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Some Reactions of CF_3OO Derivatives with Inorganic Nitrogen Compounds. Synthesis and Vibrational Spectrum of Trifluoromethyl Peroxynitrate[1]

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Trifluoromethyl peroxynitrate, CF_3OONO_2, is obtained in high yield by the reaction of trifluoromethyl hydroperoxide with dinitrogen pentoxide or fluoroperoxytrifluoromethane with dinitrogen tetroxide. Physical and chemical properties of the new compound are reported along with an assignment of the vibrational spectrum based on C_s symmetry.

Introduction

Trifluoromethyl peroxygen derivatives of nonmetals are of considerable interest because of their relatively high thermal stabilities. In many instances, these compounds are unique and provide the only examples of a C-O-O-X molecular skeleton. In our work with fluorocarbon polyoxides, trifluoromethyl hydroperoxide, CF_3OOH,[2-4] fluoroperoxytrifluoromethane, CF_3OOF,[5] and bis(trifluoromethyl) trioxide, CF_3OOOCF_3,[5-7] have been useful reagents in the synthesis of new CF_3OO derivatives of nonmetals. Only one example was known for group V, $CF_3OO\ P(O)F_2$.[4] A study of the reactions of CF_3OOH, CF_3OOF, and CF_3OOOCF_3 with several nitrogen compounds was undertaken to isolate CF_3OO derivatives of nitrogen. It was hoped that both III and V valent derivatives of nitrogen could be obtained; however, only one, a N(V) compound, was found. Trifluoromethyl peroxynitrate, CF_3OONO_2, is obtained in a variety of reactions and is the most stable peroxynitrate known.

Experimental Section

General. Although most of the peroxy materials involved in this study appeared to be well behaved and relatively stable, such compounds must all be regarded as potentially hazardous. *CF_3OONO_2 in particular should be handled with caution* as its stability may be a function of its purity (see text).

All work was carried out on standard vacuum lines as previously described.[2] Nmr spectra were recorded on a Varian A 56/60 spectrometer using 10 mol % solutions in $CFCl_3$. Routine ir spectra were recorded on a Beckman IR-10 or a Perkin-Elmer 337 with 10-cm glass or Monel cells with AgCl windows. Ir spectra of solids were recorded using the Perkin-Elmer 337 with the sample deposited on a KBr window at −196°. Gas-phase spectra for assignments were taken on a Perkin-Elmer 180 spectrometer using glass cells fitted with AgCl or polyethylene windows.

Raman spectra were taken on liquid samples sealed in glass capillaries cooled to *ca.* −25° by cold N_2(g). A Spex 1401 double monochromator with photon counting was employed. The 4880-A line of a Coherent Radiation Laboratory Model 52G Ar^+ laser was used for excitation with 150 mW power. Polarization measurements were made using method V as described by Claassen, Selig, and Shamir.[8] Mass spectra were observed on an AEI MS9 at 70 eV with a source temperature of 100°.

The gases NO, N_2O_4, N_2O, and NH_3 were obtained from Matheson Gas Products. N_2O_3 and N_2F_4 were obtained from Air Products and Chemicals, Inc. N_2O_5 was prepared by dehydration of HNO_3 with P_4O_{10}.[9] Preparation and purification of CF_3OOH,[2] CF_3OOF,[3,10] and CF_3OOOCF_3[11] were carried out as previously described.

Reactions. The reactions carried out are summarized in Table I. In a typical case, the reactants were condensed into the vessel at −196° after being either weighed or measured *via* PV/RT. After reaction under the conditions shown, the vessel was cooled to −196° and checked for noncondensables which were pumped away. The remaining mixture was then fractionated through cold traps and the various fractions measured and identified *via* ir and molecular weight.

Reaction of CF_3OOH with N_2O_5 and CF_3OOF with N_2O_4 follow with additional details because of their synthetic value.

