Stabilities of Carbocations in Solution. 14. An Extended Thermochemical Scale of Carbocation Stabilities in a Common Superacid

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Abstract: Until now, thermodynamic stabilities of carbocations have been limited to (1) relatively stable resonance delocalized ions which are ranked on the pK_R scale and (2) relatively unstable aliphatic and alicyclic ions which have been compared in the gas phase by ion cyclotron resonance or by calorimetry in SbF_5/SO_2ClF superacid at −50 to −120 °C in our laboratory. The present paper will present an extensive series of new measurements which is designed to close the gap between the stable triarylmethyl cations and the unstable ions so as to put them all on a common energy scale. Carbinols were used as precursors in $SbF_5/HSO_3F/SO_2ClF$ at −40 °C. As we reported recently (*J. Am. Chem. Soc.*, **104**, 3522 (1982)), these conditions are necessary to avoid complications which appear to be introduced by ion-pairing when the alcohols are treated with the SbF_5/SO_2ClF system which was used previously to ionize alkyl chlorides. The results from the present work place 39 typical carbocations representing saturated, secondary, and tertiary, and aliphatic, bicyclic, and substituted cumyl, benzhydryl, and trityl systems on a common scale. Correlations and interpolation equations for relating other measurements in the gas phase and solution will be presented. The results provide useful comparisons of the σ^+ and σ^{C+} scales for correlating carbocation stabilities and provide new data for several classic questions in the field such as the ranking of methyl, phenyl, and cyclopropyl groups for stabilizing ions and also the reactions of carbocations with water.

Introduction

The basic rules for relating the structures of carbocations to their stabilities have been the conceptual key to understanding many areas of organic chemistry. Until recently, the only quantitative guide to thermodynamic stabilities lay in the indicator equilibrium studies based on applying the acidity function method to ionization of aryl carbinols in aqueous sulfuric acid solutions.[1-6] This method requires that the carbocations under study be kinetically stable on the time scale of the indicator study and also that they show appropriate spectroscopic evidence of ionization. These limitations rule out many kinds of ions, including aliphatic and alicyclic ones.

During the past decade much progress has been made in comparing thermodynamic stabilities of the simpler carbocations which were unapproachable by classical acidity function methods. Gas-phase ionization methods, most notably ion cyclotron resonance, have provided the energies for producing nearly 100 carbocations from neutral precursors such as alkyl halides of alkenes.[7-10] However, the gas-phase studies have been limited so far mostly to the aliphatic and alicyclic ions with virtually no overlap with the familiar carbinol–cation pK_{R^+} series.

Recently, we have developed thermochemical methods for measuring directly the heats of ionization of appropriate precursors to carbocations at low temperature in superacidic media where their structures and kinetic stabilities can be monitored by NMR.[11-16] Our original emphasis has been on the same types of saturated and relatively unstable ions which have been studied in the gas phase and which were previously unapproachable by acidity function methods. We have demonstrated remarkably consistent relationships between the heats of formation of many ions in several nonbasic solvents and in the gas phase. Furthermore, a surprisingly good correlation between these energies of ionization and free energies of activation for solvolysis of a series of alkyl, alicyclic, and aralkyl chlorides was found.

The present paper describes our efforts to extend the thermochemical method to determination of heats of formation of the stabler carbocations in order to provide the basis for a single stability scale in solution ranging from relatively unstable saturated secondary ions (e.g., isopropyl or cyclopentyl) to the more familiar triarylmethylcarbenium ions. If this were accomplished, future workers could use a scale to interpolate and include almost any ion whose ionization energy can be related directly or indirectly to the gas-phase scale, the pK_R scale, the thermochemical scales, or solvolysis rates.

