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Stable Carbonium Ions. V.^{1a} Alkylcarbonium Hexafluoroantimonates

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Propyl, butyl, and pentyl fluorides gave with excess antimony pentafluoride remarkably stable solvated alkylcarbonium hexafluoroantimonates. The stability of the systems allowed infrared, ultraviolet, and nuclear magnetic resonance investigation of the dimethyl-, trimethyl-, and dimethylethylcarbonium ions, including that of the completely deuterated and C¹³-labeled analogs. In the strong acid systems used, both *n*-propyl and isopropyl fluoride yield only the secondary dimethylcarbonium ion, all four butyl fluorides give the tertiary trimethylcarbonium ion, and all seven pentyl fluorides give the dimethylethylcarbonium ion. The spectroscopic observations, discussed in detail, fully substantiate the planar sp²-hybridized structure of the simple alkylcarbonium ions. The chemical reactivity of alkylcarbonium hexafluoroantimonates was investigated in hydrolysis and reactions with alcohols, H₂S, mercaptans, amines, acids, and aromatic hydrocarbons.

Introduction

The majority of simple alkylcarbonium ions that have been discussed in the chemical literature have been considered only as transient entities. Their existence has been inferred from the study of the course of certain reactions. No reliable physical measurements other than electron impact measurements have so far been reported for any of the simple alkylcarbonium ions.

The formation of gaseous organic cations under electron bombardment of haloalkanes, alkanes, etc., has been widely investigated in mass spectral studies.^{2,3}

Measurements by electron impact methods have led to experimental stabilization energies of a number of alkylcarbonium ions. Muller and Mulliken⁴ compared these with calculated values obtained by a procedure based on the LCAO-MO approximation, the large stabilization energies found for carbonium ions being attributed to the combined effects of hyperconjugation and charge redistribution. Their data are summarized in Table I.

TABLE I
STABILIZATION ENERGIES OF ALKYL CARBONIUM IONS (IN KCAL./MOLE)⁴

	Obsd.	Calcd.
CH ₃ ⁺	0	0
CH ₃ CH ₂ ⁺	36	41
CH ₃ CH ⁺ CH ₃	66	66
(CH ₃) ₃ C ⁺	84	83
CH ₂ =CHCH ₂ ⁺	58	64

The heat of formation, ΔH_f , of a series of alkylcarbonium ions from electron impact data calculated by Field and Franklin from their tabulated data² is shown in Table II.

From the ΔH_f values in Table II, it can be seen that the isopropyl cation is more stable than the *n*-propyl cation by some 26 kcal./mole. Similarly the *t*-butyl cation is substantially more stable than any of the other butyl cations, as is the *t*-pentyl cation compared with any of the other pentyl cations. These considera-

(1) (a) Part IV: G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963); (b) The Dow Chemical Co., Midland, Mich.

(2) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

(3) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press, Inc., New York, N. Y., 1963.

(4) N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

TABLE II

HEAT OF FORMATION OF ALKYL CARBONIUM IONS, ΔH_f ²

	ΔH_f , kcal./ mole		ΔH_f , kcal./ mole
CH ₃ ⁺	262	(CH ₃) ₃ C ⁺	166
CH ₃ CH ₂ ⁺	224	(CH ₃) ₂ CHCH ₂ ⁺	211
CH ₃ CH ₂ CH ₂ ⁺	216	(CH ₃) ₃ CCH ₂ ⁺	194
CH ₃ CH ⁺ CH ₃	190	(CH ₃) ₂ C ⁺ CH ₂ CH ₃	152
CH ₃ CH ₂ CH ₂ CH ₂ ⁺	207	(CH ₃) ₂ CHCHCH ₃	170
CH ₃ CH ₂ CH ⁺ CH ₃	181	CH ₂ =CHCH ₂ ⁺	220

tions are based upon the energetics of ions in the gas phase and as such can give only qualitative interpretations for their behavior in solutions. It would of course be very useful if the energies of the ions in solution were available. Unfortunately, the heats and entropies of solvation of gaseous ions have never been measured directly. However, several methods of estimating the energies of solvation have been proposed. These methods of course could be looked upon as approximations, but they have provided some insight into the behavior of ions in solution.²

Evans⁵ calculated the solvation energy of a number of alkylcarbonium ions. He assumed that the carbon atom would be in an sp²-state of hybridization and would thus be planar. The ion would be solvated by one molecule of the solvating agent (water) each above and below of the plane of the charged carbon and by two molecules in the plane of the ion. With the aid of bond lengths and van der Waals radii, the in-plane and out-of-plane energies were estimated separately, and the total solvation energy could thus be determined. Franklin⁶ estimated the solvation energies of several carbonium ions using graphically determined average ionic radii. The solvation energies were somewhat different from those estimated by Evans, but the conclusion concerning stabilization of the ions by solvation were similar.

Electronic absorption spectra of alcohols in strong proton acids (H₂SO₄) were obtained by Rosenbaum and Symons.⁷ They observed for a number of simple aliphatic alcohols absorption maxima in the 290 m μ region and ascribed this absorption to the corresponding simple alkylcarbonium ions. An alternate explanation, e.g., that the absorption maxima are due to oxidized

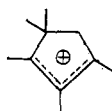
(5) A. G. Evans, *Trans. Faraday Soc.*, **42**, 719 (1946).

(6) J. L. Franklin, *ibid.*, **48**, 443 (1952).

(7) J. Rosenbaum and M. C. R. Symons, *Proc. Chem. Soc.*, 92 (1959); *Mol. Phys.*, **3**, 205 (1960).

allylic ions, was considered by these authors but was rejected.

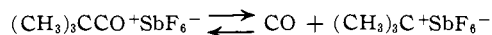
Deno and co-workers⁸ recently questioned the validity of the assignment of the 290 $m\mu$ absorption of sulfuric acid solutions of alcohols to the corresponding simple alkylcarbonium ions. They demonstrated in the case of *t*-butyl alcohol (based on n.m.r., ultraviolet, and infrared spectra as well as equilibrium constants and H-D exchange) that the products formed in concentrated sulfuric acid are 50% higher alkanes and cycloalkanes plus 50% of polymethylcyclopentenyl and cyclohexenyl cations. One of the predominant cations was characterized as the 1,2,3,4,4-pentamethylcyclopentenyl cation.



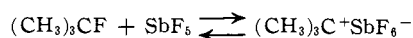
The transitory existence of alkylcarbonium ions has also been inferred from a variety of other observations, such as vapor pressure depressions of CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ in the presence of gallium chloride,⁹ the electric conductivities of aluminum chloride in ethyl chloride,¹⁰ and of alkyl fluorides in boron trifluoride,¹¹ as well as the effect of ethyl bromide on the dipole moment of aluminum bromide.¹² However, in no case have well-defined stable ionic salts or complexes been isolated, even at low temperatures.

Results and Discussion

In previous work¹ we have found that the isolated *t*-butyloxocarbonium (pivalylium) hexafluoroantimonate loses carbon monoxide easily in sulfur dioxide solution even at low temperature, and a new, electrodeficient species, the trimethylcarbonium ion, is formed



In order to establish the identity of the trimethylcarbonium ion, the *t*-butyl fluoride–antimony pentafluoride system was investigated. It was found that when purified antimony pentafluoride was treated with vapor of *t*-butyl fluoride by passing the fluoride over the surface of the liquid antimony pentafluoride (with exclusion of moisture and oxygen) a stable complex layer is formed on the top of the antimony pentafluoride. When this layer was separated and its proton magnetic resonance investigated (see subsequent discussion of further spectroscopic and chemical properties), the spectrum was found to be identical with that of the least-shielded species formed by decarbonylation of the *t*-butyloxocarbonium salt



The possibility of obtaining stable alkylcarbonium hexafluoroantimonate salts by interaction of alkyl fluorides with antimony pentafluoride (neat or in sulfur

(8) N. C. Deno, Abstracts, p. 77Q, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962; N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Hauser, and M. J. Wisotzky, *J. Am. Chem. Soc.*, **84**, 2016 (1962); N. C. Deno, personal communications; N. C. Deno, Abstracts, p. 47Q, 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(9) H. C. Brown, H. Pearsall, and L. P. Eddy, *J. Am. Chem. Soc.*, **72**, 5347 (1950).

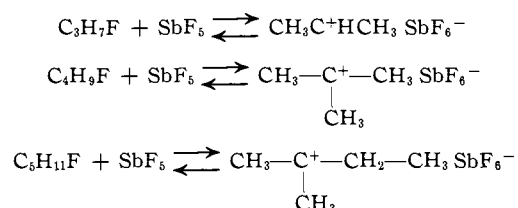
(10) E. Wertyporoch and T. Firla, *Ann.*, **500**, 287 (1933).

(11) G. Olah, S. Kuhn, and J. Olah, *J. Chem. Soc.*, 2174 (1957).

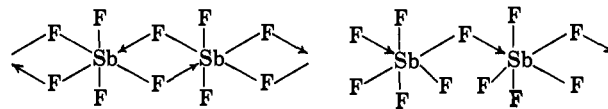
(12) F. Fairbrother, *ibid.*, 503 (1945).

dioxide solution) was then evaluated in detail, extending the investigations to all isomeric C_3 -, C_4 -, and C_5 -alkyl fluorides.

Propyl, butyl, and pentyl fluorides gave with excess antimony pentafluoride substantially stable ionic complexes



(see subsequent discussion of spectroscopic investigations and chemical reactivity). The complexes always contained excess antimony pentafluoride over that needed for the 1:1 complex formation. It was indeed found necessary to have excess antimony pentafluoride present in order to obtain stable alkylcarbonium hexafluoroantimonate complexes. Antimony pentafluoride is a low dielectric constant ($\epsilon \sim 3$), liquid Lewis acid fluoride (b.p. 148–150°), which has been shown by fluorine n.m.r. studies in both the liquid state and in solution to exist in both cyclic and acyclic polymeric forms involving fluorine bridges. The antimony is in approximately octahedral coordination with predominant bridging by coordinating fluorines.¹³



As fluorine generally does not show bridging properties, the structure of antimony pentafluoride itself indicates the very high acidity and coordinating ability of the compound. The conjugate acid HSbF_6 has a Hammett acidity function H_0 value of -16.6 (in HF), indicating again the very high acid strength.¹⁴ The very high Lewis acidity of antimony pentafluoride obviously causes the easy cleavage of the C–F bonds of alkyl fluorides, together with the energy of Sb–F bond formation compensating that of the cleavage of the C–F bond.

The role of excess antimony pentafluoride can best be explained by assuming that it is capable of solvating the alkylcarbonium ion salt through interaction of the fluorine unshared electron pairs into the vacant p -orbital of the sp^2 -hybridized planar central carbon atom of the carbonium ion. The alkylcarbonium ion in the low dielectric system is present not in the “free” form, but as a tightly bound ion-pair; solvation affects this species rather than the free ion.

That the acid strength and the role of solvation are essential in the investigated systems was shown when attempting to obtain related alkylcarbonium ions in other Lewis acid halide–alkyl halide systems, and when diluting the alkyl fluoride–antimony pentafluoride systems with other solvents.

Attempts to obtain alkylcarbonium complexes by dissolving alkyl chlorides (bromides) in other liquid Lewis acid halides (stannic chloride, titanium(IV)

(13) R. J. Gillespie and R. A. Rothenbury, *Chem. Can.*, **15**, No. 8, 46 (1963).

