Formation of Adducts between Fluorinated Ketones and Metal Fluorides

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Adducts of hexafluoroacetone were prepared from different metal fluorides in acetonitrile and in a variety of other polar organic solvents. It was demonstrated that certain alicyclic chlorofluoro ketones and cyclic perfluoro ketones formed similar adducts. A study of adduct formation was made under various conditions and the probability of adduct formation and the relative stability of the adducts were related to the lattice energies of the salts involved; those salts with high lattice energies, *e.g.*, NaF, being unable to form adducts.

The formation of an adduct complex was observed between hexafluoroacetone and a metal fluoride in an aprotic solvent at this laboratory and has now been reported in the literature[2] (eq 1).

$$(CF_3)_2C{=}O + MF \rightleftarrows (CF_3)_2CFO^-M^+ \qquad (1)$$

The stability of this adduct is mainly due to the strong electron-withdrawing effect of the CF_3– groups. As this reaction provides a simple route to the salts of perfluorinated alcohols, it was deemed of interest to investigate the scope of the reaction. The findings are reported in this paper.

Results and Discussion

Reaction of Hexafluoroacetone with Different Metal Fluorides in Acetonitrile.—The procedure can be described briefly as follows. Hexafluoroacetone was added to a slurry of the metal fluoride in acetonitrile. When an adduct was formed, a rise in temperature was observed, the metal fluoride went into solution, and hexafluoroacetone did not reflux. The adduct was precipitated by the addition of a large amount of benzene. In the cases where the adduct was too unstable to be isolated and identified, its formation was demonstrated when further reaction gave a stable derivative.[3]

The results of this study are given in Table I.

TABLE I

FORMATION OF ADDUCTS BETWEEN HEXAFLUOROACETONE AND DIFFERENT METAL FLUORIDES[a]

Metal fluoride	Lattice energy[b] of metal fluoride, kcal/mol	Temp change, °C	Adduct formed
CsF	176	28	Yes[c]
KF	192	17	Yes[c]
AgF	220	10	Yes
$(C_2H_5)_4NF$	...	...	Yes[c]
NaF	215	2	No
LiF	243	0	No
BeF_2	...	1	No
SnF_2	...	1	No
MgF_2	684	4	No
CuF_2	627	2	No
HgF_2	626	12	No

[a] All reactions run in acetonitrile, 1 *M* solution. [b] T. C. Waddington, *Advan. Inorg. Chem. Radiochem.*, **1**, 157 (1959). [c] Adduct isolated.

It may be seen that adducts were formed from CsF, KF, AgF, and $(C_2H_5)_4NF$ while none was obtained from NaF, LiF, ZnF_2, MgF_2, CuF_2, and BeF_2. These results are best interpreted in terms of the lattice energies of the salts. Thus, in the alkali metal fluoride series, LiF and NaF with large lattice energies are unable to form adducts, whereas the others (presumably also RbF) do form adducts. Also, the stability of the adduct decreases with increasing lattice energy, the CsF adduct being more stable than the KF adduct.

Silver fluoride forms an adduct in acetonitrile while sodium fluoride does not, in spite of the fact that the lattice energy of silver fluoride is higher. This is probably due to the complexing of silver ions with acetonitrile[4] which makes the solvation energy in this solvent higher than the salvation energy of the alkali metal fluorides.

The solubility of the metal fluorides in water is dependent on the lattice energy of the salt. The ability of a salt to form an adduct is thus related to its solubility in water, and only those salts which are very soluble in water are able to form an adduct with hexafluoroacetone. The one exception to the rule is beryllium fluoride; this material is very soluble in water but it has been found completely unreactive toward hexafluoroacetone in any solvent. This abnormal reaction is probably due to the exceedingly strong solvation of beryllium ions in water; the solvation energy is much lower in organic solvents. The correlation between water solubility and adduct formation is useful in predicting the behavior of those metal fluorides whose lattice energies are not known.

This part of the study can be summarized as follows: fluorides found to form adducts with hexafluoroacetone include CsF, KF, AgF, and quaternary ammonium fluorides. The reactivity of these compounds is due to their low lattice energies, and the property is reflected in the high solubilities of these salts in water.

Adducts with Ketones Other than Hexafluoroacetone.—A study was also made of the formation of adducts by other fluorocarbonyl compounds and the results are summarized in Table II.

A series of chlorofluorinated acetones was studied. The compounds CF_3COCF_2Cl, $(CF_2Cl)_2CO$, and $CF_2ClCOCFCl_2$ formed adducts and the reactivity of the ketone decreased with increasing amount of chlorine. This was shown by the temperature measurements and by the fact that $CF_2ClCOCFCl_2$ formed an adduct only with CsF and not with KF. The adduct with $(CFCl_2)_2CO$ probably has borderline stability

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[1] Sandoz Pharmaceutical Co., Basel, Switzerland.

