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## Direct Synthesis of Fluorinated Peroxides. 8. Synthesis and Properties of $(CF_3)_3COOF$ and Evidence for the Trioxide $(CF_3)_3COOC(CF_3)_3$

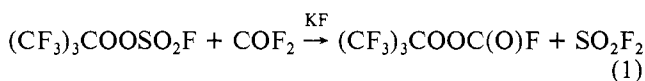
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The preparation of  $(CF_3)_3COOF$  has been achieved by the low-temperature reaction of fluorine with the novel peroxy anion  $(CF_3)_3COO^-$ . The latter is generated in situ by nucleophilic attack of fluoride on  $(CF_3)_3COOSO_2F$ . The compound 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  $(CF_3)_3COOC(CF_3)_3$ .

### Introduction

Several members of the new class of fluorinated peroxides containing the perfluoro-*tert*-butyl group have recently been described.<sup>2</sup> 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.

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 monochromator with photon counting detection. A low-temperature cell similar to that described by Brown et al.<sup>11</sup> 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  $KOC(CF_3)_3$ .<sup>12</sup> 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.<sup>13</sup> 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  $(CF_3)_3COOC(CF_3)_3$  identified by IR and NMR spectroscopy and molecular weight. The -95 °C trap contained nearly pure  $(CF_3)_3COOF$  with small amounts of  $(CF_3)_3COF$ .<sup>15</sup> 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,

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

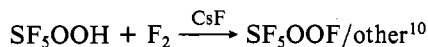
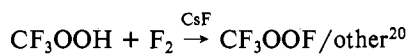
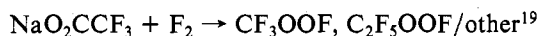
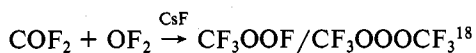
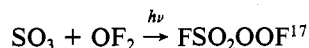
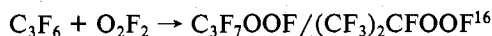
For comparison, the Raman spectrum of  $(\text{CF}_3)_3\text{COF}$  was also recorded at  $-10^\circ\text{C}$ : 1286, br; 1100, 0.7, p; 995, 0.6, p; 870, 2.2, p; 758, 10.0, p; 724, 1.0, p; 650, 0.4, dp; 560, 0.7, dp; 530, 0.9, dp; 498, 0.6, dp; 434, 0.3, p; 354, 3.3, p; 318, 1.9, dp; 300, 4.5, p; 282,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

**Reaction of  $(\text{CF}_3)_3\text{COOF}$  with  $\text{KOC}(\text{CF}_3)_3$ .** In a typical reaction, 1.0 mmol of  $(\text{CF}_3)_3\text{COOF}$  was condensed onto 4.0 mmol of  $\text{KOC}(\text{CF}_3)_3$  contained in a 100-mL glass vessel at  $-196^\circ\text{C}$ . The reaction was allowed to warm from  $-90$  to  $-40^\circ\text{C}$  over 24 h. The contents were then pumped via a short connection through traps at  $-60$  and  $-196^\circ\text{C}$  as the reactor warmed slowly in the air from  $-78^\circ\text{C}$ . The  $-196^\circ\text{C}$  trap contained  $\text{CF}_4$ ,  $(\text{CF}_3)_2\text{CO}$ ,  $\text{C}_2\text{F}_6$ , and other products. A white solid collected in the  $-60^\circ\text{C}$  trap. This material was very unstable at  $22^\circ\text{C}$  and pumping from one container, as it warmed slowly, to another vessel at  $-196^\circ\text{C}$  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  $-60^\circ\text{C}$  with an NMR tube attached to the bottom of the trap. The compound was washed into the NMR tube with cold  $\text{CFCl}_3$  (below  $-40^\circ\text{C}$ ). The NMR spectrum showed a single, somewhat broadened resonance at  $\phi^*$  69.8.

