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Direct Synthesis of Fluorinated Peroxides. 8. Synthesis and Properties of $(CF_3)_3COOF$ and Evidence for the Trioxide $(CF_3)_3COOOC(CF_3)_3$

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The preparation of $(CF_3)_3COOF$ has been achieved by the low-temperature reaction of fluorine with the novel peroxo anion $(CF_3)_3COO^-$. The latter is generated in situ by nucleophilic attack of fluoride on $(CF_3)_3COOSO_2F$. The compound has been characterized by ^{19}F NMR, infrared, and Raman spectroscopy and by its thermal decomposition and addition to chlorotrifluoroethylene. Reaction of $(CF_3)_3COOF$ with $KOC(CF_3)_3$ forms the unstable trioxide $(CF_3)_3COOOC(CF_3)_3$.

Introduction

Several members of the new class of fluorinated peroxides containing the perfluoro-*tert*-butyl group have recently been described.[2] These new compounds were obtained from $(CF_3)_3COOC(O)F$ which was obtained by a novel nucleophilic displacement reaction with $(CF_3)_3COOSO_2F$ in the presence of COF_2 and KF (eq 1). This reaction probably involves the formation of the unstable anion $(CF_3)_3COO^-$. By employing CsF instead of KF, it has now been possible to generate this anion at low temperature and to carry out its controlled oxidation by fluorine, forming $(CF_3)_3COOF$ in excellent yield. This new method of preparation may have general applicability.

$$(CF_3)_3COOSO_2F + COF_2 \xrightarrow{KF} (CF_3)_3COOC(O)F + SO_2F_2 \tag{1}$$

In previous work by us on the synthesis of fluorinated peroxygen compounds containing the trifluoromethyl and pentafluorosulfur groups, the hydroperoxides CF_3OOH[4–7] and SF_5OOH[8–10] have been key reagents. The corresponding perfluoro-*tert*-butyl hydroperoxide, $(CF_3)_3COOH$, is much more difficult to prepare and is thus of less use in the direct synthesis of $(CF_3)_3COO$ derivatives. The easy synthesis of $(CF_3)_3COOF$ described here makes it the most accessible reagent for this purpose. This paper presents details for its preparation and describes some of its physical and chemical properties.

Experimental Section

General Procedures. Volatile compounds were handled in a glass and stainless steel vacuum system equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge, series 1500. All reactions were carried out in 75-mL 304 stainless steel reactors or glass bulbs fitted with glass–Teflon valves. Separation of volatile products was by trap-to-trap distillation and GLC using columns packed with 40% halocarbon 11-21 polymer oil on Chromosorb P.

Infrared spectra were recorded on Perkin-Elmer Model 180 or 337 spectrophotometers using a 10-cm gas cell fitted with AgCl windows. Raman spectra were recorded at low temperatures using a Spex 14018 monochromater with photon counting detection. A low-temperature cell similar to that described by Brown et al.[11] was employed. Excitation was by the 514.5-nm line of an argon laser or by a tunable CW dye laser output in the 610-nm region. NMR spectra were recorded with a Varian XL-100-15 spectrometer in CW or pulsed FT modes using ~15 mol % solutions in $CFCl_3$.

Reagents. Fluorine, CsF, KH, CF_2CFCl, and $(CF_3)_3COH$ were obtained from commercial sources. $(CF_3)_3COOSO_2F$ was prepared by the reaction of $S_2O_6F_2$ with $KOC(CF_3)_3$.[12] Peroxydisulfuryl difluoride was prepared by heating stoichiometric amounts of $2SO_3$ and F_2 at 160 °C in a 150-mL bomb, loosely packed with Ag-coated copper gauze. The vessel was heated with 5 atm of F_2 at 200 °C before adding SO_3 and F_2. On a 100-mmol scale, yields were quite high with small amounts of unreacted SO_3, O_2, and SO_2F_2. Treatment with concentrated H_2SO_4 and collection at −78 °C provided pure $S_2O_6F_2$. Preparation of $KOC(CF_3)_3$ was by reaction of the alcohol with KH in ether at 0 °C, followed by filtration and evaporation of the diethyl ether solvent.[13] Fluorine was passed through a NaF scrubber before use. CsF was dried in a metal reactor at 80 °C under dynamic vacuum for 17 h and then treated with ~2 atm of F_2 for several hours. The metal reactor contained several nickel balls up to $^1/_4$ in. During treatment with F_2, the vessel was agitated violently on a paint shaker for ~5 min.