Reaction of CF_3OOH with N_2O_5. CF_3OOH (1.93 mmol) was condensed atop N_2O_5 (2.02 mmol) in a glass tube reactor at −196°. The mixture was placed in a $CFCl_3$ bath at −78° where it remained for about 20 hr, warming to −35° in the process. No solid remained. The mixture was cooled to −78° and the volatiles removed, leaving 0.166 g of material in the reaction tube. Infrared analysis showed the residue to be HNO_3 with traces of COF_2, CF_3OOOCF_3, and SiF_4. The material removed at −78° had an average molecular weight of 136.3. It was passed through a −111° trap where 1.04 mmol of pure CF_3OONO_2 collected (54% yield). In a subsequent reaction, 0.560 g of CF_3OOH (5.49 mmol) was condensed atop excess N_2O_5 and held at −78° overnight. The next day it was warmed to *ca.* −50° for 5.5 hr. After purifying as described above, 0.741 g of CF_3OONO_2 was recovered (92% yield).

Reaction of CF_3OOF with N_2O_4. N_2O_4 (0.0971 g, 1.06 mmol) and CF_3OOF (1.07 mmol) were condensed into a 75-cm^3 stainless steel reactor at −196°. It was placed in an ice-filled dewar and held at 0° for 17 hr. The reactor was cooled to −196° and opened; a trace of noncondensables was observed. The contents were then rapidly fractionated through −78, −111, and −196° traps. The −78° trap contained N_2O_4 (0.08 mmol), the −111° trap contained 0.137 g of CF_3OONO_2 (0.93 mmol), and the −196° trap contained a mixture of FNO_2 and COF_2 (1.16). This represents an 87% yield of CF_3OONO_2 based on the CF_3OOF used.

Trifluoromethyl Peroxynitrate, CF_3OONO_2: mol wt 147.4, calcd 147.0; mp, becomes glass; bp +0.9° (extrapolated). The static vapor pressure over a range of temperatures is as follows [P(mm), t(°C)]: 8.0, −79.3; 10.1, −79.0; 25.1, −64.2; 28.4, −64.0; 70.0, −48.2; 68.7, −48.7; 112.0, −39.4; 115.3, −39.4; 229.9, −27.2; 234.4, −26.8. $\log P(\text{mm}) = 7.567 - (1284.4/T)$. $\Delta H_{\text{vap}} = 5.88$ kcal/mol, $\Delta S_{\text{vap}} = 21.4$ eu. The liquid density over a range of temperatures is as follows [ρ(g/cm^3), t(°C)]: 1.806, −104.0; 1.763, −89.0; 1.763, −88.0; 1.763, −86.3; 1.722, −71.6; 1.682, −58.0. $\rho(t) = 1.531 - 00263t$. The infrared and Raman spectra are presented in Table II. The nmr spectrum shows one peak at $\phi^* = +69.4$. The mass spectrum showed no parent ion but was consistent with the proposed structure. In a crude shock sensitivity test, a melting point capillary containing about 6 mg of CF_3OONO_2 was struck with a hammer behind shields; a significant report was heard suggesting detonation.

Analysis of CF_3OONO_2 was carried out *via* quantitative decomposition in a stainless steel vessel at 130°. A 0.1143-g sample yielded 0.0509 g of COF_2, 0.0366 g of NO_2, and 0.54 mmol of O_2 (noncon-

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Table I. Summary of Reactions

