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AN ABSTRACT OF THE THESIS OF

Patricia Diane Weeks for the M.S. in Chemistry
(Name) (Degree) (Major)

Date thesis is presented: May 19, 1970.

Title: THE CHEMISTRY OF TRIFLUOROTHIOACETIC ACID

Abstract approved:
(Major Professor)

Addition reactions of perfluorothiolacetic acid (TFTAA) with organic and inorganic substrates were studied and six new compounds containing the trifluoroacetyl group have been prepared. Two types of reactions were observed, free radical and nucleophilic addition. Under the influence of ultraviolet light, TFTAA (CF_3COSH) adds to olefins to form 1:1 adducts. The $\text{CF}_3\text{COS}\cdot$ radical appears to be the adding species. Three new olefin adducts were prepared: $\text{CF}_3\text{COSCFHCF}_2\text{H}$, $\text{CF}_3\text{COSCH}_2\text{CF}_2\text{H}$, and $\text{CF}_3\text{COSCH}_2\text{CFH}_2$. In addition, this was found to be a new way to prepare $\text{CF}_3\text{COSCH}_2\text{CH}_3$, which had been previously prepared by another route¹. Physical constants, analytical data, infrared, ultraviolet,

¹ M. Hauptschein, C. S. Stokes, and E. A. Nodiff, J. Am. Chem. Soc. 74, 4005 (1952).

nmr and mass spectra are presented supporting the proposed structures for these compounds.

Nucleophilic addition adducts were formed with TFTAA and some organic and inorganic materials. TFTAA is a strong acid and the CF_3COS^- ion was found to act as a nucleophile with several substrates. With hexafluoroacetone, addition of TFTAA across the carbonyl gave $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$. This structure is supported by analytical data, gas chromatographic data, infrared, ultraviolet, nmr, and mass spectra. Ethylene oxide and TFTAA react to produce the alcohol addition product, $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}$, which is supported by analytical data, nmr infrared, and mass spectra. Sulfur trioxide was studied as a representative inorganic molecule. TFTAA adds to this Lewis acid to form the sulfonate, $(\text{CF}_3\text{COS})_2\text{SO}_2$. Analytical data, infrared, ultraviolet, nmr and mass spectra are reported here.

All of the reactions, except the free radical reactions, occurred spontaneously and exothermically upon mixing the two reactants.

A new method of preparing CF_3COSH , by reacting KSH with $(\text{CF}_3\text{CO})_2\text{O}$, is also presented.

THE CHEMISTRY OF TRIFLUOROTHIOACETIC ACID

by

PATRICIA DIANE WEEKS

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

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in

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1970

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May 19, 1970

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I. INTRODUCTION

Trifluorothiolacetic acid (TFTAA) was first prepared in 1960 by W. A. Sheppard and E. L. Muetterties by reacting trifluoroacetic anhydride, $(\text{CF}_3\text{CO})_2\text{O}$ and H_2S at 200°C with a 45% yield.¹ These conditions are much more drastic than those needed for the hydrocarbon analogs. TFTAA is a pale yellow liquid with the overpowering onion-like thioacid odor. It was found to be a much stronger acid than the hydrocarbon analog, with an ionization constant of approximately 0.6, which is more comparable to that of CF_3COOH (0.5), than to that of CH_3COSH (4.7×10^{-4}).

Sheppard and Muetterties found that the fluorinated thioacids appeared to react similarly to the hydrocarbon analogs:

and

No other work with this type of compound has appeared in the literature until 1969, when W. V. Rochat and G. L. Gard, of this laboratory, published a paper on CF_3COSH and its derivatives.² They found that TFTAA acts characteristically like an organic acid, ionizing to form the CF_3COS^- ion and the H^+ ion. It forms a salt with the bases pyridine or aniline:

and

TFTAA also appeared to exhibit acid chloride behavior in some reactions. For example, with water,

the SH being replaced by OH. This reaction explains not only the instability of aqueous solutions of fluorinated thioacids, which prevented Sheppard and Muetterties from measuring accurate conductivities of these solutions, but also was the reason for the failure of earlier attempts at preparation of this type of fluorocarbon by hydrolyzing the thiolester.¹ The products obtained in these early attempts were acids and thiols, as would be expected from the above reaction with water.

It seemed likely that the TFTAA anion, CF_3COS^- , might add nucleophilically to Lewis acids like SO_3 and BBr_3 , and to the electron depleted carbons of fluorinated olefins. Six new compounds were prepared illustrating this behavior.

TFTAA was found to form 1:1 adducts with fluoroolefins, although the reaction was not spontaneous and had to be initiated with UV light. With hexafluoroacetone, TFTAA added across the carbonyl, producing a hemi-mercaptal-like addition product, $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$. With ethylene oxide, the alcohol addition product was formed, $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}$. These reactions occurred spontaneously, without any catalyst or solvent.

With inorganic Lewis acids, spontaneous adduct formation was also found. Sulfur trioxide reacted forming $(\text{CF}_3\text{COS})_2\text{SO}_2$. Borontri-

bromide, nitrosylchloride and ammonia also reacted but the products were less clear, possibly the trisubstituted adduct of boron, $B(CF_3COS)_3$. The nitrosyl chloride reaction formed a green intermediate (CF_3COSNO ?) as in a study of other perfluoroalkylnitroso compounds (CF_3SNO) done by J. Mason.³ The intensely colored intermediate gradually faded to a colorless solution which was found to be the disulfide, $(CF_3COS)_2$, previously characterized by Rochat and Gard.² The reaction of TFTAA with NH_3 split out H_2S , forming CF_3CONH_2 . These last three reactions were not pursued further and rigorous identification of the products was not made, but they certainly appeared to be an interesting topic for future study.

The reactions which have given new compounds are summarized in Table I.

TABLE I
NEW ADDUCTS PREPARED BY REACTIONS OF CF_3COSH

Compound	Reaction		
$CF_3COSCH_2CFH_2$	$CF_3COSH + CH_2=CHF$	=	$CF_3COSCH_2CFH_2$
$CF_3COSCH_2CF_2H$	$CF_3COSH + CH_2=CF_2$	=	$CF_3COSCH_2CF_2H$
$CF_3COSCHFCH_2H$	$CF_3COSH + CHF=CF_2$	=	$CF_3COSCHFCH_2H$
$CF_3COSC(CF_3)_2OH$	$CF_3COSH + (CF_3)_2C=O$	=	$CF_3COSC(CF_3)_2OH$
$(CF_3COS)_2SO_2$	$2CF_3COSH + 2SO_3$	=	$(CF_3COS)_2SO_2 + H_2SO_4$
$CF_3COSCH_2CH_2OH$	$CF_3COSH + \overset{O}{\underset{\text{CH}_2}{\text{CH}_2}}$	=	$CF_3COSCH_2CH_2OH$

A new method of preparing TFTAA is also presented. It was found that combining KSH with trifluoroacetic anhydride, $(\text{CF}_3\text{CO})_2\text{O}$, produces CF_3COSH and CF_3COOK . This method eliminated the need for heat and pressure.

II. EXPERIMENTAL

APPARATUS

Vacuum System

The vacuum system used in this work consisted of a manifold connected to a Duo Seal vacuum pump. The manifold was constructed of 22mm and 8mm I.D. Pyrex glass tubing and was connected to a two leg mercury manometer and several taps. The taps consisted of Eck and Krebs 2mm high vacuum stopcocks, and ended in 10/30 W outer Pyrex glass joints. The pump was protected by a large concentric trap which was cooled with liquid nitrogen. A swivel McLeod gauge measured the vacuum, which usually attained 10^{-3} torr. All joints were lubricated with Halocarbon 25-5S grease. The vacuum system is illustrated in Figure 1.

Reaction Vessels

.2 Liter Glass Vessels. Reactions involving solids were run in a .2 liter Pyrex glass bulb closed with a Kontes high vacuum teflon valve of 0-4mm bore and tipped with a 10/30 W inner Pyrex glass joint.

One Liter Glass Vessels. Reactions involving condensation of liquids or gases together, in which warming to room temperature caused reaction, were done in one liter Pyrex glass vessels. These vessels were equipped with a cold finger at the bottom for condensing the materials and were closed with 2mm high vacuum Eck and Krebs glass stopcocks, lubricated with Halocarbon 25-5S grease. The vessels were tipped with 10/30 W inner glass joints for attaching to the vacuum line.

- A Eck and Krebs 2 mm high vacuum stopcock.
- B 9/16" ball and socket joint.
- C 10/30 ♀ female glass joint.
- D Eck and Krebs 4 mm high vacuum stopcock.

