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Preparation and Reactions of *F*-*N*-Methanesulfenylacetimidoyl Chloride. Reactions with Nucleophiles

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Photolysis or thermolysis in a polar solvent of a mixture of trifluoromethanesulfenyl chloride, CF_3SCl, with trifluoromethylacetonitrile, CF_3CN, produces *F*-*N*-methanesulfenylacetimidoyl chloride, $CF_3SN=C(Cl)CF_3$. This new imidoyl chloride which has two nucleophilic centers at the sulfur and three-coordinate carbon undergoes base-catalyzed nucleophilic attack by CsF, alcohols [CF_3CH_2OH and $(CF_3)_2CHOH$], and amines [NH_3, CH_3NH_2, $(CH_3)_2NH$] to give rise to $CF_3SN=C(F)CF_3$, $CF_3SN=C(OCH_2CF_3)CF_3$, $CF_3SN=C[OCH(CF_3)_2]CF_3$, $CF_3SN=C(NH_2)CF_3$, $CF_3SN=C(N-HCH_3)CF_3$, and $CF_3SN=C[N(CH_3)_2]CF_3$. With CH_3NH_2 and $(CH_3)_2NH$, $CF_3SN(H)CH_3$ and $CF_3SN(CH_3)_2$ are also formed. The relative susceptibility of each center to attack as a function of the nucleophile used is discussed with respect to the product(s) isolated.

Introduction

Imidoyl halides, compounds of the type R—C(X)=N—R′ (X = halogen), contain a halo group with increased reactivity due to electronic assistance from the heteroatom attached to the carbon. This increased reactivity and the reactivity of imidoyl halides toward oxygen–hydrogen, sulfur–hydrogen, nitrogen–hydrogen bonds, etc. have been the subject of a number of reports.[1-3]

The addition reactions of trifluoromethanesulfenyl chloride to nitriles has been investigated,[4] e.g.
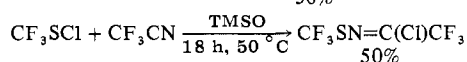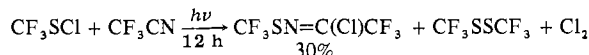
$$R_2NC\equiv N + CF_3SCl \rightarrow R_2NC(Cl)=NSCF_3 \quad (R = CH_3, C_2H_5)$$
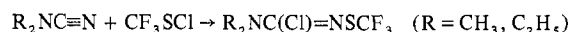
We find that CF_3SCl can be reacted similarly with trifluoromethylacetonitrile, CF_3CN, to form the new imidoyl chloride, $CF_3SN=C(Cl)CF_3$.

Earlier in this laboratory it was demonstrated that *F*-*N*-isopropylacetimidoyl chloride underwent reactions with alcohols and thiols to form totally and partially fluorinated imido esters and imido thioesters.[5,6] Similar reactions between $CF_3SN=C(Cl)CF_3$ and alcohols, thiols, or amines show that the imidoyl chloride is susceptible to nucleophilic attack at the sulfenyl sulfur as well as at the three-coordinate carbon. This factor allows for an alternate reaction route which greatly influences the reaction products obtained. The extent to which the nucleophiles reacted at each of the sites available is discussed theoretically and also is discussed in the context of the concept of hard and soft acids and bases.

Results and Discussion

F-*N*-Methanesulfenylacetimidoyl chloride, $CF_3SN=C(Cl)CF_3$, is synthesized from trifluoromethanesulfenyl chloride, CF_3SCl, and trifluoromethylacetonitrile, CF_3CN, either photolytically or thermally in the presence of a strongly polar solvent, i.e.

$$CF_3SCl + CF_3CN \xrightarrow[12\ h]{h\nu} CF_3SN=C(Cl)CF_3 + CF_3SSCF_3 + Cl_2$$
$$30\%$$

$$CF_3SCl + CF_3CN \xrightarrow[18\ h,\ 50\ °C]{TMSO} CF_3SN=C(Cl)CF_3$$
$$50\%$$

The latter is the preferred synthesis of $CF_3SN=C(Cl)CF_3$ because the competing reaction which occurs under photolytic conditions and results in a loss of the reactant, CF_3SCl, is not possible in this polar environment, i.e.

