

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).

$$\delta_{i\text{-C}_4\text{H}_9}X_{i\text{-C}_4} + \delta_{t\text{-C}_4\text{H}_9}X_{t\text{-C}_4\text{H}_9} = \delta_{\text{meas}} \quad (6)$$

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

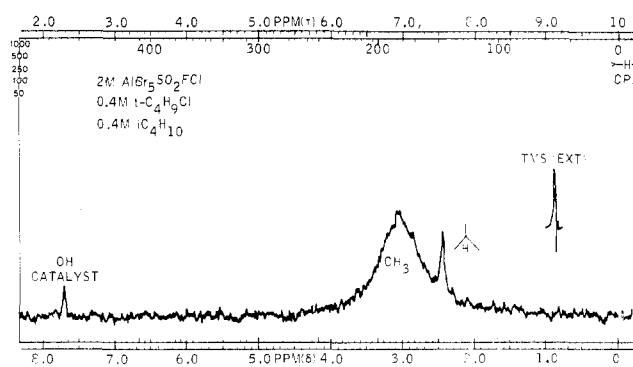


Figure 2. ^1H NMR spectrum of an equimolar solution of the *tert*-butyl cation and isobutane undergoing intermolecular hydride transfer, -50 °C.

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 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*- $\text{C}_4\text{H}_9\text{Cl}$ and 0.4 M *i*- 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 $\text{AlBr}_3/\text{SO}_2\text{FCl}$ 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*- 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- $\text{Cl}_2\text{C}_2\text{H}_4$ stabilize high concentrations of tertiary alkyl cations at temperatures ca. -30 °C. NMR indicates that aluminum bromide forms $\text{R}^+\text{Al}_2\text{Br}_6\text{X}^-$ salts while GaCl_3 forms both $\text{R}^+\text{Ga}_2\text{X}_7^-$ 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 $t\text{-C}_4\text{H}_9^+ + \text{RH}$ 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.

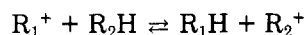
Strong acid systems have the ability to stabilize tertiary and in some cases secondary alkyl cations for a sufficient

time to permit their observation by NMR spectroscopy.^{1,2} In principle this should permit the study of ionic equilibria

engendered by the fast intermolecular hydride-transfer reaction between the ions and alkanes that was studied under other conditions by Bartlett, Condon, and Schneider.³

Direct measurement of the position of ionic equilibria in solution provides information on the importance of solvation in stabilizing the reacting pairs when compared with gas-phase equilibria. The latter can be estimated from tabulations of ionic heats of formation⁴ or measured directly by recently developed mass spectroscopic techniques.^{5,6}

Unfortunately, equilibria of the sort



are difficult to assess in many of the SbF_5 systems used to stabilize cations because these acids often oxidize all the alkanes to ions.

In principle, oxidation might be minimized by forming the ions from alkyl halides in aprotic media like SbF_5/SO_2FCl . This has been used to measure the position of the isopropyl ion plus cyclopentane equilibrium,⁷ but interfering oxidation by the acid or trace protonic impurities makes it difficult to study equilibria involving tertiary cations and alkanes.

Oxidation is not a serious problem in aprotic solutions of $AlBr_3/CH_2Cl_2$, $AlBr_3/CH_2Br_2$, and $GaCl_3/CH_2Cl_2$. These have all been found capable of stabilizing concentrated solutions of tertiary ions and they have been used in assessing hydride-transfer equilibria between the *tert*-butyl cation and isopentane, 2,3-dimethylbutane, 3,4-dimethylpentane, methylcyclopentane, adamantane, and several other hydrocarbons. These data are compared with prior values obtained with $AlBr_3$ in SO_2FCl ⁷ and gas-phase determinations.

It has generally been found that the vapor-phase equilibria are slightly muted in these acid systems. The solution equilibria might be expected to reflect ion pairing or specific solvation effects and these are believed to be relatively important in the *tert*-butyl ion/methylcyclopentane and *tert*-butyl ion/adamantane systems.