Figure 1. Vacuum System

Five Liter Ultraviolet Reaction Vessel. For most of the ultraviolet work, done with the olefins, a five liter round bottom flask was used. This vessel was equipped with a cold finger for condensing the reactants on one side. On the other side there was an arm tipped with a 10/30 F inner glass joint for attaching to the vacuum line. This was closed with an Eck and Krebs 2mm glass high-vacuum stopcock. Figure 2 shows a diagram of the vessel. A large center cold finger made of quartz suspended the Hanovia 100W mercury arc lamp so that the entire vessel was exposed to the light. Water was circulated through the cold finger while the light was running. The entire set-up was enclosed in aluminum foil during the reaction to prevent eye injury from the light. The joints of the vessel were lubricated with silicone lubricant, which can withstand higher temperatures, and the quartz cold finger joint was cooled with a stream of air during the reaction.

One Liter Ultraviolet Reaction Vessel. Some of the reactions were run in a one liter vessel, shown in Figure 3, equipped to use the same quartz cold finger as the larger vessel. This vessel had a ball and socket joint on one side that led to an arm tipped by an inner 10/30 F glass joint for attaching to the vacuum line. The arm was closed with an Eck and Krebs 2mm glass high-vacuum stopcock. The same mercury lamp, silicone lubricant and cooling conditions were used with this vessel as described for the five liter vessel.

Metal Reaction Vessels. TFTAAs were prepared in a 200 cm³ nickel pressure vessel equipped with an Autoclave Space-saver* valve, and a metal 10/30 F inner joint for attaching to the vacuum line.

* Ordered from Autoclave Engineers, Inc., 2930 West 22nd St, Erie, Pa.

- A Eck and Krebs 2 mm high vacuum stopcock.
- B 10/30 T inner glass joint.
- C 19/38 ground glass joint.
- D 60/50 ground glass joint.
- E Quartz cold finger.

Figure 2. Five Liter Ultraviolet Apparatus.

- A 2 mm Eck and Krebs high vacuum stopcock.
- B 10/30 glass male joint.
- C 9/16" ball and socket joint.
- D 60/50 ground glass joint.
- E Quartz cold finger.

Figure 3. One Liter Ultraviolet Reaction Vessel.

PHYSICAL METHODS

Fractional Distillation

The products of the reactions were purified by fractional distillation, often under reduced pressure. A Bantam-Ware (Kontes) distillation apparatus was used, and was equipped with a multiple fraction collector head for low pressure distillations. The distilling column was connected to the vacuum line or atmosphere through a -78°C trap.

Gas Chromatography

The purity of the products was checked by gas chromatography using an Auto-Prep Model 700 gas chromatograph. A 5' x 3/8" column of 60/80 "Chromosorb W" was used. This was coated with 5% QF-1, a fluorinated alkyl silicone preparation.

Chemical Analysis

Chemical analysis were performed by Beller Microanalytical Laboratory in Göttingen, West Germany.

Vapor Pressure

Vapor pressure as a function of temperature was measured in the apparatus shown in Figure 4. The sample was condensed into a bulb (E) which opened to a mercury manometer (F). Air was initially removed from the system through valves (D_1 , D_2). Valve D_2 was then closed, the sample condensed in, and air pumped out of it by warming and cooling several times and pumping through valve D_1 . To measure the vapor pressure at various temperatures, the whole apparatus was immersed in

- A Eck and Krebs 2 mm high vacuum stopcock.
- B 10/30 $\frac{7}{8}$ inner ground glass joint.
- C 10/30 $\frac{7}{8}$ ground glass joint.
- D Kontes high vacuum teflon valve, 0-4 mm bore.
- E Sample bulb.
- F Manometer.

Figure 4. Vapor Pressure Apparatus

a controlled temperature bath to the top of stopcock D₁. Mercury levels were read with a cathetometer* after thermal equilibrium had been reached. The data was plotted on log P vs 1/T graphs and a straight line was drawn through the points. Heat of vaporization and Trouton constants were calculated from the slope.

Index of Refraction

Indices of refraction were determined using a Bausch and Lomb Abbe-3L refractometer.

Infrared Spectra

Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord Spectrophotometer. Gaseous samples were contained in a 8.25 cm Monel cell fitted with NaCl windows and a Whitey-Brass valve which was connected to a glass 10/30 W joint for attaching to the vacuum line.

Ultraviolet Spectra

The ultraviolet spectra of the new adducts were obtained using a Cary Model 14 recording ultraviolet spectrophotometer. Liquid spectra were taken with a cell having a path length of 1.00 cm. The compounds were diluted with Gas Chromatographic-Spectrophotometric quality cyclohexane (J. T. Baker Co.).

Nuclear Magnetic Resonance Spectra

The fluorine nuclear magnetic resonance spectra were recorded on a Varian Model HA-100 high resolution nmr spectrophotometer. The

* The author wishes to thank Professor David W. McClure for the use of the Cathetometer.

spectra were run at 94.07 Mcps and freon-11 was used as an external reference. The proton spectra were recorded on a Varian Model A-60 analytical nmr spectrometer.

Mass Spectra

Mass spectra were taken on a CEC 21-110B double focus Mass Spectrometer equipped with a 6 KV ion accelerator and operated at 72 volts. Polyfluoroamine (PFA) was used as an internal standard.

REAGENTS

Trifluorothiolacetic Acid

TFTAA was prepared by the method of Rochat and Gard,² in which $(\text{CF}_3\text{CO})_2\text{O}$ and H_2S are heated to 90-140°C with an I_2 catalyst for 3-3/4 hours. It was purified by shaking with mercury to remove the I_2 and distilled using a spinning band column. The fraction boiling at 37.5°C was collected. Its purity was further checked by infrared analysis and vapor density.

Trifluoroethylene

The trifluoroethylene was purchased from Penninsular Chemresearch, Inc., and was used without further purification. The purity of the olefin was checked by infrared analysis.

Vinylidene Fluoride

Vinylidene fluoride was purchased from Penninsular Chemresearch, Inc., and used without further purification. Purity was checked by infrared analysis.

Vinyl Fluoride

Vinyl fluoride was purchased from Penninsular Chemresearch, Inc., and was used without further purification. Purity was checked by infrared analysis.

Sulfur Trioxide

Sulfur trioxide was obtained from Allied Chemical Co., as Sulfan B, a stabilized liquid, and used without further purification.

Ethylene Oxide

Ethylene oxide was purchased from the Matheson Co., and used without further purification. It was checked for purity by infrared analysis.

Hexafluoroacetone

Hexafluoroacetone was obtained from Allied Chemical Co., and used without further purification.

Boron Tribromide

Boron tribromide was obtained from the Matheson Co., and used without further purification.

Nitrosyl Chloride

Nitrosyl chloride was purchased from Research Organic/Inorganic Chemical Co., and used without further purification.

Nitrogen

Dry nitrogen gas was obtained from a commercial cylinder from Airco and used without further purification.

Ammonia

Dry ammonia was obtained from a commercial cylinder and was dried through a $P_2O_5/CaCl_2$ column before use. Purity was checked by infrared analysis.

III. SYNTHESIS OF NEW ADDUCTS OF TRIFLUOROTHIOACETIC ACID

THE REACTION OF TRIFLUOROTHIOACETIC ACID WITH FLUOROOLEFINS

Introduction

The reaction of trifluoromethane thiols with fluoroolefins,⁴

and of thiolacetic acid with vinyl fluoride,⁵

suggest that TFTAA may react similarly. It was found that in the presence of UV light, TFTAA would add to fluoroolefins in the manner expected. The following reactions were studied:

Ethyl thioltrifluoroacetate, $\text{CF}_3\text{COSCH}_2\text{CH}_3$, has been prepared previously by Hauptschein, Stokes and Nodiff⁶ by the reaction of ethyl mercaptan and trifluoroacetic anhydride.

Since these reactions occur at a negligible rate when the reactants are combined at room temperature, but proceed readily when irradiated with UV light, it seems likely that free radicals play an important part in the mechanism. Harris and Stacey⁴ found, in their free radical studies with CF_3SH and fluoroolefins, that the $\text{CF}_3\text{S}\cdot$

radical was the adding species. In this work only one isomer was found (as with CF_3SH) for each reaction, and the products can be correlated on the basis of the intermediate radical stability, postulated by Haszeldine and co-workers.^{7,8} The products found are those deriving from the predicted more stable intermediate radical. Haszeldine found that the order of radical stability is tertiary > secondary > primary, and that the order of stability of primary and secondary radicals can vary depending upon the substituents involved. The designations "tertiary," "secondary" and "primary" are determined solely by the number of atoms or groups other than hydrogen on the carbon atom bearing the odd electron and do not necessarily refer to the carbon skeleton. Substituents vary in their stabilizing ability, e.g. $\text{H} < \text{F} < (\text{Cl}, \text{CF}_3, \text{RO})$. Thus, the relative order of stability of free radicals produced here would be:

The new adducts are colorless liquids with a strong onion-like odor. They decompose slowly at room temperature under a nitrogen atmosphere producing a yellow impurity. The trifluoroethylene adduct was less stable than the others, darkening in a vacuum during the vapor pressure study, while the others remained unchanged. The trifluoro-adduct was slowly attacked by water, forming a white solid, which was not further characterized.

