3100 *Inorg. Chem.* **1988**, *27*, 3100-3104

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Reactions of (Difluoroamino)difluoroacetonitrile and (Difluoroamino)difluoroacetamidoxime

Earnest Obed John and Jean'ne M. Shreeve*

Received March 14, 1988

(Difluoroamino)difluoroacetonitrile, NF_2CF_2CN, was reacted with ammonia, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, hydroxylamine and hydrazine to give the corresponding amidine, imidates, amidoxime, and diamidine. After being heated at 135 °C for 2 days, (difluoroamino)difluoroacetamidine undergoes cyclization to form 1-amino-3,5-bis[(difluoroamino)difluoromethyl]triazine. While the monosubstituted hydrazine $F_2NCF_2C(=NH)NHNH_2$ is only stable in solution, the bis(iminomethyl)hydrazine $F_2NCF_2C(=NH)NHNHC(=NH)CF_2NF_2$ is a stable sublimable solid. (Difluoroamino)difluoroacetamidoxime, $F_2NCF_2C(=NOH)NH_2$, is acylated with perfluoroacyl chlorides $R_fC(O)Cl$ ($R_f = CF_3$, C_2F_5, C_3F_7) to form $F_2NCF_2C(=NOC(O)R_f)NH_2$. The latter are cyclized by dehydration with P_4O_{10} to give the respective 1,2,4-oxadiazoles, $F_2NCF_2C{=}NOC(R_f){=}N$. With phosgene, $F_2NCF_2C(=NOC(O)Cl)NH_2$ is formed. Thermolysis of the latter at 100 °C results in loss of HCl giving $F_2NCF_2C{=}NOC(O)NH$. The acetamidoxime with perfluorosuccinic acid (1:1) gives $(-CF_2C{=}NC{=}N(CF_2NF_2)O)_2$ in the presence of P_4O_{10}.

Introduction

Highly fluorinated nitrogen compounds that contain the $-NF_2$ functionality are high-energy materials that may be explosively unstable.[1] Recently we have reported a high-yield synthesis of (difluoroamino)difluoroacetonitrile from the reaction of tetrafluorohydrazine with 1,1-difluoroethene in the presence of KF.[2] The enhanced reactivity of perfluoroalkanenitriles toward nitrogen, oxygen and sulfur bases compared to nonfluorinated nitriles has been recorded and is not surprising, based on the increased electropositive character of the cyano carbon in fluorine-containing nitriles.[3-7]

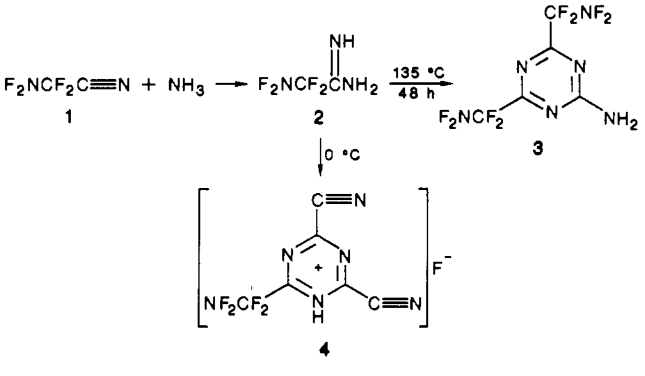
Since reactions of nitriles have been thoroughly studied, only a few examples from the literature that relate to our present work are cited here. Dimerization or trimerization of nitriles is effected under a variety of conditions. Hydrogen cyanide derivatives tend to polymerize to form dimers, trimers or polymers. In the presence of acid catalysts,[8] cyanogen chloride trimerizes very easily to cyanuric chloride. Cyanamide is dimerized smoothly by alkali to dicyanodiamide[9] and trimerization to melamine is suitable as a preparative method starting from dicyanodiamide and ammonia under pressure.[10] 1,3,5-Tris(trifluoromethyl)triazine can be produced in a two-step reaction. Trichloroacetonitrile was first cyclized to 1,3,5-tris(trichloromethyl)triazine by saturation with HBr in the presence of $AlCl_3$ or $AlBr_3$ as catalyst. Fluorination of the trichloromethyl group was then accomplished by using a mixture of SbF_3 and $SbCl_5$.[11] Traditionally, triazines are obtained by trimerization of the appropriate nitrile under pressure (70–900 psi) at elevated temperatures (300–350 °C).[12] However, condensation reactions of amidines under less rigorous conditions give yields of triazines of about the same magnitude.[13] Nitriles also normally react exothermically with alcohols to form their respective imidates in the presence of trialkylamines as basic catalysts.[14] A number of (perfluoroacyl)amidoximes have been synthesized[14,15] with each having the possibility of two tautomeric forms, $R_fC(=NOH)NH_2$ (I)[16] and $R_fC(=NH)NHOH$ (II),[17] each being favored by different authors.

In this paper we report condensation and cyclization reactions of (difluoroamino)difluoroacetonitrile. In addition, we have examined the reactions of (difluoroamino)difluoroacetamidoxime, $F_2NCF_2C(=NOH)NH_2$, with perfluoroacyl chlorides to form 1,2,4-oxadiazoles.

Results and Discussion

Compounds that contain the $-NF_2$ moiety do not always behave predictably either in their modes of reaction or in their innate stability. (Difluoroamino)difluoroacetonitrile behaves differently toward various nucleophiles. Most frequently the reaction is with the nitrile functionality, but occasionally defluorination of the $-NF_2$ group occurs.[18]

(a) Reaction of F_2NCF_2CN with NH_3.



Ammonia with **1** gives the volatile, viscous compound (difluoroamino)difluoroacetamidine (**2**). In the infrared spectrum of **2** were absorption bands at 3330 and 3140 (ν_{NH_2}), 3480 (ν_{NH}), and 1663 ($\nu_{C=N}$) cm^{-1}. Resonance bands at ϕ 18.01 (broad singlet, NF_2) and −110.8 (triplet, CF_2) are seen in the ^{19}F NMR spectrum. On heating, **2** was converted to 1-amino-3,5-bis[(difluoroamino)difluoromethyl]triazine, **3**. A proposed mechanism for this cyclization is presented.

---

(1) (a) Banks, R. E.; Barlow, M. G. *Fluorocarbon Relat. Chem.* **1971**, *1*, 98; **1974**, *2*, 204; **1976**, *3*, 207. (b) *Fluorocarbons and Their Derivatives*, 2nd ed.; MacDonald: London, 1970. (c) Freeman, J. P. *Adv. Fluorine Chem.* **1970**, *6*, 287. (d) Ruff, J. K. *J. Am. Chem. Soc.* **1958**, *80*, 5004.

(2) Marsden, H. M.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 169 and references therein.

(3) Eloy, F.; Lenaers, R. *Chem. Rev.* **1962**, *62*, 155.

(4) Husted, D. U.S. Patent 2676785, 1954.

