ion by about eightfold. Secondly, the cationic polymer binds both of the anionic reactants and thereby increases their local concentration and, consequently, the rate of reaction.

In the absence of polymer, the rate constant for the hydrolysis of o-acetoxybenzaldehyde, at pH 7.8, is 4.52×10^{-1} min^{-1}, and the first-order rate constants for the reaction of salicylaldehyde with 3-nitro-4-acetoxybenzoic acid, in the concentration range of $0.25-2.0 \times 10^{-3}$ M salicylaldehyde, vary from 0.16 to 1.21×10^{-3} min^{-1}. In the presence of polymer, the rate constant for the hydrolysis of o-acetoxybenzaldehyde is 4.76×10^{-1} min^{-1}, and the first-order rate constant for the reaction of salicylaldehyde with 3-nitro-4-acetoxybenzoic acid is 0.19 min^{-1}. Thus, in the presence or absence of polymer the rate-limiting step is the transfer of the acyl group from the nitrophenyl ester to o-hydroxybenzaldehyde. Although, the first step in this reaction is accelerated by the polymer, there is no significant acceleration of the second step, i.e., the hydrolysis of o-acetoxybenzaldehyde.

Since there is no significant increase in the rate of hydrolysis of o-acetoxybenzaldehyde in the presence of the polymer and, in this pH region, the rate is linear in (OH$^-$),[7] we presume that there is very little binding of this neutral small molecule to the macromolecule. Therefore, in the overall reaction scheme given in eq 5, the hydrolysis of o-acetoxybenzaldehyde is shown to occur free in solution.

An interesting feature of the catalyzed reaction in the presence of the polymer, illustrated in Figure 4, is the initial increase in the first-order rate constant, followed by the gradual decrease as the polymer concentration is increased. As the total number of binding domains is increased, the probability that the two reactants will be bound at separated sites also increases. Consequently, the amount of nonproductive binding increases at very high polymer concentration and the rate of reaction decreases.

Overall the results indicate that an efficient bifunctional reagent for the hydrolysis of labile ester substrates can be devised by having a formyl group proximal to a nucleophilic group that is capable of an intermolecular attack on the ester substrate. The catalytic efficiency of this system has been demonstrated to be enhanced by a binding polymer. Further studies are underway to devise other bifunctional reagents containing a carbonyl moiety proximal to a nucleophilic group possessing greater nucleophilicity than the phenoxide ion.

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Effect of Solvents of Decreasing Nucleophilicity (Sulfur Dioxide, Sulfuryl Chloride Fluoride, Sulfuryl Fluoride, and Methylene Fluoride) on the Complex Formation and Ionization of Alkyl Fluorides (Chlorides) with Antimony and Arsenic Pentafluoride[1]

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Abstract: C_1 to C_5 alkyl fluorides (chlorides) were complexed and/or ionized with antimony and arsenic pentafluoride in the following solvents of decreasing nucleophilicity: sulfur dioxide, sulfuryl chloride fluoride, sulfuryl fluoride, and methylene fluoride. ^{1}H and ^{13}C NMR spectroscopy were used to investigate the formation of the corresponding alkyl cations and/or complexes. Carbocation or complex formation is dependent on the stability of the species, the strength of Lewis acid, and the nucleophilicity of the solvent.

Introduction

Methods developed in our preceding work allowing the study of carbocations under stable ion conditions have helped to elucidate the structure of a large number of carbocationic reaction intermediates.[2] The use of higher valency Lewis acid fluorides such as antimony and arsenic pentafluoride and their

derived conjugate protic superacids, together with the use of low nucleophilic solvents such as sulfur dioxide, sulfuryl chloride fluoride, and sulfuryl fluoride at low temperatures, has made possible the generation and study of a wide variety of stable carbocations. Despite the continuously increasing number of studies on carbocations, the role of the solvents in

Table I. ^{1}H and ^{13}C NMR Spectral Parameters of Methyl Fluoride with Antimony and Arsenic Pentafluoride in SO_2, SO_2ClF, and SO_2F_2 Solutions

RX	MF_5	solvent	ion or complex	^{1}H NMR[a]		^{13}C NMR[a]		^{19}F NMR[a]	
				δ_{Me_4Si}	J_{HCF}	δ_{Me_4Si}	J_{CH}	J_{CF}	δ_{CCl_3F}
CH_3F		SO_2F_2	CH_3F	4.17 (d)	47.0	70.3 (dq)	150.1	158.2	270.6 (q)
CH_3F	SbF_5[b]	SO_2	CH_3^+OSO	5.50 (s)		74.9 (q)	162.9		
CH_3F	SbF_5	SO_2ClF	$CH_3^+OSOClF$	5.63 (s)		81.8 (q)	165.8		−90.8 (s)
CH_3F	SbF_5	SO_2F	$CH_3F \rightarrow SbF_5$	5.68 (d)	41.2	96.8 (dq)	164.4	126.0	162.2 (br)
CH_3F	AsF_5[c]	SO_2	CH_3^+OSO	5.52 (s)		74.7 (q)	162.9		
CH_3F	AsF_5	SO_2ClF	$CH_3F \rightarrow AsF_5$	5.33 (d)	41.4	87.7 (dq)	160.8	133.7	
CH_3F	AsF_5	SO_2F_2	$CH_3F \rightarrow AsF_5$	5.14 (d)	41.3	86.8 (dq)	160.6	134.1	198.4 (bq)
CH_3F	AsF_5		$CH_3F \rightarrow AsF_5$			86.4 (dq)	160.6	134.1	

[a] Measured at −80 °C. [b] The molar ratio of CH_3F to SbF_5 is 1:1 to 1:4. [c] The molar ratio of CH_3F to AsF_5 is 1:1 to 1:4.

these systems has not yet been systematically investigated.

In typical substitution reactions the solvent can participate in the ionization process (a) by assisting the displacement of the departing leaving group, (b) by stabilizing the developing electron-deficient center (i.e., solvation), or (c) by reacting itself with the electron-deficient center (i.e., solvolysis). The role of the solvent in stable carbocationic systems depends on the strength of the acidic ionizing agent, the stability (and reactivity) of the carbocationic intermediate, and the nucleophilicity of the solvent. Solvent participation by definition is expected to be limited in these systems (otherwise no stable, long-lived carbocations could be observed) unless the carbocations are of an extremely reactive nature (incipient primary or some secondary cations).