CF_3OO compd[a]	Nitrogen compd[a]	Reactor[b]	Conditions	Products[a]
CF_3OOH, 1.36	N_2O, 1.42	M	25°, 24 hr	COF_2-N_2O, 2.53; HF, 1.13; O_2, 0.3; CF_3OONO_2 0.18
0.87	N_2O_3, 0.89	M	−78°, 12 days	COF_2, 0.94; NO_2-HF, 1.38
1.93	N_2O_5, 2.02	G	−35°, 20 hr[c]	CF_3OONO_2, 1.04; HNO_3-COF_2-CF_3OOOCF_3-SiF_4, 2.6
5.49	N_2O_5, excess	G	−50°, 5.5 hr	CF_3OONO_2, 5.03
1.00	N_2F_4, 1.15	GG	25°, 2 days	NF_3-COF_2-SiF_4, 2.67; NO_2, 0.95
1.16	N_2F_4, 1.20	M[d]	25°, 40 hr	COF_2, FNO, NF_3
1.22	NH_3, ~10	G	−60°, 1 hr	O_2, NH_3, solids[e]
CF_3OOF, 0.51	NO, 1.01	M	0°, 6 hr[c]	COF_2, 0.57; N_2O_3, 0.53
1.32	N_2O, 1.31	M	86°, 3 days	O_2, 0.81; CF_4, 0.30; CF_3OF, 0.34; CF_3OOCF_3, 0.31; N_2O, 1.27
0.94	N_2O_3, 0.95	M	−78°, 10 days	COF_2, 0.6; FNO_2, 0.4; NO_2, 1.2; CF_3OONO_2, 0.3
1.07	N_2O_4, 1.06	M	20°, 17 hr[c]	COF_2-FNO_2, 1.16; N_2O_4, 0.08; CF_3OONO_2, 0.93
1.17	N_2O_5, 1.14	M	−10°, 5 days	O_2, 0.25; COF_2-FNO_2, 0.88; N_2O_5-CF_3OONO_2, 1.00
1.16	N_2F_4, 1.20	M	25°, 7 days	NF_3, 1.31; CF_3OOCF_3, 0.05; CF_3ONF_2, 0.85; CF_3OOOCF_3, 0.07; CF_3-$OONO_2$, 0.11; NO_2, 0.13
CF_3OOOCF_3, 1.05	NO, 2.09	M	25°, 1 days	COF_2-FNO-FNO_2-CF_3OOOCF_3, 2.73; NO_2, 0.80
1.77	NO_2, 1.72	M	25°, 2 days	O_2, 0.25; COF_2-CF_3OOOCF_3, 2.20; NO_2
0.99	N_2O_5, 0.98	M	25°, 24 hr	O_2, 0.52; CF_3OOOCF_3, 1.05; N_2O_4, 0.95

[a] Millimole. [b] M is a 75-cm³ stainless steel cylinder with Kel-F soft-seat valve; G is a 30-cm³ Pyrex tube with Teflon-glass valve; GG is identical with G but 150 cm³. [c] Warmed slowly from −196° to temperature listed during time given. [d] 15 g of NaF in the reactor. [e] Qualitative examination showed no oxidizing power toward acidic KI solution. Ir and mp suggests a mixture containing $(NH_2)_2C{=}O$.

densable at −196°, *m/e* 32). These data are consistent with the equation

$$CF_3OONO_2 \xrightarrow[17\ \text{hr}]{130^\circ} COF_2 + NO_2 + {}^1/_2O_2 + [MF]$$

in which M represents the metal of the vessel. Additional evidence of the composition of CF_3OONO_2 comes from its decomposition in a Pyrex infrared cell at ~50° to give COF_2 and FNO_2, which are easily observed, plus a gas, noncondensable at −196°, presumably O_2.

These data are consistent with the structure CF_3OONO_2, for which we propose the name trifluoromethyl peroxynitrate.

Results and Discussion

Trifluoromethyl peroxynitrate is obtained in high yield by the reaction of CF_3OOH with N_2O_5 or CF_3OOF with N_2O_4.

$$CF_3OOH + N_2O_5 \rightarrow CF_3OONO_2 + HONO_2$$

$$CF_3OOF + N_2O_4 \rightarrow CF_3OONO_2 + FNO_2$$

It is a colorless liquid which is quite sensitive toward water and undergoes slow thermal decomposition at 22°