(14) G. A. Olah in “Friedel–Crafts and Related Reactions,” G. A. Olah, Ed., Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 212, 880.

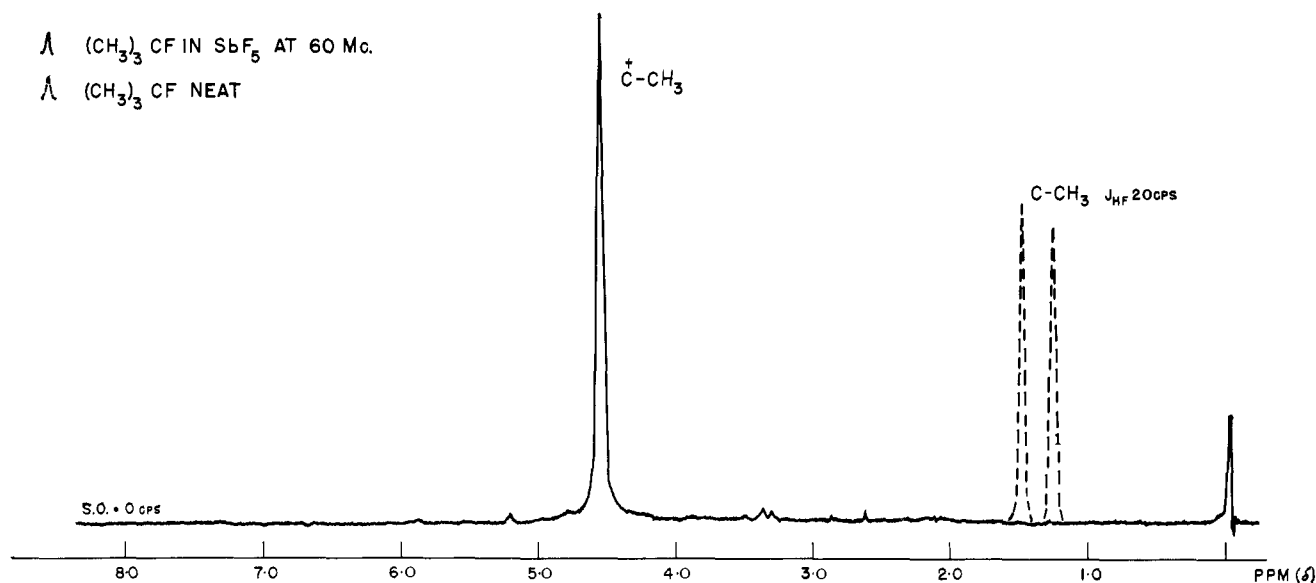


Figure 1.

chloride, antimony pentachloride, etc.) were unsuccessful. Although stable solutions at low temperature could be obtained with, for example, *t*-butyl chloride, the observed n.m.r. chemical shifts were generally not larger than 0.5 p.p.m. and thus could be attributed only to weak donor-acceptor complexes, but not to the carbonium ions. The negative result of these investigations seems to indicate that either the Lewis acids used were too weak to cause sufficient ionization of the C-Cl bond or that the solvating effect of the halides was not sufficient to stabilize the carbonium ion salts formed (an equilibrium containing a certain concentration of the carbonium ion cannot be excluded in any of these systems, but in order to obtain suitable n.m.r. spectra a concentration of 3-4% of the carbonium ion would be needed). It is also possible that the donor (base) strength of the alkyl halide also plays an important role. This could explain why alkyl fluorides were found to ionize readily with antimony pentafluoride. The bond energy of the C-F bond to be cleaved is compensated for by the bond energy of the Sb-F bond to be formed in the case of ionization. It is rather unfortunate that owing to halogen exchange alkyl fluorides generally cannot be used in investigations involving other halogen-containing Lewis acid halides.

When the alkyl fluoride-antimony pentafluoride systems in excess antimony pentafluoride were diluted with other solvents (first of all in order to enable freezing point depression of the solutions needed for low temperature spectroscopic and chemical investigations) it was found that the *t*-alkyl fluoride solutions could be substantially diluted without appreciable change (up to 10-15% excess antimony pentafluoride). Diluting solvents used were liquid sulfur dioxide and to a smaller degree arsenic pentafluoride or phosphorus pentafluoride. (Neither of these fluorides was found to yield alkylcarbonium salts similarly to antimony pentafluoride. However, as in the case of liquid boron trifluoride, the temperatures used with the liquid fluorides were so low that the ionization of the C-F bonds must have been made more difficult.) When solutions of a secondary carbonium salt (dimethylcarbonium hexafluoroantimonate) were diluted to the same extent, irreversible

changes were observed and the spectra indicated the formation of new, cyclized alkylcyclopentenyl ions. The best explanation for the formation of these ions, previously found by Deno in solutions of alcohols in sulfuric acid, is that they are secondary products of cycloalkylation of olefin (formed in deprotonation of the decreased stability, less solvated carbonium ion) with excess of the carbonium ion salt present.

The fact that solutions of the *t*-alkylcarbonium hexafluoroantimonates containing some excess antimony pentafluoride were found stable in cold sulfur dioxide allowed the simplified preparation of these complexes. Accordingly, it is possible to obtain sulfur dioxide solutions of the tertiary carbonium ion complexes by mixing cold solutions of the alkyl fluoride and excess antimony pentafluoride.

Nuclear Magnetic Resonance Investigations.—The observation that stable solutions of alkyl fluorides and antimony pentafluoride can be obtained and, further, that solutions involving tertiary halides can be substantially diluted with liquid sulfur dioxide without observable change, offered an excellent possibility for the nuclear magnetic resonance investigation of these solutions.

A modification of the high resolution n.m.r. spectrograph of Baker and Burd¹⁵ was used for recording the H², C¹³, and F¹⁹ resonance spectra, whereas the H¹ spectra were obtained on Varian Associates Model HR 60 and A-60 spectrographs, using low temperature probes when needed.

Proton Spectra.—Proton spectra of the antimony pentafluoride complexes of *t*-butyl, isopropyl, and *t*-amyl fluoride in excess antimony pentafluoride (in concentrations of 10-20%) are displayed in Fig. 1, 2, and 3. The spectra are given in p.p.m. relative to the (CH₃)₄Si (TMS) as internal standard present in a capillary tube centered in the middle of the n.m.r. tubes. (It is convenient to have a long stem capillary tube with a bulb at the end containing the standard inserted through a hole in the cap of the n.m.r. tube, thus easily kept centered.) Figures 1 and 2 represent spectra obtained on a Varian A-60 instrument without temperature con-

(15) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957); **34**, 238 (1963).

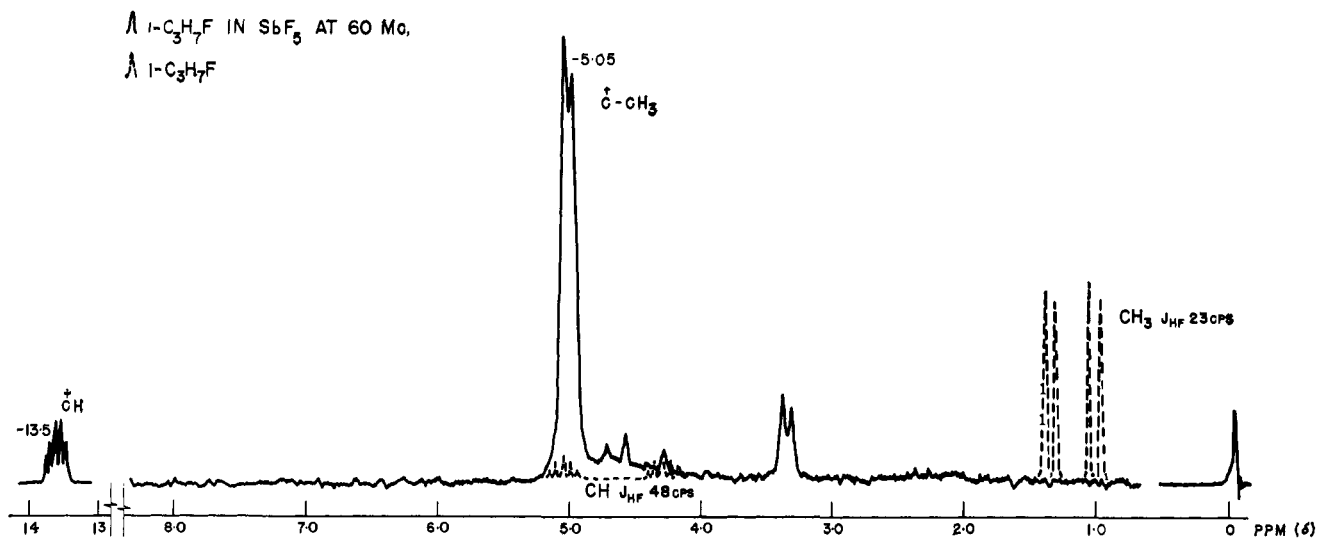


Figure 2.

trol, at an average probe temperature of about 37° . They illustrate the high stability of the carbonium ion complexes in the antimony pentafluoride solvent system even at this temperature. The spectrum of the *t*-butyl cation consists of one sharp peak at -4.35 p.p.m. The resolution of the isopropyl cation under these conditions is not very good (due to obvious exchange), but still the methyl group is a fairly well resolved doublet at -5.03 p.p.m. with the CH group being an only partially resolved septuplet at -13.5 p.p.m. The resolution improves with lowering the temperature, but exchange is still appreciable at $+2^\circ$, the lowest temperature obtainable due to the relatively high freezing point of SbF_5 .

t-Amyl fluoride in antimony pentafluoride at room or slightly elevated temperature gives only one hybrid band around -4.6 p.p.m. Taking the spectrum on the Varian HR 60 instrument at 0 – 2° gave only partial resolution as shown in Fig. 3A. Substantial exchange is not sufficiently slowed down at this temperature. The sulfur dioxide dilution technique allows the temperature to be lowered further, avoids freezing of antimony pentafluoride (antimony pentafluoride solutions are getting too viscous to handle around 0°), and obtains non-viscous solutions. Figure 3B shows the H^1 spectrum of *t*-amyl fluoride at -30° (in about 10% solution), with good resolution of the dimethylethylcarbonium ion (*t*-amyl cation). This spectrum was obtained on a Varian A-60 instrument using a low temperature probe. The $\text{C}^+-\text{C}-\text{CH}_3$ triplet is at -2.27 p.p.m. It is interesting to find strong coupling of approximately 7 c.p.s. through the sp^2 -hybridized positive carbon resulting in a well resolved triplet of the $\text{CH}_3-\text{C}^+-\text{CH}_2-$ methyl groups at -4.50 p.p.m. and a 10-line group centered at -4.93 p.p.m. for the methylene group.

The coupling between protons is quite characteristic of the bond angles of the C–C bonds to which they are attached. Karplus¹⁶ and Conroy¹⁷ discussed this problem theoretically using the valence bond treatment and a molecular orbital treatment, re-

(16) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(17) H. Conroy, quoted by J. N. Shoolery in "NMR and EPR Spectroscopy," Paper of Third Varian Workshop, Pergamon Press, New York, N. Y., 1960, p. 114.