(5) Brown, H. C.; Pilipovich, D. *J. Am. Chem. Soc.* **1960**, *82*, 4700.

(6) Reilly, W. L.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6032.

(7) Josey, A. D. *J. Org. Chem.* **1964**, *29*, 707.

(8) Diel, O. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 692.

(9) Pink, L. A. *Inorg. Synth.* **1950**, *3*, 43.

(10) Soc. pour l'Ind. Chim. Swiss Pat. 189, 406; *Chem. Abstr.* **1937**, *31*, 6678.

(11) Norton, T. R. *J. Am. Chem. Soc.* **1950**, *72*, 3527.

(12) Reilley, W. L.; Brown, H. C. *J. Am. Chem. Soc.* **1956**, *78*, 6022; Reilley, W. L.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 698.

(13) Bissell, E. R. *J. Org. Chem.* **1963**, *28*, 1717.

(14) Brown, H. C.; Wetzel, C. R. *J. Org. Chem.* **1965**, *30*, 3724.

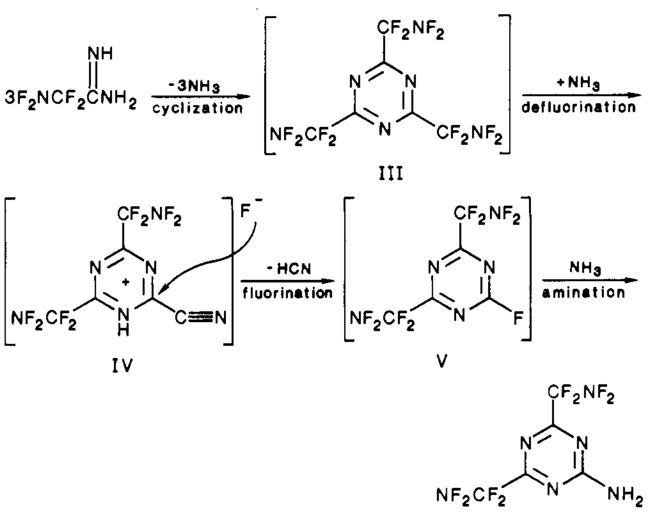
(15) Tiemann, F.; Kruger, P. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1685.

(16) Ungnade, C. L.; Kissinger, L. W. *J. Org. Chem.* **1958**, *23*, 1112.

(17) Bell, C. L.; Nambury, C. N. V.; Bauer, L. *J. Org. Chem.* **1961**, *29*, 2873.

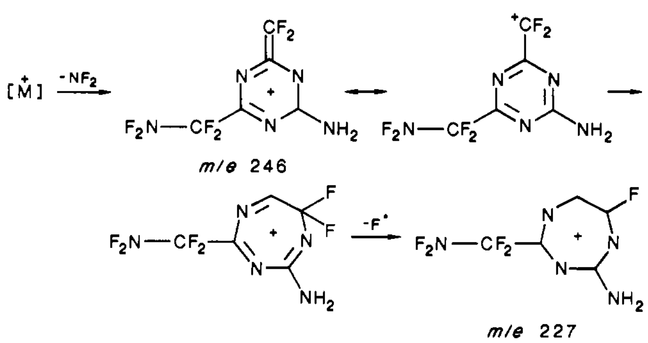
(18) Mitsch, R. A.; Neuvar, E. W. *J. Org. Chem.* **1968**, *33*, 3675.

0020-1669/88/1327-3100$01.50/0

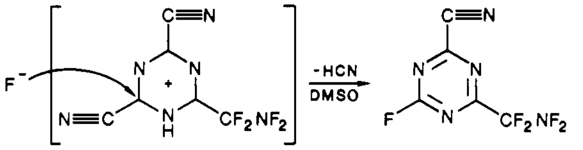


3

Compound **3** is a white, sublimable solid. In its infrared spectrum, bands appropriate to ν_{NH_2} and to the triazine ring are observed at 3350, 3220, 1660, 1590, 1531, and 1425 cm^{-1}. The EI mass spectrum shows a molecular ion at *m/e* 298 and the base peak at *m/e* 246 (M^+-NF_2). A unique fragmentation pattern in the spectrum supports the proposed structure. The peak at *m/e* 227, is similar to the tropolium ion, which is a characteristic fragment for alkyl-substituted six-membered aromatic rings like toluene.



At low temperature, a compound, 1,3-dicyano-5-[(difluoroamino)difluoromethyl]triazonium fluoride (**4**), that is somewhat similar to intermediate IV could be isolated. The infrared spectrum of **4** showed a broad absorption band between 3338 and 2600 cm^{-1} and also a broad complex peak at 1510 cm^{-1} characteristic of triazines.[13] A strong band at 2010 cm^{-1} is assigned to $\nu_{C\equiv N}$. In the ^{19}F NMR spectrum of **4**, it was not possible to observe a resonance that could be assigned to F^-. However, we did observe a small additional peak at ϕ −80.5 in addition to resonances at ϕ 16.39 (NF_2) and −110.9 (CF_2). The ^1H NMR spectrum has a single peak at δ 3.33. The appearance of the resonance at ϕ −80.5 suggests that intramolecular fluorination occurred upon addition of solvent displacing the cyano group.

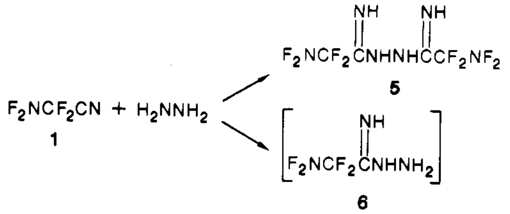


(b) Oligomerization of 1 by UV Radiation.

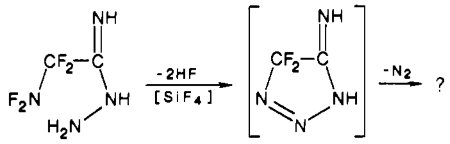
$$F_2NCF_2C{\equiv}N \xrightarrow[\text{4 weeks}]{\text{UV/quartz}} (F_2NCF_2C{=}N\text{-})_n$$

Oligomerization was initiated by a trace of chlorosuccinimide. A mixture of oligomers was trapped at −40 °C. The value of *n* ranges between 2 and 5. The infrared spectrum showed two broad peaks centered at 1773.5 and 1715.7 cm^{-1}, which is the characteristic region for $>C{=}N-$. The framework of the polymer contained CF_2NF_2 as indicated by the IR spectrum and confirmed by ^{19}F NMR spectroscopy with complex multiplets centered at ϕ −106 (CF_2) and 19 (NF_2). The highest peak in the EI mass spectrum was *m/e* 606 ($n = 5.03 - F_2$). Also observed was a fragment at *m/e* 346 for $n = 3 - F_2$. Some solid material was also formed but was not examined.

(c) Reaction of 1 with Hydrazine.

