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SOME REACTIONS OF POTASSIUM PERFLUORO-t-BUTOXIDE WITH STRONG OXIDIZING AGENTS

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Summary

Several reactions of potassium perfluoro-t-butoxide with strong oxidizing agents have been studied. The new compounds $(CF_3)_3COOSO_2F$ and $(CF_3)_3CONO_2$ have been prepared by reactions with peroxydisulfuryl difluoride and nitryl fluoride, and their properties are reported. Evidence is also presented for the formation of the novel peroxy salt KOOCF, in the reaction with bis(fluoroxy)difluoromethane. A mechanism for the reaction of -OF compounds with $KOC(CF_3)_3$ is proposed.

Introduction

Perfluorinated alkoxide derivatives of metals have been very useful in synthetic chemistry. This is especially true in the case of potassium and caesium trifluoromethoxide, where nearly all CF_3O derivatives have been derived from these compounds, either by direct reaction or by reactions of compounds formed initially from these salts. Our interest in these compounds relates to the many novel oxidations they undergo to yield relatively stable peroxides, polyoxides and hypohalites such as CF_3OOSO_2F [1], CF_3OOF [2, 3], CF,OOC(O)F [3, 4], CF_3OOOCF_3 [5] and CF_3OX [6 - 8] (X = Cl, F). A limited number of similar reactions with other higher perfluoroalkoxides have been carried out, but, in general, the corresponding compounds have been relatively unstable.

The recent synthesis of the stable alkali-metal derivatives of perfluoro-t-butanol [9] makes these compounds readily available for similar studies. Three oxidizing agents containing the perfluoro-t-butyl group have been previously reported, *i.e.* $(CF_3)_3COX$ [10,11] (X = F, Cl) and $(CF_3)_3COOC(CF_3)_3$ [12], and their stability makes the synthesis of other related derivatives likely. We have investigated several reactions of $KOC(CF_3)_3$ with several strong oxidizing agents, and the new compounds $(CF_3)_3COOSO_2F$ and $(CF_3)_3CONO_2$ have been prepared and characterized. Evidence was also obtained for the novel peroxo derivative KOOCF, in the reaction of $CF_2(OF)_2$ with $KOC(CF_3)_3$.

Experimental

General

Volatile compounds were handled in a Pyrex and stainless-steel vacuum system equipped with Teflon/glass valves and Kel-F, soft-seat, stainless-steel valves. Pressures were measured using a Wallace and Tiernan FA-145 differential pressure gauge. Amounts of reactants and products were measured by direct weighing or from the relation $n = PV/RT$, assuming ideal gas behavior. Molecular weights were determined by vapor density measurements. Vapor pressures were determined using the method of Kellogg and Cady [13], and the data analyzed by a computer-assisted least-squares fit to both linear and quadratic equations.

Infrared spectra were recorded on Perkin–Elmer model 337 and 180 spectrometers using 10 cm glass cells fitted with AgCl windows. NMR spectra were measured at 20 °C on a Varian XL 100-15 spectrometer using 90 mol% trichlorofluoroethylene as an internal standard and solvent.

Reagents

Oxygen difluoride was obtained from the Ozark Mahoning Co., N_2O_4 from the Matheson Co., $(CF_3)_3COH$ from PCR, Inc. and KH and CsF from Research Inorganic Chemical Co. The compounds CF_3OOSO_2F [1], CF_3OF [6], $CF_2(OF)_2$ [7], CF_3OOF [2], CF_3OOOCF_3 [5], $S_2O_6F_2$ [14] and SF_5OF [15] were prepared by literature methods. Nitryl fluoride was obtained by the reaction of CF_3OOF with N_2O_4 [16]. Potassium perfluoro-t-butoxide was prepared using the method of Dear and co-workers employing a small excess of $(CF_3)_3COH$ [9]. After removal of the ether under vacuum, the compound was pumped under high vacuum until removal of $(CF_3)_3COH$ ceased.

Reactions

The reactions are summarized in Table 1. They were carried out by condensing the volatile reactant on to the $KOC(CF_3)_3$ held at −196 °C in a 100 cm^3 glass bulb fitted with a Teflon/glass valve. After reaction was complete, the products were separated by trap-to-trap distillation after removing any O_2 at −196 °C. Complete separation of all products was not attempted but separation was sufficient to identify known compounds by their infrared spectra when present in reasonable amounts. Purification of $(CF_3)_3COOSO_2F$ was accomplished by GLC at 40 °C using a 25 cm × 9 mm stainless-steel column packed with 40% Halocarbon oil (11 - 21) on Chromasorb P. The properties of $(CF_3)_3COOSO_2F$ and $(CF_3)_3CONO_2$ are as follows:

