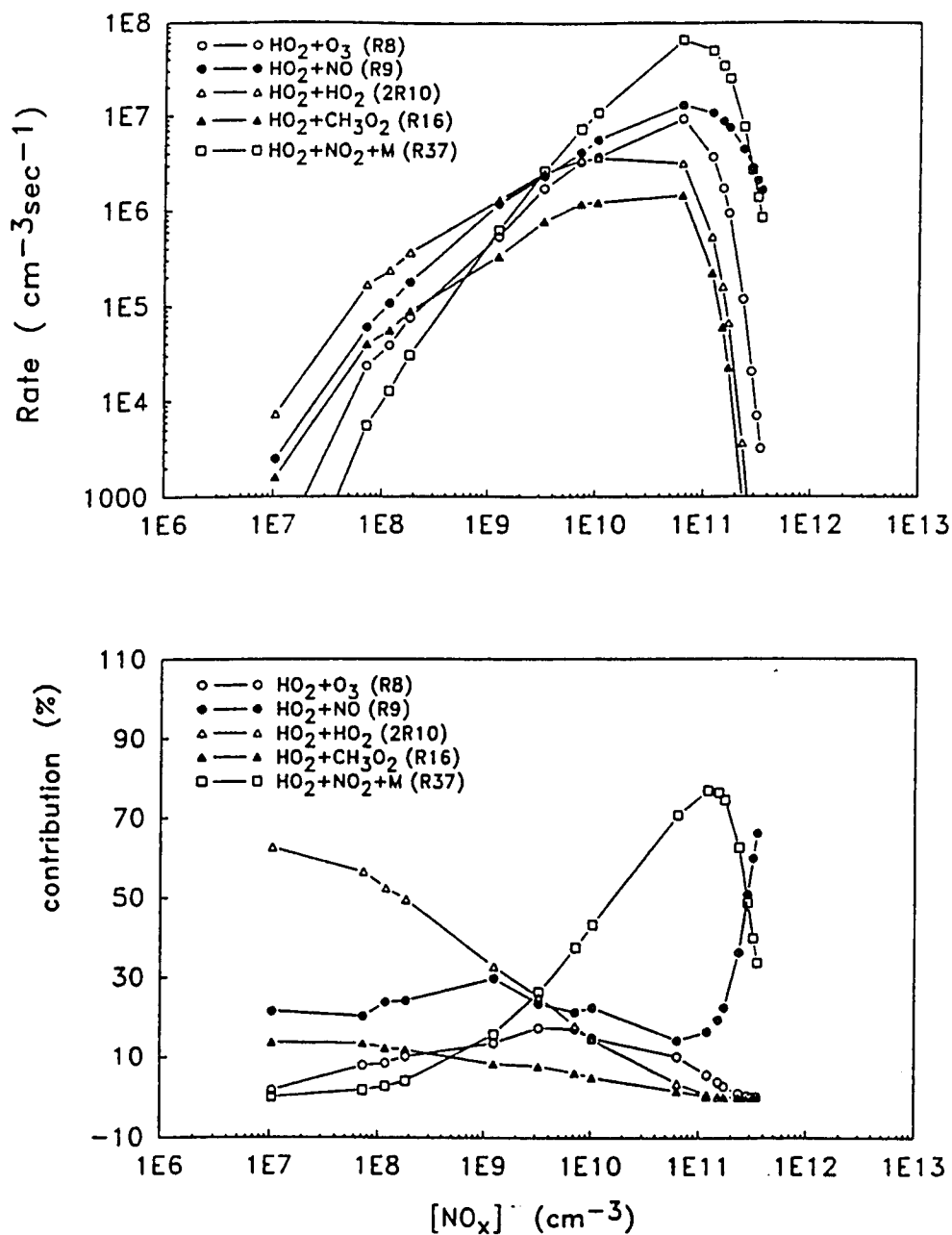


Figure 25. Selected Removal Rates of $[\text{HO}_2]$ vs. $[\text{NO}_x]$. The top figure shows how the values of each rate vary with NO_x , and the bottom figure shows the relative percentage of each rate vs. NO_x . Conditions are same as Figure 19.

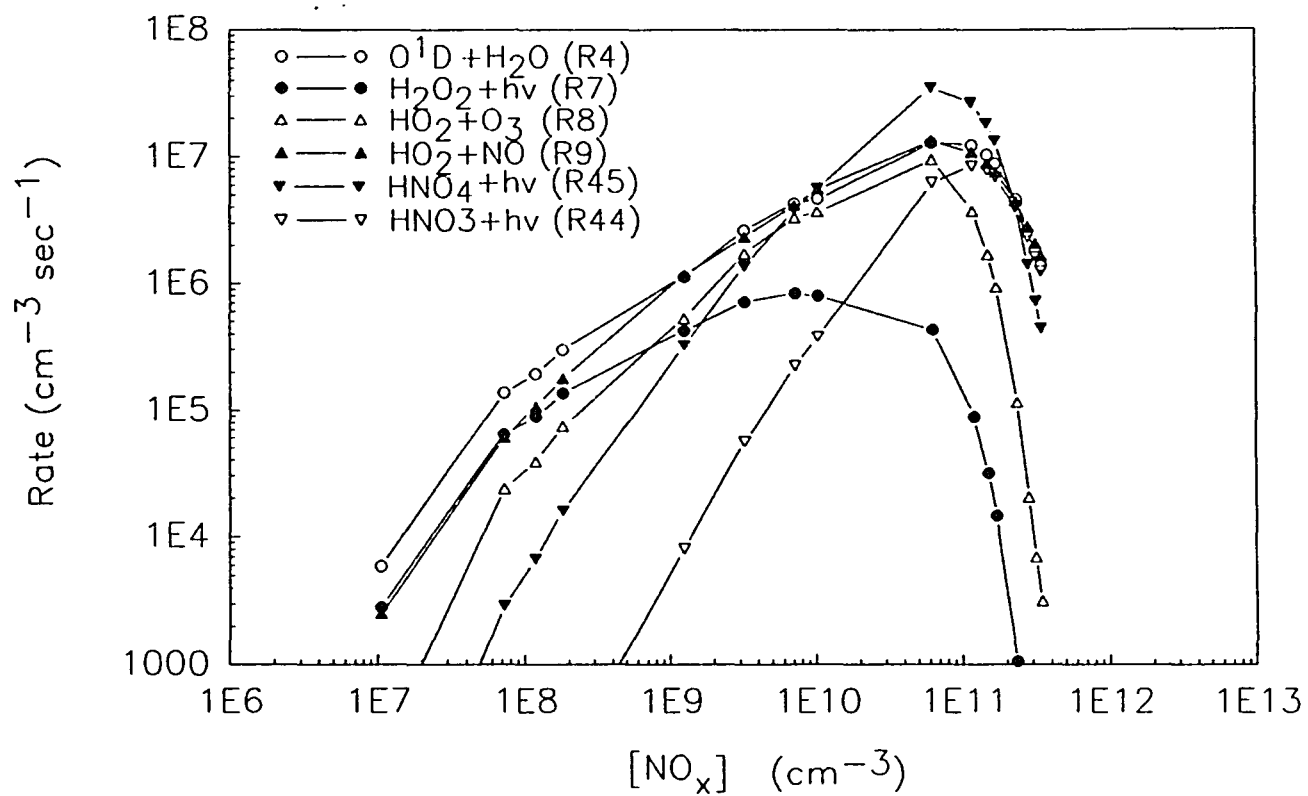


Figure 26. Variation of selected source rates for $[HO]$ with $[NO_x]$. Conditions are same as Figure 19.

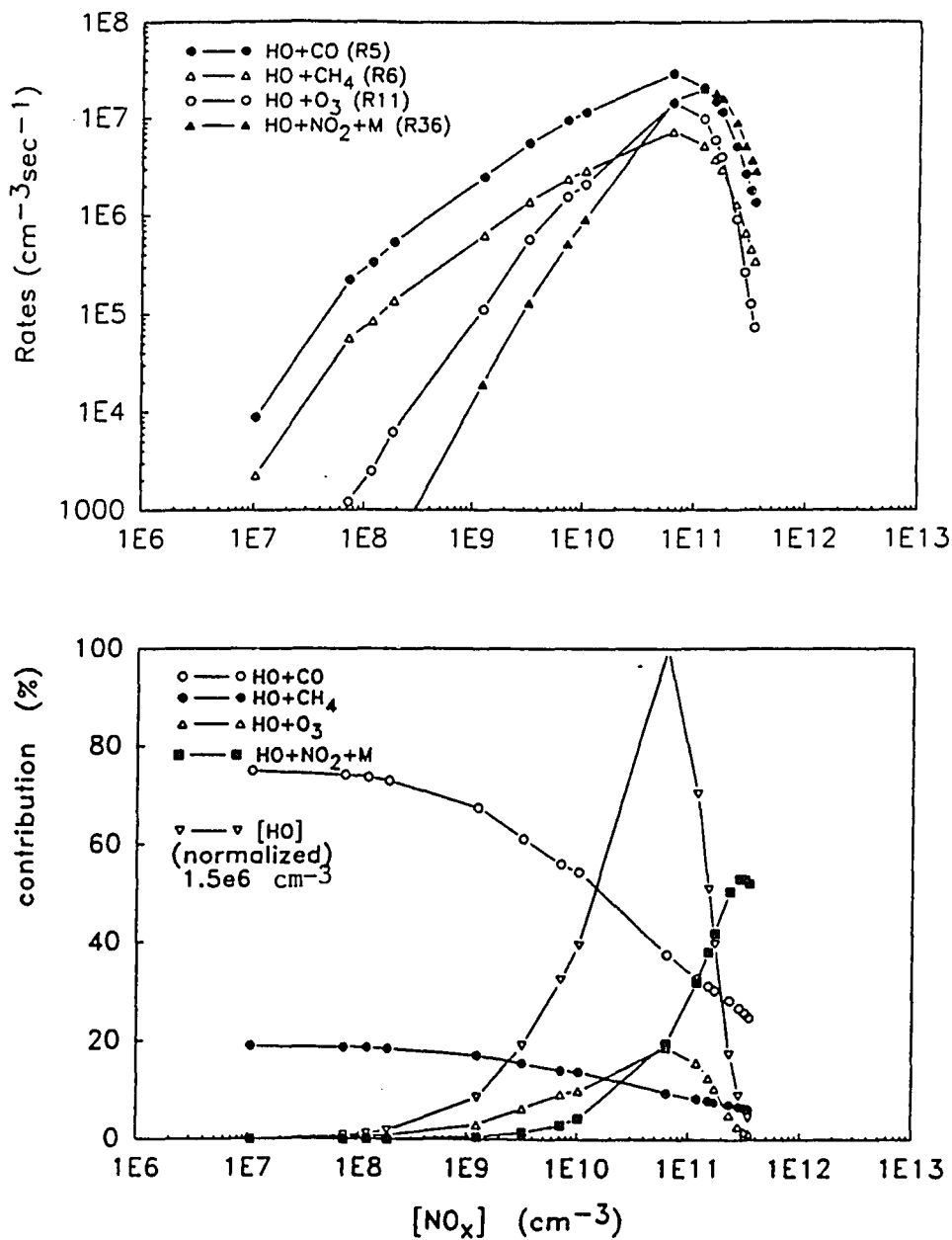


Figure 27. Selected Removal Rates of $[\text{HO}]$ vs. $[\text{NO}_x]$. The top figure shows the values of each rate vs. NO_x , and the bottom figure shows the relative percentage of each rate vs. NO_x . Also, normalized $[\text{HO}]$ has been plotted for comparison. Conditions are same as Figure 19.

minimum in Figure 23 is shown to be due to the reaction of HO with NO_2 to form HNO_3 , dominating the reaction of HO with CO. The more stable HNO_3 is usually removed by wet deposition, thus, there is no long-term positive feedback for HO_2 .

The investigation of nonlinearity among trace gases in the troposphere is a longtime interest for both modelers and experimenters. In the Lin et al. (71) and Liu et al. (72) papers, they revealed the nonlinearity of ozone production with respect to NO_x and NMHC (non-methane hydrocarbon). Although our study eliminates the impact from NMHC, for the time being, the above examination clearly has disclosed the influence from perturbing NO_x alone. In the absence of NMHC, the major NO_x losses during daytime are through the reactions (we exclude PAN formation since it requires NMHC)



Here, the most interesting subject is the study of inflection points at which most species' concentrations start to decline after their maximum has been reached. These phenomena happen around the region of $1 \text{ ppb} < \text{NO}_x < 4 \text{ ppb}$. NO_x is known as a precursor of ozone production and of tropospheric chemistry driven by the oxidizing ability of nitrogen oxide. According to Stewart (73), this sort of non-linear behavior is caused by the scavenging of odd hydrogen radicals by their reaction with odd nitrogen and the consequent decrease in effectiveness of the methane oxidation

chain, resulting in a substantial ozone decrease and the removal of NO_2 , which is a primary source for formation of ozone, by NO_2 's reaction with OH to form HNO_3 . White (74) interpreted the nonlinearity by the reason that NO_2 , NO and O_3 are controlled by PSS (i.e., NO_2 must increase with NO_1 as long as O_3 does. see Figure 28), and due to the interdiction of the photochemical chain by $\text{HO} + \text{NO}_2$, the NO_2 concentration cannot continue to rise indefinitely without reducing the O_3 yield from O_3 photolysis below break-even. Logan (6) explained that this behavior reflects the increasing importance of reaction R36 as a sink for odd hydrogen. With the investigation of the relative strength of removal of HO, we have found that when $\text{HO} + \text{O}_3$ and $\text{HO} + \text{NO}_2 + \text{M}$ cross over, $[\text{HO}]$ has reached its peak (Figure 27).

Furthermore, we have found that where the reactions of $\text{HO}_2 + \text{NO}$ (R9) and $\text{HO} + \text{NO}_2 + \text{M}$ (R36) cross at $\text{NO}_1 = 2.5$ ppb, all species except H_2CO , HNO_2 , HNO_3 , NO_2 , NO have reached their summits (Figures 20 & 21). This interesting phenomenon is illustrated in Figure 27 and can be easily explained. The former is a governing reaction for converting NO_2 , which is a primary source for ozone, from NO. In other words, the ozone concentration will continuously increase until the latter reaction surpasses the former one. With respect to the link between NO_1 and HO_1 , the dominance of $\text{HO} + \text{NO}_2 + \text{M}$ over either $\text{HO}_2 + \text{NO}$ or $\text{HO} + \text{O}_3$ indicates that the role HO_1 plays is no longer productive but destructive of ozone. The analysis

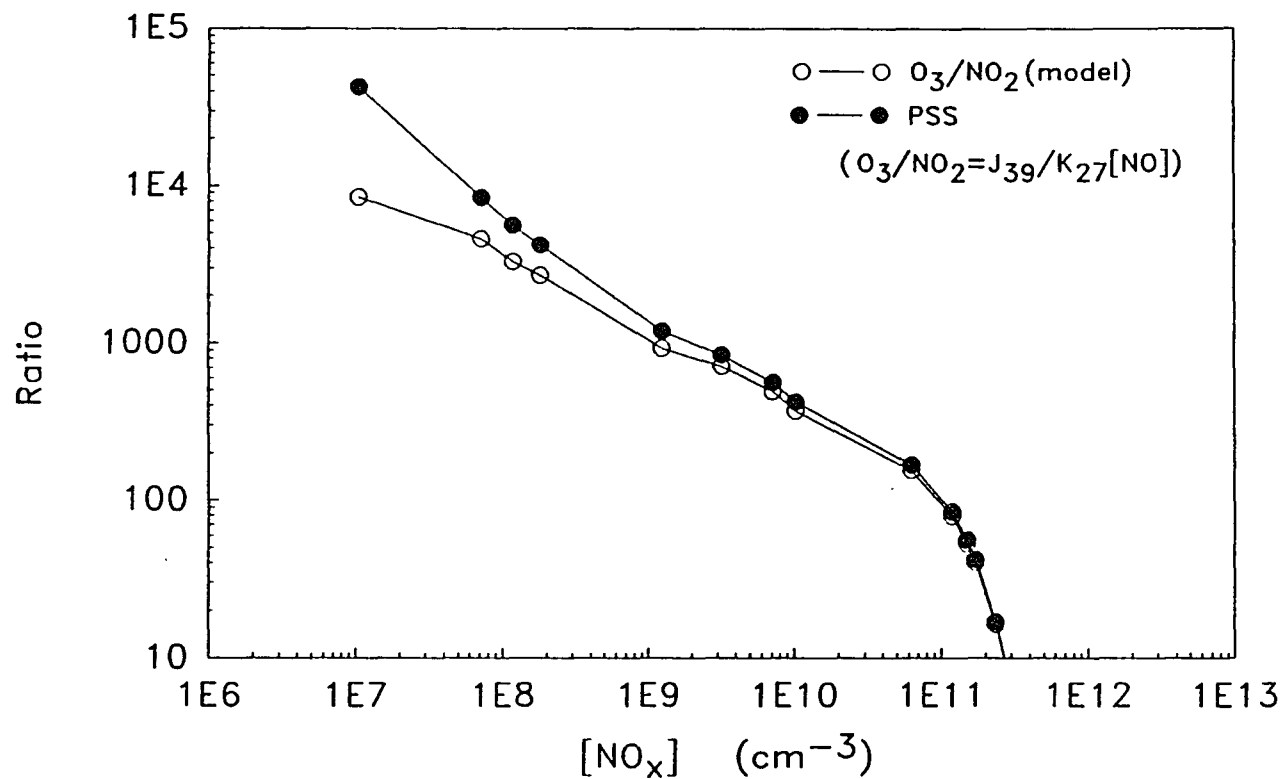


Figure 28. Variation of the ratio of ozone to nitrogen dioxide with [NO_x], comparison of numerical integration with photostationary state. Conditions are same as Figure 20.

confirms that HNO_3 is real sink of HO_x . It is realized that the decreasing conversion of HO_x causes the fast consumption of HO_2 , which plays an important role in the formation of ozone. Here, it is clear that the ratio of HO_2 to HO can be calculated, and it depends upon the ratio of $k_{11}[\text{O}_3]$ to $k_9[\text{NO}]$ at the inflection point, due to the fact the two reactions R9 & R11 meet (Figure 29). i.e., $\text{HO}_2/\text{HO} = 30$. Furthermore, once the ratio of $\text{HO} + \text{CO}$ to $\text{HO} + \text{NO}_2$ is equal to unity, all species except NO and NO_2 declined even further. The extracted data show that the dominant sink of HO depends on reactions with CO and CH_4 until the concentration of NO_x reaches about 4 ppb, then the reaction with NO_2 becomes the major sink of HO (Figure 27). At this point, one third of the removal of HO is caused by reacting with CO , one third is caused by reacting with NO_2 , and the last one third is caused by reacting with other species. Note that the importance of HO and HO_2 in odd oxygen photochemistry is equivalent to the importance of HNO_3 and HNO_4 in odd nitrogen photochemistry. The increasing nitrogen oxide enhances the role of HNO_3 and HNO_4 as sinks for HO_x .

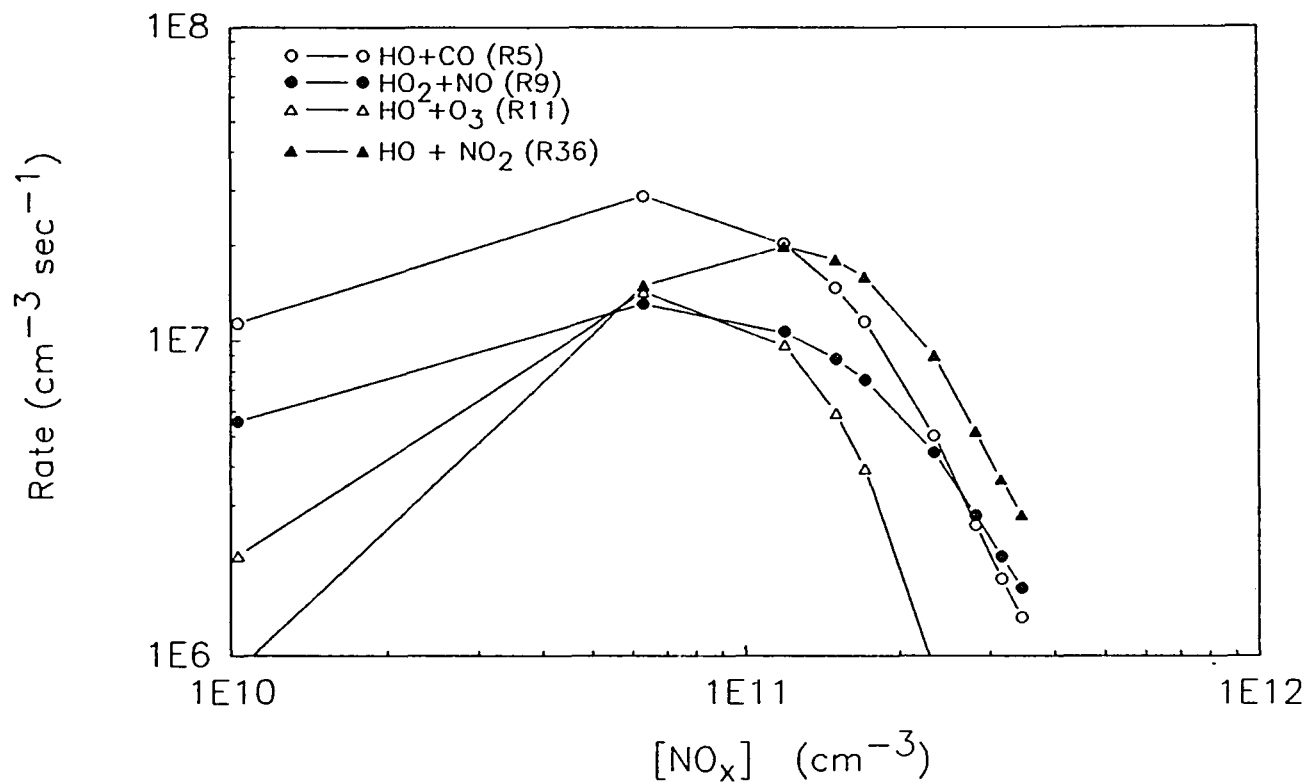


Figure 29. Illustration of how rate 36 dominates over rate 5, 9 & 11 as $[NO_x]$ increases. Rate 36 starts to outweigh rates 9 & 11 about $[NO_x] = 6\text{e}10$ and surpasses rate 5 when $[NO_x] > 1.5\text{e}11$.

CHAPTER VI

DEVELOPMENT OF SSA-BASED EQUATIONS

INTRODUCTION

The basic idea of all computer programs has been described in chapter IV & V. The goals of computer modeling here are reemphasized again. That are (a) to seek valid simplicity in the complex system. (b) to link any cause and effect in terms of specific species of interest. (c) to benefit the experimenter by providing insight and simple but reliable equations to understand the interplay in the tropospheric chemistry.

SSA EQUATIONS FOR HO_x IN CLEAN AIR

The clean air mechanism (Table I) has been taken as an example to illustrate the idea of a computer experiment. Since focusing on HO_x is our interest, the details of how to derive the equations of HO and HO_2 will be described. Some rules are listed as follows:

1. Follow the order of SSR ratio, taking the smallest one first and so on.
2. Minimize the involvement of the odd nitrogen compounds in the equation.
3. Avoid the mixing of HO with HO_2 in one equation so

that a pair of simultaneous equations need not be solved.

4. The resultant equations should be valid over the entire clean region of troposphere ($\text{NMHC}=0$ and $\text{NO}_x < 1$ ppb).

5. Seek the simplest form of equations.

6. All species left in the final equations should be measurable according to current techniques.

The investigation of the mechanism started with HO_2 . The reason is that HO_2 is believed to be more stable than HO and the concentration is about two orders of magnitude higher; from this information, we can deduce that it should have fewer dependent variables in terms of HO_2 than in terms of HO . In the region where $[\text{NO}_x] < 1$ ppb, the procedures have been implemented as follows. The simple criterion for ignoring all reactions which involved NO_x is used. The reason not involving NO_x is due to all NO_x terms are insignificant or having inherent cancellation which is described as follows. Comparing the SSR ratios for all species at noon, we can be sure that it is feasible to apply steady state for those species with small ratio. From Table III, the descending order of ratios shows $\text{O}(^1\text{D})$ is the best steady state species with insignificant error. Similarly, the steady state assumption is valid for all species except H_2CO , H_2O_2 , $\text{CH}_3\text{O}_2\text{H}$ & HNO_3 . If we consider all NO_x ($=\text{NO}+\text{NO}_2+\text{NO}_3+\text{N}_2\text{O}_5+\text{HNO}_2+\text{HNO}_4+\text{HNO}_3$) species only, with a factor of 2 for N_2O_5 , i.e., $d\text{NO}/dt+d\text{NO}_2/dt+d\text{NO}_3/dt+d\text{HNO}_2/dt+d\text{HNO}_4/dt+d\text{HNO}_3/dt+2(d\text{N}_2\text{O}_5/dt)$, then it ends up that the sum of rainout of HNO_2 , HNO_3 & HNO_4 is equal to zero (i.e., $\text{R46}+\text{R47}+\text{R48}=0$).

This results from the lack of NO_x sources in the mechanism, such sources, if included, would then equal the depositional processes for a net nitrogen balance. Since the goal is to investigate local steady-state chemistry, we ignore all NO_x species while dealing with clean air. We went through different combinations. It turned out that the combination of four species HO , HO_2 , CH_3O & CH_3O_2 is the best choice. Appendix B list all data with different nitric oxide concentration and the details of manipulation are described as an example in the Appendix C.

$$\begin{aligned} d[\text{HO}]/dt = & 2R_4 + R_8 + R_9 + 2R_7 + R_{18} - R_{17} - R_5 - R_6 \\ & - R_{11} - R_{12} - R_{14} - R_{15} \end{aligned}$$

$$\begin{aligned} d[\text{HO}_2]/dt = & R_5 + R_{11} + R_{12} + R_{14} + R_{15} + R_{22} + 2R_{23} \\ & - R_8 - R_9 - 2R_{10} - R_{16} \end{aligned}$$

$$d[\text{CH}_3\text{O}]/dt = R_{18} + 2R_{19} + R_{21} - R_{22}$$

$$d[\text{CH}_3\text{O}_2]/dt = R_6 + R_{17} - R_{16} - 2R_{19} - R_{21}$$

By applying the steady state assumption, the net rate of the sum of HO , HO_2 , CH_3O_2 and CH_3O is obtained by summing the above equations, yielding the following formula after canceling.

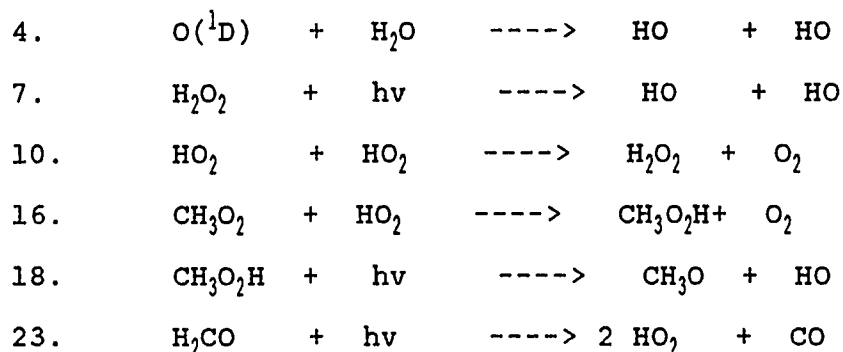
$$2R_4 + 2R_7 + 2R_{18} + 2R_{23} - 2R_{10} - 2R_{16} = 0;$$

or

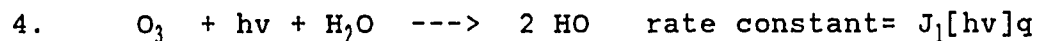
$$R_4 + R_7 + R_{18} + R_{23} = R_{10} + R_{16}$$

HO₂ Equation

Two questions arise: can these six reactions represent HO₂ chemistry at low NO, and it is possible to reduce the equation further. Check the six reactions on the left hand side:



The reaction 4 should be replaced by the following reaction if the steady state assumption is applied to O(¹D).



where q is the quantum yield for HO formation from O(¹D)

All work mentioned above can be done easily through the program SSEGEN whose purpose is allowing the user to generate useful steady state equations based on the steady state data. Some criteria used are :

1. The inherent cancellation will reduce the complexity.
2. The rule of thumb for dropping rates is on the basis of their relative contributions of rates in the system and the relationships among them.
3. The rule of choice of species depends on the measurability and reliability of atmospheric concentration data on that species.

4. Alternatively, the seeking of an inequality indicating upper or lower limits is essential if equality doesn't exist.

Using SSEGEN, the combination of constituents HO, HO₂, CH₃O, CH₃O₂ results in data Table VII obtained at [NO] = 1e7 molecules cm⁻³. Other data tables with different [NO] are in Appendix B. The last two columns show the relative importance of individual reactions. Table VIII shows the desired steady state equation for HO₂. As an example of the further irreducibility of this equation, the deletion of R4 alone leads to an error around -40% in terms of [HO₂]. On the other hand, c%, which represents the cumulative error, shows almost no increase in error if we only keep the top 6 reactions and drop all the rest. The data and resultant HO₂ equation after dropping terms can be found in Table IX and X.

Figures 30 & 31 show selected source and removal rates for HO₂ based on the results after combining the four species HO, HO₂, CH₃O & CH₃O₂. Figure 32 shows how well 4 dominant production reactions (R4+R7+R18+R23) and 2 dominant removal reactions (R10+R16) represent the whole HO₂ chemistry cycle at [NO_x] less than 1 ppb. If additional rates 44 & 36 are added for production & sink, respectively, then the agreement will extend up to [NO_x] ≈ 5ppb. The dependence of 6 rates upon [NO_x] is shown as percentages in Figure 33 & 34. Through this process, the dominance of individual reactions decreases and the discrepancy between production and sink enlarges. In other words, at high NO_x, the simple relationship used to represent

the concentration of HO_2 is no longer valid.

Several important points should be addressed here. Since the photolysis of ozone is vital for the existence of HO_x , it rules out the possibility of elimination of reaction 4. In order to balance HO_x , it is necessary to keep the dominant removal reaction 10 which acts as net sink for HO_x . Therefore, there are only 4 reactions left to be considered for further reduction. Dropping of the removal reaction 16 is the first try on the basis of simplicity (avoiding the quadratic form). In addition, in clean air, both reactions 18 and 23 act as sources for HO_2 and are less significant compared with reactions 4 and 7 (75,76 and Figure 31).

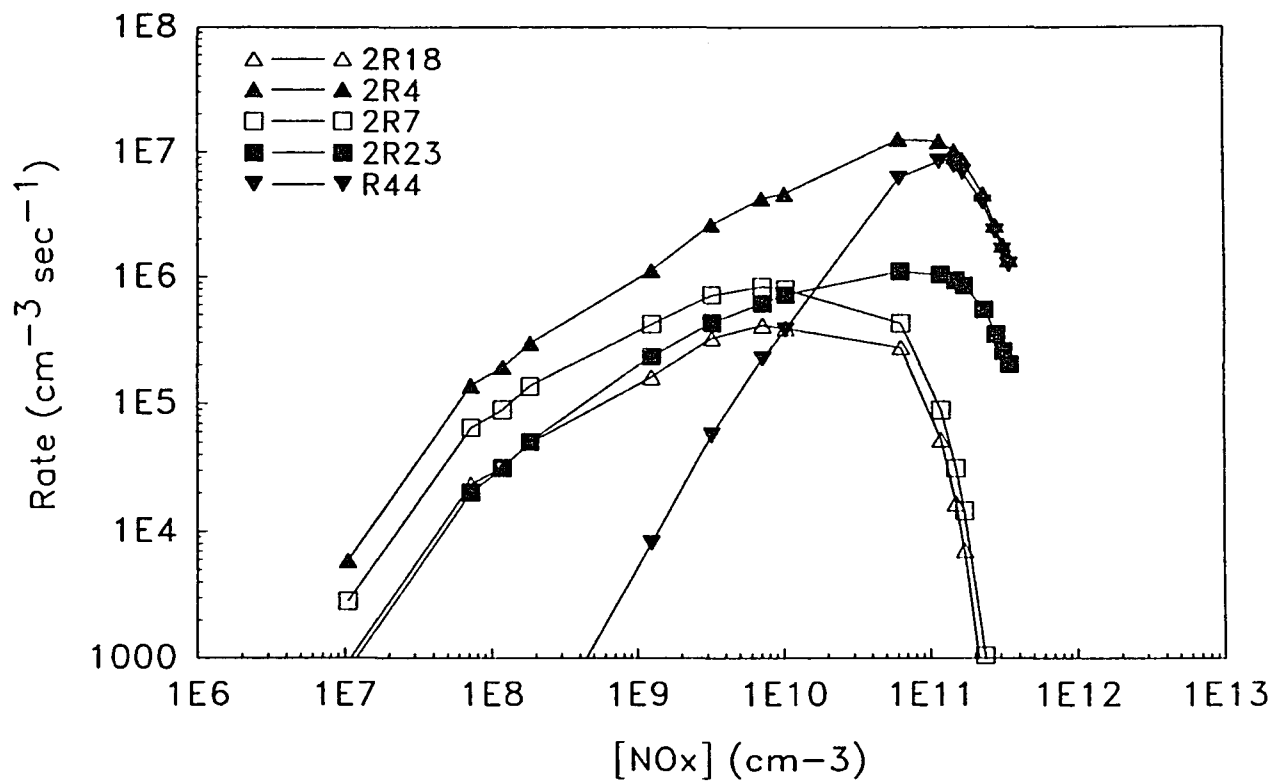


Figure 30. Variation of selected source rates for $[HO_2]$ after combination of HO , HO_2 , CH_3O , CH_3O_2 . It is obvious that rate 44 is insignificant until $[NO_x]$ reaches around 1×10^{10} (0.5 ppb).

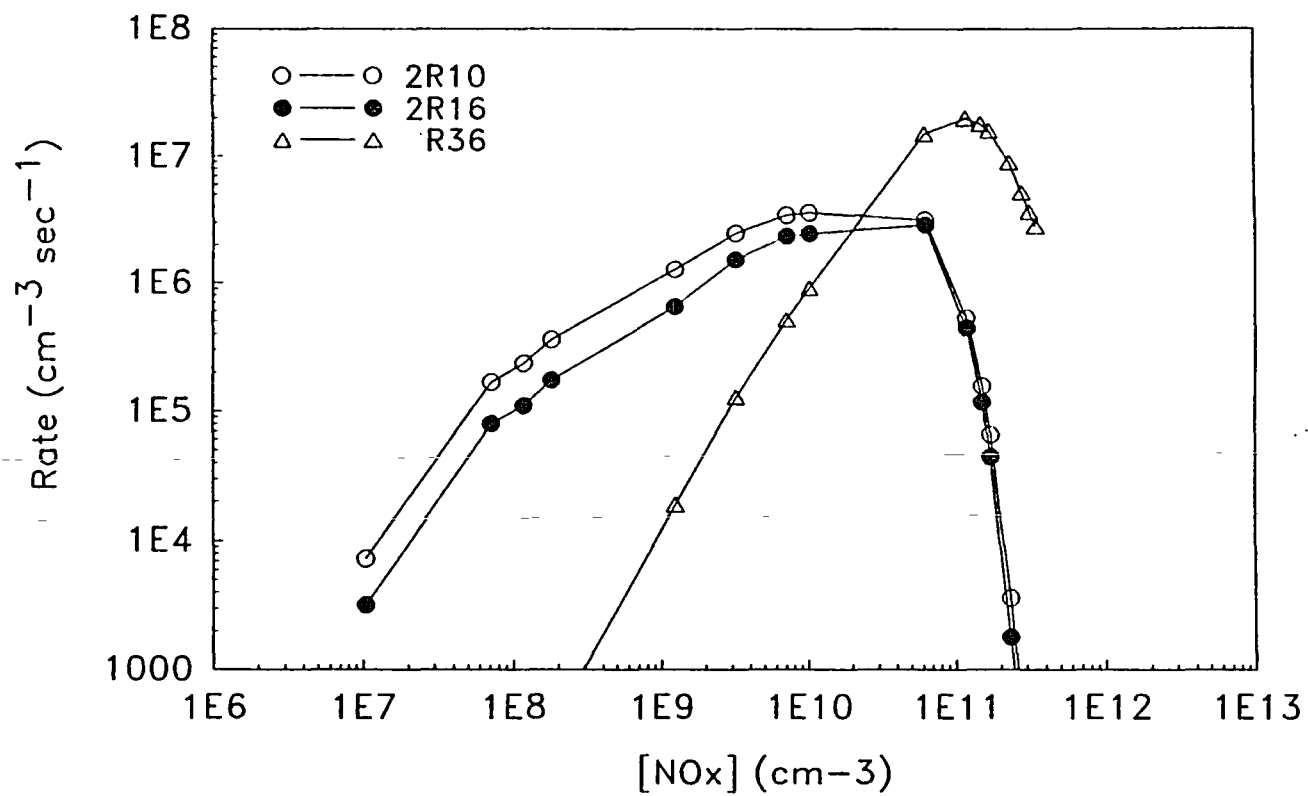


Figure 31. Variation of selected removal rates for $[HO_2]$ after combination of HO , HO_2 , CH_3O , CH_3O_2 . Similarly, rate 36 is insignificant until $[NO_x]$ reaches around 2×10^{11} (1 ppb).

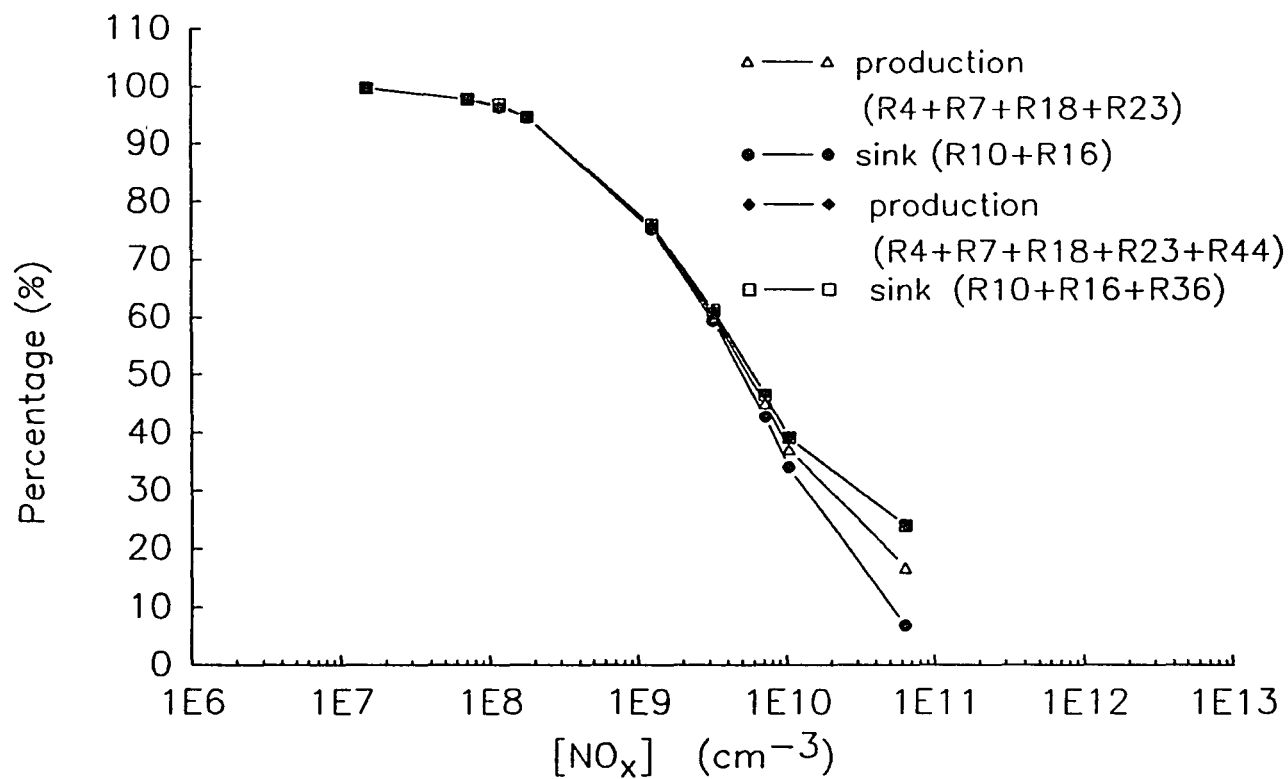


Figure 32. Variation of SSA for $[\text{HO}_2]$ with $[\text{NO}_x]$. The graph shows how well 4 dominant production reactions (R4+R7+R18+R23) and 2 dominant removal reactions (R10+R16) represent the whole HO_2 chemistry cycle at $[\text{NO}_x]$ less than 1 ppb. See text for detail (p. 89).