$$CF_3SCl \xrightarrow{h\nu} CF_3S\cdot + Cl\cdot$$

$$2CF_3S\cdot \rightarrow CF_3SSCF_3$$

$$2Cl\cdot \rightarrow Cl_2$$
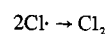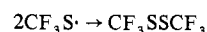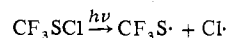
At temperatures less than 50 °C no secondary reactions are observed for the reaction carried out in tetramethylenesulfone

(TMSO). The reaction is slow at ambient temperatures, and at 50 °C after 18 h a conversion of 50% is obtained. Although with longer reaction times this conversion is improved, the amount of improvement does not compensate for the extra time required. A better procedure is to recycle the unreacted starting materials after increasing their concentrations. The use of higher reaction temperatures is hampered by the formation of bis(trifluoromethyl)disulfane with a concomitant decrease in the yield of the imidoyl chloride.

The reaction chemistry of $CF_3SN=C(Cl)CF_3$ is, in part, that of a typical imidoyl chloride in that the chlorine is labile and the adjacent carbon is subject to attack by nucleophiles, e.g., with cesium fluoride

$$CF_3SN=C(Cl)CF_3 + CsF \rightarrow CF_3SN=C(F)CF_3 + CsCl$$
$$(\sim100\%)$$
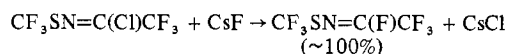
Reaction also occurs with alcohols, in the presence of a suitable base, i.e.

$$CF_3SN=C(Cl)CF_3 + ROH \xrightarrow{(CH_3)_3N} CF_3SN=C(OR)CF_3$$
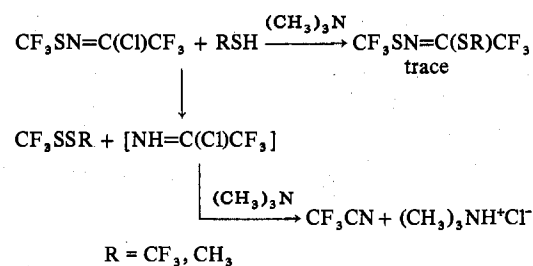$$+ (CH_3)_3NH^+Cl^-$$

$$R = CF_3CH_2, (CF_3)_2CH$$
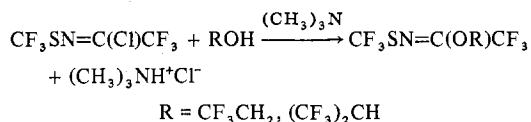
In the case of reactions with amines to form amidines, a twofold excess of the amine is used in order to allow for the formation of the chloride salt of the amine.

$$CF_3SN=C(Cl)CF_3 + 2RR'NH \rightarrow CF_3SN=C(NRR')CF_3 + RR'NH_2^+Cl^-$$

	A	B	C
R =	H	H	CH_3
R′ =	H	CH_3	CH_3
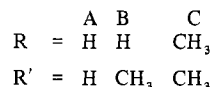
These new compounds are colorless or light yellow liquids at 25 °C which are stable indefinitely when stored in Pyrex glass at 25 °C. The infrared spectra of the new derivatives show characteristic absorption bands for the CF_3 groups in the 1000–1200-cm^{-1} region. The absorption band due to the C=N stretch varies from 1622 cm^{-1} [$CF_3SN=C(CF_3)$-$N(CH_3)_2$] to 1729 cm^{-1} [$CF_3SN=C(F)CF_3$] and is dependent on the group bonded to the carbon. [For $FSO_2N=C(C-F_3)N(CH_3)_2$, $\nu_{C=N}$ is 1620 cm^{-1}.[3]] Weakening of the C=N bond and therefore absorbance at a lower wavenumber are occurring due to an interaction with the heteroatom of the new group which results in a delocalization of the electron density. The absorption bands for the C=N bonds in the amine derivatives occur at lower wavenumbers than those for the alcohol derivatives and the imidoyl fluoride has the absorption band at 1729 cm^{-1}, indicating the strongest C=N bond of the compounds studied. The ^{19}F NMR spectra of the compounds show a resonance assignable to the CF_3S– group in the ap-
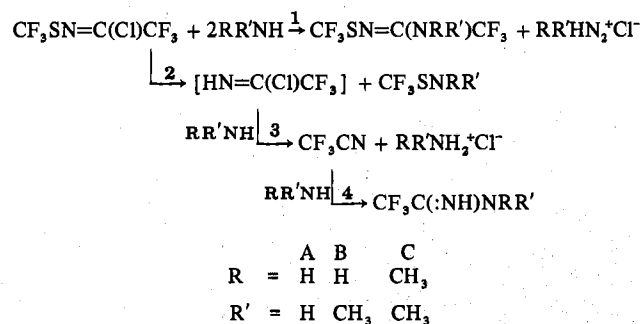
proximate range ϕ^* 50–54. The mass spectra contain strong molecular ion peaks as well as a strong peak for $(M - CF_3)^+$ and appropriate fragmentation patterns for all imidoyl compounds synthesized.