**Reaction of  $(\text{CF}_3)_3\text{COOF}$  with  $\text{CF}_2\text{CFCl}$ .** One millimole of  $(\text{CF}_3)_3\text{COOF}$  and 5.0 mmol of  $\text{CF}_2\text{CFCl}$  were condensed into a metal reactor containing 15 g of  $\text{CsF}$  at  $-196^\circ\text{C}$ . The  $\text{CsF}$  was used simply as a moderator for the reaction. The vessel was allowed to warm slowly to  $22^\circ\text{C}$  and the product was collected at  $-78^\circ\text{C}$ . GLC showed only one major component, yield  $\sim 75\%$ .  $(\text{CF}_3)_3\text{COOCF}_2\text{CF}_2\text{Cl}$  (1)– $(\text{CF}_3)_3\text{COOCFClCF}_3$  (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)  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR  $(\text{CF}_3)_3\text{COOCF}_2\text{CF}_2\text{Cl}$   $\phi^*$  69.42 (A, t), 83.0 (B, m), 71.1 (C, t),  $J_{\text{AB}} = 2.5$ ,  $J_{\text{BC}} = 9.0$ ,  $J_{\text{AC}} \approx 0$  Hz;  $(\text{CF}_3)_3\text{COOCFClCF}_3$   $\phi^*$  69.50 (A, d), 83.2 (B, m), 81.0 (C, d),  $J_{\text{AB}} = 0.4$ ,  $J_{\text{BC}} = 2.5$ ,  $J_{\text{AC}} \approx 0$  Hz.

## Results and Discussion

The synthesis of fluoroperoxides of the type  $\text{R}_f\text{OOF}$  has previously been accomplished by several different methods as shown in the equations

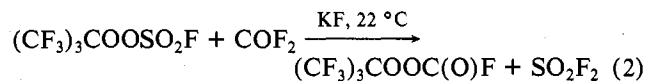


Of these, only the reaction of hydroperoxides with  $\text{F}_2/\text{CsF}$  appears to have any general applicability.

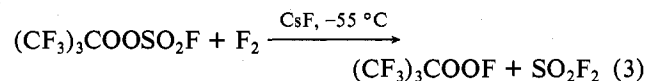
As part of a study to develop reagents for the synthesis of a variety of  $(\text{CF}_3)_3\text{COO}$  peroxides, we had prepared  $(\text{CF}_3)_3\text{COOH}$  and planned to use this compound to synthesize other reactive compounds such as  $(\text{CF}_3)_3\text{COOF}$  and  $(\text{CF}_3)_3\text{COOCl}$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

The most accessible peroxide containing the  $(\text{CF}_3)_3\text{COO}$  group is  $(\text{CF}_3)_3\text{COOSO}_2\text{F}$ . We had shown that this fluorosulfate could be used to generate the  $(\text{CF}_3)_3\text{COO}$  anion by

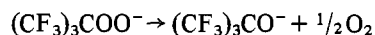
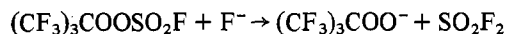
nucleophilic attack of fluoride on sulfur and could be chemically trapped by reaction with  $\text{COF}_2$  (eq 2).<sup>2</sup> The



oxidation of  $(\text{CF}_3)_3\text{COO}^-$  with  $\text{F}_2$  appeared to be a potential route to  $(\text{CF}_3)_3\text{COOF}$ . Substitution of  $\text{CsF}$  for  $\text{KF}$  and lowering of the temperature to  $\sim -55^\circ\text{C}$  provided high yields of this compound ( $\sim 80\%$ ) (eq 3). This reaction does not



occur without  $\text{CsF}$  and the following reaction scheme is reasonable to explain the observed products.



A few percent of  $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$  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  $(\text{CF}_3)_3\text{COO}^\cdot$  and  $(\text{CF}_3)_3\text{CO}^\cdot$  radicals. These radicals could combine to form  $(\text{CF}_3)_3\text{CO}_n\text{C}(\text{CF}_3)_3$  ( $n = 2, 3, 4$ ), 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  $(\text{CF}_3)_3\text{CO}_n\text{C}(\text{CF}_3)_3$  ( $n > 2$ ).