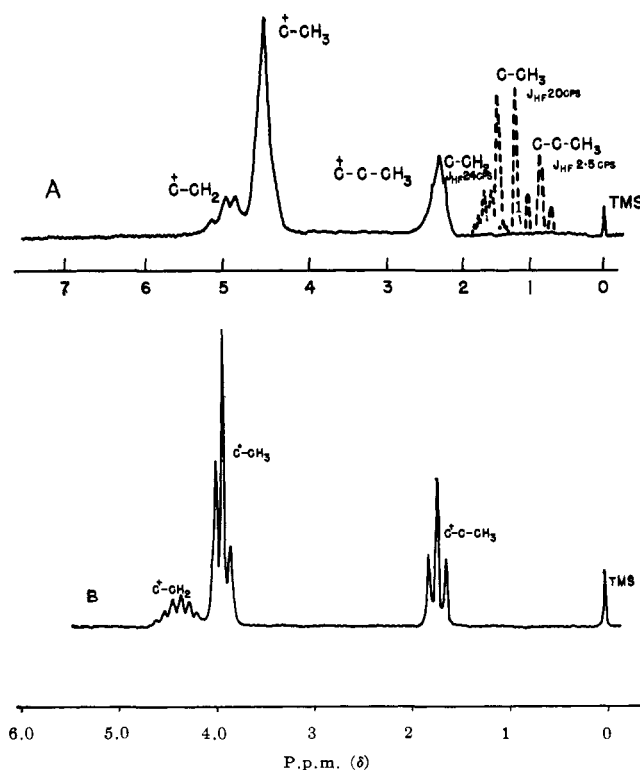


Fig. 3.—A: - - - $(\text{CH}_3)_2\text{CFCH}_2\text{CH}_3$, ——— $(\text{CH}_3)_2\text{CF}-\text{CH}_2\text{CH}_3$ in SbF_5 at 60 Mc. and 0° ; B: $(\text{CH}_3)_2\text{CCH}_2\text{CH}_3\text{SbF}_6$ in SO_2-SbF_5 at 60 Mc. and -30° .

spectively. J_{HH} was found to be strongly dependent on the bond angles in molecules which have a fixed orientation. Thus the observed coupling of the methyl and methylene groups across the sp^2 carbon atom in the fixed planar configuration of the carbonium ion is to be expected and its maximum value could be as much as 10 c.p.s., which is in good agreement with experimental observation.

Table III summarized the proton resonance data of the neat alkyl fluorides and their complexes in antimony pentafluoride.

Because of the concentration dependence of the chemical shifts of the alkylcarbonium ions, it was attempted to keep the concentration of the alkylcarbonium hexafluoroantimonate solutions approximately con-

TABLE III

NUCLEAR MAGNETIC PROTON RESONANCE SHIFTS (δ_{TMS} P.P.M.) OF ALKYL FLUORIDES AND THEIR ANTIMONY PENTAFLUORIDE COMPLEXES (IN SbF_5)

R	R-F, δ , p.p.m.	J_{HF} , c.p.s.	R ⁺ SbF ₆ ⁻ , δ , p.p.m.	Peak area ratio
CH ₃ -CH-CH ₃	-1.23	23.5	-5.06	5:95:1
	-4.64	48	-13.5	
CH ₃ CH ₃ -C-CH ₃	-1.30	20	-4.35	
CH ₃ -C-CH ₂ -CH ₃ CH ₃	-1.25	2.5	-2.27	2.96:5.97:2
	-1.55	20	-4.50	
	-1.85	24	-4.93	

stant. The neat antimony pentafluoride solutions (15–20%) were generally, however, more concentrated than those diluted with sulfur dioxide (10–15%). Smaller deviations in the comparison of the chemical shifts are therefore possible. Exact determination of the concentration of the carbonium ion salts in the used solvents represents difficulty, thus prohibiting the usual extrapolation of the chemical shifts to zero concentrations.

It was observed that *n*-propyl and isopropyl fluorides gave the identical secondary carbonium ion complex with antimony pentafluoride (*e.g.*, dimethylcarbonium ion). Similarly *t*-butyl, *sec*-butyl, isobutyl, and *n*-butyl fluorides all gave the same tertiary carbonium ion complex (*e.g.*, trimethylcarbonium ion) and all the seven isomeric pentyl fluorides, including neopentyl fluoride gave the same tertiary carbonium ion (*e.g.*, dimethylethylcarbonium ion). Thus in the strongly acidic antimony pentafluoride complete isomerization to the thermodynamically most stable carbonium ion takes place and this is the only ion observed.

The main feature of the observed proton spectra is the very substantial deshielding of the protons in the carbonium ions as compared with the starting alkyl fluorides. No H¹-F¹⁹ coupling was observed in any of the spectra of the carbonium ion complexes, which would of course not be expected in the ionic forms (where the covalent C-F bond of the starting alkyl fluorides must be cleaved). However, this observation can be used only as supporting, but not as conclusive, evidence for the ionic dissociation. Fast exchange in a highly polar donor-acceptor complex, in the strongly acidic solvent, could equally well result in the absence of observable H¹-F¹⁹ coupling.

There is no doubt that local charges have a most important effect on hydrogen shifts. There is good correlation between shifts and electronegativity, for example, in many saturated compounds.^{18–20} However, electric charges are not the only reason which can cause chemical shifts. When a molecule is placed in a magnetic field, currents are set up in the molecule and the additional magnetic field at the nucleus due to these currents causes shifts. Such currents flow around atoms, within bonds, and from atom to atom in conjugated ring compounds. Each of these currents effect the hydrogen shifts differently.²¹

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

(19) B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955).

(20) J. N. Shoolery, *J. Chem. Phys.*, **21**, 1899 (1953).

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

Fraenkel²² considered the effect of charge in a 2p_y-orbital above a C-H bond on the chemical shift of the C-H hydrogen. He found a linear relationship between charge and shift

$$\delta = 10q$$

Musher²³ has calculated the effect of electric fields on chemical shifts of hydrogens. Using these treatments it can be found that sp² C⁺-H should be about -10 p.p.m. from sp² C-H (uncharged).

The problem is to estimate the chemical shift of uncharged sp² C-H hydrogens. Benzene is about 7.25 p.p.m. from SiMe₄. Correcting for the ring current in benzene leaves a value of about 5.0 p.p.m., in the same region as observed for ethylene. This value is, however, not the correct one because there are paramagnetic currents in ethylene due to the admixture by the magnetic field of the ground nearest excited state wave functions. Such a paramagnetic shift may amount to 2 p.p.m. Thus the shift in C⁺-H could be as much as 9 p.p.m. and as little as 7 p.p.m. from uncharged sp² C-H. Thus the shifts of hydrogen attached to the positively charged sp² carbon in the secondary dimethylcarbonium ion, CH₃-CH⁺-CH₃, is in the correct magnitude, and similar shifts are to be expected in other secondary (and primary) carbonium ions.

In order to establish how far the observed large chemical shifts are effected by solvent (antimony pentafluoride as discussed is a rather unique solvent whose properties relating nuclear magnetic investigations were not so far reported), we compared the proton spectra of a known ionic compound, tetramethylammonium hexafluoroantimonate in antimony pentafluoride and sulfur dioxide solutions (Table IV).

TABLE IV

SOLVENT EFFECT ON THE H¹ RESONANCE OF THE (CH₃)₄N⁺ ION (P.P.M. FROM TMS)

Ion	Solvent	δ
(CH ₃) ₄ N ⁺ SbF ₆ ⁻	SbF ₅	-3.86
(CH ₃) ₄ N ⁺ SbF ₆ ⁻	SO ₂	-3.55

The data show that the shielding difference is about 0.3 p.p.m. (higher deshielding observed in SbF₅). Consequently, we compared the proton resonance spectra of trimethyl- and dimethylethylcarbonium hexafluoroantimonate in the same two solvents (Table V). It must be emphasized, however, that in the sulfur dioxide solution there is excess SbF₅ present in order to effect stabilizing solvation of the carbonium ion; thus the comparison is not entirely realistic.

TABLE V

SOLVENT EFFECT ON THE H¹ RESONANCE OF ALKYL CARBONIUM IONS (δ , P.P.M., FROM TMS)

Ion	Solvent	Temp., °C.	C ⁺ -CH ₂ - C ⁺ -CH ₃ C ⁺ -C-CH ₃		
			C ⁺ -CH ₂ -	C ⁺ -CH ₃	C ⁺ -C-CH ₃
(CH ₃) ₃ C ⁺ SbF ₆ ⁻	SbF ₅	0-+2		-4.35	
	SO ₂	0-+2		-4.07	
(CH ₃) ₂ C ⁺ CH ₂ CH ₃ SbF ₆ ⁻	SbF ₅	0-+2	-4.93	-4.50	-2.27
	SO ₂	-30	-4.30	-3.97	-1.72

Data again indicate that the solvent effect of antimony pentafluoride on the deshielding values is not too large.

(22) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(23) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

Deuteron Spectra.—In order to obtain further evidence for the validity of assignment of the proton shifts to the investigated alkylcarbonium ions, it was felt worthwhile to prepare the corresponding completely deuterated carbonium ions and obtain their H^2 resonance spectra.

Perdeuterated isopropyl, *t*-butyl, and *t*-amyl fluorides were prepared from the corresponding deuterated alkyl chlorides (bromides) by halogen exchange. The perdeuterated alkyl fluorides were then used in the formation of the deuterated carbonium ions under similar conditions as described previously for the proton complexes. The H^2 resonance spectra were obtained at 9.2 Mc. and the data are summarized in Table VI.

TABLE VI

H^2 RESONANCE OF DEUTERATED ALKYL CARBONIUM IONS (9.2 Mc., P.P.M. FROM D_2O AND CONVERTED TO TMS)			
	$-CD_3$	$-CD_2$	$-CD$
$(CD_3)_3C^+SbF_6^-$	-4.35		
$(CD_3)_2CD^+SbF_6^-$	-4.90		-13.48
$(CD_3)_2C^+CD_2SbF_6^-$	-2.25	-4.47	-4.89

The data indicate good agreement with those of the H^1 resonance data. Thus it was possible to reproduce the chemical shifts of the alkylcarbonium ions in an independent system; when corrected for the ratio of magnetogyric ratios the chemical shifts are well in the limit of experimental error.

F^{19} Spectra.—The F^{19} spectra were obtained at 56.5 Mc. The spectra of the carbonium hexafluoroantimonate complexes indicated the absence of covalent C-F bonds in accordance with the uniformity of fluorine atoms in the ionic SbF_6^- forms.

However, there is no evidence to exclude the possibility of an exchanging, highly polarized $R-F \rightarrow SbF_6^-$ system.

The possibility of fluorine exchange in a highly polarized complex of the type $R-F \rightarrow SbF_6^-$, where the C-F bond must be considerably weakened (and in the limiting case ionized) must be considered. There is also a possibility of exchange involving solvent SbF_6^- . Attempts were made to see if at lower temperature, due to the decreased exchange, differences are observable between the SbF_6^- line and the one corresponding to an exchanging $F \rightarrow SbF_6^-$ system, but this was not the case.

C^{13} -Resonance Investigations.—To substantiate further, that in the systems investigated we indeed were able to obtain stable, solvated alkylcarbonium hexafluoroantimonate complexes, we carried out C^{13} -resonance investigations of labeled complexes, with the potentially electropositive sp^2 carbon atom being C^{13} -labeled. Owing to the fact that the solubility of the complexes in the solvent employed is generally not more than 10%, it was necessary to prepare the complexes with the highest C^{13} -isotopic concentration ($\sim 60\%$) available, as the complexes are tenfold diluted on solution.