Experimental Section

The acid solutions used in this program were prepared with freshly sublimed $AlBr_3$ or $GaCl_3$. The $AlBr_3/CH_2Cl_2$ system requires extra care because at ambient conditions it undergoes an exothermic halide exchange which could lead to dangerous overheating or an explosion. The exchange ultimately forms $AlCl_3$ which precipitates and renders the systems less useful for the equilibrium studies. This problem can be avoided by warming a mixture of $AlBr_3/CH_2Cl_2$, prepared at $-80^\circ C$, until the $AlBr_3$ dissolves and then cooling to about $-40^\circ C$. In this manner clear

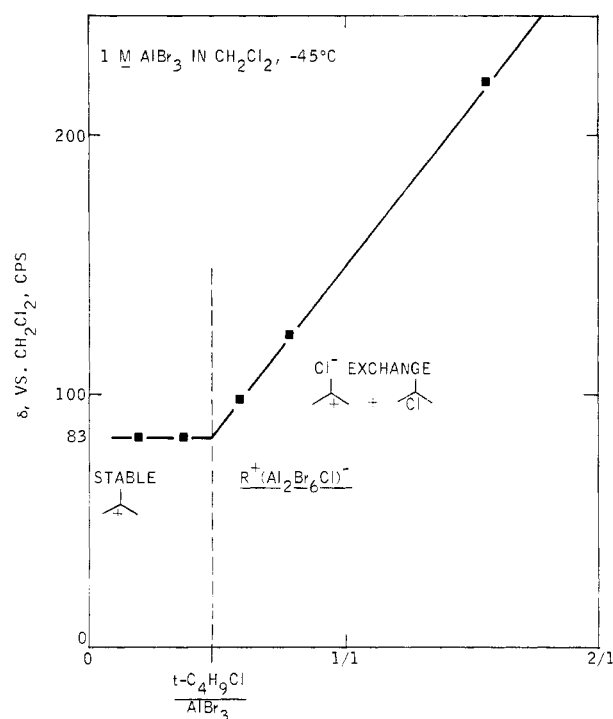


Figure 1. Aluminum bromide forms 2:1 salt.

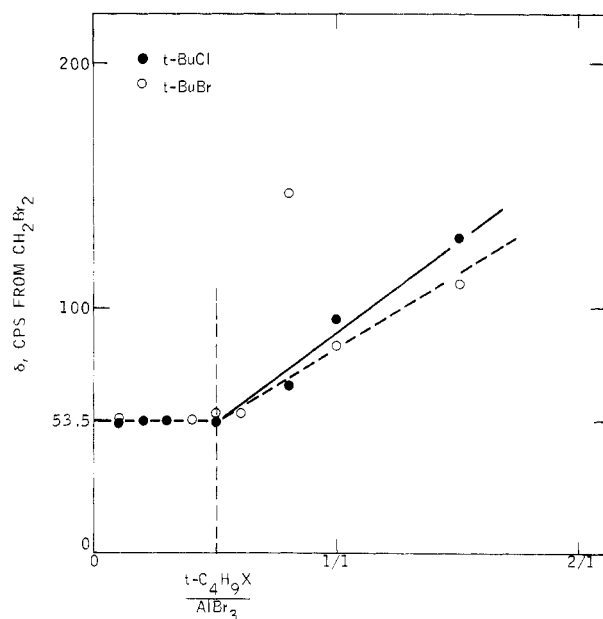


Figure 2. Comparison of *t*-BuX solutions in 1 M $AlBr_3/CH_2Br_2$ at $-50^\circ C$.

1 M solutions are obtained which NMR indicates contain only traces of CH_2BrCl .

In preparing the strong acid solutions it is necessary to keep the solutions away from atmospheric moisture. Therefore much of the work was done in an N_2 drybox or using sealed systems under a nitrogen atmosphere. The solvents were also dried over $CaSO_4$ (anhydrous) for at least 24 h before use.

All NMR experiments were done in a Varian A-60 instrument operating at 60 MHz.

The initial preparation of carbonium ions in the acid solutions was done in the drybox. Exactly 0.5 cm^3 of the acid solution was added to an NMR tube at the appropriate temperature in a cooling bath (i.e., $-50^\circ C$). Then the appropriate amount of the *t*-BuX was added to obtain the desired concentration. This procedure was followed for all the NMR shift data and temperature dependence data.

The above technique was replaced by a more efficient process which was used for the equilibrium data. For these experiments

(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) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

(2) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).

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

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(5) (a) J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **97**, 2625 (1975); (b) J. J. Solomon and F. H. Field, *ibid.*, **95**, 4483 (1973); (c) M. Meot-Ner, J. J. Solomon, and F. H. Field, *ibid.*, **98**, 1025 (1976); (d) J. J. Solomon and F. H. Field, *ibid.*, **98**, 1567 (1976); (e) J. J. Solomon, M. Meot-Ner, and F. H. Field, *ibid.*, **96**, 7552 (1974).

(6) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).

(7) G. M. Kramer *Int. J. Mass Spectrosc.*, **19**, 139 (1976).