The new fluoroperoxide  $(\text{CF}_3)_3\text{COOF}$  is surprisingly stable and its decomposition is sensitive to impurities and other influences. The compound explodes, when warmed to  $22^\circ\text{C}$  in a sealed tube, where the volume is small enough to leave a liquid phase. On the other hand, in the gas phase at  $22^\circ\text{C}$ , 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  $\text{AgCl}$  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  $22^\circ\text{C}$ . The products were mainly  $(\text{CF}_3)_2\text{CO}$ ,  $\text{CF}_3\text{OF}$ , and  $\text{CF}_3\text{OOOCF}_3$ , with small amounts of  $\text{CF}_3\text{OOCF}_3$ ,  $\text{COF}_2$ , and  $\text{SiF}_4$ . Essentially no oxygen is formed and the total moles of gas indicate a twofold increase in volume.

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

In Table I, some salient features of  $\text{R}_f\text{OOF}$  are given for the seven known fluoroperoxides along with related data for

Table I. Comparison of  $^{19}\text{F}$  NMR,  $\nu_{\text{OF}}$ , and  $\nu_{\text{OO}}$  of  $\text{R}_f\text{OF}$  and  $\text{R}_f\text{OOF}$ 

	$\nu_{\text{OF}}$ , $\text{cm}^{-1}$	$\nu_{\text{OO}}$ , $\text{cm}^{-1}$	$\phi^*(\text{OF})$	ref
$\text{CF}_3\text{OF}$	882		-147.1	22, 23
$\text{CF}_3\text{OOF}$	760	873	-292	20
$\text{SF}_5\text{OF}$	949		-189.0	10, 24
$\text{SF}_5\text{OOF}$	727	873	-330	10
$\text{FSO}_2\text{OF}$	878		-249.0	25, 26
$\text{FSO}_2\text{OOF}$	738	890	-291	17, 27
$(\text{CF}_3)_3\text{COF}$	885		-149.6	15
$(\text{CF}_3)_3\text{COOF}$	741	902	-295	this work
$\text{C}_3\text{F}_7\text{OF}$	888		-144.3	15
$\text{C}_3\text{F}_7\text{OOF}$	?	?	-292	16
$(\text{CF}_3)_3\text{CFOF}$	885		-153.9	15
$(\text{CF}_3)_2\text{CFOOF}$	?	?	-292	16
$\text{C}_2\text{F}_5\text{OF}$	909		-139.4	15
$\text{C}_2\text{F}_5\text{OOF}$	752	?	-291.6	19

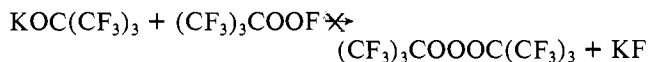
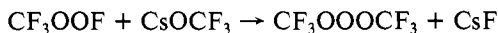
the analogous  $\text{R}_f\text{OF}$  derivatives. It can be seen from this that all carbon derivatives show a very consistent pattern with regard to  $\nu_{\text{OF}}$ ,  $\nu_{\text{OO}}$ , and  $\phi^*(\text{OF})$  values, and clearly the O-F bonds in the fluoroperoxides are rather different from 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  $\text{CF}_3\text{OOF}$  by electron diffraction suggests that the compound has some of the features of  $\text{O}_2\text{F}_2$  with a significantly shorter O-O bond and longer O-F bond than expected for a typical peroxide or FO derivative such as  $\text{CF}_3\text{OOCF}_3$  or  $\text{CF}_3\text{OF}$ .<sup>28</sup> One would expect similar results for the other fluoroperoxides which contain a highly electronegative R group.

Further structural proof for  $(\text{CF}_3)_3\text{COOF}$  is provided by the reaction with  $\text{C}_2\text{F}_3\text{Cl}$  (eq 4). Two isomeric peroxides are

$$(\text{CF}_3)_3\text{COOF} + \text{CF}_2\text{CFCl} \rightarrow (\text{CF}_3)_3\text{COOCF}_2\text{CF}_2\text{Cl}(1) / (\text{CF}_3)_3\text{COOCFCICF}_3(7) \quad (4)$$

formed corresponding to the free-radical addition of  $(\text{CF}_3)_3\text{COOF}$  to the olefin. The magnitude of  $J_{\text{FF}}$  for coupling between the  $(\text{CF}_3)_3\text{C}$  group and the  $\alpha$  fluorines in the alkyl group clearly indicates the compounds are peroxides and not ethers. In the analogous ethers, the corresponding  $J_{\text{FF}}$  values are approximately 4 times larger.<sup>29</sup> This reaction also serves to indicate the utility of  $(\text{CF}_3)_3\text{COOF}$  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.