$$H_2O + CF_3OONO_2 \rightarrow CF_3OOH + HONO_2$$

$$CF_3OONO_2 \rightarrow COF_2 + FNO_2 + {}^1/_2O_2$$

It is the only well characterized example of an alkyl peroxynitrate and has considerable stability compared to other known peroxynitrates such as $RC(O)OONO_2$[12] and $NO_2CH_2(OONO_2)HR$.[13] The latter compounds are quite unstable, and while CF_3OONO_2 appears to detonate under high impact, it has not shown any signs of explosive decomposition during routine handling, as a solid, liquid, or gas. The thermal decomposition of CF_3OONO_2 is analogous to that of $FONO_2$ into FNO_2 and O_2[14] and $CF_3OOP(O)F_2$ to OPF_3, COF_2, and O_2.[4] It is possible that the decomposition of CF_3OONO_2 is catalyzed by impurities or certain metal fluorides. The extent of decomposition varied considerably during handling in glass and stainless steel vacuum lines.

The ^{19}F nmr of CF_3OONO_2 shows a singlet at $\phi^* = 69.4$ which is characteristic of the CF_3OO group and is usually found at $\phi^* \approx 69$ in most CF_3OO derivatives.[2,6,15] The infrared and Raman spectra of CF_3OONO_2 shown in Figure 1 and Table II provide further proof for the presence of CF_3O-, -OO-, and $-ONO_2$ groups. Assuming C_s symmetry with the $-ONO_2$ plane parallel to the FCOON plane as shown in Figure 2, the 21 normal modes factor into 14 A′ and 7 A″ species. Using the structural parameters established for $FONO_2$[16] and CF_3OF,[17] C-O-O and N-O-O angles of 105°, and an O-O bond distance of 1.4 Å, the principal moments of inertia are $I_A = 129.7$, $I_B = 558.9$, and $I_C = 600.5$ amu Å². These values indicate the molecule is an asymmetric top and their relative magnitudes are consistent with the absence of well defined band types under medium resolution.

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Table II. Infrared and Raman Frequencies (cm^{-1}) of Trifluoromethyl Peroxynitrate

Infrared			Raman			
Gas	Intensity (g)	Solid	Liquid	Intensity	Polarization	Assignment
253	M		264	VVS	p	ν_{14}
284	W		287	M	p	ν_{13}
371	M		371	VS	p	ν_{12}
436	W		446	S	p	ν_{11}
485	M	491	497	VS	p	ν_{10}
562	M	564	567	S	wp	ν_{17}
600	M	604	607	W	wp	ν_9
669	M	668	672	M	wp	ν_8
702	M	704	698	W	wp	ν_{16}
732	W					
738	W	744	754	VVW		$\nu_{10} + \nu_{14}$
742	W					$2\nu_{12}$
783	VS	777	783	S	p	ν_7
862	M	855 br				$\nu_9 + \nu_{14}$
		877	880	S	p	ν_6
953	S	953	955	M	wp	ν_5
1049	W	1054				$\nu_{10} + \nu_{17}$
1186	VVS	1174	1175 br	VW		ν_{15}
1244	VS	1225	1235 br	VW		ν_4
1292	VS	1281	1285 sh			ν_3
		1303	1305	S	p	ν_2
			1318 sh			
1412	W		1412	VW		$2\nu_{16}$
1440 br	VW					$\nu_6 + \nu_{17}$
1482	VW					
1572 br	VW					
1592 br	VW					
1626	W					
1760	VS	1746	1760 br	W	wp	ν_1
1766 sh						
1832 br	W					
1980	VVW					
2060	VW					$\nu_3 + \nu_7$
2116	VW					$\nu_6 + \nu_4$
2138	VW					$\nu_{15} + \nu_5$
2168	VVW					
2258	VVW					
2364	VW					$2\nu_{15}$
2424	VVW					
2480	VW					$2\nu_4$
2532	VVW					
2582	VW					$\nu_2 + \nu_3$
2602	VW					$2\nu_2$
2710	VVW					
2950	VVW					
3052	W	3020				$\nu_1 + \nu_3$
3160	VVW					
3502	VW					$2\nu_1$

Table III. Normal Vibrations of Trifluoromethyl Peroxynitrate[a] (cm^{-1})

