run to run as would be desired (see Table V). The data are plotted in Figure 1. The slopes and intercepts are in good agreement, considering the experimental problems.

Hydrogen Exchange with *p*-Dodecylbenzenesulfonic Acid. The sulfonic acid, obtained from Pilot Chemical Co., was purified by chromatography over alumina. The Stern–Volmer quenching constant for quenching naphthalene fluorescence was 22 M^{-1} in isooctane. Hydrogen exchange was studied in the system $C_{10}D_8$/*p*-dodecylbenzenesulfonic acid. The hydrocarbon (6.0 × 10^{-3} M) and the acid (0.20 M) were irradiated together for 18 h. GC/MS analysis of the photolysate indicated that the quantum yield of hydrogen exchange ($C_{10}D_8 \rightarrow C_{10}D_7H$) was 0.05.

Reaction of 1-Chloronaphthalene with TFA in Ether. The solutions contained 5.0 × 10^{-3} M 1-chloronaphthalene and 0.2 M CF_3CO_2H in dry ether. After 14-h irradiations, the extent of reaction was 90%, while control samples without TFA had reacted to the extent of 56%. A similar experiment using CF_3CO_2D in place of CF_3CO_2H was analyzed by GC/MS. The ratio of *m/e* 163 to *m/e* 162 in the irradiated samples was 0.130, compared with 0.110 for the unirradiated 1-chloronaphthalene. For the naphthalene produced the ratio of *m/e* 129 to *m/e* 128 was 0.150, compared with 0.110 for an authentic compound.

Attempted Sensitization of TFA-Assisted Dechlorination of 1-Chloronaphthalene by *m*-Methoxyacetophenone. Solutions containing 1-chloronaphthalene (5.0 × 10^{-3} M) and TFA (0.2 M) were prepared with and without *m*-methoxyacetophenone (0.05 M). After 2.5 h of irradiation, the solutions were analyzed by GLC. The percent decomposition was 15% for the samples without added "sensitizer" and 2.8% in the sensitized samples. The percent light absorbed by *m*-methoxyacetophenone was 95%.

TFA-Assisted Reaction of 1-Chloronaphthalene in Solvents Other Than Ether. Concentrations of 1-chloronaphthalene and of TFA were 5.0 × 10^{-3} M and 0.2 M, respectively. The percent decomposition was compared for each solvent in the presence and absence of TFA after 3-h irradiation. For cyclohexane, the precent reaction was not influenced by adding TFA; in the case of tetrachloroethylene as solvent, the percent reaction was 74 and 51% with and without TFA. When 1-octene was the solvent, the percent reaction was typically 16% without TFA and 17% with TFA, though it was variable from run to run.

Dechlorination of 1-Chloronaphthalene in the Presence of *p*-Dodecylbenzenesulfonic Acid. The solutions contained 1-chloronaphthalene (5.0 × 10^{-3} M) and the acid (0.2 M). After 2.5-h irradiation, percent reactions were 11 and 50% in the absence and in the presence of the acid.

Acknowledgments. We thank the National Research Council of Canada for financial support and Pilot Chemical Co. for a gift of *p*-dodecylbenzenesulfonic acid.

Registry No. Naphthalene, 91-20-3; 1-fluoronaphthalene, 321-38-0; 1-chloronaphthalene, 90-13-1; biphenyl, 92-52-4; 4,4′-dichlorobiphenyl, 2050-68-2; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 2-fluoronaphthalene, 323-09-1; 2-chloronaphthalene, 91-58-7; 1-methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; isooctane, 540-84-1; benzene, 71-43-2; 1-octene, 111-66-0; tetrachloroethylene, 127-18-4; acetonitrile, 75-05-8; dioxane, 123-91-1; ether, 60-29-7; ethanol, 64-17-5; methylbenzene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1; isopropylbenzene, 98-82-8; butylbenzene, 104-51-8; isobutylbenzene, 538-93-2; CF_3CO_2D, 599-00-8; 4-chlorobiphenyl, 2051-62-9; CF_3CO_2H, 76-05-1; benzophenone, 119-61-9; *p*-dodecylbenzenesulfonic acid, 121-65-3; $C_{10}D_8$, 1146-65-2; $C_{10}D_7H$, 887-68-3; *m*-methoxyacetophenone, 586-37-8; cyclohexane, 110-82-7.

