Fully fluorinated alkoxides. Part II. Ethoxides, propoxides, and butoxides

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Ionic, fully fluorinated, ethoxides, *n*-propoxides, isopropoxides, and *n*-butoxides of the heavier alkali metals may be made by the reaction of the appropriate acyl fluoride, or of hexafluoroacetone, with the metal fluoride. Factors affecting the stability and possible synthetic use of such compounds are discussed, together with n.m.r. (nuclear magnetic resonance) and infrared spectral data.

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We (1) have shown previously that the reaction of carbonyl fluoride with fluorides of the heavier alkali metals produces ionic trifluoromethoxides as stable, crystalline solids.

$$MF + COF_2 \rightleftharpoons MOCF_3,$$

where $M = K$, Rb, or Cs.

The scope of this reaction has now been extended to include the preparation of ionic, fully fluorinated ethoxides, *n*-propoxides, isopropoxides, and *n*-butoxides by the reaction of alkali metal fluorides with trifluoroacetyl fluoride, pentafluoropropionyl fluoride, hexafluoroacetone, and heptafluoro-*n*-butyryl fluoride respectively.

$$MF + R_fCOF \rightleftharpoons MOCF_2R_f$$

$$MF + (CF_3)_2CO \rightleftharpoons MOCF(CF_3)_2,$$

where M = Rb or Cs and $R_f = CF_3$, C_2F_5, or C_3F_7.

As might be expected, these compounds are considerably less stable than the trifluoromethoxides. In discussing factors affecting the formation of the latter, we suggested that, although the negative charge in the ion OCF_3^- formally rests on the oxygen atom, the great electronegativity of the three fluorine atoms would tend to distribute the charge more evenly over the ion, and hence enhance its stability. With fluorinated alkoxides containing more than one carbon atom, this effect would be reduced. With the pentafluoroethoxide, $CF_3CF_2O^-$, for example, the carbon atom carrying the oxygen has attached to it two fluorine atoms and a trifluoromethyl group, and the lesser electronegativity of the latter as compared with a fluorine atom would lead to a lower stability than that found in the trifluoromethoxide ion. Similarly, a lower stability still would be expected for the pentafluoroisopropoxide ion, $(CF_3)_2CFO^-$, where the carbon atom attached to oxygen carries two trifluoromethyl groups.

The criterion of stability used in this work has been the rate of thermal decomposition of the solids on heating *in vacuo*, when all decomposed readily to give the metal fluoride and carbonyl compound. Other factors, such as the different lattice structures of the solids, will clearly influence the resistance to decomposition under these conditions, but the data reproduced in Figs. 1 and 2 are in general agreement with the above argument.

At 50°, the decomposition of rubidium heptafluoroisopropoxide is much more rapid than that of rubidium heptafluoro-*n*-propoxide, whereas the three cesium salts are much more stable. Decomposition of the cesium salts becomes more rapid at 80°, but there is no significant difference between the rates of decomposition of the cesium ethoxide, *n*-propoxide, or isopropoxide.

The influence of cation size on the stability of the solid alkoxides is in accord with that previously found for the trifluoromethoxides: that the larger ions produce the more stable compounds. With potassium fluoride, an adduct was obtained with trifluoroacetyl fluoride, but the solid decomposed even at 20°. No evidence was found for formation of an adduct between sodium fluoride and trifluoroacetyl fluoride

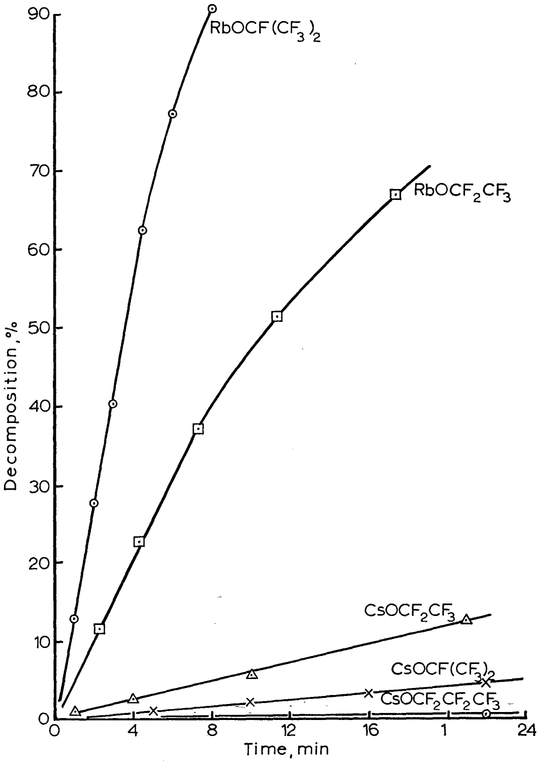


FIG. 1. Decompositions at 50°.

