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N,N-Difluoro-O-pentafluorosulfanylhydroxylamine

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Received July 15, 1965

The reaction of tetrafluorohydrazine with pentafluorosulfur hypofluorite produced the new compound, N,N-difluoro-O-pentafluorosulfanylhydroxylamine. Several reactions of this material and the related N,N-difluorohydroxylamine O-fluorosulfonate are discussed.

The chemistry of pentafluorosulfur hypofluorite has been the subject of several recent investigations.[1-3] Addition of a fluorine atom and the SF_5O group to substrates such as sulfur dioxide or perfluoroolefins has been observed as well as fluorination of the substrate. It was found in this study that the interaction of pentafluorosulfur hypofluorite and tetrafluorohydrazine produced N,N-difluoro-O-pentafluorosulfanylhydroxylamine. A limited comparison of the chemical reactivity of N,N-difluoro-O-pentafluorosulfanylhydroxylamine with that of N,N-difluorohydroxylamine O-fluorosulfonate[4] was made since both compounds contain an ONF_2 group bonded to sulfur. Marked differences were observed when the two compounds were allowed to interact with a Lewis acid or several anionic nucleophiles.

Experimental

Preparation of SF_5ONF_2.—A typical procedure for the preparation of SF_5ONF_2 is given below. The data are taken from one of the better runs. The reactor employed in this run had been used for two previous runs and contained an unidentified nonvolatile white solid. A 1.471-mmole sample of SF_5OF and N_2F_4 (1.474 mmoles) were condensed together into a 250-ml. Pyrex bulb. The mixture was allowed to stand for 10 hr. before vacuum line fractionation through −78°, −130° (*n*-pentane slush bath), and −196° cold baths. The contents of the −196° trap consisted of 0.668 mmole of NF_3 along with smaller amounts of NO, SO_2F_2, and SF_4O. The product, 1.126 mmoles, contaminated with SF_4O and SO_2F_2 was found in the −130° trap. Refractionation served to remove these contaminants.

Anal. Calcd. for SF_5ONF_2: N, 7.18; F, 68.2. Found: N, 7.04; F, 66.5.

Reaction of SF_5ONF_2 with BF_3.—A 1.769-mmole sample of SF_5ONF_2 and BF_3 (1.738 mmoles) were condensed together into a 250-ml. Pyrex bulb. The mixture was allowed to warm slowly to 25° and stand for 3 hr. The volatile products were fractionated through −126° (methylcyclohexane slush bath) and −196° cold traps. Sulfur hexafluoride, 1.672 mmoles, was obtained in the −196° trap together with approximately 0.01 mmole each of SF_5ONF_2, SO_2F_2, and SiF_4. The −126° trap contained 0.04 mmole of SF_5ONF_2 and 0.01 mmole of $S_2O_5F_2$. Nitrosonium tetrafluoroborate, 0.1755 g., remained in the reactor.

Anal. Calcd. for $NOBF_4$: N, 11.99; F, 65.1. Found: N, 11.72; F, 64.6.

Reaction of FSO_2ONF_2 with NaCl.—A 0.796-mmole sample of FSO_2ONF_2 was condensed into a glass reactor containing 0.15 g. of NaCl in 2 ml. of dry CH_3CN. The mixture was stirred 2 hr. before fractionation. A 0.758-mmole sample of NF_2Cl was obtained in the −196° trap. Only traces of volatile sulfur-containing compounds were formed.

Reaction of FSO_2ONF_2 with CsF.—A 0.721-mmole sample of FSO_2ONF_2 was condensed into a 150-ml. Monel bomb containing 5 g. of CsF. The mixture stood for 2 hr. at 25°. The workup of the product was performed in an all-metal vacuum line which had been prefluorinated. A total of 1.41 mmoles of volatile products was obtained. Infrared analysis, using a Monel cell equipped with BaF_2 windows, showed only NOF, SO_2F_2, and a trace of NO_2. These volatile products were then treated with 0.821 mmole of BF_3. A white solid formed which was identified as $NOBF_4$ by its infrared spectrum. Fractionation of the remaining volatile products yielded 0.701 mmole of SO_2F_2 and traces of NO_2 and BF_3.

Analyses.—Weighed gaseous samples were analyzed for nitrogen by the Dumas method and for fluorine by hydrolysis with aqueous 30% KOH. The fluoride ion liberated was titrated with thorium nitrate.