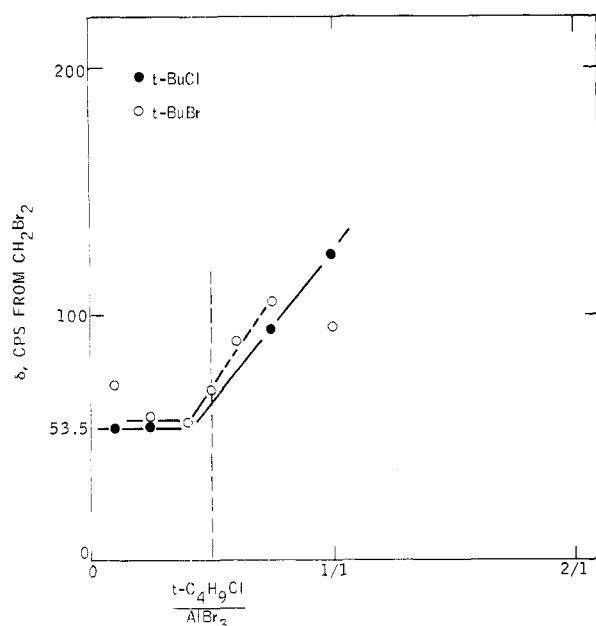


Figure 3. Comparison of *t*-BuX solution in 2 M $\text{AlBr}_3/\text{CH}_2\text{Br}_2$ at -30°C .

solutions of alkyl halides and hydrocarbons in the appropriate solvent were blended into solutions of the Lewis acids in the same solvent. The mixtures were prepared at -50 or -80°C while stirring in a nitrogen atmosphere.

Results

The chemical shift in hertz of the ^1H NMR spectra of *tert*-butyl halides interacting with 1 or 2 M solutions of the acids are shown in Figures 1, 2, and 3. [Also shown is data for $\text{GaCl}_3/1,2\text{-Cl}_2\text{C}_2\text{H}_4$ solutions which are also capable of stabilizing $t\text{-C}_4\text{H}_9^+$. These were not used for equilibria measurements because they gave evidence of instability (they turn from clear to purple).]

The chemical shift of the methyl resonance is plotted vs. the ratios of *tert*-butyl halide to Lewis acid. At low ratios the *tert*-butyl ion is found at a limiting shift of 83 Hz from CH_2Cl_2 . With AlBr_3 , this shift is maintained as the *tert*-butyl halide/ AlBr_3 ratio is raised to 1:2. With more alkyl halide, a single peak is seen whose position moves to higher field.

When adding *tert*-butyl chloride to $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$ the upfield shift occurs without the formation of detectable additional absorptions which might indicate the occurrence of side reactions. In $\text{AlBr}_3/\text{CH}_2\text{Br}_2$, on the other hand, there is a small but detectable development of additional bands at ratios above 1:2.

Other evidence of instability in the $\text{AlBr}_3/\text{CH}_2\text{Br}_2$ system was obtained from studies of the temperature dependence of the spectra. In general it was found that heating solutions above -30°C , even when RX/AlBr_3 was less than 1:2, led to nonreversible shifts of the butyl signal and the formation of small additional bands 1.98 and 2.61 ppm more shielded than solvent which were not assigned.

Figure 2 illustrates the behavior of *tert*-butyl chloride and *tert*-butyl bromide in 1 M $\text{AlBr}_3/\text{CH}_2\text{Br}_2$ solutions at -50°C . Both alkyl halides provide a limiting shift of 53.5 ± 0.5 Hz at low alkyl halide concentrations. At or near the 1:2 ratio there is a break just as in $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$ solutions. Figure 3 contains a similar comparison made with a 2 M AlBr_3 solution at -30°C . The points in parentheses indicate that side reactions were evident in the spectra.

In 2 M $\text{GaCl}_3/\text{CH}_2\text{Cl}_2$ solutions, Figure 4, the limiting shift of the *tert*-butyl signal is observed at 78.8 Hz, slightly

