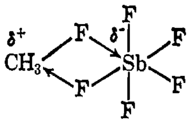
indicates a rapidly exchanging donor–acceptor complex system.

The laser Raman spectrum of a CH_3F–SbF_5–SO_2 solution[8] contains lines at 526, 653, 685, 738, 1010, 1150, 1330, 2863, and 2950 cm^{-1}. These lines are nearly identical with those obtained for the additive Raman spectra of SbF_5 and CH_3F in SO_2 solution. The intense line usually assigned to the ν_1 vibration of SO_2 in the $SO_2 \rightarrow SbF_5$ complex at 1106 cm^{-1} is not observed in the CH_3F–SbF_5–SO_2 spectrum. This indicates that CH_3F is a stronger n base than SO_2 in these solutions leading to the exclusive formation of a $CH_3 \rightarrow SbF_5$ donor–acceptor complex. Furthermore, the fact that there is no apparent interaction (*i.e.*, exchange) observed between excess CH_3F and the complex $CH_3F \rightarrow SbF_5$ on either the Raman or nmr time scale suggests a strong $CH_3F \rightarrow SbF_5$ bonding interaction. On the other hand, the similarities in the fundamental Raman-active vibrations of CH_3F and methyl fluoride in the $CH_3F \rightarrow SbF_5$ complex shows that the weakening of the C–F bond in methyl fluoride is not sufficient to significantly alter the tetrahedral geometry the molecule possesses in neutral solution.

Nmr and Raman data for the CH_3F–SbF_5 complex in SO_2 solution described above indicates a polarized donor–acceptor complex undergoing rapid fluorine exchange in what amounts to front-side attack (**1**).

The pmr spectrum of a 1:1 (mol:mol) antimony pentafluoride–methyl fluoride mixture in sulfur dioxide solution showed only a single peak for the complex with no evidence of excess CH_3F. Thus a 1:1 relationship is established, thereby supporting structure **1**.



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In neat SbF_5 as solvent, clearly a dimeric (or polymeric) antimony pentafluoride would be the complexing agent, but the self-condensation reaction of methyl fluoride under these conditions (*vide infra*) does not allow the study of this system. To our knowledge, the CH_3F–SbF_5 complex is the first well-characterized example of a Friedel–Crafts donor–acceptor complex.

The methyl fluoride–antimony pentafluoride complex is a powerful new methylating agent capable of oxygen, sulfur, aromatic and aliphatic carbon, and even halogen substitution.

Dimethyl ether, for example, is methylated to the trimethyloxonium ion, dimethyl sulfide to the trimethylsulfonium ion (eq 1 and 2). Aromatic hydrocarbons

$$CH_3OCH_3 + CH_3F\text{–}SbF_5 \longrightarrow (CH_3)_3O^+SbF_6^- \qquad (1)$$

$$CH_3SCH_3 + CH_3F\text{–}SbF_5 \longrightarrow (CH_3)_3S^+SbF_6^- \qquad (2)$$

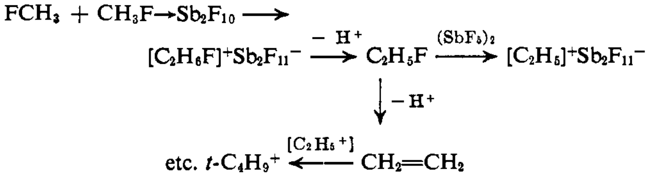
are methylated (eq 3) and even alkanes undergo methylation (eq 4). The powerful methylating ability of

$$ArH + CH_3F\text{–}SbF_5 \longrightarrow ArCH_3 + HF + SbF_5 \qquad (3)$$

$$RH + CH_3F\text{–}SbF_5 \longrightarrow RCH_3 + HF + SbF_5 \qquad (4)$$

CH_3F–SbF_5 toward saturated aliphatic carbon is further evidenced by its self-condensation reaction.