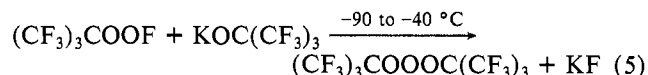
An additional  $(\text{CF}_3)_3\text{COOF}$  reaction of considerable interest is the reaction with  $\text{KOC}(\text{CF}_3)_3$  which resulted in the formation of the trioxide. An earlier attempt to prepare  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$  from  $\text{KOC}(\text{CF}_3)_3$  and  $\text{OF}_2$  was unsuccessful, although this reaction is clearly analogous to that used for the successful preparation of  $\text{CF}_3\text{OOOCF}_3$ .<sup>30</sup>



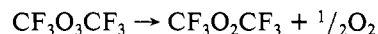
The reaction of  $\text{OF}_2$  with metal salts of the above type is rather slow at 22 °C and below. If this reaction were more favorable at low temperature, it would probably form both  $(\text{CF}_3)_3\text{COOF}$  and  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$  in reasonable yields. But at 22 °C, neither compound is observed. This is to be expected based on the properties of  $(\text{CF}_3)_3\text{COOF}$  described above.

On the other hand,  $\text{CF}_3\text{OOF}$  is more reactive than  $\text{OF}_2$  in the reaction with  $\text{CsOCF}_3$ , and a similar difference is expected for the reaction of  $(\text{CF}_3)_3\text{COOF}$  with  $\text{KOC}(\text{CF}_3)_3$  compared

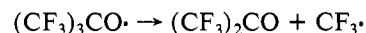
to the reaction with  $\text{OF}_2$ . Thus, with  $(\text{CF}_3)_3\text{COOF}$  available, we reasoned that the trioxide might be obtainable. Reaction of  $(\text{CF}_3)_3\text{COOF}$  with  $\text{KOC}(\text{CF}_3)_3$  at low temperature forms an unstable white solid, believed to be the trioxide (eq 5).



Unfortunately, the trioxide could not be characterized in a completely satisfactory manner. The  $^{19}\text{F}$  NMR spectrum obtained at low temperature shows a singlet at  $\phi^* 69.8$  as expected for  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$ . An IR band at 1020  $\text{cm}^{-1}$ , in addition to bands common for  $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$ , 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  $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$  and  $(\text{CF}_3)_2\text{CO}$ . Perhaps the best evidence for  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$  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  $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$ ,  $(\text{CF}_3)_2\text{CO}$ ,  $\text{C}_2\text{F}_6$ , and  $\text{O}_2$  as the major products, with small amounts of other products. These results are very consistent with the decomposition of other trioxides.<sup>10,31</sup>



These reactions involve  $\text{CF}_3\text{O}\cdot$  and  $\text{SF}_5\text{O}\cdot$  radicals which have reasonable stability in the gas phase. If the decomposition of  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$  involves the  $(\text{CF}_3)_3\text{CO}\cdot$  radical,  $(\text{CF}_3)_2\text{CO}$  and  $\text{C}_2\text{F}_6$  would be expected as major products due to the reactions<sup>2,12</sup>



In conclusion, while the direct evidence for  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$  is somewhat meager, we believe the compound is indeed formed in the low-temperature reaction of  $\text{KOC}(\text{CF}_3)_3$  with  $(\text{CF}_3)_3\text{COOF}$  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,  $\text{CF}_3\text{OOOCF}_3$ ,  $\text{CF}_3\text{OOOC}_2\text{F}_5$ , and  $\text{CF}_3\text{OOOCF}_2\text{OOCF}_3$ .<sup>30</sup>

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**Registry No.**  $(\text{CF}_3)_3\text{COOF}$ , 66793-67-7;  $(\text{CF}_3)_3\text{COF}$ , 2203-56-7;  $\text{KOC}(\text{CF}_3)_3$ , 29646-16-0;  $\text{CF}_2\text{CFCl}$ , 79-38-9;  $(\text{CF}_3)_3\text{COOOC}(\text{CF}_3)_3$ , 66793-66-6;  $(\text{CF}_3)_3\text{COOCF}_2\text{CF}_2\text{Cl}$ , 66793-65-5;  $(\text{CF}_3)_3\text{COOCFCICF}_3$ , 66793-64-4;  $(\text{CF}_3)_3\text{COOSO}_2\text{F}$ , 55064-77-2;  $\text{F}_2$ , 16984-48-8.