A′ species	
1 Antisym NO_2 stretch	1760
2 Sym NO_2 stretch	1305 (R)
3 Sym CF_3 stretch	1281
4 Antisym CF_3 stretch	1244
5 CO stretch	953
6 OO stretch	880 (R)
7 Sym NO′ stretch	783
8 Sym CF_3 deformation	669
9 Sym NO_2 bend	600
10 Antisym CF_3 deformation	485
11 Antisym NO_2 rock	436
12 Antisym CF_3 rock	371
13 COO skeletal bend	287 (R)
14 OON skeletal bend	264 (R)
A″ species	
15 Antisym CF_3 stretch	1186
16 Sym NO_2 out of plane bend	702
17 Antisym CF_3 deformation	562
18 Antisym CF_3 rock	b
19 OONO torsion	b
20 FCOO torsion	b
21 COON torsion	b

[a] All frequencies are gas-phase infrared except as noted by (R) for Raman. [b] Not observed.

The alternative model for the structure of CF_3OONO_2 would be to have the $-ONO_2$ plane perpendicular to the FCOON plane. This does not change the classification of the molecule as an asymmetric top but would lead to a 13 A and 8 A″ species for the C_s point group. This would result in classification of the antisymmetric NO_2 stretch as an A″ species and the interchange of ν_{11} and ν_{16}. Our data do not allow a clear choice between these two models but the available data for $HONO_2$, $FONO_2$, $ClONO_2$, and CH_3ONO_2 make the alternative model unlikely as all of these nitrates appear to have the planar type structure.

The fundamental vibrational modes of CF_3OONO_2 along with their approximate descriptions are given in Table III. Seventeen of the 21 fundamentals are accounted for with the three torsional modes and a CF_3 rocking mode not observed. The torsional modes should lie well below 200 cm^{-1} and thus below the spectral region examined by us. The missing CF_3 rock may lie below 200 cm^{-1} or alternatively it may coincide with another vibrational mode. The assignment of the vibrational spectrum of CF_3OONO_2 might appear straightforward at first sight but in fact there is considerable difficulty in arriving at an unambiguous assignment for the observed frequencies. Most of our assignments are made by comparison to those of $XONO_2$[18-21] (X = H, D, CH_3, Cl, F), CF_3OX (X = F,[22] CF_3O,[23] CF_3OO[24,25]), and other CF_3X derivatives.[26,27] Assignments for ν_1-ν_6 and ν_{15} are straightforward. While ν_2 and ν_3 overlap strongly in the infrared, the intensity and polarization of ν_2 in the Raman clearly indicate it should be assigned as the symmetric NO_2 stretch. The remaining assignments must be regarded as tentative until a more detailed investigation of CF_3OONO_2 is made and additional studies on related molecules become available.

The most recent studies of $XONO_2$ molecules[20,21] agreed substantially with earlier assignments, except that for the series X = H, F, and Cl the previous assignments for the symmetric NO_2 bend and the NO′ stretch were reversed, placing the former at a higher value. We have followed the earlier examples, assigning the NO′ stretch to a higher value than the symmetric NO_2 deformation. If the more recent assignments for $XONO_2$ are followed, we feel any value that can be assigned to ν(NO′) is unreasonably low. Thus, ν_7 at 783 cm^{-1} is assigned to the NO′ stretch. This frequency is too high for assignment to any of the remaining CF_3OO modes and must belong to the nitrate group. The 702-cm^{-1} band in the infrared with a weak Raman couterpart, which ap-