Alkyl Cation Formation and Hydride Transfer in the $AlBr_3/SO_2FCl$ System

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Until now the primary acidic systems which have been reported to be able to stabilize high concentrations of alkyl cations contain antimony pentafluoride. The ions have been detected and characterized principally by nuclear magnetic resonance spectroscopy. This report deals with an aluminum bromide system that can also stabilize high concentrations of tertiary alkyl cations. The NMR spectra of solutions of C_4 thru C_7 alkyl halides in $AlBr_3/SO_2FCl$ are the same as those found with SbF_5 in many solvents. The cations exhibit ^1H NMR shifts which are a function of the $RX/AlBr_3$ ratio and $AlBr_3$ concentration. Limiting shifts are found in 2 M solutions with ratios below 0.2. Regardless of the isomeric halide dissolved in the acid, the initial ions appear to isomerize rapidly to the most favored structures which are then observed. Thus the *tert*-butyl and *tert*-amyl ions are formed from butyl and amyl halides. The C_6 and C_7 systems yield a mixture of tertiary cations. The ions in $AlBr_3/SO_2FCl$ undergo extremely rapid hydride transfer reactions with hydride donors. The acid system is partially miscible with hydrocarbons and two-phase systems can easily be developed in which rapid transfer occurs in both phases.

At about the same time, two groups of investigators reported the detection by NMR spectroscopy of stable alkyl cations in systems containing antimony pentafluoride.[1] Whether the species being observed were truly stable ions or ions participating in rapid equilibrating processes was not established, but the spectral results were so striking as to make it likely that if an averaging process were involved, ions were heavy contributors.

The ^1H NMR spectra of solutions of alkyl halides in the SbF_5 containing systems are unique in that absorptions are obtained significantly donwfield of those in the parent compounds. In addition, first-order patterns are generally observed which could be rationalized with a model for the appropriate cation. One does not know a priori where the resonance of a stable cation would be, but the effects of charge and rehydribization of an sp^3 center to sp^2 should both result in downfield shifts of neighboring groups.

A wealth of information concerning cation behavior has developed from these studies. The initial systems included SbF_5 neat,[2] SbF_5 + HF,[1b] SbF_5 + SO_2,[1] SbF_5 + HSO_3F,[3]

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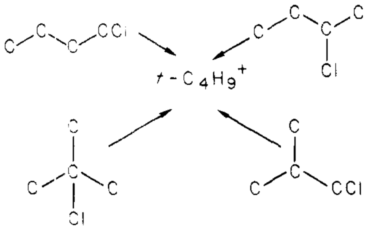
[1] (a) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963); (b) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).

[2] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

[3] G. A. Olah, and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2227 (1967).

Scheme I



$SbF_5 + HSO_3F + SO_2$,[4] $SbF_5 + HSO_3F + SO_2FCl$,[5] and others all containing antimony pentafluoride and relatively nonbasic solvents. In all systems, simple tertiary cations such as *tert*-butyl or *tert*-amyl exhibit similar spectra. Formation of the stable ions has been attributed both to the fact that SbF_5 is a very strong Lewis acid and to the low basicity of the various solvents.

This report is concerned with another strong Lewis acid, aluminum bromide. Till now, the stabilization of simple tertiary cations in systems containing $AlBr_3$ has been limited and spectra approaching that in the SbF_5 systems have been only reported with $AlBr_3/C_6H_5Cl$ solutions at -50 °C.[6] This can hardly be attributed to difficulties in ionizing alkyl halides in view of the work of Bartlett, Condon, and Schneider[7] and the subsequent demonstration of rapid long-chain intermolecular hydride transfer between isobutane and *tert*-butyl cations.[8] Instead, the problem has been to find a nonnucleophilic solvent with which to confine the potentially reactive ions.