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## Properties of Nitroxyl as Intermediate in the Nitric Oxide-Hydroxylamine Reaction and in Trioxodinitrate Decomposition<sup>1</sup>

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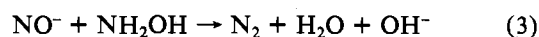
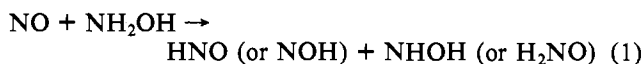
The rate of decomposition of trioxodinitrate monobasic anion ( $\text{HN}_2\text{O}_3^-$ ) in aqueous solution is unaffected by the presence of hydroxylamine, but the primary product nitroxyl (HNO) experiences a competition between dimerization to  $\text{N}_2\text{O}$  and reduction to  $\text{N}_2$ . The proportion of  $\text{N}_2$  increases with pH and with  $\text{NH}_2\text{OH}$  concentration; at pH 8, with  $\text{NH}_2\text{OH}$  in 10-fold excess over  $\text{HN}_2\text{O}_3^-$ , the reaction product is more than 97%  $\text{N}_2$ . The reaction between NO and  $\text{NH}_2\text{OH}$  produces equimolar amounts of  $\text{N}_2$  and  $\text{N}_2\text{O}$  at pH > 13, but the ratio  $\text{N}_2/\text{N}_2\text{O}$  decreases with pH; at pH 8 the product is almost entirely  $\text{N}_2\text{O}$ . The rate of reaction declines sharply with decreasing pH. Observations of reaction product ratios are complicated by simultaneous contributions of  $\text{NH}_2\text{OH}$  disproportionation, which produces  $\text{N}_2$  and  $\text{N}_2\text{O}$  in pH-dependent proportions. Tracer experiments employing  $^{15}\text{N}^{18}\text{O}$  reactant confirm a previously proposed mechanistic interpretation of the  $\text{NO}-\text{NH}_2\text{OH}$  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  $\text{N}_2\text{O}$ : I, predominantly  $^{14}\text{N}^{15}\text{N}^{18}\text{O}$ , and II, predominantly  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ . 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  $\text{NH}_2\text{OH}$  to  $\text{N}_2$  at high pH but undergoes dimerization to produce a third kind of  $\text{N}_2\text{O}$ , predominantly  $^{15}\text{N}^{15}\text{N}^{18}\text{O}$ , 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  $\text{HN}_2\text{O}_3^-$  decomposition is preferentially reduced to  $\text{N}_2$  at pH 8 in the presence of  $\text{NH}_2\text{OH}$ , while the nitroxyl produced in the  $\text{NO}-\text{NH}_2\text{OH}$  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<sup>2</sup> it has been demonstrated that sodium trioxodinitrate(II) ( $\text{Na}_2\text{N}_2\text{O}_3$ ) decomposes in aqueous solution by cleavage of the  $\text{N}=\text{N}$  bond to produce the products nitrite and nitroxyl (HNO or NOH), the latter as precursor to  $\text{N}_2\text{O}$ . This conclusion, applying to the monobasic anion  $\text{HN}_2\text{O}_3^-$  as predominating species in the pH range ~4-8, has been subsequently verified by Hughes and Wimbledon.<sup>3</sup> The existence of nitroxyl as an intermediate was first proposed by Angeli,<sup>4</sup> and its participation in the reactions of nitrogen has often been postulated. It has been directly observed by matrix isolation,<sup>5</sup> and its properties as a gas-phase species have been examined by spectroscopy<sup>6</sup> and by mass spectrometry.<sup>7</sup> 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  $\text{HN}_2\text{O}_3^-$  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.<sup>8</sup> While these experiments make a convincing case for nitroxyl and even provide a pK 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,<sup>9</sup> who report equimolar quantities of  $\text{N}_2$  and  $\text{N}_2\text{O}$  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



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  $\text{NO}-\text{NH}_2\text{OH}$  reaction, but from which we infer that