When methyl fluoride is dissolved in neat antimony pentafluoride at room temperature, a solution is formed whose pmr spectrum consists of a singlet at δ 5.50 and peaks at δ 4.35 and δ 12.5. The intensity of the latter two absorptions increases (at the probe temperature, +35°) with time. Quenching experiments indicated that the signal at δ 4.35 is the *t*-butyl cation and the peak at δ 12.5 was identified by control experiments as being due to HF. Thus methyl fluoride is seen to readily undergo a self-condensation reaction in neat SbF_5. Based on peak area integration for each mole of *t*-butyl cation, 3 mol of HF is formed.



$$\begin{tikzcd}
\mathrm{FCH_3} + \mathrm{CH_3F{\rightarrow}Sb_2F_{10}} \arrow[r] & {} & \\
{[\mathrm{C_2H_6F}]^+\mathrm{Sb_2F_{11}}^-} \arrow[r, "-\mathrm{H}^+"] & \mathrm{C_2H_5F} \arrow[r, "(\mathrm{SbF_5})_2"] \arrow[d, "-\mathrm{H}^+"] & {[\mathrm{C_2H_5}]^+\mathrm{Sb_2F_{11}}^-} \\
\text{etc. } t\text{-}\mathrm{C_4H_9}^+ & \mathrm{CH_2{=}CH_2} \arrow[l, "{[\mathrm{C_2H_5}^+]}"'] &
\end{tikzcd}$$

The condensation reaction must occur in the following manner: methyl fluoride and antimony pentafluoride form an incipient methyl cation which then methylates a second molecule of methyl fluoride on carbon to form the $C_2H_6F^+$ species. The $C_2H_6F^+$ deprotonates to ethyl fluoride which then in SbF_5 ionizes to $C_2H_5^+$ which, in turn, is ready to condense to the *t*-butyl cation, *t*-hexyl cations, etc. In a separate experiment, methylation of ethyl fluoride yielded identical condensation results.

When methyl fluoride was treated with 1:1 HF–SbF_5 or 1:1 FSO_3H–SbF_5 at 0° only a single pmr absorption at δ 5.50 (s) is originally observed. This species then slowly converts ($t_{1/2} \sim$ 1 hr) to the *t*-butyl cation (singlet at δ 4.35).

When alkyl halides, other than the fluorides, are treated with CH_3F–SbF_5, n alkylation on halogen takes place and dialkylhalonium ions are formed. The following communication reports on this new reaction and its implications to Friedel–Crafts chemistry.[9]

Acknowledgment. Partial support of the work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Received February 24, 1969

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(8) For experimental conditions see G. A. Olah and A. Commeyras, *J. Amer. Chem. Soc.*, in press.

(9) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).

(10) Postdoctoral Research Investigator.

Friedel–Crafts Chemistry. IV.[1]
Dialkylhalonium Ions and Their Possible Role in Friedel–Crafts Reactions

Sir:

In the extensive literature of Friedel–Crafts chemistry[2] the alkyl halide–Lewis acid system studied always showed 1:1 or 1:2 complex formation. No indication of 2:1 or 2:2 complex formation was obtained. Since dialkylhalonium ions were not previously

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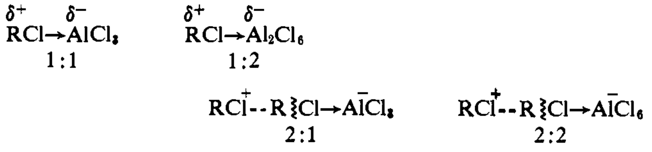
(1) Part III: G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969).

(2) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I–IV, Interscience Publishers, New York, N. Y., 1963–1965.



$$\overset{\delta+}{R}Cl \rightarrow \overset{\delta-}{Al}Cl_3 \quad (1{:}1) \qquad \overset{\delta+}{R}Cl \rightarrow \overset{\delta-}{Al}_2Cl_6 \quad (1{:}2)$$

$$R\overset{+}{Cl}\text{- -}R\wr Cl \rightarrow \overset{-}{Al}Cl_3 \quad (2{:}1) \qquad R\overset{+}{Cl}\text{- -}R\wr Cl \rightarrow \overset{-}{Al}Cl_6 \quad (2{:}2)$$

reported or observed in any way in solution,[3] their possible presence in Friedel–Crafts systems was not suggested.[4]

We have previously reported observation of a series of stable, long-lived bridged halonium ions[5] generated through halogen participation in ionization or dihalides, haloalkoxides, haloacetates, etc., in SbF_5–SO_2, FSO_3H–SbF_5, and other super acid solutions. Open-chain diarylhalonium ions have been obtained from reaction of aryldiazonium compounds with halobenzenes and aryliodoso compounds with aromatics.[6,7]

We now report the preparation and nmr investigation of a series of dialkylhalonium ions, the general methods leading to convenient preparation of this new class of halonium ions, and their possible involvement in Friedel–Crafts alkylations.