In addition to the above route of nucleophilic attack at the three-coordinated carbon, the sulfenyl sulfur is susceptible to attack also. This reaction mode is not observed with CsF or with the alcohols used, but rather the nucleophiles formed in these reactions react almost exclusively at the carbon to form the stable products. At the opposite extreme, reaction of $CF_3SN{=}C(Cl)CF_3$ with thiols (CF_3SH and CH_3SH) produced only trace amounts of the imidoyl derivatives and formed primarily the products expected from nucleophilic attack at the sulfur.

$$CF_3SN{=}C(Cl)CF_3 + RSH \xrightarrow{(CH_3)_3N} \underset{\text{trace}}{CF_3SN{=}C(SR)CF_3}$$

$$\downarrow$$

$$CF_3SSR + [NH{=}C(Cl)CF_3]$$

$$\xrightarrow{(CH_3)_3N} CF_3CN + (CH_3)_3NH^+Cl^-$$

$$R = CF_3, CH_3$$

This is in sharp contrast with the analogous reactions between $(CF_3)_2CFN{=}C(CF_3)Cl$ and thiols where the imido thioesters are formed in moderate yields.[5]

The reaction of $CF_3SN{=}C(Cl)CF_3$ with the amines tried yielded a mixture of products indicating that both sites were undergoing nucleophilic attack. The scheme is further complicated by the reaction of the amines with the trifluoromethylacetonitrile formed in the reaction.

$$CF_3SN{=}C(Cl)CF_3 + 2RR'NH \xrightarrow{1} CF_3SN{=}C(NRR')CF_3 + RR'HN_2^+Cl^-$$

$$\xrightarrow{2} [HN{=}C(Cl)CF_3] + CF_3SNRR'$$

$$\xrightarrow[RR'NH]{3} CF_3CN + RR'NH_2^+Cl^-$$

$$\xrightarrow[RR'NH]{4} CF_3C(:NH)NRR'$$

	A	B	C
R =	H	H	CH_3
R' =	H	CH_3	CH_3

Reaction 1 is a typical reaction of imidoyl chloride with amines to give amidines. Reaction 2, nucleophilic attack at the sulfur, results in the formation of CF_3SNH_2, $CF_3SN(H)CH_3$, and $CF_3SN(CH_3)_2$. Trifluoromethylmercaptoamine, CF_3SNH_2, has been reported and was identified from the literature.[9] In order to confirm the presence of $CF_3SN(H)CH_3$ and $CF_3SN(CH_3)_2$, the compounds were prepared by condensing together trifluoromethanesulfenyl chloride and an excess of the appropriate amine

$$CF_3SCl + 2R(CH_3)NH \rightarrow CF_3SN(R)CH_3 + R(CH_3)NH_2^+Cl^-$$

$$R = H, CH_3$$
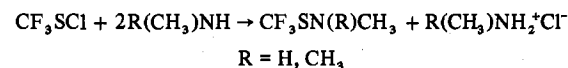
Reaction 4 accounts for the observation that smaller quantities of trifluoromethylacetonitrile than CF_3SNRR' were found in the reaction products. Trifluoromethylacetonitrile has been shown to react with amines under different conditions[10] in a similar manner to form the observed products $CF_3C(:NH)NH_2$, $CF_3C(:NH)NHCH_3$, and $CF_3C(:NH)-N(CH_3)_2$.

It is of interest to consider the above reactions with regard to the factors influencing the extent to which the nucleophiles tried attacked the susceptible sites in $CF_3SN{=}C(Cl)CF_3$. A comparison made by considering the percentage of the imidoyl

Table I

Reactant	% imidoyl deriv formed	
CsF	100	
(CF_3)_2CHOH	>95	
CF_3CH_2OH	>95	increasing
(CH_3)_2NH	90	attack at
CH_3NH_2	75	sulfur
NH_3	65	
CH_3SH	<1	
CF_3SH	<1	

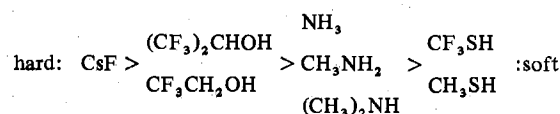derivative formed in each reaction is given in Table I.