In our preceding studies,[3] as well as those of Peterson[4] and Gillespie,[5] the reactions of methyl fluoride and ethyl fluoride with antimony pentafluoride were investigated in solvents such as SO_2, SOF_2, SO_2ClF, and SO_2F_2. From these studies it was concluded that the $CH_3F \rightarrow SbF_5$ complex is so reactive as to O-methylate both SO_2 and SO_2ClF forming $CH_3^+O=SO$ and $CH_3^+O=SOClF$, respectively. The observation of the strong $CH_3F \rightarrow SbF_5$ donor-acceptor complex was achieved in SO_2F_2 solution, but no "free" methyl cation could be observed. The alkylation of even slightly nucleophilic solvents by strong alkylating agents can be explained by their relative basicity toward the carbocationic species.[6,7]

Results and Discussion

In our present study we report in full the systematic investigation of the ionization (complexation) of C_1 to C_5 alkyl halides with SbF_5 and AsF_5 in SO_2, SO_2ClF, SO_2F_2, and CH_2F_2 as studied by ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts and J_{C-H} coupling constants were determined from proton decoupling as well as fully coupled experiments, respectively. ^{1}H and ^{19}F NMR spectra were also studied, whenever indicated. A detailed ^{19}F NMR study of these and related systems is, however, available from Gillespie's work.[5–7] ^{13}C NMR spectroscopy is particularly useful in determining the nature of the carbocationic intermediates under superacidic stable ion conditions. By relating changes due to the acid system or the solvents to the ^{13}C NMR chemical shifts of the carbocationic intermediates, it was found that it is possible to distinguish between the formation of polarized donor-acceptor complexes, completely ionized stable carbocations, or alkylation products of the solvent by the carbocations under a variety of superacidic conditions.

Methyl Fluoride. The methyl fluoride-antimony pentafluoride system has been previously studied in SO_2 and SO_2ClF solution and was shown to be a highly efficient agent for methylating practically any conceivable type of nucleophile.[8,9] The structure of these highly efficient methylating reagents is thus of particular interest.

The ^{1}H, ^{13}C, and ^{19}F NMR spectra of the system in SO_2ClF solution were measured previously. The ^{1}H NMR spectra of

both systems showed a singlet around δ_{1H} (Me₄Si) 5.5 with no observable proton-fluorine coupling.[8,9] The ^{19}F NMR spectra of both solutions indicated the presence of the $Sb_2F_{11}^-$ anion as the predominant species. The proton-decoupled ^{13}C NMR spectra of the system in SO_2 displayed a singlet without carbon to fluorine coupling and with a ^{13}C chemical shift not much deshielded from that of methyl fluorine itself. These observations were originally interpreted in terms of a fluxional $CH_3F \rightarrow SbF_5$ complex, where the methyl group is rapidly shifting from fluorine to fluorine.[8–10]
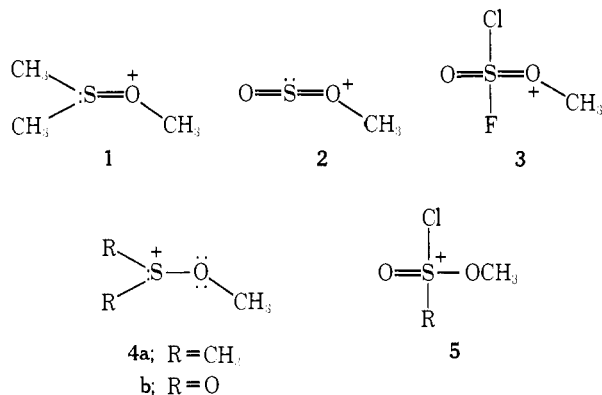
Subsequently, we were able to isolate a white solid complex from the SO_2 solution of methyl fluoride and antimony pentafluoride. Elemental analysis showed that it contains sulfur dioxide, which is given off upon warming or prolonged standing. When redissolved in SO_2 the complex showed identical spectral properties with those of the original solution. All these observations suggested that sulfur dioxide is bonded to CH_3F-SbF_5 and prompted us to reinvestigate the CH_3F-SbF_5 system in SO_2 and SO_2ClF. Independently from our work Peterson, Brackington, and Vidrine,[4] as well as Calves and Gillespie,[5] reported similar observations. The latter authors also carried out ^{19}F NMR studies and reported the x-ray structure of $CH_3OSO^+Sb_2F_{11}^-$.[5c] In addition, experiments using SO_2F_2 for the solvent and AsF_5 as the Lewis acid were carried out on methyl fluoride.[3] The NMR results are summarized in Table I. The solutions had a methyl fluoride to Lewis acid molar ratio from 1:5 to 1:15 (all ratios are molar).

The ^{13}C NMR spectrum of the CH_3F-SbF_5 system in SO_2ClF displays the methyl peak at δ_{13C} 81.8, which is clearly different from that of the system in SO_2 (δ_{13C} 74.9). The corresponding ^{1}H NMR shifts were found to be nearly identical. The different ^{13}C NMR spectra of the SO_2 and SO_2ClF solutions prove that the species responsible are different and that the similarity of the ^{1}H NMR was coincidental. An additional peak in the ^{19}F NMR spectrum of the SO_2ClF solution, which is not due to either solvent SO_2ClF or the $SO_2ClF \rightarrow SbF_5$ complex, was observed at ϕ −90.8. This is attributed to the fluorine absorption of the O-methylated sulfuryl chloride fluoride.

The methyl fluoride-antimony pentafluoride system in SO_2ClF solution also behaves differently than the corresponding system in SO_2. When the temperature of the complex in SO_2ClF was raised to 0 °C, the peak at δ_{1H} (Me₄Si) 5.63 decreased and a singlet appeared at δ_{1H} (Me₄Si) 4.59. The ^{13}C NMR absorption at δ_{13C} 49.8 clearly indicates the irreversible formation of the dimethylchloronium ion.[11] Its formation involves chloride abstraction from the sulfuryl chloride fluoride to give methyl chloride. The methyl chloride formed can either be methylated by the O-methylated complex or condensed by reaction with antimony pentafluoride to form the dimethylchloronium ion. In contrast the O-methylated complex in SO_2 is more stable and is only partially rearranged to O-methylated methyl fluorosulfite upon standing for 1 week at room tem-

perature. A similar result was observed previously in our work[12] in the reaction of methyl fluorosulfite and antimony pentafluoride in SO_2.