Experimental

Preparation. The same general method was used for all of these reactions. In a typical reaction, a slight excess of TFTAA (.39 mmol) was condensed with the fluoroolefin (.34mmol) in a five liter Pyrex round bottom flask (see Figure 2). The reactants were warmed to room temperature. Excess nitrogen was found to improve the yield for all but the vinyl fluoride reactions, and was then added to all but this reaction. The reactants were exposed to UV light and the course of the reaction was followed on a manometer. When the pressure stopped decreasing (approximately 30 minutes) irradiation was stopped. The products were pumped slowly through a liquid nitrogen trap which permitted collection of all products and excess reactants, while removing the nitrogen and possibly CO produced during the reaction. In all cases there remained behind a colorless pool of liquid at the bottom of the reaction vessel, which was assumed to be a higher polymer. The infrared spectra of this material showed more peaks than for the monomer product, in addition to having the carbonyl and CF_3 peaks present. The transferred product was distilled under reduced pressure, yielding 40 to 60% of the monomer. Preliminary identification of the product was made by infrared analysis.

Gas Chromatography. The products were analyzed with an Auto-prep gas chromatograph as described under Physical Methods, page 10. The column temperature was 35° and the helium flow rate was 30 ml/minute. Table II lists the times of appearance of the various compounds. CCl_4 , CF_3COSH and $\text{CF}_3\text{COSCH}_2\text{CH}_3$ are shown for comparison. The presence of only one peak was evidence of the purity of these adducts.

TABLE II
GAS CHROMATOGRAPH DATA FOR OLEFIN ADDUCTS

<u>Compound</u>	<u>Time (min)</u>
CCl_4	5.59
CF_3COSH	2.83
$\text{CF}_3\text{COSCH}_2\text{CH}_3$	10.23
$\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$	28.83
$\text{CF}_3\text{COSCH}_2\text{CHF}_2$	18.63
$\text{CF}_3\text{COSCHFCHF}_2$	11.93

Chemical Analysis. The compounds were analyzed by Beller Microanalytical Laboratory (see Physical Methods, page 10) for C, H, S, and F. The results are shown in Table III. There was good agreement with calculated composition except for the trifluoro-adduct. The slight deviations for this adduct are due to its thermal instability, mentioned previously.

TABLE III
ANALYTICAL DATA FOR OLEFIN ADDUCTS

Compound	Carbon		Carbon		Carbon		Carbon	
	wt%		wt%		wt%		wt%	
	Exptl/Calc		Exptl/Calc		Exptl/Calc		Exptl/Calc	
$\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}_2$	27.17	27.30	2.22	2.30	17.90	18.10	43.10	43.20
$\text{CF}_3\text{COSCH}_2\text{CHF}_2$	24.80	24.70	1.55	1.50	16.46	16.50	48.90	49.00
$\text{CF}_3\text{COSCHFCHF}_2$	22.63	22.60	1.74	0.90	14.19	15.20	47.40	53.80

Infrared Spectra. The infrared peaks for these adducts are listed in Table IV. The spectra are shown in Figures 5 and 6. All show the strong CF_3 symmetric and asymmetric stretching bands at $1285\text{--}1130\text{ cm}^{-1}$, and the CF_3 deformation bands at $750\text{ to }736\text{ cm}^{-1}$.⁹ The carbonyl stretching frequency for these compounds is found in the range 1710 cm^{-1} (ethylene adduct) to 1735 cm^{-1} (trifluoro adduct). The frequency shows a slight increase with increasing fluorine substitution of the thiol ester. Haupschein, Stokes and Nodiff⁶ explain this as follows:

1) Due to the extreme electronegativity of the fluorine atoms, a strong inductive effect (-I) is present which gives the carbonyl carbon a greater effective positive charge than in the nonfluorinated cases. As a consequence, the attractive forces between the positive carbon and negative oxygen of the carbonyl band are enhanced, and the motion of the oxygen atom relative to the carbon atom during a vibrational cycle is diminished. Thus, the force constant of the carbonyl bond is increased which is reflected in the greater frequency of the infrared band in oxygen esters.

2) Due to the greater polarizability (lower electronegativity) of the sulfur compound to the oxygen atom, the positive character of the carbonyl carbon is not enhanced nearly as much in the case of fluorinated thiolesters, i.e. the mobile electronic field of the alkyl sulfur atom is more "available" to the carbonyl carbon. The force constant of the carbonyl bond in fluorinated thiolesters is increased to a minor extent, if at all, so that almost no shift to higher frequency is observed. The absorption frequency of $\text{CF}_3\text{COSCH}_2\text{CH}_3$ is

TABLE IV
INFRARED ABSORPTION BANDS FOR OLEFIN ADDUCTS

$\text{CF}_3\text{COSCH}_2\text{CH}_3$	$\text{CF}_3\text{COSCH}_2\text{CH}_2\text{CHF}_2$	$\text{CF}_3\text{COSCH}_2\text{CHF}_2$	$\text{CF}_3\text{COSCHFCHF}_2$
2990 (w)	2940 (w)	2940 (w)	2960 (w)
2920 (w)	1710 (s)	1820 (vw)	1872 (vw)
1910 (vw)	1463 (vw)	1725 (s)	1825 (vw)
1830 (vw)	1395 (w)	1398 (m)	1735 (m)
1710 (s)	1275 (s)	1370 (m)	1373 (m)
1460 (w)	1210-1175 (s)	1280 (s)	1274 (s)
1385 (w)	1120 (m)	1240-1175 (s)	1205 (s)
1270 (vs)	1063 (m)	1114 (s)	1184 (s)
1175 (vs)	1020 (s)	1076 (s)	1108 (s)
1050 (w)	955 (s)	1017 (w)	1080 (m)
959-932 (vs)	818 (vw)	949 (s)	1058 (m)
738 (s)	738 (m)	839 (w)	983 (w)
695 (vw)		740 (m)	938 (s)
			893 (w)
			807 (m)
			779 (w)
			738 (m)

Figure 5. Infrared Spectrum of:

Top - $\text{CF}_3\text{COSCH}_2\text{CH}_3$

Bottom - $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$

Figure 6. Infrared Spectrum of:

Top - $\text{CF}_3\text{COSCH}_2\text{CHF}_2$

Bottom - $\text{CF}_3\text{COSCHFCHF}_2$

1710 cm^{-1} , close to the "normal" value of 1715 cm^{-1} for a saturated aliphatic ketone. However, as the thiolester group becomes increasingly substituted with fluorines, the electronic field of the sulfur atom becomes less "available" to the carbonyl carbon and a shift of the infrared band to higher frequencies is observed, to a value of 1735 cm^{-1} for $\text{CF}_3\text{COSCHFCHF}_2$.

The C-H stretching modes are seen in all spectra in the region 2990-2960 cm^{-1} . The ethyl ester shows the CH_3 symmetric and asymmetric bending vibrations at 1460 and 1385 cm^{-1} . The bands in the vinyl and vinylidene adducts at 1395 to 1370 cm^{-1} could be due to the CH_2 scissoring vibration.¹⁰

Ultraviolet Spectra. The ultraviolet spectra of these adducts are compared in Figure 7. The maximum absorptions found, when dissolved in cyclohexane are:

	λ_{max}	E_{max}
CF_3COSH	230	5,510
$\text{CF}_3\text{COSCH}_2\text{CH}_3$	242	8,550
$\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$	240	30,700
$\text{CF}_3\text{COSCH}_2\text{CHF}_2$	238	87,000
$\text{CF}_3\text{COSCHFCHF}_2$	232	55,500

There is a progressive blue shift from 242 $\text{m}\mu$ for the ethylene adduct to 232 $\text{m}\mu$ for the trifluoroadduct, which parallels increasing fluorine substitution on the olefin. These shifts are explained by Koch¹¹, who accounts for the absorbance band by the formation of an excited state through charge transfer involving a sulfur electron:

Figure 7. Ultraviolet Spectrum of Olefin Adducts.

It seems likely that charge transfer, rather than a purely intra-atomic valency shell transition is involved in view of the relatively high intensity of the absorption band.

Koch notes that substitution of chlorine on R produces a red shift (CH_3COSH $\lambda_{\text{max}} = 220 \text{ m}\mu$, $E_{\text{max}} = 2200$; Cl_3COSH $\lambda_{\text{max}} = 238 \text{ m}\mu$, $E_{\text{max}} = 3800$). This he attributes to the inductive effect of chlorine, which would raise the ground state relative to the excited state:

Rochat and Gard² found that substituting fluorines on R produces a red shift also, but of a lesser degree, (CF_3COSH $\lambda_{\text{max}} = 230 \text{ m}\mu$).