either as a solid residue or as a species in solution. Examination of the ^{19}F n.m.r. (nuclear magnetic resonance) spectrum of a slurry of sodium fluoride in acetonitrile with trifluoroacetyl fluoride showed the unchanged spectrum of the acyl fluoride, whereas with the fluorides of the heavier alkali metals considerable interaction was at once apparent.

With hexafluoroacetone, potassium fluoride gave a solid adduct stable at 20°, but it decomposed too rapidly at 50° for measurements of the rate to be made. The data in Fig. 1 clearly demonstrate the greater stability of cesium rather than rubidium alkoxides.

With the trifluoromethoxides, the emphasis was on the study of the solids, since no solvent could be found in which they were appreciably soluble. With the compounds studied in the present work, however, much greater solubility in polar solvents was found. This was at once apparent when the metal fluoride and the carbonyl compound were brought together in acetonitrile, in which the metal fluorides are not appreciably soluble. With trifluoroacetyl fluoride, pentafluoropropionyl fluoride, and heptafluorobutyryl fluoride, the solid fluoride at once dissolved to give a suspension containing a small amount of solid that did not have the appearance of the original fluoride. With hexafluoroacetone, all three metal fluorides readily dissolved to give completely clear solutions. Other workers have previously noted the ability of hexafluoroacetone in donor solvent to dissolve potassium fluoride (2) or cesium fluoride (3), but have not attempted to isolate the solid adducts.

Because of the solubility of the alkoxides, the removal of the solvent was much more difficult. In the preparation of the trifluoromethoxides where the product was insoluble, the solvent was removed *in vacuo* at −20° to minimize decomposition, and

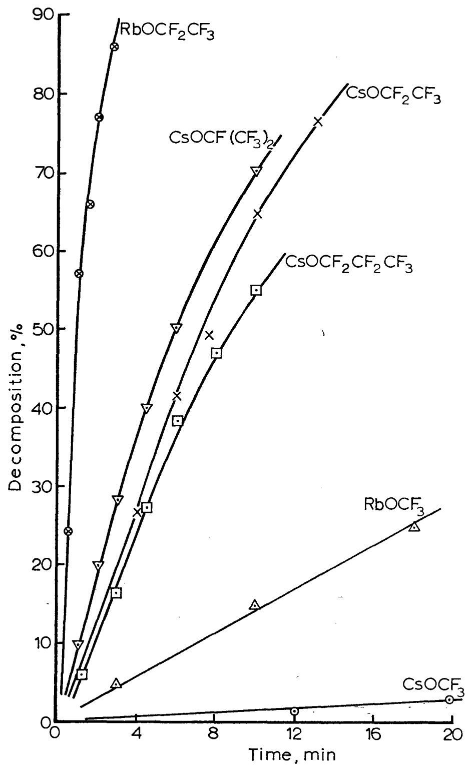


FIG. 2. Decompositions at 80°.

only in that way was it possible to prepare solids whose composition corresponded to the pure trifluoromethoxides of rubidium and cesium. In the present case, it was not possible to remove solvent at −20°. On removing acetonitrile *in vacuo* from the mixture after synthesis of the alkoxides, the solution became viscous and prolonged pumping (up to 24 h) at 20° was necessary to remove the last traces. Although most of the solids are stable at 20°, the solutions all had a tendency to decompose in this process, giving a solid residue in which the ratio of carbonyl compound to metal fluoride was always less than 1. As can be seen from Table I, the cesium alkoxides were the only ones where the composition of the solid approached a 1:1 ratio, but even with these it was apparent that some fluoride was present. For this reason, meaningful quantitative analysis of the composition of the solids was not possible.