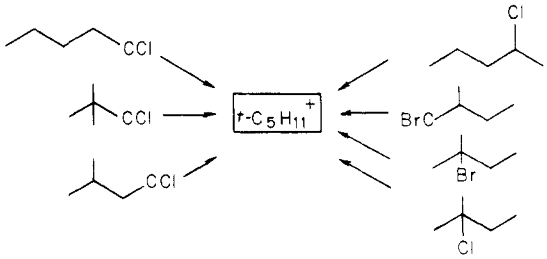
Sulfuryl fluorochloride has recently been found to be a convenient solvent for $AlBr_3$ as it is for SbF_5. The nature of the $AlBr_3$–SO_2FCl system is ill-defined at this time, but it is simple to use and possesses many of the properties of the SbF_5 systems. In particular, it allows the formation of species exhibiting the same ^1H NMR spectra as in the latter systems.

This report contains the spectral results which indicate that the tertiary ions are really participating in equilibrating processes which influence the observed chemical shift. While the nature of the process is uncertain, solutions containing "stabilized" ions with a maximum chemical shift are shown to undergo fast intermolecular hydride transfer reactions with isobutane. This leads to a shift in the methyl resonance to a point between that of t-$C_4H_9^+$ and i-C_4H_{10}. The methyl shift is used in work described in an accompanying paper to directly measure the position of hydride transfer equilibrium between t-$C_4H_9^+$ and many hydrocarbons.

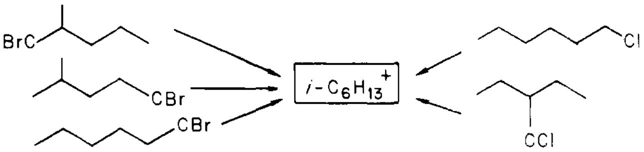
The $AlBr_3/SO_2FCl$ System. The $AlBr_3/SO_2FCl$ system is prepared by condensing commercially available SO_2FCl on N_2 blanketed $AlBr_3$ at -50 °C. At first $AlBr_3$ appears to dissolve, but upon allowing a 2 M solution to stand, a small amount of precipitate appears. The precipitate will partially dissolve upon warming. It has not been well characterized, but crude elemental analyses suggest that the liquid is still approximately 2 M. Condensing more solvent into the system leads to an increasing formation of precipitate.

The liquid phase of the nominal 2-M solution is an excellent solvent for tertiary alkyl cations. More dilute solutions are less efficient but have been used to derive additional information about the absorbing species. The acid system after the addition of alkyl halides often shows a small sharp peak at -7.6 ppm which is not identified.

Scheme II



Scheme III



Alkyl Halide Behavior. *tert*-Butyl chloride and *tert*-amyl chloride in 2 M $AlBr_3/SO_2FCl$ afford the same ^1H NMR spectrum obtained in SbF_5/HSO_3F. The chemical shifts reported below are all referred to an external Me_4Si sample, run just prior to the acid solution.

Four butyl halides have been found to yield virtually identical NMR spectra in 2 M $AlBr_3$–SO_2FCl at -50 and -30 °C. The compounds are 1-chlorobutane, 2-chlorobutane, *tert*-butyl chloride, and isobutyl chloride (Scheme I). The spectrum in each case is a sharp downfield singlet at -3.8 ppm.

Seven amyl halides yield very similar spectra in 2 M $AlBr_3/SO_2FCl$ (Scheme II). These are characterized by a triplet at -1.5 ppm, another triplet at -3.7 ppm, and a multiplet near -4.0 ppm. On the low-field side of the -3.7-ppm triplet, there is invariably a sharp singlet. The two triplets and multiplet characterize the *tert*-amyl cation, while the sharp singlet is that of the *tert*-butyl cation formed by an unknown pathway. The cleanest spectrum of the *tert*-amyl system is obtained from n-$C_5H_{11}Cl$.