Substitution of an alkyl group for hydrogen on sulfur causes a further red shift, ($\text{CF}_3\text{COSCH}_2\text{CH}_3$ $\lambda_{\text{max}} = 242 \text{ m}\mu$), due to the stabilizing electropositive effect of the alkyl group, which would help disperse the positive charge of the excited state:

The substitution of fluorines on one carbon removed from the sulfur should reduce the electron donating effect of the alkyl group slightly and results in a slight blue shift of 2 mμ for the vinyl adduct and

2 μ more for the vinylidene. Substituting fluorines on the adjacent carbon to the sulfur has a much larger counteracting effect, and the peak is shifted 6 μ shorter than the vinylidene and is almost the same as the unsubstituted thioacid.

Physical Properties. The physical properties of the olefin adducts are summarized in Table V. The molecular weights were found using a calibrated bulb and compared reasonably well with the expected values. Vapor pressure as a function of temperature was found using the apparatus shown in Figure 4, (page 11). The data is presented in Table VI. The curves drawn from this data are shown in Figure 8. The straight line was extrapolated at 760 mm to find the boiling point. From Table V, it can be seen that boiling point rises with increasing fluorine substitution until the di-substituted adduct is reacted. The trifluoro adduct has a lower boiling point than any of the others. This is analogous to the series of fluorinated methanes compared by Sheppard and Sharts¹² which shows an increase in boiling point from methane to difluoromethane and a drop for the trifluoromethane, with the lowest value for carbon tetrafluoride. This is explained by the importance of intermolecular hydrogen bonding in partially fluorinated compounds. This intermolecular hydrogen bonding, promoted by the high polarization of the molecule is probably at a maximum for the difluoro- adduct.

The slope of the vapor pressure plot was used to find ΔH_{vap} and Trouton's constant for the four adducts. These constants are listed in Table V with the physical properties. One can see that these do approximately follow the boiling point trends and support

TABLE V

PHYSICAL PROPERTIES OF THE OLEFIN ADDUCTS

Compound	M.P. °C	B.P. °C Extrap.	ΔH_{vap} kcal/mole	Trouton Const.	Vapor Density Calc.	Fnd.	Index of Refrac. 25°
$\text{CF}_3\text{COSCH}_2\text{CH}_3$		88.8	8.23	22.7	158	159.0	1.3750
$\text{CF}_3\text{COSCH}_2\text{CFH}_2$	-35.5 -33.5	97.8	9.64	26.0	176	179.5	1.3866
$\text{CF}_3\text{COSCH}_2\text{CHF}_2$		100.6	9.33	25.0	194	189.5	1.3632
$\text{CF}_3\text{COSCHFCHF}_2$		74.7	8.08	23.2	212	203.0	1.3482

TABLE VI

VAPOR PRESSURE-TEMPERATURE DATA FOR OLEFIN ADDUCTS

$\text{CF}_3\text{COSCH}_2\text{CH}_3$		$\text{CF}_3\text{COSCH}_2\text{CFH}_2$		$\text{CF}_3\text{COSCH}_2\text{CHF}_2$		$\text{CF}_3\text{COSCHFCHF}_2$	
T°K	Pmm	T°K	Pmm	T°K	Pmm	T°K	Pmm
273	8.0	283	12.9	282	13.1	282	52.4
283	31.0	294	25.0	295	26.8	284	54.9
293	54.6	304	42.9	302	39.0	294	86.35
303	82.0	312	64.6	303	42.4	304	138.0
313	128.0	313	69.4	308	53.1	312	193.6
		323	104.3	313	69.3	316	254.4
		324	107.8	322	96.3	322	302.1

a. $\text{CF}_3\text{COSCH}_2\text{CH}_3$	$\log P = 7.8 - \frac{1.8 \times 10^3}{T}$
b. $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$	$\log P = 8.7 - \frac{2.2 \times 10^3}{T}$
c. $\text{CF}_3\text{COSCH}_2\text{CHF}_2$	$\log P = 7.9 - \frac{1.9 \times 10^3}{T}$
d. $\text{CF}_3\text{COSCHFCHF}_2$	$\log P = 7.4 - \frac{1.7 \times 10^3}{T}$

Figure 8. Vapor Pressure Curves of Olefin Adducts.

the above argument.

Nuclear Magnetic Resonance Spectra. ^{19}F nmr data is presented in Table VII. The spectra of the various adducts are compared in Figures 9, 10 and 11. The proton spectrum was obtained for the trifluoro- adduct only and this is pictured in Figure 12.

All the fluorine spectra contained the single CF_3^- peak in the range +75.8 to +76.2 ppm upfield from CFCl_3 , which is the region expected for the CF_3^- group when it is attached to a carbonyl group.¹³ Rochat and Gard² found that the CF_3 resonance for CF_3COSH was +77.2 and other substituted thioacids fell in the range +73.5 to +75.8.

The fluorine spectrum of the vinyl adduct, $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$ consists of a nine line spectra with a band center of 216 ppm upfield from CFCl_3 , in the region expected for a fluorine in a CHF group.¹² The ^{19}F resonance is split into a large triplet by the two protons of the CH_2F group, $J_{\text{F1,H1}} = 47$ cps. Each of these triplets is further split into a triplet by the CH_2 protons, $J_{\text{F1,H2}} = 24$ cps. The spectrum thus confirms the direction of addition postulated by consideration of the most stable free radical intermediate.

The fluorine spectrum of the vinylidene adduct, $\text{CF}_3\text{COSCH}_2\text{CHF}_2$, consists of six lines, with a band center of 115.5 ppm upfield from CFCl_3 , as expected for a fluorine in a CHF_2 group. The ^{19}F resonance is split into a large doublet by the CHF_2 proton, $J_{\text{F2,H2}} = 55$ cps. Each component of the doublet becomes a triplet as a result of coupling between ^{19}F and the CH_2 protons, $J_{\text{F2,H1}} = 16.0$ cps. This spectrum again shows that the direction of addition is as expected.

TABLE VII
FLUORINE NUCLEAR MAGNETIC RESONANCE DATA FOR OLEFIN ADDUCTS

Proposed Structure Skeletal Atom Number				Chemical Shifts, Band Centers ^a			Coupling Constants ^b					
1	2	3	4	CF ₃	CF ₂	CF	J _{3,4} ^{H,F}	J _{4,4} ^{H,F}	J _{4,3} ^{H,F}	J _{3,3} ^{H,F}	J _{3,4} ^{F,F}	J _{4,3} ^{F,F}
CF ₃		CH ₂	CH ₃									
CF ₃		CH ₂	CFH ₂	76.1		216.2	24	47				
CF ₃		CH ₂	CHF ₂	76.0	115.8		16	55				
CF ₃		CHF	CHF ₂	76.2	127.4	179.2	?	54	5	47	19	19

^a Chemical shifts in parts per million upfield from CFC1₃ internal standard.

^b Measured in cycles per second.

Figure 9. ^{19}F NMR Spectrum of $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$.

Figure 10. ^{19}F NMR Spectrum of $\text{CF}_3\text{COSCH}_2\text{CHF}_2$.

Figure 11. ^{19}F NMR Spectrum of $\text{CF}_3\text{COSCHFCHF}_2$.

Figure 12. ^1H NMR Spectrum of $\text{CF}_3\text{COSCHFCHF}_2$.

The fluorine spectrum of the trifluoro adduct, $\text{CF}_3\text{COSCHFCHF}_2$, is more complex. In addition to the CF_3 peak, mentioned at the start as present in all the spectra, there are two ^{19}F resonance bands representing the CHF group and the CHF_2 group. The CHF resonance has a band center at 179.1 ppm upfield from CFCl_3 and contains twelve lines. The resonance is first split into a wide doublet, by the CHF proton, $J_{\text{F1,H1}} = 47$ cps. Each doublet is further split into a triplet by the CF_2H fluorine, $J_{\text{F1,F2}} = 19$ cps. Each triplet is then further split into a doublet, $J_{\text{F1,H2}} = 5$ cps, by the CF_2H proton resulting in a total of twelve lines.

The CHF_2 resonance consists of sixteen lines with a band center of 127.0 ppm upfield from CFCl_3 . The band is initially split into a large doublet by the CHF_2 proton, $J_{\text{F2,H2}} = 54$ cps. Each doublet is further divided into a doublet by the CHF fluorine, $J_{\text{F1,F2}} = 19$ cps. One would then expect each of these doublet elements to be further split into doublets by the CHF proton with a coupling constant of approximately 5 cps as in the CHF resonance coupling. However, in this case the doublet is split into a doublet with a coupling constant of 10.2 cps and each of these is again split into a doublet with a coupling constant of 3.8 cps, giving a total of sixteen lines when only 8 are expected. The difference between band centers, $\Delta\nu$, here is 52 cps and the largest coupling constants are on the order of 50 cps, giving a $\Delta\nu/J$ ratio of .4. Whenever the ratio falls below 6 or 7, first order spectra are not expected. In this spectrum it appears that the two CHF_2 fluorine atoms are not equivalent. Because the two fluorines have the same chemical shift, after

splitting by the coupled fluorine and protons these fluorine resonances can now interact to split each other into two pairs of resonances. Adding all these splittings results in the observed sixteen line pattern which is, in fact, two sets of lines predicted by the first order theory from CHF and H splitting. If this is the case, the CHF spectrum would still look the same if the coupling constant of the two equivalent fluorines are the same.