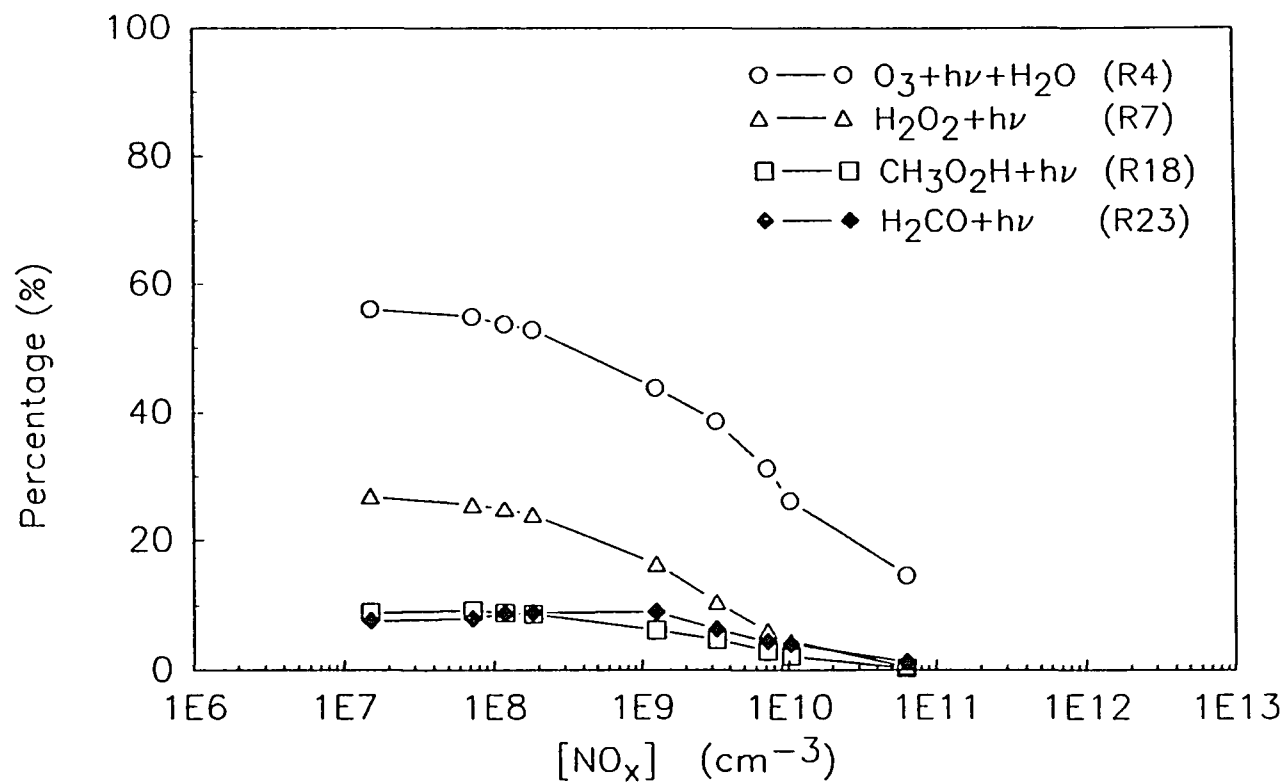


Figure 33. Variation of Selected production rates for HO₂ with [NO_x]. Ozone photolysis (followed by reaction of O(¹D) with water) and hydrogen peroxide photolysis dominate the production of hydroperoxyl radical (HO₂). The percentage of each reaction indicates the amount of contribution of formation of HO₂.

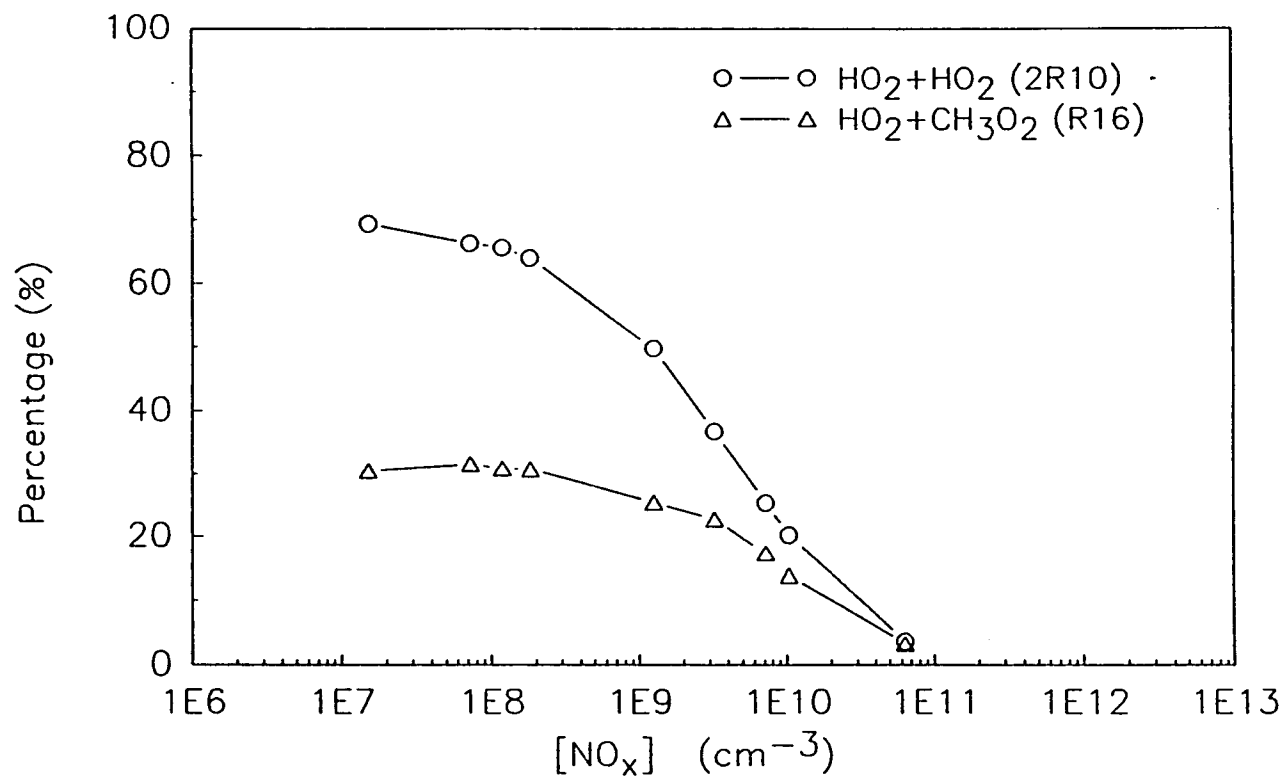


Figure 34. Variation of selected removal rates for $[\text{HO}_2]$ with $[\text{NO}_x]$. The self-reaction of HO_2 dominates through the entire range of NO_x . The percentage of each reaction indicates the amount of contribution of destruction of HO_2 .

TABLE VII
ORIGINAL DATA USED FOR EQUATION HO₂

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19
 COMMENTS : [NO]=1E7 [NO_x]=1.06e7

| | inst. | | | | | cum. | | |
|------|-------|------|------|----------|----|----------|----|----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |

| | | | | | | | | |
|----|-----------|-----|----------|------------|-------|------------|-----|-----|
| -2 | 3.659e+03 | R10 | ho2+ho2 | -7.318e+03 | 69.33 | -7.356e+03 | 226 | *** |
| 2 | 2.950e+03 | R4 | od+h2o | 5.900e+03 | 56.10 | -1.456e+03 | -40 | *** |
| -2 | 1.605e+03 | R16 | ch32+ho2 | -3.210e+03 | 30.41 | -4.666e+03 | 20 | -7 |
| 2 | 1.418e+03 | R7 | h2o2+hv | 2.836e+03 | 26.96 | -1.830e+03 | -17 | -27 |
| 2 | 4.718e+02 | R18 | ch3h+hv | 9.436e+02 | 8.97 | -8.862e+02 | -5 | -10 |
| 2 | 4.050e+02 | R23 | h2co+hv | 8.100e+02 | 7.70 | -7.616e+01 | -5 | -5 |
| -1 | 2.692e+01 | R37 | ho2+no2 | -2.692e+01 | .26 | -1.031e+02 | 0 | -0 |
| 1 | 1.417e+01 | R45 | hno4+hv | 1.417e+01 | .13 | -8.891e+01 | -0 | -0 |
| 1 | 1.275e+01 | R33 | hno4 | 1.275e+01 | .12 | -7.616e+01 | -0 | -0 |
| 2 | 2.647e-01 | R50 | od+ch4 | 5.294e-01 | .01 | -7.564e+01 | -0 | -0 |
| 1 | 4.880e-01 | R43 | hno2+hv | 4.880e-01 | .00 | -7.515e+01 | -0 | -0 |
| -1 | 4.459e-01 | R35 | ho+no | -4.459e-01 | .00 | -7.559e+01 | 0 | 0 |
| 2 | 6.609e-02 | R52 | od+h2 | 1.322e-01 | .00 | -7.546e+01 | -0 | -0 |
| -1 | 4.668e-02 | R26 | ho2+no2 | -4.668e-02 | .00 | -7.551e+01 | 0 | 0 |
| -1 | 3.969e-02 | R36 | ho+no2 | -3.969e-02 | .00 | -7.555e+01 | 0 | 0 |
| 1 | 1.781e-02 | R44 | hno3+hv | 1.781e-02 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 1.692e-05 | R31 | ho+hno2 | -1.692e-05 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 1.051e-06 | R30 | ho+hno3 | -1.051e-06 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 3.200e-07 | R32 | ho+hno4 | -3.200e-07 | .00 | -7.553e+01 | -0 | -0 |

SSR=deviation = rate/sum of production = -3.59061e-3
 sum of production = 10517.7 ; sum of sink = 10555.5

1. SPECIES = ho/ho2/ch32/ch3o represents combination of species HO, HO₂, CH₃O₂ and CH₃O.
2. All data are taken as [NO]=14 ppt.
3. Column's explanation:
 coef.= rate contribution coefficient (the minus sign indicates sink reaction while the positive sign means production reaction).
 inst. rate = value of individual instantaneous rate.
 rxn = reaction number (R1 etc.).
 code=reaction code. (i.e., ho2+ho2--> h2o2 + o2)
 contrib.= coef. multiplied by inst. rate.
 w%=contrib./(sum of production or sum of sink)
 cum. contrib.= cumulative sum of net values starting from first row.
 i%=the deviation caused by eliminating the reaction.
 c% = cumulative sum of i% starting from last reaction.
- 4 The **** sign indicates c% is over 1000%.

TABLE VIII

STEADY STATE EQUATION FOR HO₂ BASED ON TABLE VII

STEADY-STATE EQUATION :

$$[\text{ho}_2] = \frac{-2 * C}{[B + \text{SQR}(B^2 - 4 * A * C)]}$$

where

$$A = -2[k_{10}] = -8.12e-12$$

$$B = -(2[\text{ch}_3] + 1[\text{no}_2] + 1[\text{no}])$$

$$= -1.07806e-4$$

$$C = 2[\text{od} + \text{h}_2\text{o}] + 2[\text{h}_2\text{o}_2 + \text{h}\nu] + 2[\text{ch}_3\text{h} + \text{h}\nu]$$

$$+ 2[\text{h}_2\text{co} + \text{h}\nu] + 1[\text{hno}_4 + \text{h}\nu]$$

$$+ 1[\text{hno}_4] + 1[\text{hno}_2 + \text{h}\nu]$$

$$+ -1[\text{ho} + \text{no}] + 2[\text{od} + \text{ch}_4] + 2[\text{od} - \text{h}_2]$$

$$+ -1[\text{ho} + \text{no}_2] + 1[\text{hno}_3 + \text{h}\nu]$$

$$+ -1[\text{ho} + \text{hno}_2] + -1[\text{ho} + \text{hno}_3] + -1[\text{ho} + \text{hno}_4]$$

$$= 10517.2$$

APPROX. CONCENTRATION OF [ho₂] = 2.996e+07
 MODEL CONCENTRATION OF [ho₂] = 3.002e+07
 PERCENT RELATIVE ERROR(%) = -2.066e-01

TABLE IX

SELECTED DATA USED FOR EQUATION HO₂SPECIES = ho/ho₂/ch₃2/ch₃o ; # OF RATE = 6COMMENTS : [NO]=1E7, [NO_i]=1.05e7

| | | inst. | | | | cum. | | | |
|------|-----------|-------|-----------------------------------|------------|-------|------------|-----|-----|--|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% | |
| -2 | 3.659e+03 | R10 | ho ₂ +ho ₂ | -7.318e+03 | 69.51 | -7.356e+03 | 228 | *** | |
| 2 | 2.950e+03 | R4 | od+h ₂ o | 5.900e+03 | 56.25 | -1.456e+03 | -40 | *** | |
| -2 | 1.605e+03 | R16 | ch ₃ 2+ho ₂ | -3.210e+03 | 30.49 | -4.666e+03 | 20 | -7 | |
| 2 | 1.418e+03 | R7 | h ₂ o ₂ +hν | 2.836e+03 | 27.04 | -1.830e+03 | -17 | -27 | |
| 2 | 4.718e+02 | R18 | ch ₃ h+hν | 9.436e+02 | 9.00 | -8.868e+02 | -5 | -10 | |
| 2 | 4.050e+02 | R23 | h ₂ co+hν | 8.100e+02 | 7.72 | -7.680e+01 | -5 | -5 | |

deviation = rate/sum of production = -3.66077e-3

sum of production = 10489.6 ; sum of sink = 10528

TABLE X
STEADY STATE EQUATION FOR HO₂ BASED ON TABLE IX

STEADY-STATE EQUATION :

$$[\text{ho}_2] = \frac{-2 \cdot C}{[B + \text{SQR}(B^2 - 4 \cdot A \cdot C)]}$$

where $A = -2[k_{10}] = -8.12\text{e-}12$
 $B = -(2[\text{ch}_{32}]) = -1.06908\text{e-}4$
 $C = 2[\text{od} + \text{h}_2\text{o}] + 2[\text{h}_2\text{o}_2 + \text{h}\nu] + 2[\text{ch}_3\text{h} + \text{h}\nu] + 2[\text{h}_2\text{co} + \text{h}\nu]$
 $= 10489.6$

APPROX. CONCENTRATION OF [ho₂] = 2.996e+07
 MODEL CONCENTRATION OF [ho₂] = 3.002e+07
 PERCENT RELATIVE ERROR = -2.105e-01

Before going further, we should see the completeness of HO₂ cycle in Figure 35. and compare with several separate subcycles. Figure 36 indicates that both reactions 4 and 7 act as a source of HO₂ and reaction 8 acts as a sink. Figure 37 shows that both of reactions 18 and 23 are sources while reaction 16 is a sink. Figure 38 shows that reaction 7 is a source instead of reaction 18 and the rest of the reactions are same as in Figure 37. Figure 39 shows that reaction 7 substitutes for reaction 23. It is obvious that only the subcycle in Figure 35 maintains the completeness of the HO₂ cycle. Therefore one may break down 6 reactions into two subsets as shown in Figure 36 and 37. The reason for this is keeping the completeness as well as the setting of upper and lower bounds in terms of HO₂. Table XI displays the calculated

data on the basis of 6 reactions with the percentages of deviation.

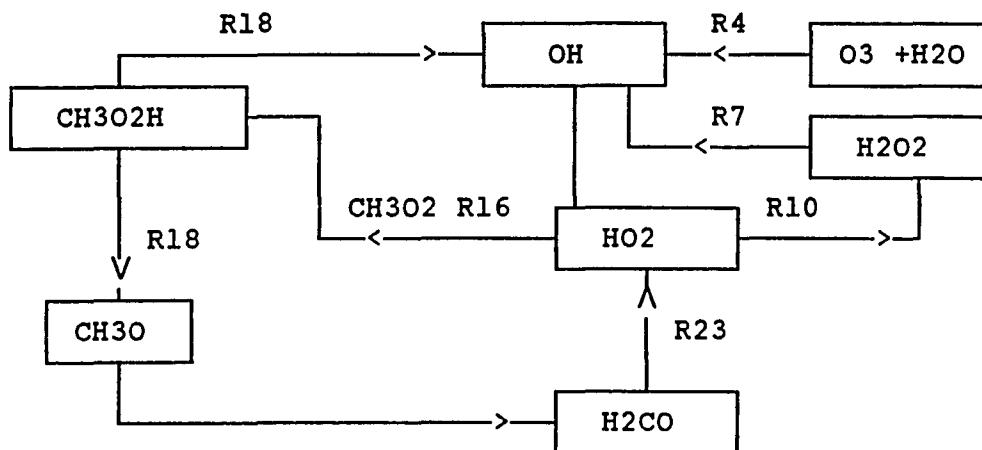


Figure 35. Completed cycle of HO_2 reaction scheme. (excluded NO_y species)

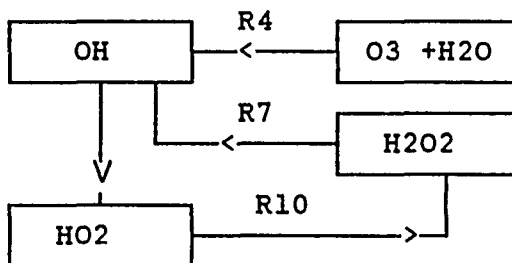


Figure 36. Subcycle of HO_2 reaction scheme I.

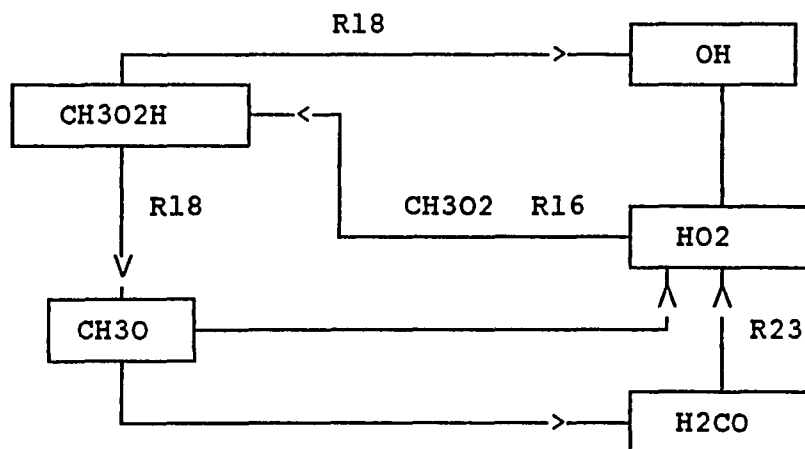


Figure 37. Subcycle of HO_2 reactions scheme II.

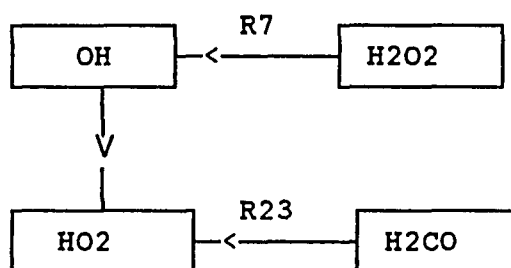


Figure 38. Subcycle of HO_2 reactions scheme III.

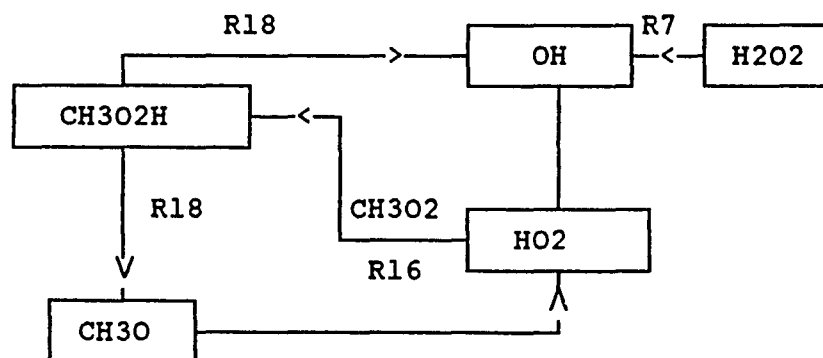


Figure 39. Subcycle of HO_2 reactions scheme IV.

TABLE XI
COMPARISON OF MODEL WITH CALCULATED HO₂
USING SIX REACTIONS

| [NO _x] | Model | Calc. | devi% |
|--------------------|---------|---------|-------|
| 1.052e7 | 3.002e7 | 2.996e7 | -0.2 |
| 7.235e7 | 1.437e8 | 1.434e8 | -0.2 |
| 1.183e8 | 1.700e8 | 1.696e8 | -0.2 |
| 1.825e8 | 2.111e8 | 2.106e8 | -0.2 |
| 1.244e9 | 3.968e8 | 3.970e8 | 0.1 |
| 3.230e9 | 5.538e8 | 5.580e8 | 0.8 |
| 7.152e9 | 6.503e8 | 6.717e8 | 3.3 |
| 1.032e10 | 6.631e8 | 6.983e8 | 5.3 |

1. 1.052e7 read as 1.052x10⁷
2. The unit is cm⁻³.
3. Deviations are calculated as
(eqn. - model)x100/model

TABLE XII
VARIATION OF DOMINANCE OF SELECTED RATES
FOR HO₂ WITH [NO_x]

| [NO _x] | A(O ₃ +H ₂ O+hv=R4) | B(H ₂ O ₂ +hv=R7) | HO ₂ +HO ₂ =R10 |
|--------------------|---|---|---------------------------------------|
| | (%) | (%) | (%) |
| 1.052e7 | 2.938e3 56 | 1.418e3 27 | 3.659e3 69 |
| 7.235e7 | 6.894e4 55 | 3.230e4 26 | 8.386e4 66 |
| 1.183e8 | 9.546e4 54 | 4.455e4 25 | 1.174e5 66 |
| 1.825e8 | 1.486e5 53 | 6.780e4 24 | 1.809e5 64 |
| 1.244e9 | 5.592e5 44 | 2.103e5 16 | 6.391e5 50 |
| 3.230e9 | 1.303e6 39 | 3.561e5 11 | 1.245e6 37 |
| 7.152e9 | 2.110e6 31 | 4.147e5 6 | 1.717e6 25 |
| 1.032e10 | 2.309e6 26 | 3.969e5 4 | 1.785e6 20 |

1. The percentages represent the role of importance of individual rates either production or destruction controlling [HO₂].
For example: the source rates of HO₂ include R4, R7, R18, R23; $R4/(R4+R7+R18+R23)=0.56$ while $R7/(R4+R7+R18+R23)=0.27$ at [NO_x]=10.52e7. Similarly, with regard to the removal rates, $R10/(R10+R16)=0.69$ at same [NO_x].
2. The graphic data are shown in Figures 33 & 34.

TABLE XIII

VARIATION OF THE COMBINATION OF R4+R7 AND R18+R23
FOR HO₂ WITH [NO_x]

| [NO _x] | Model | R4+R7 | devi% | R18+R23 | devi% |
|--------------------|---------|---------|-------|---------|-------|
| 1.052e7 | 3.002e7 | 3.276e7 | 9 | 1.640e7 | -45 |
| 7.235e7 | 1.437e8 | 1.579e8 | 9 | 7.836e7 | -45 |
| 1.183e8 | 1.700e8 | 1.857e8 | 9 | 9.709e7 | -43 |
| 1.825e8 | 2.111e8 | 2.309e8 | 9 | 1.208e8 | -42 |
| 1.244e9 | 3.968e8 | 4.354e8 | 9 | 2.371e8 | -40 |
| 3.230e9 | 5.538e8 | 6.393e8 | 15 | 2.705e8 | -51 |
| 7.152e9 | 6.503e8 | 7.886e8 | 21 | 2.836e8 | -56 |
| 1.032e10 | 6.631e8 | 8.164e8 | 23 | 2.996e8 | -54 |

1. Deviations are calculated as (eqn.-model)*100/model.
The deviation is positive means the predicated [HO₂] of combination of R4+R7 is higher than that of model if R10 is the only one removal rate.
2. All deviations of equation 6-2 are positive indicates R4+R7 is upper limit and the negative deviations indicates R18+R23 is lower limit of concentration of HO₂.
3. R10 is the removal rate for R4+R7 (Figure 36).
4. R16 is the removal rate for R18+R23 (Figure 37).

TABLE XIV

VARIATION OF THE COMBINATION OF R4+R23 AND R4+R18
FOR HO₂ WITH [NO_x]

| [NO _x] | Model | R4+R23 | devi% | R4+R18 | devi% |
|--------------------|---------|---------|-------|---------|-------|
| 1.052e7 | 3.002e7 | 2.875e7 | 4 | 2.903e7 | 3 |
| 7.235e7 | 1.437e8 | 1.397e8 | 3 | 1.411e8 | 2 |
| 1.183e8 | 1.700e8 | 1.657e8 | 3 | 1.658e8 | 2 |
| 1.825e8 | 2.111e8 | 2.072e8 | 2 | 2.x9e8 | 2 |
| 1.244e9 | 3.968e8 | 4.084e8 | -2 | 3.973e8 | 1 |
| 3.230e9 | 5.538e8 | 6.124e8 | -11 | 6.017e8 | -9 |
| 7.152e9 | 6.503e8 | 7.729e8 | -19 | 7.565e8 | -16 |
| 1.032e10 | 6.631e8 | 8.119e8 | -22 | 7.866e8 | -19 |

1. See notes of Table XIII.
2. The deviations with different signs for combination of either R4+R23 or R4+R18 indicate the lack of reliability.
3. R10 is the only one removal rate for both.

TABLE XV
 VARIATION OF THE COMBINATION OF R7+R18 AND R7+R23
 FOR HO₂ WITH [NO_x]

| [NO _x] | Model | R7+R18 | devi% | R7+R23 | devi% |
|--------------------|---------|---------|-------|---------|-------|
| 1.052e7 | 3.002e7 | 3.535e7 | 17.7 | 3.410e7 | 13.6 |
| 7.235e7 | 1.437e8 | 1.584e8 | 10.2 | 1.528e8 | 6.3 |
| 1.183e8 | 1.700e8 | 1.862e8 | 9.5 | 1.657e8 | 9.2 |
| 1.825e8 | 2.111e8 | 2.245e8 | 6.4 | 2.258e8 | 7.0 |
| 1.244e9 | 3.968e8 | 3.520e8 | -11.3 | 3.960e8 | 0.2 |
| 3.230e9 | 5.538e8 | 3.721e8 | -32.8 | 4.100e8 | -26.0 |
| 7.152e9 | 6.503e8 | 3.434e8 | -47.2 | 3.995e8 | -38.6 |
| 1.032e10 | 6.631e8 | 3.207e8 | -51.6 | 4.094e8 | -38.3 |

1. See notes of Table XIII.
2. The deviations with different signs for combination of either R7+R23 or R7+R18 indicate the lack of reliability.
3. For both combinations, R10 is the only one removal rate.

Table XII shows the relative weights of R4 and R7 as sources of HO₂ and Table XIII shows the deviations resulting from the combinations R4+R7 & R18+R23, compared with the model. Table XIV and XV illustrate all other different combinations (i.e., R4+R23, R4+R18, R7+R18 & R7+R23). The switch of sign of deviation indicates the impossibility of treating these four combinations R4+R23, R4+R18, R7+R18 & R7+R23 as boundary equations. The final resultant equation appear to be

$$\begin{array}{ll}
 \text{upper boundary} & R_4 + R_7 > R_{10} \\
 \text{lower boundary} & R_{18} + R_{23} < R_{16}
 \end{array}
 \quad (6-1)$$

Here we see that the upper limit of the concentration of HO₂ is controlled by the photolysis of ozone and hydrogen

peroxide, assuming that we can ignore the other removal reactions except for the self destruction of HO_2 . Levy (77), Leonard et al. (78), Logan et al. (6), Cox (79) & Chameides (80) have used dominant reactions to construct steady-state equations for HO_2 . The utility of these equations is limited because these equations are unnecessarily complex for low NO concentrations, or they require simultaneous solution of both equations for HO_2 . We have obtained the following more useful relationship for HO_2 based on the inequality of equation 6-1.

$$[\text{HO}_2]_{\text{upper}} = \sqrt{\frac{A+B}{k_{10}}} \quad (6-2)$$

$$[\text{HO}_2]_{\text{lower}} = \frac{S_1+S_2}{k_{16}[\text{CH}_3\text{O}_2]} \quad (6-3)$$

where $A=R_4=J_1[h\nu]q[\text{O}_3]$, $B=R_7=J_7[h\nu][\text{H}_2\text{O}_2]$, $S_1=k_{18}[\text{CH}_3\text{O}_2\text{H}]$, $S_2=k_{23}[\text{H}_2\text{CO}]$; J indicates the combined cross section and quantum yield and q is the quantum yield for HO formation from $\text{O}(^1\text{D})$. This equation indicates that the effective sources of HO_2 are ozone photolysis and hydrogen peroxide photolysis. For $[\text{NO}_x]<1$ ppb, loss of HO_2 occurs largely through its self reaction. In spite of its simplicity, equation 6-2 gives an accurate approximation to the numerical integration results. However, equation 6-3 is less important since it contains CH_3O_2 species which is lack of reliable experimental data.

HO Equation

Basically, the similar approach was applied to derive the HO equation, however, it is easier for HO since no self-reactions are involved. From the data in Table XVI, there is only 5% deviation if all but the top six reactions ignored.

TABLE XVI
ORIGINAL DATA USED FOR EQUATION HO

| SPECIES = HO ; # OF RATE = 22 | | | | | | | | | |
|---|-----------|------|---------|------------|-------|------------|-----|-----|--|
| COMMENTS : [NO]=3E8 [NO ₂]=1.06e7 | | | | | | | | | |
| | inst. | | | | | cum. | | | |
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% | |
| -1 | 2.467e+06 | R5 | ho+co | -2.467e+06 | 67.56 | -2.467e+06 | 208 | *** | |
| 1 | 1.164e+06 | R9 | ho2+no | 1.164e+06 | 31.88 | -1.303e+06 | -32 | -32 | |
| 2 | 5.614e+05 | R4 | od+h2o | 1.123e+06 | 30.75 | -1.802e+05 | -31 | -1 | |
| -1 | 6.228e+05 | R6 | ho+ch4 | -6.228e+05 | 17.06 | -8.030e+05 | 21 | -21 | |
| 1 | 5.281e+05 | R8 | ho2+o3 | 5.281e+05 | 14.46 | -2.749e+05 | -14 | -7 | |
| 2 | 2.103e+05 | R7 | h2o2+hv | 4.206e+05 | 11.52 | 1.457e+05 | -12 | 5 | |
| 1 | 3.229e+05 | R45 | hno4+hv | 3.229e+05 | 8.84 | 4.686e+05 | -9 | 13 | |
| -1 | 1.963e+05 | R14 | ho+h2 | -1.963e+05 | 5.38 | 2.723e+05 | 6 | 8 | |
| -1 | 1.088e+05 | R11 | ho+o3 | -1.088e+05 | 2.98 | 1.635e+05 | 3 | 5 | |
| -1 | 9.805e+04 | R15 | ho+h2co | -9.805e+04 | 2.69 | 6.545e+04 | 3 | 2 | |
| -1 | 8.668e+04 | R12 | ho+h2o2 | -8.668e+04 | 2.37 | -2.123e+04 | 2 | -1 | |
| 1 | 7.950e+04 | R18 | ch3h+hv | 7.950e+04 | 2.18 | 5.827e+04 | -2 | 2 | |
| -1 | 4.861e+04 | R17 | ch3h+ho | -4.861e+04 | 1.33 | 9.660e+03 | 1 | 0 | |
| -1 | 1.883e+04 | R36 | ho+no2 | -1.883e+04 | .52 | -9.170e+03 | 1 | -0 | |
| 1 | 8.072e+03 | R44 | hno3+hv | 8.072e+03 | .22 | -1.098e+03 | -0 | -0 | |
| 1 | 5.258e+03 | R43 | hno2+hv | 5.258e+03 | .14 | 4.160e+03 | -0 | 0 | |
| -1 | 4.294e+03 | R35 | ho+no | -4.294e+03 | .12 | -1.340e+02 | 0 | 0 | |
| -1 | 1.311e+02 | R30 | ho+hno3 | -1.311e+02 | .00 | -2.651e+02 | 0 | -0 | |
| 1 | 5.038e+01 | R50 | od+ch4 | 5.038e+01 | .00 | -2.147e+02 | -0 | 0 | |
| -1 | 5.016e+01 | R31 | ho+hno2 | -5.016e+01 | .00 | -2.649e+02 | 0 | -0 | |
| 1 | 1.258e+01 | R52 | od+h2 | 1.258e+01 | .00 | -2.523e+02 | -0 | 0 | |
| -1 | 2.007e+00 | R32 | ho+hno4 | -2.007e+00 | .00 | -2.543e+02 | 0 | 0 | |

SSR = rate/sum of production = -3.48242e-5

sum of production = 3.65129e+6 ; sum of loss = 3.65155e+6

See notes of Table VIII.

Thus the HO equation can be reduced and appear to be

$$[\text{HO}] = \frac{2(\text{R4}+\text{R7})+\text{R8}+\text{R9}}{k_5[\text{CO}]+k_6[\text{CH}_4]} \quad \text{or}$$

$$[\text{HO}] = \frac{2(\text{J}_1[\text{h}\nu]\text{q}[\text{O}_3]+\text{J}_7[\text{h}\nu][\text{H}_2\text{O}_2]) + [\text{HO}_2](k_8[\text{O}_3]+k_9[\text{NO}])}{k_5[\text{CO}]+k_6[\text{CH}_4]}$$

A similar HO equation can be found in Logan's paper (6). Equation (6-2) for $[\text{HO}_2]$ allows simplification of the HO equation to yield

$$[\text{HO}] = \frac{2(\text{A}+\text{B})}{\text{C}+\text{D}} \left(1 + \frac{\text{E}+\text{F}}{2\sqrt{k_{10}(\text{A}+\text{B})}}\right) \quad (6-4)$$

where $\text{A}=\text{J}_1[\text{h}\nu]\text{q}[\text{O}_3]$, $\text{B}=\text{J}_7[\text{h}\nu][\text{H}_2\text{O}_2]$, $\text{C}=k_5[\text{CO}]$, $\text{D}=k_6[\text{CH}_4]$, $\text{E}=k_8[\text{O}_3]$, and $\text{F}=k_9[\text{NO}]$. The first term in equation (6-4) represents ozone and hydrogen peroxide photolysis to form HO, with loss occurring through the methane and carbon monoxide reactions. The second term represents the "recycling" of HO_2 which occurs through HO_2 's reaction with NO and ozone to regenerate HO (Figure 23). Carbon monoxide loss dominates over methane loss ($\text{C}=1.32 \text{ s}^{-1}$ and $\text{D}=0.33 \text{ s}^{-1}$). These relative values are based upon a concentration of 200 ppb for ground level carbon monoxide, after Logan et al. (6) It seems likely that a concentration closer to 100 ppb would be more representative of clear air tropospheric concentrations at this latitude (9), which would increase $[\text{HO}]$ and the importance of CH_4 relative to CO in controlling $[\text{HO}]$. The dominant recycling term in Eq. 6-4 depends upon the ozone and NO concentration. Table XVII

presents the calculated values of E, F and recycling terms for $0.4 \text{ ppt} < [\text{NO}_x] < 500 \text{ ppt}$. Thus the parenthetical term ({})) varies from 1.3 to 3.1 over this range of $[\text{NO}_x]$.

TABLE XVII
CALCULATED VALUES OF E, F AND RECYCLING TERM (r)

| $[\text{NO}_x]$ (ppt) | E (s^{-1}) | F (s^{-1}) | 1+r | $[\text{HO}]_c$ | $[\text{HO}]_n$ |
|-----------------------|-----------------------|-----------------------|------|-----------------|-----------------|
| 1.052e7(0.4) | 6.99e-6 | 8.38e-4 | 1.34 | 7.053e3 | 6.776e3 |
| 7.235e7(3.0) | 1.64e-4 | 4.19e-4 | 1.45 | 1.776e5 | 1.688e5 |
| 1.183e8(5.0) | 2.27e-4 | 6.29e-4 | 1.57 | 2.649e5 | 2.501e5 |
| 1.825e8(7.0) | 3.54e-4 | 8.38e-4 | 1.64 | 4.273e5 | 4.005e5 |
| 1.244e9(50) | 1.33e-3 | 2.93e-3 | 2.21 | 2.049e6 | 1.846e6 |
| 3.230e9(130) | 3.10e-3 | 4.19e-3 | 2.41 | 4.815e6 | 4.153e6 |
| 7.152e9(290) | 5.02e-3 | 6.29e-3 | 2.77 | 8.431e6 | 7.068e6 |
| 1.032e10(410) | 5.50e-3 | 8.38e-3 | 3.10 | 1.011e7 | 8.590e6 |

1. 1.052e7 read as 1.052×10^7
2. The unit for $[\text{HO}]$ is molecules cm_3
3. r represents the recycling term in equation 6-4.

$$r = \frac{E+F}{2\sqrt{k_{10}(A+B)}}$$

4. $[\text{HO}]_c$ indicates $[\text{HO}]$ is calculated on the basis of equation 6-4.
5. $[\text{HO}]_n$ indicates $[\text{HO}]$ is chosen from numerical intergration model.

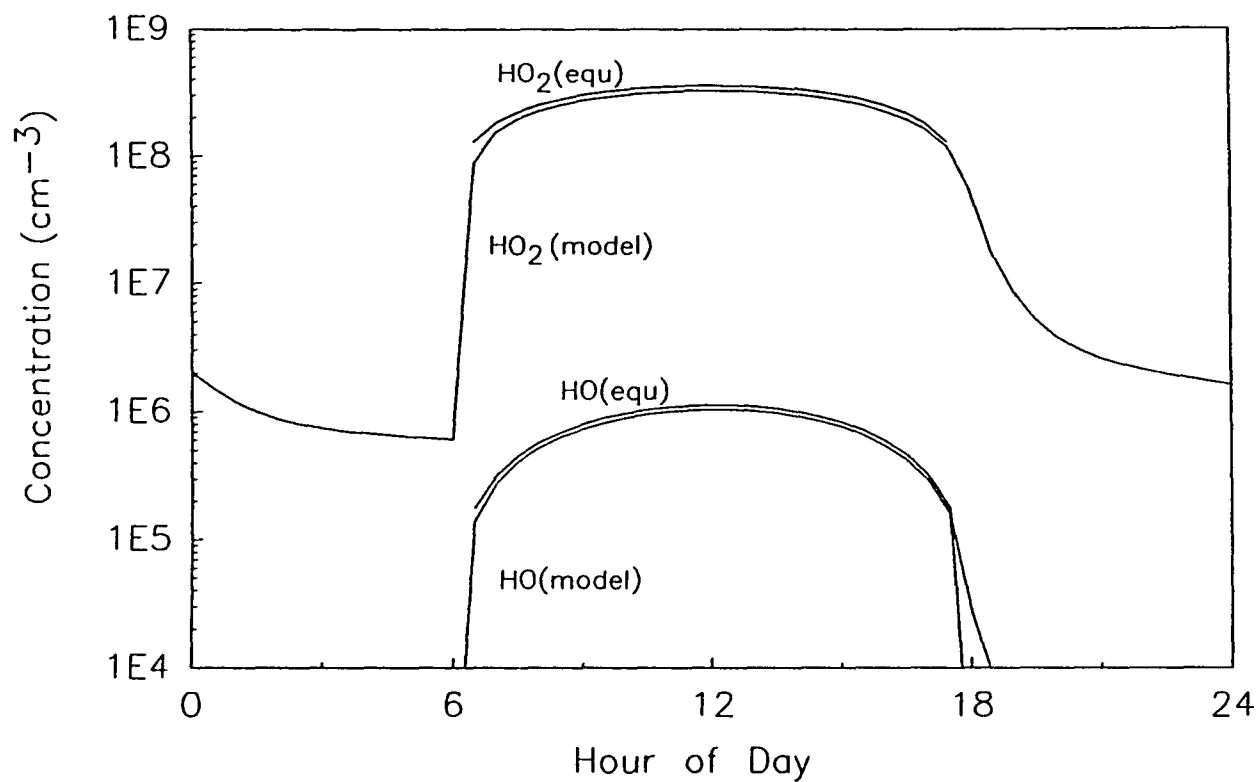


Figure 40. Comparison of diurnal profiles for HO and HO₂ as calculated by numerical integration and by equations 6-2 and 6-4. Conditions are same as Figure 19.

Note that all species in Eqns. 6-2 & 6-4 are long-lived and are thought to have negligible diurnal variation except for NO. The major source of diurnal variation in species concentration is due of course to the variation of solar intensity. These equations apply to daylight hours only. All species in Eqns. 6-2 & 6-4 are measurable with current technology. The accuracy of equations 6-2 & 6-4 is shown in Figure 40. Since the SSA has considerable error for HO₂ at sunrise and sunset (Figure 8 to 11), it is not surprising that the equations make significant error at these times when compared to numerical integration of the equation set. However, the overall accuracy of Eqns. 6-2 & 6-4 for HO₂ over the course of the day is quite good.

