[CONTRIBUTION NO. 34, EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Stable Carbonium Ions. II.[1a] Oxocarbonium[1b] (Acylium) Tetrafluoroborates, Hexafluorophosphates, Hexafluoroantimonates and Hexafluoroarsenates. Structure and Chemical Reactivity of Acyl Fluoride: Lewis Acid Fluoride Complexes[1c]

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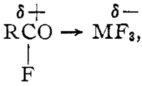
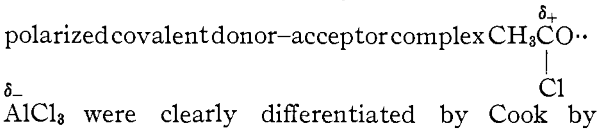
RECEIVED JANUARY 2, 1962

1:1-Addition complexes of acetyl-, propionyl- and benzoyl fluoride with antimony pentafluoride, arsenic pentafluoride and phosphorus pentafluoride were prepared and investigated together with previously-known boron trifluoride complexes. On the basis of infrared and high resolution proton and fluorine magnetic resonance spectra, the complexes were found to be predominantly oxocarbonium (acylium) salts. In the solid crystalline state the ionic structure ($RCO^+MF_{4,6}^-$) prevails for all the investigated complexes. In solutions (SO_2 and HF) there is n.m.r. evidence for a second type of fairly ionic species besides the oxocarbonium ion, most probably the highly polarized coördination complex,  $\overset{\delta+}{\underset{\underset{F}{|}}{RCO}} \rightarrow \overset{\delta-}{MF_{3,5}}$. The isolated oxocarbonium salts are reactive acylating agents in C-, O-, N- and S-acylations.

Introduction

In 1943, Seel[2] reported the isolation of the first stable well identified oxocarbonium salt. Acetyl fluoride, when allowed to react at low temperatures with boron trifluoride, gave a solid crystalline 1:1 addition compound which decomposed quantitatively into its components without melting at +20°, the boiling point of acetyl fluoride. On the bases of analytical and electrical conductivity data, the compound was characterized as the ionic methyl oxocarbonium (acetylium) tetrafluoroborate ($CH_3CO^+BF_4^-$) complex. In previous work[3] other oxocarbonium tetrafluoroborates were prepared and their application as acylating agents investigated.

The oxocarbonium structure of $CH_3COF \cdot BF_3$ was further proved by the infrared spectroscopic investigations of Susz.[4] The presence of two functional groups in an acyl halide, namely, the carbonyl donor group and the ionizable halogen atom, suggests that two types of intermediates may be possible in the interaction of acyl halides with Lewis acid type Friedel–Crafts catalysts. For the acetyl chloride aluminum chloride system, this was first suggested by Pfeiffer[5] and has recently been discussed on the basis of infrared spectroscopic data by Susz and Wuhrmann[6a] and by Cook.[6b] The ion salt $CH_3CO^+AlCl_4^-$ and the polarized covalent donor–acceptor complex  $\overset{\delta+}{\underset{\underset{Cl}{|}}{CH_3CO}}\cdot\cdot\,\overset{\delta-}{AlCl_3}$ were clearly differentiated by Cook by means of their infrared C=O absorptions. According to Susz's data, the $CH_3COF \cdot BF_3$ complex prepared and kept at low temperatures is predominantly the ionic methyl oxocarbonium tetrafluoroborate, $CH_3CO^+BF_4^-$. Only a very minor amount of the donor–acceptor complex is detectable.

Results

Preparation of Oxocarbonium Salts.—Two independent methods were used for the preparation of oxocarbonium salts.

(a) **Fluoride Method.**—Acyl fluorides, when treated with Lewis acid-type metal fluorides such as boron trifluoride, phosphorus pentafluoride, antimony pentafluoride and arsenic pentafluoride, gave stable, well defined 1:1 addition compounds.

$$RCOF + MF_{3,5} \rightleftarrows RCO\ ^+MF_{4,6}^-$$
$$R = CH_3,\ C_2H_5,\ C_6H_5;\quad M = B,\ P,\ As,\ Sb$$

Equimolar quantities of acetyl, propionyl and benzoyl fluoride and the appropriate Lewis acid fluoride (BF_3, PF_5, SbF_5, AsF_5) were allowed to react in 1,1,2-trifluorotrichloroethane (Freon 113) or difluorodichloromethane (Freon 12) solutions at temperatures ranging between −78° to 0°. After the Freon solutions of the reagents were mixed at low temperatures with effective stirring and exclusion of moisture, they were allowed to warm up gradually, in the case of Freon 113 solutions to room temperature, in the case of Freon 12 solutions to about −35°. The white crystalline precipitates formed were collected, washed with cold Freon and dried in vacuum. All operations were carried out with usual precautions for excluding moisture, preferably in a vacuum line system.

(b) **Silver Salt Method.**—Oxocarbonium salts can be prepared without the use of the sometimes inconvenient fluorides by the simple metathetic reactions of the corresponding acyl chlorides (bromides) with the appropriate anhydrous complex silver salts.[7]

$$RCOCl + AgMF_{4,6} = RCO^+MF_{4,6}^- + AgCl$$
$$R = CH_3,\ C_2H_5,\ C_6H_5;\quad M = B,\ As,\ P,\ Sb$$

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(1) (a) Part I, G. A. Olah and W. S. Tolgyesi, *J. Am. Chem. Soc.*, **83**, 5031 (1961). (b) We suggest the adoption of the carbonium ion nomenclature as a suitable system for naming simple carbonium ions. (M. S. Newman and H. L. Gildenhorn, *J. Am. Chem. Soc.*, **70**, 317 (1948). Accordingly, the electron deficient carbon atom is used as a root with the suffix "carbonium" and the attached groups are named as usual. Thus CH_3CO^+ is methyl oxocarbonium, $CH_3CH_2CO^+$ ethyl oxocarbonium and $C_6H_5CO^+$ phenyl oxocarbonium. Similarly, $(CH_3)_3CH^+$ is trimethylcarbonium, $(CH_3)_2CH^+$ dimethylcarbonium etc. (c) Partly presented as a paper at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal (Canada), August 1961, Abstracts of Papers, p. 64. (d) Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.

(2) F. Seel, *Z. anorg. allgem. Chem.*, **250**, 331 (1943).

(3) G. Olah and S. Kuhn, *Chem. Ber.*, **89**, 866 (1956).

(4) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957).

(5) P. Pfeiffer, "Organische Molekulverbindungen," 2nd Ed., F. Enke Verlag, Leipzig, 1927, p. 104.