The five hexyl halides shown in Scheme III have been found to yield a complex spectrum in 2 M $AlBr_3/SO_2FCl$. The spectrum has been reported to be due to a mixture of approximately equal concentrations of three ions by Brouwer and Mackor,[1b] 2,3-dimethylbutyl, 2-methylpentyl, and 3-methylpentyl. The 2,3-dimethylbutyl cation is observed as a doublet at -2.68 ppm.

n-Heptyl chloride provides a very complex spectrum. The temperature dependence of the spectra for this compound and for 2,3 dimethyl-2-pentanol and 2,3,3-trimethyl-2-butanol have been examined. Between -50 and +20 °C, there is a continual shift in the spectra of the first two compounds to a pattern dominated by a sharp singlet, but the peak position does not coincide with that observed with the last. The nature of the absorbing species in the C_7 system is unclear.

Factors Influencing Peak Position. The spectra of the C_4 through C_7 alkyl halides in 2 M $AlBr_3/SO_2FCl$ correspond extremely well with those found in the antimony pentafluoride systems. In more dilute solutions, however, the "ion" bands appear more shielded and are shifted to higher fields.

The aluminum bromide concentration and the alkyl halide to aluminum bromide ratio are the main factors affecting the shift. Temperature is relatively unimportant between -50 and -10 °C.

In Figure 1 are shown the peak positions of groups which have been assigned to the *tert*-amyl cation. The position

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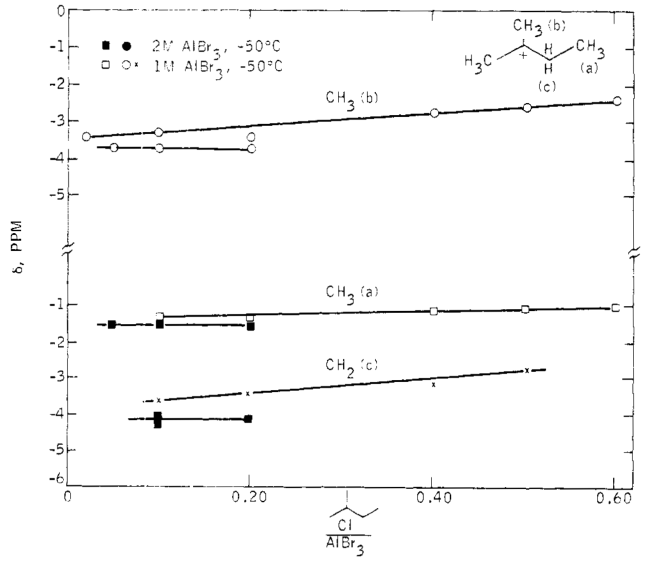
[4] G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **89**, 4736 (1967).

[5] G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 4739 (1967).

[6] G. M. Kramer, *J. Org. Chem.* **35**, 1737 (1970).

[7] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

[8] G. M. Kramer, B. E. Hudson, and M. T. Melchior, *J. Phys. Chem.*, **71**, 1525 (1967).



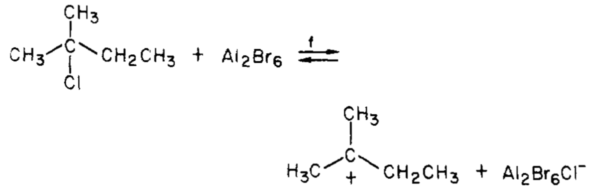
NOTE: δ= SHIFT IN PPM FROM EXTERNAL TMS.

Figure 1. *tert*-Amyl chloride/AlBr$_3$ in SO$_2$FCl.

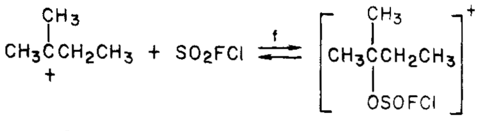
of the methyl and methylene protons adjacent to the tertiary carbon atom show a strong dependence on the amyl chloride/aluminum bromide ratio in the 1 M solution but essentially no dependence in the 2 M solution. The position of the methyl group β to the tertiary carbon also shows a smaller but distinct tendency to shift toward the value in the 2 M solution. The limiting values obtained in these solutions are essentially the same as those obtained in SbF$_5$/HSO$_3$F.