When an SO_2 solution of SbF_5–SO_2 is added to an approximate 5 mol excess of methyl chloride, bromide, or iodide at −60°, pmr spectra of the solutions show, in addition to the signals of excess alkyl halide, deshielded singlets at δ 4.13, 3.84, and 3.42, respectively. Characteristic deshielded ethyl signals were also obtained when SbF_5–SO_2 was allowed to react with excess ethyl halides. It is suggested that the species giving rise to these low-field signals are dialkylhalonium ions.

$$2RX + SbF_5\text{–}SO_2 \xrightarrow{SO_2} RXR^+SbF_5X^-$$

When $^{13}CH_3Br$ (60% enriched) is used, the ^{13}C spectra obtained by the indor method in SbF_5–SO_2 display a quartet at 156.2 ppm (relative to CS_2) with a $J_{^{13}C\text{-}H}$ of 162 Hz. A similar multiplet at 182 ppm ($J_{^{13}C\text{-}H} = 152$ Hz) is observed for excess $^{13}CH_3Br$ in the same solution. In contrast to the large $\Delta\delta$ of 26 ppm observed for $^{13}CH_3Br$ *vs.* $^{13}CH_3BrCH_3^+$, the $^{13}CH_3F$ *vs.* $^{13}CH_3F$–SbF_5 ^{13}C spectra yield a $\Delta\delta$ of 1.1 ppm. This indicates a much larger variation in $\Delta\delta$ than would be expected for the possible $^{13}CH_3Br$–SbF_5 complex. Furthermore, pmr spectra for $CH_3Br^{13}CH_3^+$ show, in addition to the expected doublet, further splitting to yield a doublet of doublets. This secondary splitting is assigned to long-range (H_1–C_2Br–$^{13}C_3^+$; $J = 1.7$ Hz) coupling interaction of proton H_1 with carbon atom $^{13}C_3$. Such long-range coupling indeed supports the conclusion that these species are the dimethylbromonium ions $^{13}CH_3Br^{12}CH_3$ and $^{13}CH_3$-$Br^{13}CH_3$ since it demonstrates the presence of two methyl groups in each molecule.

The pmr spectrum of the $CH_3F \rightarrow SbF_5$ complex in SO_2[1] shows only a singlet at δ 5.56 due to rapid intramolecular fluorine exchange in the complex. When aliquot portions of the complex solutions are added to an approximate 5 mol excess of methyl and ethyl halides the δ 5.56 signal disappears and spectra analogous to that obtained in the excess alkyl halides–SbF_5–SO_2 systems are observed. The nmr data are summarized in Table I. Since electrophilic methylation of alkyl halides (other than fluorides[8]) is expected to take place on the halide atom with its unshared electron pairs, the experimental observations are in good agreement with the formation of dialkylhalonium ions.

$$RX + CH_3F \rightarrow SbF_5 \xrightarrow{SO_2} [R\text{—}X\text{—}CH_3]^+SbF_6^-$$
$$X = Cl,\ Br,\ \text{or}\ I$$

Chemical shifts of both the methyl and the methylene protons of ethylhalonium ions **4**–**9** correlate well with those reported[5b] for bridged five-membered-ring tetramethylenehalonium ions. All of the ethylhalonium ion signals are shifted approximately 0.5 ppm to higher field relative to their bridged partners. Such diamagnetic shifts are generally observed in changing from alicyclic to open-chain species. The position of signals observed for methyl protons in dimethyl- and methylethylhalonium ions **1**–**3**, **7**, **8**, and **9** are what would be predicted based on extrapolation of data obtained from previous studies,[5] and by analogy with evidence obtained for diethyl- and diisopropylhalonium ions.

The reactions of ethyl chloride and ethyl bromide with the $CH_3F \rightarrow SbF_5$ complex in SO_2 are accompanied in each case by the formation of the corresponding methyl halides. This halogen exchange is incomplete

$$CH_3CH_2X + CH_3F \rightarrow SbF_5 \longrightarrow CH_3CH_2XCH_3^+\,SbF_6^-$$
$$CH_3CH_2XCH_3^+ + CH_3CH_2X \longrightarrow CH_3CH_2XCH_2CH_3^+ + CH_3X$$
$$X = Cl,\ Br$$