Preparation of $(CF_3)_3COOF$. The reaction of $(CF_3)_3COOSO_2F$ with fluorine in the presence of CsF was carried out under a variety of conditions. The following procedure normally produced the highest yields. Into a 75-mL metal reactor containing 15 g of activated CsF, 2.7 mmol of $(CF_3)_3COOSO_2F$ and 6.0 mmol of F_2 were added at −196 °C. The reactor was placed in a large Dewar filled with an ethanol–water slush at −55 °C. After 24 h, the bath temperature was −35 °C. The contents were collected at −196 °C and then fractionated through traps at −65, −95, and −196 °C. The −65 °C trap contained a small amount of $(CF_3)_3COOC(CF_3)_3$[14] identified by IR and NMR spectroscopy and molecular weight. The −95 °C trap contained nearly pure $(CF_3)_3COOF$ with small amounts of $(CF_3)_3COF$.[15] The −196 °C trap contained SO_2F_2 with small amounts of CF_4, C_2F_6, and other products. If there is unreacted $(CF_3)_3COOSO_2F$ (depending on the activity of the CsF), the −65 and −95 °C traps will both contain the fluorosulfate. It can only be effectively removed from $(CF_3)_3COOF$ by GLC with some loss of $(CF_3)_3COOF$ from decomposition. The best yields of $(CF_3)_3COOF$ were ~80%. $(CF_3)_3COOF$: mp −17 to −16 °C: mol wt found 270.4, calcd 270.0. IR: 1310–1260 (vs), 1069 (s), 1009 (s), 987 (s), 760 (w), 741 (s), 537 (w), 499 (w) cm^{-1}. Raman (liquid, −15 °C) [cm^{-1}, relative intensity, polarization]: 1284, br; 1003, 1.2, p; 989, sh; 902, 1.0, p; 768, 10, p; 741, 1.2, p; 724, 0.7, dp; 633, 0.2, dp; 570, 0.4, dp; 540, 0.7, dp; 503, sh; 489, 1.2, p; 489, 1.2, p; 484, sh; 441, 0.1, p; 359, 1.6, p; 331, sh; 314, 4.1, p; 304, sh; 297, sh; 233, 1.2, p; 204, 0.2, dp; 184, 0.1, p; 174, 0.1, p; 160, 0.5, dp; 136,

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0.7, dp. ^{19}F NMR $\phi^*((\mathrm{CF_3})_3\mathrm{C})$ 69.5, $\phi^*(\mathrm{OOF})$ −295.0, $J_{\mathrm{FF}} = 6.0$ Hz.

For comparison, the Raman spectrum of $(\mathrm{CF_3})_3\mathrm{COF}$ was also recorded at −10 °C: 1286, br; 1100, 0.7, p; 995, 0.6, p; 870, 2.2, p; 758, 10.0, p; 724, 1.0, p; 650, 0.4, dp; 560, 0.7, dp; 530, 0.9, dp; 498, 0.6, dp; 434, 0.3, p; 354, 3.3, p; 318, 1.9, dp; 300, 4.5, p; 282, sh, p; 224, 0.3, p; 196, 0.6, dp; 136, sh; 120, 1.1, dp.