The limiting values do not shift with temperature between -50 and -10 °C. The actual shape of the peaks change, however, in this temperature range and the various bands are all broadened as temperature is increased. The ions are more stable in the more concentrated acid solutions and are discernible at -10 °C with 2 M AlBr$_3$ but only to -30 °C with 1 M AlBr$_3$.

Variation of peak position with reactant ratio implies the existence of at least one equilibrium. If we assume that the t-C$_5$H$_{11}$$^+$ ion has the spectrum obtained in 2 M AlBr$_3$/SO$_2$FCl, then the shift observed in the 1 M solution could be rationalized by assuming an equilibrium between ionized and covalently bound *tert*-amyl compounds. For example, the equilibrium in either eq 1 or 2 if attained



$$CH_3\overset{CH_3}{\underset{Cl}{C}}CH_2CH_3 + Al_2Br_6 \xrightleftharpoons{f} H_3C\overset{CH_3}{\underset{+}{C}}CH_2CH_3 + Al_2Br_6Cl^- \quad (1)$$

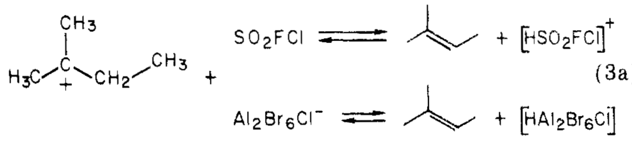


$$CH_3\overset{CH_3}{\underset{+}{C}}CH_2CH_3 + SO_2FCl \xrightleftharpoons{f} \left[CH_3\overset{CH_3}{\underset{OSOFCl}{C}}CH_2CH_3\right]^+ \quad (2)$$

rapidly could lead to the observed spectra providing the steady-state ion concentration is significantly higher than that of the covalent precursor.

Another possible reaction that could yield the averaged signal would be the rapid and reversible formation of a dialkylhalonium ion.[10] Although no such species containing tertiary alkyl groups have previously been reported and we believe they could only be a low concentration species in these acids, in a subsequent paper[11] we show that chloride exchange occurs rapidly between t-C$_4$H$_9$$^+$ and t-C$_4$H$_9$Cl in solutions of AlBr$_3$ in CH$_2$Cl$_2$. The transition state in this reaction presumably resembles this kind of intermediate.

The fact that sharp coupled peaks are observed at low temperatures means that intermolecular proton transfer coupled with exchange is not occurring or is occurring slowly. The broadening of all peaks which is observed as the temperature is raised suggests that this rate is accelerating and that the process is reversible. Possible processes are shown in eq 3a and 3b. If this interpretation



(3a)

(3b)

is correct, then the spectra clearly suggest the olefin–ion equilibrium to be on the side of the ion and further imply that the reactivity of the olefin is severely restricted. Note that if eq 3a or 3b is occurring rapidly, the NMR spectra will only be broadened if the released proton is exchanged with others before it is recaptured by the olefin.

Saunders[9] has found that the *tert*-amyl cation in SbF$_5$/SO$_2$FCl undergoes intramolecular isomerization without proton exchange to solvent, which makes eq 3a doubtful. At elevated temperatures, isomerization leads to coalescence of the pair of methyl triplets while the fine structure of the methylene protons becomes progressively sharper. The proton exchange in AlBr$_3$/SO$_2$FCl may be due to a slight nucleophilic behavior of the anion (eq 3b) or possibly to the presence of some nucleophilic impurities in SO$_2$FCl.

In summary, the major factors affecting peak position are the aluminum bromide concentration and the alkyl halide/aluminum bromide ratio. Equilibria between species which may be ionic and covalently bound compounds appear to occur in dilute acid solutions. In more concentrated solutions, the peaks reach a limited chemical shift which may be caused either by the formation of stable ions or their dominating participation in equilibrating processes.