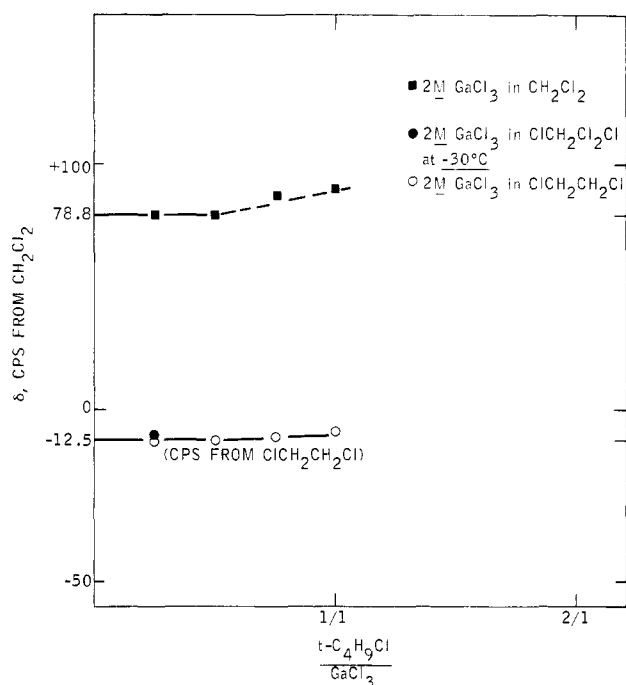


Figure 4. Comparison of 2 M GaCl_3 solutions in 1,2-dichloroethane and methylene chloride with *t*-BuCl at -50°C .

deshielded compared to the 82 Hz shift found in $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$. The shift in the gallium chloride solution is also maintained to a 1:2 *tert*-butyl chloride to GaCl_3 ratio. With added *tert*-butyl chloride one again observes a break in the curve, but it is much reduced when compared with the AlBr_3 solutions. The GaCl_3 solutions also tend to develop new peaks indicative of side products at ratios above 1:2 and when heated.

Note should be made of the $1,2\text{-Cl}_2\text{C}_2\text{H}_4/\text{GaCl}_3$ system in which there is a still smaller shift in the position of the *tert*-butyl signal up to a 1:1 alkyl halide/ GaCl_3 ratio.

The $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$, $\text{GaCl}_3/\text{CH}_2\text{Cl}_2$, and in one case the $\text{AlBr}_3/\text{CH}_2\text{Br}_2$ systems were employed in measuring the positions of hydride-transfer equilibria under the assumption that the limiting downfield shift of the butyl system represents the solvated *tert*-butyl cation. The *tert*-butyl halide/Lewis acid ratio was usually 0.2:1, and equilibria were only estimated for homogeneous mixtures with various hydrocarbons. The extent to which the added alkane may have isomerized during the experiment is not known and trapping experiments indicate that some rearrangement occasionally occurred. Since the equilibria between the *tert*-butyl ion and any of the tertiary alkanes of a given carbon number would to a first approximation be expected to be similar, the alkane rearrangements are not believed to play a major role in the measured ΔG values.

The data in Table I is not "corrected" for the number of available tertiary hydrogen atoms in the alkane. The main reason is that the extent of isomerization is unknown and even if it was known, the correction would generally be small. For example, conversion of 2,3-dimethylbutane to a methylpentane reduces the available hydride donors from two to one and would provide a "correction" to the measured free-energy change of $RT \ln 2$ or 0.3 kcal/mol at -50°C .

Table I contains a comparison of the equilibrium constants and free-energy changes for the reaction of $t\text{-C}_4\text{H}_9^+$ with various hydrocarbons. In $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$ data are also tabulated for the equilibrium reached by adding isobutane to a solution of the other cation. Agreement between the acid systems is generally excellent except for

Table I. Hydride-Transfer Equilibria
 $t\text{-C}_4\text{H}_9^+ + \text{RH} \rightleftharpoons i\text{-C}_4\text{H}_9 + \text{R}^+$

RH	1 M AlBr ₃ /CH ₂ Cl ₂ , 228 K		1 M AlBr ₃ /CH ₂ Br ₂ , 223 K	1 M GaCl ₃ /CH ₂ Cl ₂ , 223 K
	ΔG	ΔG^a	ΔG	ΔG
<i>i</i> -C ₅	-0.7	-1.1, -1.2		0, ^b -0.7 ^b
2,3-DMC ₄	-0.8			-0.9, -1.0, -1.5
2,3,3-TMC ₄	-0.1, -1.0			
2,4-DMC ₅				-1.1, -1.1, ^b -1.4
MCyC ₅	-1	-1.2, -1.3		-1.7, -1.9
adamantane		-3.2, -3.4	-0.6, +0.6	-0.1, -0.7, ^b +0.4
norbornane	+1.1	+0.3		

^a Reactants were *i*-C₄H₉ and an alkyl halide in this column. All ΔG values in kcal/mol. The standard deviation is estimated as ± 0.2 kcal/mol. ^b With 0.67 M GaCl₃.