[2] A. G. Pittman and D. L. Sharp, *Textile Res. J.*, **35**, 190 (1965); A. G. Pittman and D. L. Sharp, *J. Polym. Sci., Part B*, **3**, 379 (1965); M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **45**, 389 (1967).

[3] F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1839 (1968).

[4] K. B. Yatsimirskii and V. D. Korableva, *Zh. Neorgan. Khim.*, **9** (2), 357 (1964); *Chem. Abstr.*, **60**, 10184 (1964).

TABLE II

FORMATION OF ADDUCTS BETWEEN METAL FLUORIDES AND DIFFERENT CARBONYL COMPOUNDS[a]

Carbonyl compound	Metal fluoride	Temp change, °C	Adduct formed[b]
CF_3COCF_2Cl	KF	15	Yes
$(CF_2Cl)_2CO$	KF	7	Yes
$CF_2ClCOCFCl_2$	KF	0	No
$CF_2ClCOCFCl_2$	CsF	6	Yes
Perfluorocyclohexanone	KF	2	No
Perfluorocyclohexanone	CsF	15	Yes
Perfluorocyclopentanone	CsF	5	Yes

[a] All reactions run in acetonitrile, 1 *M* solution. [b] Formation of adduct demonstrated by the isolation of a derivative.

while $CFCl_2COCCl_3$ and hexachloroacetone will not form adducts.

Perfluorocyclohexanone[5] and perfluorocyclopentanone[5] were found to form adducts only with CsF and not with KF, showing that these ketones were also less reactive than hexafluoroacetone.

The results of this section of the study can be summarized as follows: the carbonyl compounds must be highly fluorinated in order to form an adduct. Substitution of chlorine for fluorine near the carbonyl group decreased the stability of the adduct. Cyclic ketones form adducts which are less stable than those of straight-chain ketones, probably owing to steric interaction.

Effect of Solvent on the Formation of Adducts.—The results discussed above were obtained using acetonitrile as the solvent. It was also of interest to study the reaction in other solvents. The heats of solution of hexafluoroacetone with different solvents were first determined calorimetrically in order to decide whether they would react with the ketone, either directly or by complex formation. If the heats of these reactions were much less than the heat of reaction of KF and hexafluoroacetone, then the latter reaction would be favored. The results are given in Table III. It may be seen that, in most cases, the heat of solution was small compared with the heat of reaction of KF with hexafluoroacetone.

TABLE III

HEAT OF SOLUTION OF HEXAFLUOROACETONE WITH DIFFERENT SOLVENTS

Solvent	Initial temperature of measurement, °C	ΔH/l. of solvent,[a] kcal	$(CF_3)_2CO$ %/l. of solvent
CH_3CN	22.1	0.8	~8
DMSO	21.3	1.5	8.4
$EtNO_2$	21.6	0.3	~8
Glyme	24.9	2.5	~20
DMF	24.8	3.4	12.5
H_2O[b]	25.9	20.9	12
KF in CH_3CN[c]	25.6	10.7	

[a] ΔH is the heat evolved in dissolving the maximum amount of $(CF_3)_2CO$ in 1 l. of solvent at 1-atm pressure of $(CF_3)_2CO$. [b] $(CF_3)_2CO$ forms a hydrate with water. In this run the final solution was not saturated with $(CF_3)_2CO$. [c] $(CF_3)_2CO$ was added to a 1 *M* solution of KF in the solvent. The final solution contained approximately 20% excess of $(CF_3)_2CO$.

The effect of the solvent on the formation of an adduct was then investigated and the results are given in Table IV.

TABLE IV

FORMATION OF ADDUCTS BETWEEN HEXAFLUOROACETONE AND METAL FLUORIDES IN DIFFERENT SOLVENTS[a]

Metal fluoride	Solvent	Temp change, °C	Adduct formed[b]
KF	DMF	17	Yes
KF	Butyrolactone	10	Yes
KF	Glyme	...	Yes
CsF	Glyme	13	Yes
CsF	Nitrobenzene	17	Yes
CsF	3-Methyl sulfolane	...	Yes[c]
CsF	Benzene	3	No

[a] 1 *M* solutions. [b] Demonstrated by the isolation of a stable derivative. [c] Adduct precipitated out.

A solvent which has a high heat of solution for the adduct favors the formation of the adduct. Hexafluoroacetone formed an adduct with potassium fluoride in many aprotic polar solvents, *e.g.*, DMF, butyrolactone, and dimethoxyethane. In nitrobenzene and 3-methyl sulfolane, hexafluoroacetone formed an adduct only with cesium fluoride, while in a nonpolar solvent like benzene, no adduct was formed.