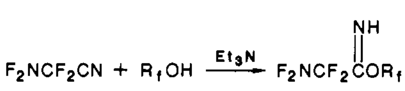


[((Difluoroamino)difluoromethyl)iminomethyl]hydrazine (**6**) is stable only in solution with explosive decomposition accompanying removal of the solvent. However, *N,N'*-bis[(difluoroamino)difluoromethyl)iminomethyl]hydrazine (**5**) is a stable, sublimable crystalline solid. The instability of **6** may be attributed to the closing of the five-membered ring with concomitant loss of 2 mol of hydrogen fluoride followed by loss of N_2.



For **5**, ν_{NH} bands were observed at 3520, 3400, and 3160 cm^{-1}, and $\nu_{C=N}$ was observed at 1635 cm^{-1} in the infrared spectrum. The EI mas spectrum contained M^+ at *m/e* 288 and also *m/e* 236 ($M^+ - NF_2$), *m/e* 186 ($M^+ - NF_2CF_2$), and *m/e* 184 ($M^+ - 2NF_2$).

(d) Reaction of 1 with Polyfluorinated Alcohols.

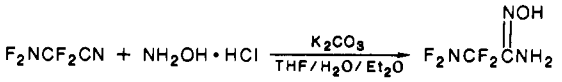


$$F_2NCF_2CN + R_fOH \xrightarrow{Et_3N} F_2NCF_2C(=NH)OR_f$$

$R_f = CF_3CH_2$ (**7**), $(CF_3)_2CH$ (**8**)

2,2,2-Trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol were reacted with **1** in the presence of triethylamine. Any unconsumed Et_3N was removed by reaction with HCl at reduced temperature. Both **7** and **8** were confirmed by the usual spectroscopic methods, and **7** also was characterized by elemental analysis. In the infrared spectra of **7** and **8**, ν_{NH} bands were observed at 3382 and 3383 cm^{-1}, ν_{CH} bands at 2983 and 2986 cm^{-1}, and $\nu_{C=N}$ bands at 1813 and 1697, and 1823 and 1704 cm^{-1}, respectively. Mass spectral fragmentation patterns of these imidates contained M^+ at *m/e* 228 for **7** and ($M^+ - F$) at *m/e* 277 for **8**.

(e) Reaction of 1 with NH_2OH.



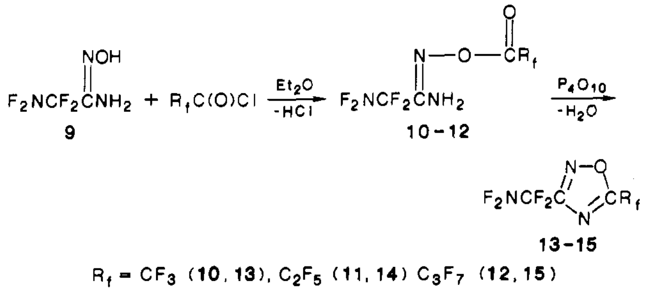
$$F_2NCF_2CN + NH_2OH\cdot HCl \xrightarrow[THF/H_2O/Et_2O]{K_2CO_3} F_2NCF_2C(=NOH)NH_2$$

9

(Difluoroamino)difluoroacetamidoxime (**9**) was prepared by modifying the earlier methods.[14,15] Through use of the latter method, in which hydroxylamine was generated in situ by the reaction of sodium methoxide with hydroxylamine hydrochloride in CH_3OH, only a very low yield of **9** was obtained. Therefore, a two-phase method was developed in which the NH_2OH was freed from the hydrogen chloride salt in the aqueous phase by the addition of an equivalent amount of K_2CO_3. The free NH_2OH was transferred to the organic phase (diethyl ether and tetrahydrofuran) where it was reacted with **1**. Although it is possible for **9** to exist in two tautomeric forms, the simplicity of the infrared spectrum supports the existence of only one form, $F_2NCF_2C(=NOH)NH_2$. The asymmetric, symmetric, and deformation bands for NH_2 appear at 3318, 3353, and 1597 cm^{-1} and the band for ν_{OH} appears at 2863 cm^{-1}. In the ^1H NMR spectrum are found two broad resonance peaks at δ 5.15 and 7.83 for hydrogen in NH_2

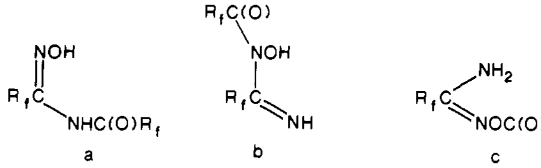
and OH, respectively. Compound **9** is a transparent, highly crystalline, low-melting (40 °C) material. In the EI mass spectrum a molecular ion at *m/e* 161 and ($M^+ - NF_2$) at *m/e* 109 are seen. The base peak is NF_2^+ at *m/e* 52.

(f) Reaction of 9 with Perfluoroacyl Chlorides. Further support for the above tautomer is obtained when **9** is reacted with $R_fC(O)Cl$ ($R_f = CF_3$, C_2F_5, C_3F_7) to form the respective (difluoroamino)difluoroacetamidoximes that undergo ready cyclization to 3-[(difluoroamino)difluoromethyl]-5-(perfluoroalkyl)-1,2,4-oxadiazoles. Standard routes to 1,2,4-oxadiazoles[14] require large amounts of starting materials, which makes them less attractive to us because of lack of a commercial source for N_2F_4. In the older method, the NF_2CF_2 portion of the molecule would be attacked by the H_3PO_4 that is formed from P_4O_{10} upon washing of the crude reaction mixture with water. Thus, since our oxadiazoles are volatile materials, dehydration was done under vacuum over P_4O_{10} followed by condensation to give pure materials (75–85% yield). Compound **9** was reacted with $R_fC(O)Cl$ as follows:



Each of these *O*-acyl(difluoroamino)difluoroacetamidoximes is a stable, sublimable solid, but each is highly susceptible to hydrolysis. However, **10** begins to decompose even at room temperature, which made elemental analysis difficult. The infrared spectra of **10**, **11**, and **12** showed asymmetric and symmetric N–H stretching bands at 3455 and 3363, 3483 and 3365, and 3447 and 3352 cm⁻¹, respectively while $\nu_{C=O}$ and $\nu_{C=N}$ were recorded at 1799, 1680, 1665; 1800, 1683, and 1665; and 1800, 1685, and 1600 cm⁻¹, respectively. The usual C–F and N–F bands were present. Electron-impact mass spectra had peaks at M^+ and $M^+ - NF_2$ at *m/e* 257 and 205, 307 and 255, and 357 and 305 for **10**, **11**, and **12**, respectively.