(6) (a) B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **40**, 971 (1957); (b) W. D. Cook, *Can. J. Chem.*, **37**, 48 (1959).

(7) G. A. Olah, H. W. Quinn and S. J. Kuhn, Abstracts of Papers XVIIth International Congress of Pure and Applied Chemistry, Munich, Germany, September, 1959, p. 92.

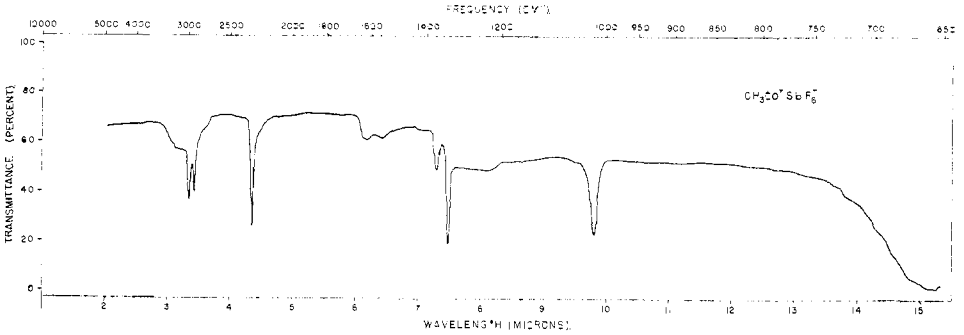

Fig. 1.

The crystalline addition complexes obtained were found by analytical data to be 1:1 addition compounds of high purity (see experimental part). Their thermal decomposition points or melting points (in sealed capillary tubes) are listed in Table I together with the previously described tetrafluoroborate salts.

TABLE I

THERMAL DECOMPOSITION AND MELTING POINTS, RESPECTIVELY, OF ACYL FLUORIDE–LEWIS ACID FLUORIDE COMPLEXES

	BF_3, dec. p., °C.	PF_5, dec. p., °C.	SbF_5, m.p., °C.	AsF_5, m.p., °C.
CH_3COF	+20	+30	+173–175	+175–178
CH_3CH_2COF	−15	− 5	+125	+110–112
C_6H_5COF	−30	−15	+150–151	+158–160

Spectroscopic Investigations

Infrared investigation of the solid complexes, using a Perkin–Elmer model 221-G spectrophotometer with sodium chloride optics, was carried out. Emulsions of the solids in mineral oil (Nujol) and a fluorinated hydrocarbon (Fluorolube, S30, Minnesota Mining and Manufacturing Co.) were pressed between silver chloride plates, all operations being carried out in a dry-box, as the compounds are extremely sensitive to moisture. No etching of the silver chloride plates was observed, in marked contrast to that observed when sodium chloride plates were used. Even barium fluoride plates were etched slightly. The main characteristic data obtained are summarized in Table II. A detailed infrared spectroscopic investigation including a comparison of $CH_3CO^+SbF_6^-$ with $CD_3CO^+SbF_6^-$ and $CH_3\overset{13}{C}O^+SbF_6^-$ was carried out by Dr. D. Cook and will be published elsewhere.

There has been general agreement[6a,b] that the strong band at 2300 cm.$^{-1}$ in the spectra of acetyl halide:Lewis acid metal halide complexes is due to the methyl oxocarbonium (acetylium) ion, (CH_3CO^+), formed in the process

$$CH_3COX + MX_n \rightleftarrows CH_3CO^+MX_{n+1}^-$$

Similarly, aromatic acid halide (benzoyl, etc.) complexes have given spectra containing a strong band at 2200 cm.$^{-1}$, indicating the presence of phenyl oxocarbonium (benzoylium) ion.

The lower frequency of the phenyl oxocarbonium ion compared with the methyl oxocarbonium ion was attributed to conjugation of the CO group with the ring, a familiar situation in infrared spectroscopy. However, in certain cases two bands in the acyl halide:Lewis acid halide complexes have been observed[6a,b,8] in the triple bond region, *e.g.*, at 2300 and 2200 cm.$^{-1}$, for which no adequate explanation has been offered. Cook recently investigated this problem[9] in more detail in the case of the $CH_3COCl:GaCl_3$ complex and suggested that the 2200 cm.$^{-1}$ band should be assigned to the CH_3CO^+ ion, while the 2300 cm.$^{-1}$ band (observed in a liquid complex) is due to a more complicated ionic species, possibly $[CH_3CO\ldots GaCl_3]^+Cl^-$, or some kind of ion-pair interaction, in accordance with the fact that whenever a linear molecule such as CH_3CO^+ forms a complex with an electron deficient material, the CO stretching frequency would be raised to a higher value than in the free ion. The carbonyl frequencies of the starting acyl halides are absent in the infrared spectra of our isolated crystalline complexes and the expected shifted lines which should appear if oxygen–electron deficient metal donor–acceptor complexes were formed are generally weak. The observed carbonyl adsorption frequencies of the complexes are in accordance with the predominant oxocarbonium structure. The polarized donor:acceptor form is present only in minor amounts, probably due also to some decomposition of the complexes during handling to obtain the spectra.

The isolation of crystalline 1:1 addition complexes of acyl halides with Lewis acid halides alone is by no means proof of the oxocarbonium structure of these addition compounds. Susz[4,6a,10] and Cook[6b,11] amply demonstrated with infrared investigations of a number of 1:1 acyl halide:Lewis acid halide addition compounds the existence of the two previously suggested forms: $RCO^+MX_{4,6}^-$ (oxocarbonium form) and $R\underset{X}{\overset{\delta+}{C}}{=}O \longrightarrow \overset{\delta-}{M}X_{3,5}$ polarized covalent complex with fixation of the Lewis acid acceptor on the carbonyl oxygen). Susz recently also suggested that in the case of $RCOCl:TiCl_4$ complexes there is evidence of a double possibility for the fixation of the acceptor on the carbonyl oxygen atom.

The oxocarbonium salt nature of the isolated new crystalline, 1:1 addition complexes of acyl

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[8] A. N. Terenin, V. N. Filiminov and D. S. Bistov, *Bull. Acad. Sci., U.S.S.R. Phys. Chem. Sect.*, **22**, 1100 (1958); *Z. Elektrochem.*, **62**, 180 (1958).

[9] D. Cook, personal communication, *Can. J. Chem.*, **40**, 480 (1962).

[10] D. Cassimatis, P. Gagnaux and B. P. Susz, *Helv. Chim. Acta*, **43**, 422 (1959); B. P. Susz and D. Cassimatis, *ibid.*, **44**, 395 (1960).