Owing to the low concentration of the ion-complexes in solution, it was not possible to observe the C^{13} -resonance directly on a 4-mm. sample, even though highly enriched. However, the resonance was observable indirectly by the INDOR (internuclear double resonance) method of Baker.²⁴ This method was well

applicable to the investigation of the $(CH_3)_3C^{13+} \cdot SbF_6^-$ complex and its comparison with the covalent starting *t*-butyl halide (there is no exchange in the complex to interfere with being able to "sit" on the proton line in order to carry out the internuclear double resonance investigation). The data obtained are shown in Table VII. (As it was found that *t*-alkyl chlorides generally also ionize well in antimony pentafluoride, it was possible to carry out the investigation with $(CH_3)_3C^{13}Cl$ without preparing the fluoride.)

TABLE VII

C^{13} -H INDOR RESONANCE OF THE $(CH_3)_3C^{13+}$ ION
 $(CH_3)_3C^{13}Cl$ at 15.090440 Mc. (CH_3 at 60.0097848 Mc.)
 $(CH_3)_3C^{13+}SbF_6^-$ at 15.094530 Mc. (CH_3 at 60.0099475 Mc.)
 $\delta_{C^{13}}$ (from $(CH_3)_3C^{13}Cl$) = 4090 c.p.s. = 273 p.p.m.
 δ_H (from $(CH_3)_3C^{13}Cl$) = 162.6 c.p.s. = 2.7 p.p.m.

The observed very substantial shift of the C^{13} resonance line in the trimethylcarbonium complex, as compared with the position of the C^{13} line in the starting covalent sp^3 -hybridized halide, amounting to 273 p.p.m., is difficult to interpret in any other way than as a direct proof (a) that the state of hybridization of the carbon atom involved is changed in the complex to sp^2 and at the same time (b) the carbon atom carries a substantial positive charge.

The C^{13} resonance investigations also provided a further possibility in the investigation of the carbonium ion complexes through evaluation of the C^{13} -H coupling values. The coupling data are shown in Table VIII for the isopropyl and *t*-butyl systems.

TABLE VIII

C^{13} -H COUPLING (J_{CH}) IN ALKYL CARBONIUM IONS AND THE CORRESPONDING ALKYL HALIDES (IN C.P.S.)		
	$>CH$	$-CH_3$
$(CH_3)_3C^*X$		128
$[(CH_3)_3C^*]^+$		130
$(CH_3)_2C^*HX$	151	127
$[(CH_3)_2C^*H]^+$	382	130

* Labeled carbon atom.

There is no significant change in the C^{13} -H couplings of the methyl groups in the covalent alkyl halides or in the carbonium ions complexes. This is of course to be expected because the state of hybridization of the methyl carbon atoms does not change on ionization of the adjacent carbon-halogen bond. When, however, the C^{13} -H coupling is considered on the central carbon atom in isopropyl fluoride it changes from 151 c.p.s. in the covalent halide to 382 c.p.s. in the sp^2 -hybridized dimethylcarbonium ion. The very substantial increase in the coupling constant is again difficult to account for otherwise than as a consequence of change of hybridization and positive character of the carbon atom in the ion.

Infrared Investigations.—A Perkin-Elmer Model 421 grating spectrophotometer was used to record the spectra. Films of the antimony pentafluoride solution of the alkylcarbonium hexafluoroantimonate complexes as well as their completely deuterated analogs were put between IRTRAN plates, all operations being carried out in a drybox. The spectra of the trimethyl-, dimethyl-, and dimethylethylcarbonium salts in excess antimony pentafluoride are shown in full in Fig. 4, 5, and 6. The IRTRAN cells are not transparent below

(24) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

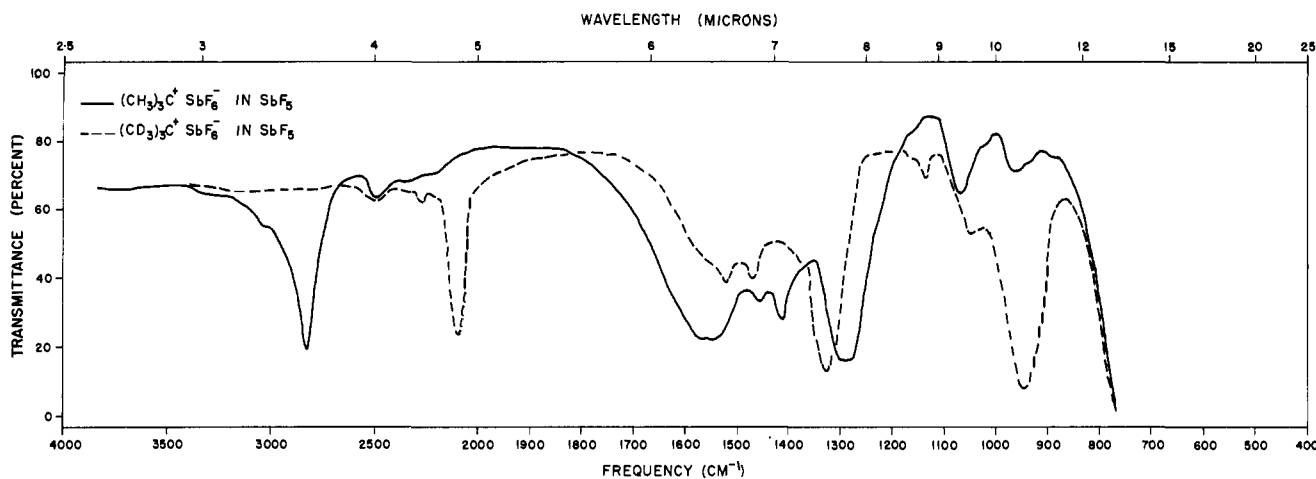


Figure 4.

770 cm^{-1} , thus obscuring the 650 cm^{-1} SbF_6^- absorption, which, however, would be overlapped by the solvent SbF_5 absorption. The broad, intense absorption band which appears in all the spectra near 1550 cm^{-1} is present in the solvent spectrum. It was found to be dependent on the purity of the SbF_5 , but the nature of the impurity was not established. It also should be mentioned that Deno found an intense absorption at 1533 cm^{-1} in the cyclohexenyl cations²⁵; thus secondary carbonium ions formed from the reaction with olefins due to deprotonation could add to this broad absorption.

TABLE IX
INFRARED FUNDAMENTAL FREQUENCIES OF ALKYL CARBONIUM
HEXAFLUOROANTIMONATE COMPLEXES AND THEIR ASSIGNMENT

$(\text{CH}_3)_3\text{C}^+$	Assignment ^a	$(\text{CD}_3)_3\text{C}^+$
Trimethylcarbonium ion (<i>t</i> -butyl cation)		
2830 s	ν_7, ν_{12} CH_3 stretch	2062 s
2500 w	$\nu_8 + \nu_9$	
1455 w	ν_8, ν_{14} CH_3 deformation	~ 1050 vw
1290 vs	ν_{16} , CCC asym. stretch	1330 s
1070 m	ν_9 CH_3 rocking	
962 mw	ν_{17} CH_3 rocking	
(~ 1300) obscured	ν_{15} CH_3 deformation	955 s
Dimethylcarbonium ion (isopropyl cation)		
$(\text{CH}_3)_2\text{CH}^+$		$(\text{CD}_3)_2\text{CD}^+$
2730 s	ν_9, ν_2 CH_3 stretch	2013 s
1499 s	ν_{16} , CH in-plane bend	930 s
1260 s	ν_{18} CCC asym. stretch	1378 s
1175 w	ν_6 , mixed mode	
930 vw	ν_7 , mixed mode	
Dimethylethylcarbonium ion (<i>t</i> -amyl cation)		
$(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$		$(\text{CD}_3)_2\text{C}^+\text{CD}_2\text{CD}_3$
2815 s	CH_3 stretch	2071 s
2505 w	1463 + 1065	
1463 s	CH_3 deformation	~ 1060 vw
1295 s	CCC asym. stretch	1377 s
1065 w	CH_3 rocking	
935 w	CH_3 rocking	
(~ 1300) obscured	Mixed mode	964 s

^a Descriptions are based on the calculated potential energy distributions for the trimethyl- and the dimethylcarbonium ions; see Appendix I.

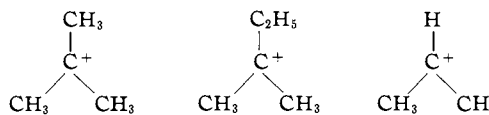
Using assumed molecular models and force constants based on the force constants derived from the paraffin series, normal coordinate calculations for the simple alkylcarbonium ions were carried out (see Appendix).

(25) N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **84**, 1498 (1962).

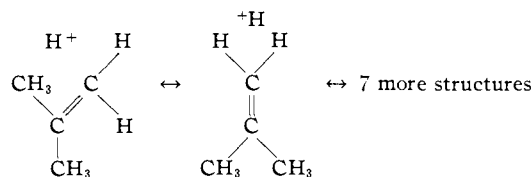
These calculations were made in order to be able to predict the vibrational spectra. Comparison with the experimentally obtained infrared spectra show that the main observed features indeed can be reasonably explained in terms of the modes calculated for the planar models of the ions.

The following conclusions can be established from the infrared spectra: (a) The C-H stretching fundamentals are exceptionally low in frequency. (b) The asymmetrical stretching mode of the carbon skeleton is exceptionally high in frequency.

The exceptional features can be reasonably interpreted in terms of the planar structure of the alkylcarbonium ions



since we may assume a number of nonbonded resonance structures such as



contributing. The effect of these structures is to: (a) lower the C-H bond strength and hence lower the C-H force constant which in turn results in a lower than normal frequency, (b) raise the C-C bond strength which similarly results in a higher than normal stretching frequency. However, part of the frequency increase is due to the planar geometry of the skeleton in the ions.

Ultraviolet Investigations.—Rosenbaum and Symons⁷ have reported that solutions of both *t*-butyl alcohol and isobutylene gave in sulfuric acid a single measurable ultraviolet band having $\lambda_{\text{max}} 293 \pm 2 \text{ m}\mu$ ($\epsilon 6.4 \times 10^3$) with a half-height width of 490 cm^{-1} . (The intensity of the absorption was later corrected to be < 2000 .)