A suitable model compound for the O-alkylated SO_2 or SO_2ClF complexes is O-methylated dimethyl sulfoxide, where the O-methyl group absorbs at δ_{13C} 63.4. The corresponding methyl absorptions in the O-methylated sulfur dioxide and sulfuryl chloride fluoride are deshielded by 11.5 and 18.4 ppm, respectively, from that of the O-methylated dimethyl sulfoxide. These differences can be rationalized if one considers the polarity of each of the three alkylated complexes. Resonance structures can place the positive charge formally on sulfur in

CH$_3$\
    S=O$^+$
CH$_3$/   \CH$_3$

O=S=O$^+$
          \CH$_3$

Cl
|
O=S=O
| $^+$\CH$_3$
F

1   2   3

R\
   S—O$^+$
R/   \CH$_3$

Cl
|
O=S$^+$—OCH$_3$
|
R

4a; R=CH$_3$ 5
b; R=O

4 and 5. The charge distribution and ^{13}C NMR shift of O-alkylated methyl groups will depend on the relative contribution of each of the resonance structures. Since the methyl groups are electron donating and oxygen is inductively electron withdrawing, it is expected that the O-alkylated methyl group in 1 will be shielded as compared to 2. In a similar sense it is expected that substitution by electron-negative chlorine and fluorine atoms will also cause deshielding. Thus, the O-methyl group in 2 will be shielded as compared to that in 3. The predicted order follow the observed values for the ^{13}C shifts of the O-alkylated methyl groups.

When methyl fluoride is dissolved in a mixture of arsenic pentafluoride and sulfur dioxide, a clear homogeneous solution is obtained (CH_3F/AsF_5 1:1 to 1:4 molar; CH_3F/SO_2 1:10 to 1:12). The ^1H and ^{13}C NMR spectra of this solution are identical with those of the CH_3F-SbF_5-SO_2 system. Thus, it can be concluded from the NMR evidence that identical $CH_3{}^+O{=}S{=}O$ complexes are formed in these solutions. The ^{19}F NMR spectrum shows at $-80\ °C$ only a single broad peak indicating a fast intermolecular exchange between excess arsenic pentafluoride and its complex anion.

Since the methyl fluoride–antimony pentafluoride complex is so reactive that it O-methylates not only SO_2, but also SO_2ClF, it was found possible to study the complex itself only in the extremely low nucleophilic solvent sulfuryl fluoride. In SO_2F_2 the $CH_3F \rightarrow SbF_5$ complex showed no evidence of interaction with the solvent. Both the ^1H and proton-decoupled ^{13}C spectra displayed a doublet due to fluorine coupling (Table I). The positions of these absorptions are independent of the ratio of CH_3 to SbF_5 and are different from those of methyl fluoride itself. When excess CH_3F is added, NMR absorptions for the complex and free CH_3F are separately observed at $-80\ °C$. The NMR observations are consistent with the formation of static (nonexchanging) $CH_3F \rightarrow SbF_5$ complex, with the fluorine atom of methyl fluoride being bound to the antimony pentafluoride. The doublets in the ^1H and ^{13}C NMR spectra of the complex demonstrate that only one fluorine atom is attached to carbon. Thus a fluorine-bridged five-coordinated structure can be ruled out, since in this case a triplet is expected in the ^1H and ^{13}C NMR spectra.

To obtain further direct proof for the methylation of SO_2 and SO_2ClF by the CH_3F-SbF_5 system we added SO_2 and

SO_2ClF, respectively, to solutions of the complex in SO_2F_2 solution. We were able to observe the formation of 2 and 3 giving identical spectra with those observed in SO_2 or SO_2ClF solution of CH_3F-SbF_5.

It should be mentioned that independently from our studies, Gillespie and Calves[5] have also studied the $CH_3F \rightarrow SbF_5$ complex in SO_2F_2 solution at low temperature and observed its ^{19}F NMR spectrum. Their results are complementary to our findings. They were able to attain a well-resolved ^{19}F NMR spectrum at $-145\ °C$ which is only consistent with a 1:1 CH_3F-SbF_5 complex. However, our ^{19}F NMR spectra of these solutions were broad even at temperatures of $\sim -120\ °C$. The differences between these solutions can be attributed to the ratios of CH_3F to SbF_5. The former study contained a large excess of CH_3F while our study involves excess amounts of SbF_5. Since SbF_5 is polymeric and forms bridged anions, it is reasonable to expect that excess SbF_5 will interact with the $CH_3F \rightarrow SbF_5$ complex causing the broadening observed in the ^{19}F NMR spectra.

When CH_3F is dissolved in neat AsF_5 or with AsF_5 in SO_2ClF or SO_2F_2, clear solutions result, which have similar spectral properties (CH_3F/AsF_5 1:3 to 1:5 molar). The ^1H and ^{13}C NMR spectra show a doublet, which is substantially deshielded from that of methyl fluoride (Table I). If additional methyl fluoride is added to the above solutions, the ^1H and ^{13}C NMR chemical shifts become shielded. Even at $-135\ °C$ the absorptions in the ^1H and ^{13}C NMR spectra do not show broadening. Thus, the exchange between free methyl fluoride and complexed methyl fluoride is still fast at this temperature and only an average absorption is observed in the NMR spectrum.

The donor–acceptor complexes of methyl fluoride with SbF_5-SO_2F_2 and AsF_5-SO_2ClF were observed by ^1H and ^{13}C NMR spectroscopy. The $CH_3F \rightarrow SbF_5$ complex is much stronger and more polar than the $CH_3F \rightarrow AsF_5$ complex, as evidenced by the static nature of the former in SO_2F_2 and its ability to alkylate SO_2ClF. In comparison, the $CH_3F \rightarrow AsF_5$ complex is weaker and less polar since it still does not alkylate sulfuryl chloride fluoride, but does alkylate sulfur dioxide. The stability and polarity of the complexes are directly related to strength of the Lewis acid ($SbF_5 > AsF_5$). Since the C–F bond of methyl fluoride is not ionized to form a free methyl cation, the methylation of the solvent will depend on the polarity of the donor–acceptor complex. This was further exemplified when the considerably weaker Lewis acid BF_3 was dissolved in a solution of CH_3F-SO_2 resulting in no significant deshielding of the ^1H NMR shift of the methyl group. Thus, the $CH_3F \rightarrow BF_3$ complex is much weaker than the SbF_5 and AsF_5 complexes.[13-16]