Table II. Hydride- and Bromide-Transfer Equilibria in Solution and Vapor Phase
 $t\text{-C}_4\text{H}_9^+ + \text{RX} \rightleftharpoons i\text{-C}_4\text{H}_9 + \text{R}^+$

RX	ΔG , kcal/mol				
	AlBr ₃ / CH ₂ Cl ₂ 223 K	AlBr ₃ / CH ₂ Br ₂ 223 K	GaCl ₃ / CH ₂ Cl ₂ 223 K	AlBr ₃ / SO ₂ FCl 223 K	gas, 300 K
<i>i</i> -C ₅ H ₁₂	-1.0		-0.4	-0.8	-2.5 ^{5e}
2,3-DMC ₄	-0.8		-1.1		-5.4 ^{5a}
adamantane	-3.3	0.0	-0.1	-0.6	
norbornane	+0.7			+1.2	-2.3 ^{5d}
MCyC ₅	-1.2		-1.8		-5.5 ^{5d}
	RBr ⁶		$\Delta H_{\text{HSO}_3\text{F}}^{298}$	$\Delta H_{\text{g}}^{298}$	
	<i>exo</i> -1-bromonorbornane		+1.5	-10	
	1-bromoadamantane		+0.2	-11	

the *tert*-butyl/adamantane data.

The data indicate that in the C₅, C₆, and C₇ series the larger ions tend to be slightly more stabilized or easier to form than *tert*-butyl.

The average values of the free-energy change found in these experiments are compared with equilibrium measurements found in SO₂FCl and the gas phase in Table II. Also tabulated are some bromide transfer reaction enthalpy changes measured by ion cyclotron resonance⁶ and deduced from solvolysis studies in HSO₃F.^{8a} The latter measurements can be used to infer the equilibrium constants of a reaction very similar to the hydride-transfer equilibrium that we directly measure, if the net entropy change is close to zero.

Other measurements of the heat of solution of alkyl chlorides and fluorides in strong acids have recently been reported by Arnett and Petro.^{8b} They generally show a close correspondence with the data discussed in this paper.

Discussion

Figures 1, 2, and 3 indicate that ionization of *tert*-butyl halides is essentially quantitative when more than 2 mol of AlBr₃ or GaCl₃ per mole of RX is employed in CH₂Cl₂ or CH₂Br₂. This is shown by the large downfield shift of the *tert*-butyl proton resonance. For example, *tert*-butyl chloride and bromide, which are normally 207 and 195 Hz upfield of CH₂Br₂ (on a 60 MHz instrument), yield a singlet at +53.5 Hz which should represent the solvated *t*-C₄H₉⁺ ion. If the ion is in equilibrium with an alkyl halide, the concentration of the latter must be very small, because the position of the *tert*-butyl signal hardly shifts as the RX/AlBr₃ ratio is increased to 1:2.

The ion formed from *tert*-butyl chloride and AlBr₃ in CH₂Cl₂ appears to exist in a more stable situation than in

the other systems studied. This is evident from the appearance of the spectra as alkyl halide is added beyond the 1:2 ratio. In this solution one observes a sharp singlet shifting progressively toward higher field as one raises the ratio to 1:1 and beyond.

The spectra indicate that at low concentrations *tert*-butyl chloride forms the *t*-C₄H₉⁺Al₂Br₆Cl⁻ salt. The cation evidently participates in halide exchange with additional *tert*-butyl chloride, which leads to the indicated shift. Thus, above the 1:2 ratio one could study halide-transfer equilibria between alkyl halides and *tert*-butyl ions. At concentrations below the 1:2 ratio the *tert*-butyl ion participates in hydride-transfer equilibria with many alkanes, leading to the data in Tables I and II.

The sharp break in the curve at 1:2 and the lack of a second break at 1:1 are consistent with the hypothesis that the shifts are due to halide exchange. Other processes which might cause the first break could include the decomposition of the 1:2 salt to a 1:1 pair of ions, *t*-C₄H₉⁺AlBr₃Cl⁻, or the formation of a dialkyl halonium salt like (*t*-C₄H₉)₂Cl⁺Al₂Br₆Cl⁻. These processes are considered to be unimportant, however, because they should have led to another break at the 1:1 ratio, but this was not observed.

The AlBr₃/CH₂Br₂ solutions appear to be more nucleophilic and less ion stabilizing than AlBr₃/CH₂Cl₂. Both *tert*-butyl bromide and chloride behaved similarly until the 1:2 ratio was reached and both yielded a shifted butyl signal at slightly higher ratios. However, at the higher ratios small amounts of additional bands appeared in the ¹H NMR spectra. These unassigned bands indicate that side reactions are occurring and the solutions of aluminum bromide in methylene chloride which do not generate these complications are therefore preferred for studying halide-transfer equilibria.