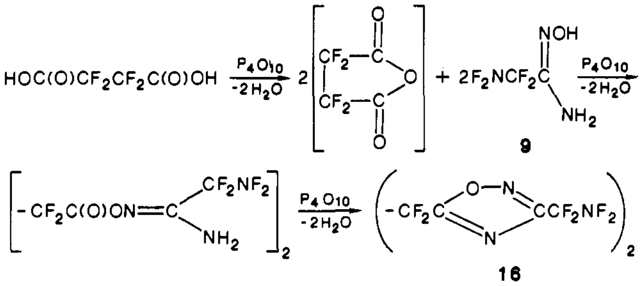
Amidoximes have three possible points of acylation that would produce the *N*-acyl- (a, b) or *O*-acylamidoxime (c). Structure



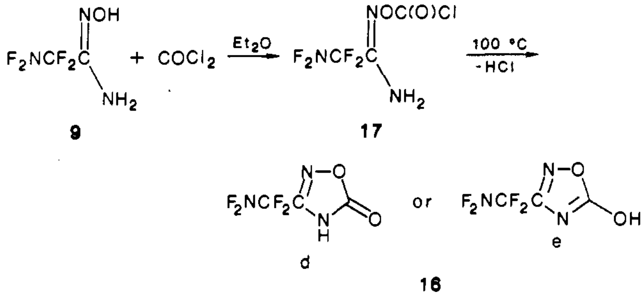
b is impossible since each of the (perfluoroacyl)amidoximes cyclized readily to the corresponding 1,2,4-oxadiazoles by dehydration.[14] Others have claimed that acylation occurred on the amino nitrogen in the case of halogenated acetamidoximes.[19] These products were shown later to be *O*-acyl derivatives.[20] The complete disappearance of the –OH band of **9** and a comparison of $\nu_{C=O}$ in the infrared spectra of the acylated derivatives with those of amides and esters shows clearly that these compounds have the –C(O)O– structure rather than –C(O)NH–.

3-[(Difluoroamino)difluoromethyl]-5-(perfluoroalkyl)-1,2,4-oxadiazoles (**13**, **14**, and **15**) are colorless, volatile, stable liquids that have characteristic infrared absorption bands at 1590–1615 and 1530–1510 cm⁻¹ due to the stretching vibrations of the two distinct >C=N moieties of the 1,2,4-oxadiazole ring.

When **9** was heated at 160 °C with perfluorosuccinic acid over P_4O_{10} a novel bis(1,2,4-oxadiazole) resulted. It is likely that the reaction proceeds via the initial formation of perfluorosuccinic acid anhydride that is then acylated and subsequently dehydrated to the bis(1,2,4-oxadiazole), i.e.



Phosgene in large excess was also used successfully as an O-acylating agent to give the *O*-(chloroformyl)(difluoroamino)difluoroacetamidoxime **17** in essentially quantitative yield.



The structure of **17** was confirmed by infrared, chemical ionization mass, and NMR spectra and elemental analysis. A single broad peak at δ 5.27 is assigned to NH_2 in the ^1H NMR spectrum and peaks at ϕ 18.9 and −108.1 in the ^{19}F NMR show retention of the NF_2CF_2– group. The presence of chlorine was clearly demonstrated by the appearance of fragments in the CI mass spectrum whose mass difference was 2 and whose intensity was 3:1, i.e., for *m/e* 223 (M^+) 6% and 225 ($M^+ + 2$) 2%. Infrared absorption bands for $\nu_{C=O}$ and $\nu_{C=N}$ were centered at 1768 and 1669 cm⁻¹. When **17** was heated, HCl gradually evolved, giving rise to **18**. Infrared spectra of **18** supported the lactone structure d rather than the alcohol structure e. In the infrared spectrum, the presence of a strong, strained ring lactone C=O stretching vibration at 1800 cm⁻¹ is noted. There was also a broad band between 3500 and 2650 cm⁻¹ assigned to ν_{NH}. No vibration attributable to ν_{OH} was found. The proton NMR spectrum contained a broad band at δ 5.46. These observations support structure d rather than structure e for **18**.

Experimental Section

Materials. Reagents were purchased as indicated: 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 1,1-difluoroethene, perfluorocarboxylic acid chlorides, and trifluoroacetonitrile (PCR); perfluorosuccinic acid (Pierce); and hydroxylamine hydrochloride (Baker). (Difluoroamino)difluoroacetonitrile was prepared by the published method.[2]

General Procedures. A Perkin-Elmer 1710 Fourier transform infrared spectrometer, a JEOL FX90Q Fourier transform nuclear magnetic resonance spectrometer, and a VG7070HS mass spectrometer were used to record the spectral data. Gases and volatile liquids were handled in a Pyrex vacuum system equipped with a Heise Bourdon tube and Televac thermocouple pressure gauges. Elemental analysis were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

Reaction of (Difluoroamino)difluoroacetonitrile (1) with Ammonia. (Difluoroamino)difluoroacetonitrile (2 mmol) and NH_3 (2 mmol) were condensed into a 50 mL Pyrex bulb at −196 °C. The bulb was allowed to warm slowly to 25 °C and the mixture was agitated for 0.5 h. A viscous liquid was trapped at −60 °C (yield ~80%). Because of the instability of $F_2NCF_2C(=NH)NH_2$ (**2**) at 25 °C only rather rough infrared, NMR, and mass spectral data were obtained: IR: (capillary): 3840 br, 3300 br, 3140 br, 1663 s, 1450 s, 1205 s, br, 1150 w, 1095, 970 s, 925 s, 675 w cm⁻¹. NMR ($CDCl_3$): ^{19}F, ϕ 17.9 (NF_2), −110.9 (CF_2); ^1H, δ 2.14 (NH_2), 6.2 (=NH). EI MS [*m/e* (species), intensity]: 146 ($M^+ + 1$), 3.1%; 145 (M^+), 46.6; 144 ($M^+ - H$), 0.8; 143 ($M^+ - 2H$),

---

[19] Steinkoff, W.; Borhmann, L. *Ber Dtsch. Chem. Ges.* **1907**, *40*, 1633.
[20] Eloy, F.; Lenaers, R.; Buyle, R. *Bull. Soc. Chim. Belg.* **1964**, *73*, 518.

10.5; 142 ($M^+ - 3H$), 9.3; 129 ($M^+ - NH_2$), 2.5; 125 ($M^+ - HF$), 0.4; 102 (CF_4N^+), 4.4; 93 ($C_2H_3F_2N_2^+$), 26.3; 77 ($C_2HF_2N^+$), 44; 52 (F_2N^+), 4.2.