The ready solubility of the fluorinated higher alkoxides was an advantage in the study of the n.m.r. spectra, described below, and also in using them as starting materials for the preparation of covalent fluorinated alkoxides. Use of the very reactive non-fluorinated alkoxides of Group I metals as synthetic intermediates has long been recognized, but with the fluorinated analogues this application is limited by the ease with which they decompose to eliminate a fluoride ion. With the trifluoromethoxides, where, through lack of solubility, reaction must be heterogeneous, fluoride elimination predominates and no covalent trifluoromethoxides have yet been prepared. With a compound such as the ionic di-alkoxides of perfluoropinacol, $[OC(CF_3)_2C(CF_3)_2O]^{2-}$, where there is no possibility of elimination of an α-fluorine atom, any number of stable covalent derivatives may be prepared (4).

In this respect the secondary heptafluoropropoxides, $(CF_3)_2CFO^-$, appeared intermediate between the primary trifluoromethoxides and tertiary pinacol derivatives. However, they only reacted with the more reactive alkyl halides, e.g. with allyl bromide to give allylheptafluoroisopropyl ether.

$$CH_2{:}CHCH_2Br + K^+[(CF_3)_2CFO^-] \rightarrow CH_2{:}CHCH_2OCF(CF_3)_2 + KBr$$

A recent publication by Pittman and Sharp (2) reports that reaction of triethylchlorosilane with the potassium fluoride – hexafluoroacetone adduct produces only the fluorosilane, rather than the heptafluoroisopropoxysilane, which they attribute to intramolecular fluorine transfer in the latter compound. In our own work, we have found a similar reaction to occur with trimethylchlorosilane, giving trimethylfluorosilane.

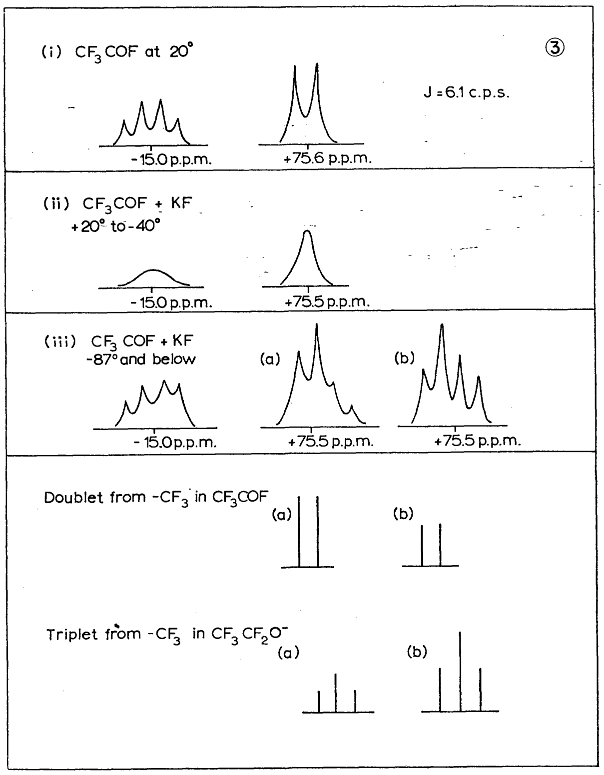
It would appear that fluoride ion abstraction is likely to predominate in the reaction of fluorinated alkoxides with compounds of moderately electropositive elements such as silicon; the limitations to their use as nucleophilic reagents have been shown by the observation of Graham and Weinmayr (3) that the heptafluoroisopropoxide ion is too feeble a nucleophile to attack tetrafluoroethylene.