Ethyl Fluoride. The ^1H and ^{19}F NMR spectra of ethyl fluoride dissolved in a solution of SbF_5-SO_2 have been studied, and were found to be similar to those of the methyl fluoride system. The ^1H NMR spectrum displayed a quartet and triplet with no evidence of fluorine coupling.[9] The ^{19}F NMR spectrum indicates the presence of the $Sb_2F_{11}{}^-$ anion.[10] The ^1H and ^{13}C NMR chemical shifts were not concentration dependent and indicated the presence of a distinct nonexchanging species. Since the observed NMR spectral properties were similar to those of the CH_3F-SbF_5-SO_2 system it was originally concluded that in both cases fluxional complexes were observed. However, on the basis of the conclusion previously discussed on the structure of the CH_3F-SbF_5 complex in SO_2, the structure of CH_3CH_2F-SbF_5-SO_2 system can also be assigned to that of the O-ethylated sulfur dioxide complex. In a similar fashion the ethyl fluoride–arsenic pentafluoride system in SO_2 shows the presence of the O-alkylated sulfur dioxide.
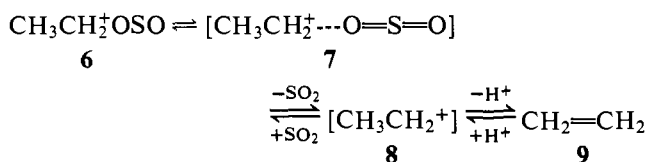
The proton-decoupled ^{13}C NMR spectrum of O-ethylated sulfur dioxide displayed two singlets at δ_{13C} 94.8 and 14.0 for the methylene and methyl groups, respectively. The α-methyl

substituent effect between the methyl group of methylated sulfur dioxide and the methylene group of O-ethylated sulfur dioxide can be calculated as about 20 ppm $(CH_3{}^+O{=}S{=}O \rightarrow CH_3{}^\alpha CH_2{}^+O{=}S{=}O)$.[17]

At first sight such a large value might indicate an equilibrium between the free ethyl cation and ethylated sulfur dioxide, since a typical α-methyl substituent effect generally is of the order of 6–10 ppm for neutral compounds.[17,18] However, ^{13}C and ^2H labeling experiments as well as variable temperature NMR experiments carried out in our preceding work indicate that this is unlikely.[9]

It was shown that there is no intermolecular hydrogen-deuterium exchange of the ethyl fluoride-SbF_5-SO_2 complex with DSO_3F-SbF_5 and DF-SbF_5 at -78 °C. However, when the temperature of the solution was raised, deuterium incorporation could be detected from the ^1H NMR spectrum. In addition, labeling experiments with CD_3CH_2F and 90% ^{13}C-enriched $^{13}CH_3CH_2F$ in SbF_5-SO_2 solution at -78 °C showed an approximately statistical distribution of the labeled atom in the ethyl group of the complex.

From these experiments it was shown that intermolecular and intramolecular exchange was taking place at different rates, the latter being much faster than the former at low temperatures. It can be thus concluded that the exchanges take place through the O-ethylated sulfur dioxide.

$$CH_3CH_2^+OSO \rightleftharpoons [CH_3CH_2^+\text{---}O{=}S{=}O]$$
$$\quad\quad\mathbf{6}\quad\quad\quad\quad\quad\quad\mathbf{7}$$

$$\overset{-SO_2}{\underset{+SO_2}{\rightleftharpoons}} [CH_3CH_2^+] \overset{-H^+}{\underset{+H^+}{\rightleftharpoons}} CH_2{=}CH_2$$
$$\quad\quad\quad\quad\mathbf{8}\quad\quad\quad\quad\quad\mathbf{9}$$

Since no intermolecular reaction between **8** and **9** was observed leading to alkylation until the temperature was raised, it can also be concluded that the intramolecular exchange observed with CD_3CH_2F and $^{13}CH_3CH_2F$ cannot proceed through an entirely free ethyl cation. If it did, one would expect approximately the same rates for both the intra- and intermolecular exchange. The intramolecular exchange can be best explained through a solvated cation **7**.

Ethyl fluoride dissolved in SbF_5 or AsF_5-SO_2ClF did not give rise to the formation of the O-ethylated sulfuryl chloride fluoride complex. If ethyl fluoride was carefully added to a solution which contained an excess of SbF_5-SO_2ClF, the diethylchloronium ion was the only species observed. Its formation is analogous to that of the dimethylchloronium ion from CH_3F in SbF_5-SO_2ClF solution. On the other hand, under less controlled conditions allowing local heating leading to cleavage-condensation reactions the *tert*-hexyl and *tert*-butyl cations were the only observed products.

From the ^{13}C NMR spectrum it is possible to identify the dimethylpropyl and the diethylmethyl carbenium ions along with a small amount of *tert*-butyl cation. Since only even-numbered carbocations were observed, the mechanism does not appear to involve carbon chain cleavage and can be explained in the following way.

Initially, ethyl fluoride can ionize to the ethyl cation which, in aprotic reaction medium, equilibrates via deprotonation-protonation with ethylene. The ethylene formed will react with excess ethyl cation to form the 1-butyl cation, which subsequently rearranges to the *tert*-butyl cation, through the *sec*-butyl cation. The butyl cations can themselves react further with ethylene to give the *tert*-hexyl cations.

Under the studied experimental conditions the ethyl cation is not a long-lived species in sulfur dioxide solution but forms O-ethylated sulfur dioxide, similar to the methyl fluoride complex (in sulfuryl chloride fluoride solution). The O-ethylated sulfuryl chloride fluoride is not observed. Ionization leads to the intermediate formation of the ethyl cation which,