Experimental Section

Preparation of $(CF_3)_2CO$–KF Adduct.—In a 2-l. reaction flask were placed 1 l. of acetonitrile, freshly distilled from P_2O_5, and 58 g (1 mol) of anhydrous potassium fluoride. Hexafluoroacetone was bubbled into the stirred suspension at room temperature until 166 g (1 mol) had been taken up. A temperature rise of 17° was noticed over the 50-min period required to add the gas. At the end of the addition, the potassium fluoride had dissolved.

The adduct was precipitated by the addition of approximately double the volume of dry benzene and filtered quickly; the yield was 91%. The white solid was very hygroscopic and readily lost hexafluoroacetone, thus giving a slightly higher ratio of KF–$(CF_3)_2CO$ (1.2:1) than theoretical. *Anal.* Calcd for C_3F_7KO: C, 16.08; K, 17.45. Found: C, 14.5; K, 20.0, H, 1.2. The presence of hydrogen indicated that some water had been picked up. Ir spectroscopy showed a strong absorption at 8.2–8.5 μ, characteristic for the C–F stretching absorption. X-Ray diffraction techniques indicated the presence of a small excess of KF. Three major peaks, probably due to the adduct, were observed at 12.1, (3.42, 3.35),[6] and 4.10 Å with relative intensities 70, 100, 100, and 40. For the analysis, use was made of Ni filtered copper Kα radiation on a Norelco wide-angle goniometer.

Preparation of $(CF_3)_2CO$–CsF.—The same procedure was employed as described above, giving a quantitative yield of the adduct. *Anal.* Calcd for C_3F_7CsO: C, 11.3; Cs, 41.8. Found: C, 10.6; Cs, 42.1; H, 1.6.

Formation of Metal Fluoride Adducts with Fluoro Ketones Other than Hexafluoroacetone.—Attempts to isolate the adducts of potassium or cesium fluoride with CF_3COCF_2Cl, $(CF_2Cl)_2CO$, $CF_2ClCOCFCl_2$, perfluorocyclohexanone,[5] and perfluorocyclopentanone,[5] prepared according to the above procedure, gave only decomposition. Thus, these adducts, and also the $(CF_3)_2CO$–AgF adduct, were studied only in solution.

Preparation of $(CF_3)_2CO$–$(C_2H_5)_4NF$ Adduct.—*Caution!* Extreme care should be taken in the handling of the perchlorate. Owing to the instability of tetraethylammonium fluoride, a slightly modified technique had to be used in this preparation.

Tetraethylammonium perchlorate was prepared from tetraethylammonium bromide and perchloric acid in water solution. The precipitated material was recrystallized from water and dried.

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[5] E. P. Moore and A. S. Milan, Jr., British Patent 1,019,788 (1966). Samples were kindly provided by Dr. A. Price, Industrial Chemicals Division, Allied Chemical Corp.

[6] Partly resolved doublet or singlet peak with scattering.

Tetraethylammonium perchlorate (230 g, 1 mol) was dissolved in acetonitrile and added to a stirred solution of $(CF_3)_2CO$–KF adduct, prepared according to the above procedure. Potassium perchlorate precipitated out leaving a solution of the desired adduct, which was then isolated as described previously.

Elemental analysis showed contamination by $KClO_4$, and considerable decomposition occurred through the loss of hexafluoroacetone.

Formation of Metal Fluoride Adducts with Hexafluoroacetone in Different Solvents.—The reaction of hexafluoroacetone and a metal fluoride was run in different solvents according to the method described above for the preparation of $(CF_3)_2CO$–KF adduct in acetonitrile. No attempts were made to isolate the adduct, but its formation was shown by further reaction yielding stable derivatives.[3] All solvents were carefully dried and distilled shortly before use.

Calorimetric Measurements of Heats of Solution of Hexafluoroacetone in Different Solvents.—The calorimeter used in these experiments was equipped with a Dry Ice condenser, thermistor, stirrer, gas inlet with a flow meter attached to measure the amount of hexafluoroacetone added, and an opening for the addition of solid material. The apparatus was kept in a dewar flask to prevent any heat loss. The calorimeter was calibrated by the determination of the heat of solution of potassium chloride in water.

The calorimeter was charged with 250 cc of the purified solvent and hexafluoroacetone was added at a rate of about 1.3 g/min until a saturated solution was obtained. The addition times were between 15 and 20 min. The evolution of heat was followed with the thermistor and the heat of solution calculated by use of the calibration curve.