[11] D. Cook, Abstract of Papers XVIIIth International Congress of Pure and Applied Chemistry, Montreal (Canada), August, 1961.

TABLE II

INFRARED FUNDAMENTAL STRETCHING FREQUENCIES (CM.$^{-1}$) OF ACYL FLUORIDE:LEWIS ACID FLUORIDE COMPLEXES[a]

	$\nu_{C=O}$	$\nu_{C\equiv O}$	ν_{C-F}	$\nu_{SbF_6^-}$	$\nu_{AsF_6^-}$	$\nu_{PF_6^-}$	$\nu_{BF_4^-}$
CH_3COF	1848vs		826s				
			809s				
$CH_3CO^+BF_4^-$[3]	1619m, 1560w	2299vs					1052b,s
$CH_3CO^+PF_6^-$	1620m, 1558w	2297vs				855s	
$CH_3CO^+\cdot SbF_6^-$	1621w, 1554w	2294vs		665b,s			
$CH_3CO^+AsF_6^-$	1620w, 1558w	2302vs			705s		
CH_3CH_2COF	1845vs		805s				
$CH_3CH_2CO^+SbF_6^-$	1610m	2290vs		650b,s			
$CH_3CH_2CO^+AsF_6^-$	1608m	2289vs			702s		
C_6H_5COF	1812vs		1020s				
$C_6H_5CO^+SbF_6^-$	1531m	2212vs		660b,s			
$C_6H_5CO^+AsF_6^-$	1546m	2228vs			702s		

[a] s = strong, vs = very strong, b = broad.

fluorides with antimony pentafluoride led us to reinvestigate the corresponding acyl chloride: antimony pentachloride complexes described by Seel[12] as oxocarbonium salts on the basis of analytical and electrical conductivity data. The characteristic infrared carbonyl absorptions of the acetyl chloride, propionyl chloride and benzoyl chloride–antimony pentachloride complexes are summarized in Table III.

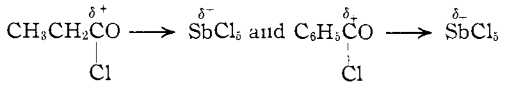
TABLE III

INFRARED FUNDAMENTAL STRETCHING FREQUENCIES (CM.$^{-1}$) OF ACYL CHLORIDE: ANTIMONY PENTACHLORIDE COMPLEXES[a]

	$\nu_{C=O}$	$\nu_{C\equiv O}$
CH_3COCl	1800vs	.....
$CH_3COCl\cdot SbCl_5$	1709m 1587w	2283vs
CH_3CH_2COCl	1828vs	.....
	1795vs	
$CH_3CH_2COCl\cdot SbCl_5$	1790sh	2232vw
	1764vs	
C_6H_5COCl	1776vs	.....
	1736vs	
$C_6H_5COCl\cdot SbCl_5$	1656vs	2215vw
	1575vs	

[a] s = strong, vs = very strong, sh = shoulder, vw = very weak.

The $CH_3COCl:SbCl_5$ complex is, accordingly, predominantly the ionic methyl oxocarbonium hexachloroantimonate $CH_3CO^+SbCl_6^-$, but the $CH_3CH_2COCl:SbCl_5$ and $C_6H_5COCl:SbCl_5$ complexes contain only a very small amount of the ionic oxocarbonium form and are basically polarized donor–acceptor complexes



$$CH_3CH_2\overset{\delta+}{\underset{\substack{| \\ Cl}}{C}}O \longrightarrow \overset{\delta-}{S}bCl_5 \text{ and } C_6H_5\overset{\delta_+}{\underset{\substack{| \\ Cl}}{C}}O \longrightarrow \overset{\delta-}{S}bCl_5$$

No corresponding complexes with phosphorus pentachloride were reported and arsenic pentachloride itself is still unknown.

Data obtained on solid crystalline addition compounds of organic halides and Lewis acid metal halides cannot be extrapolated without any further information on the structure of these compounds in solutions. Lattice energy forces operative in the crystalline compounds are replaced by solvation energy forces, as well as possible other interactions of different steric and electrostatic nature.

Nuclear Magnetic Resonance Investigation.—To obtain further information on the structure of the acyl fluoride:Lewis acid fluoride 1:1 addition complexes in solution, high resolution nuclear magnetic proton and fluorine resonance spectroscopic investigations were carried out. A modification of the high resolution n.m.r. spectrograph of Baker and Burd[13] was used. Liquid sulfur dioxide and anhydrous hydrogen fluoride were used as solvents. Since organic acylation reactions are always carried out in solution, where the interaction with solvents may have a very important role in the course and mechanisms of the reactions, it was felt that n.m.r. investigations of these complexes in solution should be of particular interest.

Some of these solutions are more stable than others. Most of them decompose in a week or so at −10°, but can be kept fairly well at Dry Ice temperature. The decomposition points of the solids are shown in Table I, and it is seen that the antimony and arsenic pentafluoride complexes are stable to higher temperatures, whereas the phosphorus pentafluoride and boron trifluoride complexes, particularly with benzoyl fluoride, are very unstable. The stability of the solutions should not necessarily be in the same order as the solids, although the solutions of the antimony pentafluoride complexes are indeed the most stable. The n.m.r. spectra of some of the solutions were obtained at low temperatures without warming for more than a few seconds. No attempt was made to study the decomposition products in a systematic manner, although such study should prove interesting.

The H^1 and F^{19} spectra obtained are shown in a partially schematic form in Figs. 1 through 6, together with the spectra of the reference substances used in interpretation of the chemical shifts. In the F^{19} spectra the acetyl (A), propionyl (P) and benzoyl (B) fluorides are shown in the same spectrum, and the F^{19}–H^1 splitting (to be discussed later) is removed, for compactness.

Proton Spectra.—The proton spectra of the complexes obtained at 60 Mc. are displayed in Figs. 1, 2 and 3 for the three acyl fluorides used,

(12) F. Seel, *Z. anorg. allgem. Chem.*, **252**, 24 (1943).

(13) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957). In the modified form of this instrument, residual field fluctuations are measured with an auxiliary proton sample and used to control the rf oscillator frequency, which is suitably divided down for measurements of nuclei other than protons. Details will be published later.