The dependence of noon HO₂ concentrations upon [NO_x] is shown in Figure 41. Calculated concentrations are compared with the numerical integration for latitude 45°N at ground level during the equinox. Both the HO and the HO₂ equations reproduce model calculations very well for [NO_x] concentrations below 1 ppb. Equations 6-2 & 6-4 indicate that clean tropospheric HO₂ chemistry may be adequately described by the reactions shown in Figure 36. Ozone and hydrogen peroxide photolysis are the major sources of HO, but this HO is converted quantitatively to HO₂. Since HO₂ is lost almost entirely through reaction with itself to form hydrogen peroxide, its steady-state equation for HO₂ is very simple at low NO_x. The next question is what additional terms are

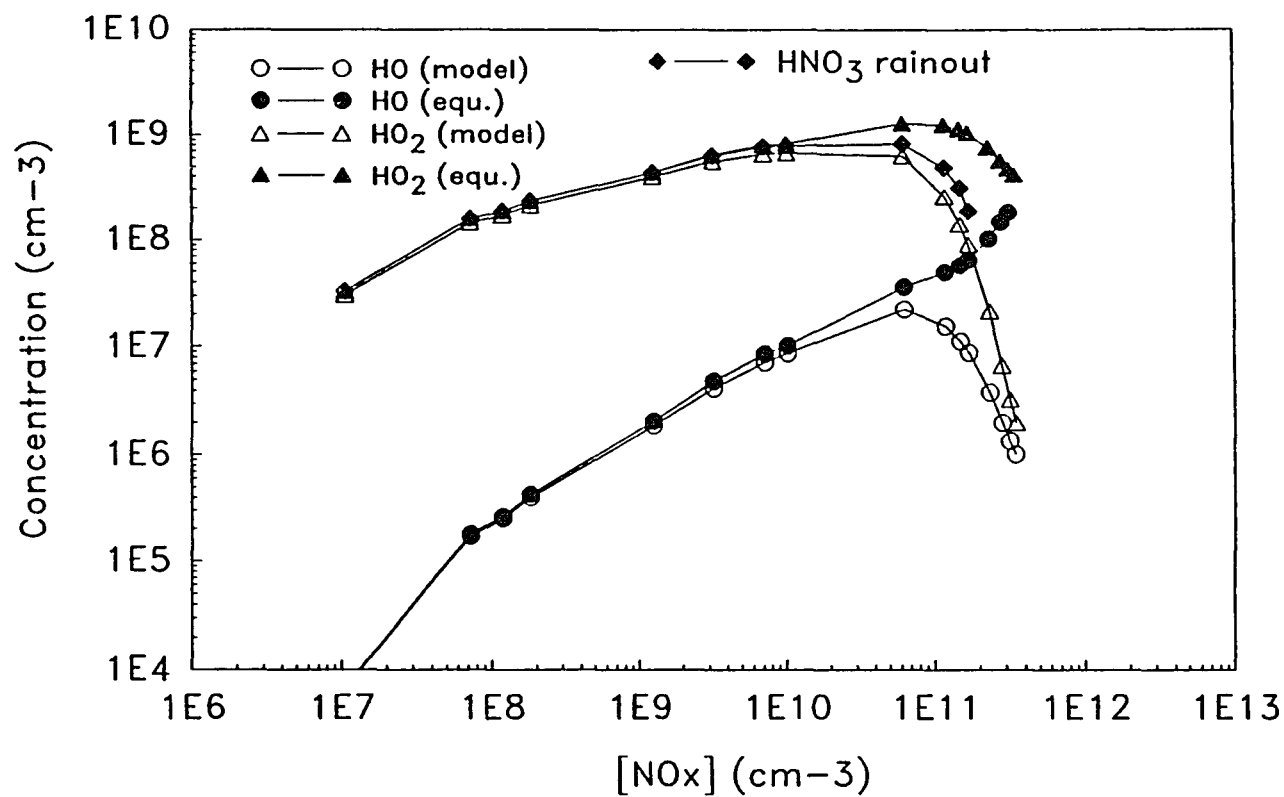


Figure 41. Variation of HO and HO₂ concentration with ambient nitric oxide concentration, comparison of numerical integration and equations 6-2 (HO₂) and 6-4 (HO). The inclusion of rainout of nitric acid (equation 6-6) is shown as well. Conditions are same as Figure 40.

necessary to include at high NO_x (> 1 ppb). Surveying all data in Appendix B, we found the chemistry of HNO_3 increases in importance until $[\text{NO}_x] \approx 2 \times 10^{11}$. Fortunately, three reactions involving HNO_3 are balanced so that it will not cause any error to ignore HNO_3 chemistry. Instead, the difference between reaction 36 ($\text{HO} + \text{NO}_2 + \text{M}$) and 44 ($\text{HNO}_3 + \text{h}\nu$) gets bigger while $[\text{NO}_x]$ increases. Obviously, we should add R36 as sink and R44 as source and equation 6-2 becomes

$$k_{10}[\text{HO}_2]^2 + k_{36}[\text{HO}][\text{NO}_2] = A + B + k_{44}[\text{HNO}_3][\text{h}\nu] \quad (6-5)$$

But the initial criterion of searching the simple equations for HO_2 is to exclude the possible combinations which contain both HO and HO_2 . However, the chemistry of HNO_3 is simple since $\text{R36} = \text{R30} + \text{R44} + \text{R47}$. Figure 42 shows the weights of individual rates with regard to depletion of HNO_3 . By ignoring R30, the relationship becomes

$$\text{R36} - \text{R44} = \text{R47} = \text{rainout of } \text{HNO}_3$$

Substituting into equation 6-5, we obtain

$$[\text{HO}_2] = \sqrt{\frac{A+B-\text{R47}}{k_{10}}} \quad (6-6)$$

The equation 6-6 works well until the numerator become negative at $[\text{NO}_x] \approx 1.7 \times 10^{11}$. It reveals that the sources for HO_2 should include photolysis of formaldehyde. The equation 6-7 is obtained after appending rate 23 to equation 6-6.

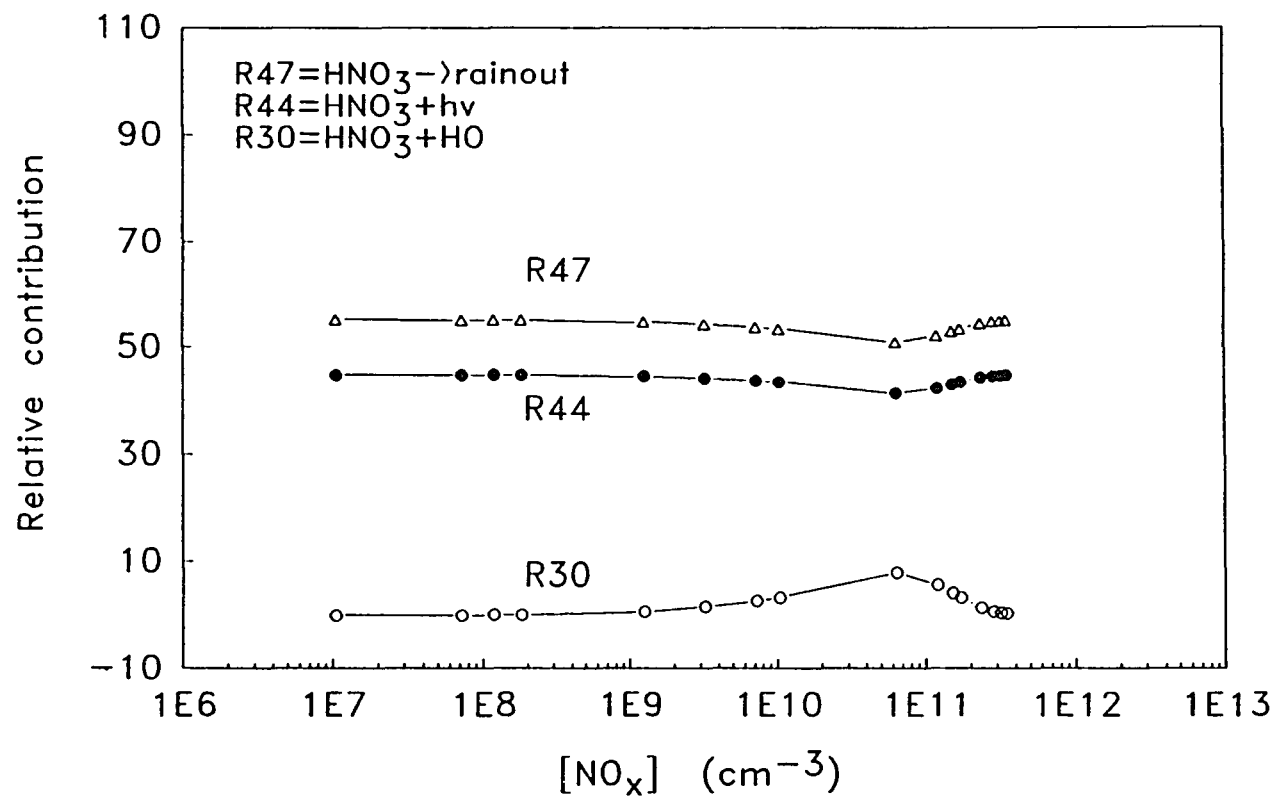


Figure 42. Variation of removal rates for nitric acid. The rainout of HNO_3 is dominant over the entire range of nitrogen oxide.

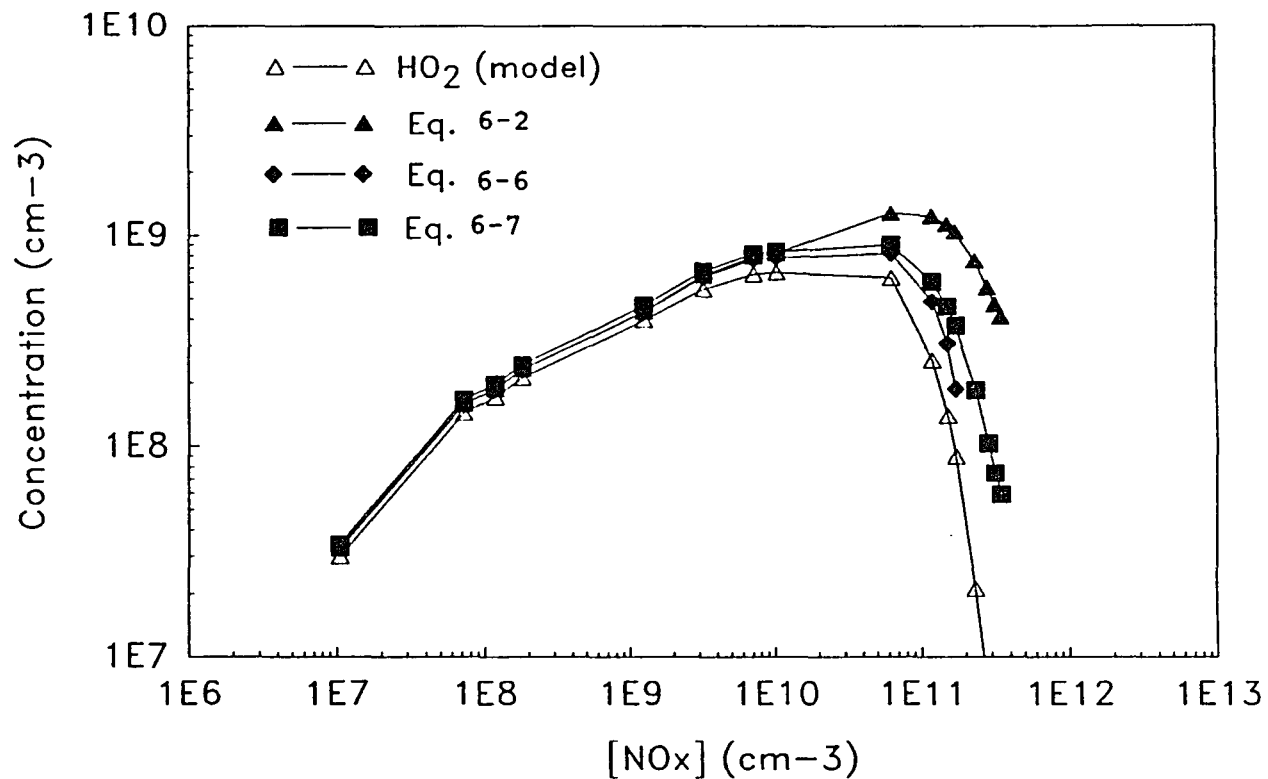


Figure 43. Variation of $[\text{HO}_2]$ with $[\text{NO}_x]$, comparison of numerical integration model with equations 6-2, 6-6 & 6-7. The numerator of equation 6-6 becomes negative when NO_x concentration is over 2×10^{11} , in other words, the equation is no longer valid for calculation of $[\text{HO}_2]$. The inclusion of formaldehyde solves the problem and reveals the importance of formaldehyde in relatively polluted air.

$$[HO_2] = \sqrt{\frac{A+B+R23-R47}{k_{10}}} \quad (6-7)$$

Figure 43 shows the comparison of model, equations 6-2, 6-6 & 6-7. If the more accurate equation is desired, then the form of equation may be totally different. However, the simplicity pays for the inaccuracy as long as the error is within the range of tolerance.

The effort to seek the approximate equation for hydroxyl radical ends with a simplified format through combination of steady state equations for HO/HO₂/CH₃O/CH₃O₂/HNO₂/HNO₃/HNO₄.

$$[HO] = \frac{2(R4+R23)-R47}{k_{30}[HNO_3]+k_{31}[HNO_2]} \quad (6-8)$$

Based on the equation 6-8, it can be shown that [HO₂] can no longer be used for predicting [HO]. Instead, HNO₃ & HNO₂ start to control the abundance of HO. Comparison of numerical integration model with equation 6-8, the modified equation for HO is shown in Figure 44.

SIMULTANEOUS EQUATION SOLVER

The Simultaneous Equation Solver (SEQS) (81) offers a tool for numerical solution of a wide variety of problems which can be expressed as a single equation or a set of simultaneous algebraic equations. The version we have is a professional version allowing use of up to 32 equations with 50 variables.

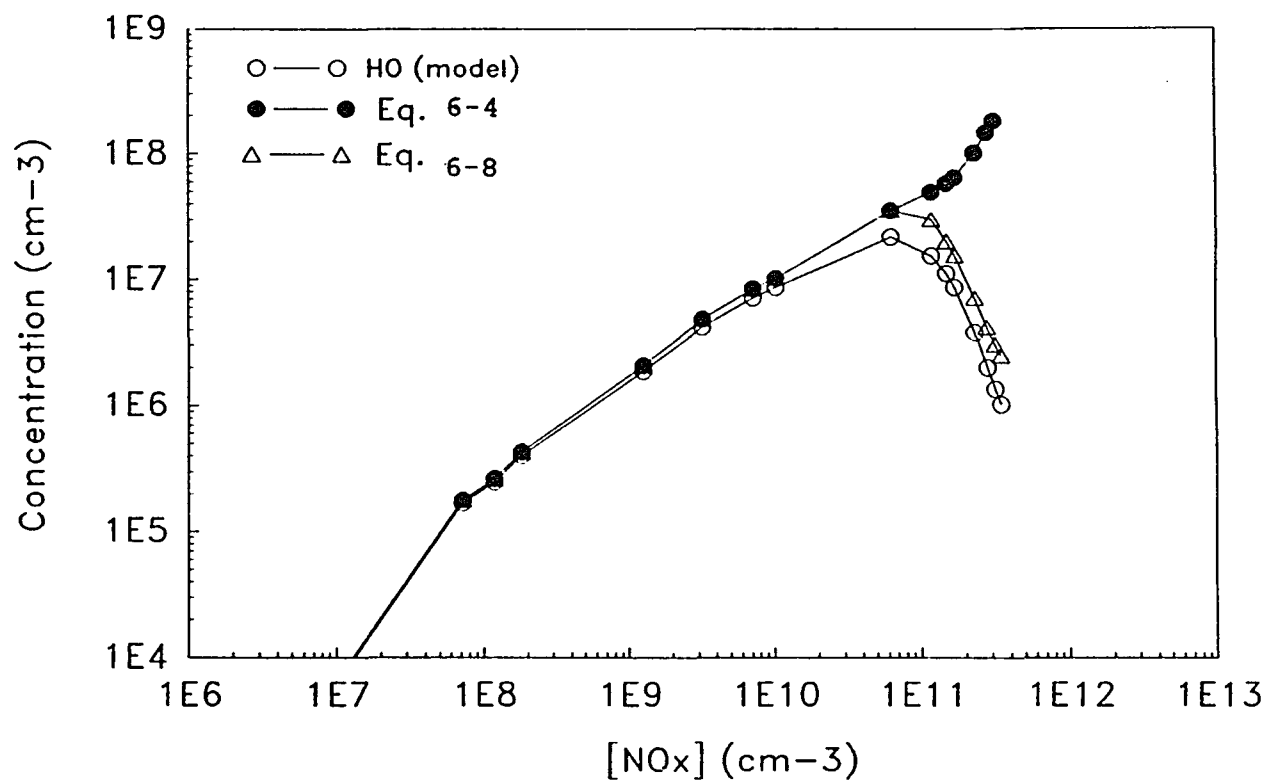


Figure 44. Variation of $[HO]$ with $[NO_x]$, comparison of numerical integration with equations 6-4, 6-8. Equation 6-4 is valid when $[NO_x]$ is below 1 ppb and eqn. 6-8 is valid if $[NO_x] > 1\text{ppb}$. This piecewise analysis of HO indicates the role of HNO_3 and HNO_2 in controlling HO at relatively polluted air.

The SEQS program is designed to enable the user to numerically solve algebraic equations. It is claimed that SEQS will solve equations which are nonlinear, transcendental, linear or some combination of these three types. The mechanism by which SEQS solves equations is an iterative one. An iterative process is simply one in which the numerical values of the supposed solutions are modified until some pre-determined criterion is met concerning the quality of the solution of the unknowns in the equations. The way in which SEQS attempts to solve the equations is to find numerical values of the unknown variables which make the two sides of the equations exactly equal. For instance, for an equation like $A=4$, SEQS would seek the A value which makes this true. SEQS interprets equations as a function like $R=A-4$ and seeks a minimum value of the product $(A-4)*(A-4)$. In other words, in solving equations, SEQS attempts to make the quantity $R \times R$ or R^2 (R is a residual) as small as possible.

The motivation for using SEQS is to confirm whether all species in the troposphere are in temporary steady state at specific time region. In order to simulate the variation of HO_x with NO_x , we try to set the concentration of NO_x as variable and run the SEQS to see if reasonable results are obtained.

Based on the clean air mechanism (Table I), a total of 15 species have been chosen to denote the set of equations, respectively. (i.e., HO , HO_2 , CH_3O_2 , NO_2 , NO_3 , N_2O_5 , HNO_2 , HNO_4 ,

CH₃O, CH₃O₂H, H₂O₂, HNO₃, H₂CO, NO, O₃). Table XVIII is the input file of clean air for SEQS. In order to constrain NO_x concentration, we compute [NO] as the difference of NO_x and NO₂. Several different cases have been analyzed and compared with the data from the numerical model. Since the simplified mechanism (8 equations) can represent HO_x chemistry in the unpolluted troposphere, the test of using the 5 species and 8 reactions on SEQS has been implemented. i.e., 5 species (HO, HO₂, H₂O₂, NO, O₃ see Table XVIII) have been chosen for the purpose of comparison with the simplified equations derived in chapter 6. In the latter case, the equations for HO₂ & HO are exactly identical to Eqns. 6-2 & 6-4, respectively, while the equation of H₂O₂ is adopted from Table XVIII and the equations for O₃ and NO are based on the modified PSS (photostationary state) relationship (82) in which NO₂ is treated implicitly as the difference of NO and NO_x which is a variable.

Figure 45 shows the variation of HO_x with NO_x. Deviations have been found when [NO_x] is less than 1×10^8 or greater than 2×10^{10} . Figure 46 shows the comparison of model's data with SEQS' data (whole system, Table XVIII) for HO_x vs. NO_x. It is not surprising that the correlation between the two approaches is so good due to the similar idea behind each. The difference only appears at low [NO_x] ($< 1 \times 10^8$). In Figure 47, the agreement between the model and SEQS for HO_x equations confirms the success of the simplification of the mechanism. Figure 48 shows the attempt to obtain the diurnal variations

of all species by using discrete values simulating the light intensity. Variations here may be due to failure of the steady-state relationships away from midday.

Figure 49 shows the results for the whole and simplified systems (Table XVIII) in which ozone is treated as constant (O_3 equation ignored). There is no deviation existing until $[NO_x]$ reaches 2×10^{10} (1 ppb). However, these convergent results may not exactly reflect reality since ozone is unlikely to be constant with NO_x . The steady-state variation of ozone with NO_x was shown in Figure 20. But from the steady-state viewpoint, all graphic data seem to indicate that it is possible to assume all species reach the steady state under noon time conditions.

TABLE XVIII

SEQS INPUT FILE FOR CLEAN TROPOSPHERE
THE WHOLE & SIMPLIFIED SYSTEMS

(THE WHOLE MECHANISM)

```

0=2*8.79e-6*[o3]*[hv]*q-2.7e-13*[ho]*[co]-8.03e-15
  *[ho]*[ch4]+2*7.6e-6*[h2o2]*[hv]+1.59e-15
  *[ho2]*[o3]+8.38e-12*[ho2]*[no]-6.97e-14*[ho]*[o3]
  -1.68e-12*[ho]*[h2o2]-7.84e-15*[ho]*[h2]-1e-11
  *[ho]*[h2co]-1.64e-12*[ho]*[ch3o2h]+5e-6*[ch3o2h]*[hv]
  -8.5e-14*[ho]*[hno3]-6.6e-12*[ho]*[hno2]
  -6.58e-12*[ho]*[no]-1.13e-11*[ho]*[no2]+1.29e-3
  *[hno2]*[hv]+9.76e-6*[hno3]*[hv]+0.15*[hno4]*[hv]
  - [HO] -
0=2.7e-13*[ho]*[co]-1.59e-15*[ho2]*[o3]-8.38e-12
  *[ho2]*[no]-2*4.06e-12*([ho2]^2)+6.97e-14*[ho]*[o3]
  +1.68e-12*[ho]*[h2o2]+7.84e-15*[ho]*[h2]+1e-11
  *[ho]*[h2co]-6e-12*[ho2]*[ch3o2]+6.36e-16*[ch3o]*[o2]
  +2*2.2e-5*[h2co]*[hv]-3e-15*[ho2]*[no2]+1.35e-1*[hno4]
  -1.73e-12*[ho2]*[no2]
  - [HO2] -
0=8.03e-15*[ho]*[ch4]-6e-12*[ch3o2]*[ho2]+1.64e-12
  *[ch3o2h]*[ho]-2*4.6e-13*[ch3o2]^2-7.0e-12*[ch3o2]*[no]
  - [CH3O2] -
0=8.38e-12*[ho2]*[no]+7.0e-12*[ch3o2]*[no]-3e-15*[ho2]
  *[no2]+1.83e-14*[no3]*[no]-3.41e-17*[o3]*[no2]+2*2e-11
  *[no]*[no3]+5e-13*[ho]*[hno4]+1.35e-1*[hno4]+4.19e-2
  *[n2o5]-1.13e-11*[ho]*[no2]-1.73e-12*[ho2]*[no2]
  -7.58e-13*[no2]*[no3]-7.6e-3*[no2]*[hv]+3.3e-2
  *[no3]*[hv]+1.6e-1*[n2o5]*[hv]+9.76e-6*[hno3]*[hv]
  - [NO2] -
0=3.41e-17*[o3]*[no2]-2e-11*[no]*[no3]+8.5e-14*[ho]*[hno3]
  +4.19e-2*[n2o5]-7.58e-13*[no2]*[no3]-1.6e-2*[no3]*[hv]
  -3.3e-2*[no3]*[hv]+1.6e-1*[n2o5]*[hv]+0.15*[hno4]*[hv]
  - [NO3] -
0=-4.19e-2*[n2o5]+7.58e-13*[no2]*[no3]-1.6e-1*[n2o5]*[hv]
  - [N2O5] -
0=3e-15*[ho2]*[no2]-6.6e-12*[ho]*[hno2]+6.58e-12*[ho]*[no]
  -1.29e-3*[hno2]*[hv]-r*[hno2]
  - [HNO2] -
0=-5e-13*[ho]*[hno4]-1.35e-1*[hno4]+1.73e-12*[ho2]*[no2]
  -0.15*[hno4]*[hv]-r*[hno4]
  - [HNO4] -
0=5e-6*[ch3o2h]*[hv]+2*4.6e-13*[ch3o2]^2+7e-12
  *[ch3o2]*[no]-6.36e-16*[ch3o]*[o2]
  - [CH3O] -

```

TABLE XVIII

SEQS INPUT FILE FOR CLEAN TROPOSPHERE
THE WHOLE & SIMPLIFIED SYSTEMS
(continued)

```

0=6e-12*[ch3o2]*[ho2]-1.64e-12*[ch3o2h]*[ho]-5e-6
  *[ch3o2h]*[hv]-r*[ch3o2h]
                                - [CH3O2H] -
0=4.06e-12*[ho2]*[ho2]-[h2o2]
  *(r+7.6e-6*[hv]+1.68e-12*[ho])
                                - [H2O2] -
0=1.3e-11*[ho]*[no2]-[hno3]*(8.5e-14*[ho]+9.76e-6*[hv]+r)
                                - [HNO3] -
0=6.36e-16*[ch3o]*[o2]-[h2co]*(1e-11*[ho]+2.2e-5*[hv]
  +2.94e-5*[hv]+r)
                                - [H2CO] -
[no]=[nox]-[no2]
                                - [NO] -
[o3]*8.79e-6*[hv]*(1-q)+7.6e-3*[hv]*[no2]+3.3e-2
*[no3]*[hv]+125000=[o3]*(8.79e-6*[hv]+1.59e-15*[ho2]
+6.97e-14*[ho]+1.83e-14*[no]+3.41e-17*[no2])
                                - [O3] -

(THE SIMPLIFIED SYSTEM)

[ho2]
=sqr((8.79e-6*[o3]*q*[hv]+7.6e-6*[h2o2]*[hv])/4.06e-12)

[h2o2]
=(4.06e-12*[ho2]*[ho2])/(rain+1.68e-12*[ho]+7.6e-6*[hv])

[ho]*(2.7e-13*[co]+8.03e-15*[ch4])=2*(8.79e-6*[o3]*q*[hv]
+7.6e-6*[h2o2]*[hv])*(1+((1.59e-15*[o3]+8.38e-12*[no])
/(2*sqr(4.06e-12*(8.79e-6*[o3]*q*[hv]+7.6e-6*[h2o2]
*[hv])))))

[no]=([nox]*7.6e-3*[hv])/(8.38e-12*[ho2]+1.83e-14*[o3]
+7.6e-3*[hv])
[o3]*(8.79e-6*[hv]+1.59e-15*[ho2]+1.83e-14*[no])
=8.79e-6*[o3]*(1-q)*[hv]+([nox]-[no])*7.6e-3*[hv]

```

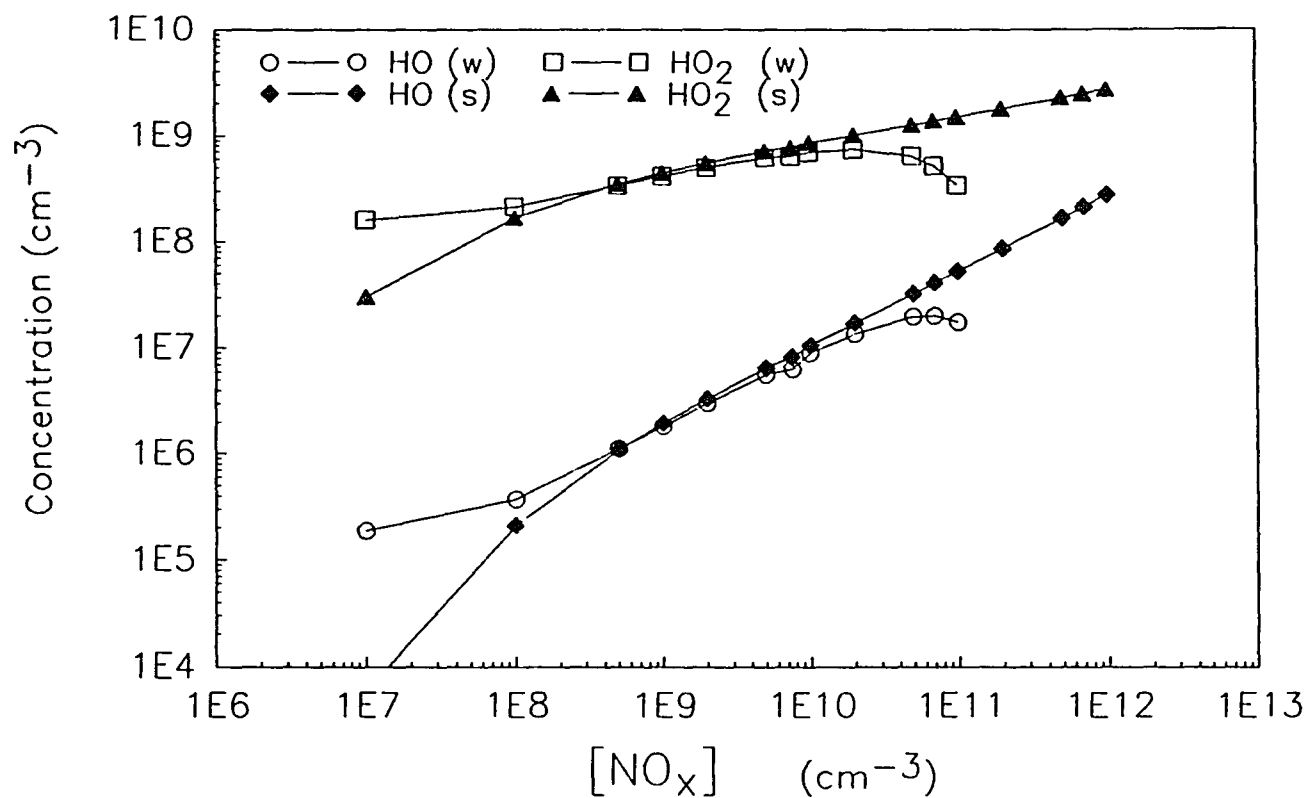


Figure 45. Variation of $[HO_i]$ with $[NO_i]$ (noon value) via simultaneous equations solver (SEQS), comparison of the whole system (w) with simplified equations system (s). Here ozone is not held constant. Both systems are shown on Table XVIII.

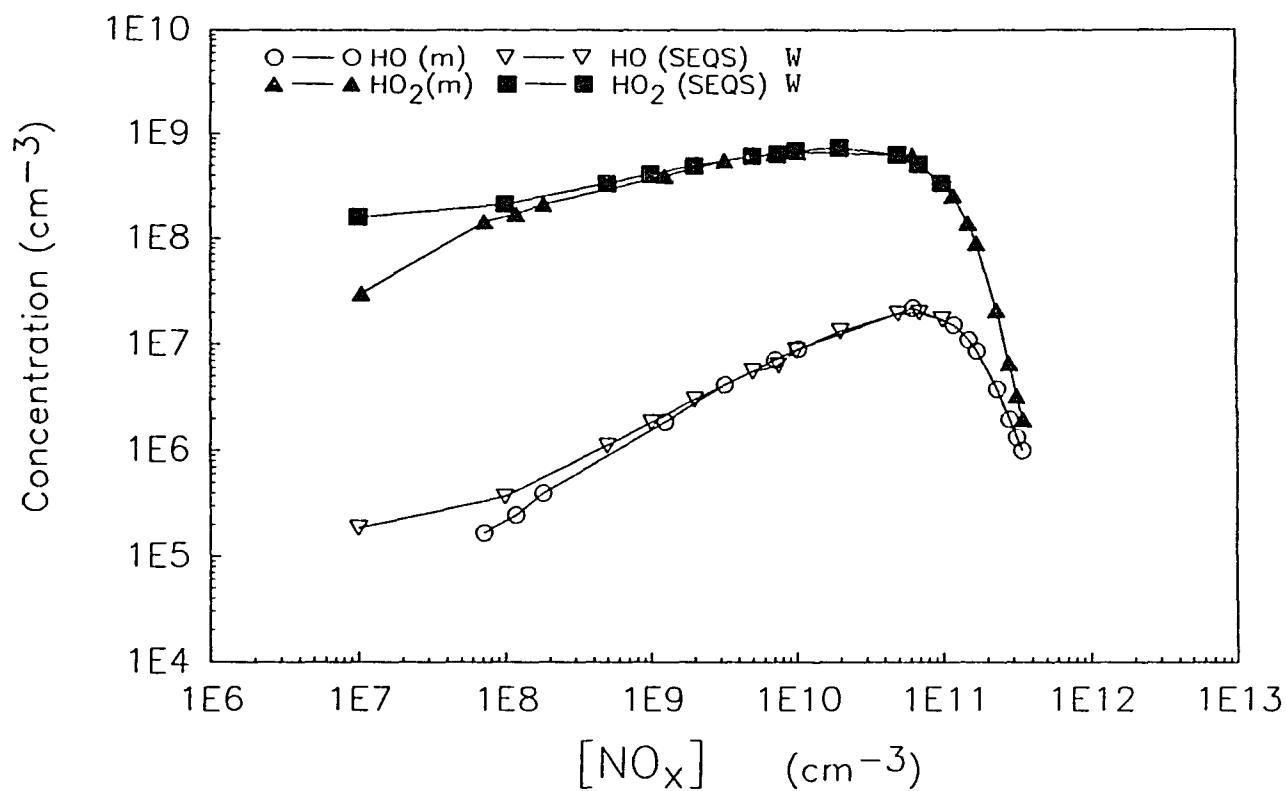


Figure 46. Variation of $[\text{HO}]$ with $[\text{NO}_x]$ (noon value), comparison of numerical integration model (m) with SEQS (whole system). The agreement is good well except for deviation at very low $[\text{NO}_x]$. Here ozone is not held constant. See Figure 20 for model's ozone.

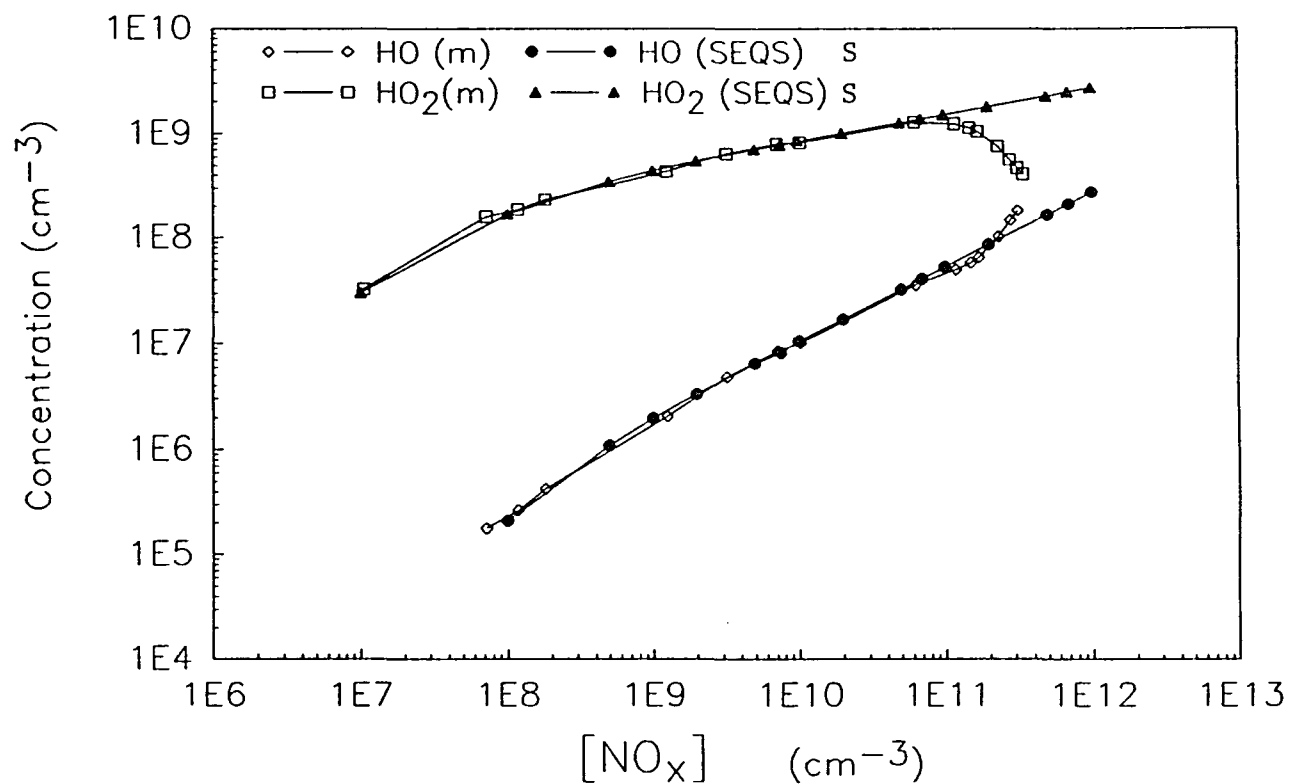


Figure 47. Variation of [HO_i] with [NO_x] (noon value), comparison of numerical integration model (m) with SEQS (simplified equations system). The agreement is good except for deviation occurred at high [NO_x]. Here ozone is not held constant. See Figure 20 for model's ozone.

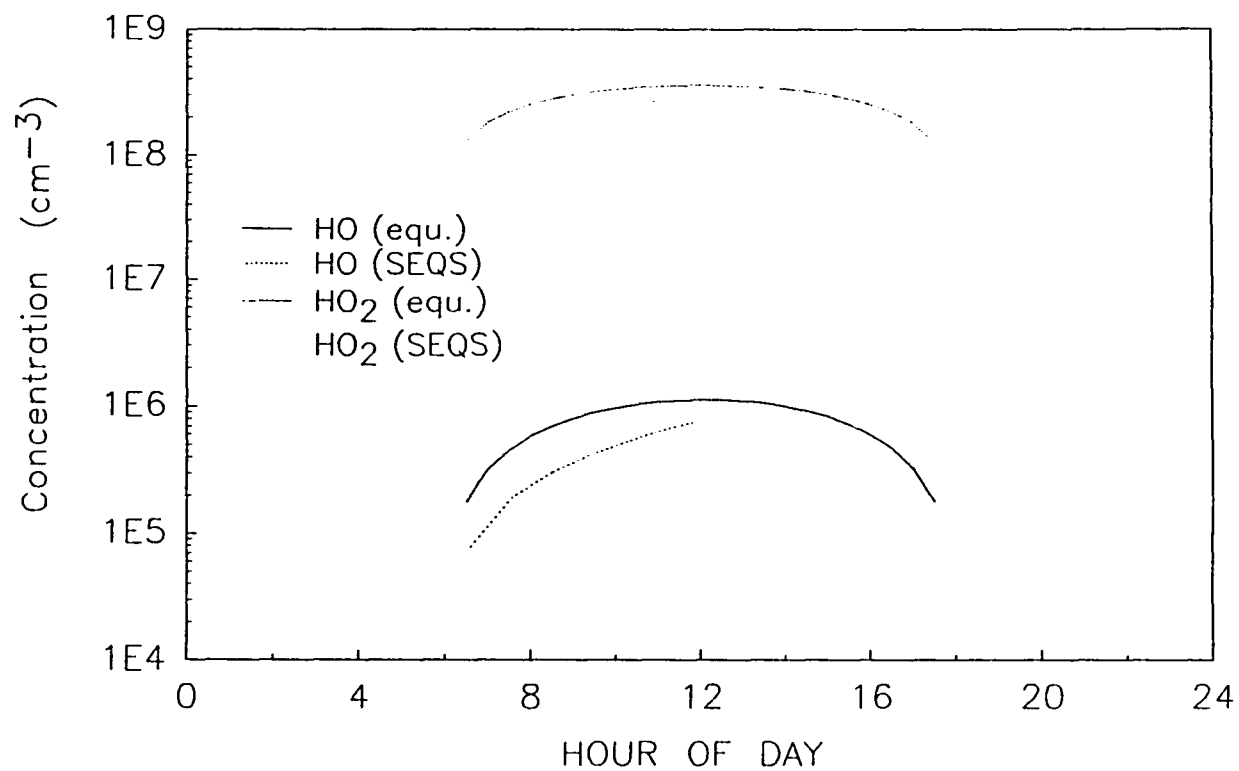


Figure 48. Comparison of diurnal profiles for HO and HO₂ as calculated by SEQS and by equations 6-2 and 6-4. The afternoon data from SEQS is exactly identical as morning data.

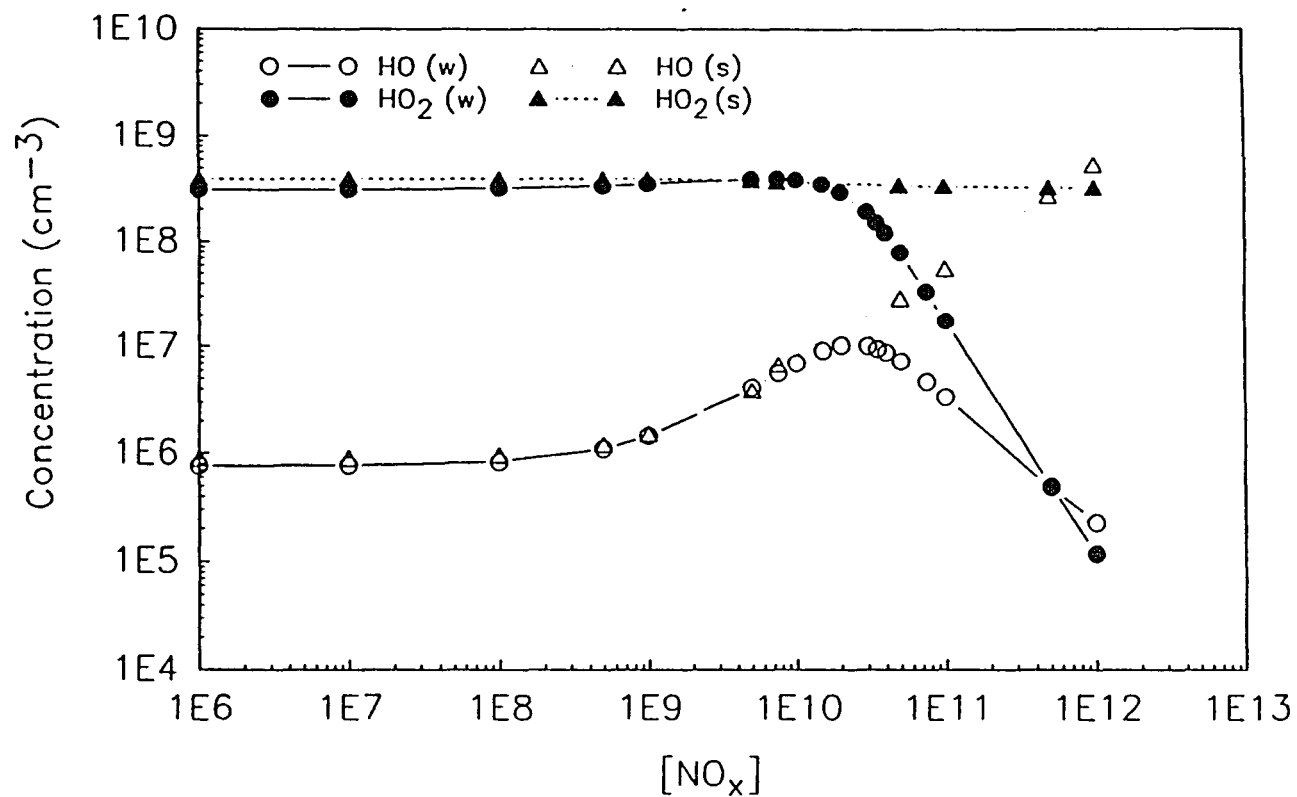


Figure 49. Variation of $[HO_x]$ with $[NO_x]$ via simultaneous equations solver (SEQS), comparison of the whole system (w) with simplified equations system (s). Conditions are same as Figure 45 except ozone concentration has been kept constant at 24 ppb ($6 \times 10^{11} \text{ cm}^{-3}$).