One might suppose that measurement of the heats of formation of relatively stable carbocations in superacid would be easier than for the thermodynamically unstable ones. However, several new problems appeared. The most serious was related to the fact that the covalent chlorides of the stabler carbocations are difficult to prepare and handle in a pure state—the stabler the cation, the less stable is the chloride. Accordingly, we examined carbinols as more suitable precursors. Unfortunately, these precursors tend to have higher intermolecular forces than chlorides do and often dissolve poorly in the nonpolar solvents used for superacidic media. A worse problem, however, was the discovery that ionization *of alcohols* by SbF_5 is remarkably dependent on the solvent, a problem which had not arisen with the halides. A strong dependence on leaving group and solvent suggested that dissociation of the carbocation salts was variable and incomplete even though ^1H NMR spectra showed that quantitative ionization had occurred.[13]

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Table I. Comparison of Various Measures of Carbenium Ion Stability[a]

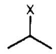
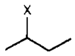
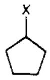
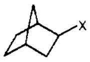
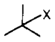
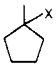
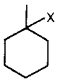
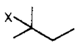
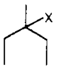
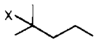
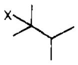
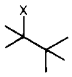
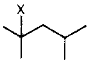
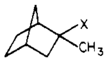
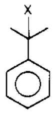
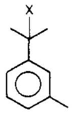
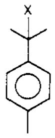
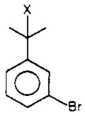
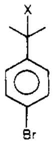
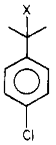
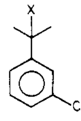
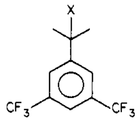
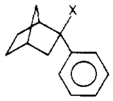
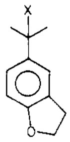
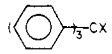
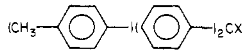
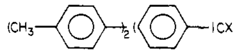
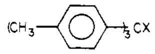
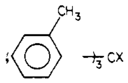
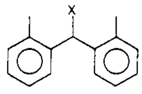
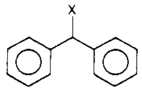
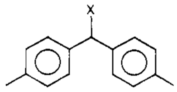
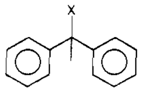
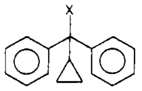
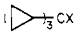
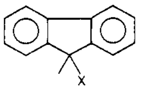
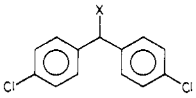
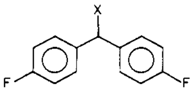
	precursor	σ^{C+}	1[c]	2[d]	3[e]	4[f]
			−15,3 ± 0,7		246,3	
			−15.9 ± 0,3		247	
			−17,3 ± 0,7		245,7	
			−21.6 ± 0.5	−31.0 ± 0,4		
			−23.6 ± 0.5	−34,6 ± 0,4	231.1	
			−24,8 ± 0.3	−35,5 ± 0,4	230.6	
			−27.1 ± 0,4	−38.3 ± 0.5	225.8	
			−26.9 ± 0,3	−37.8 ± 0.7	227.2	
			−27.1 ± 0.4	−40.3 ± 0.5	229.1	
			−27.9 ± 0.3	−36.7 ± 0.5	226.8	
			−27.1 ± 0.5		227,9	
			−27.1 ± 0.7		226.2	
			−26,9 ± 0,6		223.8	
			−28.5 ± 0,4		226.9	
			−31,0 ± 1,1	−37,1 ± 1.2	224,6	
			−30.3 ± 0.3	−40.3 ± 0.3	220	
−0.066		−0.13		−43,0 ± 1,3		
−0.311		−0.62	(−36.9)[b]	−46,3 ± 1.2		
+0.405		+0.33		−39.4 ± 0.9		
0.150		−0.19		−43,1 ± 0.8		
0.114		−0,24		−40.2 ± 0.6		

Table I (*Continued*)

	precursor	σ^{C^+}	1[c]	2[d]	3[e]	4[f]
0.52		0.56		−38.6 ± 0.5		
1.04		1.03		−31.9 ± 0.5		
			−37.0 ± 0.8			
−0.984		−2.4		−49.9 ± 1.2		
			(−38.0)[b]	−49.0 ± 1.3		−6.6
				−47.5 ± 0.5		−5.25
				−50.5 ± 0.5		−4.71
				−59.2 ± 1.1		−3.6
				−48.1 ± 0.7		−12.5
				−40.2 ± 0.7		−12.5
			(27.9)[b]	−39.3 ± 0.7		−13.3
				−41.9 ± 0.9		−10.4
				−37.5 ± 0.9		
				−44.3 ± 0.4		
				−59.2 ± 0.2		2.34
				−35.4 ± 0.4		−16.6
				−35.5 ± 0.5		
				−35.6 ± 0.8		−13.03