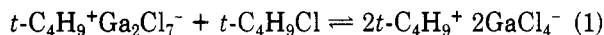
It was hoped that these spectra might be useful in deciding whether the Al₂Br₇⁻ or Al₂Br₆Cl⁻ anion would be more useful in stabilizing a cationic salt in CH₂Br₂. The chloride atom is likely to occupy a bridging position in the anion and might be expected to stabilize the structure, but no real difference could be deduced from the measurements as side products formed with equal ease from both alkyl halides.

The AlBr₃/CH₂Br₂ system was only used in measuring the equilibrium between *t*-C₄H₉⁺ and adamantane. The reaction is nearly thermoneutral and was similar to that found in GaCl₃/CH₂Cl₂.

Both methylene chloride and 1,2-dichloroethane form solutions with GaCl₃ that stabilize the *tert*-butyl ion. The ion is again formed with the least formation of side products at RCl/GaCl₃ ratios below 1:2. At ratios between this and 1:1 in methylene chloride one finds a slight upfield shift of the *tert*-butyl signal and the formation of small signals that appear as sharp singlets at +145.5, +187.5, and +232.5 Hz.

(8) (a) Calculated in ref 6 from measurements by Arnett; (b) E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 5402, 5408 (1978).

The slight shift in the butyl signal is more consistent with decomposition of Ga_2Cl_7^- to GaCl_4^- ,



than with the onset of either fast intermolecular chloride transfer or chloronium ion formation. No assignments are proposed for the small signals which indicate the formation of some stable side products. This system was used for studies of hydride-transfer equilibria with about 1:5 ratios of *tert*-butyl chloride to GaCl_3 .

The 1,2-dichloroethane solvent was also effective at stabilizing *tert*-butyl ions at similar conditions as CH_2Cl_2 , but was not used in the equilibrium measurements. The shift of the butyl signal hardly changed up to 1:1 ratios of *tert*-butyl chloride to GaCl_3 , but side products again appeared above the 1:2 ratio. Both GaCl_3 systems appear to yield both monomeric and dimeric anions with the *tert*-butyl cation.

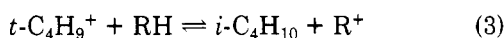
Equilibrium Measurements

Carbonium ion equilibrium measurements were made by measuring the shift of the *tert*-butyl signal in homogeneous mixtures of a *tert*-butyl halide and a hydrocarbon in an acid solution. The shift δ_{meas} is from the solvent band and is assumed to be a linear function of the mole fractions of *tert*-butyl ion ($X_{t\text{-C}_4^+}$) and isobutane ($X_{i\text{-C}_4}$) present at equilibrium, each being multiplied by the chemical shift of the pure constituent.

$$\delta_{\text{meas}} = X_{t\text{-C}_4^+}\delta_{t\text{-C}_4^+} + X_{i\text{-C}_4}\delta_{i\text{-C}_4} \quad (2)$$

In the $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$, $\text{AlBr}_3/\text{CH}_2\text{Br}_2$, and $\text{GaCl}_3/\text{CH}_2\text{Cl}_2$ systems the limiting shifts of $t\text{-C}_4\text{H}_9^+$ and $i\text{-C}_4\text{H}_{10}$ were respectively 83 and 267.6, 53.5 and 238.1, and 78.8 and 267.6 Hz.

Once the butyl components have been determined the concentrations of the other pair of reactants are calculated and the equilibria is determined for eq 3.



It is interesting that the shift of $t\text{-C}_4\text{H}_9^+$ in CH_2Cl_2 changes from +83 Hz with AlBr_3 to +78.8 Hz with GaCl_3 . This immediately suggests that the solutions contain incompletely dissociated ion pairs in which interaction with the counterion alters the shielding about the cation.

The data in Table I suggests the large cations to be slightly more stable than the *tert*-butyl ion, or alternatively that they are easier to form by hydride abstraction. This trend in the alkyl series $t\text{-C}_5^+ \rightarrow t\text{-C}_6^+ \rightarrow t\text{-C}_7^+$ should reflect the ability of the larger hydrocarbon skeleton to stabilize the charge by distributing it more extensively.

These ionic equilibria can be compared with measurements in $\text{AlBr}_3/\text{SO}_2\text{FCl}$ solutions and the vapor phase. Some of the results have already been published.⁷ They were made with 1 or 2 M solutions of AlBr_3 and the shifts were measured vs. the tetramethylammonium ion as an internal standard.