CHAPTER VII

DISCUSSION AND SUMMARY

SENSITIVITY ANALYSIS OF EQUATIONS

The validity of any analysis is limited by the reliability of input data, including rate constants and initial concentrations. Since $[HO]$ and $[HO_2]$ are given in closed form, it is straightforward to carry out a sensitivity analysis by the generalized procedure to establish uncertainty limits on the predictions of current tropospheric chemical models.

$$s_{HO_x} = \sqrt{\sum_j^N \left(\frac{\partial HO_x}{\partial j} \right)^2 s_j^2} \quad (7-1)$$

Here s_{HO_x} is the standard deviation in either $[HO]$ or $[HO_2]$ due to uncertainties or deviations in the j parameters which determine it. The term j includes rate constants and solar fluxes as well as concentrations. The relevant partial derivatives for quantum yield (q), the concentrations of HO and HO_2 are given in Appendix A. Sensitivity analysis is performed by SSESa.

HO₂ MEASUREMENTS

Because of the importance of HO, numerous efforts have been made to measure its atmospheric concentration. These measurements have used a variety of techniques and have been both ground and aircraft based (83,84,85,86,87,88,89,5,90). The initial goal of these studies is to learn whether calculated and measured HO concentrations agree. With Eq. 7-1, it is possible to use measurement uncertainties in the controlling concentrations (i.e. CH₄, CO, NO, H₂O₂, O₃, H₂O and solar intensity) and rate constants to set uncertainty limits in predicted [HO]. These limits set a goal for the necessary accuracy in the much more difficult [HO] measurement. Application of Eqn. 7-1 to Eqns. 6-2 & 6-4 results in uncertainty factors of 1.2 for [HO₂] and 1.4 for [HO], based upon recommended rate constant uncertainties (91) and an arbitrary 10% uncertainty in the controlling species concentration as well as solar intensity. The uncertainty sources are normalized to unity & tabulated vs. NO concentration in the Table XIX & XX for HO₂ and HO, respectively and Figure 50 & 51 display the results graphically. From Table XX, it is apparent that most uncertainty in calculating HO concentration comes from rate constants. Also, the relative sensitivity of [HO₂] to two different species can be easily calculated based on the data in the Table XIX & XX.

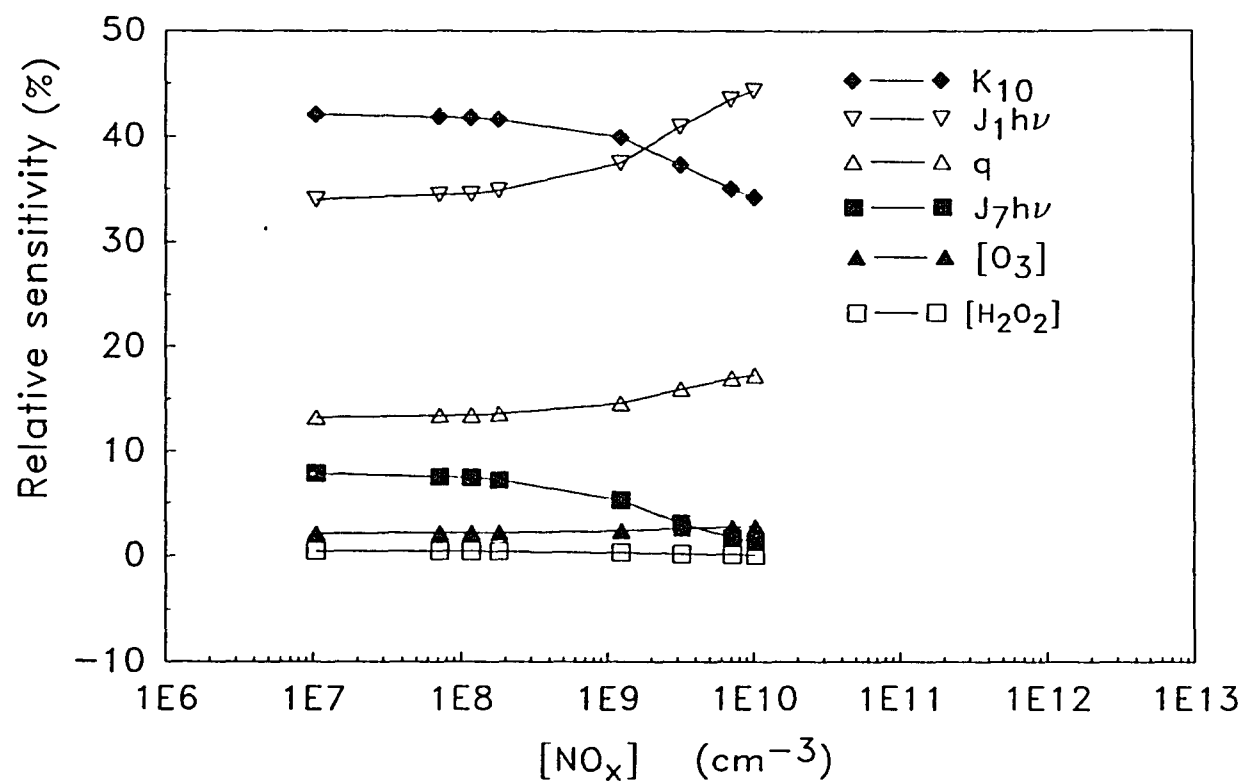


Figure 50. Variation of sensitivities of $[HO_2]$ to $[NO_x]$. The photolysis rate constant of ozone and self-reaction rate constants govern almost 80% of sensitivities of HO_2 concentration. Conditions are same as Figure 19.

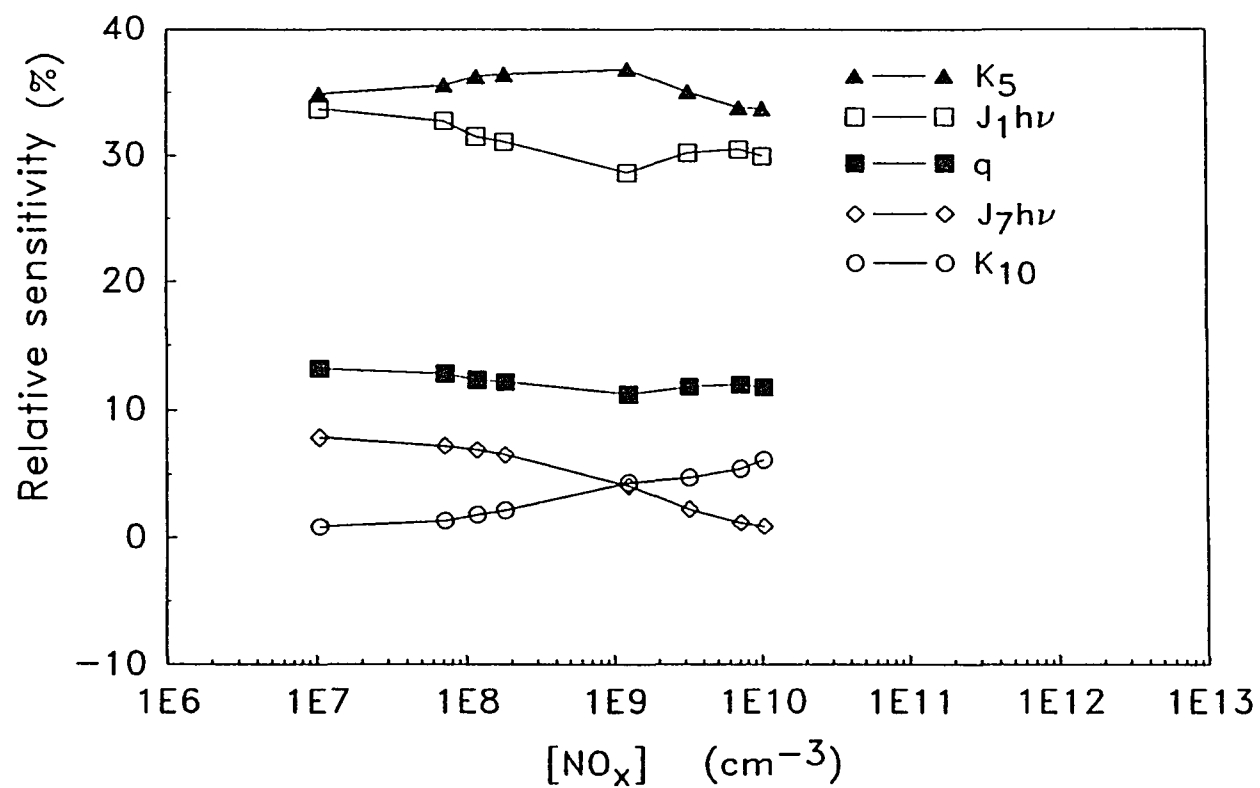


Figure 51. Variation of sensitivities of [HO] to [NO_x]. The photolysis rate constant of ozone and rate constant for reaction with CO govern almost 70% of sensitivities of HO₂ concentration. Conditions are same as Figure 19.

TABLE XIX
SPECIES, RATE CONSTANTS AND SENSITIVITIES
FOR HO₂

| SPECIES or RATE CONST. | NORMALIZED SENSITIVITIES (%) | | | | | | | | |
|------------------------------|------------------------------|------|------|------|------|------|------|------|---------------------------|
| | [NOx] (ppt) | | | | | | | | conc. rate constant |
| | 0.4 | 3 | 5 | 7 | 50 | 130 | 290 | 410 | |
| H2O2(1.1) | 0.5 | 0.5 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 | 0.1 | variable |
| O3 (1.1) | 2.1 | 2.2 | 2.2 | 2.2 | 2.3 | 2.6 | 2.7 | 2.8 | variable |
| q (1.25) | 13.3 | 13.5 | 13.5 | 13.6 | 14.6 | 16.0 | 17.0 | 17.3 | 7.6e-2 |
| J1hv(1.4) | 34.1 | 34.5 | 34.6 | 34.9 | 37.5 | 40.9 | 43.5 | 44.3 | 8.8e-6 |
| J5hv(1.4) | 7.9 | 7.6 | 7.5 | 7.3 | 5.3 | 3.1 | 1.7 | 1.3 | 7.6e-6 |
| k10(1.3) | 42.1 | 41.8 | 41.8 | 41.6 | 39.9 | 37.3 | 35.0 | 34.2 | 4.0e-1 |
| σ(HO2) | 0.25 | 0.25 | 0.25 | 0.25 | 0.26 | 0.28 | 0.31 | 0.31 | uncert. |

- Notes: 1. the number 7.6e-2 read as 7.6×10^{-2}
The unit for species is molecules cm⁻³
The unit for rate constant is cm³ sec⁻¹
2. The value in parentheses in the first column indicates the uncertainty factor.
arbitrary 10% for all species & light intensity.
the uncertainties for rate constant adopted from JPL publication 87-41. (91)
3. q = quantum yield for [HO] formation from O(¹D)
4. conditions 45°N, equinox, ground level.

TABLE XX
SPECIES, RATE CONSTANTS AND SENSITIVITIES
FOR HO

| SPECIES or RATE CONST. | NORMALIZED SENSITIVITIES (%) | | | | | | | | |
|------------------------------|------------------------------|------|------|------|------|------|------|------|---------------------------|
| | [NO _x] (ppt) | | | | | | | | conc. rate constant |
| | 0.4 | 3 | 5 | 7 | 50 | 130 | 290 | 410 | |
| CO (1.1) | 3.9 | 3.9 | 4.0 | 4.1 | 4.1 | 3.9 | 3.8 | 3.7 | 4.9e12 |
| H2O2(1.1) | 0.5 | 0.4 | 0.4 | 0.4 | 0.3 | 0.1 | 0.1 | 0.1 | variable |
| CH4(1.1) | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 4.2e13 |
| O3 (1.1) | 2.2 | 2.7 | 2.7 | 2.8 | 3.1 | 3.9 | 4.3 | 4.1 | variable |
| NO (1.1) | 0.3 | 0.3 | 0.5 | 0.5 | 0.9 | 0.7 | 0.7 | 1.0 | variable |
| q (1.25) | 13.2 | 12.8 | 12.3 | 12.2 | 11.2 | 11.8 | 11.9 | 11.7 | 7.6e-2 |
| J1hv(1.4) | 33.7 | 32.7 | 31.5 | 31.1 | 28.6 | 30.2 | 30.5 | 29.9 | 8.8e-6 |
| k5 (1.3) | 34.8 | 35.6 | 36.2 | 36.4 | 36.8 | 35.0 | 33.8 | 33.7 | 2.7e-13 |
| k6 (1.2) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 | 7.7e-15 |
| J5hv(1.4) | 7.8 | 7.2 | 6.9 | 6.5 | 4.1 | 2.3 | 1.2 | 0.9 | 7.6e-6 |
| k8 (1.3) | 0.0 | 0.4 | 0.5 | 0.8 | 1.7 | 3.4 | 4.3 | 3.8 | 2.0e-15 |
| k9 (1.2) | 1.3 | 1.3 | 1.8 | 1.9 | 3.6 | 2.8 | 3.0 | 3.9 | 8.3e-12 |
| k10(1.3) | 0.9 | 1.4 | 1.9 | 2.2 | 4.3 | 4.7 | 5.4 | 6.1 | 4.0e-12 |
| σ(HO) | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.5 | 0.5 | uncert. |

See Table XVIII for notes.

For instance, uncertainties in $J_1[\text{hv}]$ and k_5 account for over 60% of the $[\text{HO}]$ uncertainty at all NO concentrations. Since Table XX lists the squares of the uncertainty contributions, it is necessary to compare relative

sensitivities by taking the square root of the ratio of the Table XX values. For instance, the sensitivity of HO to ozone relative to its sensitivity to nitric oxide at [NO]= 50 ppt can be represented as the ratio $(3.1/0.9)^{\frac{1}{2}}$ or about 1.9. That is, a change in $[O_3]$ of 10% would produce about twice (1.9) as much change in [HO] as a 10% change in [NO]. Likewise, the relative sensitivity of [HO] to carbon monoxide vs. methane is $(4.1/0.3)^{\frac{1}{2}}$ or about 3.7, in agreement with the relative magnitude of the terms C and D in equation 6-4.

In current measurements, fairly long averaging times have been necessary for HO determination. These averaging times present potential difficulties in interpretation. It is obvious, for instance, that substitution of temporally and/or spatially averaged (via aircraft or long path absorption measurements) concentrations of controlling variables into Eqns. 6-2 & 6-4 will not necessarily yield a correct average HO_1 concentration to be compared with measurements. Thus, for n discrete values of A and B, the average $[HO_2]$ would be given by

$$[HO_2] = \frac{1}{n} \sum_{i=1}^n \sqrt{\frac{A_i + B_i}{k_{10}}} * \sqrt{\frac{\bar{A} + \bar{B}}{k_{10}}} \quad (7-2)$$

If the controlling variables can be measured on shorter time scales than HO_1 , then calculation of the correctly averaged $[HO_2]$ is accomplished by the equality in Eq. 7-2. Similar considerations apply to [HO].

Although almost all efforts to date have centered around the measurement of $[HO]$, Eqns. 6-2 and 6-4 indicate that HO_2 may be a more attractive candidate for model testing. First of all, its concentration is about 100 times higher than HO . Thus measurement uncertainties are less and/or averaging times may be significantly shorter. Second, the HO_2 concentration depends upon fewer controlling trace gases than does $[HO]$, and the uncertainty factor in its concentration (due in part to the square-root dependance) is 1.2 rather than 1.4 for $[HO]$ (Table XIX & XX).

Kasting and Singh's study (92) shows that the impact on HO & HO_2 by introducing current levels of NMHC-PAN has a seasonal variation with significant impact only in winter. The concentration of HO & HO_2 can be enhanced by factors of 5 & 50, respectively. Reactions of RCO_3 (from NMHC) with NO_2 are believed to account for the formation of PAN, which acts as a reservoir or transport agent for otherwise short-lived NO_2 .

COMPARISON OF EXPERIMENT WITH MODEL

Comparison of HO and HO_2 observations with the model has been accomplished by taking experimental data from Hard et al. (95), collected on Oregon's coast near Lincoln City. Table XXI indicates the conditions and Figure 52 & 53 shows the diurnal variation for both experiment and model for HO and HO_2 , respectively. In both sets of experimental data on HO & HO_2 , the morning fog is a factor which may have caused a lag

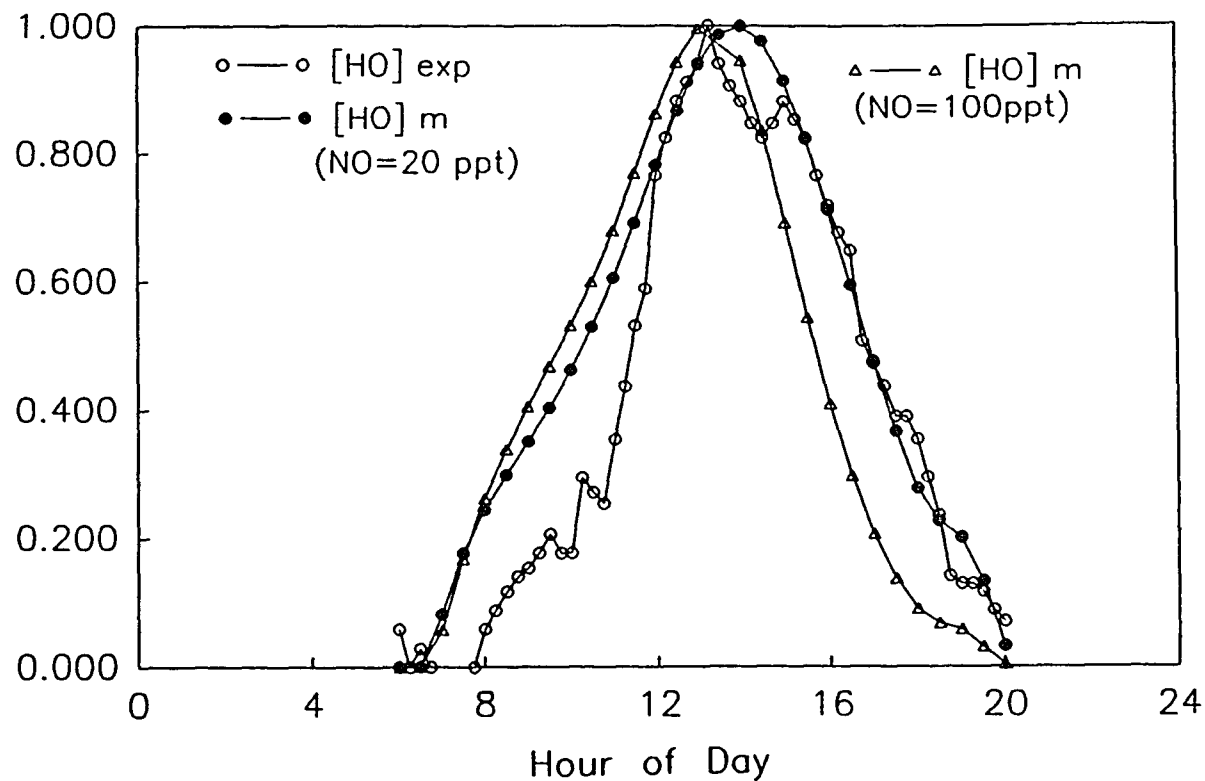


Figure 52. Diurnal variation of HO in clean air, comparison of numerical integration model with experimental data. The input data of ozone and light intensity in the model are taken from observation's data and polynomialized as a time series equation. Two [NO] values chosen were 20 ppt ($5 \times 10^8 \text{ cm}^{-3}$) and 100 ppt ($2.5 \times 10^9 \text{ cm}^{-3}$) and held constant over the course of the daytime. All data are normalized.

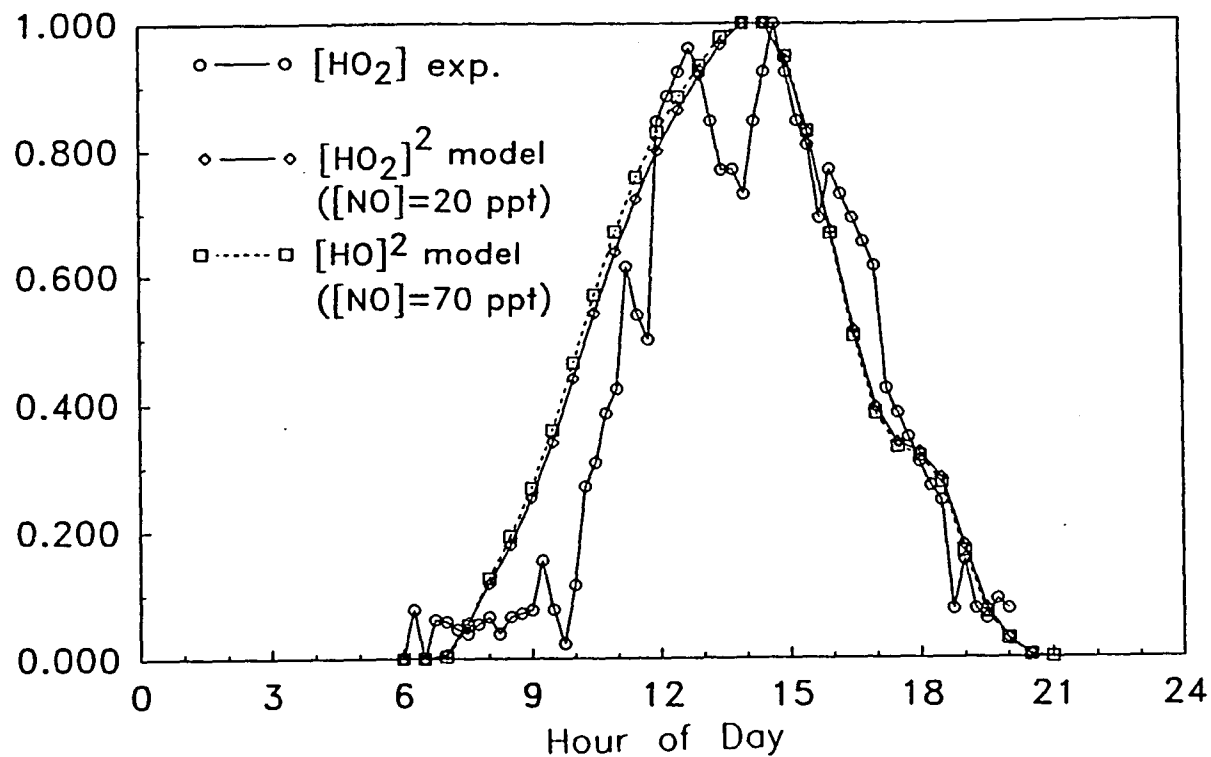


Figure 53. Diurnal variation of HO_2 in clean air, comparison of numerical integration model with experimental data. The input data of ozone and light intensity in the model are taken from observation's data and polynomialized as a time series equation. Two $[\text{NO}]$ values chosen were 20 ppt ($5 \times 10^8 \text{ cm}^{-3}$) and 70 ppt ($1.8 \times 10^9 \text{ cm}^{-3}$) and held constant over the course of the daytime. All data are normalized. The plot of $[\text{HO}_2]^2$ vs. local time evidenced that the ambient concentration of HO_2 is proportional to the square root of solar radiation

in radical concentration. The same considerations apply to the profile of [HO] compared to the model. Additionally, the wind pattern may have a significant impact on trace gas concentrations through horizontal or vertical mixing. Overall, the agreement of model with experimental data is adequate considering the preliminary nature of the experimental data.

TABLE XXI
COMPARISON OF EXPERIMENT WITH MODEL

| conditions | experiment | model |
|--------------------------------|------------------------|-------------------------------|
| latitude | 45° | 45° |
| altitude | ground level | ground level |
| season | summer | equinox |
| wind | variable | ----- |
| [H ₂ O] | 2% | 1.05% |
| [NO] ^a | ---- | 20 & 100 ppt |
| [O ₃] ^b | 30 ppb(max) | (note) |
| [HO ₂] | 6e7 (max) ^d | 3.0e8 molecs cm ⁻³ |
| [HO] | 5e6 (max) ^e | 1.6e6 molecs cm ⁻³ |
| hv ^c | real time | (note) |

- Note : a. NO analyzer was not sensitive to ppt level.
 b. diurnal data of ozone have been polynomialized to a time series equation and used as an input for modelling
 c. diurnal data of light intensity have been polynomialized and used as an input for modelling.
 d. experimental data for HO₂ are 15 min average.
 e. experimental data for HO are 2 hours average.

TRENDS IN HO CONCENTRATION

Equations 6-2 and 6-4 should be useful in several contexts of clean air atmospheric chemistry. First, multi-dimensional global air chemistry models would run more

efficiently if $[HO]$ could be accurately calculated by a single equation. Models in current use must calculate the global distribution of $[HO]$ in order to reconcile measured levels of various trace gases with emissions. For instance, global measurements of methylchloroform (CH_3CCl_3) (6,93,94,95) and of ^{14}CO (83,96) have been used to calculate globally averaged HO concentrations since reaction with HO is their only significant loss process.

Knowledge of past, present and future HO concentrations is necessary to understand how the atmosphere's trace gas composition is changing due to natural and anthropogenic processes. This is especially important for those gases which are infrared absorbers or interact with the stratospheric ozone layer.

Considerable concern has been expressed over the apparent long-term increase in measured concentrations of methane and carbon monoxide. These increases have been postulated to be causing decreases in atmospheric HO concentrations. Eq. 6-4 allows inference of changes in $[HO]$ from measured changes in $[CH_4]$ and $[CO]$. Levine et al (97) have used evidence of increasing methane and CO concentrations to calculate the effect on HO concentrations. Values chosen were 1%/year for methane and 2%/year for carbon monoxide. Changes in these concentrations will affect concentrations of nitric oxide and ozone indirectly. Rather than probing these, we illustrate four scenarios in Figure 54 to 57. In each, 1% and 2% annual

changes in methane and carbon monoxide are projected backward to 1950 and forward 50 years. The backward projections are based upon the spectroscopic measurements of Rinsland et al (98,99) and Thompson et al (10,100), forward projections are speculative. These increases are coupled with varying changes in nitric oxide and ozone, with constant hydrogen peroxide. If nitric oxide and ozone are constant over the 85-year period, [HO] drops by about 75%. (Figure 54) If nitric oxide and ozone both increase 1% annually, the net HO decrease is reduced to about 50%. (Figure 55) If ozone increases 1% and nitric oxide 2%, the HO decrease is 20%. (Figure 56) Finally, if ozone increases 2% and nitric oxide 1%, then the HO decrease is only 10% and the HO concentration goes through a minimum around 2010. (Figure 57) None of these scenarios are totally unrealistic, and the range of changes in HO is considerable, varying from a 75% decrease to almost no decrease at all. An [HO] decrease of 75% would have a profound influence on the atmosphere. For a species removed solely by reaction with HO, whose emissions remain constant, a 75% decrease in HO would (to a first-order approximation) produce a four-fold increase in the species concentration at steady-state. If emission rates of the species are increasing also, a more likely event, the species concentration would increase even further.

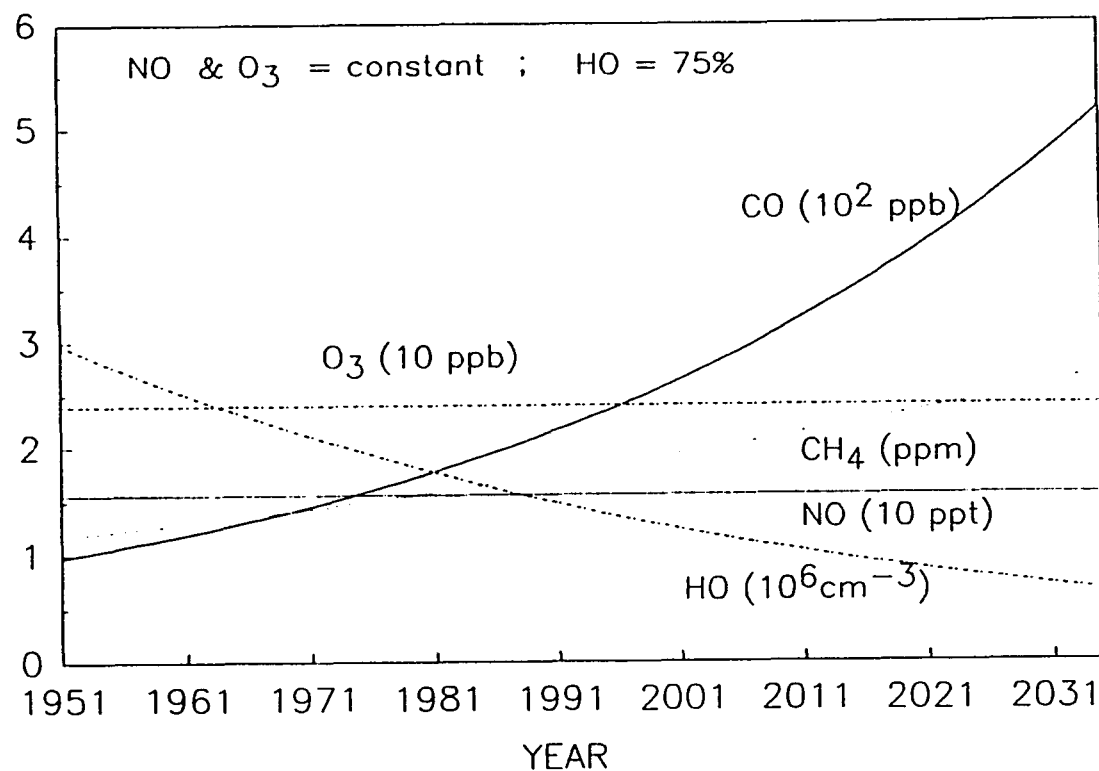


Figure 54. Past and future changes in [HO] with both nitric oxide and ozone constant. Methane and carbon monoxide concentrations are projected backwards to 1951 at respective annual rates of 1% and 2%. These changes are projected forwards arbitrarily for 50 years from the present. A 75% decrease in HO is predicted.

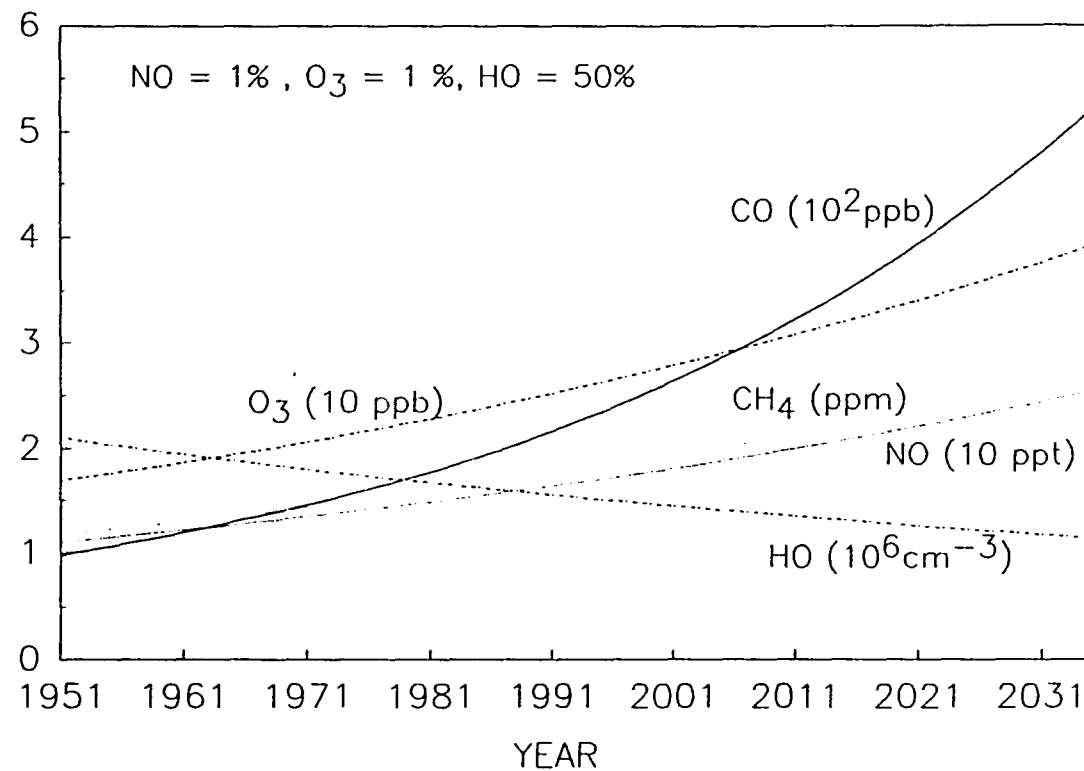


Figure 55. Past and future changes in [HO] with both nitric oxide and ozone have annual rates of 1%. Conditions are same as Figure 54. A 50% decrease in HO is predicted.

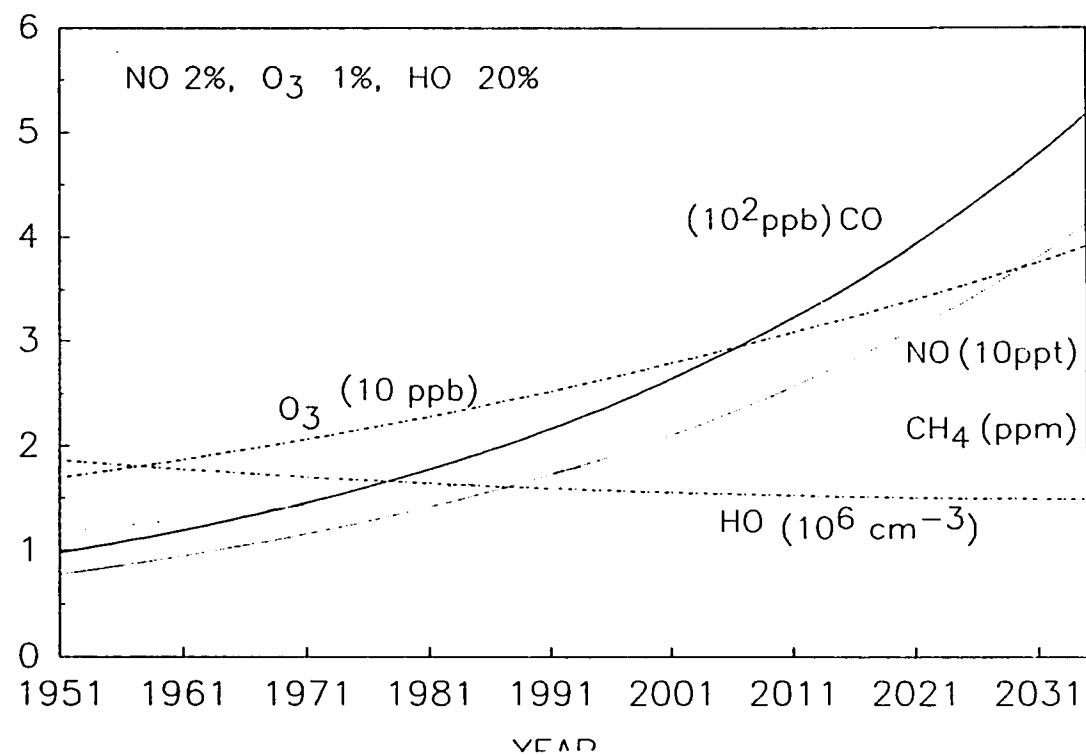


Figure 56. Past and Future changes in [HO] with both nitric oxide and ozone have annual rates of 2% and 1%, respectively. Conditions are same as Figure 54. A 20% decrease in HO is predicted.

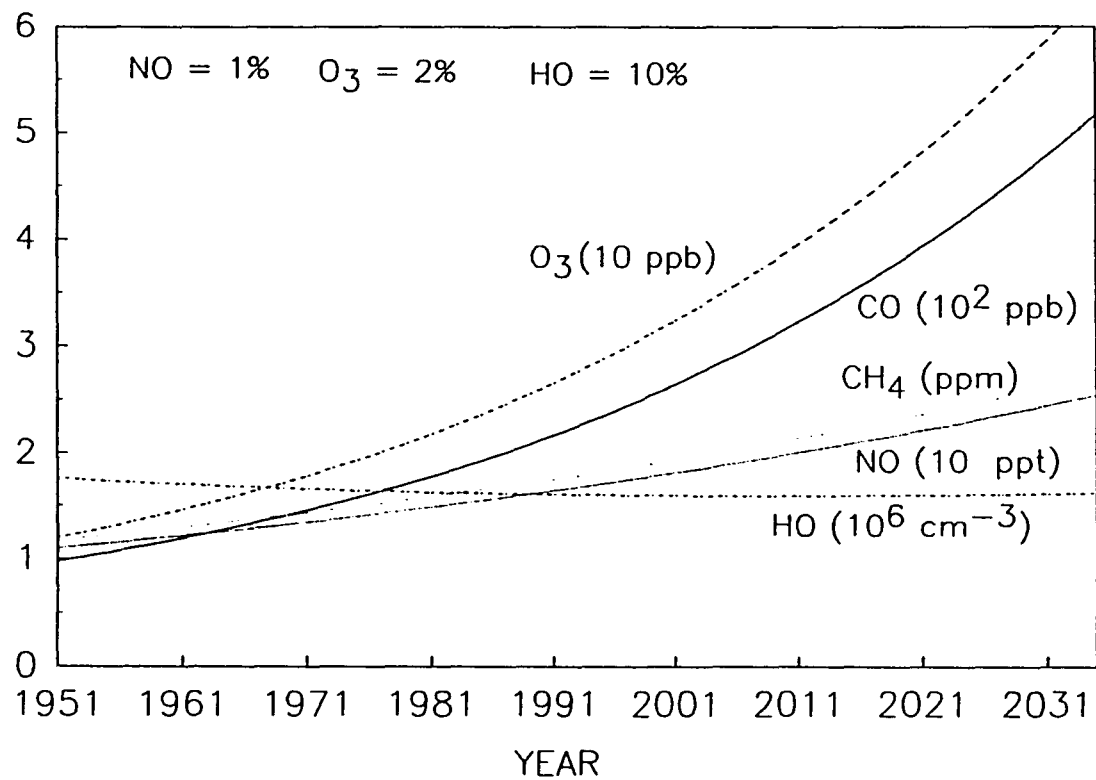


Figure 57. Past and Future changes in [HO] with both nitric oxide and ozone have annual rates of 1% and 2%, respectively. Conditions are same as Figure 54. A 10% decrease in HO is predicted.

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Note: Since the defense of this thesis was given on March 9, 1990, the literature is reviewed through the end of 1989.

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APPENDIX A

PARTIAL DERIVATIVES FOR CALCULATING SENSITIVITY ANALYSIS

QUANTUM YIELD (Q) FOR [HO] RADICAL

TABLE XXII

SUMMARY OF PARTIAL DERIVATIVES FOR QUANTUM YIELD (Q)

| parameters | partial derivatives |
|---------------|---------------------------------------|
| $[H_2O]$ | $\frac{K_4 (d - K_4 [H_2O])}{d^2}$ |
| $k_2 (1.2)^*$ | $- \frac{[N_2] K_4 [H_2O]}{d^2}$ |
| $k_3 (1.2)^*$ | $- \frac{[O_2] K_4 [H_2O]}{d^2}$ |
| $k_4 (1.2)^*$ | $\frac{[H_2O] (d - K_4 [H_2O])}{d^2}$ |

Note: $d = k_1[N_2] + k_3[O_2] + k_4[H_2O]$

All rate constants are correspond to mechanism (Table I)

The value in the parentheses with * indicates the uncertainty factor for that rate constant.