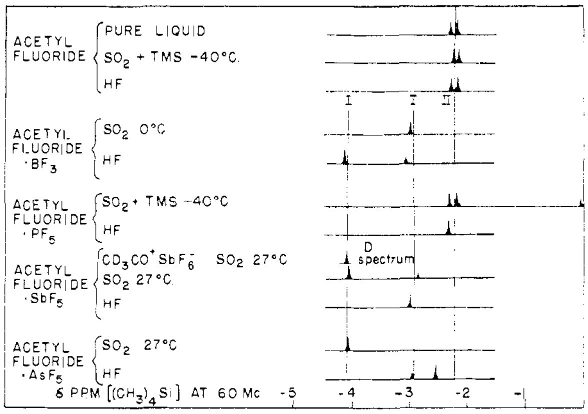


Fig. 1.—H′ spectra of acetyl fluoride complexes.

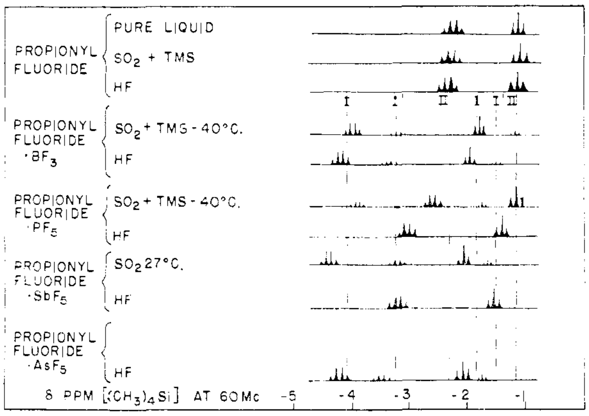


Fig. 2.—H′ spectra of propionyl fluoride complexes.

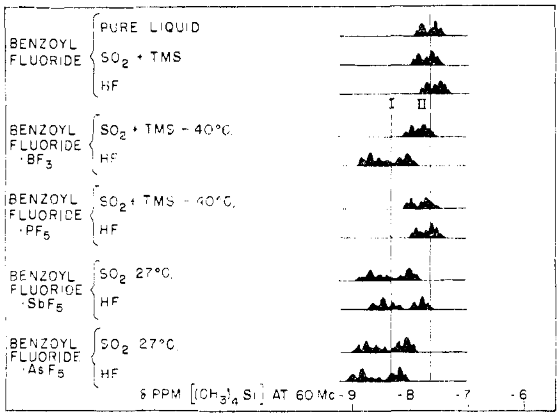


Fig. 3.—H′ spectra of benzoyl fluoride complexes.

and are compared with spectra of solutions of the acyl fluorides alone. The spectra are given in p.p.m. relative to $(CH_3)_4Si$ (TMS) as internal standard. However, the complexes react with TMS and so an external water sample was used and corrections derived from acetyl fluoride solutions in SO_2 and HF were applied. This amounted to subtracting 5.41 p.p.m. for SO_2 solutions and 5.25 p.p.m. for HF solutions. The line due to HF has been omitted from these spectra. Acetyl fluoride itself (Fig. 7) shows a methyl doublet due to F^{19} coupling, with J_{HF} = 7.0 c.p.s. This is reflected in the F^{19} spectrum as 1:3:3:1 quartet.

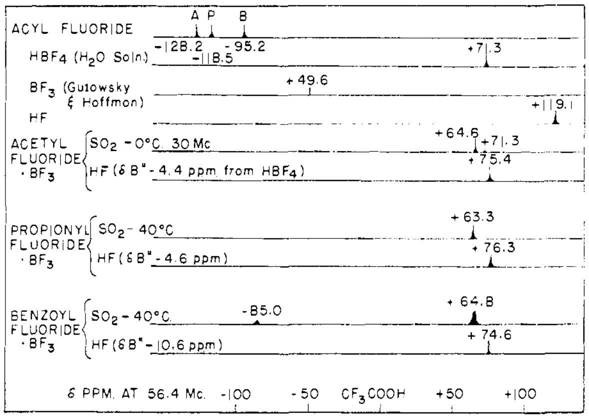


Fig. 4.—F^{19} spectra of BF_3:acyl fluoride complexes.

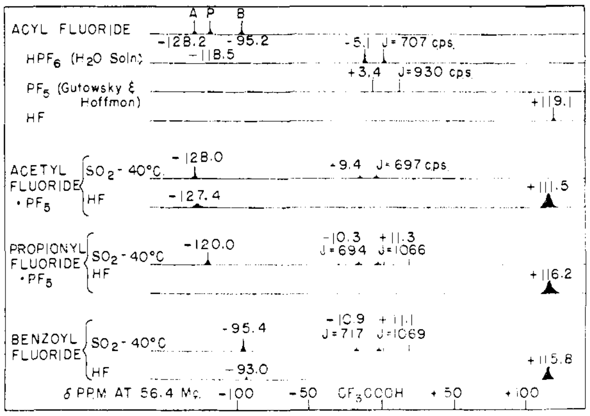


Fig. 5.—F^{19} spectra of PF_5:acyl fluoride complexes.

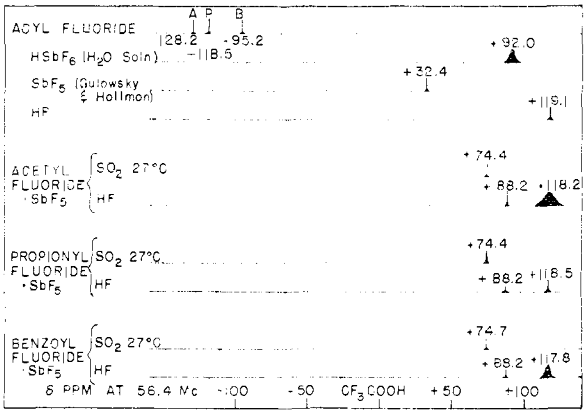
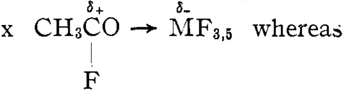


Fig. 6.—F^{19} spectra of SbF_5:acyl fluoride complexes.

Acetyl-d_3 fluoride was prepared and shows a doublet in the deuterium spectrum with a coupling to the fluorine of J_{DF} = 1.04 c.p.s. This is reflected as the expected 1:3:6:7:6:3:1 septuplet in the fluorine spectrum. The ratio J_{DF}/J_{HF} = 0.149, and the ratio of magnetogyric ratios is γ_D/γ_H = 0.153, which agreement is within experimental error. Propionyl fluoride does not exhibit such coupling at room temperature. However, at −80° the CH_2–F^{19} splitting is resolved, but the coupling is only J_{HF} = 2.8 c.p.s., which probably is due to a different average HCCF bond angle in the two molecules. None of the complexes exhibit such H^1–F^{19} coupling, which would of course not be expected in the ionic forms, but this can hardly be used as conclusive evidence of ionic dissociation, but only as supporting evidence. Fast exchange in a highly polarized donor–acceptor complex could equally well result in the absence of observable H^1–F^{19} coupling.