Synthesis of 3. Compound **2** was heated at 135 °C for 2 days in a sealed Pyrex tube. The solid product was transferred into a sublimation apparatus and sublimed under vacuum (65% yield). IR (KBr disk): 3350 s, 3320 s, 1660 s, 1590 s, 1530 s, 1425 s, 1245 s, 1227 s, 1215 s, 1210 s, 1190 w, 1105 w, 1030 m, 980 s, 930 s, 850 m, 838 m, 829 m, 780 m, 770 m, 730 br, 660 w, 610 m, 560 vw, 485 m cm^{-1}. NMR: ^{19}F, ϕ 18.01 (NF_2), −110.8 (CF_2); ^1H, δ 6.51 (NH_2). EI MS [*m/e* (species), intensity]: 298 (M^+), 0.1; 246 ($M^+ - NF_2$), 100; 227 ($C_5H_2F_5N_5^+$), 7.5; 208 ($C_5H_2F_4N_5^+$), 12.7; 194 ($C_5H_2F_4N_4^+$), 54.6; 144 ($C_4H_2F_2N_4$), 9; 118 ($C_3H_2F_2N_3^+$), 25.2; 102 ($C_3F_2N_2^+$), 10.4; 92 ($C_4H_2N_3^+$), 6.1; 91 ($C_4HN_3^+$), 25.3; 76 ($C_2F_2N^+$), 27.3; 68 ($C_2H_2N_3^+$), 84.2. Anal. Calcd for $C_5H_2F_8N_6$ (**3**): C, 20.13; H, 0.67; N, 28.18; F, 21.00. Found: C, 20.70; H, 0.50; N, 27.41; F, 49.2.

Synthesis of 4. Compound **2** (0.5 mmol) was retained in a sealed tube under vacuum for an extended period. A precipitate that had formed slowly was washed with diethyl ether and dried over P_4O_{10} to give a 40% yield of **4**. IR (KBr disk): 3500–2600 (br), 2073 w, 2015 m ($\nu_{C\equiv N}$), 1829 vw, 1687 s, 1523 s, 1497 s, 1237 s, 1110 w, 996 m, 979 m, 933 m, 808 w, 662 w cm^{-1}. NMR: ^{19}F (DMSO), ϕ 16.39 (NF_2), −80.5 (N=CF), −110.9 (CF_2); ^1H, δ 3.33. See Results and Discussion for rationale. Anal. Calcd for $C_6HF_5N_6$ (**4**): N, 33.33; F, 37.69. Found: N, 32.59; F, 37.60.

Synthesis of 5. Compound **1** (1 mmol) was condensed into anhydrous hydrazine dissolved in THF at −196 °C. The reaction mixture was slowly warmed to 25 °C and agitated for 2 h. Each time the solvent was evaporated, a mild explosion occurred. Volatile compounds (N_2, SiF_4, ?) were removed under vacuum followed by sublimation of **5** onto a cold finger (5% yield). IR (KBr disk): 3520 m, 3400 m, 1645 vs, 1560 vw, 1412 s, 1200 s, 1100 m, 965 s, 910 s, 750 w, 700 vw, 620 w cm^{-1}. NMR: ^{19}F, ϕ 18.95 (NF_2), −108.9 (CF_2); ^1H, δ 1.16 (br), 5.57 (br). EI MS [*m/e* (species), intensity]: 288 (M^+), 3.9; 250 ($M^+ - 2F$), 0.4; 236 ($M^+ - NF_2$), 6.8; 186 ($M^+ - NF_2CF_2$), 1.1; 184 ($M^+ - H_2NF_2CF_2$), 6.8; 134 ($M^+ - N_2F_4CF_2$), 2.6; 102 ($NF_2CF_2^+$), 0.6; 57 ($CH_3N_3^+$), 1.9; 52 (F_2N^+), 100; 45 (CFN^+), 36.4.

Synthesis of 7 and 8. Compound **1** (1.4 mmol) was condensed over a preformed adduct of triethylamine (0.5 mmol) and 2,2,2-trifluoroethanol (1 mmol) or 1,1,1,3,3,3-hexafluoro-2-propanol (1 mmol) at −196 °C. The reaction mixture was agitated for 1 week in the dark at 25 °C. Anhydrous HCl (0.6 mmol) was added to the reaction mixture at −196 °C. The temperature was raised slowly to 0 °C. Any unreacted HCl and **1** were quickly removed under vacuum at −78 °C. Compound **7** or **8** and small amounts of the respective alcohol were trapped at −65 °C. Fractional evaporation gave the pure imidate (**7**, 65% yield; **8**, 50% yield).

Spectral data for **7**. IR (gas phase): 3382 ($\nu_{=NH}$) m, 2983 (ν_{CH_2}) m, 1813 w ($\nu_{C=N}$(asym)) m, 1697 vs ($\nu_{C=N}$(sym)), 1425 s, 1287 vs, 1217 vs, 1186 vs, 1124 vw, 1095 s, 1015 m, 938 s, 850 m, 817 w, 761 m, 651 w cm^{-1}. ^{19}F NMR ($CDCl_3$): ϕ 18.47 (NF_2, s, br), −74.54 (CF_3, tr, $J = 8$ Hz), −108.1 (CF_2, tr, $J = 2.02$ Hz). EI MS [*m/e* (species), intensity]: 229 ($M^+ + 1$), 0.2; 228 (M^+), 2.3; 176 ($M^+ - NF_2$), 31.5; 159 ($M^+ - CF_3$), 0.5; 158 ($M^+ - CF_3H$), 8.8; 157 ($M^+ - NF_3$), 23.5; 126 ($M^+ - NF_2CF_2$), 38.9; 102 ($NF_2CF_2^+$), 16.5; 83 ($CF_3CH_2^+$), 100, 81 ($C_2F_3^+$), 34.8; 69 (CF_3^+), 34.8; 50 (CF_2^+), 17.2. Anal. Calcd for $C_4H_3F_7N_2O$: C, 21.05; H, 1.32. Found: C, 23.08; H, 1.41.

Spectral data for **8**. IR: 3383 ($\nu_{=NH}$) m, 2986 (ν_{CH}) m, 1823 ($\nu_{C=H}$(asym)) w, 1704 ($\nu_{C=N}$(sym)) vs, 1387 s, 1299 vs, 1275 vs, 1235 vs, 1122 vs, 1097 vs, 1025 vs, 980 s, 939 vs, 909 m, 848 s, 818 w, 765 m, 693 s, 653 w, 528 w cm^{-1}. NMR: ^{19}F, ϕ 19.92 (NF_2, br), −73.55 (CF_3, d, $J = 5.86$ Hz), −107 (CF_2, tr, $J = 2.07$ Hz); ^1H, δ 5.55 (septet). EI MS [*m/e* (species), intensity]: 277 ($M^+ - F$), 0.27; 244 ($M^+ - NF_2$), 11.6; 225 ($M^+ - NF_3$), 19.0; 194 ($M^+ - NF_2CF_2$), 20.7; 151 ($(CF_3)_2CH^+$), 35.4; 129 ($M^+ - (CF_3)_2CHO$), 9.3; 69 (CF_3^+), 100; 52 (NF_2^+), 1.39.