Registry No.—CsF, 13400-13-0; KF, 7789-23-3; AgF, 7775-41-9; $(C_2H_5)_4NF$, 665-46-3; NaF, 7681-49-4; LiF, 7789-24-4; BeF_2, 7787-49-7; SnF_2, 7783-47-3; MgF_2, 7783-40-6; CuF_2, 7789-19-7; HgF_2, 7783-39-3; hexafluoroacetone, 684-16-2; CF_3COCF_2Cl, 79-53-8; $(CF_2Cl)_2CO$, 127-21-9; $CF_2ClCOCFCl_2$, 79-52-7; perfluorocyclohexanone, 1898-91-5; perfluorocyclopentanone, 376-66-9.

Formation of Fluorinated Ethers in a Modified Halohydrin Reaction[1]

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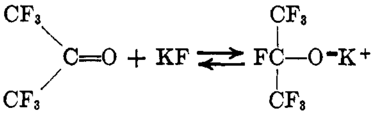
Fluorinated ethers have been prepared in a three-component reaction involving an adduct of a perhalogenated ketone or acid fluoride with a metal fluoride, an olefin, and a halogen. The reaction was shown to be general in that all three reactants could be varied. The reaction is analogous to a halohydrin reaction with the attack of a fluorinated alkoxide ion on a halonium ion or an olefin–halogen complex.

The formation of an adduct between fluorinated carbonyl compounds and a metal fluoride has been reported in the literature[3,4] (eq 1). At room temperature,



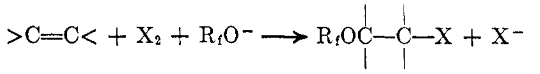
$$\mathrm{(CF_3)_2C{=}O + KF \rightleftharpoons F\overset{CF_3}{\underset{CF_3}{C}}{-}O^-K^+} \qquad (1)$$

the equilibrium in eq 1 lies very much in favor of the adduct of hexafluoroacetone. The heptafluoroisopropoxide ion has been used successfully in nucleophilic displacement reactions.[3,5] However, it is too weak a nucleophile to give nucleophilic attack on fluoroolefins.

Thus on reaction with a fluoro olefin at room temperature, the $(CF_3)_2CO$–CsF adduct was reported to give a perfluorinated alcohol.[6] Initial attack on the olefin by the fluoride ion was followed by a reaction with the free ketone present in equilibrium with the adduct (eq 2). No evidence of the formation of an ether was found.

$$CF_2{=}CF_2 + F^- \rightleftharpoons CF_3CF_2^- \xrightarrow{(CF_3)_2CO} CF_3CF_2C(CF_3)_2O^- \qquad (2)$$

We have found that, if an adduct of a perhalogenated carbonyl compound and a metal fluoride reacted with an olefin in the presence of a *halogen*, the reaction takes a different path and a fluorinated ether is formed (eq 3). This paper describes our investigation of the scope of this reaction.



$$>C{=}C< + X_2 + R_fO^- \longrightarrow R_fO\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X + X^- \qquad (3)$$

Results and Discussion

The reaction procedure can be described briefly as follows. The carbonyl compound was added to a slurry of the metal fluoride in an aprotic solvent. The olefin and halogen were added at room temperature to the adduct thus formed. The mixture was poured on ice and excess halogen reduced. The product separated out as a heavy layer.

The reaction is of a general type, in that all three reaction components can be varied, giving a large selection of this class of compounds. The scope of the reaction includes nonfluorinated as well as fluorinated olefins, and perfluorinated ketones and acyl fluorides, as well as chlorofluoro-substituted ketones. The results obtained with different ketones, olefins, and halogens will be discussed, each reactant being considered separately, and a mechanism for the reaction will be suggested.

Reactions of Different Carbonyl Compounds

In order for the ketone or acid fluoride to react, it must form an adduct with a metal fluoride (eq 1). The various factors affecting the formation of these adducts were discussed in another paper.[4] It was concluded that the carbonyl compound has to be at least partially fluorinated to give an adduct. Thus hexafluoroacetone, CF_3COCF_2Cl, $(CF_2Cl)_2CO$, perfluoro-

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[1] Paper presented at the Fourth International Symposium on Fluorine Chemistry in Estes Park, Colo., 1967.

[2] Sandoz Pharmaceutical Co., Basel, Switzerland.

[3] (a) A. G. Pittman and D. L. Sharp, *Textile Res. J.*, **35**, 190 (1965); (b) A. G. Pittman and D. L. Sharp, *J. Polym. Sci., Part B*, **3**, 379 (1965); (c) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **45**, 389 (1967).

[4] F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1837 (1968).

[5] A. G. Pittman, D. L. Sharp, and R. E. Lundin, *J. Polym. Sci., Part A-1*, **4**, 2637 (1966).

[6] D. P. Graham and V. Winemayr, *J. Org. Chem.*, **31**, 957 (1966).