Reaction of $(\mathrm{CF_3})_3\mathrm{COOF}$ with $\mathrm{KOC(CF_3)_3}$. In a typical reaction, 1.0 mmol of $(\mathrm{CF_3})_3\mathrm{COOF}$ was condensed onto 4.0 mmol of $\mathrm{KOC(CF_3)_3}$ contained in a 100-mL glass vessel at −196 °C. The reaction was allowed to warm from −90 to −40 °C over 24 h. The contents were then pumped via a short connection through traps at −60 and −196 °C as the reactor warmed slowly in the air from −78 °C. The −196 °C trap contained $\mathrm{CF_4}$, $(\mathrm{CF_3})_2\mathrm{CO}$, $\mathrm{C_2F_6}$, and other products. A white solid collected in the −60 °C trap. This material was very unstable at 22 °C and pumping from one container, as it warmed slowly, to another vessel at −196 °C resulted in considerable decomposition as evidenced by the formation of a noncondensable gas. An NMR sample was prepared by pumping the compound into a trap at −60 °C with an NMR tube attached to the bottom of the trap. The compound was washed into the NMR tube with cold $\mathrm{CFCl_3}$ (below −40 °C). The NMR spectrum showed a single, somewhat broadened resonance at ϕ^* 69.8.

Reaction of $(\mathrm{CF_3})_3\mathrm{COOF}$ with $\mathrm{CF_2CFCl}$. One millimole of $(\mathrm{CF_3})_3\mathrm{COOF}$ and 5.0 mmol of $\mathrm{CF_2CFCl}$ were condensed into a metal reactor containing 15 g of CsF at −196 C. The CsF was used simply as a moderator for the reaction. The vessel was allowed to warm slowly to 22 °C and the product was collected at −78 °C. GLC showed only one major component, yield ~75%. $(\mathrm{CF_3})_3\mathrm{COOCF_2CF_2Cl}$ (1)–$(\mathrm{CF_3})_3\mathrm{COOCFClCF_3}$ (7): mol wt found 384.0, calcd 386.5. IR 1305–1260 (vs), 1235 (s), 1190 (m), 1137 (m), 1109 (s), 1076 (s), 983 (s, br), 850 (w), 805 (w), 763 (w), 729 (m), 643 (w), 570 (w), 538 (w) cm^{-1}. ^{19}F NMR $(\mathrm{CF^A}_3)_3\mathrm{COOCF^B}_2\mathrm{CF^C}_2\mathrm{Cl}$ ϕ^* 69.42 (A, t), 83.0 (B, m), 71.1 (C, t), $J_{\mathrm{AB}} = 2.5$, $J_{\mathrm{BC}} = 9.0$, $J_{\mathrm{AC}} \approx 0$ Hz; $(\mathrm{CF^A}_3)_3\mathrm{COOCF^B ClCF^C}_3$ ϕ^* 69.50 (A, d), 83.2 (B, m), 81.0 (C, d), $J_{\mathrm{AB}} = 0.4$, $J_{\mathrm{BC}} = 2.5$, $J_{\mathrm{AC}} \approx 0$ Hz.

Results and Discussion

The synthesis of fluoroperoxides of the type $\mathrm{R_fOOF}$ has previously been accomplished by several different methods as shown in the equations

$$\mathrm{C_3F_6 + O_2F_2 \rightarrow C_3F_7OOF/(CF_3)_2CFOOF}^{16}$$

$$\mathrm{SO_3 + OF_2 \xrightarrow{h\nu} FSO_2OOF}^{17}$$

$$\mathrm{COF_2 + OF_2 \xrightarrow{CsF} CF_3OOF/CF_3OOOCF_3}^{18}$$

$$\mathrm{NaO_2CCF_3 + F_2 \rightarrow CF_3OOF,\ C_2F_5OOF/other}^{19}$$

$$\mathrm{CF_3OOH + F_2 \xrightarrow{CsF} CF_3OOF/other}^{20}$$

$$\mathrm{SF_5OOH + F_2 \xrightarrow{CsF} SF_5OOF/other}^{10}$$

Of these, only the reaction of hydroperoxides with $\mathrm{F_2/CsF}$ appears to have any general applicability.