Synthesis of 9. Compound **1** (7 mmol) was condensed onto a mixture of H_2O (3 mL), $NH_2OH{\cdot}HCl$ (7.5 mmol), K_2CO_3 (3.75 mmol), $(C_2H_5)_2O$ (2 mL), and THF (3 mL) at −196 °C. The temperature was gradually increased to ambient while the mixture was stirred. Stirring continued for 6 h. The organic layer was removed. The aqueous phase was extracted with 2 × 3 mL of diethyl ether, which was subsequently added to the earlier organic phase. The volume of the extract was reduced to 1.5 mL and dried over P_4O_{10}. After the organic phase was removed, the residue was sublimed under vacuum. It was further dried over P_4O_{10} and resublimed to ensure purity. The yield of $NF_2CF_2C({=}NOH)NH_2$ was ~64%. IR (KBr disk): 3518 m, 3353 m, 2863 m, 1691 vs, 1597 s, 1466 m, 1420 s, 1227 vs, 1196 vs, 1104 m, 969 s, 922 s, 830 m, 760 m cm^{-1}; NMR: ^{19}F, ϕ 18.65 (NF_2, br), −108.5 (CF_2, tr); ^1H, δ 5.15 (br), 7.83 (br). EI MS [*m/e* (species), intensity]: 162 ($M^+ + 1$), 0.7; 161 (M^+), 25.8; 109 ($M^+ - NF_2$), 35.6; 78 ($C_2H_2F_2N^+$), 16.8; 77 ($C_2HF_2N^+$), 6.0; 76 ($C_2F_2N^+$), 6.8; 59 ($CH_3N_2O^+$), 17.0; 52 (NF_2^+), 100; 42 ($CH_2N_2^+$), 43.9; 41 (CHN_2^+), 6.9. Anal. Calcd for $C_2H_3F_4N_3O$: C, 14.90; H, 1.86; F, 47.2. Found: C, 14.43; H, 1.83; F, 46.0.

Synthesis of 10, 11, and 12. The general procedure for the reaction of **9** with perfluoroacyl chlorides follows. To compound **9** (0.2–0.3 mmol) in anhydrous Et_2O was added $R_fC(O)Cl$ (0.5 mol; $R_f = CF_3, C_2F_5, C_3F_7$) at −196 °C. The mixture was held at −20 °C for ~0.5 h and then agitated at 25 °C for ~0.5 h. An essentially quantitative yield of **10**, **11**, and **12** was obtained after the solvent and HCl were removed.

Spectral data for **10**. IR (KBr disk): 3455 s, 3363 s, 3411 w, 3215 w, 1799 vs, 1680 vs, 1665 vs, 1349 s, 1231 s, 1184 vs, 1142 vs, 971 m, 931 ms, 737 m cm^{-1}. ^{19}F, ϕ 19.58 (NF_2, br), −73.26 (CF_3, s), −107.7 (CF_2, tr, $J = 2.5$ Hz); ^1H, δ 5.1 (NH_2, br). EI MS [*m/e* (species), intensity]: 258 ($M^+ + 1$), 0.2; 257 (M^+), 10.8; 238 ($M^+ - F$), 0.7; 219 ($M^+ - 2F$), 1.5; 205 ($M^+ - NF_2$), 26.4; 187 ($M^+ - CF_3H$), 3.9; 186 ($M^+ - CF_3H_2$), 1.6; 159 ($M^+ - CF_3COH$), 1.5; 121 ($C_2HF_2N_3O^+$), 6.7; 92 ($C_2H_2F_2N_2^+$), 12.8; 91 ($C_2HF_2N_2^+$), 11.7; 78 ($C_2H_2F_2N^+$), 28.8; 69 (CF_3^+), 100; 52 (NF_2^+), 1.3; 42 ($CH_2N_2^+$), 16.9.

Spectral data for **11**. IR (KBr disk): 3483 s, br, 3365 s, 1800 vs, 1683 s, 1665 vs, 1610 w, 1440 vw, 1340 w, 1291 s, 1218 vs, 1196 s, 1146 vs, 1030 s, 970 m, 920 s, 870 vw, 820 vw, 750 w, 730 w, 700 w, 650 vw, 620 vw, 590 w cm^{-1}. NMR: ^{16}F, ϕ 19.46 (NF_2, br), −82.88 (CF_3, tr, $J = 2.60$ Hz), −107.7 (CF_2N, tr, $J = 2.5$ Hz), −120.8 (CF_2C, q). CI MS [*m/e* (species), intensity]: 308 ($M^+ + 1$), 6.4; 307 (M^+), 2.5; 256 ($M^+ + 1 - NF_2$), 3.4; 255 ($M^+ - NF_2$), 36.3; 147 ($C_2F_5CO^+$), 5.8; 119 ($C_2F_5^+$), 100; 102 ($NF_2CF_2^+$), 3.7; 100 ($C_2F_4^+$), 33.7; 92 ($C_2H_2F_2N_2^+$), 20.5; 91 ($C_2HF_2N_2^+$), 12.3; 78 ($C_2H_2F_2N^+$), 27.1; 77 ($C_2HF_2N^+$), 3.3; 76 ($C_2F_2N^+$), 4.5; 69 (CF_3^+), 77.1; 52 (NF_2^+), 2.9; 50 (CF_2^+), 13.6; 45 (CFN^+), 17.4; 44 (CO_2^+), 39.4. Anal. Calcd for $C_5H_2F_9N_3O_2$: C, 19.54; H, 0.65; N, 13.68. Found: C, 17.83; H, 0.73; N, 13.85.

Spectral data for **12**. IR (KBr disk): 3509 vw, 3447 vw, 3352 br, 3179 w, 1800 s, 1685 vs, 1600 m, 1440 w, 1220 vs, 1200 vs, 1140 s, 1125 s, 970 s, 930 s, 850 w, 760 w, 750 w, 720 m, 630 w, 590 w, 530 vw cm^{-1}. ^{19}F NMR: ϕ 19.0 (NF_2, br), −80.51 (CF_3), −107.6 (CF_2N, tr, $J = 2.5$ Hz), −118.3 (CF_2), −126.6 (CF_2). EI [*m/e* [*m/e* (species), intensity]: 357 (M^+), 2.6; 319 ($M^+ - 2F$), 1.3; 305 ($M^+ - NF_2$), 21.6; 169 ($C_3F_7^+$), 49.1; 150 ($C_3F_6^+$), 9.0; 131 ($C_2H_2F_4N_2^+$), 11.2; 119 ($C_2F_5^+$), 14.5; 100 ($C_2F_4^+$), 15.8; 92 ($C_2H_2F_2N_2^+$), 18.2; 91 ($C_2HF_2N_2^+$), 10.6; 85 ($C_2HN_2O_2^+$), 9.5; 78 ($C_2H_2F_2N^+$), 41; 70 ($C_2NO_2^+$), 70; 69 (CF_3^+), 100; 66 ($C_2N_3^+$), 13.3; 52 (NF_2^+), 3.4; 50 (CF_2^+), 8.0; 44 (CO_2^+), 45.9; 42 ($CH_2N_2^+$), 13.9

Synthesis of 13, 14, and 15. The general procedure for the dehydration of the acetamidoximes **10**, **11**, and **12** is as follows. Compound **10**, **11**, or **12** (0.2 mmol) and P_4O_{10} (~1–2 g) were mixed thoroughly in one arm of a U-tube. The tube was evacuated, sealed, and heated at 160 °C for 3–24 h. The product was condensed into the other arm of the U-tube at −196 °C, and the arm containing the product was removed. The yield of each 1,2,4-oxadiazole was 80–90%.