The proton spectra of the acetyl fluoride complexes show only single lines, but of two types, labeled I and I′, with chemical shifts of $\delta_I = -4.08$ and $\delta_I' = -2.94$ p.p.m. Species I is thought to be the ion CH_3CO^+ itself. The exact nature of species I′ is unknown. However, it also must be considerably ionic or at least a strongly positively polarized entity causing a substantial chemical shift of the methyl protons to less shielding. Although it is less possible that I′ corresponds to ion pairs or clusters of ion pairs, whereas I to the free oxocarbonium ion, this possibility cannot be fully substantiated. It seems improbable that in fairly dilute solutions (the HF solutions were about 15–10%, the SO_2 solutions less than 10% by weight) a part of the ions should be present as solvated ion pairs, the rest as separated ions. As both species I and I′ were found in the same solutions (although generally one is predominant) it must be suggested that species I′ is most probably the highly polarized coördination complex  $CH_3\underset{\underset{F}{|}}{\overset{\delta+}{C}}O \rightarrow \overset{\delta-}{M}F_{3,5}$ whereas species I is the oxocarbonium ion. Cryoscopic investigations of SO_2 and tetramethylene sulfone solutions of oxocarbonium salts (to be published later) indicated little or no ion separation; thus the oxocarbonium ion should be present in these solutions predominantly in the form of solvated ion-pairs. More ion separation is expected in anhydrous HF solutions. Because of fast exchange, the H^1–F^{19} coupling should not be observed in the complex. The high positive polarization can account for the considerable methyl shift, although this is smaller than that observed in the case of the truly ionic species I. Some of the complexes have I and I′ present simultaneously, generally with one form predominant. In the case of acetyl fluoride:PF_5, in SO_2 solution, which is mostly present as acetyl fluoride and PF_5, some PF_6^- was found (as shown by the fluorine resonance) but neither I nor I′ is found in the proton spectrum. Instead there is a different species, which is very highly shielded, lying near TMS. This species was not found in the HF solution, but in this case the line due to CH_3COF was not split. At lower temperatures or in the crystalline state the ionic oxocarbonium form may have more importance. The SbF_6 and AsF_6 complexes of acetyl fluoride are ionic methyl oxocarbonium salts. The deuterated complex $CD_3CO^+SbF_6^-$ was prepared and examined in SO_2 solution at 9.2 Mc. Upon multiplying the shift from external D_2O by $\gamma_H/\gamma_D = 6.52$ and subtracting the correction 5.41 p.p.m. to convert to internal TMS reference, excellent agreement with the methyl group position in the corresponding proton complex was found. Using the empirical linear relation of Allred and Rochow,[14] as modified by Cavanaugh and Dailey[15] for the chemical shift δ_{CH_3} p.p.m. of a methyl group attached to a group having a Huggins electronegativity

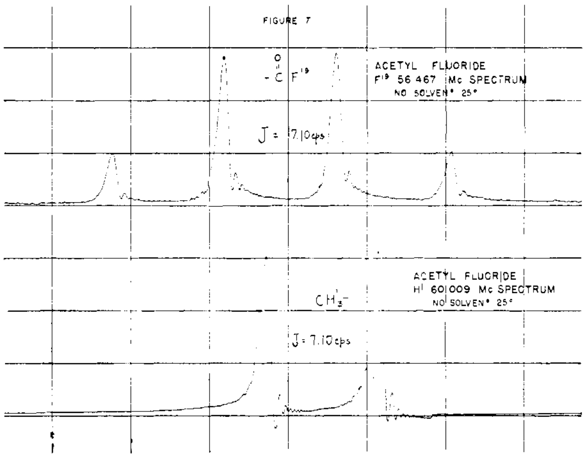


Fig. 7.

$$\epsilon = [1.29 - 0.6\delta_{CH_3}]_{TMS} \text{ e.v.}$$

we find $\epsilon_I = 3.74$ e.v. and $\epsilon_I' = 3.05$ e.v. (typical values $\epsilon_{NO_2} = 3.90$ e.v., $\epsilon_{OH} = 3.43$ e.v., $\epsilon_{COOH} = 2.660$ e.v., $\epsilon_{CN} = 2.49$ e.v.) so that both I and I′ are strongly electron withdrawing. The proton spectra of the propionyl fluoride complexes (Fig. 2) show much the same behavior as the acetyl fluoride complexes, but having the separate CH_3 and CH_2 multiplets of the ethyl groups. There are, besides the propionyl fluoride itself, two species of ions, again labeled I and I′, as may be seen from the figure. Dailey and Shoolery[16] have found an empirical linear relation between the shift difference $\Delta = \delta_{CH_3} - \delta_{CH_2}$ p.p.m. within the ethyl group and the electronegativity of the attached group.

$$\epsilon = [0.684\Delta]_{TMS} + 1.78 \text{ e.v.}$$

which with $\Delta_I = -2.25$ p.p.m., and $\Delta_I' = -1.20$ p.p.m. gives $\epsilon_I = 3.32$ e.v. and $\epsilon_I' = 2.99$ e.v. There is thus close agreement for ϵ_I' for acetyl complexes and not so close agreement for ϵ_I.

The proton spectra of the benzoyl fluoride complexes exhibit, at least grossly, a ring spectrum corresponding to the ionic (phenyl oxocarbonium) species I which is shifted to lower shielding and internally shifted by about a factor of two from benzoyl fluoride. The ring spectrum of I, believed to be $C_6H_5CO^+$, obtained in SO_2 solution of $C_6H_5COF{:}SbF_5$, shows a complicated AB_2C_2 system and was not analyzed. There is little doubt, however, that the *ortho* protons are the most and the *para* the least shielded. No complexes of ionic type were observed in the interaction of benzoyl fluoride with PF_5 (both in SO_2 and HF solutions) and with BF_3 in SO_2 solution (at the investigated temperatures). There is some ion formation, however, in liquid hydrogen fluoride solution.

F^{19} Spectra.—The F^{19} spectra obtained at 56.5 Mc. are shown in p.p.m. relative to external

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(14) A. L. Allred and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5361 (1957).

(15) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(16) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1956); see also ref. 17.