The proton spectrum of this trifluoro adduct is diagrammed in Figure 10. This is an AB system, using Pople's nomenclature.¹⁴ The chemical shift of H1 is 6.39 ppm downfield from TMS, while that of H2 is 6.06 ppm downfield from TMS. $\Delta\nu$, here is 20 cps and it is found that the coupling constants of the H_1F_1 splitting is about 45 cps, giving a $\Delta\nu/J$ ratio of .45. The spin-spin coupling constant between H_1F_2 is about 11 cps, resulting in $\Delta\nu/J$ of about 2 in this instance. Again this is not a first order spectra and deviations from first order rules are expected. A detailed analysis of this spectrum was not attempted and instead the discussion here is based on first order expectations. Enough similarities to the expected first order spectrum are present that this sort of analysis is possible and the spacing distances given here are measured distances, which may not be the actual coupling constants. Values shown as approximate varied by 1 or 2 cps either way of the expected distances in the spectrum.

The CHF proton resonance has a band center of 6.39 ppm downfield from TMS. It is split into a wide doublet by the fluorine. This doublet is then split into triplets by the adjacent CHF_2 fluorines.

Each doublet is further split into a doublet by the CHF proton.

This results in a total of twelve lines for this proton.

In all, the proton spectra should contain twenty-four lines. It would be expected that the resonance patterns of the two protons would be intermixed due to the proximity of their chemical shifts. Because of line overlap, the twenty-four line pattern is reduced to eighteen lines.

Mass Spectra. The major mass spectra peaks for the olefin adducts are listed in Tables VIII, IX, X and XI. A comparison of the major peaks shows that all of the spectra had strong peaks at $m/e = 69$, the CF_3^+ peak, as would be expected. The vinyl, vinylidene and ethyl adduct had good parent peaks, while the trifluoro adduct showed only a very weak parent peak. The unit COS^+ olefin ($\text{COSCH}_2\text{CH}_3^+$, $\text{COSCH}_2\text{CH}_2\text{F}^+$, $\text{COSCH}_2\text{CHF}_2^+$ and COSCHFCHF_2^+) was present in all. It was surprising that other units of the thioacid were not consistently present. CF_3CO^+ was present in all of the spectra, although it was very weak in the vinyl and trifluoro adduct spectra. CF_3COS^+ was very weak in the fluorinated adducts and not present in the ethyl adduct. CF_3COSH^+ was found only in the vinyl and vinylidene adducts. A 131 peak however, was present in all but the vinylidene spectra and was quite strong in the vinyl adduct spectrum. This might correspond to $\text{CF}_3\text{COSH}_2^+$.

In all cases, the mass spectra did reaffirm the proposed structure.

TABLE VIII
MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSCH}_2\text{CH}_3$

M/e	Relative Intensity	Type
26	6.8	CH_2H_2^+
27	6.8	CH_2CH^+
28	23.0	$\text{CO}^+, \text{N}_2^+$
29	100.0	$\text{CH}_3\text{CH}_2^+, \text{COH}^+$ COS^{++}
32	5.0	O_2^+, S^+
35	6.8	?
45	13.5	CSH^+
46	4.8	CH_2S^+
50	6.8	$\text{CF}_3\text{S}^{++}, \text{CF}_2^+$
57	3.6	CHCS^+
58	6.8	CH_2CS^+
59	6.8	CH_3CS^+
60	5.7	COS^+
61	11.4	$\text{CH}_3\text{CH}_2\text{S}^+$
63	3.2	?
69	53.0	CF_3^+
89	47.8	$\text{COSCH}_2\text{CH}_3^+$
97	3.8	CF_3CO^+
143	5.5	$\text{CF}_3\text{COSCH}_2^+$
158	43.0	$\text{CF}_3\text{COSCH}_2\text{CH}_3^+$

There are also minor peaks for masses: 13(CH^+), 16(O^+), 17(OH^+), 31(CF^+), 33(SH^+), 40(C_2O^+), 44(CS^+ , CO_2^+), 47(COF^+), 65($\text{CF}_3\text{COS}^{++}$), 78(CF_2CO^+), 82(CF_3CSH^+), 131($\text{CF}_3\text{COSH}_2^+$).

TABLE IX

MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}$

M/e	Relative Intensity	Type
29	100.0	COH^+
39	9.0	?
43	6.9	CH_2CHO^+
45	6.8	CHCHF^+ , CSH^+
47	33.3	$\text{CH}_2\text{CH}_2\text{F}^+$, COF^+
59	6.5	CHCHS^+
69	100.0	CF_3^+
100	13.7	CF_3S^+
107	23.7	$\text{COSCH}_2\text{CH}_2\text{F}^+$
114	6.2	?
119	9.0	?
131	28.5	CF_3COSH^+
143	6.5	$\text{CF}_3\text{COSCH}_2^+$
173	7.4	$\text{CF}_3\text{COSCCH}^+$
176	11.0	$\text{CF}_3\text{COSCH}_2\text{CH}_2\text{F}^+$

Minor peaks were also found for: 12(C^+), 13(CH^+), 26(C_2H_2^+), 28(CO^+ , N_2^+), 32(O_2^+ , S^+), 44(CS^+ , CO_2^+), 46(CH_2S^+), 50(CF_2^+), 51(SF^+), 57(CHCS^+), 58(CH_2CS^+), 60(COS^+), 70(SF_2^+), 78(CF_2CO^+), 82(CF_3SH^+), 97(CF_3CO^+), 115($\text{CF}_3\text{SCH}_2^+$), 129(CF_3COS^+), 130(CF_3COSH^+), 154($\text{CF}_3\text{COSCCH}^+$), 156($\text{CF}_3\text{COSCHCH}_2^+$), 157($\text{CF}_3\text{COSCH}_2\text{CH}_2^+$), 162(CF_3COSF^+), 164($\text{CF}_3\text{COSCH}_2\text{F}^+$).

TABLE X

MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSCH}_2\text{CHF}_2$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
18	9.6	H_2O^+	61	4.6	COSH^+
26	3.2	C_2H_2^+	63	6.9	C_2HF_2^+
28	30.8	$\text{CO}^+, \text{N}_2^+$	64	9.2	$\text{C}_2\text{H}_2\text{F}_2^+$
31	9.2	CF^+	65	92.0	$\text{CH}_2\text{CHF}_2^+$
32	9.2	$\text{C}_2^+, \text{S}^+, \text{CHF}^+$	69	100	CF_3^+
33	5.9	$\text{SH}^+, \text{CH}_2\text{F}^+$	77	13.8	$\text{CF}_3\text{COSC}_2\text{H}_2^{+2}$
44	4.0	CS^+	78	4.7	$\text{CF}_3\text{COSCH}_2\text{CH}^{+2}$
45	42.4	CSH^+	97	13.8	$\text{CF}_3\text{CO}^+,$
46	16.9	CH_2S^+			$\text{SCH}_2\text{CHF}_2^+$
47	11.5	COF^+	105	3.3	$\text{COSCH}_2\text{CF}^+$
50	9.2	CF_2^+	115	8.1	?
51	17.7	CF_2H^+	125	96.0	$\text{COSCH}_2\text{CHF}_2^+$
57	3.2	?	126	3.8	?
59	6.1	?	143	9.2	$\text{CF}_3\text{COSCH}_2^+$
60	6.1	COS^+	155	3.7	$\text{CF}_3\text{COSC}_2\text{H}_2^+$
			194	14.6	$\text{CF}_3\text{COSCH}_2\text{CHF}_2^+$

There are also minor peaks for masses: 15(CH_3^+), 17(OH^+), 19(F^+), 20(HF^+), 24(COF^{+2}), 25(CF_2^{+2}), 27(C_2H_3^+), 29(COH^+), 34(CF_3^{+2} , H_2S^+), 40($^+$), 62(C_2F_2^+), 66(COF_2^+), 74(COSCH_2^+), 83($\text{CF}_3\text{SCH}_2\text{CHF}_2^{+2}$), 98(CF_3COH^+), 100(CF_3CF^+), 101(CF_3S^+), 113(CF_3CS^+), 114(CF_3CSH^+), 128(CF_3COCF^+), 129(CF_3COS^+), 130(CF_3COSH^+), 133($\text{CF}_3\text{CH}_2\text{CF}_2^+$), 147($\text{CF}_3\text{COCF}_2^+$), 156($\text{CF}_3\text{COSCH}_2\text{CH}^+$), 166($\text{CF}_3\text{SCH}_2\text{CHF}_2^+$), 175($\text{CF}_3\text{COSCH}_2\text{CHF}^+$), 193($\text{CF}_3\text{COSCH}_2\text{CF}_2^+$).