As part of a study to develop reagents for the synthesis of a variety of $(\mathrm{CF_3})_3\mathrm{COO}$ peroxides, we had prepared $(\mathrm{CF_3})_3\mathrm{COOH}$ and planned to use this compound to synthesize other reactive compounds such as $(\mathrm{CF_3})_3\mathrm{COOF}$ and $(\mathrm{CF_3})_3\mathrm{COOCl}$. However, the synthesis of $(\mathrm{CF_3})_3\mathrm{COOH}$ turned out to be quite difficult, and the expected low-yield syntheses of $(\mathrm{CF_3})_3\mathrm{COOF}$ and $(\mathrm{CF_3})_3\mathrm{COOCl}$ from the hydroperoxide appeared to render this approach impractical. Due to the instability of $(\mathrm{CF_3})_3\mathrm{COOCl}$ prepared by an alternate route and difficulty in obtaining $(\mathrm{CF_3})_3\mathrm{COOH}$,[2] a practical synthesis of $(\mathrm{CF_3})_3\mathrm{COOF}$ was critical to our goal of developing a reagent that could be used for the preparation of $(\mathrm{CF_3})_3\mathrm{COO}$ derivatives.

The most accessible peroxide containing the $(\mathrm{CF_3})_3\mathrm{COO}$ group is $(\mathrm{CF_3})_3\mathrm{COOSO_2F}$. We had shown that this fluorosulfate could be used to generate the $(\mathrm{CF_3})_3\mathrm{COO}$ anion by nucleophilic attack of fluoride on sulfur and could be chemically trapped by reaction with $\mathrm{COF_2}$ (eq 2).[2] The

$$\mathrm{(CF_3)_3COOSO_2F + COF_2 \xrightarrow{KF,\ 22\ ^\circ C} (CF_3)_3COOC(O)F + SO_2F_2} \quad (2)$$

oxidation of $(\mathrm{CF_3})_3\mathrm{COO^-}$ with $\mathrm{F_2}$ appeared to be a potential route to $(\mathrm{CF_3})_3\mathrm{COOF}$. Substitution of CsF for KF and lowering of the temperature to ~−55 °C provided high yields of this compound (~80%) (eq 3). This reaction does not

$$\mathrm{(CF_3)_3COOSO_2F + F_2 \xrightarrow{CsF,\ -55\ ^\circ C} (CF_3)_3COOF + SO_2F_2} \quad (3)$$

occur without CsF and the following reaction scheme is reasonable to explain the observed products.

$$\mathrm{(CF_3)_3COOSO_2F + F^- \rightarrow (CF_3)_3COO^- + SO_2F_2}$$

$$\begin{tikzcd} \mathrm{(CF_3)_3COO^-} \arrow[r] \arrow[d, "\mathrm{F_2}"] & \mathrm{(CF_3)_3CO^-} + {}^1/_2\mathrm{O_2} \arrow[d, "\mathrm{F_2}"] \\ \mathrm{(CF_3)_3COOF} & \mathrm{(CF_3)_3COF} \end{tikzcd}$$

A few percent of $(\mathrm{CF_3})_3\mathrm{COOC(CF_3)_3}$ is always observed and probably arises from the free-radical nature of the reaction with fluorine. A large excess of fluorine decreases the amount of peroxide suggesting an intermediacy of $(\mathrm{CF_3})_3\mathrm{COO}\cdot$ and $(\mathrm{CF_3})_3\mathrm{CO}\cdot$ radicals. These radicals could combine to form $(\mathrm{CF_3})_3\mathrm{CO}_n\mathrm{C(CF_3)_3}$ (n = 2, 3, 4), but only the peroxide could be isolated. However, the less volatile products from this reaction always produced some oxygen on warming to room temperature, which could arise from the decomposition of small amounts of $(\mathrm{CF_3})_3\mathrm{CO}_n\mathrm{C(CF_3)_3}$ ($n > 2$).