Spectral data for **13**: IR (gas phase): 1610 m, 1530 vw, 1399 m, 1333 ms, 1240 vs, 1196 vs, 1157 s, 1122 s, 1011 s, 994 s, 965 s, 937 s, 919 s, 797 w, 762 ms, 672 w, 630 vw, 616 w cm^{-1}. ^{16}F NMR: ϕ 21.08 (NF_2, br), −65.10 (CF_3, s), −101.8 (CF_2, tr, $J = 2.44$ Hz). EI MS [*m/e* (species), intensity]: 220 ($M^+ - F$), 10.0; 184 ($M^+ - NF_2$), 88.3; 168 ($M^+ - NF_3$), 11.1; 106 ($C_2F_2N_2O^+$), 10.8; 92 ($C_2F_2NO^+$); 100; 76 ($C_2F_2N^+$), 13.3; 69 (CF_3^+), 83.8; 50 (CF_2^+), 11.1. Anal. Calcd for $C_4F_7N_3O$: C, 20.08; N, 17.57. Found: C, 19.89; N, 17.72.

Spectral data for **14**. IR (gas phase): 1599 m, 1529 vw, 1515 w, 1394 m, 1344 s, 1302 m, 1245 vs, 1196 vs, 1158 vs, 1132 m, 1046 s, 1009 ms, 957 vs, 936 vs, 918 ms, 796 m, 756 s, 737 m, 672 w, 628 m, 545 vw, 481 m cm^{-1}. ^{19}F NMR: ϕ 21.72 (NF_2, br), −83.22 (CF_3, tr, $J = 2.60$ Hz), −101.6 (CF_2N, tr, $J = 2.56$ Hz), −115.5 (CF_2C, q). CI MS [*m/e* (species), intensity] 290 ($M^+ + 1$), 44.7; 270 ($M^+ - F$), 13.8; 237 ($M^+ - NF_2$), 100; 218 ($M^+ - NF_3$), 2.9; 187 ($C_4F_5N_2O^+$), 8,6; 119 ($C_2F_5^+$), 25; 92 ($C_4N_2O^+$), 59.9; 69 (CF_3^+), 45.9. Anal. Calcd for $C_5F_9N_3O$: C, 20.76; N, 14.53. Found: C, 21.87; N, 15.49.

Spectral data for **15**. IR (gase phase): 1597 m, 1515 vw, 1394 m, 1357 s, 1278 s, 1245 vs, 1200 vs, 1153 vs, 1120 s, 1086 m, 1014 s, 1005 s, 966 m, 930 vs, 885 vs, 796 w, 752 s, 736 s, 663 m, 627 w cm^{-1}. ^{19}F NMR: ϕ 21.66 (NF_2, br), −80.33 (CF_3, tr tr), −101.8 (CF_2N, tr, $J = 2.5$ Hz), −113.6 ($CF_2C(O){=}N$, mult), −126.4 ($CF_3\mathit{CF}_2$, mult). CI MS [*m/e* (species), intensity] 340 ($M^+ + 1$), 57.4; 339 (M^+), 0.12; 320 ($M^+ - F$), 11.0; 302 ($MH^+ - 2F$), 7.6; 301 ($M^+ - 2F$), 1.3; 288 ($MH^+ - NF_2$), 7.6; 287 ($M^+ - NF_2$), 100; 169 ($C_3F_7^+$), 13.3; 119 ($C_2F_5^+$), 7.8; 76 ($C_2F_2N^+$), 10.9; 69 (CF_3^+), 57.9. Anal. Calcd for $C_6F_{11}N_3O$: C, 21.23; N, 12.39. Found: C, 21.36; N, 12.36.

Synthesis of 16. Perfluorosuccinic acid (1.0 mmol), **9** (2 mmol), and P_4O_{10} (excess) were mixed, and the mixture was sealed under vacuum and heated at 160 °C for 48 h. Compound **16** was distilled at 60 °C under dynamic vacuum. The yield was ~65%. IR: 1593 ms, 1515 m, 1344 ms, 1314 m, 1230 s, 1191 vs, 1146 s, 1120 s, 1127 m, 1007 s, 981 s, 965 s, 931 vs, 870 s, 795 ms, 769 w, 699 vw, 672 w, 624 m cm^{-1}. ^{19}F NMR: ϕ 21.90 (NF_2, br), −101.6 (CF_2N, tr, J = 2.07 Hz), −112.7 (CF_2C, br). CI MS [*m*/*e* (species), intensity] 331 ($M^+ - F_5N$), 2.57; 319 ($M^+ - CF_5N$), 1.8; 293 ($M^+ - C_2F_5N_2$), 0.9; 281 ($M^+ - CF_7N$), 4.3; 269 ($M^+ - C_2F_7N$), 2.9; 231 ($M^+ - C_2F_9N$), 5.7; 219 ($C_5HF_6N_2O^+$), 7.9; 181 ($C_5HF_4N_2O^+$), 7.8; 169 ($C_4HF_4N_2O^+$), 16.3; 149 ($C_4F_3N_2O^+$), 4.2; 131 ($C_4HF_2N_2O^+$), 17.1; 119 ($C_3HF_2N_2O^+$), 23.6; 99 ($C_3FN_2O^+$), 6.4; 81 ($C_2F_3^+$, $C_3HN_2O^+$), 14.8; 69 (CF_3^+, $C_2HN_2O^+$), 100; 57 (CHN_2O^+), 66.1. Anal. Calcd for $C_8F_{12}N_6O_2$: C, 21.81; N, 19.09. Found: C, 21.32; N, 19.31.

Synthesis of 17 and 18. A large excess of phosgene was condensed on a solution of **9** (0.5 mmol) in diethyl ether at −196 °C. The temperature was raised slowly to and held at −20 °C for 30 min and then raised to 25 °C for 30 min with shaking. The solvent was removed under vacuum leaving **17** in approximately quantitative yield. Heating **17** at 120 °C for 4 h under vacuum gave nearly quantitative conversion to **18**.