As an alternate possibility for the absorbing ion, Symons considered the oxidized butenyl cation $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2^+$. Deno⁸ recently questioned the assignment of the 293 $\text{m}\mu$ maximum in the sulfuric acid solution of butyl alcohol as due to the trimethylcarbonium

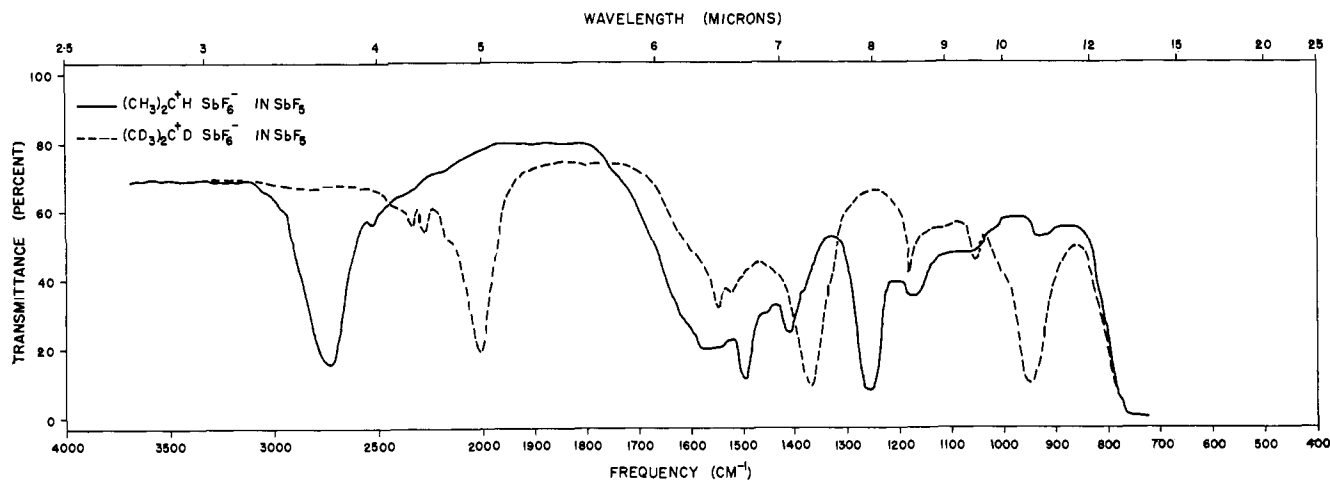


Figure 5.

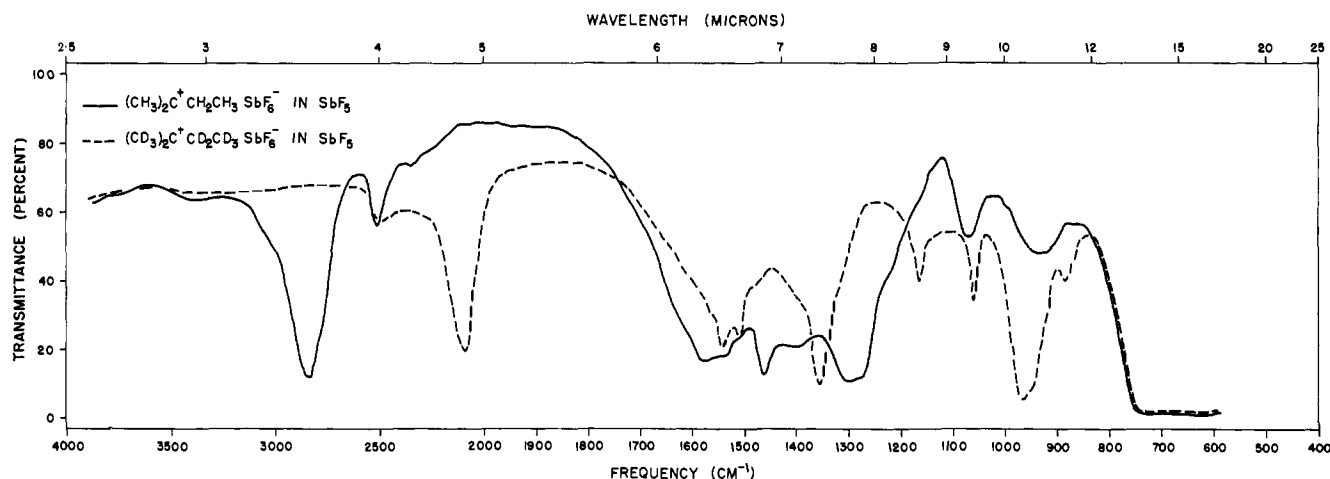


Figure 6.

ion or the isobutenyl cation and suggested, based on n.m.r. infrared and ultraviolet investigations, that it is entirely that of a mixture of cyclopentenyl and cyclohexenyl cations.

The ultraviolet spectra of complexes of alkyl fluorides with antimony pentafluoride in antimony pentafluoride solution were recorded on a Perkin-Elmer Model 350 spectrophotometer, using 1-cm. quartz cells. The determination of exact concentrations of the carbonium hexafluoroantimonate complexes in antimony pentafluoride represented difficulties, because of lack of suitable analytical methods applicable for direct determination of the dilute solutions and also because during the preparation of the complexes (see Experimental part) no exact weigh of the starting alkyl fluoride is possible. Consequently, extinction coefficients can be considered only as very approximate.

All the investigated fluorides gave a single weak absorption maximum around 290 μ with a low extinction coefficient. The solvent used does not allow observation of the spectra <250 m μ . Data obtained are summarized in Table X.

It is not possible at the present time to decide whether the observed absorptions are indeed due to the simple alkylcarbonium ions or whether secondary products formed (mainly cyclopentenyl and cyclohexenyl cation type compounds or oxidized allylic ions) or impurities present in very low concentrations are responsible for the absorption maxima. We have attempted the puri-

fication of the reagents to the limit of the experimental possibilities available and carried out all operations with careful exclusion of atmospheric moisture and oxygen without observing the disappearance or even significant change in intensity of the absorption maxima. The ob-

TABLE X
ULTRAVIOLET ABSORPTION MAXIMA OF ALKYL
FLUORIDE-ANTIMONY PENTAFLUORIDE COMPLEXES
(IN ANTIMONY PENTAFLUORIDE)

	λ_{\max} , m μ	ϵ
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	288	$\sim 3.5 \times 10^2$
$(\text{CH}_3)_2\text{CHF}$	288	
$(\text{CH}_3)_3\text{CF}$	293	$\sim 5.0 \times 10^2$
$(\text{CH}_3)_2\text{CHCH}_2\text{F}$	296	
$\text{CH}_3\text{CHFCH}_2\text{CH}_3$	292	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{F}$	296	
$(\text{CH}_3)_2\text{CFCH}_2\text{CH}_3$	294	$\sim 7.5 \times 10^2$ $\sim 1.0 \times 10^3$
$(\text{CH}_3)_3\text{CCH}_2\text{F}$	292	
$(\text{CH}_3)_2\text{CHCHFCH}_3$	292	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{F}$	291	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHFCH}_3$	293	
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{F}$	294	
$(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHCH}_2\text{F}$	293	

ervation of Deno that alkylcyclopentenyl ions are formed from simple alkylcarbonium ions in strong acid media (sulfuric acid) and that these ions have strong absorption around 300 m μ may easily explain a low intensity absorption even if only minor amounts of the secondary cyclized ions were present.

It is therefore difficult from our observation of the ultraviolet spectra to come to a definite conclusion. Although our observed extinction coefficients are substantially smaller than those reported by Symons,⁷ it is possible that the ~ 290 m μ absorptions with the observed small extinction coefficient can be assigned to the electron transfer of the trimethylcarbonium and related ions involving quasi- π -electrons and the vacant p-orbital of the positive carbon.

If the ~ 290 m μ absorption is really due to the alkylcarbonium ions, its origin needs consideration. The stability of alkylcarbonium ions can be explained predominantly in terms of resonance and hyperconjugation. Alkylcarbonium ions can be considered as hybrids of bonded and nonbonded structures, such as for the methylcarbonium ion $\text{CH}_3\text{-CH}_2^+$ (one) and H^+

$\text{CH}_2=\text{CH}_2$ (three). It is difficult to estimate the energies of various structures, but in the case of the C_2H_5^+ ion the no-bond structures may be estimated to be some 116 kcal./mole above the conventional structure. If CH_3CH_2^+ were not stabilized, the appearance potential from ethane would be the same as that of CH_3^+ from methane which leads to $H_f(\text{CH}_3\text{CH}_2^+) = 262$ kcal./mole. The sum of heats of formation of H^+ and

ethylene (the no-bond $\text{CH}_2=\text{CH}_2$ structure) is 378 kcal./mole².

Therefore, if there is ultraviolet absorption of alkylcarbonium ion above 200 m μ , it should be an electronic transition from a nonbonding atomic orbital to a higher energy molecular orbital. The $\sigma \rightarrow \sigma^*$ transitions (to σ -orbitals) are considered as allowed and should give absorption at < 200 m μ (not observable in SbF_6 as solvent). The $\sigma \rightarrow \pi^*$ transitions are considered as not allowed and should give a low intensity absorption above 200 m μ which is the one probable in the 290 m μ region.

It would seem therefore that we are concerned with transitions involving electrons in quasi- π -group orbitals having nodes in the plane of the carbon atoms.

In the methylcarbonium ion (CH_3CH_2^+) we assume that the two carbon atoms, the hydrogen atoms of the CH_2 group, and the center of gravity of the H_3 group to lie in one plane, which is the plane of the molecule. According to Mulliken, we call the π (or quasi- π) orbitals that have a node in this plane π_x -orbitals; those that have a node in the plane passing through the carbon atoms perpendicular to the plane of the molecule are called π_y -orbitals. For brevity these orbitals are sometimes called x- and y-orbitals. The methylcarbonium ion has two electrons in the energetically lowest of the three x MO's (and two more electrons in each of the lowest y MO's).

In the dimethylcarbonium ion, if hyperconjugation is neglected, the four quasi- π_x -electrons are localized in CH_3 bonding orbitals whose energy is the same as in the ethyl ion.

For the trimethylcarbonium ion, six π -electrons are assigned to three such orbitals and will be largely localized on the three methyl groups, while the excited level will be largely localized on the central carbon, being similar to the half-filled orbital in the corresponding radical. Of the three occupied levels, one is symmetrical, and the transition would be forbidden; the

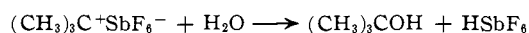
other two form a degenerate pair, and it is this level that is thought to be involved in the observed transition.

Using the results of Muller and Mulliken for trimethylcarbonium ions, Rosenbaum and Symons estimated a transition energy of about 3.87 e.v. or 89.2 kcal./mole. The approach is very approximate, but the result does suggest that the assignment of a charge transfer band in the 290 m μ region to the alkyl carbonium ions is reasonable.

Chemical Reactivity.—The alkylcarbonium hexafluoroantimonate complexes were found, in accordance with expectation, to be extremely reactive alkylating agents in C-, O-, S-, and N-alkylations as well as catalysts in olefin polymerizations.

In the present paper we report only preliminary and mainly qualitative data of the investigation of the chemical reactivity of stable alkyl carbonium salts. It is hoped that more detailed quantitative report can be given in a subsequent publication. We are confining our present data mainly to the reactions of trimethylcarbonium hexafluoroantimonate. Although the dimethyl- and dimethylethylcarbonium salts react similarly, the reaction mixtures are sometimes more complex.

(a) **Hydrolysis.**—It is expected that when an alkylcarbonium ion reacts with water the corresponding alcohol is formed. Indeed, the reaction could be

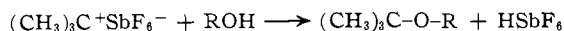


performed in a 83% yield in the case of trimethylcarbonium hexafluoroantimonate, *t*-butyl alcohol formed being isolated and analyzed by gas chromatography. It was found important, however, the way in which the hydrolysis was carried out. When the sulfur dioxide solution of the carbonium salt was added to ice-water the reaction product contained *t*-butyl alcohol, *sec*-butyl alcohol (in a ratio of about 4:1), as well a smaller amount of isobutyl alcohol, butyl ethers, and unidentified higher molecular weight products and polyisobutylene. When the reaction was, however, carried out in a way that the cold sulfur dioxide solution of the carbonium salt was added to an equally cold (-78°) dispersion of ice in sulfur dioxide and the stirred mixture allowed to react for 1 hr., upon working up the reaction mixture the product contained 83% *t*-butyl alcohol, as well as *sec*-butyl alcohol, butyl ethers, *t*-butyl fluoride, and some minor unidentified higher boiling compounds.