The new fluoroperoxide $(\mathrm{CF_3})_3\mathrm{COOF}$ is surprisingly stable and its decomposition is sensitive to impurities and other influences. The compound explodes, when warmed to 22 °C in a sealed tube, where the volume is small enough to leave a liquid phase. On the other hand, in the gas phase at 22 °C, at a pressure of 20–40 mm, decomposition is very slow and the compound can be purified by GLC. Curiously, the compound was very unstable in a glass infrared cell with AgCl windows. The thermal decomposition is quite complex and a 0.5-mmol sample in a 100-mL glass bulb was completely decomposed after 30 h at 22 °C. The products were mainly $(\mathrm{CF_3})_2\mathrm{CO}$, $\mathrm{CF_3OF}$, and $\mathrm{CF_3OOOCF_3}$, with small amounts of $\mathrm{CF_3OOCF_3}$, $\mathrm{COF_2}$, and $\mathrm{SiF_4}$. Essentially no oxygen is formed and the total moles of gas indicate a twofold increase in volume.

The infrared, Raman, and ^{19}F NMR spectra provide unequivocal proof of structure for $(\mathrm{CF_3})_3\mathrm{COOF}$. The infrared spectrum is quite similar to that of $(\mathrm{CF_3})_3\mathrm{COF}$,[15] except for the absence of ν_{OF} at 887 cm^{-1} and the new, very strong band at 1069 cm^{-1} instead of 1108 cm^{-1}. In addition, the band at 741 cm^{-1} is much stronger than the typical $\delta_{\mathrm{a}}(\mathrm{CF_3})$ found in $(\mathrm{CF_3})_3\mathrm{CO}$ compounds.[21,12] This band is clearly ν_{OF} of the peroxo compound with some intensity contribution from $\delta_{\mathrm{a}}(\mathrm{CF_3})$. The Raman spectrum of the liquid shows a polarized counterpart to the 741 cm^{-1} IR band and $\delta_{\mathrm{a}}(\mathrm{CF_3})$ is clearly visible at 724 cm^{-1} as a depolarized band. The relatively intense polarized band at 902 cm^{-1} is assigned to ν_{OO}, and the most intense band in all Raman spectra of $(\mathrm{CF_3})_3\mathrm{CO}$ derivatives, a $\delta_{\mathrm{s}}(\mathrm{CF_3})$ mode, is at 768 cm^{-1} in $(\mathrm{CF_3})_3\mathrm{COOF}$ compared to 758 cm^{-1} in $(\mathrm{CF_3})_3\mathrm{COF}$. The ^{19}F NMR exhibits a typical $(\mathrm{CF_3})_3\mathrm{CO}$ resonance at ϕ^* 69.5 and a OOF resonance at ϕ^* −295.0 as expected. The value of $J_{\mathrm{FF}} = 6.0$ Hz indicates the presence of two oxygen atoms, since J_{FF} in $(\mathrm{CF_3})_3\mathrm{COF}$ is 15.5 Hz.

In Table I, some salient features of $\mathrm{R_fOOF}$ are given for the seven known fluoroperoxides along with related data for

Table I. Comparison of ^{19}F NMR, ν_{OF}, and ν_{OO} of R_fOF and R_fOOF

	ν_{OF}, cm^{-1}	ν_{OO}, cm^{-1}	ϕ^*(OF)	ref
CF_3OF	882		−147.1	22, 23
CF_3OOF	760	873	−292	20
SF_5OF	949		−189.0	10, 24
SF_5OOF	727	873	−330	10
FSO_2OF	878		−249.0	25, 26
FSO_2OOF	738	890	−291	17, 27
$(CF_3)_3COF$	885		−149.6	15
$(CF_3)_3COOF$	741	902	−295	this work
C_3F_7OF	888		−144.3	15
C_3F_7OOF	?	?	−292	16
$(CF_3)_2CFOF$	885		−153.9	15
$(CF_3)_2CFOOF$	?	?	−292	16
C_2F_5OF	909		−139.4	15
C_2F_5OOF	752	?	−291.6	19