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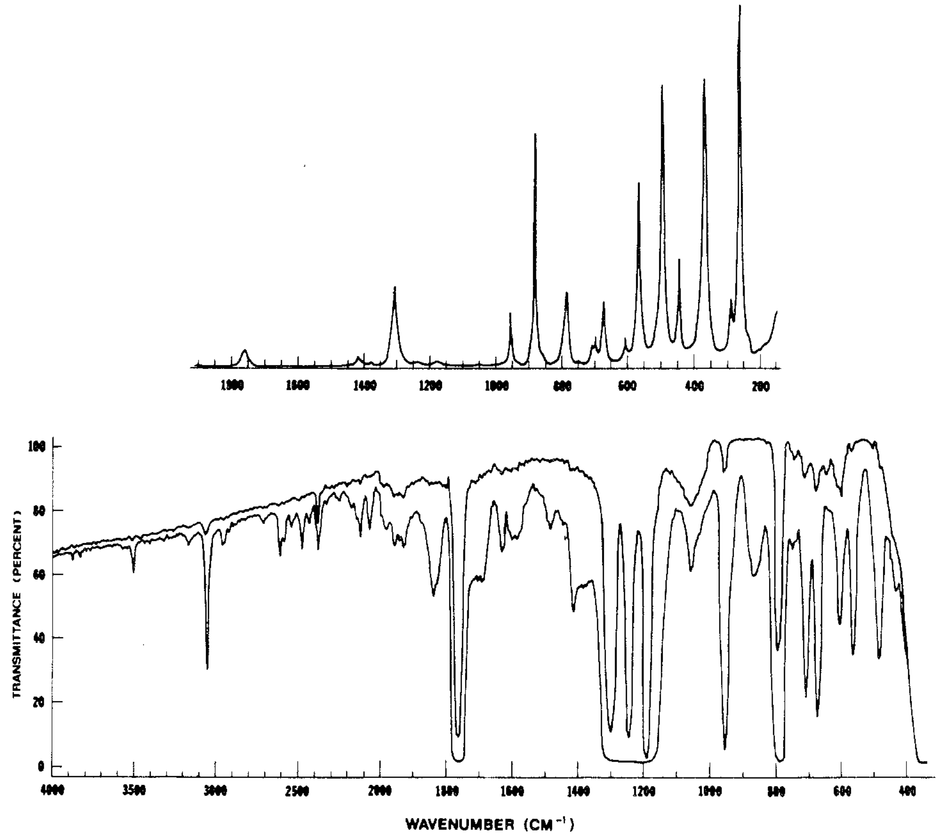

Figure 1. Raman (l) and infrared (g, 3 and 45 mm) spectra of trifluoromethyl peroxynitrate.

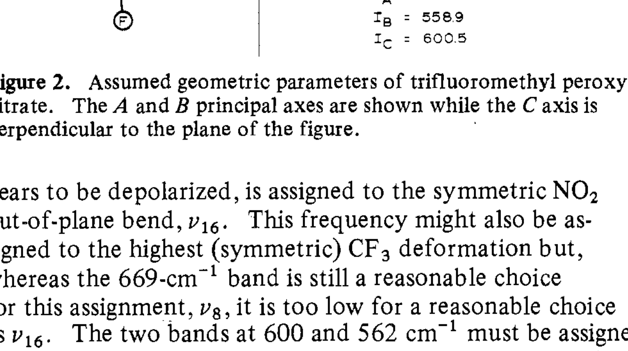

Figure 2. Assumed geometric parameters of trifluoromethyl peroxynitrate. The *A* and *B* principal axes are shown while the *C* axis is perpendicular to the plane of the figure.

pears to be depolarized, is assigned to the symmetric NO_2 out-of-plane bend, ν_{16}. This frequency might also be assigned to the highest (symmetric) CF_3 deformation but, whereas the 669-cm^{-1} band is still a reasonable choice for this assignment, ν_8, it is too low for a reasonable choice as ν_{16}. The two bands at 600 and 562 cm^{-1} must be assigned to a CF_3 deformation mode and the symmetric NO_2 bend. However, a choice between the two is rather arbitrary. We have assigned the 600-cm^{-1} band, ν_9, to the NO_2 bending mode and the 562-cm^{-1} band, ν_{17}, to the antisymmetric CF_3 deformation. Ideally, depolarization ratios should allow a definitive choice, but ours is predominantly on the basis of the symmetric CF_3 deformation mode at 669 cm^{-1}, which makes 562 cm^{-1} a more realistic choice for one of the two remaining CF_3 deformation modes.