CF_3COOH. Bulk susceptibility corrections should be of the order of 0.5 p.p.m. or less. It is expected, however, that there will be specific solvent effects.

The boron trifluoride complexes appear to be all in the BF_4^- form, although in the HF solutions the BF_4^- line and the solvent HF line are merged, presumably due to rapid exchange of fluorine between BF_4^- and HF. Similarly, because of the possibility of fluorine exchange in a highly polarized complex of the type $R\underset{\substack{|\\F}}{\overset{\delta_+}{C}}O\rightarrow\overset{\delta_-}{M}F_{3,5}$, where the C–F bond must be considerably weakened (and in the limiting case ionized) and also because of possible exchange involving solvent HF and BF_4^- ions, fluorine resonance probably cannot differentiate between the BF_4^- line and that corresponding to an exchanging $F–BF_3$ system. Attempts were made to see differences are observable at a lower temperature, but this was not the case. The benzoyl fluoride: BF_3 complex in SO_2 contains also some of a species in which the chemical shift is nearly the same as in benzoyl fluoride. This species therefore can be only benzoyl fluoride showing weak interaction with the Lewis acid or solvent, not the ionic phenyl oxocarbonium ion.[17] The boron resonance (B^{11}) spectra at 19.3 Mc. of the HF solutions were also obtained and showed only a small shift from HBF_4 in water, slightly larger for the benzoyl complex. The phosphorus pentafluoride complexes are less stable and less soluble than the boron trifluoride complexes. PF_6^- and PF_5 have nearly the same shift, but can be differentiated by the rather different $P^{31}–F^{19}$ splittings. In this case in HF solutions there may also be fluorine exchange with HF solvent, since no separate ionic species were detected, although ionic PF_6^- was observed to some extent in SO_2 solutions. This may be an intermediate exchange rate, causing a broadening of the HF line, but no HF solutions were examined at low temperatures.[18] The HF solutions gave evidence only of the presence of acyl fluoride and PF_5, but not ionic PF_6^-. The antimony pentafluoride complexes were reasonably soluble in both solvents and indicated the ion SbF_6^- in all cases. In the HF solutions exchange of fluorine from SbF_6^- to HF is slow enough to give separate lines. However, there is again no evidence to exclude the possibility of an exchanging, highly polarized $F–SbF_5$ system. The HF lines are quite broad in some cases. There is a large solvent effect for the SbF_6^- ion in SO_2 of −17.6 p.p.m. from that in H_2O, and −3.8 p.p.m. in HF, or a difference of 13.8 p.p.m. of HF solutions relative to SO_2 solutions. A similar shift occurs in solutions of the other complexes. Preliminary investigation of the arsenic pentafluoride complexes indicates the ionic form AsF_6^- in HF solutions, with fast fluorine exchange. The SO_2 solutions were examined only after standing at room temperature, and results are uncertain due to decomposition. However, freshly prepared SO_2 solutions probably contain the pure ionic form AsF_6^-.

Table IV summarizes the nature of the prepared acyl fluoride: Lewis acid fluoride complexes, based on infrared investigations of the solid, crystalline substances and n.m.r. investigations of SO_2 and HF solutions.

Chemical Reactivity.—The isolated oxocarbonium complexes are effective acylating agents in C-, O-, N- and S-acylations of a variety of organic compounds. Acylations with oxocarbonium tetrafluoroborates have been reported.[2]

TABLE IV

NATURE OF ACYL FLUORIDE: LEWIS ACID FLUORIDE COMPLEXES BASED ON INFRARED AND N.M.R. INVESTIGATIONS

I = oxocarbonium ion ($RCO^+MF_{4,6}^-$); I′ = polarized donor-acceptor complex $R\overset{\substack{F\\|\delta_+}}{C}O \longrightarrow \overset{\delta_-}{M}F_{3,5}$; II = dissociated into acyl fluoride and Lewis acid fluoride with possible weak interaction.

Fluoride		Acetyl fluoride	Propionyl fluoride	Benzoyl fluoride
Boron tri-	Solid	I		
	SO_2 soln.	I′	I (I′)	II (I)
	HF soln.	I (I′)	I (I′)	I
Phosphorus penta-	Solid	I		
	SO_2 soln.	II (I)	II (I)	II
	HF soln.	II (I)	I′	II
Antimony penta-	Solid	I	I	I
	SO_2 soln.	I (I′)	I (I′)	I
	HF soln.	I′	I′	I
Arsenic penta-	Solid	I	I	I
	SO_2 soln.	I		I
	HF soln.	I (I′)	I (I′)	I

Aromatic hydrocarbons when treated with oxocarbonium hexafluoroantimonates and hexafluorophosphates, preferably in nitromethane solution, gave the corresponding aceto-, propio- and benzophenones

$$ArH + RCO^+MF_6 \longrightarrow ArCOR + HF + MF_5 \quad (M = Sb \text{ and } As)$$

Yields of ketones obtained are listed in Table V. The reaction must be considered as a modification of the Perrier synthesis[19] of ketones. The possibility of using preprepared, crystalline stable oxocarbonium salts presents definite advantages in our opinion.

TABLE V

C-ACYLATION OF AROMATICS WITH OXOCARBONIUM SALTS

Aromatic	Yield ketone, %		
	$CH_3CO^+SbF_6^-$	$CH_3CO^+AsF_6^-$	$CH_3COF\cdot PF_5$[a]
Benzene	95	93	15
Toluene	96	92	23
Ethylbenzene	94	91	20
Fluorobenzene	90	89	Trace
Chlorobenzene	87	86	. . .

[a] Thermally unstable under acylation conditions. [b] Propionylation of the same aromatics with $CH_3CH_2CO^+SbF_6^-$ and $CH_3CH_2CO^+AsF_6^-$, respectively, gave the corresponding propiophenones with 81–93% yield. Benzoylation with $C_6H_5CO^+SOF_6^-$ and $C_6H_5CO^+AsF_6^-$ gave benzophenones with yields of 86–93%.

The acyl fluoride: PF_5 complexes (similarly to the acyl fluorides: BF_3 complexes[2]) are considerably

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(17) This work is handicapped by the lack of reference materials known to be of the polarized donor-acceptor form referred to above. At some future time this may be resolved by careful n.m.r. and infrared studies on the same sample.

(18) The HF solutions were sealed in quartz tubes with too large an outer diameter to fit into the low temperature probe.

(19) G. Perrier, *Ber.*, **33**, 815 (1900).

less suitable acylating agents in the formation of aromatic ketones than the stable oxocarbonium hexafluoroantimonates and hexafluoroarsenates. Not only is their reactivity much lower, but being thermally unstable under generally used acylation conditions the preparative yields of ketones are quite low.