There are many factors which influence nucleophilic reactivity and one author listed 17 different points of significance.[11] In considering the relative reactivity of nucleophiles in these reactions polarizability is most important since many of the other factors remain constant or do not apply to this system. Sulfenyl sulfur has two unshared pairs of outer-shell electrons and an electron cloud which may be easily distorted. If a nucleophile with similar characteristics, i.e., a polarizable nucleophile, is present, a number of possible effects warrant attention.

First, the polarization of bonding electrons in the nucleophile in the direction of the substrate lessens the repulsion between the extra electrons on the nucleophile and those on the substrate which result from the operation of the Pauli exclusion principle as well as simple electrostatic repulsion. Another factor is the polarization of nonbonding electrons on the nucleophile away from the substrate which reduces electrostatic repulsion between the nucleophile and the leaving group on the substrate.[12]

Also of significance is the possibility of the utilization of d orbitals for a degree of π bonding between the nucleophile and the substrate thereby strengthening the transition state which results from the attack at the sulfur in a manner not possible with nucleophilic attack at the carbon.

In the reactions tried we find that when the nucleophile is a sulfur-containing anion, CF_3S^- or CH_3S^-, attack occurs almost exclusively at the sulfenyl sulfur of $CF_3SN{=}C(Cl)CF_3$. Here an additional factor, which is not as significant in the other reactions, is an effect of van der Waals forces which has been observed earlier.[13] These forces are proportional to the polarizability of the atoms involved and grow small with increasing distance due to an inverse proportionality to distance; however, in the transition state they may contribute to a lowering of the energy and therefore increase the reaction rate. Such an effect would be most prominent in a reaction involving two atoms of high polarizability and it is just such a reaction with thiols in which we find, by far, the preferred site of nucleophilic attack to be the sulfenyl sulfur. The effect becomes less important as we consider the other members of the series in Table I. Therefore, as polarizability decreases, the primary point of attack shifts from the sulfur to the carbon.

Others have related the concept of hard and soft acids and bases to nucleophilic reactions[14] and specifically to nucleophilic displacement at sulfenyl sulfur.[15,16] By using this approach for $CF_3SN{=}C(Cl)CF_3$, the three-coordinate carbon is susceptible to nucleophilic attack by hard bases and the sulfenyl sulfur is susceptible to attack by soft bases. On the basis of existing tables which attempt to classify bases in a general manner[14] we would classify the reactants tried with respect to relative hardness as

$$\text{hard:} \quad CsF > \underset{CF_3CH_2OH}{\overset{(CF_3)_2CHOH}{}} > \underset{(CH_3)_2NH}{\overset{NH_3}{CH_3NH_2}} > \underset{CH_3SH}{\overset{CF_3SH}{}} \quad \text{:soft}$$

If we relate our experimental data in Table I to this order, we find that the reactants tending to be designated as hard

do react primarily at the carbon whereas those tending to be designated as soft react primarily at the sulfur. It is not possible to make a valid comparison based only on our experimental data which would relate the compounds within each grouping, i.e., alcohols or amines.

The correlation between our findings and the concept of hard and soft acids and bases is not surprising since the factor which we feel is of significance in determining the reaction route for a particular nucleophile, e.g., polarizability, is also of primary importance in classifying an acid or base as hard or soft.

Experimental Section

Material. Trifluoromethanethiol[7] and trifluoromethylsulfenyl chloride[8] were prepared by literature methods, purified using low-temperature vacuum distillation techniques, and identified by infrared spectroscopy. The following compounds were used as purchased from the sources indicated: CF_3CN, $(CF_3)_2CHOH$, and CF_3CH_2OH (PCR), CsF and $(CH_3)_3N$ (Baker), CH_3NH_2 (Linde), and $(CH_3)_2NH$ (Matheson).