Hydride-Transfer Experiments. A characteristic reaction of hydrocarbons in strong acid media is the transfer of a hydride ion to a carbonium ion. One example is the behavior of isobutane in AlBr$_3$/trichlorobenzene where hydride transfer between isobutane and a small concentration of *tert*-butyl cations has been shown to occur at an enormous rate, thereby repeatedly converting all the isobutane molecules to ions in a fraction of a second.[8]

The detection of intermolecular hydride-transfer reactions in 2 M AlBr$_3$–SO$_2$FCl would substantiate the existence of an ionic intermediate. If the peaks formed from alkyl halides represent either ions or species in equilibrium with ions, they would be expected to shift or undergo replacement by reaction with hydride donors.

Hydride transfer was shown by reacting isobutane with *tert*-amyl bromide in 2 M AlBr$_3$/SO$_2$FCl at -50 °C. Solutions of the alkyl halide (0.2 M) exhibited typical spectra of the C$_5$$^+$ cation. Adding 1.8 M isobutane replaces it with that of isobutane undergoing hydride-transfer reactions to *tert*-butyl ions

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(9) M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968).

(10) G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Suoboda, P. Schilling, and I. Olah, *J. Am. Chem. Soc.*, **96**, 884 (1974).

(11) D. Mirda, D. Rapp, and G. M. Kramer, *J. Org. Chem.*, following paper in this issue.

$$i\text{-}C_4H_{10(1.8\ M)} + t\text{-}C_5H_{11}{}^+{}_{(0.2\ M)} \rightleftarrows t\text{-}C_4H_9{}^+ + i\text{-}C_5H_{10} \quad (4)$$

$$t\text{-}C_4H_9{}^+ + i\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10} + t\text{-}C_4H_9{}^+ \quad (5)$$

Both the methyl doublet of isobutane and the multiplet of the tertiary hydrogen are collapsed to singlets as a result of the rapidity of this reaction. The position of the methyl protons, –1.42 ppm, are shifted downfield from the median position in isobutane, –0.58 ppm (both vs. external Me_4Si), because the fast exchange leads to a weighted average of the shifts of the *tert*-butyl ion (0.2 M) and isobutane (~1.8 M).

$$\delta_{i\text{-}C_4}X_{i\text{-}C_4} + \delta_{t\text{-}C_4H_9^+}X_{t\text{-}C_4H_9^+} = \delta_{\text{meas}} \quad (6)$$

Here, the δ values are the chemical shifts vs. external Me_4Si and the X values are the mole fractions of the components being averaged. The calculated position of the *tert*-butyl ion, –3.2 ppm, is in reasonable agreement with the observed spectra, –3.7 to –3.8 ppm.

At higher isobutane concentrations, two liquid phases appear. By adjusting the amount of sample in the NMR tube and varying its position in the spectrometer, it is possible to observe reactions in either phase. Thus, adding 0.125 mL of isobutane (2.3 M) to 0.5 mL of acid containing 0.4 M *tert*-butyl chloride results in a phase separation.

The NMR spectrum of the initial solution shows the *tert*-butyl cation peak at –3.69 ppm. The lower phase contains a large singlet at –3.10 ppm and a small singlet at –1.73 ppm corresponding to the methyl and tertiary protons of an isobutane–*tert*-butyl ion system containing an excess ion concentration and undergoing rapid hydride transfer.

Exactly the same reaction occurs in the upper phase. Only here, the relative concentrations are reversed and the collapsed CH_3 singlet is at –0.72 ppm. The tertiary hydrogen is at –1.33 ppm. When observing either phase, a small amount of the other is present (emulsion?), and the reactions can be seen to be occurring simultaneously in each.

There are two important points, first that the reactions occur in each phase and second that transfer between phases must be slow on the NMR time scale to enable the separate phase reactions to be seen separately.