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[a] Column 2 represents heats of reactions ΔH_{rxn} for carbinol with acid system uncorrected for heat of solution of the carbinol in SO_2ClF (see text). All heat terms are in kcal/mol and reproducibilities are given at 95% confidence levels. [b] These values interpolated from a plot of data in column 1 vs. column 2. [c] Lewis acid, SbF_5; solvent, SO_2ClF; X = Cl. [d] Lewis acid, 1:1 SbF_5/FSO_3H; solvent, SO_2ClF; X = OH. [e] Lewis acid, HIA (hydride ion affinity); solvent, gas phase; X = none. [f] Lewis acid, pK_R; solvent, H_2SO_4; X = OH.

After considerable searching we have determined that ionization of the entire range of carbinols listed in Table I is complete using SbF_5/HSO_3F in SO_2ClF. This system then provides the means for developing a single thermochemical scale ranging from some of the least stable secondary alkyl ions to some of the most stable triarylmethyl ones. We shall present these results here and discuss the results briefly with respect to several classical questions in carbocation chemistry—the relation of carbocation stability to solvolysis rates and to substituent parameters, and ^{13}C NMR shifts and rates of reaction with water.

Experimental Section

Materials. Benzhydrol, bis(*p*-fluorophenyl)methanol, and bis(*p*-chlorophenyl)methanol were obtained from Aldrich and recrystallized from ethanol. Some of the triarylmethanols (*o*-CH_3, *p*-CH_3, *p,p'*-di-CH_3, *p,p',p'''*-tri-CH_3, and the unsubstituted triphenyl) were available from a previous study.[3] Tricyclopropylmethanol was prepared from dicyclopropyl ketone (Aldrich) and cyclopropylmagnesium bromide, bp 82–83 °C at 7.6 mm.[17] Bis(*p*-methylphenyl)- and bis(*o*-methylphenyl)methanol (mp 69–70 and 119–120 °C, respectively) were prepared from the appropriate methyl-substituted bromobenzene and the appropriate methyl-substituted benzaldehyde via standard Grignard reactions and recrystallized from ethanol. The synthesis of 9-methyl-9-fluorenol was carried out by the action of MeMgI on fluorenone;[18] the product was recrystallized from ethanol, mp 173–4 °C. The syntheses of all of the substituted *tert*-cumyl alcohols have been reported previously.[19,20] All physical properties agreed with those in the literature.

The synthesis of SO_2ClF was carried out by two methods: treatment of SO_2Cl_2 with either NaF in acetonitrile[21] or pyridinium poly(hydrofluoride).[22] The latter method was preferred since smaller amounts of chlorine were generated. The SO_2ClF, thus obtained, was refluxed over a small amount (~10 g) of SbF_5 and fractionally distilled. The purity was checked by gas chromatography (Poropack Q) and infrared spectroscopy.

As a further check on purity, the alcohols were converted to their respective carbocations in the 1:1 SbF_5/HSO_3F in SO_2ClF; their 60-MHz ^1H NMR spectra were obtained and compared with data published in the literature where possible. In all cases the spectra agreed with those published or gave spectra consistent with carbocation formation. It should be noted that the concentrations used in the NMR checks were ~100 times those used in measuring the heats of reaction.

Calorimetry. The apparatus and procedure are essentially the same as described previously,[11] with only minor improvements in the stirrer and ampoule-breaking[12] process having been made. For some of the compounds, most notably those which formed "glassy" solids upon cooling to −40 °C, a slower than usual reaction occurred, as indicated by the strip chart thermograms. This resulted in larger than normal standard deviations of the heats measured. In all cases, however, the 60-MHz ^1H NMR spectra of the carbocations in the superacidic media at higher concentration (vide supra) showed clean carbocation formation.

Results

Table I presents a complete listing of thermodynamic data for carbocation stabilities in four different media. Heats of ionization, ΔH_i, of chlorides in SbF_5/SO_2ClF at −55 °C are taken from ref 11 and 12. Heats of reaction, ΔH_{rxn}, of alcohols with $HSO_3F/SbF_5/SO_2ClF$ are the results of the present research. As stated in the Experimental Section, these heats of reaction have not been converted into heats of ionization, as were the chloride data in the first column, because of the poor solubility of the solid alcohols in SO_2ClF at low temperature and because all of the heats of solution which could be measured were negligibly small. We doubt if the error in accuracy from this source will exceed 2 kcal/mol, or 5%, for any of the data presented here. In most cases it should be less than 1 kcal/mol.