The remaining bands at 485, 436, 371, 284, and 264 cm^{-1} are all moderate to very strong in the Raman and are polarized making them A′ vibrations. The 485-cm^{-1} band is assigned to the remaining (antisymmetric) CF_3 deformation, ν_{10}. The three CF_3 deformation modes are typically observed in the 700 to 500 cm^{-1} region, and, while 485 cm^{-1} is somewhat low, it is the only choice available for the third CF_3 deformation. The two bands at 436 and 371 cm^{-1} must be due to the antisymmetric NO_2 and CF_3 rocking modes. Either vibration is reasonable for the CF_3 rock, but only the 436-cm^{-1} vibration is consistent with previous assignments for the NO_2 rocking mode, and they are assigned accordingly as ν_{11} and ν_{12}.

The two remaining bands must now be assigned. Although one could logically be assigned to the remaining antisymmetric A″ CF_3 rocking mode, Raman polarizations will not allow this. Therefore, these two bands must be assigned to the COO and OON skeletal bending modes. Because the ν_5 is higher than ν_7, 284 cm^{-1}, ν_{13}, is assigned to the COO bend and 264 cm^{-1}, ν_{14}, to the OON bend. This represents a high value for a COO bend but, in consideration of the few compounds for which this vibration has been assigned, it is not unreasonable. There are no previous assignments for an OON skeletal bend and thus the validity of this assignment cannot be inferred from analogy.

In Table IV the fundamental frequencies of $XONO_2$ are given for comparison. The experimental frequencies for $HONO_2$, $FONO_2$, and $ClONO_2$ are those given by Hisatsune and coworkers, but assignments are in general consistent with those reported in earlier studies. The values for CF_3OONO_2 are in good agreement with the related $XONO_2$ molecules and, considering that the group electronegativity of CF_3O is between F and Cl, the observed trends are not unexpected.

The failure to obtain other new CF_3O derivatives *via* the reactions given in Table I is disappointing. As can be seen by the products formed, most of the reactions involved either the decomposition of the starting CF_3OO compound and (or) the oxidation of lower valent nitrogen species. The

Table IV. Correlation of $XONO_2$ Fundamentals[a]

Description	$HONO_2$	$FONO_2$	$ClONO_2$	CF_3-$OONO_2$
XO stretch	3550	928	780	880
NO antisym stretch	1708	1759	1735	1760
XON bend	1331	303	270	264
NO sym stretch	1325	1301	1292	1305
NO′ stretch	879	804	809	783
NO_2 out-of-plane	762	708	711	702
NO_2 deformation	647	633	560	600
ONO′ bend	579	454	434	436
XO torsion	456	152	121	

[a] Values are given to the nearest wave number. Description used is that of ref 20.

failure to observe CF_3OONF_2 and CF_3ONO_2 seems especially puzzling because of the ease with which CF_3ONF_2 and CF_3-$OONO_2$ are obtained. A lower stability of CF_3ONO_2 compared to CF_3OONO_2 might be expected based on the properties of CF_3OPOF_2 and CF_3OOPOF_2.[4] However, this analogy cannot apply in the case of CF_3OONF_2, and the failure to observe this compound is probably related to the detailed reaction mechanism and not to the intrinsic instability of CF_3OONF_2.

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Registry No. CF_3OOH, 16156-36-8; CF_3OOF, 34511-13-2; CF_3OOOCF_3, 1718-18-9; N_2O_5, 10102-03-1; N_2O_4, 10544-72-6; N_2O_3, 10544-73-7; N_2O, 10024-97-2; NO, 10102-43-9; N_2F_4, 10036-47-2; NH_3, 7664-41-7; CF_3OONO_2, 50311-48-3.