TABLE XI

MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSCHF}\text{CF}_2\text{H}$

M/e	Relative Intensity	Type
28	100.0	CO^+ , N_2^+
32	68.0	CHF^+ , O_2^+ , S^+
40	4.5	CCO^+
45	3.4	CHS^+
69	10.8	CF_3^+
83	4.1	$\text{CHF}\text{CF}_2\text{H}^+$
143	11.4	$\text{COSCHF}\text{CF}_2\text{H}^+$

Also present were minor peaks representing the following: 31(CF^+), 34(CF_3^{++}), 44(CS^+ , CO_2^+), 47(COF^+), 50(CF_2^+), 51(SF^+), 60(COS^+), 65($\text{CF}_3\text{COS}^{++}$), 78(CF_3CO^+), 85(CF_3O^+), 97(CF_3C^+), 129(CF_3COS^+), 131($\text{CF}_3\text{COSH}_2^+$), 141($\text{CF}_3\text{COCHF}\text{CF}^+$), 162($\text{CF}_3\text{COSCF}^+$), 196($\text{CF}_3\text{CSCHF}\text{CF}_2\text{H}^+$), 212($\text{CF}_3\text{COSCHF}\text{CF}_2\text{H}^+$).

THE REACTION OF TRIFLUOROTHIOACETIC ACID WITH HEXAFLUOROACETONE

Introduction

The reaction of hexafluoroacetone and hydrogen sulfide studied by Harris¹⁵

suggests that CF_3COSH may react similarly. The reaction of TFTAA with hexafluoroacetone occurs readily at room temperature:

The product is a colorless sweet smelling liquid, with a boiling point of 48.5°C. It is very stable in the liquid phase at room temperature, as was found to be true for fluorinated olthiols. In contrast, some unfluorinated compounds studied by Harris were found to be less stable, giving off H_2S or water. In the vapor phase this compound behaved analogously to some of Harris' less stable adducts by dissociating almost completely back into the starting materials.

Experimental

Preparation. A slight excess of thioacid (.146 mmol) was condensed with hexafluoroacetone (.133 mmol) in a one liter pyrex glass vessel with a glass stopcock (page 6). The reaction occurred spontaneously and exothermically upon warming to room temperature, producing a colorless product. The product was condensed into a

distilling flask and distilled at atmospheric pressure. The fraction boiling at 48.5° was collected, giving a yield of 57%. The infrared spectra showed new peaks (OH, only one C=O) not present in the starting materials.

Gas Chromatography. The compound was checked for purity with gas chromatography, using the column and descriptions discussed on pages 11 and 21. Two major peaks were found of equal area, one coming at 2.83 minutes, the same time as found for the thioacid (see Table II, page 19), and the other at 1.75 minutes. It is assumed that the product dissociates in the vapor phase into the starting materials in a 1:1 ratio and this data supports that proposal.

Chemical Analysis. The chemical analysis of this material was in good agreement with the expected composition for the 1:1 adduct. C 20.3% (found 20.3%), H 0.3% (found 0.4%), S 10.8% (found 10.9%).

Infrared Spectra. The infrared peaks (cm^{-1}) for the liquid and gas spectra are compared below:

$\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$ gas: 3390 (vw), 2578 (vw), 2375 (vw), 1795 (m), 1740 (s), 1378 (vw), 1324 (s), 1262 (vs), 1198 (vs), 1107 (vw), 1055 (m), 1020 (s), 986 (s), 966 (s), 889 (vw), 863 (m), 856 (m), 778 (w), 743 (m), 719 (m), 714 (m).

$\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$ liquid: 3310 (w), 1709 (s), 1385 (w), 1279 (s), 1286 (s), 1242 (s), 1220 (s), 1184 (s), 1142 (s), 1074 (w), 1064 (w), 988 (w), 948 (w), 882 (m), 744 (m), 693 (w).

The spectra are shown in Figure 13. In the liquid spectrum there is a carbonyl peak at 1709 cm^{-1} that shows that the thioacid was

Figure 13. Infrared Spectrum of $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$

Top: Liquid

Bottom: Gas

incorporated as an entity including the carbonyl group. The OH absorption at 3310 cm^{-1} supports the proposed structure of $(\text{CF}_3)_2\text{C} \begin{array}{l} \text{OH} \\ \diagup \\ \text{SC(O)CF}_3 \end{array}$. The four strong peaks in the region $1286\text{--}1142\text{ cm}^{-1}$ are the CF_3 symmetric and asymmetric stretching frequencies. The medium peak at 744 and 713 cm^{-1} are CF_3 deformation bands.⁹ The gas spectrum has a doublet at 1795 and 1740 cm^{-1} , the carbonyl region. This lends further support to the hypotheses that the adduct dissociates in the vapor state into the starting materials. The carbonyl peak for the thioacid is found at 1758 cm^{-1} and for hexafluoroacetone it is at 1820 cm^{-1} .

Ultraviolet Spectra. The ultraviolet spectra of this adduct is shown in Figure 14. The maximum absorption is $240\text{ m}\mu$, which is a higher wavelength than for the thioacid, $230\text{ m}\mu$. $E_{\text{max}} = 50,700$.

Physical Properties. The compound is a colorless liquid with a slightly sweet smell that boils at 48.5°C . The refractive index at 26° is 1.3244 , a little lower than the thioacid, which is 1.3452 and also a little lower than the other adducts which were prepared in this study (see Table V, page 28). The vapor density was found to be 146.7 . The expected value is 296 for the adduct. If complete dissociation occurs, the value should be 148 .

Mass Spectra. The major mass spectrum peaks for the hexafluoroacetone adduct are listed in Table XII. As for the olefin adducts, there is a very strong CF_3^+ peak. Also present are strong peaks for the dissociation products, CF_3COSH^+ and $\text{CF}_3\text{COCF}_3^+$. A weak peak at $M/e\ 198$, representing $(\text{CF}_3)_2\text{COS}^+$ supports the proposed structure, $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$.

Figure 14. Ultraviolet Spectrum of $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$

TABLE XII
MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSC}(\text{CF}_3)_2\text{OH}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
18	37.5	H_2O^+	69	100.0	CF_3^+
28	8.8	$\text{CO}^+, \text{N}_2^+$	70	7.1	?
31	50.0	CF^+	78	21.6	$\text{C}_2\text{F}_2\text{O}^+$
32	25.0	O_2^+, S^+	82	10.0	?
33	41.7	SH^+	83	4.6	$\text{CF}_3\text{COCF}_3^{+2}$
44	10.8	CS^+	93	3.8	?
45	5.4	CSH^+	97	100.0	CF_3CO^+
47	4.6	COF^+	98	4.2	CF_3COH^+
50	91.5	CF_2^+	100	54.0	C_2F_4^+
51	20.8	?	119	10.0	C_2F_5^+
60	29.2	COS^+	130	19.2	CF_3COSH^+
61	10.0	COSH^+	147	91.5	$\text{CF}_3\text{COCF}_2^+$
62	5.8	?	148	3.7	?
63	20.8	SCF^+	166	15.8	$\text{CF}_3\text{COCF}_3^+$

There are also minor peaks for masses: 17(OH^+), 19(F^+), 20(HF^+), 24(COF^{+2}), 25(CF_2^{+2}), 29(COH^+), 34(H_2S^+), 35(CF_3^{+2} , OF^+), 40(Ar^+), 49($\text{CF}_3\text{COH}^{+2}$), 55($\text{CF}_2\text{COS}^{+2}$), 60(COS^+), 64($\text{C}_3\text{F}_4\text{O}^{+2}$), 65($\text{CF}_3\text{COSH}^{+2}$), 66(COF_2^+), 74($\text{CF}_3\text{COCF}_2^{+2}$), 84[(CF_3) $_2\text{COH}^{+2}$], 85(CF_3O^+), 99($\text{CF}_3\text{COSCCF}_3^{+2}$), 101(CF_3S^+), 102(CF_3SH^+), 110(CF_2COS^+), 111(CF_2COSH^+), 113(CF_3CS^+), 114(CF_3CSH^+), 128($\text{C}_3\text{F}_4\text{O}^+$), 129(CF_3COS^+), 138(CF_3CF_3^+), 198[(CF_3) $_2\text{COS}^+$].

THE REACTION OF TRIFLUOROTHIOLACETIC ACID WITH ETHYLENE OXIDE

Introduction

The observed nucleophilic behavior of TFTAA led to the attempt to add it to ethylene oxide to produce the alcohol. The reaction was found to proceed spontaneously and exothermically at room temperature, proceeding through a yellow intermediate which can be observed if the reactants are condensed together and warmed slowly to room temperature. The colorless, nonvolatile liquid product polymerizes, when heated, to a white solid, with a m.p. of 179-181°, producing as a byproduct trifluoroacetic acid, CF_3COOH .