Vapor Pressure of SF_5ONF_2.—The vapor pressure of SF_5ONF_2 was determined by the method of Kellogg and Cady.[5] The data are T (°C.), P (mm.): −58.2, 58.7; −51.7, 89.6; −98.3, 107.4; −47.5, 113.0; −46.6, 121.9; −42.8, 149.5; −40.1, 172.1; −31.5, 273.4; −30.3, 288.3; −27.0, 345.6; −24.9, 393.5; −20.1, 486.0; and −17.1, 553.2. The Clausius–Clapeyron equation gives a boiling point of −10.0°, a Trouton constant of 22.8, and $\Delta H_{\text{vap}} = 5.99$ kcal./mole.

N.m.r. and Infrared Spectra.—The infrared spectrum of SF_5ONF_2 was obtained using a Perkin-Elmer Model 21 spectrophotometer. The bands were observed in the spectrum at 1042 (w), 942 (vs) 868 (ms) 845 (sh), 794 (ms), and 712 (vw) cm.$^{-1}$. The F^{19} n.m.r. spectrum of SF_5ONF_2 was obtained on a 15% solution in CCl_3F using a Varian Model V4310A spectrometer operating at 40 Mc. The chemical shifts are reported in ϕ units, which are p.p.m. relative to CCl_3F.

Mass Spectrum.—The cracking pattern of SF_5ONF_2 was obtained with a Consolidated Engineering Corp. Model 21-620 spectrometer using an ionization potential of 100 v. The mass number, species, and relative abundance for some of the more prominent peaks are listed below: 127, SF_5^+, 100%; 108, SF_4^+, 5.9%; 105, SF_3O^+, 52.2%; 89, SF_3^+, 18.4%; 86, SF_2O^+, 14.5%; 70, SF_2^+, 8.1%; 67, FSO, 14.7%; 64, SO_2^+, 2.9%; 52, NF_2^+, 61.7%; 51, SF^+, 6.6%; 48, SO^+, 5.2%; 33, NF^+, 7.5%; 32, O_2^+, 14.2%; and 30, NO^+, 55.2%. The appearance potentials were determined by the vanishing current method using argon as a voltage standard.[6] A molecular weight of SF_5ONF_2 was obtained by the effusion method.[7] Using the three peaks of mass number 127, $(SF_5)^+$, 105 (SF_3O^+), and 52 (NF_2^+), the following values were found: 188, 189, and 192, respectively. The molecular weight by vapor density was 193 (calcd. value 195).

Results and Discussion

The reaction between tetrafluorohydrazine and pentafluorosulfur hypofluorite was found to proceed readily

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[1] C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 298 (1961).

[2] G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1963).

[3] S. M. Williamson and G. H. Cady, *ibid.*, **1**, 673 (1962).

[4] M. Lustig and G. H. Cady, *ibid.*, **2**, 388 (1963).

[5] K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[6] G. S. Paulett and M. Lustig, *ibid.*, **87**, 1020 (1965).

[7] M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951).

at ambient temperature and both reactants were completely consumed.

$$N_2F_4 + SF_5OF \longrightarrow NF_3 + SF_5ONF_2$$

The reaction, however, was not as straightforward as is implied by the above equation. The yield of N,N-difluoro-O-pentafluorosulfanylhydroxylamine was not reproducible and varied between 5 and 85%. Large amounts of thionyl tetrafluoride and a nonvolatile white solid were formed in the less successful runs. The reason for this behavior is not known but it does not seem to depend on the mole ratio of the reactants or on their partial pressure as much as it does on the history of the reactor.

The infrared spectrum of N,N-difluoro-O-pentafluorosulfanylhydroxylamine contains several bands in the NF and SF regions. Definite assignment of all the bands cannot be made. However, the band at 1042 cm.$^{-1}$ is almost certainly due to the NF_2 group since a band attributed to the NF_2 group in the closely related compound, N,N-difluorohydroxylamine O-fluorosulfonate, was found at 1032 cm.$^{-1}$.[4] The band at 939 cm.$^{-1}$ probably arises from the SF_5 group since a large number of pentafluorosulfur derivatives have absorption bands in this region.

The F^{19} n.m.r. spectrum of N,N-difluoro-O-pentafluorosulfanylhydroxylamine consists of a broad band centered at $-130\ \phi$, assigned to the NF_2 group, and a series of bands in the SF region which are typical of a AB_4 group. In this AB_4 spectrum, the B shift is at $-62.3\ \phi$ and the A shift at $-57.9\ \phi$. The chemical shift difference is therefore 4.4 ϕ or 176 c.p.s. (δ_{AB}). Matching the observed peaks to the AB_4 transitions of the calculated spectra of Wibert and Nist[8] indicates the closest fit is obtained for $J/\delta = 1.0$. Use of the shift between the outermost "B" line ($-66.0\ \phi$) and the next strong line ($-63.1\ \phi$) indicates a better fit is at a J/δ of 0.90; a similar procedure for the "A" lines at 55.1 and 57.9 ϕ gives a J/δ of 0.88[9] or (using the average value of J/δ) $J_{AB} = 157$ c.p.s. The F^{19} n.m.r. spectrum of the SF_5 group was calculated using these values of J_{AB} and δ_{AB} by the NMRIT program developed by Swalen and Reilly.[10] Excellent agreement between the calculated and observed chemical shifts for the nondegenerate transitions was obtained (*i.e.*, obsd. -325 ± 3 c.p.s., calcd. -327 c.p.s.; obsd. -85 ± 2 c.p.s., calcd. -84.5 c.p.s.; obsd. 115 ± 1 c.p.s., calcd. 114.1 c.p.s.; and obsd. 199 ± 1 c.p.s., calcd. 198.6 c.p.s.).