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Nucleophilic Substitution on Nitrogen. Reactions of Hydroxylamine-*O*-sulfonate with Thiosulfate and Thiourea

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Hydroxylamine-*O*-sulfonate, $H_2NOSO_3^-$, reacts rapidly with thiosulfate, forming $H_2NSSO_3^-$ as an intermediate and tetrathionate as the final product. Thiourea reacts with $H_2NOSO_3^-$ to form the novel cation $(H_2N)_2CSNH_2^+$ isolated as the sulfate salt. Each reaction involves the rate law $-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][Nu]$, with $k_2 = 0.55\ M^{-1}\ sec^{-1}$ for $S_2O_3^{2-}$ and $1.64\ M^{-1}\ sec^{-1}$ for $(H_2N)_2CS$ at 20.4°. The reactions are interpreted in terms of nucleophilic substitution on the nitrogen center in $H_2NOSO_3^-$ with the rate constants taken as a measure of the relative nucleophilicity toward trivalent nitrogen. As found in an earlier study with several other nucleophiles $H_2NOSO_3^-$, with its nonbonded electron pair, is more reactive toward thiourea than is molecular H_3NOSO_3. Deuterium isotope effects observed for the reaction of $H_2NOSO_3^-$, compared with $D_2NOSO_3^-$ in D_2O, are $k_H/k_D = 1.12$ for $S_2O_3^{2-}$ and 1.07 for $(H_2N)_2CS$. The reaction of $S_2O_3^{2-}$ with $H_2NSSO_3^-$ was examined briefly and found to proceed with a first-order hydrogen ion dependence.

Introduction

Studies of nucleophilic substitution processes at several inorganic atom centers, notably platinum(II), peroxide oxygen, and sulfur, have been described in detail.[1] In an attempt to extend such studies to substitution at a nitrogen center, we have reported the kinetics of reactions of hydroxylamine-*O*-sulfonate ion with various nucleophiles including triphenylphosphine, iodide, and triethylamine.[2] The reactions are first order in each reactant and involve attack on nitrogen as shown in eq 1. Based on observed second-order

$$\mathrm{Nu} + H_2NOSO_3^- \rightarrow [\mathrm{Nu}\cdots\ddot{N}H_2^{\delta+}\cdots OSO_3^{(1+\delta)-}]^{\ddagger} \rightarrow \mathrm{NuNH_2}^+ + SO_4^{2-} \qquad (1)$$

rate constants, the order of nucleophilicity toward this trivalent nitrogen center is $(C_6H_5)_3P > I^- > (C_2H_5)_3N >> Br^-$, Cl^-.

We report here results for reaction of $H_2NOSO_3^-$ with thiosulfate and with thiourea. The product species anticipated as a direct consequence of attack on nitrogen are respectively $H_2NSSO_3^-$ and $(H_2N)_2CSNH_2^+$.

Thiohydroxylamine-*S*-sulfonate, $H_2NSSO_3^-$, has been prepared as the potassium salt by Gosl and Meuwsen.[3] Since a route to $H_2NSSO_3^-$ was available, we examined its role as an intermediate in the hydroxylamine-*O*-sulfonate–thiosulfate reaction. Substitution on nitrogen by thiourea would lead to the previously unreported $(H_2N)_2CSNH_2^+$ ion. This paper reports the isolation and identification of this species.

Experimental Section

Reagents. Most runs were carried out in doubly distilled water. B & A reagent grade methanol was used to prepare 50.0 wt% methanol–water solvents. Stohler 99.8% D_2O was employed in the deuterated solvent runs. Hydroxylamine-*O*-sulfonic acid and *N*-methylhydroxylamine-*O*-sulfonic acid were prepared as described earlier.[2] Reagent grade salts, $K_2S_2O_3$ (B & A), $KClO_4$, and $NaClO_4$ (used to maintain ionic strength), and the various salts for preparation of buffer solutions were used as received after drying at 110°. MCB reagent grade thiourea was recrystallized from water and dried.

Kinetics. Reactions were followed using a Cary Model 16K spectrophotometer. The decrease in absorbance at 235 nm was monitored in the case of thiourea and the increase in absorbance at 270 nm was followed in the thiosulfate reactions.

Potassium Thiohydroxylamine-*S*-Sulfonate. H_2NSSO_3K was prepared as described by Gosl and Meuwsen,[3] except that it was recrys-

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