the analogous R_fOF derivatives. It can be seen from this that all carbon derivatives show a very consistent pattern with regard to ν_{OF}, ν_{OO}, and ϕ^*(OF) values, and clearly the O–F bonds in the fluoroperoxides are rather different from those in the nonperoxides. Greater variations, but similar trends, are shown by the sulfur compounds, as might be anticipated for an element where d orbitals may be involved in the bonding. The recent structural determination of CF_3OOF by electron diffraction suggests that the compound has some of the features of O_2F_2 with a significantly shorter O–O bond and longer O–F bond than expected for a typical peroxide or FO derivative such as CF_3OOCF_3 or CF_3OF.[28] One would expect similar results for the other fluoroperoxides which contain a highly electronegative R group.

Further structural proof for $(CF_3)_3COOF$ is provided by the reaction with C_2F_3Cl (eq 4). Two isomeric peroxides are

$$(CF_3)_3COOF + CF_2CFCl \rightarrow (CF_3)_3COOCF_2CF_2Cl(1)/(CF_3)_3COOCFClCF_3(7) \quad (4)$$

formed corresponding to the free-radical addition of $(CF_3)_3COOF$ to the olefin. The magnitude of J_{FF} for coupling between the $(CF_3)_3C$ group and the α fluorines in the alkyl group clearly indicates the compounds are peroxides and not ethers. In the analogous ethers, the corresponding J_{FF} values are approximately 4 times larger.[29] This reaction also serves to indicate the utility of $(CF_3)_3COOF$ as a reagent for the direct synthesis of fluorinated peroxides. While only one example has been studied, extension of this reaction to other systems should be straightforward.

An additional $(CF_3)_3COOF$ reaction of considerable interest is the reaction with $KOC(CF_3)_3$ which resulted in the formation of the trioxide. An earlier attempt to prepare $(CF_3)_3COOOC(CF_3)_3$ from $KOC(CF_3)_3$ and OF_2 was unsuccessful, although this reaction is clearly analogous to that used for the successful preparation of CF_3OOOCF_3.[30]

$$CsOCF_3 + OF_2 \rightarrow CF_3OOF + CsF$$

$$CF_3OOF + CsOCF_3 \rightarrow CF_3OOOCF_3 + CsF$$

$$KOC(CF_3)_3 + OF_2 \nrightarrow (CF_3)_3COOF + KF$$

$$KOC(CF_3)_3 + (CF_3)_3COOF \nrightarrow (CF_3)_3COOOC(CF_3)_3 + KF$$

The reaction of OF_2 with metal salts of the above type is rather slow at 22 °C and below. If this reaction were more favorable at low temperature, it would probably form both $(CF_3)_3COOF$ and $(CF_3)_3COOOC(CF_3)_3$ in reasonable yields. But at 22 °C, neither compound is observed. This is to be expected based on the properties of $(CF_3)_3COOF$ described above.

On the other hand, CF_3OOF is more reactive than OF_2 in the reaction with $CsOCF_3$, and a similar difference is expected for the reaction of $(CF_3)_3COOF$ with $KOC(CF_3)_3$ compared to the reaction with OF_2. Thus, with $(CF_3)_3COOF$ available, we reasoned that the trioxide might be obtainable. Reaction of $(CF_3)_3COOF$ with $KOC(CF_3)_3$ at low temperature forms an unstable white solid, believed to be the trioxide (eq 5).

$$(CF_3)_3COOF + KOC(CF_3)_3 \xrightarrow{-90 \text{ to } -40\ ^\circ C} (CF_3)_3COOOC(CF_3)_3 + KF \quad (5)$$