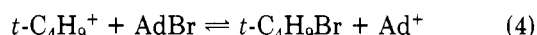
The position of equilibrium in solution for the alkyl ions is about the same in CH_2Cl_2 as in SO_2FCl . In the solvents the equilibria do not favor the larger cation as much as is found in the gas phase. This indicates that the inherent equilibrium which is manifest in the gas is slightly altered because of solvation, ion pairing, and related phenomena in solution. The overall effect of solvation is remarkably slight, probably reflecting the fact that there are a similar number of components on both sides of the equilibria studied.

Another distinction between the equilibrium measured by NMR and that which might have been inferred from

solvolytic rates is found in the *tert*-butyl/adamantane system. In $\text{GaCl}_3/\text{CH}_2\text{Cl}_2$, $\text{AlBr}_3/\text{CH}_2\text{Br}_2$, and $\text{AlBr}_3/\text{SO}_2\text{FCl}$ formation of the adamantyl ion is slightly favored over *tert*-butyl. It is favored still more in the $\text{AlBr}_3/\text{CH}_2\text{Cl}_2$ solutions.

The solution equilibria all indicate that Ad^+ is thermodynamically at least as easy to form as $t\text{-C}_4\text{H}_9^+$. Kinetically, on the other hand, it has been found that *tert*-butyl bromide¹⁰ solvolyzes $\sim 10^3$ times faster than 1-bromoadamantane.¹¹

The hydride-transfer equilibrium can be first compared with an estimate of the bromide-transfer equilibrium deduced from measurements of the heat of solution of *tert*-butyl bromide and 1-bromoadamantane, AdBr , in HSO_3F ,^{8a}



The equilibrium in general would be expected to be very similar to the hydride-transfer value as long as the bromide ion does not introduce strain or localized hydrogen-bonding interactions in one of the organic halides, and as long as the extent of solvation of the ions was comparable in the different acids.

The data in Table II show that there is in fact a great similarity in the equilibria. There is however a large difference between all the solution values and a gas phase, ion cyclotron resonance measurement which suggests the equilibrium is far on the side of the Ad^+ ion.

These differences are the basis of a scale which can be proposed to characterize the ability of aprotic media to stabilize cations. The scale arises because the planar *tert*-butyl ion can be solvated on both sides by overlap of its empty p orbital with nucleophilic donors while the bridgehead 1-adamantyl ion can only interact with solvent on its exposed apex.

In the gas phase there is no intermolecular solvation to affect the relative stability of ions, but in solution there must be. So called superacids which enable the NMR observation of cations must "solvate" to a lesser degree than solvents conventionally used in solvolysis studies such as 80% ethanol. Hence one anticipates a substantial shift in equilibria from that estimated for the fully solvated ions that ought to be generated during solvolysis to the unsolvated ions in the gas phase.

The free-energy change due to solvation is about 15 kcal/mol with ΔG being estimated as +4 from solvolysis and about -11 from the ICR data with 1-bromo-adamantane.

According to this scale the ability of the 1 M acid solutions in Table II to stabilize cations increases in the order $\text{AlBr}_3/\text{CH}_2\text{Br}_2 = \text{GaCl}_3/\text{CH}_2\text{Cl}_2 < \text{AlBr}_3/\text{SO}_2\text{FCl} < \text{AlBr}_3/\text{CH}_2\text{Cl}_2$

The position of the methylcyclopentane equilibrium favors the MCP^+ ion, but by <2 kcal. This is somewhat lower than would be expected based on solvolysis studies,⁹ which indicate that the transition state reached during the solvolysis of 1-chloromethylcyclopentane is 4 kcal/mol lower than for 1-chloromethylcyclohexane (i.e., the relief of strain accelerates the ionization process). However, the present study is concerned with the position of equilibrium in solution and if the methylcyclopentyl ion is in a tight ion pair or strongly solvated, some strain energy would

(9) H. C. Brown and M. Berkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

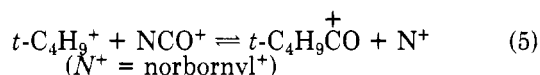
(10) (a) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957).

(11) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970).

likely be reintroduced. In any case, there is no theoretical reason for the position of equilibrium to necessarily reflect the position of the transition state in solvolytic studies.

The norbornyl cation appears to be slightly less stable than the *tert*-butyl ion in the solution equilibria. The data agree well with estimates based on heats of solution of the bromides but differ from the mass spectroscopic results in which the norbornyl ion appears to be more stable. Either in solution or in the gas phase, however, it is evident that the norbornyl ion is considerably more stable than an open-chain secondary C₇⁺ cation might be expected to be.