$(CF_3)_3COOSO_2F$: b.p., 80.5 °C; m.p., forms a glass; mol.wt., 328.2, calcd., 334.0; IR: 2730 (vw), 2460 (vw), 2425 (vw), 2390 (vw), 2242 (vw), 2215 (vw), 2170 (vw), 2055 (vw), 1965 (vw), 1922 (vw), 1896 (vw), 1858 (vw), 1804 (vw), 1769 (vw), 1734 (vw), 1707 (vw), 1664 (vw), 1548 (vw), 1528 (vw), 1497 (s), 1472 (w), 1456 (vw), 1418 (vw), 1375 (vw), 1290 (vs), 1260 (m), 1248 (m), 1192 (w), 1155 (w), 1106 (s), 1012 (s), 982 (s), 858 (s), 809 (m),

TABLE 1

Reactions of $KOC(CF_3)_3$

$KOC(CF_3)_3$[a]	Reactant[a]	Conditions	Products[b]
3.72	$S_2O_6F_2$, 3.13	−20 °C to −15 °C, 15 h	$(CF_3)_3COOSO_2F$, $[(CF_3)_3CO]_2$
2.66	FNO_2, 2.66	0 °C, 15 h	$(CF_3)_3CONO_2$, $[(CF_3)_3CO]_2CO$[c], $(CF_3)_3CO$, COF_2
1.25	CF_3OF, 2.5	−196 °C to 0 °C, 4 h	$(CF_3)_3COF$, $[(CF_3)_3CO]_2CO$, $(CF_3)_3COC(O)F$[c], $KOCF_3$, CF_3OF
1.10	SF_5OF, 1.10	−196 °C to 22 °C, 6 h	$(CF_3)_3COF$, $KOSF_5$
1.52	OF_2, 1.0	22 °C, 6 h	CF_4, O_2, OF_2, C_2F_6, COF_2, $CF_3C(O)F$, $(CF_3)_2CO$, $(CF_3)_3COC(O)CF_3$, $[(CF_3)_3CO]_2CO$
1.60	CF_3OOF, 1.60	−196 °C to 22 °C, 5 h	CF_4, O_2, COF_2, C_2F_6, $(CF_3)_3COC(O)F$[c], $[(CF_3)_3CO]_2CO$
1.02	$CF_3O_3CF_3$, 1.13	22 °C, 6 h	$(CF_3)_2CO$, O_2, $CF_3O_3CF_3$, $[(CF_3)_3CO]_2CO$
2.18	$CF_2(OF)_2$, 2.20	−111 °C to −25 °C, 11 h	$(CF_3)_3COF$, O_2, $KOOCF_3$, $KOCF_3$

[a] Amounts in mmoles.

[b] Major products. Other compounds may have been present in small amounts.

[c] These compounds are formed by reaction of the COF_2 and $CF_3C(O)F$ with $KOC(CF_3)_3$ N. S. Walker and D. D. DesMarteau, J. Fluorine Chem., 5 (1975) 135).

768 (m), 730 (s), 671 (w), 567 (vw), 538 (vw) cm^{-1}; NMR: ϕ^* 69.33 ppm [d, $(CF_3)_3CO$], −38.04 ppm [dectet, OSO_2F], $J(FF) = 1.7$ Hz; $\Delta H_{vap} =$ 8.99 kcal mol^{-1}; $\Delta S_{vap} = 25.4$ cal K^{-1} mol^{-1}; $\log P(mmHg) = 8.4370 - 1965.0/T$.

$(CF_3)_3CONO_2$: b.p., 59.4 °C; m.p., forms a glass; mol.wt., 281.0, calcd., 281.0; IR: 3470 (vw), 3035 (w), 3000 (vw), 2925 (vw), 2830 (vw), 2601 (vw), 2460 (vw), 2420 (vw), 2385 (vw), 2360 (vw), 2230 (vw), 2160 (vw), 2055 (vw), 1901 (w), 1878 (vw), 1815 (w), 1777 (w), 1745 (s), 1712 (w), 1625 (vw), 1550 (vw), 1535 (vw), 1480 (vw), 1430 (vw), 1380 (w), 1303 (s), 1280 (vs), 1228 (m), 1208 (w), 1195 (w), 1154 (m), 1078 (s), 996 (s), 980 (s), 790 (s), 748 (m), 729 (m), 665 (vw), 628 (w), 562 (w), 538 (w), 480 (vw) cm^{-1}; NMR: ϕ^* 69.14 ppm; $\Delta H_{vap} = 8.01$ kcal mol^{-1}; $\Delta S_{vap} = 24.1$ cal $K^{-1}mol^{-1}$ $\log P$ (mmHg) $= 8.1479 - 1751.5/T$.