It is curious that although the methyl protons in the example just described are at –3.10 ppm in one phase and at –0.72 ppm in the other the tertiary hydrogen undergoes only a slight shift in the difference phases, –1.33 (hydrocarbon) and –1.73 (ionic). The reason that the shift is slight is because the tertiary hydride is always in a similar environment, i.e., it is always on an isobutane molecule although it is not always the same one.

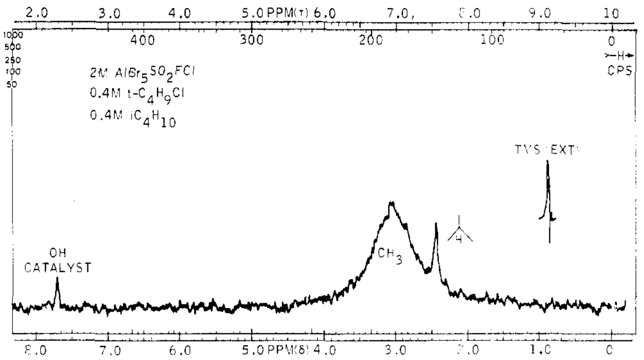

Figure 2. ^1H NMR spectrum of an equimolar solution of the *tert*-butyl cation and isobutane undergoing intermolecular hydride transfer, –50 °C.

Figure 2 provides an example of an equimolar *tert*-butyl ion/isobutane system undergoing moderately fast exchange. It is the spectrum of a homogeneous solution containing 0.4 M $t\text{-}C_4H_9Cl$ and 0.4 M $i\text{-}C_4H_{10}$. It shows a broad singlet for the methyl protons at –2.17 ppm and a sharp singlet for the exchanging methine proton at –1.57 ppm.

Behavior exactly analogous to that of isobutane has been found with isopentane and the *tert*-amyl ion. It will be recalled that the cation spectrum contains a pair of triplets for the methyl protons. These are collapsed and broadened into two singlets under hydride-transfer conditions. The low-field triplet and multiplet of the methylene group are converted by hydride transfer to upfield bands in isopentane. In the ionic phase with excess cation, there is little peak displacement but considerable broadening of all peaks.

Thus the $AlBr_3/SO_2FCl$ system has the ability to support the existence of the same absorbing species as found with SbF_5. The species appear to be involved in complex equilibrating processes and readily participate in intermolecular hydride-transfer reactions. The excellent correspondence of the spectra obtained with both Lewis acids supports the supposition that solutions of high concentrations of tertiary carbonium ions are being observed.

Registry No. $i\text{-}C_4H_{10}$, 75-28-5; *tert*-amyl bromide, 507-36-8; $AlBr_3$, 7727-15-3; SO_2FCl, 13637-84-8.

Cationic Equilibria and Behavior in $AlBr_3$ and $GaCl_3$ Containing Systems

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Solutions of $AlBr_3$ and $GaCl_3$ in CH_2Cl_2, CH_2Br_2, and $1,2\text{-}Cl_2C_2H_4$ stabilize high concentrations of tertiary alkyl cations at temperatures ca. –30 °C. NMR indicates that aluminum bromide forms $R^+Al_2Br_6X^-$ salts while $GaCl_3$ forms both $R^+Ga_2X_7{}^-$ and $R^+GaX_4{}^-$ salts. The ions participate in hydride transfer equilibria with saturated hydrocarbons which indicate that larger hydrocarbons are easier to ionize than isobutane. Free energy changes are usually within 5 kcal/mol of gas-phase values for the $t\text{-}C_4H_9{}^+ + RH$ reactions. Relative ion stabilities are in general accord with estimates from solvolysis studies, except for the adamantyl ion. The equilibria for this reaction lie within a wide range that could be anticipated from solvolysis and gas phase estimates. These values are proposed as a useful scale to characterize the extent of ionic solvation in superacid media.

Strong acid systems have the ability to stabilize tertiary and in some cases secondary alkyl cations for a sufficient time to permit their observation by NMR spectroscopy.[1,2] In principle this should permit the study of ionic equilibria