Apparatus. All gases and volatile liquids were handled in a conventional Pyrex-glass vacuum apparatus using standard *PVT* techniques. Purification of products was by low-temperature vacuum distillation techniques. In some cases, final purification was obtained by gas chromatography using a column constructed of 0.25-in. copper tubing packed with 37% FS-1265 on Chromosorb P or 25% dimethyl sulfone on Chromosorb P. Helium was used as a carrier gas. Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrophotometer by using a 10-cm gas cell fitted with KBr windows. Spectra of nonvolatile liquids were obtained by placing a drop of the compound between two KBr plates. Varian HA-100 and EM-360 nuclear magnetic resonance spectrometers were used for ^{19}F and ^1H spectra with CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The mass spectra were determined on a Hitachi Perkin-Elmer RMU 6-E mass spectrometer. Vapor pressure studies were made by an isoteniscopic method. Elemental analysis were performed by Beller Laboratories in Göttingen, Germany, or by Mr. D. Harsch at the University of Idaho.

Preparation of $CF_3SN=C(Cl)CF_3$. Photolysis. Into a 300-mL Pyrex reaction vessel equipped with a Kontes Teflon stopcock were condensed 5 mmol of CF_3CN and an excess of CF_3SCl. Upon warming to ambient temperature the mixture was photolyzed for 12 h with a Hanovia Utility ultraviolet quartz lamp. The resulting mixture was then separated via low-temperature vacuum distillation techniques; yield 30%.

Thermolysis. Into a 50-mL Pyrex reaction vessel equipped with a Kontes Teflon stopcock containing 5 mL of tetramethylene sulfone were condensed 7 mmol each of CF_3CN and CF_3SCl. The reaction mixture was allowed to warm slowly from -196 to $+50$ °C and was maintained at this temperature for 18 h. The resulting mixture was then separated via low-temperature vacuum distillation techniques and further purified using gas chromatography: conversion 50% after 18 h; IR 1647 (vs), 1607 (m), 1313 (s, sh), 1291 (vs), 1229 (vs), 1190 (vs), 1130 (vs), 1022 (w), 968 (vs), 807 (s), 766 (m), 714 (s), 552 (w), 471 cm^{-1} (m); NMR ϕ^* 49.9 (s, CF_3S), 71.0 (s, CF_3C). The equation log $P_{mm} = 7.84 - 1676.9/T$ describes the vapor pressure curve from which ΔH_v (7.67 kcal/mol), ΔS_v (22.7 eu), and the boiling point (65.0 °C) are obtained. Anal. Calcd: F, 49.4; C, 15.58. Found: F, 49.7; C, 15.63.

Preparation of $CF_3SN=C(F)CF_3$. Into a 50-mL Pyrex reaction vessel equipped with a Kontes Teflon stopcock containing an excess of dry CsF was condensed 3 mmol of $CF_3SN=C(Cl)CF_3$. The reaction mixture was allowed to warm slowly from -196 to $+50$ °C and was maintained at this temperature for several hours. The resulting mixture was then separated via low-temperature vacuum distillation techniques and further purified using gas chromatography: yield 65%; IR 1729 (s), 1343 (vs), 1323 (w, sh), 1239 (vs), 1190 (vs), 1131 (vs), 1100 (vs), 855 (m), 765 (w), 751 (w), 720 (s), 475 cm^{-1} (w); NMR ϕ^* 51.0 (s, CF_3S), 72.4 (d, CF_3C), 36.0 (t, F–C); J_{F-CF_3} = 4.46 Hz. The equation log $P_{mm} = 7.69 - 1464.9/T$ describes the vapor pressure curve from which ΔH_v (6.70 kcal/mol), ΔS_v (22.0 eu), and the boiling point (31.6 °C) are obtained. Anal. Calcd: F, 61.9; C, 16.74. Found: F, 61.7; C, 16.85.

Preparation of $CF_3SN=C(CF_3)OCH_2CF_3$ and $CF_3SN=C(CF_3)OCH(CF_3)_2$. Into a 25-mL Pyrex reaction vessel equipped with a Kontes Teflon stopcock were condensed 5 mmol each of the appropriate alcohol [CF_3CH_2OH or $(CF_3)_2CHOH$], $CF_3SN=C(Cl)CF_3$, and $(CH_3)_3N$. The reaction mixture was allowed to warm slowly from -196 to $+25$ °C and was maintained at this temperature for 2 h. The resulting mixture was then separated via low-temperature vacuum distillation techniques.