under the experimental conditions, is in equilibrium with ethylene, and is immediately alkylated to form the *tert*-butyl and *tert*-hexyl cations, respectively. Similar behavior is observed in SbF_5-SO_2F_2 solution.
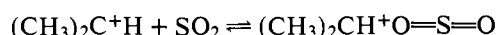
Isopropyl Fluoride (Chloride). When isopropyl fluoride is dissolved in SbF_5-SO_2 solution, the ^1H and ^{13}C NMR spectra show deshielding of both the proton and carbon resonances from those of the precursor fluoride. The deshielding of the chemical shifts and the absence of fluorine coupling confirm the ionization of the C–F bond. The relatively small deshieldings, however, indicate that an equilibrium between the O-alkylated sulfur dioxide and the isopropyl cation is present in SO_2 solution, in accordance with a comparison of the NMR spectra with that of the isopropyl cation in SO_2ClF and SO_2F_2 solutions (where no alkylation is evident) and that of O-methylated and O-ethylated sulfur dioxide. When a $(CH_3)_2$-CHF-SbF_5-SO_2 molar ratio of $1/2/22$ was used, ^{13}C chemical shifts of the C_1 and C_2 carbons were observed at δ_{13C} 22.6 and 122.7, respectively, with the latter peak broadened. In subsequent experiments sulfur dioxide was added to a solution of the isopropyl cation generated in SO_2ClF or CH_2F_2 solution. The ^{13}C NMR chemical shift of the carbenium center of isopropyl cation $(\sim\delta_{13C}$ 320) became shielded to δ_{13C} 125.5 and 128.0, respectively, upon the addition of sulfur dioxide. It thus appears that solvent SO_2 had been alkylated by the isopropyl cation in the same manner as in the case of the incipient methyl and ethyl cations. Experiments with arsenic pentafluoride showed similar ^1H and ^{13}C NMR spectra indicating that the nature of the complex with SbF_5 and AsF_5 is similar (Table II).

If the methyl substituent effects are calculated from the ^{13}C NMR chemical shifts for O-isopropylated sulfur dioxide from that of O-ethylated sulfur dioxide $(CH_3CH_2{}^+O{=}S{=}O \rightarrow (^\beta CH_3)_2{}^\alpha CHO{=}S{=}O)$, values of 29.6 and 8.6 are observed for the α and β methyl substituent effects, respectively. The β effect is in the expected range, but the α effect is much larger, as it would be expected that the α effect should be approximately within a few parts per million of the estimated value for those of methylated and ethylated sulfur dioxide, but they differ by 9.7 ppm. It is thus possible that methyl substituent effects in O-alkylated sulfur dioxide are not constant. However, this seems unlikely in comparison with the data reported for O-alkylated acetones.[20] The α effects of 14.7 ppm going from **10** to **11** and of 12.6 ppm from **11** to **12** are slightly larger than

$$\alpha = 14.7$$
$$\mathbf{11}$$

$$\alpha = 12.6, \quad \beta = 7.8$$
$$\mathbf{12}$$
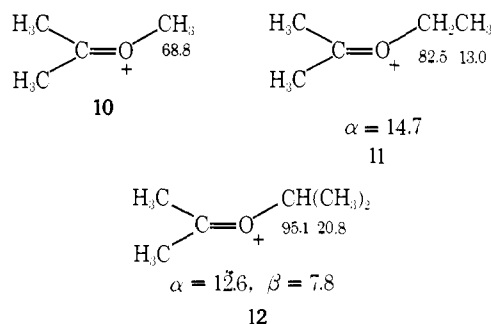
those in the case of alkanes and alcohols. However, in all cases the substituent effects decrease with multiple substitution.[17] Thus, the α-methyl substituent effect going from ethylated to isopropylated sulfur dioxide does not conform with usual substituent effects.

This discrepancy can be, however, well explained if it is assumed that isopropylated sulfur dioxide is in equilibrium with a small amount of "free" isopropyl cation. Similarly, the small changes observed in the ^{13}C

$$(CH_3)_2C^+H + SO_2 \rightleftharpoons (CH_3)_2CH^+O{=}S{=}O$$
$$\quad\quad\mathbf{13}\quad\quad\quad\quad\quad\quad\quad\mathbf{14}$$

absorptions of C_2 are related to the variations in the concen-

Table II. ¹H and ¹³C NMR Spectral Parameters of Ethyl Fluoride and Isopropyl Fluoride (Chloride) with Antimony and Arsenic Pentafluoride in Various Solvent Systems

RX	MF₅	solvent	ion	¹H NMR[a,l]			¹³C NMR[a,l]			
				CH₃(C₁)	CH₃(C₂)	J_{CH-CH}	CH₃(C₁)	CH₂(C₂)	J_{CH_3}	J_{CH_2}
CH₃CH₂F	SbF₅[h]	SO₂	CH₃CH₂⁺OSO	1.95 (t)	6.26 (q)	7	14.3	94.8	130.8	165.7
CH₃CH₂F	AsF₅	SO₂	CH₃CH₂⁺OSO	2.03 (t)	6.32 (q)	7	14.2	95.0	131.6	164.3
				CH₃	>C⁺H		CH₃	>C⁺H		J_{CH}
(CH₃)₂CH[b]							21.9	86.8	125.7	156.3
(CH₃)₂CHCl[c]	SbF₅						52.6	322.1		
(CH₃)₂CHF[d]	SbF₅	SO₂	(CH₃)₂CH⁺OSO	2.00 (d)	7.73 (sp)	6	23.0	125.2	131.2	164.2
(CH₃)₂CHF[d]	SbF₅	SO₂	(CH₃)₂CH⁺OSO				22.7	122.7		
(CH₃)₂CHF	AsF₅	SO₂	(CH₃)₂CH⁺OSO	2.28 (s)	8.10 (bs)		22.8	125.3	131.2	164.7
(CH₃)₂CHF	SbF₅[e]	SO₂ClF	(CH₃)₂⁺CH	4.4 (b)	11.4 (bs)		44.0	~264 (b)		
(CH₃)₂CHF	SbF₅[f]	SO₂ClF	(CH₃)₂⁺CH	4.4 (d)	13.8 (bsp)	5	51.0	320.3		
(CH₃)₂CHF	SbF₅[g]	SO₂ClF	(CH₃)₂⁺CH				51.2	320.8		
(CH₃)₂CHF	AsF₅	SO₂ClF	(CH₃)₂⁺CH				50.4	316.4		
(CH₃)₂CHCl	SbF₅[i]	SO₂ClF	(CH₃)₂⁺CH				50.7	317.6		
(CH₃)₂CHCl	SbF₅[k]	SO₂ClF	(CH₃)₂⁺CH				50.8	319.9		
(CH₃)₂CHCl	SbF₅[j]	SO₂ClF	(CH₃)₂⁺CH	4.45 (d)	13.08 (sp)		51.5	320.6	131.7	171.3
(CH₃)₂CHCl	SbF₅[k]	SO₂ClF	(CH₃)₂⁺CH				51.1	321.0		
(CH₃)₂CHF	SbF₅	SO₂F₂	(CH₃)₂⁺CH	4.58 (s)	13.23 (s)		51.5	321.8		
(CH₃)₂CHF	SbF₅	SO₂F₂	(CH₃)₂⁺CH	4.61 (d)	13.30 (sp)	~4	51.2	321.3	131.4	168.0
(CH₃)₂CHCl	SbF₅	CH₂F₂	(CH₃)₂⁺CH	4.18 (d)	12.85 (sp)	5	50.7	321.5		