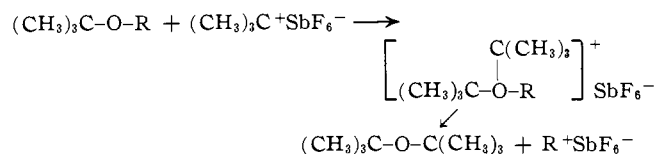
These observations indicate that the reaction of an alkylcarbonium hexafluoroantimonate salt with water is not instantaneous, although obviously at higher temperatures it is very fast. Because the carbonium salt is highly solvated (which as discussed previously is responsible for the high stability) the nucleophile can get to the carbonium ion only in a certain time. When isomerization, self-alkylation, or any other side reaction of the carbonium ion due to desolvation of the salt is becoming a competing reaction, it is understandable that the hydrolysis products are complex. If the hydrolysis is carried out under conditions where the carbonium salt is kept stable until it reacts with the nucleophile (low temperature reaction in sulfur dioxide), secondary processes are not significant and the reaction product is the expected alcohol in high yield.

Observations with the hydrolysis of dimethylethylcarbonium hexafluoroantimonate are similar to that for the trimethylcarbonium salt. The dimethylcarbonium salt could not be diluted without secondary reactions with sulfur dioxide and its hydrolysis could be investigated only by adding the antimony pentafluoride solution directly to ice-water. Under these conditions, besides isopropyl alcohol, a mixture of higher alcohols, polymeric materials, and also some cyclized products were obtained.

(b) **Alcoholysis.**—Reaction of trimethylcarbonium hexafluoroantimonate with methyl, ethyl, propyl, and butyl alcohols in sulfur dioxide solution at Dry Ice temperature resulted in formation of the corresponding *t*-butyl alkyl ethers.

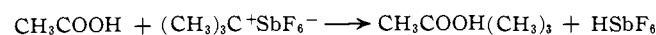


It is interesting to note that some di-*t*-butyl ether was also formed in some of the reactions. This must have resulted in the secondary reaction of the ethers with excess of the carbonium salt

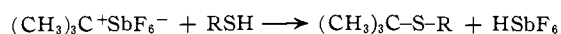
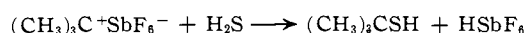


This side reaction is unimportant in the case of methyl and ethyl alcohol but is observable in reactions with propyl and butyl alcohols. Both the hydrolysis and alcoholysis of the alkylcarbonium salts can be interpreted as an electrophilic O-alkylation reaction. The same mechanism is also responsible for the ether cleavage reaction *via* oxonium ion formation.

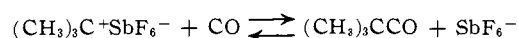
(c) **Ester Formation.**—Acetic acid, when allowed to react in sulfur dioxide solution with trimethylcarbonium hexafluoroantimonate, gave *t*-butyl acetate.



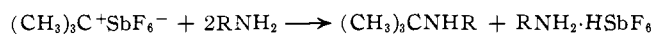
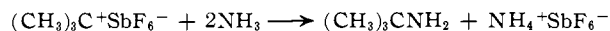
(d) **S-Alkylations.**—Hydrogen sulfide and mercaptans when treated in sulfur dioxide solution with trimethylcarbonium hexafluoroantimonate gave *t*-butyl mercaptan (with some di-*t*-butyl sulfide also present) or the appropriate *t*-butyl alkyl sulfides, although the reaction products were highly contaminated with by-products, probably due to the effects of excess SbF_6^- .



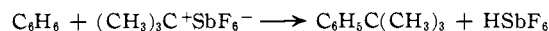
(e) **Carbonylation.**—When a sulfur dioxide solution of trimethylcarbonium hexafluoroantimonate was treated for 4 hr. with carbon monoxide and after that hydrolyzed, the product contained besides *t*-butyl alcohol and some polyisobutylene also pivalic acid, indicating the equilibrium



(f) **N-Alkylation.**—Ammonia and primary aliphatic amines are N-alkylated by trimethylcarbonium hexafluoroantimonate in sulfur dioxide solution at low temperature. However, because of the basic nature of the substrates, substantially increased amounts of polymeric materials are formed, indicating that deprotonation is increasingly involved as a competing reaction.



(g) **Aromatic Alkylation.**—Trimethylcarbonium hexafluoroantimonate alkylates benzene and toluene very readily. The alkylation products depend very substantially on the condition of the reaction.



When a sulfur dioxide solution of the carbonium salt was added to a 1:1 benzene-toluene mixture at around -20° , a relative reactivity value of $k_{\text{toluene}}:k_{\text{benzene}} \sim 6$ based on the amount of butyl benzene and butyl toluenes formed was found. (Analysis of the reaction mixtures was carried out by gas-liquid chromatography, under conditions described previously.²⁶) The alkylation products, however, consisted not only of *t*-butylated products. The butylbenzene fraction is composed of 46% *t*-butylbenzene, 36% isobutylbenzene, and 18% *sec*-butylbenzene; the butyltoluene fraction also contains all isomeric butyltoluenes, the *t*-butyltoluene composition being 98.3% *m*- and 1.7% *p*-*t*-butyltoluene. These data indicate that under the alkylation conditions used very substantial isomerization must have taken place, most probably to a substantial part even before the alkylation step. Isomerization of the alkylation products in sulfur dioxide solution by the by-product $\text{HF} + \text{SbF}_6^-$ is also possible, the latter being an exceedingly strong acid.²⁷

When the same competitive alkylation of benzene and toluene was carried out in sulfur dioxide solution at -60° the $k_{\text{toluene}}:k_{\text{benzene}}$ rate was ~ 25 . The butylbenzene fraction was composed of 85% *t*-butylbenzene and 15% *sec*-butylbenzene, whereas the butyltoluene fraction was predominantly *m*-*t*-butyltoluene, with only a small amount of *p*-*t*-butyltoluene present. These data indicate less skeletal isomerization. The very high amount of the *m*-*t*-butyltoluene indicates substantial isomerization. The extent of direct, low selectivity alkylation of the *m*-position is difficult to decide based on present data. The ease of isomerization of *t*-butyltoluene by HSbF_6^- in sulfur dioxide solution was observed even at low temperature.

(h) **Polymerization.**—Isobutylene dissolved in a mixture of methylene chloride-vinyl chloride was polymerized with exceeding speed when a catalytic amount of trimethylcarbonium hexafluoroantimonate, in the form of a sulfur dioxide solution, was added at -78° .

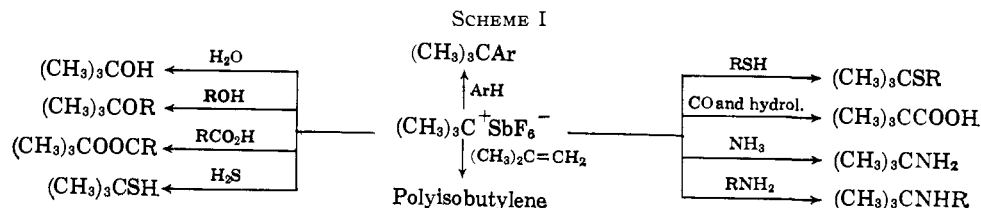
The chemical reactivity of the alkylcarbonium hexafluoroantimonate salts follows the generally expected paths, although the multiplicity of side reactions indicates the complex nature of the systems and the importance of keeping the carbonium ion in the solvated stable form during reactions. Scheme I gives a schematic summary of the main reaction paths without considering by-products.

Experimental

Materials.—Antimony pentafluoride was obtained from the Allied Chemical Co. and was freshly distilled in all-quartz distillation apparatus before use. Argentous fluoride was obtained from the Harshaw Chemical Co. Alkyl chlorides, bromides, and iodides used were commercially available materials of highest

(26) G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Am. Chem. Soc.*, **86**, 1060 (1964).

(27) H. H. Hyman, H. L. A. Quaterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).



purity, redistilled before use. Alkyl fluorides were prepared by the general method of Moissan²⁸⁻³⁰ using the halogen exchange of the corresponding alkyl bromides or iodides with argentous fluoride. The reactions were carried out either in heterogeneous systems using only excess of the alkyl halide or 1,1,3-trifluoroethane as diluent or in acetonitrile solution. After separation by usual fractional distillation methods, the alkyl fluorides were further purified, when necessary, by preparative scale gas-liquid chromatography, using a Wilkens Aerograph Model Autoprep A-700 instrument. 2-Fluorobutane, 2-fluoropentane, 3-fluoropentane, 3-fluoro-2-methylbutane, and neopentyl fluoride were prepared, in order to avoid isomerization, by the cleavage of the appropriate alkyl *p*-toluenesulfonates with anhydrous potassium fluoride.^{31,32} All the alkyl fluorides used were previously described in the literature.

Deuterated alkyl chlorides (bromides) were obtained from Merck Sharp and Dohme, Ltd., Montreal, Canada. They were fluorinated with argentous fluoride in small stainless steel pressure cylinders. The purity of the deuterated alkyl fluorides, based on gas-liquid chromatography and infrared and n.m.r. H^1 and H^2 spectra, was better than 98%.

C^{13} -Labeled alkyl chlorides (bromides) were also obtained from Merck Sharp and Dohme, Ltd. They were fluorinated, when necessary, as the deuterated halides.

Preparation of Alkylcarbonium Hexafluoroantimonates.—In order to exclude moisture and to provide an inert atmosphere, preparations were preferentially carried out in a drybox purged with dry nitrogen.

1. **Using Excess Antimony Pentafluoride as Solvent.**—Antimony pentafluoride (3.5 ml., 0.05 mole) was added in a 25-ml. flask closed with a serum cap and equipped with a drying tube. The flask was cooled in an ice bath to keep the antimony pentafluoride just above its freezing point ($5-7^\circ$). With strong agitation the alkyl fluoride (0.01 mole) was introduced from a syringe through a fine needle (26 G) above the surface of the antimony pentafluoride in 10–20 min. After 2–3 min. of further agitation in the ice bath, the mixture was allowed to separate into two phases which took about 5–10 min. The colorless lower layer consisted of antimony pentafluoride containing only traces of organic material, while the yellow to red upper layer contained the complex salt (in 15–20% concentration) with excess antimony pentafluoride dissolved in it.

For n.m.r. investigation the upper layer was used by syphoning it off with a syringe. For infrared and ultraviolet investigations the reaction mixture was homogenized by strong shaking and was transferred into the cell before the dispersion had separated.

2. **Using Sulfur Dioxide as Solvent.** (a) **For N.m.r. Investigation.**—Antimony pentafluoride (2.2 ml., 0.03 mole) was measured into a 50-ml. flask described above and 20–25 ml. of sulfur dioxide was condensed into it with Dry Ice-acetone cooling. Neat alkyl fluoride (0.02 M) was added to the well agitated solution in 10–15 min. at 18° . A neat homogeneous solution was obtained. Its color ranged from light greenish yellow to reddish yellow.

(b) **For Preparative Purpose.**—Alkyl fluoride (1 M) dissolved in 200–250 ml. of sulfur dioxide was slowly (6–8 min.) added to the sulfur dioxide (200–300 ml.) solution of antimony pentafluoride (1.5 moles) at -80° . The solution could be easily concentrated without decomposition of the complex by distilling off part of the solvent at a reduced pressure at -40 to 50° .