A brief study was made of the hydrolysis of the fluorinated alkoxides prepared in this work. It was felt to be most unlikely that hydrolysis would yield the corresponding alcohols, in view of the high probability that such compounds having a fluorine atom in an α-position to a hydroxyl group are not generally stable. As expected, the hydrolysis products were in each case the metal fluoride or bifluoride and the fluorinated acid or hexafluoroacetone.

$$R_fCF_2O^- + H_2O \rightarrow HF_2^- + R_fCOOH$$

Nuclear Magnetic Resonance Studies

The solubility of the alkoxides in acetonitrile suggested that ^{19}F n.m.r. measurements might be used to confirm their structures. This had not been possible for



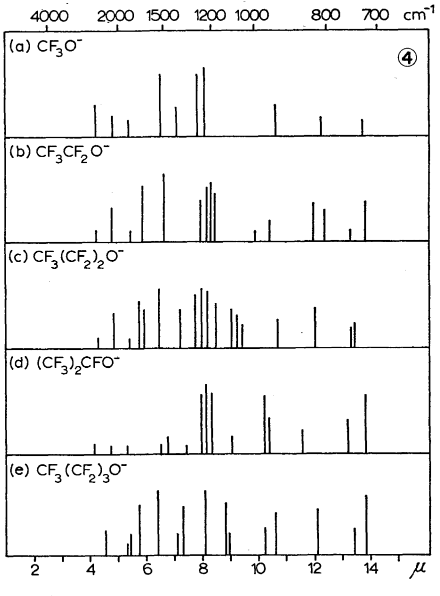


FIG. 3. ^{19}F n.m.r. spectra of $CF_3CF_2O^-$.
FIG. 4. Infrared spectra of perfluoroalkoxides.

the trifluoromethoxides because of their insolubility, and would in any case have been of little interest because only a single absorption peak would have been expected from the ion OCF_3^-.

The spectra of the various carbonyl compounds were first examined and had the expected appearance. Trifluoroacetyl fluoride in acetonitrile showed a doublet at +75.6 p.p.m. (all chemical shifts relative to external fluorotrichloromethane) associated with the $—CF_3$ group and a quartet at −15.0 p.p.m. derived from the —COF group as shown in Fig. 3 (i). The coupling constant between the two types of fluorine was 6.1 c.p.s. When potassium fluoride was dissolved in the solution at 20°, the absorptions were present at the same positions, but the fine structure had disappeared. This suggests rapid exchange of fluorine between pentafluoroethoxide ion and excess trifluoroacetyl fluoride.

$$CF_3CF_2O^- + CF_3COF \rightleftharpoons CF_3COF + CF_3CF_2O^-$$

Exchange involving dissolved fluoride ions would also be possible, but would have less importance because the slight solubility of potassium fluoride would limit the concentration of fluoride ion.

To reduce the rate of exchange, the solution was progressively cooled to −100°, using propionitrile (f.p. −92°) in preference to acetonitrile (f.p. −46°) as solvent in the lower temperature region. Resolution of the absorption peaks appeared below about −50°, and at −87° both formed well-resolved but irregular quartets, shown in Fig. 3 (iii). It would be expected that the $—CF_3$ group in CF_3COF would give a doublet near +75 p.p.m., as in the original acyl fluoride, whereas the $—CF_3$ group in $CF_3CF_2O^-$ would give a triplet. We suggest that the quartet at +75 p.p.m. in Fig. 3 (iii*a*) is the result of the superposition of these two signals, as shown at the bottom of Fig. 3. The best way of establishing this point would have been to prepare a sample containing pure pentafluoroethoxide with no excess trifluoroacetyl fluoride, but this proved to be impossible because some dissociation of the pentafluoroethoxide always occurred. However, it was possible to prepare a sample in which the ratio of excess trifluoroacetyl fluoride to pentafluoroethoxide was lower, and this gave absorption near +75 p.p.m., as shown in Fig. 3 (iii*b*). The greater intensity of the peaks assigned to the triplet in $CF_3CF_2O^-$ gives support to the above suggested assignment.

The remaining absorption in Fig. 3 (iii), that at −15.0 p.p.m., must contain the quartet of the —COF group in CF_3COF. Its irregular appearance is presumably caused by the presence of a second quartet from the absorption of $—CF_2O^-$ in $CF_3CF_2O^-$, but the resolution attainable does not permit any definite assignment to be made.

When the spectra of the acyl fluorides CF_3CF_2COF and $CF_3CF_2CF_2COF$ with rubidium fluoride in acetonitrile were examined, a similar effect was found at room temperature. The various splittings in the spectra of the pure compounds were lost when the metal fluoride was added, suggesting a rapid exchange between acyl fluoride and alkoxide. However, the larger fluorocarbon group gave these acyl fluorides a lower solubility in acetonitrile at low temperatures, making it impossible to resolve their spectra by cooling.