Unfortunately, the trioxide could not be characterized in a completely satisfactory manner. The ^{19}F NMR spectrum obtained at low temperature shows a singlet at ϕ^* 69.8 as expected for $(CF_3)_3COOOC(CF_3)_3$. An IR band at 1020 cm^{-1}, in addition to bands common for $(CF_3)_3COOC(CF_3)_3$, was observable in the gas phase. On standing at 22 °C, this band rapidly disappeared, and the observed IR spectrum appeared to be that of $(CF_3)_3COOC(CF_3)_3$ and $(CF_3)_2CO$. Perhaps the best evidence for $(CF_3)_3COOOC(CF_3)_3$ comes from its decomposition. When a sample is collected at low temperature and warmed to room temperature, oxygen is rapidly given off. After complete decomposition, separation of the products shows $(CF_3)_3COOC(CF_3)_3$, $(CF_3)_2CO$, C_2F_6, and O_2 as the major products, with small amounts of other products. These results are very consistent with the decomposition of other trioxides.[10,31]

$$CF_3O_3CF_3 \rightarrow CF_3O_2CF_3 + {}^1/_2O_2$$

$$SF_5O_3SF_5 \rightarrow SF_5O_2SF_5 + {}^1/_2O_2$$

These reactions involve $CF_3O\cdot$ and $SF_5O\cdot$ radicals which have reasonable stability in the gas phase. If the decomposition of $(CF_3)_3COOOC(CF_3)_3$ involves the $(CF_3)_3CO\cdot$ radical, $(CF_3)_2CO$ and C_2F_6 would be expected as major products due to the reactions[2,12]

$$(CF_3)_3CO\cdot \rightarrow (CF_3)_2CO + CF_3\cdot$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6$$

In conclusion, while the direct evidence for $(CF_3)_3COOOC(CF_3)_3$ is somewhat meager, we believe the compound is indeed formed in the low-temperature reaction of $KOC(CF_3)_3$ with $(CF_3)_3COOF$ and that its decomposition at 22 °C is fast. Thus, the only well-characterized fluorinated trioxides stable at 22 °C remain the three trifluoromethyl derivatives, CF_3OOOCF_3, $CF_3OOOC_2F_5$, and $CF_3OOOCF_2OOCF_3$.[30]

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Registry No. $(CF_3)_3COOF$, 66793-67-7; $(CF_3)_3COF$, 2203-56-7; $KOC(CF_3)_3$, 29646-16-0; CF_2CFCl, 79-38-9; $(CF_3)_3COOOC(CF_3)_3$, 66793-66-6; $(CF_3)_3COOCF_2CF_2Cl$, 66793-65-5; $(CF_3)_3COOCFClCF_3$, 66793-64-4; $(CF_3)_3COOSO_2F$, 55064-77-2; F_2, 16984-48-8.

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Properties of Nitroxyl as Intermediate in the Nitric Oxide–Hydroxylamine Reaction and in Trioxodinitrate Decomposition[1]