The equilibrium results do not address the question of the structure of the norbornyl cation. They are, however, in accord with other indications of ion stability such as obtained from carbonylation equilibria. Thus we estimate the free-energy change in reaction 5 to be +1.6 kcal/mol from the data of Hogeveen, Baardman, and Roobeek.¹²



This is in excellent accord with the values of +0.7 in AlBr₃/CH₂Cl₂ and +1.2 in AlBr₃/SO₂FCl.

Summary

Four new low-temperature acid systems have been found that can stabilize high concentrations of tertiary alkyl

(12) H. Hogeveen, F. Baardman, and C. F. Roobeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 227 (1970).

cations. These are AlBr₃/CH₂Cl₂, AlBr₃/CH₂Br₂, GaCl₃/CH₂Cl₂, and GaCl₃/1,2-Cl₂C₂H₄.

Solutions (1 M) of the Lewis acids generally are able to stabilize up to 0.5 M solutions of *t*-C₄H₉⁺ below ca -30 °C. NMR studies indicate that AlBr₃ forms an R⁺Al₂Br₆X⁻ salt while GaCl₃ appears to form both R⁺Ga₂Cl₇⁻ and R⁺GaCl₄⁻ salts. When RX/acid is >1:2, small amounts of side products tend to form, the least in the mixed halide AlBr₃/CH₂Cl₂ system.

The carbonium ions generally participate in intermolecular hydride and halide exchange processes, and the former were studied. Equilibrium measurements with large tertiary hydrocarbons generally show that they ionize more easily than isobutane. The equilibria in solution are usually more thermoneutral than in the vapor phase, and agree well with other estimates that can be made from heats of solution of bromides and equilibrium carbonylation studies.

In some cases the equilibria are widely different from what might be inferred from the kinetics of solvolytic processes. This is not much of a surprise but reinforces the fact that solvolysis rates be used with care in estimating equilibrium properties. The differences found with the *tert*-butyl/adamantyl system are suggested to be due to differences in solvating the open and bridgehead ions and these have been used to establish a scale to measure the ion stabilizing capabilities of superacid media.

Registry No. *i*-C₅, 78-78-4; 2,3-DMC₄, 79-29-8; 2,2,3-TMC₄, 464-06-2; 2,4-DMC₅, 108-08-7; MCyC₅, 96-37-7; adamantane, 281-23-2; norbornane, 279-23-2; *tert*-butylcarbonium ion, 14804-25-2; AlBr₃, 7727-15-3; CH₂Cl₂, 75-09-2; CH₂Br₂, 74-95-3; GaCl₃, 13450-90-3.

Organic Disulfides and Related Substances. 42. Synthesis and Properties of Some Tertiary Disulfides, Especially Involving Penicillamine¹

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Five approaches to the synthesis of unsymmetrical tertiary disulfides are illustrated. Penicillamine (1) was thioalkylated with acyclic (2, 4) and cyclic (6) thiosulfonates to give 3, 5, and 7. 5-(Dimethylamino)-1-naphthyl methoxycarbonyl disulfide hydrochloride (12), prepared from the arenesulfonyl chloride (dansyl chloride, 8) via the thiol (9), led to an impure disulfide with *N*-acetylpenicillamine (13) but to a pure one (17) with a more typical tertiary thiol; the thiol 9 fluoresced more strongly than 8, but the disulfides less so. In an alternative synthetic approach, 13 was used as its thionitrite (18) or thiosulfonate (22) to thioalkylate a typical primary thiol, reactions that may deserve attention for coupling penicillamine derivatives with protein SH. Several tertiary disulfides resist disproportionation for 24 h in water at 100 °C. When R of RSSCMe₂CH(NH₂)CO₂H was (CH₂)₂NH₃⁺Cl⁻, however, disproportionation atypically began much more rapidly (4 h) than for the amide (24 h), and when R was (CH₂)₄SO₂Na more rapidly still (1 h).

The chemistry of organic disulfides has been reviewed recently.² In previous studies of organic disulfides,^{1a} our attention to unsymmetrical tertiary disulfides has been relatively slight and usually in connection with general

interests.^{1a,3} Such disulfides are the focus of this paper, with emphasis on disulfides of penicillamine (1). Disulfides of 1 are especially interesting representatives of the tertiary class because of the biological and biomedical activities of 1,⁴ as well as because derivatives of 1 are unusual in forming an atypically stable sulfenyl iodide⁵ and thionitrite.⁶

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