$CF_3SN=C(CF_3)OCH_2CF_3$: yield 95%; IR 3472 (m), 1686 (vs), 1419 (s), 1342 (vs), 1269 (vs), 1222 (m), 1185 (vs), 1179 (s, sh), 1155 (s), 1132 (vs), 1033 (m), 980 (s), 977 (s), 925 (s), 890 (w), 841 (m), 749 (s), 691 (m), 670 (w), 560 (m), 511 (w), 422 cm^{-1} (w); NMR ϕ^* 53.7 (s, CF_3S), 70.6 (s, $CF_3C=N$), 74.7 (t, CF_3CH_2); τ 5.5 (q, CH_2CF_3); $J_{CH_2CF_3}$ = 7.8 Hz. The equation log $P_{mm} = 7.92 - 1878.3/T$ describes the vapor pressure curve from which ΔH_v (8.56 kcal/mol), ΔS_v (23.1 eu), and the boiling point (99.6 °C) are obtained. Anal. Calcd: N, 4.75; C, 20.34; H, 0.68. Found: N, 4.92; C, 20.42; H, 0.72.

$CF_3SN=C(CF_3)OCH(CF_3)_2$: yield 95%; IR 2985 (m), 1699 (s), 1382 (s), 1333 (s), 1298 (vs), 1272 (s), 1239 (vs), 1215 (vs), 1190 (vs), 1179 (vs), 1161 (vs), 1129 (vs), 1120 (s, sh), 1068 (m), 943 (s), 908 (m), 861 (m), 748 (s), 692 (m), 658 (w), 560 (w), 516 (w), 482 (w), 439 cm^{-1} (w); NMR ϕ^* 53.6 (s, CF_3S), 70.5 (s, $CF_3C=N$), 74.0 (d, CF_3CO); τ 4.3 (septet, CH); J_{HF} = 5.8 Hz. The equation log P_{mm} = 7.70 – 1752.4/T describes the vapor pressure curve from which ΔH_v (8.02 kcal/mol), ΔS_v (22.0 eu), and the boiling point (90.7 °C) are obtained. Anal. Calcd: N, 3.86; C, 19.83; H, 0.28. Found: N, 3.95; C, 19.57; H, 0.34.

Preparation of $CF_3SN=C(CF_3)NH_2$, $CF_3SN=C(CF_3)N(H)CH_3$, and $CF_3SN=C(CF_3)N(CH_3)_2$. Into a Pyrex reaction vessel as above were condensed 5 mmol of $CF_3SN=C(Cl)CF_3$ and 10 mmol of ammonia or the appropriate amine [NH_3, CH_3NH_2, or $(CH_3)_2NH$]. The reaction mixture was allowed to warm slowly from -196 to $+25$ °C and was maintained at this temperature for 2 h. The resulting mixture was then separated via low-temperature vacuum distillation techniques.

$CF_3SN=C(CF_3)NH_2$: yield 65%; IR 3492 (m), 3398 (m), 3200 (w), 1673 (s), 1612 (m), 1412 (s), 1220 (s, sh), 1175 (s, sh), 1150 (vs), 1118 (vs), 1009 (w), 860 (w), 769 (m), 755 (m), 682 cm^{-1} (m); NMR ϕ^* 50.00 (s, CF_3S), 72.7 (s, CF_3C); τ 4.96 (s, br, NH_2). The equation log $P_{mm} = 8.02 - 2080.3/T$ describes the vapor pressure curve over a range 49–117 °C. The boiling point is 110 °C (390 mm). Slight decomposition begins at approximately 117 °C. Anal. Calcd: N, 13.21; C, 16.98; H, 0.94. Found: N, 13.43; C, 16.86; H, 1.21.

$CF_3SN=C(CF_3)N(H)CH_3$: yield 75%; IR 3470 (m), 3050 (w), 2950 (w), 2903 (w), 1681 (m, sh), 1650 (vs), 1532 (s), 1465 (m), 1426 (m), 1404 (s), 1238 (m, sh), 1198 (vs), 1150 (vs), 1118 (vs), 1035 (m), 1000 (m), 883 (m), 762 (m), 742 (s), 698 (s) cm^{-1}; NMR ϕ^* 53.12 (s, CF_3S), 70.97 (s, CF_3C); τ 4.8 (br, NH), 7.15 (d, CH_3). The equation log $P_{mm} = 7.28 - 1821.3/T$ describes the vapor pressure curve over a range 66–114 °C. The boiling point is 114 °C (402 mm). Some decomposition begins at approximately 114 °C. Anal. Calcd: N, 12.38; C, 21.23; H, 1.76. Found: N, 12.19; C, 21.14; H, 1.68.