Oxocarbonium salts are also highly effective acylating agents for O-acylation of alcohols giving esters

$$ROH + R'CO^+MF_6^- \longrightarrow RCOOCR' + HF + MF_5$$

for S-acylation of mercaptans giving thiolesters

$$RSH + R'CO^+MF_6^- \longrightarrow RSOCR' + HF + MF_5$$

and for N-acylation of primary and secondary amides yielding amides

$$2RNH_2 + R'CO^+MF_6^- \longrightarrow RNHOCR' + RNH_2HMF_6$$

Results of acylations are shown in Tables VI, VII and VIII, respectively.

TABLE VI

O-ACYLATION OF ALCOHOLS WITH OXOCARBONIUM SALTS[a]

Alcohol	Yield alkyl ester, %		
	$CH_3CO^+SbF_6^-$	$CH_3CO^+AsF_6^-$	$CH_3COF \cdot PF_5$[a]
Methanol	62	70	37
Ethanol	70	65	40
1-Propanol	75	70	35
1-Butanol	80	75	40
t-Butyl alc.	77	80	40
1-Octanol	87	82	39

[a] Propionylation and benzoylation of the same alcohols with ethyl oxocarbonium and phenyl oxocarbonium salts gave yields comparable to acetylations. Propionylation yields varied between 39–85%, benzoylation yields between 18 and 85%.

TABLE VII

S-ACYLATION OF MERCAPTANS WITH OXOCARBONIUM SALTS[a]

Mercaptan	Yield thiolester, %		
	$CH_3CO^+SbF_6^-$	$CH_3CO^+AsF_6^-$	$CH_3COF \cdot PF_5$[b]
Methyl thiol-	50	40	10
Ethyl thiol-	60	55	17
n-Octyl thiol-	61	58	27

[a] Propionylation and benzoylation of the same thiols with ethyl oxocarbonium and phenyloxocarbonium salts gave yields comparable to acetylations. [b] Thermally unstable under acylation conditions.

TABLE VIII

N-ACYLATION OF AMINES WITH OXOCARBONIUM SALTS[a]

Amine	Yield amide, %		
	$CH_2CO^+SbF_6^-$	$CH_3CO^+AsF_6^-$	$CH_3COF \cdot PF_5$
Ammonia	84	82	85
Ethylamine	87	90	84
Diethylamine	80	84	79
Aniline	84	85	83

[a] Propionylation and benzoylation of the same amine with ethyl oxocarbonium and phenyl oxocarbonium salts gave yields comparable to acetylations.

All yields reported in the Tables V–VIII were obtained from preparative runs. Although acylations seem to be practically quantitative (as analyzed in a certain number of runs by gas–liquid chromatography) losses during preparative operations, mainly during water washing of the products, lowered preparative yields. The kinetic step of the oxocarbonium ion formation in the Friedel–Crafts ketone syntheses is eliminated when preprepared oxocarbonium salts are used. This offers a good way for the investigation of the main reaction step between oxocarbonium salts and aromatics. Relative rates and isomer distributions were determined in competitive acylation of alkylbenzene and halobenzene systems with methyl oxocarbonium hexafluoroantimonate. Details of this work will be reported in a forthcoming paper.

Experimental

The acyl fluorides used (acetyl, propionyl and benzoyl) were prepared as described.[20] Antimony pentafluoride was obtained from the Harshaw Chemical Co., Cleveland, O., and was freshly distilled before use. Phosphorus and arsenic pentafluorides were obtained from the Ozark–Mahoning Co., Tulsa, Okla. CD_3COOD was obtained from Merck Ltd., Montreal, Can. Anhydrous $AgBF_4$ was prepared according to Olah and Quinn.[21] Argentous fluoride was obtained from the Harshaw Chemical Corp., Cleveland, O.

Preparation of Anhydrous $AgPF_6$ in Nitromethane Solution.—Argentous fluoride (AgF, 0.5 mole) and 100 g. of nitromethane were placed in a flask equipped with a gas inlet tube and protected from the atmospheric moisture by a calcium chloride tube. Phosphorus pentafluoride was introduced into the flask which was vigorously shaken until the weight increase of the flask indicated that 0.5 mole of phosphorus pentafluoride had been absorbed, and all the solid material went into solution. The obtained homogeneous solution was filtered to remove any solid impurities, then the nitromethane was distilled off under reduced pressure. Overheating should be avoided to prevent decomposition of the salt.

Preparation of Anhydrous $AgSbF_6$.—Antimony pentafluoride (0.4 mole) was dissolved in 200 ml. of cold anhydrous HF. The mixture was kept in a Dry Ice–acetone-bath and 0.4 mole of solid AgF was added into the solution. The reaction mixture was shaken at this temperature for a few minutes, then allowed to warm up to 0° with continuous shaking; $AgSbF_6$ precipitates as it is formed. The solid was rapidly collected, washed with ligroin, then pumped dry in vacuum. The yield is 125 g. (91.9%).

Preparation of Anhydrous $AgPF_6$ and $AgAsF_6$ in Liquid HF Solution.—Argentous fluoride AgF, 0.4 mole) was dissolved in 200 ml. of anhydrous HF and the solution then saturated, while kept at about −30°, with phosphorus and arsenic pentafluoride. After saturating the solution the temperature was allowed slowly to rise to 0°. Solid impurities were removed by filtration and the clear HF solution then evaporated under slightly reduced pressure, the yield of $AgPF_6$ was 91 g. (90.9%), of $AgSsF_6$, 105 g. (89.3%). All operations involving anhydrous HF were carried out in fused silica equipment with usual standard joints greased with fluorolube or in plastic equipment. The anhydrous silver salts could be recrystallized from liquid SO_2 and were found to be analytically pure.

Oxocarbonium Tetrafluoroborates, Hexafluorophosphates, Hexafluoroantimonates and Hexafluoroarsenates. (a) **Fluoride Method.**—Acyl halide (0.2 mole) was dissolved in 70 ml. of 1,1,2-trifluorotrichloroethane (Freon 113) and the solution was cooled to −20 to −25°. Into the stirred solutions BF_3, PF_5 or AsF_5 was introduced (approximately 0.2 mole plus a slight excess). In the case of the preparation of the oxocarbonium hexafluoroantimonates the Freon solution of the acyl fluoride was allowed to react at −5° to 0° with an equimolar solution of freshly distilled antimony pentafluoride solution to the stirred cold acyl fluoride solution. After half an hour of continued stirring, the white, crystalline precipitate formed was collected, washed with cold Freon 113 and dried in vacuum. The boron and phosphorus salts were collected cold because of decomposition at room temperature. The arsenates and antimonates can be collected at room temperature, washed with Freon 113 and pumped dry.