The n.m.r. spectrum of hexafluoroacetone in acetonitrile showed a single absorption peak at +76.1 p.p.m. from CCl_3F. On adding potassium fluoride, the peak became distinctly broadened on the high field side at 20°, and cooling to −98° separated the broadening into two peaks, one at +76.1 p.p.m. (sharp) and a second at +79.9 p.p.m. (smaller and broader). The former absorption peak is presumably due to hexafluoroacetone, whereas the second, from its chemical shift, may be assigned to the absorption associated with the $—CF_3$ group in $(CF_3)_2CFO^-$. This should of course be a doublet, split by coupling with the remaining fluorine atom in the ion, but it was not resolved at the lowest temperature attainable. The remaining expected absorption peak, associated with the other fluorine atom in $(CF_3)_2CFO^-$, should be a septet of low intensity; this was not observed.

Infrared Spectra

Essential features of the infrared spectra of the fluorinated alkoxides (as rubidium or cesium salts) are shown in Fig. 4. In many cases, the absorption peaks were broad and their positions could not be determined with great accuracy. Detailed assignments have not been made, but the strong absorption usually found in the region 1 510 – 1 560 cm^{-1} is tentatively assigned to the C—O stretching frequency by analogy with that present in the ions CO_3^{2-} (1 410 – 1 450 cm^{-1}), $HCOO^-$ and CH_3COO^- (near 1 570 cm^{-1}), and CF_3COO^- (1 700 cm^{-1}). It is noticeable, however, that the intensity of this band is considerably less in the ion $(CF_3)CFO^-$.

Absorption associated with C—F stretching frequencies is found in the region 1 180 – 1 280 cm^{-1}. This is the normal region for such absorption to occur, and the ions differ in this respect from the ion $CF_3BF_3^-$, isoelectronic with $CF_3CF_2O^-$, where the C—F absorption bands are shifted to the region 960–990 cm^{-1} (5). In the trifluoromethylfluoroborate ion, this effect was ascribed to the decrease in the force constants of the C—F bonds associated with the distribution of the negative charge over all six fluorine atoms in the ion. On this basis, it would appear that the negative charge is not so widely distributed in the fluorinated alkoxide ions, which may be due to the smaller difference in electronegativity between fluorine and oxygen compared with that between fluorine and boron.

EXPERIMENTAL

General techniques and methods of preparing anhydrous metal fluorides have been described previously (1). As before, careful attention was paid to the rigorous exclusion of moisture throughout. The identity and purity of reactants and products was established by infrared spectroscopic examination (gas phase, unless otherwise stated) using Beckman IR-5A or IR-10 instruments.

Perfluoroacyl Fluorides

These compounds were prepared by the reactions of the corresponding acyl chlorides with sodium fluoride in acetonitrile. Reactions were carried out in sealed tubes using a fourfold molar excess of sodium fluoride.

In a typical preparation, pentafluoropropionyl chloride (7.2 g, 40 mmoles) was condensed onto sodium fluoride (7.1 g, 170 mmoles) in acetonitrile (20 ml) in a heavy-walled Pyrex reaction tube (60 ml). The tube was kept at 20° for 24 h with occasional shaking, then the volatile contents fractionated to give pentafluoropropionyl fluoride (6.5 g, 39 mmoles, 98% yield).

Similar treatment of trifluoroacetyl chloride and heptafluorobutyryl chloride gave the corresponding fluorides in high yield.

Reaction of Perfluoroacyl Fluorides and of Hexafluoroacetone with Metal Fluorides

Reactions were carried out by condensing acetonitrile onto the metal fluoride in an evacuated tube at −196°, followed by the acyl fluoride or ketone. A molar ratio of about 4:1 of acyl fluoride to metal fluoride was generally used. On sealing the tube and warming to 20° with shaking, reaction was immediately evident as the metal fluorides, which are insoluble in acetonitrile, dissolved partially (with the acyl fluorides) or completely (with hexafluoroacetone). To obtain solid alkoxides, the solvent and excess acyl fluoride were then removed *in vacuo* and the composition of the solid then deduced from the amount of volatile material recovered. In most cases, removal of the solvent was slow and pumping for periods up to 24 h was required.