as shown by the presence of additional low-field pmr quartets at δ 4.62 and 4.64, respectively. These signals are assigned to methylene protons of halonium ions **8** and **9** and appear in a 2:3 ratio with singlet absorptions at δ 3.60 and 3.90 which are in turn due to methyl protons of the respective CH_3BrEt^+ and CH_3ClEt^+ methylethylhalonium ions. Similarly the signals of methyl protons of the ethyl groups in chloronium ions **5** and **9** appear as nearly superimposed triplets centered at δ 1.51 and 1.54, respectively. Such a pattern is not observed for the solution of bromonium ions **4** and **8**, and only a relatively broad triplet appears at δ 1.44. This signal is assigned to the methyl protons of the ethyl groups in both **4** and **8**. Only one well-resolved ethyl signal at δ 4.23 is observed for the Et–I case, with a relatively low-field methyl singlet at δ 3.28, indicating that only methylethyliodonium ion is formed. The diethyliodonium ion **6** was prepared and observed separately in SbF_5–SO_2. Relative areas of the quartets to methylethylhalonium ions **8** and **9** suggest that the ratio of monoethyl- to diethylhalonium ions decreases in the order I > Br > Cl. This trend can be interpreted as a qualitative measure of the decrease in the stability

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(3) Dialkylhalonium ions were indicated as products of rearrangements in unimolecular fragmentation following electron impact in mass spectroscopic studies [F. W. McLafferty, *Anal. Chem.*, **34,** 2 (1962)] and in ion cyclotron resonance studies of molecular ion reactions [J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89,** 4569 (1967)].

(4) Professor H. C. Brown in private discussion informed us (Feb. 14, 1969) that F. P. DeHaan in his laboratories (Ph.D. Dissertation, Purdue University, 1961) obtained evidence in the CH_3Cl–$GaCl_3$ system through chlorine-36 exchange indicating dimethylchloronium ion as unstable intermediate.

(5) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89,** 4744 (1967); **90,** 947, 2587, 6988 (1968); (b) G. A. Olah and P. E. Peterson, *ibid.*, **90,** 4675 (1968).

(6) A. N. Nesmeyanov, L. G. Makarova and T. P. Tolstaya, *Tetrahedron*, **1,** 145 (1957), and references therein.

(7) I. Masson and E. Race, *J. Chem. Soc.*, 1718 (1937); I. Masson and C. Argument *ibid.*, 1702 (1938).

(8) Due to the high electronegativity of fluorine, alkyl fluorides are not alkylated on the fluorine atom, but under favorable conditions carbon alkylation takes place.[1]

Table I. Pmr Data of Dialkylhalonium Ions[a]

Ion		CH_3X^+	$-CH_2X-^+-CHX-^+$	CH_3CX-^+	$-CH_2CX-^+$	CH_3CCX-^+
$CH_3ICH_3^+$	**1**	3.42				
$CH_3BrCH_3^+$	**2**	3.84				
$CH_3ClCH_3^+$	**3**	4.13				
$(CH_3CH_2)_2Br^+$	**4**		4.66	1.44		
$(CH_3CH_2)_2Cl^+$	**5**		4.72	1.54		
$(CH_3CH_2)_2I^+$	**6**		4.20	1.83		
$CH_3ICH_2CH_3^+$	**7**	3.28 (3)	4.23 (2)	1.76 (3)		
$CH_3BrCH_2CH_3^+$	**8**	3.60 (3)	4.64 (2)	1.44 (3)		
$CH_3ClCH_2CH_3^+$	**9**	3.90 (3)	4.64 (2)	1.51 (3)		
$[(CH_3)_2CH]_2Br^+$	**10**		5.39 (1)	1.50 (6)		
$[(CH_3)_2CH]_2Cl^+$	**11**		5.76 (1)	1.56 (6)		
$[(CH_3)_2CH]_2I^+$	**12**		5.29	1.72		
$CH_3ClCH(CH_3)_2^+$	**13**	4.03	5.44	1.56		
$[CH_3(CH_2)_2]_2I^+$	**14**		4.12 (2)		1.50 (2)	0.66 (3)
$[CH_3(CH_2)_2]_2Br^+$	**15**		4.48 (2)		1.70 (2)	0.73 (3)

[a] From TMS in an external capillary tube. Spectra were recorded at −60° in SO_2 solution at 60 MHz. Relative peak areas are shown in parentheses. Usual multiplicities and couplings for alkyl groups were observed. The central position of the complex multiplet or of the overlapping peaks is given.

of the monoethylhalonium ions originally formed and of increasing tendency for exchange. This is also the expected order of stability since the larger halogen atoms are more capable of localizing positive charge leading to a greater stability of the CH_3XEt^+ species and hence less exchange with excess EtX to yield diethylhalonium ions.