The addition of TFTAA to the epoxide is hypothesized to proceed as follows:

Protonation of the epoxide by the TFTAA, a strong acid, would be followed by a nucleophilic attack of the TFTAA anion on the backside of a CH_2 group. Attachment of the TFTAA anion would be concurrent with breaking of the C-O bond to form the alcohol.

Experimental

Preparation. A slight excess of epoxide (.319 mmol) was condensed with TFTAA (.269 mmol) in a pyrex glass reaction vessel with

a bottom cold finger and a glass stopcock connected to a 10/30 $\frac{1}{8}$ inner glass joint for attaching to the vacuum line (page 5). The reactants were slowly warmed. At -198° some yellow solid was seen to form at the upper boundry of the cold finger, so apparently the reaction proceeds at a slow rate at even this low temperature. At -78° the product was a bright yellow liquid (in contrast with the thioacid which is pale yellow). Upon further warming to room temperature, a very exothermic reaction took place producing a colorless liquid, which is a solid at -78° . The product was poured into a distilling flask since it was too nonvolatile to vacuum transfer. The fraction boiling at 134° at 1 atm. pressure was collected. Preliminary identification was made by the infrared spectra.

Chemical Analysis. The chemical analysis, as done by Beller Microanalytical Laboratory in West Germany, was in good agreement with the expected composition for the 1:1 adduct. C 27.6 (found 27.6), H 2.9 (found 2.7), S 18.4 (found 18.1). For the polymer, C = 35.99, H = 4.88, S = 38.73.

Infrared Spectra. The infrared spectra is shown in Figure 15. The peaks present are as follows: cm^{-1}

3570 (w), 2940 (w), 2560 (w), 2460 (vw), 2270 (vw), 1790 (s), 1710(m), 1545 (w), 1450 (m), 1415 (w), 1390 (m), 1340 (m), 1290 (m), 1230-1120 (s), 1080 (w), 1010 (m), 955 (m), 935 (m), 867 (w), 832 (w), 773 (m), 740 (w), 730 (m), 696 (vw).

The OH peak at 3570 cm^{-1} supports the alcohol structure. The carbonyl band at 1790 cm^{-1} is a little higher than expected possibly due to strengthening of the C=O dipole through hydrogen bonding as

Figure 15. Infrared Spectrum of $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}$.

well as through the electron withdrawing effect of the CF_3 group. CF_3 absorption bands are present. Symmetric and asymmetric stretching bands are seen at 1290, 1230-1120 cm^{-1} . Deformation bands are at 740 and 730 cm^{-1} .

Nuclear Magnetic Resonance Spectra. The fluorine spectra, taken at 94.07 MHz contained only one peak, 7119 Hz upfield from CFCl_3 . This is the expected region for a CF_3 group attached to a carbonyl group.⁸

Proton Spectra. The proton spectra of $\text{CF}_3^1 \text{COS}^2 \text{CH}_2^3 \text{CH}_2\text{OH}^4$ is composed of three groups of resonances with amplitudes in the ratio of 1:2:2. The OH resonance appears as a triplet with a chemical shift of 1.53 ppm downfield from TMS. The adjacent (number four) CH_2 group causes the splitting into a triplet with $J = 9.0$ cps..

The number four CH_2 group resonance has a chemical shift of 2.86 ppm downfield from TMS. It is split into a doublet by the adjacent OH, $J = 9.0$ cps. The doublet is further split into a triplet by the number three CH_2 group, $J = 6.5$ cps. This gives a total of six peaks, but the center peaks are hard to distinguish due to overlap.

The number three CH_2 group resonance has a chemical shift of 4.45 ppm downfield from TMS. It is split into a triplet by the adjacent CH_2 group, $J = 6.5$ cps.

This spectra affirms the proposed structure, $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}$.

Mass Spectra. The major mass spectra peaks of the ethylene oxide adduct are listed in Table XIII. Strong peaks for CF_3^+ , $\text{CH}_2\text{CH}_2\text{OH}^+$ and $\text{CF}_3\text{COSC}_2\text{H}_3^+$ support the proposed structure.

TABLE XIII

MAJOR MASS SPECTRA PEAKS FOR $\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
21	4.9	?	57	3.6	?
26	7.7	C_2H_2^+	58	9.8	$\text{C}_2\text{H}_2\text{S}^+$
27	34.4	C_2H_3^+	59	30.0	$\text{C}_2\text{H}_3\text{S}^+$
28	7.7	CO^+ , N_2^+ , C_2H_4^+	60	91.5	COS^+
29	6.0	COH^+	61	34.2	COSH^+
31	5.1	CF^+	62	4.9	HCOSH^+
33	3.0	SH^+	69	100.0	CF_3^+
35	8.8	OF^+	78	3.2	?
42	4.2	CH_2CO^+	86	3.2	$\text{COSC}_2\text{H}_2^+$
43	28.8	CH_2CHO^+	96	5.8	?
44	4.5	$\text{CH}_2\text{CH}_2\text{O}^+$	98	3.1	?
45	35.6	$\text{CH}_2\text{CH}_2\text{OH}^+$	112	3.8	$\text{CF}_3\text{C}_2\text{H}_3\text{O}^+$
46	6.7	CH_2S^+	126	6.2	?
47	42.4	CH_2SH^+	141	30.2	CF_3COSC^+
50	9.7	CF_2^+	155	10.5	$\text{CF}_3\text{COSC}_2\text{H}_2^+$
51	5.2	?	156	10.1	$\text{CF}_3\text{COSC}_2\text{H}_3^{-1}$
			157	5.2	$\text{CF}_3\text{COSCH}_2\text{CH}_2^+$

There are also minor peaks for masses: 17(OH^+), 19(F^+), 24(C_2^+ , COF^{+2}), 25(CF_2^{+2} , C_2H^+), 32(O_2^+ , S^+), 34(H_2S^+), 48($\text{CF}_3\text{CO}^{+2}$), 63(CH_2SOH^+), 75($\text{SCH}_2\text{CH}_2\text{O}^+$), 76($\text{SCH}_2\text{CH}_2\text{O}^+$), 77($\text{SCH}_2\text{CH}_2\text{OH}^+$), 102($\text{COSC}_2\text{H}_2\text{O}^+$), 104($\text{COSC}_2\text{H}_4\text{O}^+$), 111($\text{CF}_3\text{C}_2\text{H}_2\text{O}^+$), 113($\text{CF}_3\text{CH}_2\text{CH}_2\text{O}^+$), 114($\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}^+$), 142($\text{CF}_3\text{COSCH}^+$), 143($\text{CF}_3\text{COSCH}_2^+$), 144($\text{CF}_3\text{CS}_2\text{H}_3\text{O}^+$), 158($\text{CF}_3\text{COSCHO}^+$), 159($\text{CF}_3\text{COSCH}_2\text{O}^+$), 172($\text{CF}_3\text{COSCH}_2\text{CH}_2\text{O}^+$), 174($\text{CF}_3\text{COSCH}_2\text{CH}_2\text{OH}^+$).

THE REACTION OF TRIFLUOROTHIOACETIC ACID WITH SULFUR TRIOXIDE

Introduction

The previously noted acid behavior of CF_3COSH and the nucleophilic behavior of its anion, CF_3COS^- , suggested that one might get a Lewis adduct with SO_3 . The reaction was found to proceed with the elimination of water:

The product is a colorless liquid that melts above -78° . It has a sharp odor. The boiling point is 61° at 10 mm. It is stable at room temperature. With water it reacts to give H_2S and H_2SO_4 and CF_3COOH according to the following equation:

Experimental

An excess of SO_3 (.275 mmol) was condensed with the thioacid (.376 mmol) in the cold finger of a glass pyrex vessel with a glass stopcock. The mixture was slowly warmed to room temperature. A colorless vapor condensed on the upper part of the cold finger as it warmed up. The product was poured into a distilling flask, which caused fuming. It was distilled under reduced pressure and the fraction boiling at 61° at 10 mm was collected, giving a yield of 76%. The infrared spectra showed new peaks not present in the starting materials.

Chemical Analysis. Analysis for C, H, S, and F was done by Beller Microanalytical Laboratory in West Germany. The results agreed with the expected composition for $(\text{CF}_3\text{COS})_2\text{SO}_2$; C 14.9 (found 17.0), H 0.0 (found < 0.2), S 29.9 (found 31.0), and F 35.4 (found 36.8).

Infrared Spectra. The following peaks are seen in the infrared spectrum, shown in Figure 16: cm^{-1}

3440 (vw), 2370 (vw), 2180 (vw), 1920 (vw), 1840 (m), 1750 (s), 1375 (w), 1325 (w), 1275 (s), 1210-1165 (s), 1020 (vw), 985 (w), 970 (m), 925-848 (s), 795 (vw), 735 (s), 690 (m).