(JPL publication 87-41) (91)

Equations

$$Q = \frac{K_4 [H_2O]}{K_2 [N_2] + K_3 [O_2] + K_4 [H_2O]} = \frac{K_4 [H_2O]}{d}$$

$$\begin{aligned}
 \frac{\partial q}{\partial [H_2O]} &= \frac{1}{d} \partial [K_4 [H_2O] + K_4 [H_2O] \partial \frac{1}{d}] \\
 &= \frac{K_4}{d} - \frac{K_4 [H_2O] K_4}{d^2} \\
 &= \frac{K_4 (d - K_4 [H_2O])}{d^2}
 \end{aligned}$$

$$\frac{\partial q}{\partial K_2} = K_4 [H_2O] \partial \frac{1}{d} = - \frac{K_4 [H_2O] [N_2]}{d^2}$$

$$\frac{\partial q}{\partial K_3} = K_4 [H_2O] \partial \frac{1}{d} = - \frac{K_4 [H_2O] [O_2]}{d^2}$$

$$\begin{aligned}
 \frac{\partial q}{\partial K_4} &= \frac{1}{d} \partial [K_4 [H_2O] + K_4 [H_2O] \partial \frac{1}{d}] \\
 &= \frac{[H_2O]}{d} - \frac{K_4 [H_2O] K_4}{d^2} \\
 &= \frac{[H_2O] (d - K_4 [H_2O])}{d^2}
 \end{aligned}$$

[HO₂]

TABLE XXIII
SUMMARY OF PARTIAL DERIVATIVES OF [HO₂]

| Parameters | Partial derivatives |
|----------------------------------|---|
| [O ₃] | $\frac{J_1 [hv] q}{2 \sqrt{aK_{10}}}$ |
| [H ₂ O ₂] | $\frac{J_7 [hv]}{2 \sqrt{aK_{10}}}$ |
| $J_1 [hv] (1.4)^*$ | $\frac{[O_3] q}{2 \sqrt{aK_{10}}}$ |
| $J_7 [hv] (1.4)^*$ | $\frac{[H_2O_2]}{2 \sqrt{aK_{10}}}$ |
| $K_{10} (1.3)^*$ | $-\sqrt{\frac{a}{4 K_{20}^3}}$ |
| $q (1.25)$ | $\frac{J_1 [O_3] [hv]}{2 \sqrt{aK_{10}}}$ |

Note: $a = J_1[O_3][hv] q + J_7[H_2O_2][hv]$; see Table XXII.

$$q = \frac{K_4 [H_2O]}{K_2 [N_2] + K_3 [O_2] + K_4 [H_2O]} = \frac{K_4 [H_2O]}{d}$$

Equations

$$[HO_2] = \sqrt{\frac{J_1 [hv] [O_3] q + J_7 [H_2O_2] [hv]}{K_{10}}} = \sqrt{\frac{a}{K_{10}}}$$

$$\begin{aligned} \frac{\partial [HO_2]}{\partial [O_3]} &= \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \partial \left(\frac{J_1 [hv] [O_3] q + J_7 [H_2O_2] [hv]}{K_{10}} \right) \\ &= \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(\frac{J_1 [hv] q}{K_{10}} \right) = \frac{J_1 [hv] q}{2 \sqrt{a} K_{10}} \end{aligned}$$

$$\frac{\partial [HO_2]}{\partial [H_2O_2]} = \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(\frac{J_7 [hv]}{K_{10}} \right) = \frac{J_7 [hv]}{2 \sqrt{a} K_{10}}$$

$$\frac{\partial [HO_2]}{\partial J_1 [hv]} = \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(\frac{[O_3] q}{K_{10}} \right) = \frac{[O_3] q}{2 \sqrt{a} K_{10}}$$

$$\frac{\partial [HO_2]}{\partial J_7 [hv]} = \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(\frac{[H_2O_2]}{K_{10}} \right) = \frac{[H_2O_2]}{2 \sqrt{a} K_{10}}$$

$$\frac{\partial [HO_2]}{\partial q} = \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(\frac{J_1 [O_3] [hv]}{K_{10}} \right) = \frac{J_1 [O_3] [hv]}{2 \sqrt{a} K_{10}}$$

$$\begin{aligned} \frac{\partial [HO_2]}{K_{10}} &= \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \partial \left(\frac{a}{K_{10}} \right) = \frac{1}{2} \sqrt{\frac{K_{10}}{a}} \left(-\frac{a}{K_{10}^2} \right) \\ &= -\frac{1}{\sqrt{4}} \left(\frac{\sqrt{a}}{K_{10}^{1.5}} \right) = -\sqrt{\frac{a}{4 K_{10}^3}} \end{aligned}$$

[HO]

TABLE XXIV

SUMMARY OF PARTIAL DERIVATIVES OF [HO]

| Parameter | Partial derivatives |
|--------------------|---|
| $[O_3]$ | $\frac{1}{b} (2J_1 [hv] q + k_8 \sqrt{\frac{a}{k_{10}}} + \frac{J_1 [hv] qc}{2\sqrt{ak_{10}}})$ |
| $[H_2O_2]$ | $(\frac{J_7 [hv]}{b}) (2 + \frac{c}{2\sqrt{ak_{10}}})$ |
| $[CO]$ | $- (\frac{k_5}{b^2}) (2a + c\sqrt{\frac{a}{k_{10}}})$ |
| CH_4 | $- (\frac{k_6}{b^2}) (2a + c\sqrt{\frac{a}{k_{10}}})$ |
| NO | $\frac{k_9}{b} \sqrt{\frac{a}{k_{10}}}$ |
| $J_1 [hv] (1.4)^*$ | $\frac{[O_3] q}{b} (2 + \frac{c}{2\sqrt{ak_{10}}})$ |
| $k_5 (1.3)^*$ | $- \frac{[CO]}{b^2} (2a + c\sqrt{\frac{a}{k_{10}}})$ |
| $k_6 (1.2)^*$ | $- \frac{[CH_4]}{b^2} (2a + c\sqrt{\frac{a}{k_{10}}})$ |

TABLE XXIV

SUMMARY OF PARTIAL DERIVATIVES OF [HO]
(continued)

| Parameter | Partial derivatives |
|--------------------|--|
| $J_7 [hv] (1.4)^*$ | $\frac{[H_2O_2]}{b} (2 + \frac{c}{2\sqrt{ak_{10}}})$ |
| $k_8 (1.3)^*$ | $\frac{[O_3]}{b} \sqrt{\frac{a}{k_{10}}}$ |
| $k_9 (1.2)^*$ | $\frac{[NO]}{b} \sqrt{\frac{a}{k_{10}}}$ |
| $q (1.25)$ | $\frac{[O_3] J_1 [hv]}{b} (2 + \frac{c}{2\sqrt{ak_{10}}})$ |
| $k_{10} (1.3)^*$ | $-\frac{c}{2b} \sqrt{\frac{a}{k_{10}^3}}$ |

Note: see TABLE XXII

$$a = J_1 [O_3] [hv] q + J_7 [H_2O_2] [hv] ; \quad b = k_5 [CO] + k_6 [CH_4]$$

$$c = k_8 [O_3] + k_9 [NO] ; \quad d = k_2 [N_2] + k_3 [O_2] + k_4 [H_2O]$$

$$q = \frac{k_4 [H_2O]}{k_2 [N_2] + k_3 [O_2] + k_4 [H_2O]}$$

Equations

$$[HO] = \frac{2a}{b} \left(1 + \frac{c}{2\sqrt{ak_{10}}}\right)$$

$$\frac{\partial [HO]}{\partial J_1 [hv]} = \frac{2[O_3]q}{b} + \frac{1}{2} \left(\frac{c}{b\sqrt{k_{10}}} \right) = \frac{[O_3]q}{b} \left(2 + \frac{c}{2\sqrt{ak_{10}}}\right)$$

$$\frac{\partial [HO]}{\partial q} = \frac{2[O_3]J_1 [hv]}{b} + \frac{1}{2} \left(\frac{c}{b\sqrt{k_{10}}} \right) = \frac{[O_3]J_1 [hv]}{b} \left(2 + \frac{c}{2\sqrt{ak_{10}}}\right)$$

$$\begin{aligned} \frac{\partial [HO]}{\partial [O_3]} &= \partial \left(\frac{2a}{b} \right) + \partial \left(\frac{c}{b} \sqrt{\frac{a}{k_{10}}} \right) = \frac{2qJ_1 [hv]}{b} \\ &+ \frac{qJ_1 [hv] k_8 [O_3] + qJ_1 [hv] k_9 [NO]}{b\sqrt{ak_{10}}} + \frac{2k_8 [O_3] a}{b\sqrt{k_{10}}} \\ &= \frac{1}{b} \left(2qJ_1 [hv] + \frac{qJ_1 [hv] c}{2\sqrt{ak_{10}}} + k_8 \sqrt{\frac{a}{k_{10}}} \right) \end{aligned}$$

$$\begin{aligned} \frac{\partial [HO]}{\partial [H_2O_2]} &= \partial \left(\frac{2a}{b} + \frac{c}{b} \sqrt{\frac{a}{k_{10}}} \right) = \frac{2J_7 [hv]}{b} + \frac{J_7 [hv] c}{2b\sqrt{ak_{10}}} \\ &= \frac{J_7 [hv]}{b} \left(2 + \frac{c}{2\sqrt{ak_{10}}} \right) \end{aligned}$$

$$\begin{aligned} \frac{\partial [HO]}{\partial [CO]} &= \partial \left(\frac{2a}{b} \right) \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) = - \frac{2ak_5}{b^2} \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \\ &= - \frac{k_5}{b^2} \left(2a + c \sqrt{\frac{a}{k_{10}}} \right) \end{aligned}$$

$$\begin{aligned} \frac{\partial [HO]}{\partial [CH_4]} &= \partial \left(\frac{2a}{b} \right) \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) = - \frac{2ak_6}{b^2} \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \\ &= - \frac{k_6}{b^2} \left(2a + c \sqrt{\frac{a}{k_{10}}} \right) \end{aligned}$$

$$\frac{\partial [HO]}{\partial [NO]} = \frac{1}{b} \sqrt{\frac{a}{k_{10}}} \partial(k_9 [NO]) = \frac{k_9}{b} \sqrt{\frac{a}{k_{10}}}$$

$$\begin{aligned} \frac{\partial [HO]}{\partial k_5} &= \partial \left(\left(\frac{2a}{b} \right) \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \right) = - \frac{2a[CO]}{b^2} \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \\ &= - \frac{[CO]}{b^2} (2a + c\sqrt{\frac{a}{k_{10}}}) \end{aligned}$$

$$\begin{aligned} \frac{\partial [HO]}{\partial k_6} &= \partial \left(\left(\frac{2a}{b} \right) \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \right) = - \frac{2a[CH_4]}{b^2} \left(1 + \frac{c}{2\sqrt{ak_{10}}} \right) \\ &= - \frac{[CH_4]}{b^2} (2a + c\sqrt{\frac{a}{k_{10}}}) \end{aligned}$$

$$\frac{\partial [HO]}{\partial J_7 [hv]} = \partial \left(\frac{2a}{b} + \frac{c}{b} \sqrt{\frac{a}{k_{10}}} \right) = \frac{[H_2O_2]}{b} \left(2 + \frac{c}{2\sqrt{ak_{10}}} \right)$$

$$\frac{\partial [HO]}{\partial k_8} = \frac{1}{b} \sqrt{\frac{a}{k_{10}}} \partial(k_8 [O_3]) = \frac{[O_3]}{b} \sqrt{\frac{a}{k_{10}}}$$

$$\frac{\partial [HO]}{\partial k_9} = \frac{1}{b} \sqrt{\frac{a}{k_{10}}} \partial(k_9 [NO]) = \frac{[NO]}{b} \sqrt{\frac{a}{k_{10}}}$$

$$\frac{\partial [HO]}{\partial k_{10}} = \partial \left(\frac{2a}{b} + \frac{c}{b} \sqrt{\frac{a}{k_{10}}} \right) = - \frac{c\sqrt{a}}{2b} \left(\frac{1}{k_{10}^{1.5}} \right) = - \frac{c}{2b} \sqrt{\frac{a}{k_{10}^3}}$$

APPENDIX B

DATA TABLE FROM COMBINATION OF $\text{HO}/\text{HO}_2/\text{CH}_3\text{O}/\text{CH}_3\text{O}_2$

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=1E7 [NO_x]=1.06e7

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| -2 | 3.659e+03 | R10 | ho2+ho2 | -7.318e+03 | 69.33 | -7.356e+03 | 226 | *** |
| 2 | 2.950e+03 | R4 | od+h2o | 5.900e+03 | 56.10 | -1.456e+03 | -40 | *** |
| -2 | 1.605e+03 | R16 | ch32+ho2 | -3.210e+03 | 30.41 | -4.666e+03 | 20 | -7 |
| 2 | 1.418e+03 | R7 | h2o2+hv | 2.836e+03 | 26.96 | -1.830e+03 | -17 | -27 |
| 2 | 4.718e+02 | R18 | ch3h+hv | 9.436e+02 | 8.97 | -8.862e+02 | -5 | -10 |
| 2 | 4.050e+02 | R23 | h2co+hv | 8.100e+02 | 7.70 | -7.616e+01 | -5 | -5 |
| -1 | 2.692e+01 | R37 | ho2+no2 | -2.692e+01 | .26 | -1.031e+02 | 0 | -0 |
| 1 | 1.417e+01 | R45 | hno4+hv | 1.417e+01 | .13 | -8.891e+01 | -0 | -0 |
| 1 | 1.275e+01 | R33 | hno4 | 1.275e+01 | .12 | -7.616e+01 | -0 | -0 |
| 2 | 2.647e-01 | R50 | od+ch4 | 5.294e-01 | .01 | -7.564e+01 | -0 | -0 |
| 1 | 4.880e-01 | R43 | hno2+hv | 4.880e-01 | .00 | -7.515e+01 | -0 | -0 |
| -1 | 4.459e-01 | R35 | ho+no | -4.459e-01 | .00 | -7.559e+01 | 0 | 0 |
| 2 | 6.609e-02 | R52 | od+h2 | 1.322e-01 | .00 | -7.546e+01 | -0 | -0 |
| -1 | 4.668e-02 | R26 | ho2+no2 | -4.668e-02 | .00 | -7.551e+01 | 0 | 0 |
| -1 | 3.969e-02 | R36 | ho+no2 | -3.969e-02 | .00 | -7.555e+01 | 0 | 0 |
| 1 | 1.781e-02 | R44 | hno3+hv | 1.781e-02 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 1.692e-05 | R31 | ho+hno2 | -1.692e-05 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 1.051e-06 | R30 | ho+hno3 | -1.051e-06 | .00 | -7.553e+01 | -0 | -0 |
| -1 | 3.200e-07 | R32 | ho+hno4 | -3.200e-07 | .00 | -7.553e+01 | -0 | -0 |

deviation = rate/sum of production = -3.59061e-3

sum of production = 10517.7 ; sum of sink = 10555.5

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=5E7 , [NO_x]=7.24e7

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| -2 | 8.386e+04 | R10 | ho2+ho2 | -1.677e+05 | 66.25 | -1.687e+05 | 196 | *** |
| 2 | 6.920e+04 | R4 | od+h2o | 1.384e+05 | 54.89 | -3.033e+04 | -39 | *** |
| -2 | 3.988e+04 | R16 | ch32+ho2 | -7.976e+04 | 31.51 | -1.101e+05 | 21 | -6 |
| 2 | 3.230e+04 | R7 | h2o2+hv | 6.460e+04 | 25.62 | -4.549e+04 | -17 | 27 |
| 2 | 1.165e+04 | R18 | ch3h+hv | 2.330e+04 | 9.24 | -2.219e+04 | -6 | -11 |
| 2 | 1.009e+04 | R23 | h2co+hv | 2.018e+04 | 8.00 | -2.008e+03 | -5 | -5 |
| -1 | 5.558e+03 | R37 | ho2+no2 | -5.558e+03 | 2.20 | -7.566e+03 | 1 | 0 |
| 1 | 2.925e+03 | R45 | hno4+hv | 2.925e+03 | 1.16 | -4.641e+03 | -1 | -1 |
| 1 | 2.633e+03 | R33 | hno4 | 2.633e+03 | 1.04 | -2.008e+03 | -1 | -1 |
| 1 | 6.453e+01 | R43 | hno2+hv | 6.453e+01 | .03 | -1.944e+03 | -0 | 0 |
| -1 | 5.554e+01 | R35 | ho+no | -5.554e+01 | .02 | -2.000e+03 | 0 | 0 |
| -1 | 4.264e+01 | R36 | ho+no2 | -4.264e+01 | .02 | -2.042e+03 | 0 | 0 |
| 1 | 1.936e+01 | R44 | hno3+hv | 1.936e+01 | .01 | -2.023e+03 | -0 | -0 |
| 2 | 6.210e+00 | R50 | od+ch4 | 1.242e+01 | .00 | -2.010e+03 | -0 | -0 |
| -1 | 9.638e+00 | R26 | ho2+no2 | -9.638e+00 | .00 | -2.020e+03 | 0 | 0 |
| 2 | 1.550e+00 | R52 | od+h2 | 3.100e+00 | .00 | -2.017e+03 | -0 | -0 |
| -1 | 5.573e-02 | R31 | ho+hno2 | -5.573e-02 | .00 | -2.017e+03 | 0 | 0 |
| -1 | 2.846e-02 | R30 | ho+hno3 | -2.846e-02 | .00 | -2.017e+03 | 0 | 0 |
| -1 | 1.646e-03 | R32 | ho+hno4 | -1.646e-03 | .00 | -2.017e+03 | 0 | 0 |

deviation = rate/sum of production = -3.99978e-3

sum of production = 252137. ; sum of sink = 253146.

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=7E7, [NO_x]=1.18e8

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -2 | | 1.174e+05 | | R10 | ho2+ho2 | -2.348e+05 | 65.57 | -2.362e+05 | 190 | *** |
| 2 | | 9.582e+04 | | R4 | od+h2o | 1.916e+05 | 53.73 | -4.456e+04 | -38 | *** |
| -2 | | 5.513e+04 | | R16 | ch32+ho2 | -1.103e+05 | 30.79 | -1.548e+05 | 21 | -6 |
| 2 | | 4.455e+04 | | R7 | h2o2+hv | 8.910e+04 | 24.98 | -6.572e+04 | -16 | -27 |
| 2 | | 1.583e+04 | | R18 | ch3h+hv | 3.166e+04 | 8.88 | -3.406e+04 | -5 | -11 |
| 2 | | 1.565e+04 | | R23 | h2co+hv | 3.130e+04 | 8.78 | -2.765e+03 | -5 | -5 |
| -1 | | 1.274e+04 | | R37 | ho2+no2 | -1.274e+04 | 3.56 | -1.550e+04 | 2 | 0 |
| 1 | | 6.707e+03 | | R45 | hno4+hv | 6.707e+03 | 1.88 | -8.798e+03 | -1 | -2 |
| 1 | | 6.036e+03 | | R33 | hno4 | 6.036e+03 | 1.69 | -2.762e+03 | -1 | -1 |
| 1 | | 1.440e+02 | | R43 | hno2+hv | 1.440e+02 | .04 | -2.618e+03 | -0 | 0 |
| -1 | | 1.234e+02 | | R35 | ho+no | -1.234e+02 | .03 | -2.741e+03 | 0 | 0 |
| -1 | | 1.224e+02 | | R36 | ho+no2 | -1.224e+02 | .03 | -2.864e+03 | 0 | 0 |
| 1 | | 5.484e+01 | | R44 | hno3+hv | 5.484e+01 | .02 | -2.809e+03 | -0 | -0 |
| -1 | | 2.210e+01 | | R26 | ho2+no2 | -2.210e+01 | .01 | -2.831e+03 | 0 | 0 |
| 2 | | 8.600e+00 | | R50 | od+ch4 | 1.720e+01 | .00 | -2.814e+03 | -0 | -0 |
| 2 | | 2.147e+00 | | R52 | od+h2 | 4.294e+00 | .00 | -2.809e+03 | -0 | -0 |
| -1 | | 1.842e-01 | | R31 | ho+hno2 | -1.842e-01 | .00 | -2.810e+03 | 0 | 0 |
| -1 | | 1.194e-01 | | R30 | ho+hno3 | -1.194e-01 | .00 | -2.810e+03 | 0 | 0 |
| -1 | | 5.591e-03 | | R32 | ho+hno4 | -5.591e-03 | .00 | -2.810e+03 | 0 | 0 |

deviation = rate/sum of production = -3.93894e-3

sum of production = 356663. ; sum of sink = 358068.

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=1E8, [NO_x]=1.83e8

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -2 | | 1.809e+05 | | R10 | ho2+ho2 | -3.618e+05 | 63.88 | -3.641e+05 | 177 | *** |
| 2 | | 1.492e+05 | | R4 | od+h2o | 2.984e+05 | 52.90 | -6.569e+04 | -38 | *** |
| -2 | | 8.686e+04 | | R16 | ch32+ho2 | -1.737e+05 | 30.67 | -2.394e+05 | 21 | -6 |
| 2 | | 6.780e+04 | | R7 | h2o2+hv | 1.356e+05 | 24.04 | -1.038e+05 | -16 | -27 |
| 2 | | 2.511e+04 | | R23 | h2co+hv | 5.022e+04 | 8.90 | -5.359e+04 | -6 | -11 |
| 2 | | 2.460e+04 | | R18 | ch3h+hv | 4.920e+04 | 8.72 | -4.387e+03 | -5 | -5 |
| -1 | | 3.014e+04 | | R37 | ho2+no2 | -3.014e+04 | 5.32 | -3.453e+04 | 3 | 0 |
| 1 | | 1.586e+04 | | R45 | hno4+hv | 1.586e+04 | 2.81 | -1.867e+04 | -2 | -3 |
| 1 | | 1.427e+04 | | R33 | hno4 | 1.427e+04 | 2.53 | -4.397e+03 | -2 | -2 |
| -1 | | 3.735e+02 | | R36 | ho+no2 | -3.735e+02 | .07 | -4.771e+03 | 0 | 0 |
| 1 | | 3.123e+02 | | R43 | hno2+hv | 3.123e+02 | .06 | -4.459e+03 | -0 | -0 |
| -1 | | 2.635e+02 | | R35 | ho+no | -2.635e+02 | .05 | -4.722e+03 | 0 | 0 |
| 1 | | 1.673e+02 | | R44 | hno3+hv | 1.673e+02 | .03 | -4.555e+03 | -0 | -0 |
| -1 | | 5.226e+01 | | R26 | ho2+no2 | -5.226e+01 | .01 | -4.607e+03 | 0 | 0 |
| 2 | | 1.339e+01 | | R50 | od+ch4 | 2.678e+01 | .00 | -4.580e+03 | -0 | -0 |
| 2 | | 3.343e+00 | | R52 | od+h2 | 6.686e+00 | .00 | -4.574e+03 | -0 | -0 |
| -1 | | 6.398e-01 | | R31 | ho+hno2 | -6.398e-01 | .00 | -4.574e+03 | 0 | 0 |
| -1 | | 5.835e-01 | | R30 | ho+hno3 | -5.835e-01 | .00 | -4.575e+03 | 0 | 0 |
| -1 | | 2.117e-02 | | R32 | ho+hno4 | -2.117e-02 | .00 | -4.575e+03 | 0 | 0 |

deviation = rate/sum of production = -4.05529e-3

sum of production = 564063. ; sum of sink = 566351.

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19
COMMENTS : [NO]=5E8, [NO_x]=3.23e9

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 1.308e+06 | R4 | od+h2o | 2.616e+06 | 38.63 | 2.591e+06 | -31 | *** |
| -1 | 2.616e+06 | R37 | ho2+no2 | -2.616e+06 | 38.49 | -2.503e+04 | 35 | *** |
| -2 | 1.245e+06 | R10 | ho2+ho2 | -2.490e+06 | 36.64 | -2.515e+06 | 60 | 33 |
| -2 | 7.710e+05 | R16 | ch32+ho2 | -1.542e+06 | 22.69 | -4.057e+06 | 19 | -26 |
| 1 | 1.377e+06 | R45 | hno4+hv | 1.377e+06 | 20.33 | -2.680e+06 | -16 | -46 |
| 1 | 1.239e+06 | R33 | hno4 | 1.239e+06 | 18.30 | -1.441e+06 | -14 | -30 |
| 2 | 3.561e+05 | R7 | h2o2+hv | 7.122e+05 | 10.52 | -7.288e+05 | -8 | -16 |
| 2 | 2.146e+05 | R23 | h2co+hv | 4.292e+05 | 6.34 | -2.996e+05 | -5 | -8 |
| 2 | 1.619e+05 | R18 | ch3h+hv | 3.238e+05 | 4.78 | 2.417e+04 | -4 | -3 |
| -1 | 1.281e+05 | R36 | ho+no2 | -1.281e+05 | 1.88 | -1.039e+05 | 1 | 1 |
| 1 | 5.655e+04 | R44 | hno3+hv | 5.655e+04 | .84 | -4.738e+04 | -1 | -1 |
| 1 | 1.766e+04 | R43 | hno2+hv | 1.766e+04 | .26 | -2.972e+04 | -0 | 0 |
| -1 | 1.366e+04 | R35 | ho+no | -1.366e+04 | .20 | -4.338e+04 | 0 | 0 |
| -1 | 4.536e+03 | R26 | ho2+no2 | -4.536e+03 | .07 | -4.792e+04 | 0 | 0 |
| -1 | 2.045e+03 | R30 | ho+hno3 | -2.045e+03 | .03 | -4.996e+04 | 0 | 0 |
| -1 | 3.752e+02 | R31 | ho+hno2 | -3.752e+02 | .01 | -5.034e+04 | 0 | 0 |
| 2 | 1.174e+02 | R50 | od+ch4 | 2.348e+02 | .00 | -5.010e+04 | -0 | -0 |
| 2 | 2.931e+01 | R52 | od+h2 | 5.862e+01 | .00 | -5.004e+04 | -0 | -0 |
| -1 | 1.906e+01 | R32 | ho+hno4 | -1.906e+01 | .00 | -5.006e+04 | 0 | 0 |

deviation = rate/sum of production = -3.69654e-3
sum of production = 6.7717e+6 ; sum of sink = 6.79674e+6

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=7E8, [NO_x]=7.15e9

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -1 | | 7.203e+06 | | R37 | ho2+no2 | -7.203e+06 | 53.12 | -7.201e+06 | 63 | *** |
| 2 | | 2.118e+06 | | R4 | od+h2o | 4.236e+06 | 31.24 | -2.965e+06 | -27 | *** |
| 1 | | 3.791e+06 | | R45 | hno4+hv | 3.791e+06 | 27.95 | 8.262e+05 | -24 | -4 |
| -2 | | 1.717e+06 | | R10 | ho2+ho2 | -3.434e+06 | 25.33 | -2.608e+06 | 36 | 21 |
| 1 | | 3.412e+06 | | R33 | hno4 | 3.412e+06 | 25.16 | 8.042e+05 | -22 | -15 |
| -2 | | 1.174e+06 | | R16 | ch32+ho2 | -2.348e+06 | 17.32 | -1.544e+06 | 16 | 7 |
| 2 | | 4.147e+05 | | R7 | h2o2+hv | 8.294e+05 | 6.12 | -7.144e+05 | -5 | -10 |
| 2 | | 3.066e+05 | | R23 | h2co+hv | 6.132e+05 | 4.52 | -1.012e+05 | -4 | -4 |
| -1 | | 5.113e+05 | | R36 | ho+no2 | -5.113e+05 | 3.77 | -6.125e+05 | 3 | -1 |
| 2 | | 2.054e+05 | | R18 | ch3h+hv | 4.108e+05 | 3.03 | -2.017e+05 | -3 | -4 |
| 1 | | 2.232e+05 | | R44 | hno3+hv | 2.232e+05 | 1.65 | 2.155e+04 | -1 | -1 |
| 1 | | 4.531e+04 | | R43 | hno2+hv | 4.531e+04 | .33 | 6.686e+04 | -0 | 0 |
| -1 | | 3.488e+04 | | R35 | ho+no | -3.488e+04 | .26 | 3.198e+04 | 0 | 0 |
| -1 | | 1.374e+04 | | R30 | ho+hno3 | -1.374e+04 | .10 | 1.824e+04 | 0 | 0 |
| -1 | | 1.249e+04 | | R26 | ho2+no2 | -1.249e+04 | .09 | 5.747e+03 | 0 | 0 |
| -1 | | 1.639e+03 | | R31 | ho+hno2 | -1.639e+03 | .01 | 4.108e+03 | 0 | 0 |
| 2 | | 1.901e+02 | | R50 | od+ch4 | 3.802e+02 | .00 | 4.488e+03 | -0 | -0 |
| 2 | | 4.745e+01 | | R52 | od+h2 | 9.490e+01 | .00 | 4.583e+03 | -0 | -0 |
| -1 | | 8.932e+01 | | R32 | ho+hno4 | -8.932e+01 | .00 | 4.494e+03 | 0 | 0 |

deviation = rate/sum of production = 1.65675e-4

sum of production = 1.35614e+7 ; sum of sink = 1.35591e+7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=1E9, [NO_x]=1.03e10

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -1 | | 1.069e+07 | | R37 | ho2+no2 | -1.069e+07 | 60.34 | -1.073e+07 | 85 | *** |
| 1 | | 5.626e+06 | | R45 | hno4+hv | 5.626e+06 | 31.83 | -5.108e+06 | -29 | *** |
| 1 | | 5.063e+06 | | R33 | hno4 | 5.063e+06 | 28.65 | -4.476e+04 | -26 | -16 |
| 2 | | 2.318e+06 | | R4 | od+h2o | 4.636e+06 | 26.23 | 4.591e+06 | -24 | 10 |
| -2 | | 1.785e+06 | | R10 | ho2+ho2 | -3.570e+06 | 20.15 | 1.021e+06 | 27 | 34 |
| -2 | | 1.223e+06 | | R16 | ch32+ho2 | -2.446e+06 | 13.81 | -1.425e+06 | 13 | 7 |
| -1 | | 9.046e+05 | | R36 | ho+no2 | -9.046e+05 | 5.11 | -2.329e+06 | 4 | -7 |
| 2 | | 3.969e+05 | | R7 | h2o2+hv | 7.938e+05 | 4.49 | -1.536e+06 | -4 | -11 |
| 2 | | 3.580e+05 | | R23 | h2co+hv | 7.160e+05 | 4.05 | -8.196e+05 | -4 | -7 |
| 2 | | 1.944e+05 | | R18 | ch3h+hv | 3.888e+05 | 2.20 | -4.308e+05 | -2 | -4 |
| 1 | | 3.781e+05 | | R44 | hno3+hv | 3.781e+05 | 2.14 | -5.266e+04 | -2 | -2 |
| 1 | | 7.126e+04 | | R43 | hno2+hv | 7.126e+04 | .40 | 1.860e+04 | -0 | 0 |
| -1 | | 5.652e+04 | | R35 | ho+no | -5.652e+04 | .32 | -3.792e+04 | 0 | 1 |
| -1 | | 2.829e+04 | | R30 | ho+hno3 | -2.829e+04 | .16 | -6.621e+04 | 0 | 0 |
| -1 | | 1.854e+04 | | R26 | ho2+no2 | -1.854e+04 | .10 | -8.475e+04 | 0 | 0 |
| -1 | | 3.132e+03 | | R31 | ho+hno2 | -3.132e+03 | .02 | -8.789e+04 | 0 | 0 |
| 2 | | 2.080e+02 | | R50 | od+ch4 | 4.160e+02 | .00 | -8.747e+04 | -0 | -0 |
| -1 | | 1.611e+02 | | R32 | ho+hno4 | -1.611e+02 | .00 | -8.763e+04 | 0 | 0 |
| 2 | | 5.192e+01 | | R52 | od+h2 | 1.038e+02 | .00 | -8.753e+04 | -0 | -0 |

deviation = rate/sum of production = -2.47621e-3

sum of production = 1.76735e+7 ; sum of sink = 1.77172e+7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=2E9, [NO_x]=6.33e10

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -1 | | 6.544e+07 | | R37 | ho2+no2 | -6.544e+07 | 74.28 | -6.708e+07 | 336 | *** |
| 1 | | 3.444e+07 | | R45 | hno4+hv | 3.444e+07 | 39.83 | -3.264e+07 | -48 | *** |
| 1 | | 3.100e+07 | | R33 | hno4 | 3.100e+07 | 35.85 | -1.636e+06 | -43 | -41 |
| -1 | | 1.494e+07 | | R36 | ho+no2 | -1.494e+07 | 16.96 | -1.658e+07 | 20 | 2 |
| 2 | | 6.313e+06 | | R4 | od+h2o | 1.263e+07 | 14.60 | -3.950e+06 | -17 | -18 |
| 1 | | 6.177e+06 | | R44 | hno3+hv | 6.177e+06 | 7.14 | 2.227e+06 | -8 | -1 |
| -2 | | 1.574e+06 | | R10 | ho2+ho2 | -3.148e+06 | 3.57 | -9.208e+05 | 4 | 8 |
| -2 | | 1.439e+06 | | R16 | ch32+ho2 | -2.878e+06 | 3.27 | -3.799e+06 | 4 | 3 |
| -1 | | 1.171e+06 | | R30 | ho+hno3 | -1.171e+06 | 1.33 | -4.970e+06 | 2 | -1 |
| 2 | | 5.489e+05 | | R23 | h2co+hv | 1.098e+06 | 1.27 | -3.872e+06 | -2 | -2 |
| 2 | | 2.130e+05 | | R7 | h2o2+hv | 4.260e+05 | .49 | -3.446e+06 | -1 | -1 |
| 1 | | 4.208e+05 | | R43 | hno2+hv | 4.208e+05 | .49 | -3.025e+06 | -1 | -0 |
| -1 | | 3.580e+05 | | R35 | ho+no | -3.580e+05 | .41 | -3.383e+06 | 0 | 0 |
| 2 | | 1.365e+05 | | R18 | ch3h+hv | 2.730e+05 | .32 | -3.110e+06 | -0 | -0 |
| -1 | | 1.135e+05 | | R26 | ho2+no2 | -1.135e+05 | .13 | -3.224e+06 | 0 | 0 |
| -1 | | 4.685e+04 | | R31 | ho+hno2 | -4.685e+04 | .05 | -3.271e+06 | 0 | 0 |
| -1 | | 2.499e+03 | | R32 | ho+hno4 | -2.499e+03 | .00 | -3.273e+06 | 0 | 0 |
| 2 | | 5.666e+02 | | R50 | od+ch4 | 1.133e+03 | .00 | -3.272e+06 | -0 | -0 |
| 2 | | 1.414e+02 | | R52 | od+h2 | 2.828e+02 | .00 | -3.272e+06 | -0 | -0 |

deviation = rate/sum of production = -1.89197e-2

sum of production = 86462016 ; sum of sink = 88097849

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=5E9, [NO_x]=1.20e11

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|-----|-----|
| -1 | | 5.030e+07 | | R37 | ho2+no2 | -5.030e+07 | 69.09 | -5.058e+07 | 843 | *** |
| 1 | | 2.647e+07 | | R45 | hno4+hv | 2.647e+07 | 36.50 | -2.411e+07 | -52 | *** |
| 1 | | 2.382e+07 | | R33 | hno4 | 2.382e+07 | 32.84 | -2.891e+05 | -46 | -46 |
| -1 | | 1.979e+07 | | R36 | ho+no2 | -1.979e+07 | 27.18 | -2.008e+07 | 38 | 0 |
| 2 | | 6.073e+06 | | R4 | od+h2o | 1.215e+07 | 16.75 | -7.933e+06 | -24 | -38 |
| 1 | | 8.375e+06 | | R44 | hno3+hv | 8.375e+06 | 11.55 | 4.419e+05 | -16 | -14 |
| -1 | | 1.117e+06 | | R30 | ho+hno3 | -1.117e+06 | 1.53 | -6.751e+05 | 2 | 2 |
| 2 | | 5.144e+05 | | R23 | h2co+hv | 1.029e+06 | 1.42 | 3.537e+05 | -2 | -0 |
| 1 | | 5.433e+05 | | R43 | hno2+hv | 5.433e+05 | .75 | 8.970e+05 | -1 | 2 |
| -2 | | 2.622e+05 | | R10 | ho2+ho2 | -5.244e+05 | .72 | 3.726e+05 | 1 | 3 |
| -1 | | 5.037e+05 | | R35 | o+no | -5.037e+05 | .69 | -1.311e+05 | 1 | 2 |
| -2 | | 2.186e+05 | | R16 | ch32+ho2 | -4.372e+05 | .60 | -5.683e+05 | 1 | 1 |
| 2 | | 4.398e+04 | | R7 | h2o2+hv | 8.796e+04 | .12 | -4.803e+05 | -0 | -0 |
| -1 | | 8.722e+04 | | R26 | ho2+no2 | -8.722e+04 | .12 | -5.676e+05 | 0 | 0 |
| 2 | | 2.595e+04 | | R18 | ch3h+hv | 5.190e+04 | .07 | -5.157e+05 | -0 | -0 |
| -1 | | 4.256e+04 | | R31 | ho+hno2 | -4.256e+04 | .06 | -5.582e+05 | 0 | 0 |
| -1 | | 1.351e+03 | | R32 | ho+hno4 | -1.351e+03 | .00 | -5.596e+05 | 0 | -0 |
| 2 | | 5.450e+02 | | R50 | od+ch4 | 1.090e+03 | .00 | -5.585e+05 | -0 | -0 |
| 2 | | 1.361e+02 | | R52 | od+h2 | 2.722e+02 | .00 | -5.582e+05 | -0 | -0 |

deviation = rate/sum of production = -3.84849e-3

sum of production = 7.25243e+7 ; sum of sink = 72803431

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19
 COMMENTS : [NO]=7E9, [NO₂]=1.51e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|------|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| -1 | 3.437e+07 | R37 | ho2+no2 | -3.437e+07 | 63.73 | -3.444e+07 | 1336 | ** |
| 1 | 1.809e+07 | R45 | hno4+hv | 1.809e+07 | 33.59 | -1.635e+07 | -52 | ** |
| -1 | 1.791e+07 | R36 | ho+no2 | -1.791e+07 | 33.21 | -3.426e+07 | 51 | -47 |
| 1 | 1.628e+07 | R33 | hno4 | 1.628e+07 | 30.23 | -1.798e+07 | -47 | -98 |
| 2 | 5.120e+06 | R4 | od+h2o | 1.024e+07 | 19.01 | -7.744e+06 | -29 | -51 |
| 1 | 7.702e+06 | R44 | hno3+hv | 7.702e+06 | 14.30 | -4.221e+04 | -22 | -22 |
| 2 | 4.651e+05 | R23 | h2co+hv | 9.302e+05 | 1.73 | 8.880e+05 | -3 | 0 |
| -1 | 7.424e+05 | R30 | ho+hno3 | -7.424e+05 | 1.38 | 1.456e+05 | 2 | 3 |
| 1 | 5.684e+05 | R43 | hno2+hv | 5.684e+05 | 1.06 | 7.140e+05 | -2 | 1 |
| -1 | 5.462e+05 | R35 | ho+no | -5.462e+05 | 1.01 | 1.678e+05 | 2 | 2 |
| -2 | 7.812e+04 | R10 | ho2+ho2 | -1.562e+05 | .29 | 1.155e+04 | 0 | 1 |
| -2 | 5.814e+04 | R16 | ch32+ho2 | -1.163e+05 | .22 | -1.047e+05 | 0 | 0 |
| -1 | 5.960e+04 | R26 | ho2+no2 | -5.960e+04 | .11 | -1.643e+05 | 0 | 0 |
| -1 | 3.219e+04 | R31 | ho+hno2 | -3.219e+04 | .06 | -1.965e+05 | 0 | -0 |
| 2 | 1.554e+04 | R7 | h2o2+hv | 3.108e+04 | .06 | -1.654e+05 | -0 | -0 |
| 2 | 8.270e+03 | R18 | ch3h+hv | 1.654e+04 | .03 | -1.489e+05 | -0 | -0 |
| 2 | 4.595e+02 | R50 | od+ch4 | 9.190e+02 | .00 | -1.480e+05 | -0 | -0 |
| -1 | 6.673e+02 | R32 | ho+hno4 | -6.673e+02 | .00 | -1.486e+05 | 0 | 0 |
| 2 | 1.147e+02 | R52 | od+h2 | 2.294e+02 | .00 | -1.484e+05 | -0 | -0 |

deviation = rate/sum of production = -1.37783e-3

sum of production = 5.38594e+7 ; sum of sink = 5.39336e+7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19
 COMMENTS : [NO]=1E10, [NO₂]=1.72e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|---------|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| -1 | 2.501e+07 | R37 | ho2+no2 | -2.501e+07 | 59.43 | -2.504e+07 | 1805 | ** |
| -1 | 1.581e+07 | R36 | ho+no2 | -1.581e+07 | 37.57 | -4.085e+07 | 63-173 | |
| 1 | 1.316e+07 | R45 | hno4+hv | 1.316e+07 | 31.30 | -2.769e+07 | -52 | ** |
| 1 | 1.185e+07 | R33 | hno4 | 1.185e+07 | 28.18 | -1.584e+07 | -47-110 | |
| 2 | 4.366e+06 | R4 | od+h2o | 8.732e+06 | 20.77 | -7.111e+06 | -35 | -63 |
| 1 | 6.859e+06 | R44 | hno3+hv | 6.859e+06 | 16.31 | -2.521e+05 | -27 | -28 |
| 2 | 4.229e+05 | R23 | h2co+hv | 8.458e+05 | 2.01 | 5.937e+05 | -3 | -1 |
| 1 | 5.811e+05 | R43 | hno2+hv | 5.811e+05 | 1.38 | 1.175e+06 | -2 | 3 |
| -1 | 5.688e+05 | R35 | ho+no | -5.688e+05 | 1.35 | 6.060e+05 | 2 | 5 |
| -1 | 5.164e+05 | R30 | ho+hno3 | -5.164e+05 | 1.23 | 8.958e+04 | 2 | 3 |
| -2 | 3.240e+04 | R10 | ho2+ho2 | -6.480e+04 | .15 | 2.478e+04 | 0 | 1 |
| -2 | 2.202e+04 | R16 | ch32+ho2 | -4.404e+04 | .10 | -1.926e+04 | 0 | 0 |
| -1 | 4.337e+04 | R26 | ho2+no2 | -4.337e+04 | .10 | -6.263e+04 | 0 | 0 |
| -1 | 2.570e+04 | R31 | ho+hno2 | -2.570e+04 | .06 | -8.833e+04 | 0 | 0 |
| 2 | 7.216e+03 | R7 | h2o2+hv | 1.443e+04 | .03 | -7.389e+04 | -0 | -0 |
| 2 | 3.531e+03 | R18 | ch3h+hv | 7.062e+03 | .02 | -6.683e+04 | -0 | -0 |
| 2 | 3.918e+02 | R50 | od+ch4 | 7.836e+02 | .00 | -6.605e+04 | -0 | -0 |
| -1 | 3.793e+02 | R32 | ho+hno4 | -3.793e+02 | .00 | -6.643e+04 | 0 | 0 |
| 2 | 9.780e+01 | R52 | od+h2 | 1.956e+02 | .00 | -6.623e+04 | -0 | -0 |

deviation = rate/sum of production = -7.87534e-4

sum of production = 4.20504e+7 ; sum of sink = 4.20835e+7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=2E10, [NO₂]=2.34e11