Results are summarized in Table I.

TABLE I

Combining ratio, acyl fluoride to metal fluoride, in solid adducts

Acyl fluoride or ketone	KF	RbF	CsF
CF_3COF	0	0.61	0.91
CF_3CF_2COF	N.A.*	0.57	0.93
$(CF_3)_2CO$	0.34	0.80	0.98
$CF_3(CF_2)_2COF$	N.A.*	0.45	N.A.*

*N.A. = isolation of solid adduct not attempted.

In the reaction of trifluoroacetyl fluoride with potassium fluoride, an adduct initially remained when volatile materials were removed. However, it evolved trifluoroacetyl fluoride continuously at 20° and had all decomposed in 24 h.

In preparing samples in solution for n.m.r. studies, the reactants were usually mixed directly in the n.m.r. sample tube. Alternatively, the n.m.r. tube was sealed onto a larger reaction tube, the solution decanted in, and the n.m.r. tube sealed off. Samples of the solid alkoxides (usually containing some unreacted fluoride) were prepared for infrared examination as KBr pellets, the pellets being made up in a dry atmosphere and protected from hydrolysis during examination by being enclosed between two clear KBr pellets.

Thermal Decomposition Studies

With the exception of potassium pentafluoroethoxide, the solid alkoxides showed no tendency to decompose at 20°. Samples kept in sealed, evacuated tubes showed no gas pressure on opening after several weeks. On heating to 50–80°, however, all evolved their respective acyl fluoride or ketone, leaving a residue of metal fluoride. Quantitative measurements of the rate of decomposition were made by introducing a sample of the alkoxide into a heated, continuously evacuated Pyrex tube. Evolved gases were led through a series of traps which were cooled to −196° and arranged so that the gas flow could be diverted from one to the next at regular intervals, the contents of each trap being subsequently weighed. The temperature was finally raised to 120° and heating continued until gas evolution ceased, which was considered to represent 100% decomposition of the alkoxide present. Results of decomposition studies at 50° and 80° are shown in Figs. 1 and 2.

Hydrolysis

Qualitative hydrolysis studies were performed by condensing a slight molar excess of water onto the solid alkoxides. Immediate reaction occurred, giving as the volatile products trifluoroacetic acid and pentafluoropropionic acid from the pentafluoroethoxides and heptafluoro-*n*-propoxides respectively. The isopropoxides evolved a mixture of hexafluoroacetone and hexafluoroacetone hydrate (hexafluoropropane-2,2-diol). Small amounts of silicon tetrafluoride were also present in all hydrolysis products.

Reaction of Cesium Heptafluoroisopropoxide with Allyl Bromide

Hexafluoroacetone was added to a suspension of cesium fluoride (2.0 g, 13.2 mmoles) in diglyme (25 ml) in a reaction tube (45 ml) until a clear solution was attained. Allyl bromide (3.0 g, 25 mmoles) was added and the tube sealed and kept at 55° for 12 h, when a white precipitate had developed. Fractionation, followed by purification by vapor-phase chromatography, gave allylheptafluoroisopropyl ether, b.p. 58°.

Anal. Calcd. for $C_6H_5F_7O$: C, 31.9; H, 2.2; F, 58.8. Found: C, 32.3; H, 2.4; F, 58.8.

The proton n.m.r. and infrared spectra of the ether were fully consistent with the assigned structure, the latter showing absorptions at 3 100 cm^{-1} (C—H), 1 640 cm^{-1} (C═C), 1 150 - 1 130 cm^{-1} (C—F), and 1 070 cm^{-1} (C—O—C).

Reaction of Cesium Heptafluoroisopropoxide with Trimethylchlorosilane

Hexafluoroacetone was condensed onto cesium fluoride (1.0 g, 6.6 mmoles) in diglyme (45 ml) until a clear solution was produced. Trimethylchlorosilane (1.0 g, 9.9 mmoles) was added and the mixture allowed to warm to room temperature, when immediate reaction occurred to give a white precipitate. Fractionation of volatile materials gave only hexafluoroacetone and trimethylfluorosilane.

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