[a] All measurements were obtained at −80 °C except those denoted by b,c, and d. [b] Spectra measured at −60 °C. [c] Spectra measured at 20 °C. [d] Spectra measured at −70 °C. [e] The molar ratio of alkyl fluoride to antimony pentafluoride is 1:1, respectively. [f] Same as e except 1:2. [g] Same as e except 1:4. [h] The molar ratio of alkyl fluoride to antimony pentafluoride is 1:4, respectively, of those not designated by a superscript letter. [i] The molar ratio of alkyl fluoride to sulfuryl chloride fluoride is 1:70.4. [j] Same as i except 1:6.7. [k] Repeated above measurement with the SO₂ClF distilled over SbF₅. [l] All shifts are measured from external Me₄Si.

tration of the SO₂ solutions. Since the average chemical shifts for C₂ is directly related to the concentrations of 13 and 14, the relative amounts of 13 and 14 can be found from the observed ¹³C shifts of 13 in SO₂F₂ and the estimated shifts of 14. A chemical shift of δ_{13C} 114.7 is calculated for C₂ of 14 using the α-methyl substituent effect of 20 ppm. By solving simultaneous equations with the ¹³C chemical shift of C₂ in the equilibrium mixture of 13 and 14 and that of C₂ in 13 alone, it was estimated that the mixture in SO₂ contained 95% isopropylated sulfur dioxide and 5% isopropyl cation.

Based on the preceding data, it is further possible to estimate the ¹³C shift for C₁ in O-isopropylated sulfur dioxide. With the known shift for C₁ of the isopropyl cation in SO₂F₂ and the observed value of C₁ in sulfur dioxide a value of δ_{13C} 21.1 is estimated for the ¹³C shift of C₁ in the O-isopropylated sulfur dioxide. This value would lower the β effect by only 1.8 ppm, which is still in the range of normal β effects. All the data are in accordance with a small amount of 9 equilibrating with 10, rather than the static ion 10. Under the experimental conditions the isopropyl cation is not deprotonated, but alkylates sulfur dioxide.

When the solvent is changed from SO₂ to SO₂ClF the ¹³C spectrum shows a dramatic deshielding of C₂ and C₁ to δ_{13C} 320 and δ_{13C} 51, respectively. The isopropyl cation is clearly formed in SO₂ClF solution as evidenced by the large deshieldings of the ¹H and ¹³C NMR spectra. Dilution experiments were also carried out by adding more SO₂ClF to decrease the relative concentration of the isopropyl cation. The ¹³C NMR chemical shifts of C₂ and C₁ became slightly shielded to δ_{13C} 317.6 and 50.7, respectively (Table II). The small shielding differences that are observed in the ¹³C chemical shifts, as the concentration of the cation is reduced in the SO₂ClF solution, can be attributed to SO₂ present as impurity in the SO₂ClF solvent. The isopropyl cation is in dynamic equilibrium with a low concentration of the O-isopropylated sulfur dioxide.

Experiments replacing SbF₅ by AsF₅ resulted in a larger shielding of C₂ and C₁ to δ_{13C} 316.4 and δ_{13C} 50.4, respectively. Again these shieldings can be attributed to the isopropyl cation

exchanging with the alkylated sulfur dioxide. Since arsenic pentafluoride forms a weaker complex with SO₂ than antimony pentafluoride, there is a relatively higher concentration of free SO₂ in the AsF₅–SO₂ClF solution than in the SbF₅–SO₂ClF solution.[7] Thus, more of O-isopropylated sulfur dioxide is formed and the average chemical shift of the isopropyl cation and the O-isopropylated sulfur dioxide will become more shielded relative to the SbF₅–SO₂ClF solutions. Further the isopropyl cation is not very stable in the AsF₅–SO₂ClF solution toward deprotonation, as evidenced by the formation of the three isomeric tert-hexyl cations in the solution, resulting from the isopropylation of propene formed via deprotonation.

The isopropyl cation generated in SbF₅–SO₂F₂ or CH₂F₂ solution showed a further deshielding in the ¹³C NMR spectra, with shifts for C₂ of δ_{13C} 321.3 and 321.5, and for C₁ of δ_{13C} 51.2 and 50.7, respectively.[21,22] As SO₂F₂ and CH₂F₂ are even less nucleophilic solvent systems than is SO₂ClF, solvent alkylation in these systems is considered to be negligible or nonexistent. When the isopropyl cation is generated in the solvents less nucleophilic than SO₂ClF, no solvent interaction is observed as evidenced by the constancy of the deshielded chemical shifts of C₁ and C₂ in the ¹³C NMR spectra in both SO₂F₂ and CH₂F₂ solutions.[5,23] Thus, the strong covalent solvent interactions observed before are minimal if any in SO₂F₂ and CH₂F₂. The solvent alkylation by the isopropyl cation in SO₂ClF seems to be due only to the reversible alkylation of the small impurity SO₂ present and sulfuryl chloride fluoride itself does not interact.

It should be noted that the isopropyl cation generated from either the fluoride or chloride precursor produced the same ¹³C NMR chemical shifts. Experiments where the molar ratio of alkyl fluoride to antimony pentafluoride were varied displayed differences in the ¹³C chemical shifts. Particularly, when the molar ratio was 1:1 for isopropyl fluoride to antimony pentafluoride decomposition to rearranged products as well as somewhat broadened ¹³C chemical shifts were observed. Above a molar ratio of 1:2 the ¹³C NMR spectra appeared to be constant and without the presence of extraneous absorptions.