All operations were carried out under usual conditions for excluding moisture, preferably in closed vacuum systems. Yields are generally close to quantitative.

(b) **Silver Salt Method.** (1) In **Nitromethane Solution.**—Anhydrous silver salt ($AgBF_4$, $AgPF_6$, $AgSbF_6$, $AgAsF_6$; 0.1 mole) was dissolved in 150 ml. of dry nitromethane. A

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(20) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **26**, 237 (1961).

(21) G. A. Olah and H. W. Quinn, *J. Inorg. Nucl. Chem.*, **14**, 295 (1960).

Table IX

		Chlorine, %		Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_3COF \cdot BF_3$	(130)	58.46	58.18	18.46	18.15	2.3	2.1
$CH_3COF \cdot AsF_5$	(232)	49.0	48.8	10.34	10.23	1.30	1.20
$CH_3CH_2COF \cdot AsF_5$	(246)	46.3	45.0	14.63	14.30	2.03	1.95
$C_6H_5COF \cdot AsF_5$	(294)	38.74	38.90	28.58	28.30	1.70	1.80
$CH_3COF \cdot PF_5$	(188)	60.63	59.21	12.77	12.50	1.59	1.43
$CH_3COF \cdot SbF_5$	(279)	40.88	41.1	8.61	8.53	1.08	1.04
$CH_3CH_2COF \cdot SbF_5$	(293)	38.93	38.59	12.30	12.18	1.72	1.79
$C_6H_5COF \cdot SbF_5$	(341)	33.44	33.10	24.66	24.60	1.47	1.42

solution of 0.1 mole of acyl chloride or bromide in 25 ml. of nitromethane was then added to the well-stirred silver salt solution kept at −30° to 0° with external cooling. Stirring was continued for another 10 minutes, the precipitated silver halide was then filtered and the solvent, together with any excess of Lewis acid halide, removed by distillation. Thermally instable BF_3 and PF_5 salt are difficult to separate from the solutions by this method.

(2) In **Liquid SO_2 Solution.**—Into a stirred solution of 0.1 mole of complex anhydrous silver salt in 100 ml. of liquid SO_2 kept at −25° was dropped a solution of 0.1 mole of acyl chloride dissolved in 25 ml. of SO_2. The stirring was continued for another 20 minutes. Precipitated silver halide was filtered and solvent SO_2 removed by distillation at this temperature under slightly reduced pressure.

The oxocarbonium salts could be recrystallized from liquid SO_2 solutions and were obtained as colorless crystalline compounds with high purity. Melting points (in sealed tubes) and thermal decomposition points, respectively, are given in Table I. Elementary analysis of the complexes is summarized in Table IX; $CH_3CH_2COF \cdot BF_3$, $CH_3CH_2COF \cdot PF_5$, $C_6H_5COF \cdot BF_3$ and $C_6H_5COF \cdot PF_5$ were thermally not stable enough to allow elementary analyses. The 1:1 ratio of these complexes was determined from weight increase in the complex formation.

Acyl Chloride:$SbCl_5$ Complexes.—Equimolar quantities of the appropriate acyl chloride (acetyl, propionyl, benzoyl) and antimony pentachloride were allowed to react in Freon 113 solutions according to the preparation of the previously described acyl fluoride:SbF_5 complexes.

CD_3COF.—Benzoyl fluoride (0.6 mole) and CD_3COOD (0.2 mole) were placed in flask equipped with a small Widmer type column. The flask was heated slowly and the CD_3COF formed was collected in the cooled receiver; upon redistillation b.p. 21.5°, yield 10.1g., 77.6%. The infrared spectrum of the compound does not show the presence of C–H impurities.

$CD_3CO^+SbF_6^-$.—CD_3COF (0.1 mole) was dissolved in 25 ml. of Freon 113 and cooled to −5 to −10°. Into this solution 0.1 mole of freshly distilled SbF_5, dissolved in 25 ml. of cold Freon 113, was added with continuous stirring. After the addition was completed the mixture was stirred for 5 more minutes, filtered, washed with Freon 113 and pumped dry; yield 26 g. (90.3%), m.p. 174–176°. Calcd.: F, 40.4; C, 8.5; D, 2.14. Found: F, 39.8; C, 8.4; D, 2.05.

Reaction of Oxocarbonium Salts with Aromatic Compounds. (a) **Without Solvent.**—The appropriate oxocarbonium salt (0.2 mole) was added into 0.5 mole of well stirred aromatic. The complex salts are generally not soluble in the aromatics. In most cases the reaction starts at room temperature but in some cases heating is necessary to start it. The ketones formed give complexes with the by-product Lewis acids and separate from the excess aromatics as a lower layer. After cooling, the reaction mixture is washed out twice with water, dried over Na_2SO_4 and fractionated.

(b) **In Solution.**—In these experiments the reaction was carried out in nitromethane solution in which the aromatics and the oxocarbonium salts are both soluble. The reactions are, however, much slower in solvent and due to the partial decomposition of the oxocarbonium salts in nitromethane the yields are lower.

Reaction of Oxocarbonium Salts with Alcohols.—Oxocarbonium salt (0.3 mole) was added as nitromethane solution or in small portions into 0.6 mole of the appropriate stirred and cooled alcohol. A rapid reaction takes place. The resulting mixture was washed with water, dried over Na_2SO_4 and fractionated.

Reaction of Oxocarbonium Salts with Mercaptans.—Oxocarbonium salt (0.3 mole) was added in nitromethane solution or in small fractions into 0.6 mole of well stirred and cooled mercaptan. The reaction is very fast. After completion of the reaction the mixture was washed 3 times with water, dried over Na_2SO_4 and fractionated.

Reaction of Oxocarbonium Salts with Amines.—As these reactions are very difficult to handle without solvent, they were carried out always in nitromethane or ether solutions. The solution of 0.3 mole of oxocarbonium salt was added to 0.6 mole of the stirred and cooled primary or secondary amine. The products, after water washings, were isolated either by distillation or crystallization.

Acknowledgment.—The authors are grateful to D. Cook for the infrared data, and to O. U. Anders, Radiochemistry Laboratory, The Dow Chemical Co., Midland, Mich., for neutron activation fluorine analyses.