Hydrolysis of Trimethylcarbonium Hexafluoroantimonate.

(a) **Reaction with Ice-Water.**—A sulfur dioxide solution of the salt prepared according to method 2b was slowly added (15–20 min.) to a strongly stirred mixture (1.5 l.) of ice and water. The temperature of the mixture was raised to $20-25^\circ$ and stirred for

half an hour to decompose the solid hydrate of sulfur dioxide and remove most of the dissolved sulfur dioxide. Ether (150 ml.) was added to the mixture and it was neutralized by small portions of solid sodium carbonate. After separating the precipitate by filtration, the aqueous layer was extracted four times with 100 ml. portions of ether. The united organic layers were washed with water and the aqueous layer twice extracted with 50 ml. of ether. The united ether solution was dried over sodium sulfate and concentrated by distilling off part of the ether.

Vapor phase chromatographic analysis of the ethereal solution was used to determine the products formed, comparing the products with pure standard materials.

(b) **Reaction with Cold Dispersion of Ice in Sulfur Dioxide.**—Reaction was carried out at -78° by treating a well stirred sulfur dioxide solution of 0.05 mole of trimethylcarbonium hexafluoroantimonate with a 10-mole excess of a dispersion of ice in cold sulfur dioxide. The reaction mixture was stirred for an hour. After that it was allowed to warm to -20° , poured on ice-water, and worked up as under (a).

O-Alkylations with Trimethylcarbonium Hexafluoroantimonate. (a) **Reaction of Alcohols.**—A sulfur dioxide solution of 0.05 mole of the carbonium ion salt, prepared as previously, was treated at Dry Ice temperature with a 10-mole excess of the corresponding alcohol (methyl, ethyl, propyl, and butyl alcohols). The reaction mixture was stirred for 30 min. at -78° , then allowed to warm up to room temperature. The mixture was neutralized by small portions of solid sodium carbonate. After separating the precipitate by filtration, the organic layer was analyzed by gas-liquid chromatography. The products formed were identified by comparison with standard materials. They contained besides the *t*-butyl alkyl ethers also some *sec*-butyl and isobutyl ethers.

(b) **Reaction of Acetic Acid.**—A sulfur dioxide solution of 0.05 mole of the carbonium ion salt was treated at Dry Ice temperature with a 10-mole excess of acetic acid in sulfur dioxide. The reaction mixture was stirred for an hour. After that it was allowed to warm up to room temperature and was poured on ice-water. Ether (150 ml.) was added and the organic layer after separation was neutralized with sodium carbonate. The precipitated salt was filtered and the aqueous solution was extracted with ether. The combined organic layer was analyzed by gas-liquid chromatography.

N-Alkylations with Trimethylcarbonium Hexafluoroantimonate.—A sulfur dioxide solution of 0.05 mole of the carbonium ion salt was treated at Dry Ice temperature with a tenfold excess of anhydrous ammonia or amine dispersed as its complex in sulfur dioxide. The reaction mixture was stirred for an hour. After that it was allowed to warm up, then poured on ice-water. After basification, the organic layer was extracted with ether, dried, and analyzed by gas-liquid chromatography.

Alkylation of Benzene and Toluene with Trimethylcarbonium Hexafluoroantimonate.—A sulfur dioxide solution of the carbonium salt (0.1 M) prepared according to method 2b was slowly added (10–15 min.) to a well stirred sulfur dioxide (300 ml.) solution of 1 mole of aromatic (benzene, toluene, or a 1:1 mixture of the two) between -60 and -70° . The reaction mixture was stirred for 15 min. at the same temperature, then it was poured on ice-water. After decomposition of the sulfur dioxide hydrate ether (150 ml.) was added to the mixture and it was neutralized by small portions of solid sodium carbonate. After filtering the precipitate the aqueous layer was extracted four times with 100-ml. portions of ether. The united organic layer was washed with water, dried, and concentrated by distilling off part of the ether. The products were analyzed by gas-liquid chromatography.

Acknowledgment.—Prof. R. J. Gillespie, McMaster University, is thanked for use of facilities making part of the low temperature n.m.r. work possible and Mr. J. Bacon for help in obtaining the spectra. Dr. J. P.

(28) H. Moissan, *Compt. rend.*, **110**, 952 (1890).

(29) H. Moissan, *Ann. chim. phys.*, [6] **19**, 272 (1891).

(30) F. Swarts, *Bull. soc. chim. Belges*, **30**, 302 (1921).

(31) G. V. D. Tiers, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

(32) W. F. Edgell and L. Parts, *ibid.*, **77**, 4899 (1955).

Heeschen is thanked for taking part of the low temperature resonance spectra. It is a pleasure for J. C. E. to acknowledge many helpful discussions of the normal coordinate calculations with Dr. G. R. Scherer.

Appendix

Normal Coordinate Calculations (J. C. Evans).

Trimethylcarbonium Ion.—The molecular structure assumed for this ion is that drawn in Fig. 7, with a planar carbon atom skeleton and C_{3h} symmetry. The molecular dimensions assumed are also given; the C-C bond length of 1.50 Å. is that characteristic of the bond between an sp^3 carbon and an sp^2 carbon atom. For this model only the a'' and e' modes are infrared active, but since nothing was to be gained by leaving out the other species all modes were included in the calculation.

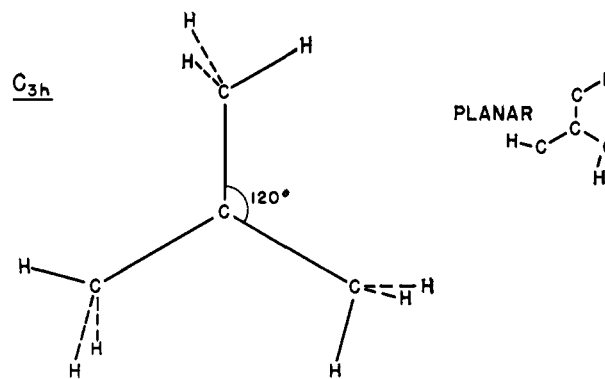
A suitable potential energy function must be assumed and the Urey-Bradley force field was adopted. It is not in general possible to start with the observed frequencies and to calculate the force constants directly. The usual procedure is to start with a reasonable set of assumed force constants and to refine these to fit the experimental frequency data; for this to succeed it is essential that the number of frequency parameters be greater than the number of force constants to be determined. In this problem the minimum number of force constants required exceeds the number of significant frequency data so that the only logical approach is to adopt a complete set of force constants, to calculate a set of frequencies from these, and to compare these calculated frequencies with the experimental data. If the model assumed is a valid one, the two sets of data should be comparable.

Fortunately, extensive calculations on a series of paraffins were recently made³³ and a good set of Urey-Bradley force constants upon which to base the present calculation was available. Some modifications of the paraffin set are required for our model; Table XI gives the paraffin force constants and the set used here. A stronger C-C bond, *i.e.*, a larger value of K_{CC} is required; a plot of K_{CC} vs. bond length indicated a value of 3.0. Resonance structures which may be written for the ion indicate a weaker than normal CH bond and the unusually low-lying bands in the CH stretching region support this. Other force constant changes are undoubtedly required, but since these are not as directly suggested either by the model or by the spectra the other force constants were not changed.

Calculations were made using the computer programs³⁴ prepared by J. R. Scherer for the IBM 7090 computer. The calculation yielded values for all 33 modes of the ion but, since only the a'' and e' modes are of immediate interest, Table XII only records these modes. Also quoted are the potential energy distributions for these modes. The table should be read thus taking as an example ν_{16} at 1298 cm^{-1} . Reading across the table we find that 49% of the potential energy change which occurs during this vibrational mode is contributed by those terms in the potential energy expression which contain the force constant K_{CC} ; 1% is contributed by terms containing K_{CH} , 11% by terms containing H_{CC} , and so on across the table. This mode can then be very approximately

(33) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(34) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **32**, 1720 (1960).



DIMENSIONS

$$C-C = 1.50 \text{ \AA}$$

$$C-H = 1.11 \text{ \AA}$$

$$\widehat{CC} = 120^\circ$$

CH₃ ANGLES TETRAHEDRAL

Fig. 7.—Model assumed for the trimethyl carbonium ion.

labeled a carbon-carbon stretching mode, and since it is in the e' species, as the doubly degenerate antisymmetric CC stretching mode. The corresponding mode in the D-compound is even more accurately described by this label because it contains a 60% contribution from K_{CC} . This mode is little affected by D-substitution.

TABLE XI

UREY-BRADLEY FORCE CONSTANTS FOR $(CH_3)_3C^+$

Force constants	Description	SS ^a set (paraffins)	Set used
K_{CC}	C-C stretching	2.23	3.0
K_{CH}	C-H stretching	4.43	3.9
H_{CC}	CCC bending	0.68	0.65
H_{CH}	HCC bending	.32	.32
H_{HH}	HCH bending	.52	.52
H_o	Skeletal out-of-plane bending	..	0.2
F_{CC}	C...C interaction	0.32	.32
F_{CH}	C...H interaction	.55	.55
F_{HH}	H...H interaction	.05	.05
C_{CH}	C...C (<i>cis</i>) interaction	..	.05
ρ	Intramolecular tension	0.025	.025
t	Torsion	0.024	.024

^a SS denotes Schachtschneider and Snyder.³³ Units: K_{ij} , F_{ij} in mdynes/Å.; H_{ij} , ρ , and t in mdynes Å./rad.².

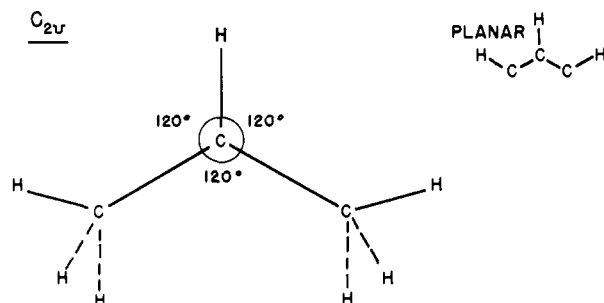
Turning now to the observed infrared spectra, we find that there are only a few prominent features. The CH and CD stretching modes, which depend almost entirely on K_{CH} , are reasonably well produced by the calculation. Both D- and H-compounds show strong bands near 1300 cm^{-1} , that in the D-compound being higher by ~ 30 cm^{-1} than that in the H-compound. The calculated values of ν_{16} strongly suggest that this is the correct assignment for these bands; the difference in direction of band shift with D-substitution in the calculated and observed spectra are probably due to some minor inadequacy, perhaps an interaction force constant not included, in the force field. The agreement between observed and calculated frequencies cannot normally be expected to be better than ± 50 cm^{-1} unless a refinement is made; in the latter case much better agreement can be expected.