Temperature-dependent pmr spectra of excess *i*-PrBr with SbF_5 in SO_2 solution displays two sets of septets (δ 3.76, 4.66) and doublets (δ 1.08, 1.44) at −95°. As the temperature is raised these peaks begin to merge, and they coalesce to a single well-resolved septet (δ 4.55) and doublet (δ 1.28) at −40°. Changes in concentration of *i*-PrBr apparently do not alter the equilibrium indicating that *i*-PrBr is taking part in both forward and reverse equilibrium processes. The only change observed was the increase in intensity of the septet at δ 3.76 and doublet at δ 1.08, demonstrating that these signals are those of nonassociated *i*-PrBr. These data are consistent with an equilibrium between diisopropylbromonium ion (**10**) and *i*-PrBr. Similar results were

$$2(CH_3)_2CHBr + SbF_5\text{–}SO_2 \xrightarrow{SO_2} \underset{\textbf{10}}{(CH_3)_2CH\overset{+}{Br}CH(CH_3)_2}\ SbF_5Br^-$$

$$(CH_3)_2CH\overset{+}{Br}CH(CH_3)_2 + (CH_3)_2CHBr \rightleftharpoons (CH_3)_2CH\overset{+}{Br}CH(CH_3)_2 + (CH_3)_2CHBr$$

obtained with *i*-PrCl; however, the equilibrium is apparently fast even at −90° and cannot be frozen out.

Isopropylhalonium ions **10**, **11**, and **12** are also formed from *n*-propyl chloride, bromide, and iodide in SbF_5–SO_2 and CH_3F–SbF_5–SO_2, with methylisopropylchloronium ion **13** being the only cross-product detected. The *n*-propyl → isopropyl rearrangement occurs to varying degree in the order Cl (~100%) > Br (~40%) > I (~2%). Characteristic spectra were obtained from di-*n*-propyliodonium ion **14** and bromonium ion **15** present in the *n*-PrI and *n*-PrBr solutions.

The observation of dialkylhalonium ion formation in alkyl halide–antimony pentafluoride systems raises the question of their involvement in Friedel–Crafts alkylations and isomerizations. Alkyl halide–Lewis acid halide complexes (or for that matter any carbonium ion) can obviously alkylate excess alkyl halides (other than fluorides) to form dialkylhalonium ions; 1:1 or 1:2 alkyl halide–Lewis acid complexes can give 2:1 or 2:2 dialkylhalonium ion complexes. The dialkylhalonium

$$R\text{—}Cl\text{---}R\,\wr Cl\rightarrow AlCl_3 \qquad R\text{—}Cl\text{---}R\,\wr Cl\rightarrow Al_2Cl_6$$

ions must be assumed to exchange rapidly under ordinary Friedel–Crafts conditions with excess alkyl halides and also to dissociate according to the equilibrium

$$\overset{\delta^+}{R}\text{—}Cl\,\wr\, R\text{---}\overset{\delta^+}{Cl}\text{—}R \qquad R\text{—}X\text{—}\overset{+}{R}\,\wr\, M_xX_y^- \rightleftharpoons RX + RX\rightarrow M_xX_{y-1}$$

That dialkylhalonium ions can be alkylating agents was shown in experiments using solutions of dialkylhalonium fluoroantimonates in sulfur dioxide solution at −70° in the presence of excess alkyl halides with no "free" antimony pentafluoride being present in the systems.

Further work with a variety of weaker Lewis acids is in progress. $GaCl_3$ in excess methyl bromide, for example, in SO_2 solution at −80° shows the presence of dimethylbromonium ion **2**.

Acknowledgment. Partial support of the work by the Petroleum Reserved Fund, administered by the American Chemical Society, and the U. S. Army Research Office (Durham) is gratefully acknowledged.

(9) Postdoctoral Research Investigator.

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The Synthesis and Solvolysis of 1-Cyclopropyl-1-iodoethylene. Generation of an Unusually Stable Vinyl Cation

Sir:

The increasing number of instances in which vinyl cations (general structure **1a**) are being suggested as intermediates in organic solution reactions[1] indicates

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(1) For some recent examples, see (a) M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968); *Compt. Rend.*, **259**, 2251 (1964); **266**, 231 (1968); (b) M. Hanack and J. Häffner, *Tetrahedron Letters*, 2191 (1964); *Chem. Ber.*, **99**, 1077 (1966); M. Hanack and I. Herterich, *Tetrahedron Letters*, 3847 (1966); M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967); (c) R. Garry and R. Vessiere, *Bull. Soc. Chim. France*, 1542 (1968); (d) W. D. Closson and S. A. Roman, *J. Am. Chem. Soc.*, **88**, 6015 (1966); (e) H. R. Ward and P. Dwight Sherman, Jr., *ibid.*, **89**,