The mass spectrum cracking pattern of N,N-difluoro-O-pentafluorosulfanylhydroxylamine contains strong peaks corresponding to the molecular ions SF_5^+, NF_2^+, NO^+, and SF_3O^+. The appearance potentials of the SF_5^+ ion and the NF_2^+ ion were found to be 13.3 ± 0.2 and 16.2 ± 0.2 e.v., respectively. The value obtained for the NF_2^+ ion is close to that found when the same ion was formed from pentafluorosulfur difluoramine.[6] Assuming the process

$$SF_5ONF_2 \xrightarrow{-e} NF_2^+ + SF_4O + F$$

the O–N bond dissociation energy was calculated from the expression

$$D_{ON} = \text{A.P.}_{NF_2^+} - \text{I.P.}_{NF_2} - D_{S-F}$$

It was found to be 30 kcal./mole, which is close to the value of 35 kcal./mole calculated for D_{O-N} in N,N-difluorohydroxylamine O-fluorosulfonate.[6] As was found for the case of pentafluorosulfur difluoramine no process could be written which is compatible with the low value of the appearance potential of the SF_5^+ ion and therefore an estimate of the S–O bond energy could not be made.

N,N-Difluoro-O-pentafluorosulfanylhydroxylamine is a colorless gas which may be handled in glass apparatus. It is thermally stable to 150° in a Monel reactor as is N,N-difluorohydroxylamine O-fluorosulfonate. However, treatment of N,N-difluoro-O-pentafluorosulfanylhydroxylamine with boron trifluoride at ambient temperature resulted in a rapid reaction and sulfur hexafluoride and nitrosonium tetrafluoroborate were isolated in high yield.

$$SF_5ONF_2 + BF_3 \longrightarrow SF_6 + NOBF_4$$

No reaction was observed between boron trifluoride and N,N-difluorohydroxylamine O-fluorosulfonate under the same conditions.

A difference in reactivity of the two difluorohydroxylamine derivatives toward nucleophiles was also noted. N,N-Difluoro-O-pentafluorosulfanylhydroxylamine was found to be inert to such anions as chloride or fluoride in acetonitrile or to solid cesium fluoride at 150°. On the other hand, N,N-difluorohydroxylamine O-fluorosulfonate was readily attacked by such anions either in solution or in the dry state. Thus treatment with sodium chloride in acetonitrile solution resulted in the formation of chlorodifluoroamine in 90% yield.

$$FSO_2ONF_2 + Cl^- \longrightarrow FSO_3^- + ClNF_2$$

The presence of the fluorosulfate anion was confirmed by infrared analysis.[11] An attempt to extend this reaction to include sodium azide was not successful and only equimolar quantities of sulfuryl fluoride, nitrogen, and dinitrogen oxide were isolated. When N,N-difluorohydroxylamine O-fluorosulfonate was treated with cesium fluoride a different type of reaction appeared to occur. Sulfuryl fluoride and nitrosyl fluoride were produced instead of the expected nitrogen trifluoride.

$$FSO_2ONF_2 \xrightarrow{F^-} FSO_2F + NOF$$

It is probable that the chloride and fluoride ions attack at different sites in the molecule, as has been observed previously.[12,13]

Acknowledgment.—The author wishes to thank Drs. F. A. Johnson and G. S. Paulett for the n.m.r. interpretation and appearance potential measurements. This work was performed under Contract No. DA-01-021 ORD-11878 (Z) Modification No. 11.

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[8] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

[9] C. I. Merrill, S. M. Williamson, G. H. Cady, and O. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

[10] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

[11] D. W. A. Sharp, *J. Chem. Soc.*, 3761 (1957).

[12] J. K. Ruff, *Inorg. Chem.*, **4**, 567 (1965).

[13] Note Added in Proof.—*After submission of this article for publication, an article on the preparation of N,N-difluoro-O-pentafluorosulfanylhydroxylamine appeared:* W. H. Hale, Jr., and S. M. Williamson, *Inorg. Chem.*, **4**, 1342 (1965).