$CF_3SN=C(CF_3)N(CH_3)_2$: yield 90%; IR 3440 (m, br), 1641 (m, sh), 1622 (vs), 1422 (w), 1400 (s), 1275 (m), 1242 (m), 1188 (vs), 1130 (vs, br), 922 (m), 760 (w), 743 (m), 705 (w) cm^{-1}; NMR ϕ^* 55.3 (s, CF_3S), 63.9 (s, CF_3C); τ 7.22 [s, br, $N(CH_3)_2$]. The proton spectrum appears to be temperature dependent. The equation log $P_{mm} = 8.86 - 2392.3/T$ describes the vapor pressure curve from which ΔH_v (9.65 kcal/mol), ΔS_v (24.1 eu), and the boiling point (126.9 °C) are obtained. Anal. Calcd: N, 11.67; C, 25.00; H, 2.50. Found: N, 11.57; C, 25.38; H, 2.63.

Preparation of $CF_3SN(H)CH_3$ and $CF_3SN(CH_3)_2$. These compounds result as by-products in the reactions of CH_3NH_2 and $(CH_3)_2NH$, respectively, with $CF_3SN=C(Cl)CF_3$. For purposes of comparison, they have also been synthesized by an alternate route. Into a Pyrex reaction vessel were condensed 3 mmol of CF_3SCl and 6 mmol of the appropriate amine [CH_3NH_2 or $(CH_3)_2NH$]. The reaction mixture was allowed to warm slowly from -196 to $+25$ °C and was maintained at this temperature for 2 h. The resulting mixture was then separated via low-temperature vacuum distillation techniques.

$CF_3SN(H)CH_3$: yield 95%; IR 3402 (m), 2950 (s), 2900 (m, sh), 2820 (w), 2250 (w, br), 1460 (m), 1290 (m), 1170 (vs), 1135 (vs), 1095 (m), 1070 (m, sh), 975 (m), 790 (w), 754 (m), 515 (m), 467 (w) cm^{-1}; NMR ϕ^* 53.0 (CF_3); τ 6.2 (br, NH), 7.5 (CH_3). Coupling is complex and temperature dependent. The mass spectrum contains a strong molecular ion peak at m/e 131 as well as strong peaks for CF_3SN^+ (m/e 114) and $CH_3N(H)S^+$ (m/e 62).

$CF_3SN(CH_3)_2$: yield 95%; IR 3000 (m), 2942 (s), 2890 (s), 2845 (m), 2804 (m), 1460 (s), 1285 (w), 1250 (m), 1202 (s), 1160 (vs), 1130 (vs), 1100 (m, sh), 1040 (m), 976 (s), 747 (m), 668 (m), 560 (m), 465 (m) cm^{-1}; NMR ϕ^* 47.6 (septet, CF_3); τ 7.05 (q, CH_3); $J_{CH_3CF_3}$ = 1.2 Hz. The mass spectrum contains a strong molecular ion peak at m/e 145 as well as strong peaks for CF_3SN^+ (m/e 114) and $(CH_3)_2NS^+$ (m/e 76).

CF_3CN, 353-85-5; CF_3SCl, 421-17-0; CsF, 13400-13-0; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3.

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Stoichiometry of the Reaction of Sulfites with Hydrogen Sulfide Ion

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The aqueous reaction of sulfites with HS$^-$ ion to yield $S_2O_3^{2-}$ ion is dependent upon [H$^+$], and the stoichiometry of the reaction has been investigated. A molar equivalency of sulfur to hydrogen has been found to be essential for reaction such that if HS$^-$ ion is the sulfide species, the protonated sulfite, HSO$_3^-$ ion, may be considered the sulfite species, and the equation for the reaction should be written $2HS^- + 4HSO_3^- \rightarrow 3S_2O_3^{2-} + 3H_2O$. Free SO_3^{2-} ion will not react with HS$^-$ ion at room temperature.