Table III. ^{13}C NMR Chemical Shifts of the *tert*-Butyl and *tert*-Amyl Cations in Various Solvent Systems

RX	MF₅	solvent	ion	°C	^{13}C NMR (CH₃)₃			C⁺
$(CH_3)_3CF$	$SbF_5{}^a$	CH_2Cl_2	$(CH_3)_3C^+$	−80	49.0			333.5
$(CH_3)_3CF$	$SbF_5{}^a$	SO_2	$(CH_3)_3C^+$	−70	48.0			334.6
$(CH_3)_3CF$	$SbF_5{}^a$	SO_2ClF	$(CH_3)_3C^+$	−80	47.5			335.2
$(CH_3)_3CF$	$SbF_5{}^a$	SO_2F_2	$(CH_3)_3C^+$	−80	47.2			335.9
$(CH_3)_3CF$	$SbF_5{}^a$	CH_2F_2	$(CH_3)_3C^+$	−80	46.7			335.8
$(CH_3)_3CCl$	$SbF_5{}^a$		$(CH_3)_3C^+$	20	48.3			337.9
$(CH_3)_3CF$	AsF_5	SO_2	$(CH_3)_3C^+$	−60	47.9			334.6
					(CH₃)₂	(CH₃)	(CH₂)	C⁺
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5	CH_2Cl_2	$(CH_3)_2C^+CH_2CH_3$	−70	45.9	10.1	58.1	334.6
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5	SO_2	$(CH_3)_2C^+CH_2CH_3$	−70	44.9	9.5	57.3	334.6
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5	SO_2ClF	$(CH_3)_2C^+CH_2CH_3$	−80	44.6	9.3	57.4	335.4
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5	SO_2F_2	$(CH_3)_2C^+CH_2CH_3$	−80	44.4	8.9	57.4	336.0
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5	CH_2F_2	$(CH_3)_2C^+CH_2CH_3$	−80	43.6	7.9	56.5	335.7
$(CH_3)_2C(Cl)CH_2CH_3$	SbF_5		$(CH_3)_2C^+CH_2CH_3$	20	45.3	10.9	59.3	337.1
$(CH_3)_2C(Cl)CH_2CH_3$	AsF_5	SO_2	$(CH_3)_2C^+CH_2CH_3$	−80	44.8	9.3	57.2	334.7

a The mean ratio of alkyl halide to Lewis acid is 1:4 or greater.

An additional sample of the isopropyl cation was prepared from the chloride precursor using neat SbF_5. The ^{13}C NMR spectrum showed ^{13}C chemical shifts of δ 52.6 and 322.1 for C_1 and C_2, respectively (Table II). The chemical shifts of C_1 and C_2 are both deshielded by ~0.1 ppm from that measured in SO_2F_2 and CH_2F_2 solutions. The small but constant variance of the ^{13}C chemical shifts indicates that the effect of these solvents cannot involve covalent interactions with the carbocation as observed in sulfur dioxide solutions. A larger effect is expected only if the solvent system displays marked nucleophilicity. There is no evidence under the experimental conditions for any chloronium ion formation (using excess SbF_5). Fluoronium ion formation in solution was never observed. At low temperatures (<−100 °C) when ionization is yet incomplete, initial donor–acceptor complex formation between the alkyl halides and antimony pentafluoride may take place, leading subsequently to the corresponding ions.[22]

The isopropyl cation is much more stable than the ethyl cation as shown by its observation in SO_2ClF, SO_2F_2, and CH_2F_2 solutions. Its electrophilic reactivity is consequently also less than that of the ethyl cation, since no static O-isopropylated sulfur dioxide is formed, whereas O-ethylated sulfur dioxide is stable.

tert-Butyl and tert-Amyl Fluoride (Chloride). Ionization of *tert*-butyl and *tert*-amyl fluoride (chloride) by SbF_5 or AsF_5 in SO_2, SO_2ClF, and SO_2F_2 produces the tertiary cations as shown by the absence of C–F coupling and the large deshielding in the ^{13}C NMR spectra of both cations (Table III).[5,17] A small deshielding of the carbenium center's ^{13}C shifts can be probably related to the different nucleophilicity of the solvents. Whereas an equilibrium could be considered for the tertiary cations similar to that of the isopropyl cation in SO_2, it would be, obviously, far to the left with only a min-

$$(CH_3)_2^+CR + SO_2 \rightleftharpoons (CH_3)_2CR-O^+=S=O$$

$$R = CH_3$$
$$R = CH_3CH_2$$
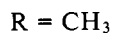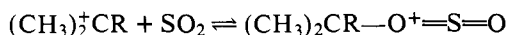
imal amount (if any) of the alkylated sulfur dioxide present. This can explain the relative shielding of the carbenium center when comparing the 13[13]C shifts in SO_2ClF, SO_2F_2, and CH_2F_2, respectively.

In dilution experiments of the tertiary cations in SO_2 solution changing the alkyl cation to solvent ratio of 1:3 to 1:120 the ^{13}C NMR chemical shifts remained constant within 1 ppm. Thus, the effect of solvents on the tertiary alkyl cations is minimal in contrast to the much more electrophilic secondary or incipient or primary cation systems. The tertiary cations

Table IV. ^{13}C NMR Chemical Shift of the Cyclopentyl Cation in SO_2, SO_2ClF, and SO_2F_2 Solutions

RX	MF₅	Solvent	$\delta_{TMS}{}^{CMR}$
c-C₅H₉Cl	$SbF_5{}^a$	SO_2	96.7
c-C₅H₉Cl	$SbF_5{}^a$	SO_2ClF	98.6
c-C₅H₉Cl	$SbF_5{}^a$	SO_2F_2	98.5

a The molar ratio of alkyl halide to precursor is 1:4 or larger.

could also be prepared in methylene chloride solutions. The chemical shifts of the carbenium center in this case are shielded relative to those observed in other lower nucleophilicity solvents. This can be rationalized either by reversible alkylation of methylene chloride or by an equilibrium of the carbocations with the corresponding alkyl chloride in this more nucleophilic medium.

Cyclopentyl Chloride. Our previous NMR studies showed that the cyclopentyl cation is a degenerate equilibrating secondary carbocation system.[17] When cyclopentyl chloride (or fluoride) is ionized by SbF_5 in SO_2, SO_2ClF, and SO_2F_2, a single absorption is observed in the proton-decoupled ^{13}C NMR spectrum.[17] Formally, the cyclopentyl cation is a secondary cation and might be expected to show similar solvent-dependent properties as the isopropyl cation. The ^{13}C NMR chemical shifts, however, in SO_2, SO_2ClF, and SO_2F_2 solutions are not much different, but small shieldings are again observed in the order of increasing nucleophilicity of the solvents (Table IV). This indicates that the equilibrating cyclopentyl cation is thermodynamically more stable than the isopropyl cation, whereas it is less stable than the *tert*-butyl cation. Accordingly the stable cyclopentyl cation could not be prepared in methylene chloride solution.