TABLE XII
 CALCULATED FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTIONS FOR $(\text{CH}_3)_3\text{C}^+$

Mode	Calcd. freq.	K_{CC}	K_{CH}	H_{CC}	H_{CH}	H_{HH}	H_{O}	F_{CC}	F_{CH}	F_{HH}	ρ	t
a'' ν_7	2800	0	0.93	0	0	0	0	0	0.06	0.01	0	0
ν_8	1444	0	.01	0	0.05	0.86	0	0	.05	0.04	0	0
ν_9	1076	0	.01	0	.42	.10	.05	0	.44	0	0.02	0
ν_{10}	315	0	0	0	.02	.01	.95	0	.02	0	0	0
ν_{11}	271	0	0	0	0	0	0	0	0	0	0	1.0
ν_{12}	2802	0	0.93	0	0	0	0	0	0.06	0.01	0	0
ν_{13}	2737	0	.89	0	0	0	0	0	.07	.03	0	0
e' ν_{14}	1445	0.01	.01	0	0.05	0.03	0	0	.05	.04	0	0
ν_{15}	1354	.02	.02	0	.28	.46	0	0	.22	.03	0.03	0
ν_{16}	1298	.49	.01	.11	.09	.08	0	.01	.22	0	0	0
ν_{17}	941	.20	.01	0	.33	.04	0	.02	.41	0	-0.1	0
ν_{18}	403	.03	.01	.64	.03	.01	0	.25	.04	0	0	0
a'' ν_7	2076	0	.93	0	0	.01	0	0	.05	0.01	0	0
ν_8	1037	0	.01	0	0.04	.87	0	0	.03	0.05	0	0
ν_9	892	0	0	0	.41	.07	0.10	0	.44	0	-0.02	0
ν_{10}	272	0	0	0	.05	.01	0.90	0	.05	0	0	0
ν_{11}	192	0	0	0	0	0	0	0	0	0	0	1.0
ν_{12}	2082	0	0.93	0.01	0	0.01	0	0	0.05	0	0	0
ν_{13}	1964	0	0.89	0	0	.01	0	0	.07	0.03	0	0
e' ν_{16}	1277	0.60	0	0.10	0.07	.03	0	0.01	.19	0	0	0
ν_{14}	1038	0	0.01	.01	.01	.91	0	0	.01	0.05	0	0
ν_{15}	1022	0.01	.03	.02	.28	.42	0	0.01	.23	0.03	-0.02	0
ν_{17}	748	.12	.01	.03	.35	.02	0	.03	.45	0	-0.01	0
ν_{18}	340	.02	.01	.59	.06	.03	0	.23	.07	0	0	0

Two less prominent features at 1070 and 960 cm^{-1} are assigned to ν_9 and ν_{17} which are essentially CH_3 rocking modes, while a weak feature near 1450 cm^{-1} , which is partially obscured by solvent absorptions, may well be ν_8 and/or ν_{14} ; ν_{15} may be contributing to the strong band near 1300 cm^{-1} . In fact, in order to explain the unexpectedly intense band near 950 cm^{-1} in the D-compound, we are obliged to assign this band to ν_{15} which is calculated at 1022 cm^{-1} . This indicates

However, the situation is probably not as hopeless as this might indicate because the rather marked similarity of the main features in the spectra of this and the trimethylcarbonium ion suggests that we should look closely at the CC stretching modes again.



DIMENSIONS

$$\text{C-C} = 1.50 \text{ \AA}$$

$$\text{C-H} = 1.11 \text{ \AA}$$

CH_3 ANGLES TETRAHEDRAL

Fig. 8.—Model assumed for the dimethylcarbonium ion.

that the calculated ν_{15} in the H-compound is too high at 1354 cm^{-1} so that it probably is coincident with ν_{16} . It is noticeable that a narrowing of this broad band near 1300 cm^{-1} occurs in the D-compound; ν_{15} is essentially a CH_3 deformation mode. Table IX summarizes the assignments.

Dimethylcarbonium Ion.—The model assumed for this ion is drawn in Fig. 8. This has C_{2v} symmetry and 20 of the 24 normal modes are infrared active.

 TABLE XIII
 FORCE CONSTANTS FOR $(\text{CH}_3)_2\text{CH}^+$

Force constants	Description	Value	No.
K_{CC}	C-C stretching	3.0	1
K_{CH}	C-H stretching	3.9	2
H_{CC}	CCC bending	0.65	3
H_{CH}	HCC bending	.30	4
H_{CH}	HCC bending in CH_3	.32	5
H_{HH}	HCH bending	.52	6
H_{γ}	Out-of-plane bending	.2	7
t	Torsion	.024	8
F_{CC}	C...C interaction	.30	9
F_{CH}	C...H interaction (CH_3)	.55	10
F_{HH}	H...H interaction	.05	11
ρ	Intramolecular tension	.025	12
C_{HH}	H...H interaction (<i>cis</i>)	.02	13
F_{CH}	C...H interaction	.50	14

 TABLE XIV
 CALCULATED FREQUENCIES FOR $(\text{CH}_3)_2\text{CH}^+$ AND $(\text{CD}_3)_2\text{CD}^+$

		$(\text{CH}_3)_2\text{CH}^+$		$(\text{CD}_3)_2\text{CD}^+$			
a_1	ν_1	2863	2100	b_1	ν_{13}	2800	2076
	ν_2	2800	2078		ν_{14}	2737	1965
	ν_3	2733	1961		ν_{15}	1443	1032
	ν_4	1443	1037		ν_{16}	1388	884
	ν_5	1362	958		ν_{17}	1348	1051
	ν_6	1127	1110		ν_{18}	1156	1251
	ν_7	892	734		ν_{19}	964	735
	ν_8	420	355	b_2	ν_{20}	2800	2076
	ν_9	2799	2075		ν_{21}	1449	1040
a_2^a	ν_{10}	1446	1038		ν_{22}	1071	880
	ν_{11}	974	742		ν_{23}	670	501
	ν_{12}	106	76		ν_{24}	119	90

^a a_2 modes are infrared inactive.

TABLE XV
 SELECTED POTENTIAL ENERGY DISTRIBUTION DATA FOR THE DIMETHYLCARBONIUM ION

Mode	Frequency	K_{CC}	K_{CH}	H_{CC}	H_{CH}	H_{CH}	H_{HH}	H_{γ}	t	F_{CC}	F_{CH}	F_{HH}	ρ	C_{HH}	F_{CH}
(CH ₃) ₂ C+H															
a ₁	ν_4	1443	0	0.01	0	0	0.04	0.87	0	0	0.04	0.04	0	0	0
	ν_5	1362	0.05	.01	0	0	.28	.46	0	0	0.01	.18	0.03	-0.03	0
	ν_6	1127	.16	.01	0.08	0.02	.26	.06	0	0	.01	.34	0	-0.01	0
	ν_7	892	.39	.02	0	0	.15	.02	0	0	.05	.30	0	0	0.02
b ₁	ν_{15}	1443	0	.01	0	0	.04	.87	0	0	0	.03	0.04	0	0
	ν_{16}	1388	0.05	.02	0	0.33	.09	.12	0	0	0	.17	.01	0	0.01
	ν_{17}	1348	.16	0	0	.12	.22	.34	0	0	0	.09	.02	-0.02	.01
	ν_{18}	1156	.46	0.01	0	.07	.02	.02	0	0	0	.19	0	-	.02
	ν_{19}	964	.06	.01	0	0	.40	.07	0	0	0	.44	0	-	.02
(CD ₃) ₂ C+D															
a ₁	ν_6	1110	0.33	0.01	0.02	0.01	0.19	0.26	0	0	0.03	0.08	0.02	-0.02	0
	ν_4	1037	0	.01	.01	0	.01	.91	0	0	0	.01	.05	0	0
	ν_5	958	0.06	.02	.08	0.02	.25	.17	0	0	0.01	.35	.01	-	.01
	ν_7	734	.22	.01	.01	0	.25	.04	0	0	0.05	.40	0	-	.01
b ₁	ν_{18}	1251	.61	0	0	0.13	.04	.03	0	0	0	.15	0	0	0
	ν_{17}	1051	.01	0.02	0	.12	.14	.46	0	0	0	.10	0.03	-0.02	0
	ν_{15}	1032	0	.02	0	.01	.09	.77	0	0	0	.07	.04	-	.01
	ν_{16}	884	0.08	.01	0	.26	.05	.11	0	0	0	.15	.01	-	.01
	ν_{19}	735	0.02	.01	0	.02	.43	.04	0	0	0	.47	0	-	.01

The force constants used were based on the previous set (Table XI), but additional constants were required because of the presence of the unique H atom on the central carbon atom. Table XIII presents the assumed constants while Table XIV gives the calculated frequencies. A selected portion of the potential energy distribution data is reproduced in Table XV, where the modes most likely to arise in the region of experimental accessibility are collected.

Looking first for modes involving considerable K_{CC} contributions, we find ν_{18} in the b₁-species which, in the D-compound, has a 61% contribution. This mode is the antisymmetric CCC stretching mode and, although the calculated values are lower than the observed bands by about 100 cm.⁻¹ in both H and D compounds, we assign these strong bands to ν_{16} ; see Table IX. The agreement between observed and cal-

culated values could readily be improved by assuming a higher K_{CC} value. This implies a greater delocalization of the charge in this ion than in the trimethylcarbonium ion where the same K_{CC} value was found to be adequate.

The other outstanding band which remains to be assigned is that near 930 cm.⁻¹ in the D-compound, and this is probably to be associated with the band near 1500 cm.⁻¹ in the H-compound. If we argue by analogy with the trimethylcarbonium ion, we would require that these be CD₃ and CH₃ deformation modes, probably ν_{15} . However, another assignment seems to be more attractive and that is to ν_{16} which is approximately described as the in-plane bending mode of the CH bond involving the unique H. The calculated values are both low but could be increased by assuming a larger H_{CH} constant. Of course, ν_5 and ν_{16} may both be contributing to the 930 cm.⁻¹ band.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

The Hydrolysis of Dicarboxonium Ions. Kinetics and Mechanism^{1,2}

BY HAROLD HART AND NORMAN R. ROOBOL

RECEIVED OCTOBER 11, 1963

The hydrolysis of dicarboxonium ions of the type I in concentrated aqueous sulfuric acid proceeds in a stepwise fashion, *via* an oxocarboxonium (acylium) ion as a discrete intermediate. The nucleophile in 90–99.75% sulfuric acid is most likely the water molecule. Factors which influence the hydrolysis rates of different dicarboxonium ions are discussed.

Certain substituted benzotrichlorides ionize in 100% sulfuric acid with the loss of two chloride ions, resulting in long-lived dicarboxonium ions (I)³; the evidence for the structures of these ions will not be reviewed here, but it might be mentioned that crystalline salts of these dications can be prepared.⁴ Hydrolysis of I gave the corresponding benzoic acid quantitatively.

(1) Paper VI on Dicarboxonium Ions; for the previous paper in this series, see H. Hart, T. Sulzberg, and R. R. Rafos, *J. Am. Chem. Soc.*, **85**, 1800 (1963).

(2) We are indebted to the National Science Foundation for financial support and to the Dow Chemical Co. for a summer fellowship to N. R. R.

(3) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960); **83**, 4460 (1961).

To examine factors which influence the stability of these ions, it would be desirable to measure their pK' s of formation, by studying the ionization in sulfuric acid of varying strength. Unfortunately, hydrolysis of these ions in less than 100% acid prevents such experiments.⁵ It seemed that the rates of these hydrolyses might reflect the relative energies of dicarboxonium ions, because one would expect the reaction of a doubly charged carbonium ion with a nucleophile to be highly

(4) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

(5) Although such experiments were thwarted in the present instance, they are possible for oxocarboxonium (acylium) ions: H. Hart, C. Y. Wu, and J. T. Fleming, manuscript in preparation.