Results and discussion

Reactions of potassium perfluoro-t-butoxide with strong oxidizing agents were carried out in attempts to isolate novel $(CF_3)_3CO$ derivatives which are themselves strong oxidizing agents. The reactions summarized in Table 1 show that reactions with $S_2O_6F_2$ and FNO_2 give the expected products in high yield.

$$KOC(CF_3)_3 + S_2O_6F_2 \rightarrow KOSO_2F + (CF_3)_3COOSO_2F$$

$$KOC(CF_3)_3 + (CF_3)_3COOSO_2F \rightarrow KOSO_2F + (CF_3)_3COOC(CF_3)_3$$

$$KOC(CF_3)_3 + FNO_2 \rightarrow KF + (CF_3)_3CONO_2$$

The side-reaction shown for the reaction of $S_2O_6F_2$ decreases the yield of the fluorosulfate, but provides a convenient alternate synthesis of the previously reported peroxide $(CF_3)_3COOC(CF_3)_3$ [12]. Identification of the new compounds was readily established from their IR and NMR spectra and from their molecular weights as given in the experimental section. The IR spectra of the compounds show characteristic $\nu(SO)$ and $\nu(NO)$ antisymmetric and symmetric frequencies at 1447 cm^{-1} and 1248 cm^{-1} for the fluorosulfate group, and at 1745 cm^{-1} and 1303 cm^{-1} for the nitrate group. In addition, the fluorosulfate group shows a characteristic $\nu(SF)$ frequency at 858 cm^{-1}, and the nitrate a $\nu(NO')$ frequency at 790 cm^{-1}. Both compound exhibit the very characteristic IR spectrum of the $(CF_3)_3CO$ group which normally consists of a very strong band at 1270 - 1300 cm^{-1}, a strong band at *ca.* 1050 - 1150 cm^{-1}, two strong absorptions 950 - 1030 cm^{-1} and a strong band at *ca.* 730 cm^{-1}. The ^{19}F NMR spectra contain chemical shifts ϕ^* at 69 - 70 ppm typical of the $(CF_3)_3CO$ group and at 69.33 ppm and 69.14 ppm typical of the fluorosulfate and nitrate respectively.

Both $(CF_3)_3COOSO_2F$ and $(CF_3)_3CONO_2$ are readily decomposed by heating, with the nitrate exhibiting the lower stability. The decomposition of the related compounds $(CF_3)_3COX$ [10, 11] (X = F, Cl) occurs essentially quantitatively to give CF_3X and $(CF_3)_2CO$, and a similar mode of decomposition was shown for $(CF_3)_3COOSO_2F$ and $(CF_3)_3CONO_2$.

$$(CF_3)_3COOSO_2F \xrightarrow{100\ ^\circ C} CF_3OSO_2F + (CF_3)_2CO + \text{other products}$$

$$(CF_3)_3CONO_2 \xrightarrow{95\ ^\circ C} CF_3NO_2 + (CF_3)_2CO + \text{other products}$$

The other products observed in both cases included C_2F_6. The presence of the latter may indicate that the decomposition is free radical in nature as suggested by the following mechanism for the fluorosulfate:

$$(CF_3)_3COOSO_2F \rightarrow (CF_3)_3CO\cdot + SO_3F\cdot$$

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

$$CF_3\cdot + SO_3F\cdot \rightarrow CF_3OSO_2F$$

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

In the case of the nitrate, $(CF_3)_3CONO^*$ is observed together with COF_2 and NO_2, and the decomposition is only *ca.* 50% complete as shown, compared to the decomposition of the fluorosulfate which is > 90% complete as shown.

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[*] This compound is readily obtained by reaction of N_2O_4 with $KOC(CF_3)_3$. It was previously obtained by S. Andreades, J. Org. Chem., 27 (1962) 4163.

The reaction of $KOC(CF_3)_3$ with O-F-containing compounds is interesting, although it does not lead to the simple peroxides;

$$ROF + KOC(CF_3)_3 \not\rightarrow KF + ROOC(CF_3)_3$$

In the case of CF_3OF and SF_5OF the reaction goes cleanly as shown:

$$ROF + KOC(CF_3)_3 \rightarrow KOR + (CF_3)_3COF$$

In our opinion, this raises interesting questions regarding the relative charge on the fluorine atom bound to the oxygen in these compounds. The compounds behave as if they are true hypofluorites. It can be argued that these results are simply due to a combination of thermodynamic and/or kinetic factors which favor the course of the reaction as shown. However it would seem that the free energy for the reaction would be more favorable for the formation of KF rather than KOR, given that all the O-F bonds and the O-O bonds are probably of similar strengths. Because these reactions are heterogeneous any mechanistic considerations are rather tenuous, but these reactions can be viewed as a nucleophilic attack by the $(CF_3)_3CO^-$ ion on the fluorine atom of ROF to form the RO^- ion and $(CF_3)_3COF$. It is interesting to note that the reaction of SF_5OF with $CsOCF_3$ forms CF_3OF and $CsOSF_5$ in high yield [17], which would establish a relative nucleophilicity of $(CF_3)_3CO^- > CF_3O^- > SF_5O^-$. These results would also be consistent with electrophilic fluorination of certain organic compounds by ROF which has been shown to occur in many instances [18].