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|------|------|
| -1 | | 8.913e+06 | | R36 | ho+no2 | -8.913e+06 | 51.46 | -8.914e+06 | 116 | *** |
| -1 | | 7.627e+06 | | R37 | ho2+no2 | -7.627e+06 | 44.04 | -1.654e+07 | 4303 | ** |
| 2 | | 2.293e+06 | | R4 | od+h2o | 4.586e+06 | 26.48 | -1.196e+07 | -60 | ** |
| 1 | | 4.014e+06 | | R45 | hno4+hv | 4.014e+06 | 23.18 | -7.941e+06 | -52 | -156 |
| 1 | | 3.940e+06 | | R44 | hno3+hv | 3.940e+06 | 22.75 | -4.001e+06 | -52 | -104 |
| 1 | | 3.613e+06 | | R33 | hno4 | 3.613e+06 | 20.86 | -3.883e+05 | -47 | -52 |
| -1 | | 6.201e+05 | | R35 | ho+no | -6.201e+05 | 3.58 | -1.008e+06 | 8 | -5 |
| 1 | | 6.157e+05 | | R43 | hno2+hv | 6.157e+05 | 3.56 | -3.927e+05 | -8 | -13 |
| 2 | | 2.740e+05 | | R23 | h2co+hv | 5.480e+05 | 3.16 | 1.553e+05 | -7 | -5 |
| -1 | | 1.293e+05 | | R30 | ho+hno3 | -1.293e+05 | .75 | 2.599e+04 | 2 | 2 |
| -1 | | 1.323e+04 | | R26 | ho2+no2 | -1.323e+04 | .08 | 1.276e+04 | 0 | 0 |
| -1 | | 1.187e+04 | | R31 | ho+hno2 | -1.187e+04 | .07 | 8.901e+02 | 0 | 0 |
| -2 | | 1.802e+03 | | R10 | ho2+ho2 | -3.604e+03 | .02 | -2.714e+03 | 0 | 0 |
| -2 | | 9.092e+02 | | R16 | ch32+ho2 | -1.818e+03 | .01 | -4.532e+03 | 0 | 0 |
| 2 | | 5.282e+02 | | R7 | h2o2+hv | 1.056e+03 | .01 | -3.476e+03 | -0 | -0 |
| 2 | | 2.058e+02 | | R50 | od+ch4 | 4.116e+02 | .00 | -3.064e+03 | -0 | -0 |
| 2 | | 1.961e+02 | | R18 | ch3h+hv | 3.922e+02 | .00 | -2.672e+03 | -0 | -0 |
| 2 | | 5.137e+01 | | R52 | od+h2 | 1.027e+02 | .00 | -2.569e+03 | -0 | -0 |
| -1 | | 5.044e+01 | | R32 | ho+hno4 | -5.044e+01 | .00 | -2.620e+03 | 0 | 0 |

deviation = rate/sum of production = -7.56352e-5
sum of production = 1.73187e+7 ; sum of sink = 1.732e+7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=5E10, [NO₂]=2.82e11

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|------|------|
| -1 | | 5.144e+06 | | R36 | ho+no2 | -5.144e+06 | 60.45 | -5.145e+06 | 192 | *** |
| -1 | | 2.671e+06 | | R37 | ho2+no2 | -2.671e+06 | 31.39 | -7.816e+06 | 7901 | ** |
| 2 | | 1.282e+06 | | R4 | od+h2o | 2.564e+06 | 30.13 | -5.252e+06 | -96 | *** |
| 1 | | 2.290e+06 | | R44 | hno3+hv | 2.290e+06 | 26.91 | -2.962e+06 | -86 | -196 |
| 1 | | 1.406e+06 | | R45 | hno4+hv | 1.406e+06 | 16.52 | -1.556e+06 | -53 | -111 |
| 1 | | 1.265e+06 | | R33 | hno4 | 1.265e+06 | 14.87 | -2.908e+05 | -47 | -58 |
| -1 | | 6.445e+05 | | R35 | ho+no | -6.445e+05 | 7.57 | -9.353e+05 | 24 | -11 |
| 1 | | 6.368e+05 | | R43 | hno2+hv | 6.368e+05 | 7.48 | -2.985e+05 | -24 | -35 |
| 2 | | 1.735e+05 | | R23 | h2co+hv | 3.470e+05 | 4.08 | 4.845e+04 | -13 | -11 |
| -1 | | 3.906e+04 | | R30 | ho+hno3 | -3.906e+04 | .46 | 9.392e+03 | 1 | 2 |
| -1 | | 6.383e+03 | | R31 | ho+hno2 | -6.383e+03 | .08 | 3.009e+03 | 0 | 0 |
| -1 | | 4.632e+03 | | R26 | ho2+no2 | -4.632e+03 | .05 | -1.623e+03 | 0 | 0 |
| -2 | | 1.793e+02 | | R10 | ho2+ho2 | -3.586e+02 | .00 | -1.982e+03 | 0 | 0 |
| 2 | | 1.151e+02 | | R50 | od+ch4 | 2.302e+02 | .00 | -1.752e+03 | -0 | -0 |
| -2 | | 7.455e+01 | | R16 | ch32+ho2 | -1.491e+02 | .00 | -1.901e+03 | 0 | -0 |
| 2 | | 5.952e+01 | | R7 | h2o2+hv | 1.190e+02 | .00 | -1.782e+03 | -0 | -0 |
| 2 | | 2.873e+01 | | R52 | od+h2 | 5.746e+01 | .00 | -1.724e+03 | -0 | -0 |
| 2 | | 1.844e+01 | | R18 | ch3h+hv | 3.688e+01 | .00 | -1.687e+03 | -0 | -0 |
| -1 | | 9.180e+00 | | R32 | ho+hno4 | -9.180e+00 | .00 | -1.697e+03 | 0 | 0 |

deviation = rate/sum of production = -9.96916e-5
sum of production = 8.50924e+6 ; sum of sink = 8.51009e+6

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=7E10, [NO₂]=3.16e11

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|------|------|
| -1 | | 3.615e+06 | | R36 | ho+no2 | -3.615e+06 | 63.84 | -3.615e+06 | 264 | *** |
| 2 | | 8.904e+05 | | R4 | od+h2o | 1.781e+06 | 31.45 | -1.834e+06 | -130 | ** |
| 1 | | 1.613e+06 | | R44 | hno3+hv | 1.613e+06 | 28.48 | -2.211e+05 | -118 | ** |
| -1 | | 1.368e+06 | | R37 | ho2+no2 | -1.368e+06 | 24.16 | -1.589e+06 | *** | *** |
| 1 | | 7.202e+05 | | R45 | hno4+hv | 7.202e+05 | 12.72 | -8.689e+05 | -53 | -116 |
| -1 | | 6.542e+05 | | R35 | ho+no | -6.542e+05 | 11.55 | -1.523e+06 | 48 | -63 |
| 1 | | 6.482e+05 | | R33 | hno4 | 6.482e+05 | 11.45 | -8.749e+05 | -47 | -111 |
| 1 | | 6.462e+05 | | R43 | hno2+hv | 6.462e+05 | 11.41 | -2.287e+05 | -47 | -64 |
| 2 | | 1.271e+05 | | R23 | h2co+hv | 2.542e+05 | 4.49 | 2.554e+04 | -19 | -17 |
| -1 | | 1.862e+04 | | R30 | ho+hno3 | -1.862e+04 | .33 | 6.920e+03 | 1 | 2 |
| -1 | | 4.382e+03 | | R31 | ho+hno2 | -4.382e+03 | .08 | 2.538e+03 | 0 | 0 |
| -1 | | 2.373e+03 | | R26 | ho2+no2 | -2.373e+03 | .04 | 1.651e+02 | 0 | 0 |
| 2 | | 7.991e+01 | | R50 | od+ch4 | 1.598e+02 | .00 | 3.250e+02 | -0 | -0 |
| -2 | | 4.362e+01 | | R10 | ho2+ho2 | -8.724e+01 | .00 | 2.377e+02 | 0 | 0 |
| 2 | | 1.995e+01 | | R52 | od+h2 | 3.990e+01 | .00 | 2.776e+02 | -0 | -0 |
| -2 | | 1.659e+01 | | R16 | ch32+ho2 | -3.318e+01 | .00 | 2.444e+02 | 0 | -0 |
| 2 | | 1.519e+01 | | R7 | h2o2+hv | 3.038e+01 | .00 | 2.748e+02 | -0 | -0 |
| 2 | | 4.326e+00 | | R18 | ch3h+hv | 8.652e+00 | .00 | 2.835e+02 | -0 | -0 |
| -1 | | 3.182e+00 | | R32 | ho+hno4 | -3.182e+00 | .00 | 2.803e+02 | 0 | 0 |

deviation = rate/sum of production = 2.47491e-5
sum of production = 5.66284e+6 ; sum of sink = 5.6627e+6

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 19

COMMENTS : [NO]=1E11, [NO₂]=3.46e11

| | inst. | coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-------|-----------|------|------|----------|------------|-------|------------------|------|------|
| -1 | | 2.787e+06 | | R36 | ho+no2 | -2.787e+06 | 64.89 | -2.787e+06 | 334 | *** |
| 2 | | 6.823e+05 | | R4 | od+h2o | 1.365e+06 | 31.77 | -1.423e+06 | -164 | ** |
| 1 | | 1.245e+06 | | R44 | hno3+hv | 1.245e+06 | 28.99 | -1.778e+05 | -149 | ** |
| -1 | | 8.334e+05 | | R37 | ho2+no2 | -8.334e+05 | 19.40 | -1.011e+06 | *** | *** |
| -1 | | 6.592e+05 | | R35 | ho+no | -6.592e+05 | 15.35 | -1.670e+06 | 79 | -121 |
| 1 | | 6.512e+05 | | R43 | hno2+hv | 6.512e+05 | 15.16 | -1.019e+06 | -78 | -200 |
| 1 | | 4.386e+05 | | R45 | hno4+hv | 4.386e+05 | 10.21 | -5.806e+05 | -53 | -122 |
| 1 | | 3.947e+05 | | R33 | hno4 | 3.947e+05 | 9.19 | -1.859e+05 | -47 | -69 |
| 2 | | 1.003e+05 | | R23 | h2co+hv | 2.006e+05 | 4.67 | 1.468e+04 | -24 | -22 |
| -1 | | 1.086e+04 | | R30 | ho+hno3 | -1.086e+04 | .25 | 3.820e+03 | 1 | 2 |
| -1 | | 3.338e+03 | | R31 | ho+hno2 | -3.338e+03 | .08 | 4.824e+02 | 0 | 1 |
| -1 | | 1.445e+03 | | R26 | ho2+no2 | -1.445e+03 | .03 | -9.626e+02 | 0 | 0 |
| 2 | | 6.124e+01 | | R50 | od+ch4 | 1.225e+02 | .00 | -8.401e+02 | -0 | -0 |
| -2 | | 1.554e+01 | | R10 | ho2+ho2 | -3.108e+01 | .00 | -8.712e+02 | 0 | -0 |
| 2 | | 1.529e+01 | | R52 | od+h2 | 3.058e+01 | .00 | -8.406e+02 | -0 | -0 |
| -2 | | 5.613e+00 | | R16 | ch32+ho2 | -1.123e+01 | .00 | -8.518e+02 | 0 | -0 |
| 2 | | 5.550e+00 | | R7 | h2o2+hv | 1.110e+01 | .00 | -8.407e+02 | -0 | -0 |
| 2 | | 1.505e+00 | | R18 | ch3h+hv | 3.010e+00 | .00 | -8.377e+02 | -0 | -0 |
| -1 | | 1.465e+00 | | R32 | ho+hno4 | -1.465e+00 | .00 | -8.392e+02 | 0 | 0 |

deviation = rate/sum of production = -9.76982e-5
sum of production = 4.29487e+6 ; sum of sink = 4.29529e+6

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=1E7, [NO_x]=1.05e7

| | coef | rate | inst. | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|-------|------------|-----|------------------|----|----|
| -2 | 3.659e+03 | R10 | ho2+ho2 | -7.318e+03 | 69.51 | -7.356e+03 | 228 | *** | | |
| 2 | 2.950e+03 | R4 | od+h2o | 5.900e+03 | 56.25 | -1.456e+03 | -40 | *** | | |
| -2 | 1.605e+03 | R16 | ch32+ho2 | -3.210e+03 | 30.49 | -4.666e+03 | 20 | -7 | | |
| 2 | 1.418e+03 | R7 | h2o2+hv | 2.836e+03 | 27.04 | -1.830e+03 | -17 | -27 | | |
| 2 | 4.718e+02 | R18 | ch3h+hv | 9.436e+02 | 9.00 | -8.868e+02 | -5 | -10 | | |
| 2 | 4.050e+02 | R23 | h2co+hv | 8.100e+02 | 7.72 | -7.680e+01 | -5 | -5 | | |

deviation = rate/sum of production = -3.66077e-3
 sum of production = 10489.6 ; sum of sink = 10528

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=5E7, [NO_x]=7.24e7

| | coef | rate | inst. | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|-------|------------|-----|------------------|----|----|
| -2 | 8.386e+04 | R10 | ho2+ho2 | -1.677e+05 | 67.77 | -1.687e+05 | 210 | *** | | |
| 2 | 6.920e+04 | R4 | od+h2o | 1.384e+05 | 56.15 | -3.032e+04 | -40 | *** | | |
| -2 | 3.988e+04 | R16 | ch32+ho2 | -7.976e+04 | 32.23 | -1.101e+05 | 22 | -6 | | |
| 2 | 3.230e+04 | R7 | h2o2+hv | 6.460e+04 | 26.21 | -4.548e+04 | -17 | -28 | | |
| 2 | 1.165e+04 | R18 | ch3h+hv | 2.330e+04 | 9.45 | -2.218e+04 | -6 | -11 | | |
| 2 | 1.009e+04 | R23 | h2co+hv | 2.018e+04 | 8.19 | -2.000e+03 | -5 | -5 | | |

deviation = rate/sum of production = -4.05712e-3
 sum of production = 246480 ; sum of sink = 247480

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=7E7, [NO_x]=1.18e8

| | coef | rate | inst. | rxn. | code | contrib. | w% | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|-------|------------|-----|------------------|----|----|
| -2 | 1.174e+05 | R10 | ho2+ho2 | -2.348e+05 | 68.05 | -2.362e+05 | 212 | *** | | |
| 2 | 9.582e+04 | R4 | od+h2o | 1.916e+05 | 55.76 | -4.452e+04 | -40 | *** | | |
| -2 | 5.513e+04 | R16 | ch32+ho2 | -1.103e+05 | 31.95 | -1.548e+05 | 21 | -6 | | |
| 2 | 4.455e+04 | R7 | h2o2+hv | 8.910e+04 | 25.92 | -6.568e+04 | -17 | -28 | | |
| 2 | 1.583e+04 | R18 | ch3h+hv | 3.166e+04 | 9.21 | -3.402e+04 | -6 | -11 | | |
| 2 | 1.565e+04 | R23 | h2co+hv | 3.130e+04 | 9.11 | -2.720e+03 | -6 | -6 | | |

deviation = rate/sum of production = -3.95694e-3
 sum of production = 343700 ; sum of sink = 345060

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=1E8, [NO_x]=1.83e8

| | coef | rate | rxn. | code | contrib. | w% | inst. | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|----------|------------|-------|------------------|----|----|
| -2 | 1.809e+05 | R10 | ho2+ho2 | -3.618e+05 | 67.56 | -3.639e+05 | 208 | *** | | |
| 2 | 1.492e+05 | R4 | od+h2o | 2.984e+05 | 55.94 | -6.550e+04 | -40 | *** | | |
| -2 | 8.686e+04 | R16 | ch32+ho2 | -1.737e+05 | 32.44 | -2.392e+05 | 22 | -6 | | |
| 2 | 6.780e+04 | R7 | h2o2+hv | 1.356e+05 | 25.42 | -1.036e+05 | -16 | -28 | | |
| 2 | 2.511e+04 | R23 | h2co+hv | 5.022e+04 | 9.41 | -5.340e+04 | -6 | -11 | | |
| 2 | 2.460e+04 | R18 | ch3h+hv | 4.920e+04 | 9.22 | -4.200e+03 | -6 | -6 | | |

deviation = rate/sum of production = -3.93686e-3
 sum of production = 533420 ; sum of sink = 535520

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=3E8, [NO_x]=1.25e9

| | coef | rate | rxn. | code | contrib. | w% | inst. | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|----------|------------|-------|------------------|----|----|
| -2 | 6.391e+05 | R10 | ho2+ho2 | -1.278e+06 | 66.18 | -1.276e+06 | 197 | *** | | |
| 2 | 5.614e+05 | R4 | od+h2o | 1.123e+06 | 58.06 | -1.530e+05 | -42 | *** | | |
| -2 | 3.266e+05 | R16 | ch32+ho2 | -6.532e+05 | 33.82 | -8.062e+05 | 23 | -2 | | |
| 2 | 2.103e+05 | R7 | h2o2+hv | 4.206e+05 | 21.75 | -3.856e+05 | -14 | -25 | | |
| 2 | 1.157e+05 | R23 | h2co+hv | 2.314e+05 | 11.97 | -1.542e+05 | -7 | -12 | | |
| 2 | 7.950e+04 | R18 | ch3h+hv | 1.590e+05 | 8.22 | 4.800e+03 | -5 | -5 | | |

deviation = rate/sum of production = 1.24108e-3
 sum of production = 1933800 ; sum of sink = 1931400

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6
 COMMENTS : [NO]=5E8, [NO_x]=3.23e9

| | coef | rate | rxn. | code | contrib. | w% | inst. | cum. contrib. | i% | c% |
|----|-----------|------|----------|------------|----------|------------|-------|------------------|----|----|
| 2 | 1.308e+06 | R4 | od+h2o | 2.616e+06 | 64.10 | 2.665e+06 | -48 | *** | | |
| -2 | 1.245e+06 | R10 | ho2+ho2 | -2.490e+06 | 61.76 | 1.752e+05 | 165 | *** | | |
| -2 | 7.710e+05 | R16 | ch32+ho2 | -1.542e+06 | 38.24 | -1.367e+06 | 28 | 8 | | |
| 2 | 3.561e+05 | R7 | h2o2+hv | 7.122e+05 | 17.45 | -6.546e+05 | -10 | -20 | | |
| 2 | 2.146e+05 | R23 | h2co+hv | 4.292e+05 | 10.52 | -2.254e+05 | -6 | -10 | | |
| 2 | 1.619e+05 | R18 | ch3h+hv | 3.238e+05 | 7.93 | 9.840e+04 | -4 | -4 | | |

deviation = rate/sum of production = 1.20553e-2
 sum of production = 4081200 ; sum of sink = 4032000

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=7E8, [NO₂]=7.15e9

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 2.118e+06 | R4 | od+h2o | 4.236e+06 | 69.56 | 4.543e+06 | -53 | *** |
| -2 | 1.717e+06 | R10 | ho2+ho2 | -3.434e+06 | 59.39 | 1.109e+06 | 159 | *** |
| -2 | 1.174e+06 | R16 | ch32+ho2 | -2.348e+06 | 40.61 | -1.239e+06 | 33 | 23 |
| 2 | 4.147e+05 | R7 | h2o2+hv | 8.294e+05 | 13.62 | -4.092e+05 | -6 | -10 |
| 2 | 3.066e+05 | R23 | h2co+hv | 6.132e+05 | 10.07 | 2.040e+05 | -3 | -5 |
| 2 | 2.054e+05 | R18 | ch3h+hv | 4.108e+05 | 6.75 | 6.148e+05 | -1 | -1 |

deviation = rate/sum of production = 5.04812e-2

sum of production = 6089400 ; sum of sink = 5782000

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=1E9, [NO₂]=1.03e10

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 2.318e+06 | R4 | od+h2o | 4.636e+06 | 70.95 | 5.155e+06 | -54 | *** |
| -2 | 1.785e+06 | R10 | ho2+ho2 | -3.570e+06 | 59.34 | 1.585e+06 | 168 | *** |
| -2 | 1.223e+06 | R16 | ch32+ho2 | -2.446e+06 | 40.66 | -8.614e+05 | 36 | 33 |
| 2 | 3.969e+05 | R7 | h2o2+hv | 7.938e+05 | 12.15 | -6.760e+04 | -3 | -3 |
| 2 | 3.580e+05 | R23 | h2co+hv | 7.160e+05 | 10.96 | 6.484e+05 | -2 | -0 |
| 2 | 1.944e+05 | R18 | ch3h+hv | 3.888e+05 | 5.95 | 1.037e+06 | 2 | 2 |

deviation = rate/sum of production = 7.93622e-2

sum of production = 6534600 ; sum of sink = 6016000

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=2E9, [NO₂]=6.33e10

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 6.313e+06 | R4 | od+h2o | 1.263e+07 | 87.54 | 2.102e+07 | -56 | *** |
| -2 | 1.574e+06 | R10 | ho2+ho2 | -3.148e+06 | 52.24 | 1.787e+07 | 412 | *** |
| -2 | 1.439e+06 | R16 | ch32+ho2 | -2.878e+06 | 47.76 | 1.500e+07 | 119 | 336 |
| 2 | 5.489e+05 | R23 | h2co+hv | 1.098e+06 | 7.61 | 1.609e+07 | 69 | 218 |
| 2 | 2.130e+05 | R7 | h2o2+hv | 4.260e+05 | 2.95 | 1.652e+07 | 74 | 149 |
| 2 | 1.365e+05 | R18 | ch3h+hv | 2.730e+05 | 1.89 | 1.679e+07 | 75 | 75 |

deviation = rate/sum of production = .582189

sum of production = 14422800 ; sum of sink = 6026000

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=5E9, [NO_x]=1.19e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|------|------|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 6.073e+06 | R4 | od+h2o | 1.215e+07 | 91.22 | 2.450e+07 | 14 | ** |
| 2 | 5.144e+05 | R23 | h2co+hv | 1.029e+06 | 7.73 | 2.553e+07 | 347 | ** |
| -2 | 2.622e+05 | R10 | ho2+ho2 | -5.244e+05 | 54.53 | 2.500e+07 | 2963 | ** |
| -2 | 2.186e+05 | R16 | ch32+ho2 | -4.372e+05 | 45.47 | 2.457e+07 | 407 | 1137 |
| 2 | 4.398e+04 | R7 | h2o2+hv | 8.796e+04 | .66 | 2.465e+07 | 365 | 730 |
| 2 | 2.595e+04 | R18 | ch3h+hv | 5.190e+04 | .39 | 2.471e+07 | 365 | 365 |

deviation = rate/sum of production = .927779

sum of production = 13314660 ; sum of sink = 961600

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=7E9, [NO_x]=1.51e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|------------|------|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| -1 | 2.787e+06 | R36 | ho+no2 | -2.787e+06 | 64.89 | -2.787e+06 | 334 | *** |
| 2 | 5.120e+06 | R4 | od+h2o | 1.024e+07 | 91.28 | 2.119e+07 | -73 | *** |
| 2 | 4.651e+05 | R23 | h2co+hv | 9.302e+05 | 8.29 | 2.212e+07 | -4 | *** |
| -2 | 7.812e+04 | R10 | ho2+ho2 | -1.562e+05 | 57.33 | 2.196e+07 | 1090 | ** |
| -2 | 5.814e+04 | R16 | ch32+ho2 | -1.163e+05 | 42.67 | 2.184e+07 | 4 | 4 |
| 2 | 1.554e+04 | R7 | h2o2+hv | 3.108e+04 | .28 | 2.187e+07 | -0 | -0 |
| 2 | 8.270e+03 | R18 | ch3h+hv | 1.654e+04 | .15 | 2.189e+07 | -0 | -0 |

deviation = rate/sum of production = .975707

sum of production = 11217820 ; sum of sink = 272520

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=1E10, [NO_x]=1.72e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|------|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 4.366e+06 | R4 | od+h2o | 8.732e+06 | 90.97 | 1.822e+07 | -72 | *** |
| 2 | 4.229e+05 | R23 | h2co+hv | 8.458e+05 | 8.81 | 1.907e+07 | -5 | *** |
| -2 | 3.240e+04 | R10 | ho2+ho2 | -6.480e+04 | 59.54 | 1.900e+07 | 1742 | ** |
| -2 | 2.202e+04 | R16 | ch32+ho2 | -4.404e+04 | 40.46 | 1.896e+07 | 3 | 3 |
| 2 | 7.216e+03 | R7 | h2o2+hv | 1.443e+04 | .15 | 1.897e+07 | -0 | -0 |
| 2 | 3.531e+03 | R18 | ch3h+hv | 7.062e+03 | .07 | 1.898e+07 | -0 | -0 |

deviation = rate/sum of production = .988662

sum of production = 9599294 ; sum of sink = 108840

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=2E10, [NO_x]=2.34e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|------|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 2.293e+06 | R4 | od+h2o | 4.586e+06 | 89.30 | 9.716e+06 | -68 | *** |
| 2 | 2.740e+05 | R23 | h2co+hv | 5.480e+05 | 10.67 | 1.026e+07 | -6 | *** |
| -2 | 1.802e+03 | R10 | ho2+ho2 | -3.604e+03 | 66.47 | 1.026e+07 | 7432 | ** |
| -2 | 9.092e+02 | R16 | ch32+ho2 | -1.818e+03 | 33.53 | 1.026e+07 | 1 | 1 |
| 2 | 5.282e+02 | R7 | h2o2+hv | 1.056e+03 | .02 | 1.026e+07 | -0 | 0 |
| 2 | 1.961e+02 | R18 | ch3h+hv | 3.922e+02 | .01 | 1.026e+07 | -0 | -0 |

deviation = rate/sum of production = .998944

sum of production = 5.13545e+6 ; sum of sink = 5422.4

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=5E10, [NO_x]=2.83e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 1.282e+06 | R4 | od+h2o | 2.564e+06 | 88.07 | 5.475e+06 | -66 | *** |
| 2 | 1.735e+05 | R23 | h2co+hv | 3.470e+05 | 11.92 | 5.822e+06 | -6 | *** |
| -2 | 1.793e+02 | R10 | ho2+ho2 | -3.586e+02 | 70.63 | 5.821e+06 | *** | *** |
| -2 | 7.455e+01 | R16 | ch32+ho2 | -1.491e+02 | 29.37 | 5.821e+06 | 0 | 0 |
| 2 | 5.952e+01 | R7 | h2o2+hv | 1.190e+02 | .00 | 5.821e+06 | -0 | -0 |
| 2 | 1.844e+01 | R18 | ch3h+hv | 3.688e+01 | .00 | 5.821e+06 | -0 | -0 |

deviation = rate/sum of production = .999826

sum of production = 2.91116e+6 ; sum of sink = 507.7

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=7E10, [NO_x]=3.16e11

| | inst. | | | | | cum. | | |
|------|-----------|------|----------|------------|-------|-----------|-----|-----|
| coef | rate | rxn. | code | contrib. | w% | contrib. | i% | c% |
| 2 | 8.904e+05 | R4 | od+h2o | 1.781e+06 | 87.51 | 3.816e+06 | -65 | *** |
| 2 | 1.271e+05 | R23 | h2co+hv | 2.542e+05 | 12.49 | 4.070e+06 | -6 | *** |
| -2 | 4.362e+01 | R10 | ho2+ho2 | -8.724e+01 | 72.45 | 4.070e+06 | *** | *** |
| -2 | 1.659e+01 | R16 | ch32+ho2 | -3.318e+01 | 27.55 | 4.070e+06 | 0 | 0 |
| 2 | 1.519e+01 | R7 | h2o2+hv | 3.038e+01 | .00 | 4.070e+06 | -0 | -0 |
| 2 | 4.326e+00 | R18 | ch3h+hv | 8.652e+00 | .00 | 4.070e+06 | -0 | -0 |

deviation = rate/sum of production = .999941

sum of production = 2.03504e+6 ; sum of sink = 120.42

SPECIES = ho/ho2/ch32/ch3o ; # OF RATE = 6

COMMENTS : [NO]=1E11, [NO₂]=3.46E11

| | inst. | | | | | | | | |
|------|-----------|------|----------|------------|-------|------------------|-----|-----|--|
| coef | rate | rxn. | code | contrib. | w% | cum. contrib. | i% | c% | |
| -1 | 2.787e+06 | R36 | ho+no2 | -2.787e+06 | 64.89 | -2.787e+06 | 334 | *** | |
| 2 | 6.823e+05 | R4 | od+h2o | 1.365e+06 | 87.18 | 2.930e+06 | -64 | *** | |
| 2 | 1.003e+05 | R23 | h2co+hv | 2.006e+05 | 12.82 | 3.130e+06 | -7 | *** | |
| -2 | 1.554e+01 | R10 | ho2+ho2 | -3.108e+01 | 73.46 | 3.130e+06 | *** | *** | |
| -2 | 5.613e+00 | R16 | ch32+ho2 | -1.123e+01 | 26.54 | 3.130e+06 | 0 | 0 | |
| 2 | 5.550e+00 | R7 | h2o2+hv | 1.110e+01 | .00 | 3.130e+06 | -0 | -0 | |
| 2 | 1.505e+00 | R18 | ch3h+hv | 3.010e+00 | .00 | 3.130e+06 | -0 | -0 | |

deviation = rate/sum of production = .999973

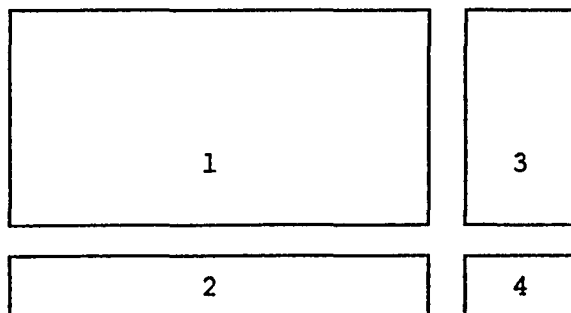
sum of production = 1.56521e+6 ; sum of sink = 42.306

APPENDIX C

DETAILS OF SSE SERIES OF SOFTWARE

SSECHEM

In SSECHEM, the graphic mode is shown below:



window 1 : concentrations or rates displayed in graphic form.
window 2 : command & comment area.
window 3 : concentrations or rates listed in numeric form in descending order.
window 4 : label window.

Figure 58. Display window of SSECHEM program

A chief feature of the program is the ability to formulate the required differential equations from an input chemical mechanism. Free-format design reduces the user's burden by avoiding tedious, error-prone work. There are up to three reactants and four products available for each reaction. Non-integral stoichiometric coefficients are allowed so that composite chemical reactions become possible. Preassigned constants, steady-state and plotted species simplify program control. In addition, a small built-in editor allows the user to edit, change, delete or save the input file without exiting the environment. This feature allows the program to be used by

people totally unfamiliar with the computer, operating system or programming language. However, any other editors or word processor can be used to create the input file which is then saved as an ASCII file, However, one must beware any hidden tabs in the editor or word processor output.

In order to reduce the burden on the user, all the user has to do is to type the free-format mechanism and run the program named as SSECONV (part of editor menu, F-6) to convert into the special format from which the SSECHEM will read the whole mechanism. The free-format mechanism should meet the requirements as follows:

1. Four characters for each species, these can include any printable ASCII characters except slash / and exclamation !, (either reactants or products) and coefficients.
2. Rate constants should have consistent units through the whole mechanism.
3. The stoichiometric coefficients of reactants are always equal to unity (1). The stoichiometric coefficients of products default to unity (1.00) unless specified as non-integer (i.e., 0.3, 0.56). But the maximum number of digits after decimal point is three, since only four characters are allowed for each number (e.g. 0.987 not allowed, but .987 is acceptable).
4. Global dilution, i.e., all species (excluding constant species) are affected by dilution, can be invoked by entering YES for dilution in the program SSECHEM.

An example of the free-format input file and corresponding converted runnable format are shown in Table XXV & XXVI, respectively. The detail of free-format input mechanism is described as

TABLE XXV
FREE-FORMAT OF CHLORINE MECHANISM

| | no. |
|------------------------------------|-----|
| !chlorine chemistry | 1 |
| 1/cl2+hv=2.0*cl+hv/1e-3/0.0 | 2 |
| 2/cl+o3=clo+o2/1.2e-11/0.0 | 3 |
| 3/clo+clo=cl2+o2/4.5e-15/0.0 | 4 |
| 4/clo+clo=2.0*cl+o2/3.11e-15/0.0 | 5 |
| 5/clo+clo=oclo+cl/1.5e-15/0.0 | 6 |
| 6/oclo=clo+o/1e-2/0.0 | 7 |
| 7/o3=o2+o/1.25e-4/0.0 | 8 |
| 8/cl+oclo=2.0*clo/5.89e-11/0.0 | 9 |
| 9/o+o2+m=o3+m/5.68e-34/0.0 | 10 |
| 10/o+o3=2.0*o2/7.95e-15/0.0 | 11 |
| 11/clo+clo+m=cl2+o2+m/3.46e-35/0.0 | 12 |
| 12/o+clo=cl+o2/3.96e-1/0.0 | 13 |
| !initial concentration | 14 |
| 1/cl2=1.25e15 | 15 |
| 2/o3=1.25e15 | 16 |
| 3/m=2.5e19 | 17 |
| 4/hv=1.00 | 18 |
| !step-range-store/2.0/200/5 | 19 |
| !constant/m/hv | 20 |
| !sse/cl/o | 21 |
| !plot/cl/clo/oclo/o3/hv | 22 |

DESCRIPTION

- The last column is line number which is only good for tracing, not part of the input file.
- First line-->title,exclamation is required.
- Second line to 13th line are chemical reactions.
- The design for each line is

number/reactants=product(s)/rate constant/energy

- The leading number before first slash is for counting.
- The symbol * separates the product and coefficient.
- The symbol + distinguishes the different reactants or products.
- The symbol = separates reactants from products.
- The slash / separates reaction number (i.e., the leading number), rate constant and energy from chemical reaction.
- The rate constant of reaction is the value at temperature $T=300\text{K}$.
- The form for energy is E_a/R while R is gas constant and E_a is activation energy for specific reaction.
- The mechanism may be simplified if desired.

for instance:

line #12 (reaction #11) can be rewritten as

11/clo+clo=cl2+o2/8.65e-16

by removing m and recalculating the rate constant (in

this case at 1 atm pressure, $k[m] = 3.46e-35 \times 2.5e19 =$

$8.65e-16$). If pressure remains constant, the third body (M) is implicit so that less memory is needed and the speed of calculation is increased. However, the termolecular form reaction should be kept when considering the effect of pressure.

- Line 14 with the symbol ! is required to tell the program to start reading the non-zero initial

concentration. One line is for each species.

- The format for non-zero initial concentration is species no./species code= initial concentration.
- Line 19 with the symbol ! is required for step size/range of time /how often to store data.
- Line 20 with the symbol ! is required for constant species. Each constant species is separated by a slash. Even if no species are assigned as constant,(!constant/) is still required.
- Lines 21 & 22 are similar to line 20, the difference is that line 21 inputs pre-set steady state species and line 22 inputs default plotting species.
- If the number of constant, pre-set steady state or plotting species is more than one line, it is OK to use second line for more species without the symbol ! (exclamation).
- It is essential for the input file to have a total of six ! symbols since the program uses the ! as indicator to distinguish main chemical reaction part, initial concentration, preset step size, range, frequency of storing, constant species, preset steady state species, and plotting species. Even if no species are set as constant or steady-state, the blank line with ! is still necessary.
- The free-format file cannot be run directly through the program SSECHEM. it should be converted to the so-called CHEMK format by using SSECONV.EXE (either invoked from the SSECHEM or separately).

- In converted format, the numeric value in the first row should correspond to the exact number of reactions. Therefore, if a new reaction is added or an old reaction is deleted, the number at the first line should be incremented or reduced by one, respectively.
- The numbers of allowed reactions and species are 200 and 100, respectively. Meanwhile, the maximum number of species pre-assigned as constant, steady state and plotted is 40.

The resultant input file looks as Table XXVI and the graphic output is shown in Figure 60.

plotting

There are several features in the plotting file. Single or multiple data file input is allowed. Six different plot options allow the user to generate various data plots and to calculate the maximum value, average value and last value of each data set. In addition, the user is able to choose any range for the independent variable.

Screen dump

The built-in screen dump function allows the user to copy the screen from color or monochrome monitors onto dot-matrix printers either from the main program or the plotting file. This can be done during an interrupt at any point of the calculation.

TABLE XXVI
CHEMK FORMAT OF CHLORINE MECHANISM

```

12
*comment line*
1cl2 hv      2.00cl  1.00hv      1.000e-03    0.
2cl  o3      1.00clo 1.00o2      1.200e-11    0.
3clo clo     1.00cl2 1.00o2      4.500e-15    0.
4clo clo     2.00cl  1.00o2      3.110e-15    0.
5clo clo     1.00oclo1.00cl      1.500e-15    0.
6oclo        1.00clo 1.00o       1.000e-02    0.
7o3          1.00o2 1.00o        1.250e-04    0.
8cl  oclo    2.00clo              5.890e-11    0.
9o   o2 m    1.00o3 1.00m        5.680e-34    0.
10o  o3      2.00o2              7.950e-15    0.
11clo clo m  1.00cl2 1.00o2  1.00m 3.460e-35    0.
12o  clo     1.00cl  1.00o2      3.960e-01    0.
*comment line*
  4      5.00e+00  5.00e+00
  cl2 o3 m hv
1.250e+151.250e+152.500e+191.000e+00
*comment line*
      2.000e+02      1.000e-02 2.000e-00
halt
!constant/m/hv
!steady-state/cl/o
!plot/cl/clo/oclo/o3/hv

```

Note: *comment line" means any comments can be inserted without influencing the entire chemical mechanism.

Color graphics output

If a color printer (e.g., Tektronix 4696 inkjet printer) is available, colorful graphic output can be generated, identifying plotted integration curves with listed values in the same colors.

Data storage

Data may be stored in either linear or logarithmic scale and three different data sets (concentration, individual rate, ratio) are saved at each preset storing time. Useful information is saved as a file header so that the plotting program can obtain the information necessary to execute the plotting. The option of appending the complete chemical mechanism at the end of the data file provides the chance for user to retrieve the initial conditions.

Experimental data input

Input of time-varying experimental data constrained by a polynomial equation (curve-fitting) is allowable. This enables the results of modelling to be interpreted more realistically.

Interrupt (interactive) features

Attempts have been made to emulate real laboratory experiments with the software. The program allows the user to interrupt the execution of the program temporarily and change concentrations, step size, light intensity, etc. The interactive mode widens the use of this modelling software and allows people to develop a good intuitive feeling for complex chemical process. For instance, you can examine what will happen by interrupting the reaction and changing one of species' concentration (at this moment, all species codes should appear on information window).

Variation of light intensity

Simulation of atmospheric chemistry by diurnal solar variation or analytical chemistry by laser pulse-initiation can be performed with this feature. The mathematical formulas available for the variation are sine wave, gaussian curve and square wave. Diurnal variation of solar intensity allows tropospheric or stratospheric photochemistry to be simulated. Sample excitation with pulsed laser radiation is also allowed so that non-linear optical phenomena can be simulated.

View & modify data

The user is able to look up any current data including the input file, initial conditions, current concentration, rate, ratio and important mechanism information. Moreover, both values of rate constants and concentrations may be modified. Through this option, it is fast & easy to examine the difference in results by varying the rate constants. The other way to modify the mechanism is implemented via the editor.

Data display : graphic & table

Most existing programs, especially those written in Fortran, do not have real-time graphic data display. In order to view data in graphic mode, a separate plot program needs to be provided. The program SSECHEM displays real-time data in graphic mode as well as in tabular format and allows easy grasp of the behavior of the whole system. In choosing the

graphic mode, all data plotted on the screen are sorted according to magnitude and displayed numerically & synchronously in a color-coded information window at the right of the screen. More important, the graphic data display is not restricted to the typical concentration vs. time trajectory, but also rate vs. time, concentration vs. concentration, rate vs. concentration or concentration vs. rate. On the other hand, there are three options, i.e., concentration, ratio and rate, for displaying data in the tabular form.

Applications of software

The variety of applications includes any form of chemical kinetics: enzyme kinetics, atmospheric chemistry, oscillating chemical reaction, laser excitation, some types of population dynamics, etc.

On-line help

On-line help (SSEHELP.EXE) can be invoked by simply pressing the key while the program is idle.

Plot file

The plot file program SSEPLOT.EXE used to replot data from storage can be invoked either from the program SSECHEM or independently. There are several features in the plotting file. Single or multiple data file input is allowed. Six different plot options, i.e., linear-linear, linear-log, log linear, log-log, linear-normalized to log-normalized, allow the user to generate various data plots. The choice of maximum

value, average value and last value for each data set simplify the procedures to trace data. In addition, the user is able to choose any interesting range of independent variable to plot, i.e., the program allows zooming.

Testing and Application of Programs

To test the feasibility and reliability of programs for integrating macroscopic chemical systems, we first take the cesium mechanism (102) as a test mechanism. Excluding the intention for competition in speed, excellent agreement with Edelson' results is reached and the graphic output is shown in Figure 59. Simulation of the impact of chlorine on ozone depletion is shown in Figure 60, and the Lotka-Volterra reaction population dynamics problem in Figure 61. Additionally, the Oregonator mechanism (103,104,105) has been taken in order to test phase plot for an oscillating reaction. There is very satisfactory agreement between the generated and published data (Figure 62). We illustrate the application of SSECHEM to butane pyrolysis (106) in Figure 63. The plot of multiple data files (101) is shown in Figure 64. The unique interactive function of allowing a continuous or a discrete pulse generator is demonstrated for laser-pulse excitation in Figure 65. It is believed that active involvement with this software leads to a great intuitive understanding of chemical dynamics. Steady state analyses of the troposphere have been carried out through this series of programs. In chapter V & VI, the details of using this series of programs will be

provided. The summary of key features of SSECHEM compared to HAVCHEM (70) is given in Table XXIX.