Introduction

Generally, the reaction of sulfites with sulfides in aqueous solution is considered to produce thiosulfate ion with the possibility of additional, more complex polythionates. Furthermore, the reaction appears to proceed by a stepwise mechanism and involves an unstable thiosulfurous ion intermediate.[1] The dependency of the overall reaction upon hydrogen ion concentration, however, has not been adequately determined.

Isotopic labeling experiments indicate the stepwise nature of the reaction.[2,3] Thiosulfate ion produced by the reaction of H_2S^{35} with HSO$_3^-$ ion, SO_3^{2-} ion, and SO_2 in NaOH has been hydrolyzed in acid solution to recover the elemental sulfur. Of the elemental sulfur recovered, $^2/_3$ was ^{35}S promoting the conclusion that $^2/_3$ of the sulfur originated from the H_2S, while the remaining $^1/_3$ was provided by the sulfite species. Equations 1 and 2 were suggested whereby elemental sulfur is generated initially followed by subsequent addition of the sulfur to excess sulfite ions.

$$2H_2{}^{35}S + SO_3{}^{2-} \rightarrow 2H_2O + 2{}^{35}S + S \tag{1}$$

$$3SO_3{}^{2-} + 2{}^{35}S + S \rightarrow 2{}^{35}SSO_3{}^{2-} + SSO_3{}^{2-} \tag{2}$$
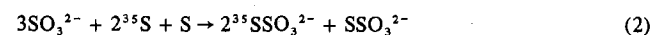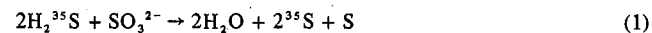
Foerster et al,[4,5] had shown earlier that thiosulfate ion, $S_2O_3^{2-}$, decomposes in acid solution to yield HSO$_3^-$ ion and elemental sulfur by an equilibrium reaction. Consequently, sulfur adds to HSO$_3^-$ ion to produce $S_2O_3^{2-}$ ion, and eq 2 may involve HSO$_3^-$ ion instead of the nonprotonated form, SO_3^{2-}.

The two-step mechanism given by eq 3 and 4 is proposed and has been investigated. The noteworthy feature of this

$$2HS^- + HSO_3{}^- \rightarrow 3S + 3^-OH \tag{3}$$

$$S + HSO_3{}^- \rightarrow S_2O_3{}^{2-} + H^+ \tag{4}$$

mechanism is that HSO$_3^-$ is necessary in both steps. Adding

eq 3 and 4 leads to the overall reaction given by eq 5.

$$2HS^- + 4HSO_3{}^- \rightarrow 3S_2O_3{}^{2-} + 3H_2O \tag{5}$$
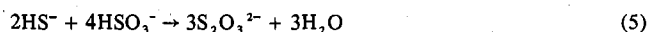
Hydrogen sulfide ion, HS$^-$, has been chosen as the sulfide species for this investigation because it is the predominant sulfide species present in solution in the pH range ($\sim$5–9) of interest.

Experimental Section

A Fisher Accumet Model 120 pH meter in conjunction with a combination electrode was used for all pH measurements. The pH measurements were made without undue delay to avoid contamination of the electrode by HS$^-$ ion.

Precipitated sulfur was identified from infrared spectra measured using a Perkin-Elmer Model 457 infrared spectrophotometer. Carbon disulfide solvent and a 0.1 mm NaCl cell were used. Spectra were obtained with respect to air reference in the spectral region of 600–400 cm^{-1} to observe the characteristic sulfur absorption at 466 cm^{-1}.

Potassium Hydrogen Sulfide, KHS, Solution. The KHS solution used throughout this study was prepared by neutralizing H_2S with an equivalent amount of standard aqueous KOH.

The H_2S was bubbled through KOH solution with nitrogen carrier gas until the weight of the solution increased by a weight equivalent to the neutralization products dictated by eq 6. Nitrogen carrier

$$H_2S + KOH \rightarrow KHS + H_2O \tag{6}$$

gas was used as a diluent to slow the neutralization reaction.

The KHS was determined by reacting the sulfide with excess standard iodine solution and back-titrating the excess I_2 with standard $Na_2S_2O_3$ solution using starch indicator for end point detection. Standard HCl solution was used to acidify the iodine solution, and the KOH was determined by back-titration of the acid with standard NaOH to the phenolphthalein end point. Any HCl not recovered was considered to have been consumed by the KOH and directly equivalent to the KOH concentration. Since the determination of KHS produces hydriodic acid, HI, which is also titrated by NaOH, compensation