Spectral data for **17**. IR (KBr disk): 3442 s, 3361 s, br, 3268 w, 3212 w, 1772 vs, 1675 vs, 1440 w, 1226 vs, 1134 vs, 970 s, 923 s, 870 w, 740 w, 700 vw, 625 vw cm^{-1}. NMR: ^{19}F, ϕ 19.00 (NF_2, br), −108.1 (CF_2); ^{1}H, δ 5.27 (NH_2). CI MS [*m*/*e* (species), intensity]: 226 ($M^+ + 3$), 2.6; 225 ($M^+ + 2$), 2.1; 224 ($M^+ + 1$), 7.5; 223 (M^+), 5.9; 204 ($M^+ - F$), 0.7; 185 ($M^+ - 2F$), 1.5; 173 ($M^+ - NF_2$, ^{37}Cl isotope), 12.4; 171 ($M^+ - NF_2$), 37.4; 160 ($M^+ - CClO$), 1.5; 102 ($NF_2CF_2^+$), 7.9; 92 ($C_2F_2NO^+$), 63.5; 91 ($C_2HF_2N_2^+$), 23.6; 83 ($NF_2CF_2^+$), 3.9; 78 ($C_2H_2F_2N^+$), 49.8; 65 ($C^{37}ClO^+$), 31.6; 63 ($C^{35}ClO^+$), 100; 42 ($CH_2N_2^+$), 47.5. Anal. Calcd for $C_3H_2ClF_4N_3O_2$: C, 16.14; H, 0.89; N, 18.83. Found: C, 15.53; H, 1.01; N, 19.27.

Spectral data for **18**. IR (KBr disk): 3500–2500 br, 1801 (ν_{CO}) br, s, 1673 ($\nu_{C=N}$) s, 1599 m, 1510 m, 1436 w, 1331 m, 1235 vs, 1200 w, 1175 vs, 1115 m, 976 m, 932 vs, 904 ms, 814 vw, 793 m, 747 m, 702 w, 675 w, 655 w, 615 w, 536 vw, 514 vw cm^{-1}. NMR: ^{19}F, ϕ 22.18 and 19.34 (NF_2, endo and exo), −104.0 and −107.8 (CF_2, endo and exo); ^{1}H, δ 5.46 (s, br). EI MS [*m*/*e* (species), intensity]: 161 ($M^+ - O$), 18.6; 149 ($M^+ - 2F$), 2.5; 123 ($C_2F_3N_3^+$), 2.3; 109 ($C_2F_3N_2^+$), 2.7; 91 ($C_2HF_2N_2^+$), 10.2; 90 ($C_2F_2N_2^+$), 5.9; 85 ($C_2HN_2O_2^+$), 60.4; 77 ($C_2HF_2N^+$), 7.6; 76 ($C_2F_2N^+$), 7.2; 52 (NF_2^+), 90.9; 44 (CO_2^+), 100. Anal. Calcd. for $C_3HF_4N_3O_2$: C, 19.25; H, 0.53; N, 22.45. Found: C, 19.08; H, 0.65; N, 22.52.

Acknowledgment for financial support is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to NSF Grants CHE-8404974 and CHE-8703790, and to AFOSR Grant 87-0067.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Kinetics and Mechanism of the Oxidation of Coordinated Thiosulfate by Peroxymonosulfate

Michael D. Johnson and Robert J. Balahura*

Received October 29, 1987

Peroxymonosulfate, HSO_5^-, reacts cleanly with $[(NH_3)_5CoS_2O_3]^+$ to form $[(NH_3)_5CoS_2O_5]^+$. The reaction proceeds via two consecutive nucleophilic additions of the terminal peroxy oxygen to the coordinated thiosulfate. The kinetics of these reactions are reported along with an ^{18}O tracer study.

Introduction

The oxidation reactions of free thiosulfate have been examined by using a variety of oxidants.[1-3] Many important analytical procedures utilize these reactions.[4] The usual products are sulfate or tetrathionate, but in some cases, a mixture of these two products is obtained. A few studies involve the activation of thiosulfate by coordination to a metal ion.[5,6] For example, the oxidation of $S_2O_3^{2-}$ by molecular oxygen is known to be slow, but in the presence of a copper(II) ammine complex the reaction rates are dramatically increased. It was postulated that coordination of $S_2O_3^{2-}$ to the metal center catalyzed the redox reaction with O_2. However, in these systems, the metal ion is labile and no definitive structure–reactivity relationship can be elucidated. In order to further probe the effects of metal ions on thiosulfate oxidations, the reactions of a substitution-inert Co(III)–$S_2O_3^{2-}$ complex were investigated by using peroxymonosulfate, HSO_5^-, a versatile oxidizing agent.

Peroxymonosulfate is a strong oxidant and has been employed in a wide range of oxidation reactions.[7,8] Thus far, two major reaction pathways have been proposed. The most common involves a two-electron oxidation where transfer of the terminal peroxy oxygen occurs. For example, HSO_5^- reacts with $[(NH_3)_5CrN_3]^{2+}$ to form $[(NH_3)_5CrNO]^{2+}$ and N_2.[9] Recently, Thompson et al. have demonstrated the role of the sulfate radical ion, $SO_4^{\bullet -}$, in the reaction of HSO_5^- with VO^{2+}, a one-electron reductant.[10] Surprisingly, the kinetic results were relatively simple, which is in contrast with other radical-ion reactions.

In this paper, a study of the reaction of $[(NH_3)_5CoS_2O_3]^+$ with HSO_5^- is reported. Unlike the case of most other thiosulfate redox reactions, a simple kinetic pathway was observed and a new oxysulfur cobalt(III) complex produced.

Experimental Section

Peroxymonosulfate solutions were prepared from OXONE ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) purchased from Aldrich. Solutions were made as needed and standardized by using iodometric techniques.[10] No appreciable decomposition (<2%) of HSO_5^- was detectable after standing for a 24-h period.

$[Co(NH_3)_5S_2O_3](ClO_4)$ was prepared by the method of Ray[11] and was purified by using CM25 Sephadex cation-exchange resin.

The final yellow product from the reaction of the thiosulfate complex with HSO_5^- was isolated from the reaction mixture by adding solid $NaClO_4$. Recrystallization from water gave a pure compound. Elemental analysis was performed by Galbraith Laboratories.

---

(1) Howelett, K. E.; Wedzicha, B. L. *Inorg. Chim. Acta* **1976**, *18*, 33.
(2) Baldea, I.; Niac, G. *Inorg. Chem.* **1970**, *9*, 110.
(3) Dennis, C. R.; Leipoldt, J.; Basson, S. S.; Lamprecht, G. J. *Polyhedron* **1985**, *4*, 1621.
(4) Nickless, G. *Inorganic Sulfur Chemistry*; Elsevier: Amsterdam, 1968; p 199.
(5) Byerley, J.; Safaa, A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 889.
(6) Byerley, J.; Safaa, A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1975**, 1329.
(7) Anbar, M.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 6243.
(8) Secco, F.; Venturini, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1410.
(9) Thompson, R. C.; Wieland, P.; Appleman, E. H. *Inorg. Chem.* **1979**, *18*, 1974.
(10) Thompson, R. C. *Inorg. Chem.* **1981**, *20*, 3745.
(11) Ray, P. R. *Q. J. Indian Chem. Soc.* **1927**, *4*, 71.

0020-1669/88/1327-3104$01.50/0 © 1988 American Chemical Society