TABLE XXVII
BUTANE REACTION MECHANISM

| | | | |
|--------------------------|------------------|-----------|----|
| 79 | | | |
| BUTANE REATION MECHANISM | | | |
| 1C4HT | 1.00C2H51.00C2H5 | 1.010e+02 | 0. |
| 2C4HT | 1.00CH3 1.00NPRO | 1.710e+02 | 0. |
| 3C2H6 | 1.00CH3 1.00CH3 | 1.940e+00 | 0. |
| 4C3H8 | 1.00CH3 1.00C2H5 | 5.390e+01 | 0. |
| 5CH3 CH3 | 1.00C2H6 | 2.100e-12 | 0. |
| 6CH3 C2H5 | 1.00C3H8 | 4.590e-12 | 0. |
| 7C2H5C2H5 | 1.00C4HT | 1.680e-12 | 0. |
| 8CH3 NPRO | 1.00C4HT | 4.630e-12 | 0. |
| 9CH3 IPRO | 1.00C4HT | 4.630e-12 | 0. |
| 10CH3 C3H5 | 1.00C4H8 | 4.630e-12 | 0. |
| 11H C2H5 | 1.00CH3 1.00CH3 | 6.600e-11 | 0. |
| 12H NPRO | 1.00CH3 1.00C2H5 | 1.670e-10 | 0. |
| 13H IPRO | 1.00CH3 1.00C2H5 | 1.670e-10 | 0. |
| 14H 1BUT | 1.00C2H51.00C2H5 | 3.600e-11 | 0. |
| 15H 1BUT | 1.00CH3 1.00NPRO | 1.310e-10 | 0. |
| 16H 2BUT | 1.00CH3 1.00NPRO | 1.310e-10 | 0. |
| 17H 2BUT | 1.00C2H51.00C2H5 | 3.600e-11 | 0. |
| 18CH3 NPRO | 1.00C2H51.00C2H5 | 1.100e-11 | 0. |
| 19C2H5C2H5 | 1.00CH3 1.00NPRO | 4.410e-12 | 0. |
| 20C2H5NPRO | 1.00CH3 1.001BUT | 6.600e-12 | 0. |
| 21C2H5 | 1.00H 1.00C2H4 | 1.110e+05 | 0. |
| 22NPRO | 1.00CH3 1.00C2H4 | 5.870e+05 | 0. |
| 23NPRO | 1.00H 1.00C3H6 | 1.230e+05 | 0. |
| 24IPRO | 1.00H 1.00C3H6 | 3.070e+05 | 0. |
| 251BUT | 1.00C2H51.00C2H4 | 4.690e+05 | 0. |
| 262BUT | 1.00CH3 1.00C3H6 | 9.410e+05 | 0. |
| 27C2H3 | 1.00H 1.00C2H2 | 2.780e+04 | 0. |
| 28H C2H5 | 1.00H2 1.00C2H4 | 3.300e-12 | 0. |
| 29H NPRO | 1.00H2 1.00C3H6 | 1.670e-11 | 0. |
| 30H IPRO | 1.00H2 1.00C3H6 | 8.350e-11 | 0. |
| 31H 1BUT | 1.00H2 1.00C4H8 | 1.670e-11 | 0. |
| 32H 2BUT | 1.00H2 1.00C4H8 | 8.350e-11 | 0. |
| 33H C2H3 | 1.00H2 1.00C2H2 | 3.300e-12 | 0. |
| 34CH3 C2H5 | 1.00CH4 1.00C2H4 | 1.320e-12 | 0. |
| 35CH3 NPRO | 1.00CH4 1.00C3H6 | 2.100e-12 | 0. |
| 36CH3 IPRO | 1.00CH4 1.00C3H6 | 4.190e-12 | 0. |
| 37CH3 1BUT | 1.00CH4 1.00C4H8 | 3.330e-12 | 0. |
| 38CH3 2BUT | 1.00CH4 1.00C4H8 | 1.670e-12 | 0. |
| 39CH3 C2H3 | 1.00CH4 1.00C2H2 | 1.320e-12 | 0. |
| 40C2H5C2H5 | 1.00C2H41.00C2H6 | 8.530e-13 | 0. |
| 41C2H5NPRO | 1.00C2H61.00C3H6 | 8.350e-13 | 0. |
| 42C2H5IPRO | 1.00C2H61.00C3H6 | 2.640e-12 | 0. |
| 43C2H51BUT | 1.00C2H61.00C4H8 | 8.350e-13 | 0. |
| 44C2H52BUT | 1.00C2H61.00C4H8 | 2.640e-12 | 0. |

TABLE XXVII
BUTANE REACTION MECHANISM
(continued)

| | | | |
|---|------------------|-----------|----|
| 45C2H5C2H3 | 1.00C2H61.00C2H2 | 4.260e-13 | 0. |
| 46C2H5C2H3 | 1.00C2H41.00C2H4 | 4.260e-13 | 0. |
| 47NPROC2H5 | 1.00C3H81.00C2H4 | 8.350e-13 | 0. |
| 48IPROC2H5 | 1.00C3H81.00C2H4 | 2.100e-12 | 0. |
| 491BUTC2H5 | 1.00C4HT1.00C2H4 | 8.350e-13 | 0. |
| 502BUTC2H5 | 1.00C4HT1.00C2H4 | 1.330e-12 | 0. |
| 51H C2H2 | 1.00C2H3 | 4.370e-13 | 0. |
| 52H C2H4 | 1.00C2H5 | 4.370e-13 | 0. |
| 53H C3H6 | 1.00NPRO | 1.030e-13 | 0. |
| 54H C3H6 | 1.00IPRO | 2.000e-13 | 0. |
| 55H C4H8 | 1.002BUT | 2.000e-13 | 0. |
| 56CH3 C2H4 | 1.00NPRO | 1.440e-16 | 0. |
| 57CH3 C3H6 | 1.002BUT | 1.910e-17 | 0. |
| 58H C2H6 | 1.00H2 1.00C2H5 | 4.910e-12 | 0. |
| 59H C3H8 | 1.00H2 1.00NPRO | 4.910e-12 | 0. |
| 60H C3H8 | 1.00H2 1.00IPRO | 5.340e-12 | 0. |
| 61H C4HT | 1.00H2 1.001BUT | 4.910e-12 | 0. |
| 62H C4HT | 1.00H2 1.002BUT | 1.060e-11 | 0. |
| 63H C2H4 | 1.00H2 1.00C2H3 | 2.360e-12 | 0. |
| 64H C3H6 | 1.00H2 1.00C3H5 | 3.070e-12 | 0. |
| 65CH3 C2H6 | 1.00CH4 1.00C2H5 | 1.180e-14 | 0. |
| 66CH3 C3H8 | 1.00CH4 1.00NPRO | 1.940e-14 | 0. |
| 67CH3 C3H8 | 1.00CH4 1.00IPRO | 2.110e-14 | 0. |
| 68CH3 C4HT | 1.00CH4 1.001BUT | 8.040e-15 | 0. |
| 69CH3 C4HT | 1.00CH4 1.002BUT | 1.610e-14 | 0. |
| 70CH3 C2H4 | 1.00CH4 1.00C2H3 | 6.930e-15 | 0. |
| 71CH3 C3H6 | 1.00CH4 1.00C3H5 | 5.340e-15 | 0. |
| 72C2H5C3H8 | 1.00C2H61.00NPRO | 1.940e-14 | 0. |
| 73C2H5C3H8 | 1.00C2H61.00IPRO | 2.110e-14 | 0. |
| 74C2H5C4HT | 1.00C2H61.001BUT | 8.040e-15 | 0. |
| 75C2H5C4HT | 1.00C2H61.002BUT | 1.610e-14 | 0. |
| 76NPROC2H6 | 1.00C3H81.00C2H5 | 3.460e-15 | 0. |
| 77IPROC2H6 | 1.00C3H81.00C2H5 | 1.280e-15 | 0. |
| 78NPROC2H4 | 1.00C3H81.00C2H3 | 6.930e-15 | 0. |
| 79IPROC2H4 | 1.00C2H31.00C3H8 | 6.400e-16 | 0. |
| INITIAL CONCENTRATION | | | |
| 1 | 5.000e-05 | 5.000e-05 | |
| C4HT | | | |
| 6.300e+16 | | | |
| 1.000e-02 3.000e+02 1.000e-02 1.000e-05 | | | |
| HALT | | | |
| !constant/ | | | |
| !SS/ | | | |
| !plot/C4HT/IPRO/CH3/CH4/C2H2 | | | |

TABLE XXVIII

LASER INDUCED REACTION MECHANISM

| | | | | | | | | | |
|------------------------|---------|---|----------|------|----|----|----------|----|--|
| 41 | | | | | | | | | |
| Laser Induced Reaction | | | | | | | | | |
| 103 | HV | Z | O* | O2 | Z | HV | 4.50E+06 | 0. | |
| 20* | H2O | | 2.000H2 | | | | 1.20E+03 | 0. | |
| 30* | H2O | | 2.000H11 | | | | 2.88E+03 | 0. | |
| 40* | H2O | | 2.000H00 | | | | 9.12E+03 | 0. | |
| 50 | H00M | | OH | M | | | 1.32E+03 | 0. | |
| 60 | H11M | | OH1 | M | | | 1.32E+03 | 0. | |
| 70 | H2 M | | OH1 | M | | | 1.20E+01 | 0. | |
| 80 | H1 M | | OH2 | M | | | 1.20E+01 | 0. | |
| 90 | H11M | | OH00 | M | | | 1.20E+01 | 0. | |
| 100 | H00M | | OH11 | M | | | 1.20E+01 | 0. | |
| 110 | H1 M | | OH | M | | | 1.20E+01 | 0. | |
| 120 | H M | | OH1 | M | | | 1.20E+01 | 0. | |
| 130 | H00H2O | | OH | H2O | | | 1.32E+04 | 0. | |
| 140 | H11H2O | | OH1 | H2O | | | 1.32E+04 | 0. | |
| 150 | H2 H2O | | OH1 | H2O | | | 2.70E+03 | 0. | |
| 160 | H1 H2O | | OH2 | H2O | | | 2.70E+03 | 0. | |
| 170 | H11H2O | | OH00 | H2O | | | 1.14E+03 | 0. | |
| 180 | H00H2O | | OH11 | H2O | | | 1.14E+03 | 0. | |
| 190 | H1 H2O | | OH | H2O | | | 1.14E+03 | 0. | |
| 200 | H H2O | | OH1 | H2O | | | 1.14E+03 | 0. | |
| 210* | M | | O | M | | | 1.26E+03 | 0. | |
| 220 | HV | Z | OH1* | Z | HV | | 1.50E+08 | 0. | |
| 230 | H00HV | Z | OH1* | Z | HV | | 5.10E+07 | 0. | |
| 240 | H* M | | OH | M | | | 3.00e+03 | 0. | |
| 250 | H1*M | | OH* | M | | | 3.00e+03 | 0. | |
| 260 | H1*M | | OH | M | | | 3.00e+03 | 0. | |
| 270 | H* H2O | | OH | H2O | | | 4.74E+04 | 0. | |
| 280 | H1*H2O | | OH* | H2O | | | 0.00E+00 | 0. | |
| 290 | H1*H2O | | OH | H2O | | | 0.00E-00 | 0. | |
| 300* | IBUH | | O | IBUH | | | 1.50E+04 | 0. | |
| 310* | IBUH | | OH | SBU | | | 1.50E+04 | 0. | |
| 320 | IBUH | | OH | SBU | | | 1.11E+00 | 0. | |
| 330 | H IBUH | | H2O | SBU | | | 1.32E+02 | 0. | |
| 340* | IBUH | | BUOH | | | | 3.00E+04 | 0. | |
| 350 | H1*IBUH | | OH* | IBUH | | | 2.10E+05 | 0. | |
| 360 | H1*IBUH | | OH | IBUH | | | 2.11e+05 | 0. | |
| 370 | H1*IBUH | | OH* | IBUH | | | 1.51e+04 | 0. | |
| 380 | H* | | OH | | | | 1.46E-04 | 0. | |
| 390 | H1* | | OH | | | | 1.46e-04 | 0. | |
| 400 | H1*HV | Z | OH | HV | Z | HV | 1.20E+09 | 0. | |
| 41 | H2O2HV | Z | OH | OH | | | 2.81E+04 | 0. | |
| !INITIAL CONCENTRATION | | | | | | | | | |

TABLE XXVIII
LASER INDUCED REACTION MECHANISM
(continued)

```

7          3.000E-00 3.000E-00
H2O IBUHO3 OH HV Z M
4.40e-09 1.23e-09 1.34e-14 0.00e-00 0.00e-00 7.90e-11 2.68e-07
          300          298          5.00E-02 3.00E-00
HALT
!CONSTANT/M/Z/H2O/O2/IBUH
!ss/
!plot/OH/OH*/OH1/HV/O*/OH2/OH00/OH1*

```

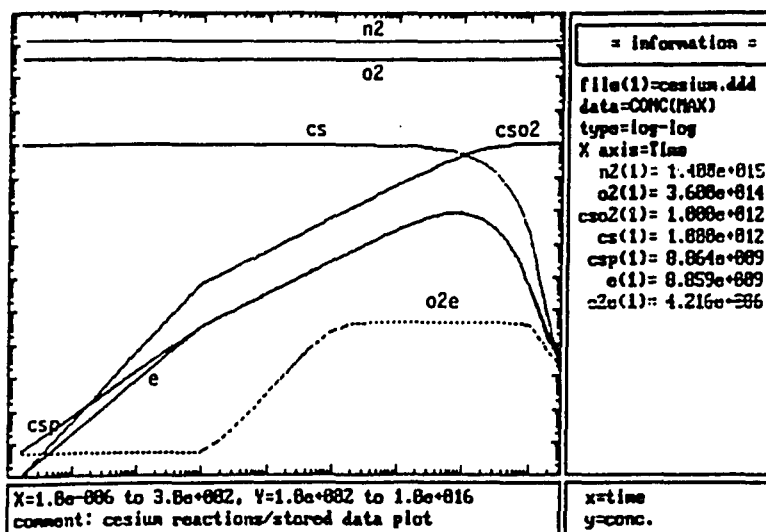
TABLE XXIX
SUMMARY OF FEATURES OF SSECHEM COMPARED TO HAVCHEM

| | SSECHEM | HAVCHEM ^a |
|-----------------------|--|---|
| 1. language | Microsoft C 5.1 | Turbo Pascal |
| 2. computer | IBM/compatible PC | IBM/compatible PC |
| 3. integrator | Euler's method (Implicit Euler Runge-Kutta 4th) | Gear DIFSUB |
| 4. input file | free-format | fixed format |
| 5. data output | real-time graphic or table display/ store and plot later.plot up to 40 species | print/ store and plot later. plot 1-3 species |
| 6. data stored | linear/log scale | ----- |
| 7. editor | built-in | ----- |
| 8. pulse variation | sine, gaussian & square functions | ----- |
| 9. interactive | allow to change conc., step size, pulse while reaction takes place. | ----- |

TABLE XXIX
SUMMARY OF FEATURES OF SSECHEM COMPARED TO HAVCHEM
(continued)

| | SSECHEM | HAVCHEM ^a |
|-----|--|--|
| 10. | information allow view data anytime. library | ----- |
| 11. | steady state preset or internal | internal |
| 12. | plotting either run inside main file program or separately. | separately. |
| 13. | step size manual | auto. |
| 14. | experimental allow input of experimental data input data as a constraint in the form of polynomial equation. | ----- |
| 15. | on-line help available | ----- |
| 16. | reaction elementary/composite type reactions | elementary reaction |
| 17. | no. of reaction 200 | 30 |
| | no. of species 80 | 20 |
| 18. | no. of reactants 3 | 3 |
| | no. of products 4 (each reaction) | 3 |
| 19. | modification two ways via of reaction editor or view scheme window. | editor |
| 20. | constant species preset | preset |
| 21. | isothermal no; recalculates rate constants based on temp. & activation energy. | yes |
| 22. | features a. linear/log conc. in vs. linear/log time. plotting b. normalized conc. vs. subroutine linear/log time. c. multiple data files d. calculate average within selected range. | a. linear/log conc. vs. time b. ----- c. multiple data files d. ----- |

Note: a. see reference 104.

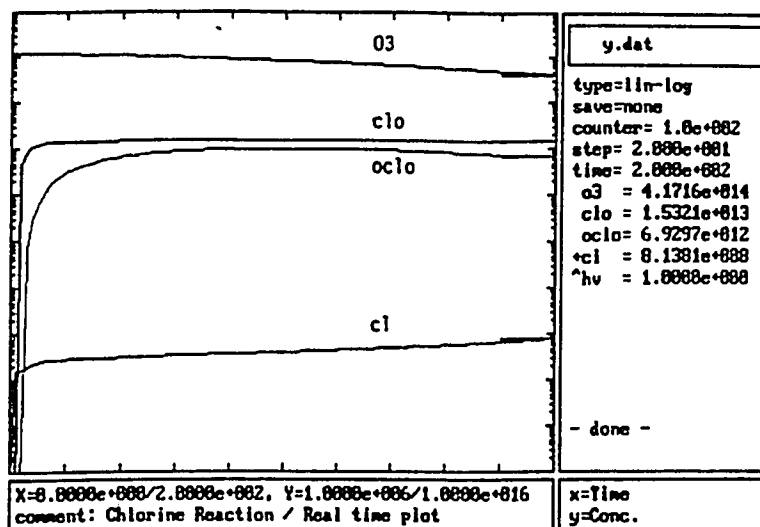


Cesium Reaction Mechanism :

```

7
#cesium reactions#
1o2e csp 1.00cs 1.00o2 5.000e-08 0.
2csp e 1.00cs 1.000e-12 0.
3cs 1.00csp 1.00e 3.240e-03 0.
4o2e 1.00o2 1.00e 4.000e-01 0.
5o2 cs x 1.00cs2 1.00e 1.000e-31 0.
6o2 e o2 1.00o2e 1.00o2 1.240e-30 0.
7o2 e n2 1.00o2e 1.00n2 1.000e-31 0.
INITIAL CONCENTRATION
5.000e+00 5.000e+00
e o2e csp cs n2 o2 x
1.000e+023.200e+026.200e+021.000e+121.400e+153.600e+141.760e+15
#ranges/temperature/tolerance/initial step size#
3.000e+02 3.000e+02 1.000e-02 1.000e-03
NALT
!constant/n2/o2/x
!no sse/
!plot/s/csp/cs/o2e
  
```

Figure 59. The Cesium reaction mechanism. It has been used to test the reliability of the numerical integration program. SSECHEM gives excellent agreement with the results of Edelson (102). The plot was done from a stored data file (cesium.data) and the digit in parenthesis indicates the first open data file (up to 5 data files allowed). The data=CONC(MAX) shows data is concentration (the other two options are rate and ratio). The plot type is log(conc.) vs. log(time). Time is chosen for the X axis (other options are conc. and rate). All data are displayed in descending order of maximum concentration order. The digit in the parenthesis for each species indicates the data file number. The lower left hand window is used for displaying the ranges for X and Y axes as well as comments.

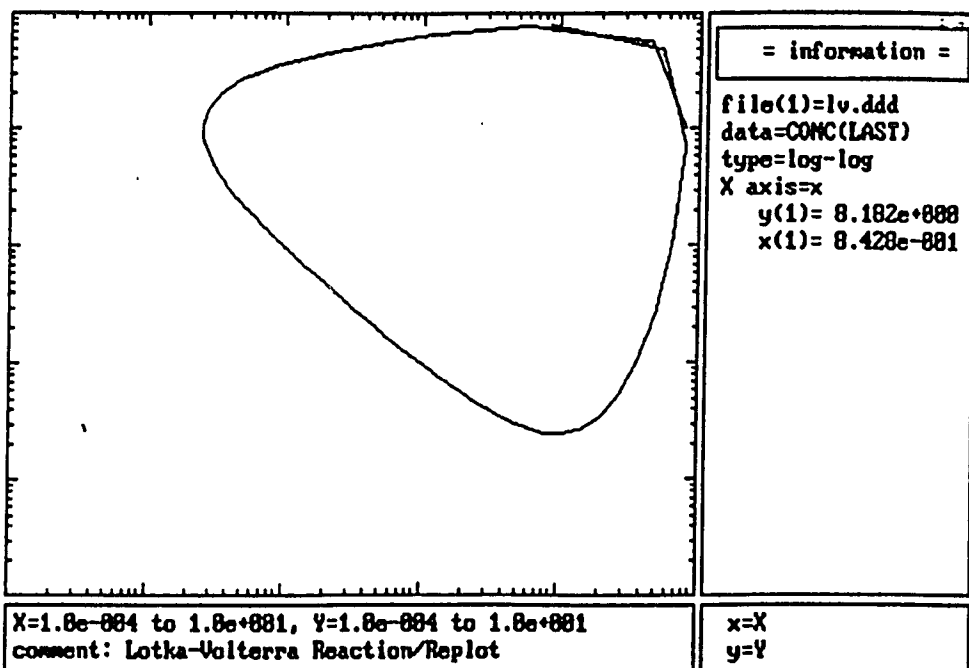


```

121
*Chlorine Reaction*
1cl2 hv      2.0 cl 1.00hv      1.000e-03  0.
2cl o3      clo o2      1.200e-11  0.
3clo clo     cl2 o2      4.500e-15  0.
4clo clo     2.0 cl o2      3.110e-15  0.
5clo clo     oclo cl      1.500e-15  0.
6oclo clo     o      1.000e-02  0.
7o3 o2      o      1.250e-04  0.
8cl oclo     2.0 clo      5.890e-11  0.
9o o2      o3      5.680e-34  0.
10o o3      2.0 o2      7.950e-15  0.
11clo clo    cl2 o2      3.460e-35  0.
12o clo     cl o2      3.960e-01  0.
run
4      5.00e+00 5.00e+00
cl2 o3      hv
1.250e+151.250e+152.500e+191.000e+00
*range/temperature/tolerance/step size*/
2.000e+02      1.000e-02 2.000e-00
halt
!constant/a/hv
!steady-state/cl/o
!plot/cl/clo/oclo/o3/hv

```

Figure 60. Real time simulation of the impact of chlorine on ozone depletion. The name of input mechanism is displayed in the top right small window. The counter indicates the number of integration steps and step indicates the step size. The caret (^) in front of hv indicates hv is a constant species through all reaction time and the plus sign indicates cl is treated as a steady state species. The other species are integrated numerically. All numerical values are the most recent during the integration. The graphic output may be dumped to the printer at any point in the calculation.

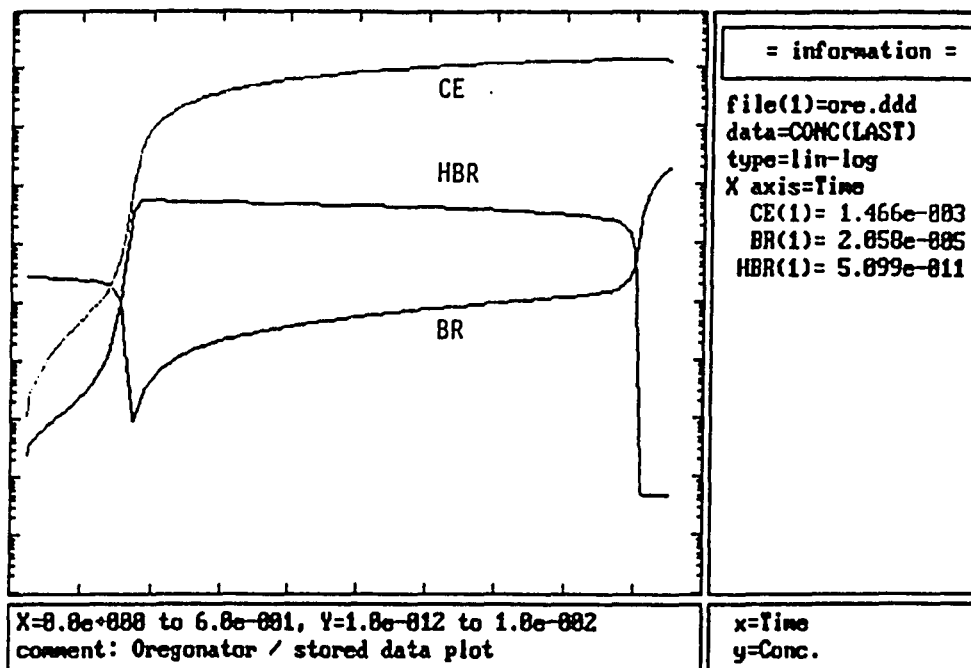


```

3
*Lotka-Volterra Reaction
1a x      2.00x      1.000e-01  0.
2x y      2.00y      3.000e-01  0.
3y b      1.00e      1.00b      1.000e-01  0.
INITIAL CONCENTRATION
4      2.000e-01 2.000e-01
x y a b
8.000e+001.000e+003.000e+003.000e+00
*range/temperature/tolerance/step size*
4.000e-01 3.000e+02 1.000e-02 1.000e-02
HALT
!const/a/b
!s/
!plot/y

```

Figure 61. Lotka-Volterra equations for population dynamics. The plot displays the predator (Y) vs. prey (X) population variation. Plot from stored data file.



```

5
/*Oregonator Reaction Mechanism*
1A BR 1.00HBR 1.340e+00 0.
2HBR BR 1.00P 1.600e+09 0.
3B HBR 2.0 HBR 2.0 CE 8.000e+03 0.
4HBR HBR 1.00Q 4.000e+07 0.
5CE 0.5 BR 1.000e+00 0.
INITIAL CONCENTRATION
4 5.000e-03 5.000e-03
A B BR HBR
6.000e-026.000e-023.000e-070.000e-00
*range/temperature/tolerance/step size*
5.000e+01 3.000e+02 1.000e-02 2.000e-04
HALT
!CONSTANT/A/B
!SS/
!PLOT/HBR/BR/CE

```

Figure 62. Oscillation reactions in the Oregonator. It was selected for testing sharp transients existing in the system. CE represents Ce^{4+} ion, BR represents Br^- ion while HBR is equivalent to HBrO_2 .

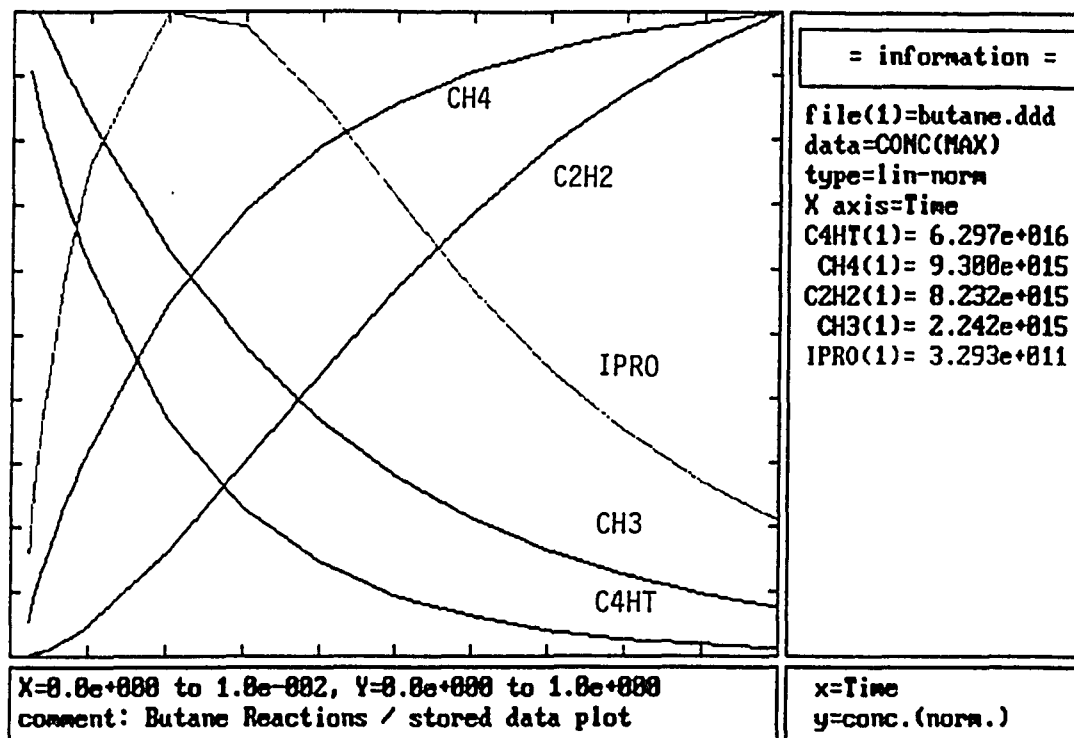
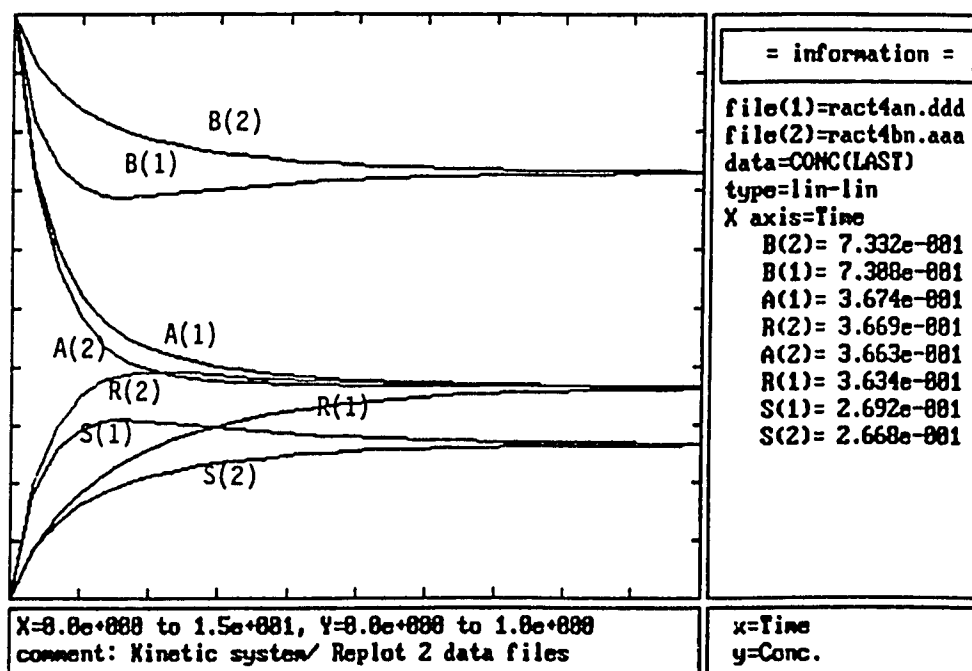


Figure 63. Analysis of the thermal decomposition of butane at 1300^oK. All stored data are normalized. The detailed mechanism can be found on Table XXVII (106).



```

4
*kinetic system*
1A      1.00R      2.00e-01    0.
2R      1.00A      2.00e-01    0.
3A  B    1.00S      5.00e-01    0.
4S      1.00A      5.00e-01    0.
INITIAL CONCENTRATION
2      5.00e-01 5.00e-01
A  B
1.00e+00 1.00e+00
*range/temperature/tolerance/step size*/
1.50e+01 3.00e+02 1.00e-02 1.00e-01
HALT
!CONSTANT/
!SSE/
!PLOT/A/R/S

```

Figure 64. An example of a multiple data file plot. The difference between the two output files is due to a variation of rate constants (101). Rate constants used for the first data file are $k_1=k_2=0.2$, $k_3=k_4=0.5$ and $k_1=k_2=0.2$, $k_3=k_4=0.5$ for the second data file. The digits in parenthesis indicate the file number.

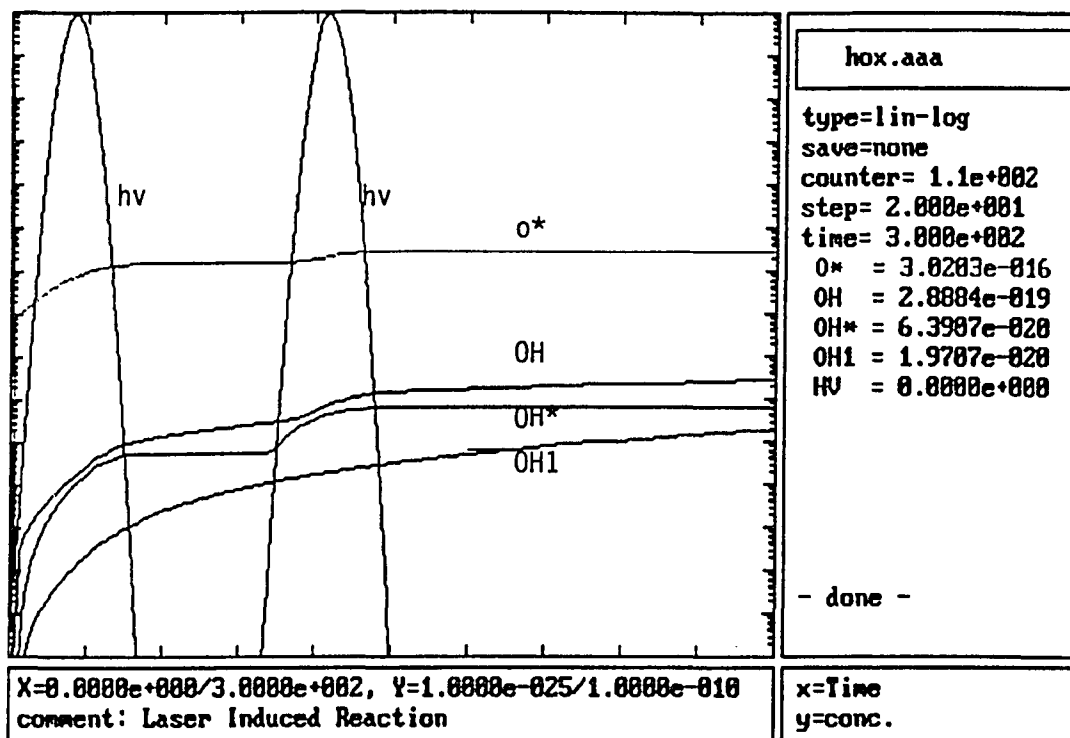


Figure 65. Excitation of hydroxyl (HO) radicals produced in ozone photolysis by 2 successive laser pulses. Plotted is concentration of various intermediates vs. time in nanoseconds. Mechanism is on Table XXVIII

CALNUM

Introduction

In CALNUM, combination theory has been applied to calculate the number of possible combinations in a given mechanism with a specific number of species. The number of combination of i species out of a total N species at a time is described as

$$C_i^N = \binom{N}{i} = \frac{N!}{(N-i)! i!}$$

In general, total combinations are

$$\sum_{i=2}^N \binom{N}{i}$$

Steady state equations can contain terms with either positive or negative sign. Changing the sign (from + to -) may yield different results, so each combination should be multiplied by the sign factor $(2^i - 1)$. Here, the reason to subtract one is that there is no difference between $-(a+b)$ and $(-a-b)$. Further, if one allows a factor of two for self-reaction of species, then a second term occurs, continuing the same combination multiplied by

$$\sum_{j=1}^{i-1} \binom{i}{j} = \sum_{j=1}^{i-1} (i, j)$$

Consequently, the possible combination is

$$\sum_{i=2}^N [(\frac{N}{i})(2^i - 1) + (\frac{N}{i})(2^i - 1) \sum_{j=1}^{i-1} (\frac{i}{j})]$$

$$= \sum_{i=2}^N [(\frac{N}{i})(2^i - 1) (1 + \sum_{j=1}^{i-1} (\frac{i}{j}))]$$

Application

The format of the result is as follows :

FIRST COLUMN : # OF SPECIES

SECOND COLUMN : # OF COMBINATIONS

THIRD COLUMN : CONSIDER DIFFERENT SIGN (-+)

FOURTH COLUMN : CONSIDER MULTIPLICATION BY 2

FIFTH COLUMN : SUM OF 3RD, 4TH COLUMN

TOTAL NUMBER OF SPECIES = 5; TAKE i FROM N AT A TIME

| # | (N,i) | (N,i)*(2 ⁱ -1) | (N,i)*(2 ⁱ -1)*(Σ(i,j)) | SUM |
|---|-------|---------------------------|------------------------------------|------|
| 2 | 10 | 30 | 60 | 90 |
| 3 | 10 | 70 | 420 | 490 |
| 4 | 5 | 75 | 1050 | 1125 |
| 5 | 1 | 31 | 930 | 961 |

In the example shown above, it is assumed the total number of species is 5 in a given mechanism. For instance, the combination of taking 2 out of 5 is equivalent to $(N,i)=5!/3!2!=10$. If the possibility of different sign (+-) is counted, the number becomes 30 through multiplying 10 by 2^i-1 . An additional possibility occurs when chemical self-reactions are considered. Then the sum of combinations equals $60 = (N,i) \times (2^i-1) \times (\Sigma(i,j))$. Finally, the total number of combinations is the sum of 30 & 60, for combining 2 out of 5. Similarly, 490 is the result of combining 3 out of 5, and 1125

of combining 4 out of 5, etc.

The program CALNUM thus provides information on how many possibilities exist for a given mechanism when considering the combination with different number of species.

SSECOM

The program SSECOM is designed for evaluating the combination and the number of resultant rates for species of interest, which will give a rough idea how to choose the species for steady-state equation generator (SSEGEN).

The maximum number of species chosen at a time by SSECOM is 20. Therefore, if the number of species is more than 20, one must run SSECOM several times. The easy way to run SSECOM is selectively, namely, only input the species codes of interest rather than those of all species.

SSECOM seeks the link between sources and sinks for a simple chemical system. The details of this search will be described at the end of this chapter. The results of SSECOM will list the combined different steady state species as well as the number of remaining rate terms. Taking the chemical mechanism of Table I (omitting R2, R3, R49, R50, R51, R52, R53, leaving 46 reactions) and examining the frequency of appearance relative to the number of remaining rate terms, one can explore the approach to a normal distribution by combining more species at a time. Figs. 66 to 69 show that the frequency distribution approaches to the normal distribution.

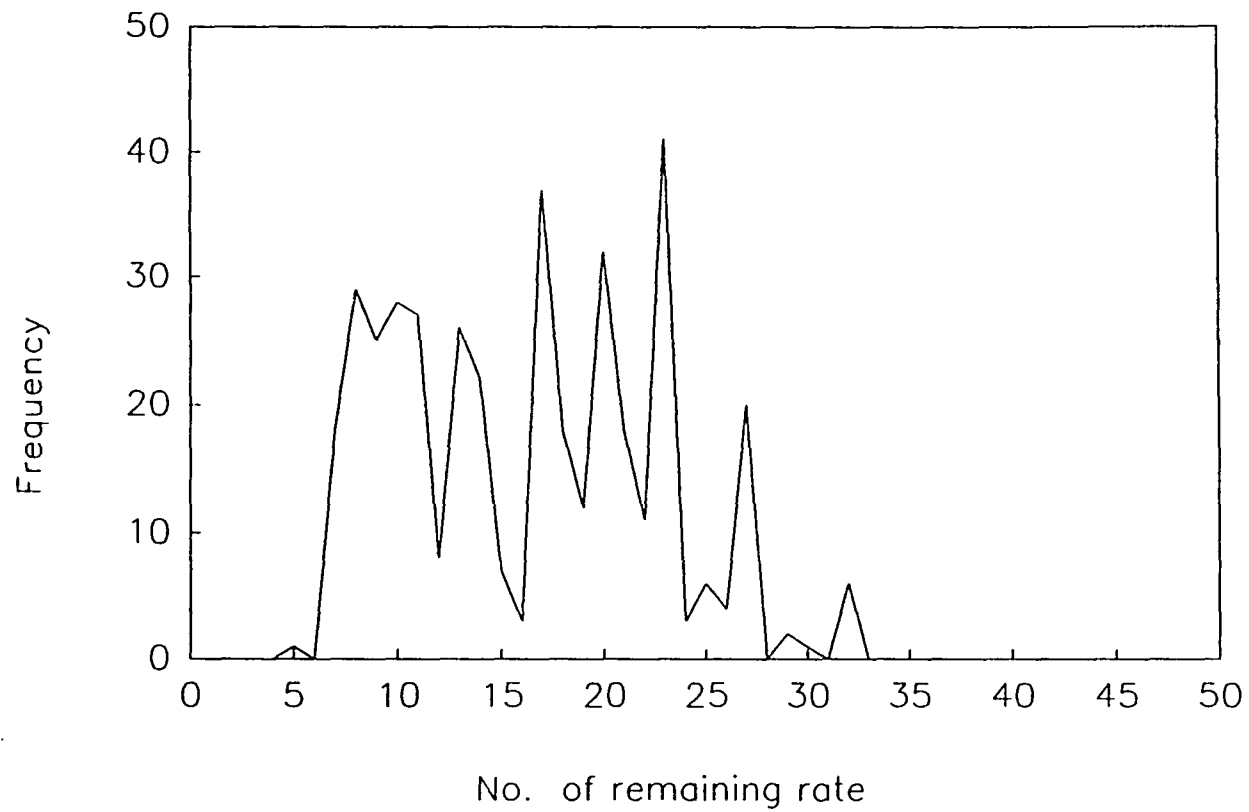


Figure 66. The plot of frequency vs. remaining rate terms after combining 2 species.