In dilution experiments in SO_2 or SO_2ClF solution, the ^{13}C NMR chemical shifts were constant within 1 ppm. The lesser stability of the cyclopentyl cation in SO_2 solution is probably due to increased ability in the higher nucleophilicity toward proton elimination, rather than an increased ability to alkylate the solvent.

Conclusions

The results observed can be rationalized in terms of the reactivity of the corresponding carbocations or the formed donor–acceptor complexes and the nucleophilicity of the solvents. In SO_2, the most nucleophilic of the solvents studied, O-methylated, ethylated, and isopropylated complexes are formed.

In the cases of the *tert*-butyl and *tert*-amyl cations, which exist as stable carbocations even in SO_2 solution, only a small

shielding is observed in the ^{13}C NMR spectra. This can be attributed either to the lesser solvent shielding effect or a very small amount of the O-alkylated sulfur dioxide being only in equilibrium with the tertiary carbocations. The rapidly equilibrating cyclopentyl cation (a secondary cation) does not alkylate solvent SO_2. Its behavior thus seems to be similar to that of the tertiary carbocations rather than the secondary isopropyl cation.

In SO_2ClF, $CH_3F \rightarrow SbF_5$ alkylates the solvent even though it is of lower nucleophilicity. However, O-methylated SO_2ClF is not as stable as O-methylated SO_2 and readily decomposes to the dimethylchloronium ion. Neither the ethyl cation nor O-ethylated SO_2ClF is observed in this solvent, only the secondarily formed *tert*-butyl and *tert*-hexyl cations. This is indicative of the intermediate formation of the ethyl cation, with subsequent proton elimination to give ethylene, which is then ethylated by the remaining ethyl cation. The isopropyl cyclopentyl, *tert*-butyl, and *tert*-amyl cations are all stable in SO_2ClF solution.

In SO_2F_2, the limiting nonnucleophilic solvent system, the CH_3F-SbF_5 complex is directly observed by NMR spectroscopy. Similar NMR spectral properties are observed for the isopropyl, cyclopentyl, *tert*-butyl, and amyl cations in SO_2F_2 as SO_2ClF. The isopropyl, *tert*-butyl, and *tert*-amyl cations were also observed in CH_2F_2 solution indicating the extremely low nucleophilicity of this solvent. The similarities in the ^{13}C NMR chemical shifts of the *tert*-butyl and *tert*-amyl cations in SO_2, SO_2ClF, SO_2F_2, CH_2Cl_2, and CH_2F_2 demonstrate that nucleophilic solvation is minimal for the tertiary carbocations.

When the ionizing Lewis acid was changed from the extremely strong SbF_5 to the somewhat weaker AsF_5, a substantial change in the properties of the solutions occurred, as reflected in their NMR spectra. O-Methylated and ethylated sulfur dioxide was still observed in SO_2 solutions, and the $CH_3F \rightarrow AsF_5$ complex, itself, was observed in SO_2ClF and SO_2F_2 solutions. As in the case with SbF_5, neither the ethyl cation nor a stable ethyl fluoride complex could be prepared using AsF_5. The isopropyl and *tert*-butyl cations showed similar ^{13}C NMR properties using AsF_5 instead of SbF_5. Thus in the studied low nucleophilic solutions the interaction of the complex fluoride anions with the formed carbocations is insignificant and independent of the nature of the carbocationic systems.

Experimental Section

Starting Materials. Methyl, ethyl, isopropyl, *tert*-butyl, *tert*-amyl, and cyclopentyl fluoride (chloride) were commercially available (Cationics Inc.) of sufficient purity. Solvent SO_2, SO_2ClF, SO_2F_2, CH_2F_2, and CH_2Cl_2 were also commercially available (Cationics). Antimony pentafluoride was doubly distilled and stored in Teflon bottles. Arsenic pentafluoride (Ozark-Mahoning) was used without further purification.

Preparation of Complexes and Carbocation Solutions. All the solutions were prepared at -78 °C (dry ice–acetone bath). Attempts to prepare the ethyl cation were carried out at temperatures as low as -140 °C (ethanol–liquid nitrogen slush bath). The C_2 to C_5 alkyl fluoride (chloride) (0.10–0.60 g) were dissolved in the corresponding solvent (~2.0 g) used for the measurement. These solutions were carefully added to a well-stirred solution of the Lewis acid (SbF_5 or AsF_5, 2–5 g), dissolved in the same solvent. The molar ratio of ethyl fluoride to the Lewis acid was 1:2 to 1:4, respectively. In the case of

C_3 to C_5 alkyl halides, the ratio was 1:1 to 1:4. The ratio of alkyl halide to solvent varied from 1:4 to 1:120 depending on the experiment.

Solutions of CH_3F were prepared by introducing gaseous methyl fluoride into a solution of the Lewis acid fluoride and solvent until the needed weight increase was observed. The molar ratio of methyl fluoride to Lewis acid was 1:1 to 1:4.

In the dilution experiments, a weighed amount of solution of known concentration was diluted with a weighed amount of the same solvent. In each successive experiment, a portion of the previous solution was used to obtain the further diluted solution. Thus, the alkyl halide to Lewis acid ratio was kept at a constant value.

Nuclear Magnetic Resonance Spectroscopic Studies. The ^1H NMR studies were carried out on a Varian Associates Model A56-60 spectrometer equipped with a variable low-temperature probe. The ^{13}C NMR spectra were obtained using a Varian XL-100-15 NMR spectrometer equipped for proton decoupling, a variable temperature probe, and a 620/L computer with 16K data points. The instrument was run in the FT pulse mode with either proton decoupling or a pulse routine that gives a fully coupled spectrum with some nuclear Overhauser enhancement. The pulse width (H_1 field) in typical experiments was 2–15 μs, where a 42-μs pulse is equivalent to a 90° pulse. Acquisition times were between 0.3 and 0.8 s with pulse delays of 0–9 s depending on the experiment. The total number of transients for suitable S/N for each absorption varied from 100 to 7000 passes. The radio frequency was 25.16 MHz with signals referenced from external Me_4Si in CCl_3F.

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(22) It should be noted that Professor M. Saunders has recently been able to observe the isopropyl chloride–antimony pentafluoride complex before ionization by ^{13}C NMR spectroscopy using his molecular beam method. He observed ionization to the cation at -100 °C. In our experiments the slow ionization was not observed since the solutions were usually made at -78 °C. Personal communication from Professor Saunders.
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