With $CF_2(OF)_2$, the reaction is analogous to that of CF_3OF and SF_5OF except that a strongly oxidizing salt is formed.

$$CF_2(OF)_2 + KOC(CF_3)_3 \rightarrow (CF_3)_3COF + [KOOCF,]$$

The salt, which is believed to be KOOCF,, decomposes above 0 °C forming $O_2, KOCF_3$ and some COF_2. The formation of $CsOOCF_3$ was previously suggested as an intermediate in the reaction of $CsOCF_3$ with $CF_2(OF)_2$ [3], but it could not be isolated. The existence of KOOCF, was also postulated as an intermediate in the reaction of KF, CF_3OOSO_2F and CF_3OF to form $CF_3O_3CF_3$, but it was not isolated. In the reaction of $CsOCF_3, COF_2$ and $CF_2(OF)_2$, the formation of $CF_3OOC(O)F$ is believed to occur by the reaction

$$CsOOCF_3 + COF, \rightarrow CsF + CF_3OOC(O)F$$

To add support to this mechanism and to further identify the $KOOCF_3$ formed, the following reactions were carried out:

$$[KOOCF_3] + COF_2 \rightarrow CF,OOC(O)F + KF$$

$$KF + COF_2 + CF_3OOSO_2F \rightarrow KF + CF,OOC(O)F + SO_2F_2$$

In both cases appreciable amounts of $CF_3OOC(O)F$ were formed, and these results add considerable weight to the previously suggested mechanism for the formation of $CF_3OOC(O)F$ and show that $KOOCF_3$ is indeed the species formed in the reaction of $KOC(CF_3)_3$ with $CF_2(OF)_2$. Further studies of the chemistry of KOOCF, are planned.

The remaining reactions studied were these of $KOC(CF_3)_3$ with CF_3OOF, $CF_3O_3CF_3$ and OF_2. The trioxide reacted only slowly at 22 °C yielding a variety of products, but none of the expected trioxide, $CF_3OOOC(CF_3)_3$, or peroxide, $CF_3OOC(CF_3)_3$. The reactions with CF_3OOF and OF_2 did not proceed in the same manner as those of CFsOF, SF_5OF and $CF_2(OF)_2$, because no $(CF_3)_3COF$ was observed. This is not surprising if one considers the reactions of OF_2 and CFsOOF with $CsOCF_3$[2]:

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

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

These reactions can be viewed as a nucleophilic attack of the CF_3O^- ion on oxygen, displacing the F^- ion from OF_2 and CFsOOF. We believe the reactions of CFsOOF and OF, with $KOC(CF_3)_3$ proceed by a similar mechanism but that $CF_3OOOC(CF_3)_3$ and $(CF_3)COOF$ (which are presumably formed) are unstable.

It is instructive to compare the reactions of CFsOOF and CF_3OF with similar substrates:

$KOC(CF_3)_3$ + CFsOOF → $[CF_3OOOC(CF_3)_3]$ + KF

$KOC(CF_3)_3$ + CFsOF → KOCF, + $(CF_3)_3COF$

KOSF, + CF_3OF → no reaction at 22 °C

KOSF, + CFsOOF → no reaction at 22 °C

KOCF, + CF_3OF → possible exchange at 22 °C

KOCF, + CF_3OOF → KF + $CF_3O_3CF_3$

These results suggest, obviously, that the reaction of -OF derivatives with nucleophiles depends in a qualitative manner on the relative basicity of the attacking and leaving group. Of much greater interest, however, is the suggestion that attack can occur at either the oxygen or fluorine atom depending, in some way, on the relative ionic character of the OF bond. If ^{19}F chemical shifts of the OF group are used as a qualitative indication of the electron density at the fluorine atom, those of CF_3OOF and OF, (ϕ^* -292 and -250 ppm) occur at much lower fields than those of CFsOF and SF_5OF (ϕ^* -142 and -178 ppm), which implies that a more covalent bond occurs in CFsOOF and OF_2. We tentatively conclude that compounds with OF chemical shifts lower than ca. ϕ^* -250 ppm will undergo attack at the fluorine atom. This work raises the possibility that new -OF derivatives, which cannot be synthesized by reactions involving elemental fluorine, might be preparable by reactions of nucleophiles with compounds such as CF_3OF and SF_5OF.

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