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The rate of decomposition of trioxodinitrate monobasic anion ($HN_2O_3^-$) in aqueous solution is unaffected by the presence of hydroxylamine, but the primary product nitroxyl (HNO) experiences a competition between dimerization to N_2O and reduction to N_2. The proportion of N_2 increases with pH and with NH_2OH concentration; at pH 8, with NH_2OH in 10-fold excess over $HN_2O_3^-$, the reaction product is more than 97% N_2. The reaction between NO and NH_2OH produces equimolar amounts of N_2 and N_2O at pH >13, but the ratio N_2/N_2O decreases with pH; at pH 8 the product is almost entirely N_2O. The rate of reaction declines sharply with decreasing pH. Observations of reaction product ratios are complicated by simultaneous contributions of NH_2OH disproportionation, which produces N_2 and N_2O in pH-dependent proportions. Tracer experiments employing $^{15}N^{18}O$ reactant confirm a previously proposed mechanistic interpretation of the NO–NH_2OH reaction in detail: an N-bound H atom is abstracted by NO to form HNO and the radical NHOH. The radical combines with a second NO molecule to form nitrosohydroxylamine, which in turn produces two kinds of N_2O: I, predominantly $^{14}N^{15}N^{18}O$, and II, predominantly $^{15}N^{14}N^{16}O$. The asymmetry of the intermediate is reflected in a higher proportion of I than II in the product at high pH, but these proportions become equalized at pH 8, probably because of tautomerism in the intermediate. Nitroxyl is entirely reduced by NH_2OH to N_2 at high pH but undergoes dimerization to produce a third kind of N_2O, predominantly $^{15}N^{15}N^{18}O$, to an extent that increases with decreasing pH. The tracer experiments also provide support for the hypothesis that nitroxyl is a primary product of hydroxylamine disproportionation. Since the nitroxyl produced in $HN_2O_3^-$ decomposition is preferentially reduced to N_2 at pH 8 in the presence of NH_2OH, while the nitroxyl produced in the NO–NH_2OH reaction is almost entirely consumed by self-reaction at the same pH, different intermediate species are produced in these two reactions. Possible explanations for this difference are discussed.

Introduction

In a previous communication from this laboratory[2] it has been demonstrated that sodium trioxodinitrate(II) ($Na_2N_2O_3$) decomposes in aqueous solution by cleavage of the N=N bond to produce the products nitrite and nitroxyl (HNO or NOH), the latter as precursor to N_2O. This conclusion, applying to the monobasic anion $HN_2O_3^-$ as predominating species in the pH range ~4–8, has been subsequently verified by Hughes and Wimbledon.[3] The existence of nitroxyl as an intermediate was first proposed by Angeli,[4] and its participation in the reactions of nitrogen has often been postulated. It has been directly observed by matrix isolation,[5] and its properties as a gas-phase species have been examined by spectroscopy[6] and by mass spectrometry.[7] The gas-phase species described in the literature is invariably HNO, and NOH has not been detected, to the best of our knowledge. It has therefore become customary to designate solution species nitroxyl as HNO, although there appears to be no clear evidence distinguishing between the two possible tautomers in any particular case. The unresolved question of location of the proton in $HN_2O_3^-$ may have a strong bearing on this distinction in the case of the trioxodinitrate decomposition reaction. Nitroxyl in solution has been reported in the literature of radiation chemistry; in particular, pulse radiolysis experiments involving hydrated electrons and hydrogen atoms impacting dissolved NO molecules give rise to a species that has been identified as HNO.[8] While these experiments make a convincing case for nitroxyl and even provide a p*K* value of 4.7 for this species, there does not appear to be any basis in the experiments themselves to distinguish between tautomeric possibilities.

An interesting reaction for which nitroxyl intermediate has been proposed is the reduction of NO by hydroxylamine. This reaction has been studied in 0.5 M NaOH solutions by Cooper, Chilton, and Powell,[9] who report equimolar quantities of N_2 and N_2O as products and a tracer experiment indicating the appearance of one N atom of NO origin in each of the two product molecules. These authors have postulated the participation of a nitroxyl intermediate, in an interpretation of these facts, in the mechanism

$$NO + NH_2OH \rightarrow HNO \text{ (or NOH)} + NHOH \text{ (or } H_2NO) \qquad (1)$$

$$NHOH + NO \rightarrow ON\text{–}NHOH \rightarrow N_2O + H_2O \qquad (2)$$

$$NO^- + NH_2OH \rightarrow N_2 + H_2O + OH^- \qquad (3)$$

We have given further experimental attention to this reaction, in the conviction that if a nitroxyl intermediate does participate, there should be conditions in which it undergoes the dimerization reaction characteristic of the nitroxyl intermediate observed in trioxodinitrate decomposition. In this paper we report the results of studies which confirm the role of nitroxyl in the NO–NH_2OH reaction, but from which we infer that

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