Evidence for the C=O group is seen in the strong peak at 1750 cm^{-1} . This is in the region expected for a carbonyl group adjacent to a perfluoroalkyl group.⁷ The CF_3 symmetric and asymmetric stretching bands are present in the band from 1210 to 1165 cm^{-1} , as is characteristic for this group.⁷ The CF_3 deformation band is a strong peak at 735 cm^{-1} . SO_2 symmetric stretching frequencies are expected in the 1150 to 1170 cm^{-1} region, and since this is overlapping the CF_3 stretching bands they are found with this large peak on the spectra. Asymmetric SO_2 stretching frequencies are expected in the 1340 to 1360 cm^{-1} region and the weak band at 1375 cm^{-1} is evidence for this.¹⁶ These frequencies represent a shift to higher frequencies over the SO_3 group bonded to carbons, which indicate increasing strength of the S=O bonds due to increased double bond character.¹⁶

Ultraviolet Spectra. The ultraviolet spectra of this compound is shown in Figure 17. The maximum absorption is at $240 \text{ m}\mu$, which is the region found for the other adducts and, again, is higher than

Figure 16. Infrared Spectrum of $(\text{CF}_3\text{COS})_2\text{SO}_2$.

Figure 17. Ultraviolet Spectrum of $(\text{CF}_3\text{COS})_2\text{SO}_2$.

the thioacid. The presence of only one peak implies symmetry of environment of the two carbonyl groups. Ultraviolet absorption by the SO_2 group would be expected below $180 \text{ m}\mu$,¹⁰ out of range of cyclohexane, which was used as a solvent.

Physical Properties. The dithiosulfonate has a boiling point of 61° at 10 mm pressure. The refractive index was found to be 1.4346 at 25°C . The melting point is above -78°C .

Nuclear Magnetic Resonance Spectra. The fluorine spectra was obtained at 94.07 Hz. One peak was found, at 7006 Hz, which is the region expected for a CF_3 group attached to a carbonyl group. The fact that only one peak was found implies symmetry of the molecule with respect to the two CF_3 groups present. The proton nmr spectra was taken with a Varian Model A-60 nmr spectrophotometer operating at 60 mcps. No peak was found, showing the absence of hydrogen.

Mass Spectra. The mass spectra contained a large number of peaks corresponding to fragments of the parent molecule ion. No parent peak was found. The peaks that were found, their relative intensities and identity are given in Table XIV. Peaks of less than 3% intensity were omitted unless of special significance, and then are given at the bottom of the table.

OTHER REACTIONS INVOLVING TRIFLUOROTHIOACETIC ACID

The Reaction of BBr_3 with CF_3COSH

The thioacid was condensed with BBr_3 in the attempt to produce a Lewis adduct. It was slowly warmed to room temperature. A gas (HBr) was evolved as the product was formed. A pink liquid was

TABLE XIV
MAJOR MASS SPECTRA PEAKS FOR $(\text{CF}_3\text{COS})_2\text{SO}_2$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
28	14.3	CO^+ , N_2^+	83	2.2	?
31	22.3	CF^+	85	2.5	CF_3O^+
32	33.2	O_2^+ , S^+	94	2.8	$\text{CF}_3\text{COSSCO}^{++}$
		SO_2^{++} , S_2^{++}	96	3.0	SSO_2^+
33	19.0	COF_2^{++}	97	95.0	CF_3CO^+
34	4.8	CF_3^{++}	98	2.7	$\text{CF}_3\text{COSSOF}^{++}$
44	12.7	CS^+ , CO_2^+	101	1.9	?
45	6.3	?	113	9.6	CF_3CO_2^+
47	2.1	COF^+	114	7.9	?
50	39.7	CF_2^+	129	14.3	CF_3COS^+
51	12.7	SF^+	130	6.4	?
60	58.8	COS^+	131	2.1	$\text{CF}_3\text{SSO}_2\text{COCF}_3^{++}$
61	63.5	?	133	5.6	?
62	4.8	COSSO_2^{++}	135	1.7	$\text{CF}_2\text{COSSO}_2\text{COCF}_3^{++}$
63	19.0	?	145	4.0	$(\text{CF}_3\text{CO})_2\text{SSO}_2^{++}$
64	81.0	SO_2^+ , S_2^+	157	20.6	?
65	23.8	$\text{CF}_3\text{COS}^{++}$	161	25.4	$\text{CF}_3\text{COSS}_2^+$
66	7.9	COF_2^+			$\text{CF}_3\text{COSO}_2^+$
69	100.0	CF_3^+	189	15.9	$\text{CF}_3\text{COSSCO}^+$
70	6.4	SF_2^+	193	7.9	$\text{CF}_3\text{COSSO}_2^+$
76	3.5	$\text{COSSO}_2\text{CO}^{++}$, CS_2^+	221	4.9	$\text{CF}_3\text{COSSO}_2\text{CO}^+$
			230	3.8	?
78	5.6	CF_2CO^+	290	14.3	$\text{CF}_3\text{COSSO}_2\text{COCF}_3^+$
82	11.1	?			

There are also minor peaks for masses: 29(COS^{++}), 35(CF_3^{++}), 40(CCO^+), 209($\text{CF}_3\text{COSSOSCF}_3^+$), 225($\text{CF}_3\text{COSSO}_2\text{S}^+$), 294($\text{CF}_3\text{SSO}_2\text{SCOCF}_3^+$).

formed which was very nonvolatile and had to be poured into the distilling flask. On exposure to air, fuming was noted, which possibly was due to the hydrolysis of B to H_3BO_3 . The syrupy liquid was heated to 60° while being pumped on and did not distill over. On cooling, it formed a solid. The hypothesis is that the trisubstituted adduct was formed: $(CF_3COS)_3B + 3HBr$.

The Reaction of NOCl with CF_3COSH

R. N. Haszeldine⁷ describes the preparation of CF_3NO by the irradiation of a mixture of trifluoriodomethane and nitric oxide in the presence of mercury. CF_3NO is intensely colored, deep blue, as a gas, a deep blue liquid and a purple solid. Mason (Banus)¹⁴ describes perfluoroalkylnitroso compounds as deep blue gases with a tinge of green, inky blue liquids and purple solids. Mason³ prepared CF_3SNO in 1969 by adding NOCl to the thiomercurial $Hg(SCF_3)_2$ at 196° and distilling out the product at -100° . It was also found that CF_3SH and NOCl gave the thionitrite but with lower yield and there was more difficulty in separating the product from the reactants. CF_3SNO is a deep red liquid and a red-black solid at -196° that boils at -3° and decomposes upon warming to NO and CF_3SSCF_3 .

When CF_3COSH was condensed with NOCl at -198° , a green solid immediately formed at the top of the cold finger region and a green liquid was produced as soon as the reactants were allowed to start warming. When cooled back down to -198° , a purplish-red solid was seen. On warming to room temperature, a yellow-green liquid resulted and a red-brown gas. An IR confirmed the presence of HCl gas.

The solution gradually faded to colorless. The melting point was approximately -3° (CF_3COS)₂ = 0.5° . Possibly the reaction formed the trifluorothiolacetylnitrite which then decomposed to NO and the disulfide: $\text{CF}_3\text{COSH} + \text{NOCl} = \text{CF}_3\text{COSNO} + \text{HCl}$; $2\text{CF}_3\text{COSNO} = (\text{CF}_3\text{COS})_2 + \text{NO}$.

This reaction would be of interest for future study not only for the preparation of an interesting new compound, but also because of the possibility of trapping stable intermediates and the promise of interesting magnetic susceptibility properties of the intensely colored compounds.

Reaction of NH_3 with CF_3COSH

CF_3COSH is known to react with organic nitrogen bases, pyridine and aniline, to produce the 1:1 adducts:²

and

It was thought that possibly the thioacid might react with ammonia, NH_3 , to produce the 1:1 adduct, $\text{CF}_3\text{COSH} \cdot \text{NH}_3$. The reactants were condensed together in a glass 200 ml pyrex reaction vessel, with a teflon stopcock. A white solid was produced as soon as the acid became liquid. After removal of volatiles (H_2S), the solid was sublimed for purification. The m.p. was $56-59^{\circ}$. The infrared spectra corresponded with CF_3CONH_2 (m.p. $72-75^{\circ}$).

A NEW METHOD OF SYNTHESIS OF TRIFLUOROTHIOACETIC ACID

Trifluoroacetic anhydride was added slowly from a dropping funnel to KSH in a round bottom flask connected to a -78° trap. The reaction occurred spontaneously producing the yellow CF_3COSH :

The volatiles were collected in a -198° trap. The product must be distilled in a spinning band column to collect the pure thioacid at 37.5° free from acid and anhydride impurities.

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