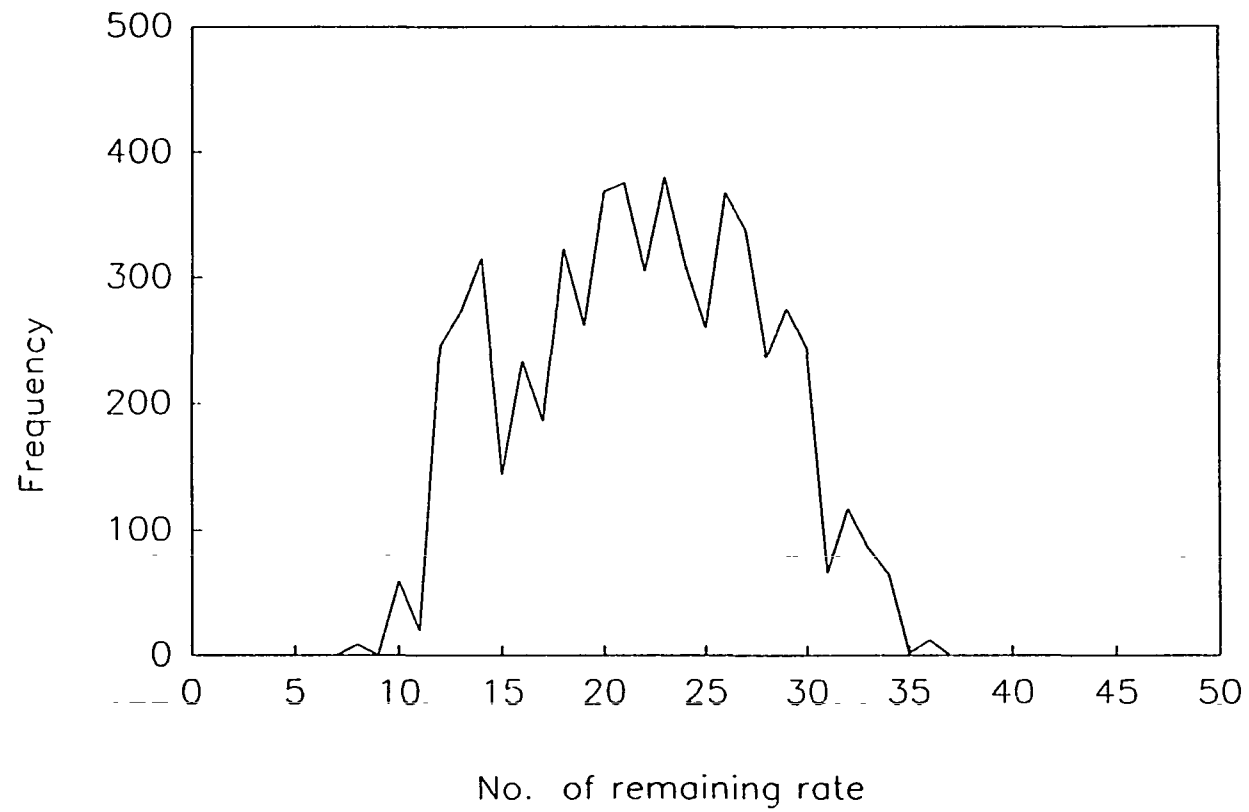


Figure 67. The plot of frequency vs. remaining rate terms after combining 3 species.

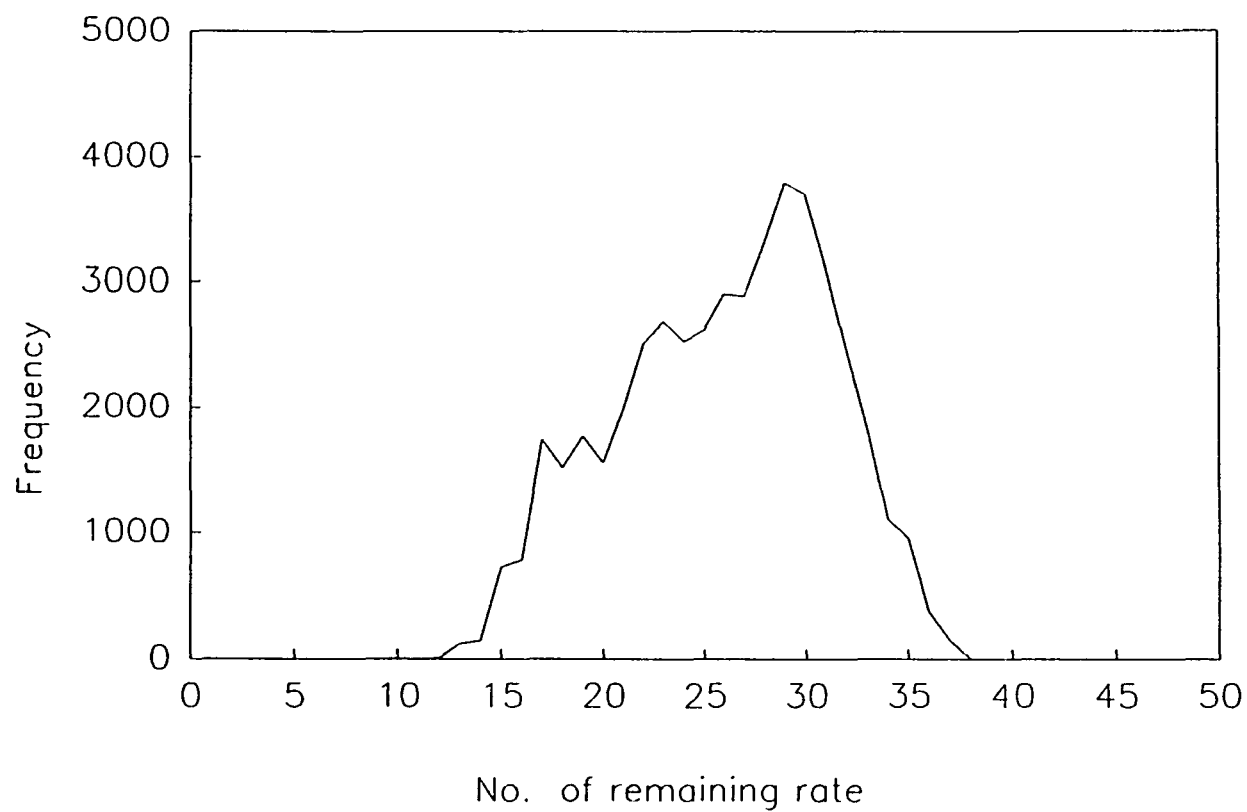


Figure 68. The plot of frequency vs. remaining rate terms after combining 4 species.

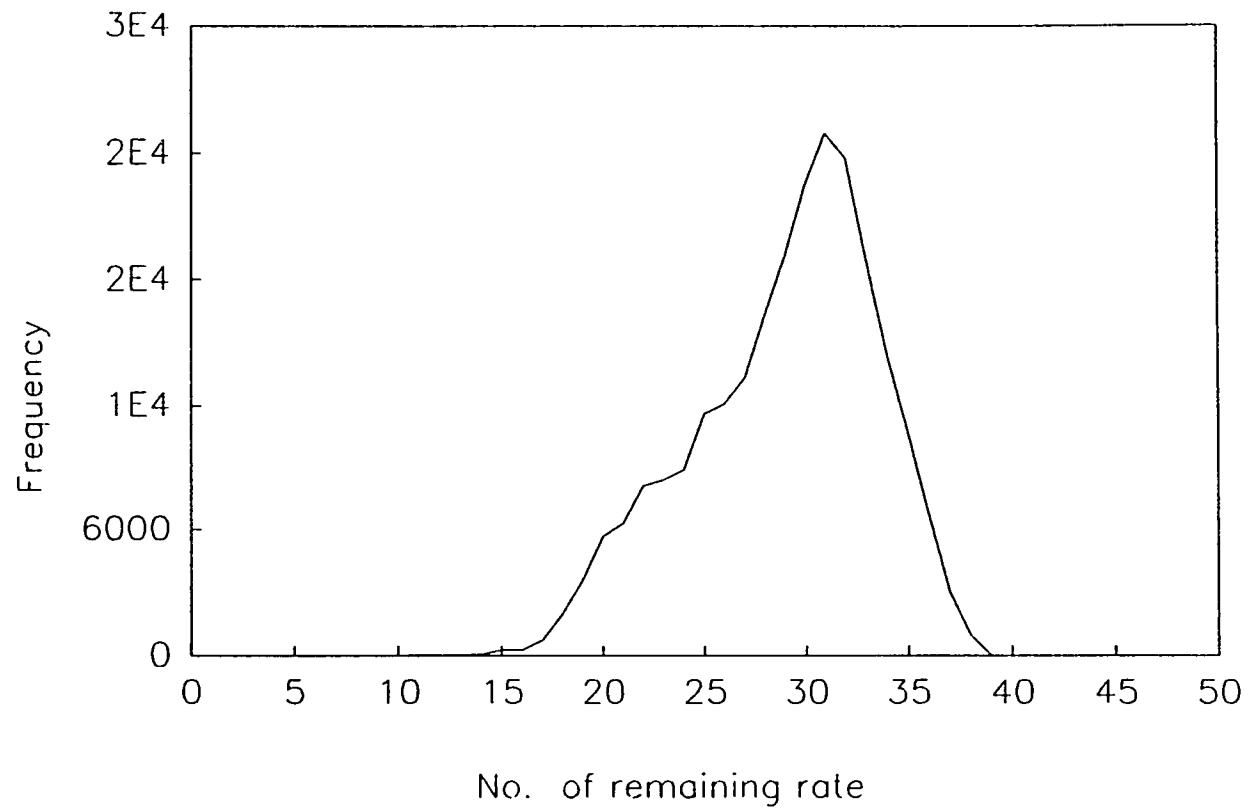


Figure 69. The plot of frequency vs. remaining rate terms after combining 5 species.

SSEGENTB

Introduction

This program is designed to create a table providing the primary information for generation of steady state equations implemented in the SSEGEN program. The chemical system used for this example is listed in Table XXV. All Data generated by the program SSEGENTB are listed in Table XXX. First part of table is the list of rate of reaction while the second part illustrated the matrix of rate coefficients (axb). The a represents the number of species and b represents the number of reactions (total number of reaction is 12). Since the m (third molecule in the reaction) is kept a constant, all values of the last row for m are zero. Take first species (Cl_2) as an example, i.e.,

$$d[\text{Cl}_2]/dt = -R_1 + R_3 + R_{11}$$

It corresponds to -1,0,1,0,0,0,0,0,0,0,1,0

The third part of table is the list of rate constants of the reaction mechanism and the last is the list of concentrations of species at the specified time.

TABLE XXX

DATA TABLE GENERATED BY SSEGENTB

12/8/mech. file=chlor.sse,data file=chlor.dat/
time picked=2300
(no. of reaction/ no. of species/ source files/ time)
cl2 o3 o2 cl clo
oclo o m (species code)
R1 /12.36820e+11/cl2 (rxn no./value of rate/
R2 /41.48610e+11/cl+o3 reaction code)
R3 /10.50810e+11/clo+clo
R4 /72.62270e+10/clo+clo
R5 /35.02700e+10/clo+clo
R6 /89.40050e+09/oclo
R7 /77.25770e+09/o3
R8 /29.45400e+10/cl+oclo
R9 /40.40750e-02/o+o2+m
R10 /13.56740e-02/o+o3
R11 /20.19900e+10/clo+clo+m
R12 /16.70900e+10/o+clo

| R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 | R9 | R10 | R11 | R12 | |
|----|----|----|----|----|----|----|----|----|-----|-----|-----|------|
| -1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | cl2 |
| 0 | -1 | 0 | 0 | 0 | 0 | -1 | 0 | 1 | -1 | 0 | 0 | o3 |
| 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | -1 | 2 | 1 | 1 | o2 |
| 2 | -1 | 0 | 2 | 1 | 0 | 0 | -1 | 0 | 0 | 0 | 1 | cl |
| 0 | 1 | -2 | -2 | -2 | 1 | 0 | 2 | 0 | 0 | -2 | -1 | clo |
| 0 | 0 | 0 | 0 | 1 | -1 | 0 | -1 | 0 | 0 | 0 | 0 | oclo |
| 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | -1 | -1 | 0 | -1 | o |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | m |

| | | | | |
|------------|------------|-----------------|------------|------------|
| 1.0000e-03 | 1.2000e-11 | 4.5000e-15 | 3.1100e-15 | 1.5000e-15 |
| 1.0000e-02 | 1.2500e-04 | 5.8900e-11 | 5.6800e-34 | 7.9500e-15 |
| 3.4600e-35 | 3.9600e-01 | (rate constant) | | |

| | | | | |
|------------|------------|------------|------------|------------|
| 1.2368e+15 | 6.1595e+14 | 1.0341e+15 | 5.6119e+08 | 1.5282e+13 |
| 8.9232e+12 | 2.7540e-02 | 2.5000e+19 | | |

There are four tables generated as shown in the above boxes, and SSEGN (for details see below) will use this information to generate SSE equations of your choice.

SSEGN

Introduction

The program SSEGN is a steady-state equation generator. Some external information is required before one can run this program, such as a data table generated via SSEGNTB. The following are examples of the SS table and SS equation :

TABLE XXXI

DATA TABLE GENERATED BY SSEGN

| SPECIES = cl ; # OF REACTION = 6 | | | | | | | |
|--|-----------|-----|---------|------------|---------------|------|------|
| COMMENTS : take [cl] only | | | | | | | |
| coef. | inst.rate | rxn | code | contrib. | cum. contrib. | i% | c% |
| -1 | 4.149e+12 | R2 | cl+o3 | -4.149e+12 | -4.148e+12 | 1406 | **** |
| 2 | 1.237e+12 | R1 | cl2 | 2.474e+12 | -1.675e+12 | -56 | **** |
| 2 | 7.262e+11 | R4 | clo+clo | 1.452e+12 | -2.222e+11 | -33 | -37 |
| 1 | 3.503e+11 | R5 | clo+clo | 3.503e+11 | 1.281e+11 | -8 | -5 |
| -1 | 2.945e+11 | R8 | cl+oclo | -2.945e+11 | -1.665e+11 | 7 | 3 |
| 1 | 1.671e+11 | R12 | o+clo | 1.671e+11 | 6.080e+08 | -4 | -4 |
| deviation = net rate ÷ sum of production = | | | | 6.84152e-5 | | | |

note: This table shows cl species involved in six reactions (1,2,4,5,8,12).

Interpretation

- First line shows the chosen species (cl) and the number of rate terms which determine it.
- Second line is for comments only.

- Third line - description of columns.

coef.= rate contribution coefficient (1,2 with plus or minus sign).

inst. rate = value of individual instantaneous rate.

rxn = reaction number (R1 etc.).

rxn code=reaction code. (i.e., cl+o3-->product)

contrib.= coef. multiplied by ind. value.

cum. contrib.= cumulative sum of net values starting from first reaction.

$$\frac{([Cl]_{\text{without given reaction}} - [Cl]_{ss})}{[Cl]_{ss}} \times 100 \%$$

c% = cumulative sum of i% starting from last reaction

The steady state concentration is calculated by applying the steady state assumption and counting all involved reactions. An example will show how the values of i% or c% are calculated. In general, the dropping of rate contributions starts with the smallest one. Therefore, if the last row (R12) is dropped, (i.e., assuming an insignificant contribution from reaction 12 to [cl]), the calculated concentration of cl will deviate by -4% compared to the steady state concentration. The negative sign indicates [cl] after dropping R12 is about 4% less than the SS conc. Similarly, the dropping of R8 alone will cause 7% deviation and so on. The cumulative error is of greater interest and is given in the 8th column under ac% in Table XXVII. The easy way to view the c% is to add each i% to

previous c% starting from the bottom of the list (for instance, $3 = -4 + 7$, $-5 = 3 - 8$). Due to roundoff of displayed numeric values, 1% error may result (for instance, $-38 = -5 - 33$, but the display is the correct values, -37). Thus c% gives the error in the steady state expression for c1 resulting from omission of progressively small terms.

The last line shows the value of SSR which is defined as the ratio of sum of individual rate divided by the sum of production term for specific species (in this case, for c1); the smaller of the value, the smaller the deviation. In this case, there is no doubt of the validity of SSA.

After screening the data table and using Function key 7, the steady state equation will be generated for chlorine radical as :

STEADY-STATE EQUATION

TABLE XXXII

SS EQUATION GENERATED BY SSEGEN

| |
|--|
| $[c1] = \frac{2[c1^2] + 2[cl + clo] + 1[clo + clo] + 1[o + clo]}{1[o3] + 1[oclo]}$ |
| APPROX. CONCENTRATION OF [c1] = 5.613e+08 MODEL CONCENTRATION OF [c1] = 5.612e+08 PERCENT RELATIVE ERROR = 1.184e-02 |

The approx. conc. based on the above steady state equation is calculated for comparison with the value calculated from

the model.

2[cl2] means two times the rate of photolysis of chlorine,
i.e., $\text{cl}_2 \rightarrow \text{cl} + \text{cl}$. the percent relative error is
defined as $(\text{approx.} - \text{model}) / (\text{model})$

Once the steady state equation has been established under
certain conditions within the error tolerance, a sensitivity
analysis of the equation is useful for practical application

SENSITIVITY ANALYSIS OF SS EQUATION (SSESA)

Introduction

This program is designed to calculate the uncertainty
caused by the deviation of measured variables. The general
form of uncertainty is defined as :

$$\text{Uncertainty} \quad s = \sqrt{\sum \left(\frac{\partial f}{\partial i} \right)^2 (\delta i)^2}$$

where f is an arbitrary function, such as a steady state
expression, and (df/di) is the partial derivative of f with
respect to i and is the Jacobian derivative; δ_i is deviation
of the measured variable. If variables i & j are mutually
dependent, then covariance caused by variables of i & j should
be considered and the calculation of covariance can be
implemented via Function key 9 in the program SSESA.

$$\text{covariance} = 2 \left(\frac{\partial f}{\partial i} \right) \left(\frac{\partial f}{\partial j} \right) \delta i \delta j$$

The weight of uncertainty in terms of each variable is defined as the ratio of the square of the individual uncertainty term to the square of the total uncertainty, multiplied by 100.

$$weight = \frac{(\frac{\partial f}{\partial i})^2 (\delta i)^2}{s_k^2} \times 100$$

EQUATION SYNTAX SSESA PROGRAM

It is essential to calculate the Jacobian derivatives prior to computation of the sensitivity analysis. There are two ways to get the Jacobian derivative. First, the Jacobian derivatives generated by the program SOLVER-Q (which is a numerical analysis & equation handling computer program, developed by Professor Fernando L. Alvarado, University of Wisconsin-Madison, College of Engineering), can be used for the input of the SSESA program. Secondly, if SOLVER-Q is not available, an alternative way to create the input file for the SSESA program is to type the original equation and all Jacobian derivatives (calculated by hand) separated by a semicolon (see example).

In order to take the derivatives resulting from SOLVER-Q, most rules required by SOLVER-Q are followed:

- All variable names must start with a lower-case

letter.

- All names of functions must be entirely upper-case.
- Variable names must not contain numbers.

The following functions are recognized by the program :

TABLE XXXIII
SYNTAX OF SSES

| | | | | | |
|---|--|--------|------------------|-----|-----------------|
| + | addition, | - | subtraction, | * | multiplication |
| / | division, | ^ | exponentiation | . | decimal point |
| E | power of ten (1E2=1x10 ²) | EXP | (EXP(x)) | LN | LN(x)=loge(x) |
| SQUARE | (x)=x ² , | SQRT | (x)=√, | INV | INV(x)=1/x |
| ABS | (x)= x , | | parenthesis () | | |
| LOG | (x)=log10(x), | COS | (x)=COS(radian), | SIN | (x)=SIN(radian) |
| TAN | (x)=TAN(radian), | ARCTAN | (x)=arctan(x) | | |
| all angles are calculated in radians, not degrees | | | | | |

Some useful hints should be pointed out here

- Characters not allowable for parts of input are
[], { }, & , % , \$, # , @ , ! , ~ , ? , < , > , \ , ` , | , ' , :
- The semicolon ; should be the last character of each equation.
- if the length of equation is too long, it can be written as two lines delimited by ;
- if the set of equations is not obtained from SOLVER-Q, then the order of equations should be followed as
first equ. -- original equation

second equ. - derivative equation and so on.

(see example)

The following are the examples and data generated by this program. Taking the equation (6-2)

$$[HO_2] = \sqrt{\frac{J_7[h\nu][H_2O_2] + J_1[h\nu]q[O_3]}{k_{10}}}$$

one codes it into the following form

$$\text{SQRT}((\text{hvjf}*\text{hhoo}+\text{oz}*q*\text{hvjo})/\text{kz})$$

where hvjf= $J_7[h\nu]$, hhoo= $[H_2O_2]$, hvjo= $J_1[h\nu]$, oz= $[O_3]$,

$$\text{kz}=k_{10}.$$

The following examples demonstrates two allowable input data files; one is generated by SOLVER-Q type (Table XXXIV), the other is the regular type (Table XXXV). However, both give the same results. The difference of regular type from SOLVER-Q is input equation format only.

TABLE XXXIV

SOLVER-Q FORMAT FOR SSES

```

{Original Equations:
SQRT((hvjf*hhoo+oz*q*hvjo)/kz);
Jacobian Terms: }
{d(eqn1)/d(kz)=}
(-(hvjf*hhoo+oz*q*hvjo))/SQUARE(kz)*INV(SQRT((hvjf*
hhoo+oz*q*hvjo)/kz))*0.5;
{d(eqn1)/d(hvjo)=}
oz*q*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)
/kz))*0.5;
{d(eqn1)/d(q)=}
oz*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)
/kz))*0.5;
{d(eqn1)/d(oz)=}
q*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)
/kz))*0.5;
{d(eqn1)/d(hhoo)=}
hvjf*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)
/kz))*0.5;
{d(eqn1)/d(hvjf)=}
hhoo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)
/kz))*0.5;

```

TABLE XXXV

REGULAR FORMAT FOR SSES

```

SQRT((hvjf*hhoo+oz*q*hvjo)/kz);
(-(hvjf*hhoo+oz*q*hvjo))/SQUARE(kz)*INV(SQRT((hvjf*hhoo+
oz*q*hvjo)/kz))*0.5;
oz*q*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5;
oz*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5;
q*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5;
hvjf*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5;
hhoo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5;

```

Next, the deviation value (i.e., δ_i) for each variable involved in the steady state equation should be input either from file or keyboard.

The following example is the format of disk input

TABLE XXXVI
FILE INPUT OF DEVIATION VALUES

| |
|----------------|
| hhoo=2.5e10,10 |
| hvjf=7.6e-6,50 |
| hvjo=8.8e-6,50 |
| q=7.6e-2,10 |
| oz=6e11,10 |
| kz=4.7e-12,30 |

Syntax : variable code=numeric value,deviation (%).
Two formats are allowable for input deviation
(i.e., numerical values or percentage(%));
This is an example of percentage.

INTERPRETATION OF WEIGHT OF UNCERTAINTIES

From Table XXXVII, a change in q (or oz) of 10% would produce the same change in the value of $[H_2O_2]$ as a 50% change in $hvjo$. That is, q , oz and $hvjo$ play same weights (24.57%) in controlling the value of $[H_2O_2]$. And, comparing oz with $hhoo$, the ratio of relative sensitivities is $(0.03/24.57)^{1/2}$ or about 0.03. That is, a change in $hhoo$ of 10% would produce only about 3 % as much change in final value of $[H_2O_2]$ as a 10% change in oz . The best and easy way to learn and understand the concepts described in this appendix is to practice the programs.

TABLE XXXVII

DATA FILE GENERATED BY SSES

```

Equation :
SQRT((hvjf*hhoo+oz*q*hvjo)/kz)
Variables :
    hvjf    hhoo    oz    q    hvjo    kz
The value of variables :
1.000e+00 2.000e+00 3.000e+00 4.000e+00 5.000e+00 6.000e+00
The value of deviation :
1.000e-01 2.000e-01 3.000e-01 4.000e-01 5.000e-01 6.000e-01
jacobian derivative with respect to [kz] :
==>
(-(hvjf*hhoo+oz*q*hvjo))/SQUARE(kz)*INV(SQRT((hvjf*hhoo+
oz*q*hvjo)/kz))*0.5
jacobian derivative with respect to [hvjo] :
oz*q*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))*0.5
jacobian derivative with respect to [q] :
oz*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5
jacobian derivative with respect to [oz] :
q*hvjo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))
*0.5
jacobian derivative with respect to [hhoo] :
hvjf*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))*0.5
jacobian derivative with respect to [hvjf] :
hhoo*kz/SQUARE(kz)*INV(SQRT((hvjf*hhoo+oz*q*hvjo)/kz))*0.5

== uncertainty s = ( Σ(df/di)*δi )^ 1/2 ==

(df/di)* :
7.176e-02 9.677e-02 1.512e-01 2.688e-01 6.720e-04 2.688e-03
(df/di)*δi* :
2.583e-02 2.419e-02 2.419e-02 2.419e-02 2.688e-05 2.688e-05
Σ (df/di)*δi* = 9.84681e-2
Uncertainty s = .313796
=== Weight of uncertainty in term of each variable ===
    kz    -----> 26.24 %
    hvjo    -----> 24.57 %
    q    -----> 24.57 %
    oz    -----> 24.57 %
    hhoo    -----> .03 %
    hvjf    -----> .03 %

```

TABLE XXXVIII
SIMPLE CHEMICAL SYSTEM

| | | | | | | |
|--------------------------------|-----------|-----------|-----------|-----------|-----------|----|
| 11 | | | | | | |
| *simple reaction* | | | | | | |
| 1NO | O3 | 1.00NO2 | | 1.500e+01 | | 0. |
| 2NO2 | HV | 1.00NO | 1.00O3 | 1.600e-01 | | 0. |
| 3O3 | HV | 2 | HO | 9.400e-06 | | 0. |
| 4CO | HO | 1.00HO2 | | 4.500e+02 | | 0. |
| 5HO2 | NO | 1.00NO2 | 1.00HO | 1.200e+04 | | 0. |
| 6HO | NO2 | 1.00HNO3 | | 1.800e+04 | | 0. |
| 7S | | 1.00O3 | | 3.000e-07 | | 0. |
| 8S | | 1.00CO | | 7.000e-07 | | 0. |
| 9NOX | | 1.00NO | 1.00NOX | 1.000e+00 | | 0. |
| 10NOX | E | 2 | NOX | 5.000e+00 | | 0. |
| 11HO | HO2 | 1.00P1 | | 4.400e-02 | | 0. |
| INITIAL CONCENTRATION | | | | | | |
| 6 | | 1.000e+05 | 1.000e+05 | | | |
| S | HV | NOX | E | O3 | CO | |
| 1.000e+00 | 1.000e+00 | 1.000e-07 | 1.905e-08 | 5.000e-02 | 1.000e-01 | |
| *comment* | | | | | | |
| | | 1.000e+07 | 3.000e+02 | 1.000e+01 | 1.000e+02 | |
| HALT | | | | | | |
| !CONST/S/HV/E | | | | | | |
| !SSE/HO/NO/NO2/HO2/O3/CO | | | | | | |
| !PLOT/HO/NO/NO2/HO2/O3/CO/HNO3 | | | | | | |

Application of SSECOM

Here is an example to illustrate the usefulness of the SSECOM program. We start to take the simple chemical system listed in the Table XXXVIII. The purpose here is to seek the relationship of individual rates in terms of sources and sink rates. According to the given mechanism, R7, R8 & R9 represent the only source reaction and R6 is the only sink reaction, because HNO_3 is the only product that is not a reactant.

The first try is via the traditional approach. We have to build the differential form for the changes of individual

species concentrations with time :

$$d[\text{HO}]/dt = 2R_3 - R_4 + R_5 - R_6 - R_{11}$$

$$d[\text{HO}_2]/dt = R_4 - R_5 - R_{11}$$

$$d[\text{NO}]/dt = -R_1 + R_2 - R_5 + R_9$$

$$d[\text{NO}_2]/dt = R_1 - R_2 + R_5 - R_6$$

$$d[\text{O}_3]/dt = -R_1 + R_2 - R_3 + R_7$$

$$d[\text{NO}_x]/dt = -R_6 + R_9 + R_{10}$$

$$d[\text{HNO}_3]/dt = R_6$$

$$d[\text{HO}_x]/dt = 2R_3 - R_6 - 2R_{11}$$

$$d([\text{O}_3] - [\text{NO}])/dt = R_3 + R_9 - R_5 - R_7$$

In Table XXXV, the matrix summarizes relationships between reaction and species. The table allows us to investigate the inherent cancellation in a given mechanism.

TABLE XXXIX
THE ELEMENTS OF MATRIX

| rxn. # | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|----------------------|----|----|----|----|----|----|----|----|----|----|----|
| NO | -1 | +1 | | | -1 | | | | +1 | | |
| O ₃ | -1 | +1 | -1 | | | | +1 | | | | |
| NO ₂ | +1 | -1 | | | +1 | -1 | | | | | |
| HO | | | +2 | -1 | +1 | -1 | | | | | -1 |
| HO ₂ | | | | +1 | -1 | | | | | | -1 |
| CO | | | | -1 | | | | +1 | | | |
| (O ₃ -NO) | | | -1 | | +1 | | +1 | | -1 | | |
| HO _x | | | +2 | | | -1 | | | | | -2 |
| NO _x | | | | | | -1 | | | +1 | +1 | |
| HNO ₃ | | | | | | +1 | | | | | |

Through Table XXXIX, it is clear that the following possible steady state relationships can be established with no

further work.

$$\text{NO} \rightarrow \text{R2} + \text{R9} = \text{R1} + \text{R5}$$

$$\text{NO}_2 \rightarrow \text{R1} + \text{R5} = \text{R2} + \text{R6}$$

$$\text{O}_3 \rightarrow \text{R2} + \text{R7} = \text{R1} + \text{R3}$$

$$\text{HO} \rightarrow 2\text{R3} + \text{R5} = \text{R4} + \text{R6} + \text{R11}$$

$$\text{HO}_2 \rightarrow \text{R4} = \text{R5} + \text{R11}$$

$$\text{CO} \rightarrow \text{R8} = \text{R4}$$

Additional steady state expressions are obtained from algebraic sums of the equations for the above species, such as $\text{HO} + \text{HO}_2$, $\text{NO} + \text{NO}_2$ and $\text{O}_3 - \text{NO}$, as well as algebraic rearrangements.

$$\text{R6} = \text{R9}; \quad (\text{C-1})$$

$$\text{R4} = \text{R8} \quad (\text{C-2})$$

$$\text{R11} = \text{R4} - \text{R5} \quad (\text{C-3})$$

$$\text{R7} + \text{R5} = \text{R3} + \text{R9} \Rightarrow \text{R5} = \text{R3} + \text{R9} - \text{R7} \quad (\text{C-4})$$

$$2\text{R3} = \text{R6} + 2\text{R11} \Rightarrow \text{R11} = \text{R3} - \text{R9}/2 \quad (\text{C-5})$$

Substituting Eqn. C-4 into Eqn. C-3, the equation C-6 is formed by eliminating R5

$$\text{R11} = \text{R4} - \text{R3} - \text{R9} + \text{R7} \quad (\text{C-6})$$

Comparison of Eqns. C-5 & C-6 leads to

$$2\text{R3} = \text{R4} - \text{R9}/2 + \text{R7} = \text{R7} + \text{R8} - \text{R9}/2 \quad \text{or}$$

$$\text{R3} = \text{R7}/2 + \text{R8}/2 - \text{R9}/4 \quad (\text{C-7})$$

Substituting of Eqn. C-7 into C-4,

$$\text{R5} = -\text{R7}/2 + \text{R8}/2 - 3\text{R9}/4 \quad (\text{C-8})$$

Since R3 in Eqn. C-7 is in terms of source and sink rates, equation C-5 now becomes

$$\begin{aligned}
 R_{11} &= R_7/2 + R_8/2 - R_9/4 - R_9/2 \\
 &= R_7/2 + R_8/2 - 3R_9/4
 \end{aligned}
 \tag{C-9}$$

Up to this point, we have derived each reaction except R1 & R2 in terms of source rates of CO, O₃ & NO_x, by inspection and algebraic manipulation.

Now we describe the automatic procedures and results of the SSECOM program. First of all, it is essential to input the original mechanism through Function key 1. After the information has been read and converted to useful data for later use, the choice of specific species codes can be done via pressing Function key 3. Then, the algebraic combinations can be initialized by invoking Function key 4. Here is a sample of data format created from the above mechanism. In this case, species codes are equivalent to 1=NO, 2=O₃, 3=NO₂, 4=HV, 5=HO, 6=CO, 7=HO₂, 8=HNO₃, 9=S, 10=NO_x, 11=E, 12=Pl.

```

(1)**1&2/# OF RATES =6 *reduced by*
(2)**(2)1&(1)2/# OF RATES =6 *reduced by*
(3)**(1)1&(2)2/# OF RATES =6 *reduced by*
(4)**-1&2/# OF RATE =4 *reduced by*
(5)**(2)-1&(1)2/# OF RATES =6 *reduced by*
(6)**(1)-1&(2)2/# OF RATES =6 *reduced by*
(7)**1&-2/# OF RATES =4 *reduced by*
(8)**(2)1&(1)-2/# OF RATES =6 *reduced by*
(9)**(1)1&(2)-2/# OF RATES =6 *reduced by*

```

Explanations

- The first number in parenthesis is the iteration number
- The symbol {-} in front of the number means a change of sign of all rates for the specified species' code.
- Double ** is used for separation. The number in

parenthesis represents the multiplying factor and the number without parenthesis represents the species' code; the symbol of {&} means {combine}.

- {# of rates = 6} represents the net number of rates left after combination. (via subtraction, cancellation and reduction).
- {reduced by *} means the existing relationships can be eliminated to make even simpler form (see below).
- For example, see iteration (9) :
 namely, combine species 1 (one), species 2 (twice and change sign), and obtain the net number of rates equal to 6. Assuming the six rates are R1, -R3, R6, R8, R9, R10 and the correlation among rates R3, R6 & R9 is known as $R3=R6+R9$ (or $-R3+R6+R9=0$), thus, the outcome of SSECOM of this iteration will become

$$(9)**(1)1\&(2)-2/\# \text{ OF RATES } =3 \text{ *reduced by R3,R6,R9*}$$
- Based on the stored data, it can be decided whether it is worthwhile to generate further equations.

The program SSECOM not only creates the information of combination, but also provides the ability to generate the desired equations. Through Function key 9, you will be allowed to view the specified stored data by selecting the number of terms and to rearrange the equation by input of selected rate codes. The screen display can be dumped by pressing "P".

In order to achieve the correlation of individual rate with sources & sink rates, the desired source rates R7, R8 &

R9 should be selected as independent variables and kept in the same side. The equation will be created and displayed along with the information of combination.

```
(10)**1&3/# OF RATE =2 *reduced by*
Equ. --> (1)R6 = (1)R9
(127)**6&7/# OF RATE =3 *reduced by*
Equ. --> (1)R5+(1)R11 = (1)R8
(4)**-1&2/# OF RATE =4 *reduced by*
Equ. --> (1)R3+(-1)R5 = (1)R7+(-1)R9
(7)**1&-2/# OF RATE =4 *reduced by*
Equ. --> (-1)R3+(1)R5 = (-1)R7+(1)R9
(46)**2&3/# OF RATE =4 *reduced by*
Equ. --> (1)R3+(-1)R5+(1)R6 = (1)R7
(128)**(2)6&(1)7/# OF RATE =4 *reduced by*
Equ. --> (1)R4+(1)R5+(1)R11 = (2)R8
```

It is obvious that the equality of rate 6s and 9 results (see equation C-1) from to the combination of species 1 & 3 (NO & NO_2) shown in iteration 10 above. It reveals that the source of NO_2 is balanced by the sink. In addition, comparing the iteration 127 and 128, i.e., substitution of $(1)R5+(1)R11=(1)R8$ into $(1)R4+(1)R5+(1)R11=(2)R8$, it ends up $R4=R8$ after cancellation. Although this equality is already known via examining species CO (see equation C-2), it demonstrates that the program SSECOM is capable to abstract the inherent relationships within the system. Now, due to the discovery of $R4=R8$ & $R6=R9$, we can treat either R4 or R6 as an equivalent independent variable. Taking this advantage, some useful information can be easily obtained, such as:

```
R5+R11 = R8           combining species 6(CO) & 7(HO2)
R3-R5 = R7-R9         combining species 1(NO) (change sign) &
                        3(NO2).
2R3+R5-R11 = R8+R9    combining species 5(HO) & 6(CO)
```

Then, three rates (R3, R5 & R11) can be obtained through the three equations depicted above. The answers are

$$4R3 = 2R7+2R8-R9 \quad \text{equivalent to equation C-7.}$$

$$4R5 = -2R7+2R8+3R9 \quad \text{equivalent to equation C-8.}$$

$$4R11 = 2R7+2R8-3R9 \quad \text{equivalent to equation C-9.}$$

With respect to R1 & R2, the equation of $2R1-2R2 = 2R9-2R5$ can be obtained through combining species 1(NO) and reverse species 3($-\text{NO}_2$). After substituting R5, the equation becomes

$$R1-R2 = R7/2-R8/2+R9/4 \quad (\text{C-10})$$

Look at the calculations above which are all based on the results by combining two species only. Different combinations may produce same results. Now, by combining more than two species at one time, the existing relationships will be more easily revealed.

For instance, assuming R6 ($R6=R9$), R7, R8, R9 are known and treating all as independent variables, then, the outcome of combination of species NO(1), NO_2 (3) & CO(6) shows that R4 is equal to R8. Different combinations of species 1, 3 & 6 lead to the same results. Since the connection of rate 4 to a source rate has been found (i.e., $R4=R8$), the group of source rates now includes R4, R6 (due to $R6=R9$), R7, R8, R9. The remaining work to be done is to find the relationship in terms of source and sink for R3, R5, R11 & R1-R2. Through the combination of species 2+3-5, the outcome is obtained as equation (C-11).

$$3R3-R11 = R4+R7 \quad (C-11)$$

Similarly, the combinations of species $-5+(2)6+7$ and $-1+(2)2+3$ will end up equations C-12 and C-13, respectively.

$$2R3+2R5 = R6+2R8 \quad (C-12)$$

$$2R3-2R5 = -R6+2R7-R9 \quad (C-13)$$

It is clear that rate $R3$ & $R5$ can be easily figured out by adding, subtracting equations (C-12) and (C-13). Consequently, two equations similar to equations (C-7) & (C-8) will result. Then the equation for $R11$ can be obtained by substituting $R3$ into equation (C-11). Finally, the equation for $R1-R2$ will be found via combining species $NO-CO-HO_2$. In summary, the program SSECOM has found four useful combinations demonstrating the inherent relationships present in the data.

Since $R1$ & $R2$ can't be separated, it is necessary to consider both simultaneously. we have found that $R1-R2$ is exactly equivalent to photostationary state (PSS). The equation (C-10) goes to show that as long as the photostationary state holds, the following equation is true.

$$R9 = 2(R8 - R7) \quad (C-14)$$

APPENDIX D

EIGENVALUE IN KINETIC SYSTEM

The kinetic system can be treated as the system of ordinary differential equations and solved by the use of matrix and vector methods. For example, the system

$$\begin{aligned} \dot{x}_1 &= x_1 + x_2 \\ \dot{x}_2 &= 4x_1 + x_2 \end{aligned} \quad (D-1)$$

and rewritten as a single vector equation

$$\dot{X} = A X$$

where X is a vector and A is the matrix

$$\begin{aligned} X &= \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \\ A &= \begin{bmatrix} 1 & 1 \\ 4 & 1 \end{bmatrix} \\ \dot{X} &= \begin{bmatrix} 1 & 1 \\ 4 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \\ &= AX \end{aligned}$$

To seek the solution for the system, the concept of eigenvector and eigenvalue has introduced, namely, suggesting $x_i = e^{\lambda_i t} v_i$ as a solution for the system, where vector v_i ($v_i \neq 0$) is known as an eigenvector of the matrix A and the corresponding value of λ_i is called an eigenvalue of the matrix A .

Substituting $x_i = e^{\lambda_i t} v_i$, $dx_i/dt = \lambda_i e^{\lambda_i t} v_i$ into the system gives

$$\begin{aligned} \dot{X} &= AX \\ \lambda_i e^{\lambda_i t} v_i &= A e^{\lambda_i t} v_i \\ \text{i.e. } Av_i &= \lambda_i v_i \end{aligned}$$

Consequently, the system can be stated in the form of an eigenvalue-eigenvector equation.

$$AV = \lambda V$$

where $V = [v_1, v_2, \dots]^{-1}$ and $\lambda = [\lambda_1, \lambda_2, \dots]^{-1}$

To obtain eigenvalues and eigenvectors for any system, we rewrite

$$(A - \lambda I)V = 0$$

where I is the unit matrix of appropriate size.

Taking the example D-1 and writing the equation in the form

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ 4 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$$

$$A - \lambda I = \begin{bmatrix} 1-\lambda & 1 \\ 4 & 1-\lambda \end{bmatrix}$$

$$A - \lambda I = (1-\lambda)^2 - 4 = \lambda^2 - 2\lambda - 3 = 0 \quad (D-2)$$

from equation D-2, the eigenvalues are $\lambda_1 = -1$, $\lambda_2 = 3$.

For $\lambda_1 = -1$, we calculate corresponding eigenvector v_1

$$\begin{bmatrix} 1-\lambda & 1 \\ 4 & 1-\lambda \end{bmatrix} = \begin{bmatrix} 2 & 1 \\ 4 & 2 \end{bmatrix} v_1 = 0$$

v_1 can be obtained by writing $v_1 = [p_1, q_1]^{-1}$ and finding a non-trivial solution of the two equation in p_1 and q_1 . In this case, $p_1 = 1$ and $q_1 = -2$, Note that there is no unique eigenvector corresponding to $\lambda_1 = -1$, therefore a constant (c_1) should be included, i.e, $v_1 = c_1[1, -2]^{-1}$. Similarly, for $\lambda_2=3$, $v_2 = c_2[1, 2]^{-1}$. Therefore

$$x_1 = c_1 e^{-t} \begin{bmatrix} 1 \\ -2 \end{bmatrix}, \quad x_2 = c_2 e^{3t} \begin{bmatrix} 1 \\ 2 \end{bmatrix}$$

Thus the two solutions form a set of solutions and the general solution of the system is given by

$$x = c_1 e^{-t} \begin{bmatrix} 1 \\ -2 \end{bmatrix} + c_2 e^{3t} \begin{bmatrix} 1 \\ 2 \end{bmatrix}$$

Overall, the difference of two eigenvalues of -1 and 3 in this simple cases is not quite large, i.e, $|-1| / |3| = 0.33$, there is no stiffness problem in the system at all.

Considering a simple kinetic reaction in the form of differential equation $dx/dt = -L[x]$, the solution is $x = e^{-Lt}[x_0]$, where $[x_0]$ represents the initial concentration. Here $|-L|$ is equivalent to the eigenvalue.