Gas-phase hydride ion abstraction values in the third column are taken either from ref 7 or references cited in ref 12. They correspond to reaction of the carbocation shown with a hydride ion. Numbers in the fourth column are pK_R values from ref 4 for equilibrium between the carbocation and the corresponding carbinol in aqueous sulfuric acid referred to a highly dilute solution of the solute in water at 25 °C as the standard state.

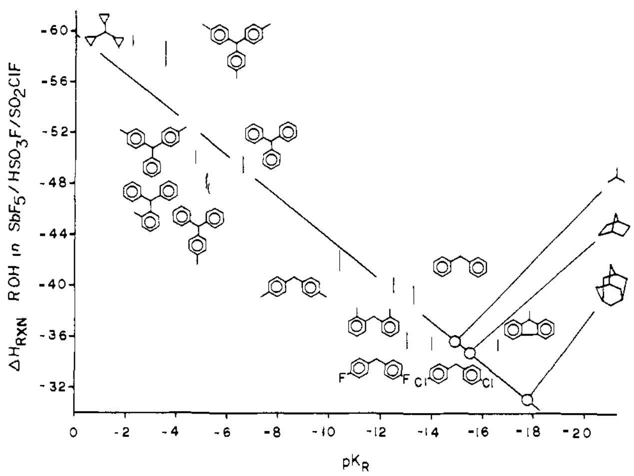

Figure 1. Correlation of heats of reaction. ΔH_{rxn} of various carbinols to produce charge-delocalized carbocations in $SbF_5/FSO_3H/SO_2ClF$ vs. pK_R's for equilibria of the same cations with their carbinols in aqueous H_2SO_4.[4,5] Error bars show the different precision for measuring ΔH_{rxn} compared to pK_R. Open circles represent interpolated pK_R's for *tert*-butyl, 2-norbornyl, and 1-adamantyl cations. Correlation equation, based on 12 points: $\Delta H_{rxn} = (-1.65pK_R - 59.8)$ kcal/mol ($r = 0.95$).

Correlation equations which may be used for interpolating new values from these results and others cited in the text are as follows. ΔH_{rxn} (ROH, $SbF_5/HSO_3F/SO_2ClF$) vs. ΔH_i(RCl, SbF_5/SO_2ClF); $r = 0.97$ for 9 points

$$\Delta H_{rxn} = 1.03(\Delta H_i) - 9.81 \tag{1}$$

ΔH_{rxn} vs. pK_R; $r = 0.95$ for 12 points

$$\Delta H_{rxn} = -1.65pK_R - 59.8 \tag{2}$$

ΔH_{rxn} vs. σ^+;[26] $r = 0.96$ for 9 points

$$\Delta H_{rxn} = 8.68\sigma^+ - 42.2 \tag{3}$$

ΔH_i vs. log *k* for ethanolysis of RCl at 25 °C;[11c] $r = 0.98$ for 10 points

$$\Delta H_i = 1.62 \log k_{solv} - 37.4 \tag{4}$$

ΔH_i vs. gas-phase hydride affinity HIA; $r = 0.97$ for 15 points

$$\Delta H_i = 0.600\text{HIA} - 163 \tag{5}$$

All ΔH values are expressed in kcal/mol.

Discussion

Table I presents the most complete listing which we can assemble at this time of thermochemical stability data for carbocations using heats of ionization of chlorides from previous work[11,12] and heats of ionization of alcohols in $SbF_5/HSO_3F/SO_2ClF$. Also listed are gas-phase ionization data[23,24] and pK_R's.[2-4] In the following discussion we shall consider graphical comparisons and correlation equations for relating these properties to each other and interpolating new values in the future. The new measurements presented here for the alcohols are a bridge linking previous measurements in the gas phase and SO_2ClF to conventional pK_R data. Unfortunately, the degree of ion pairing remains unknown for all of these systems and we have shown that it may be a very significant thermochemical factor in some cases.[13] In view of the good correlation between many of the present results and gas-phase values for which ion-pairing cannot be involved, we will assume, until confronted with evidence to the contrary, that differential

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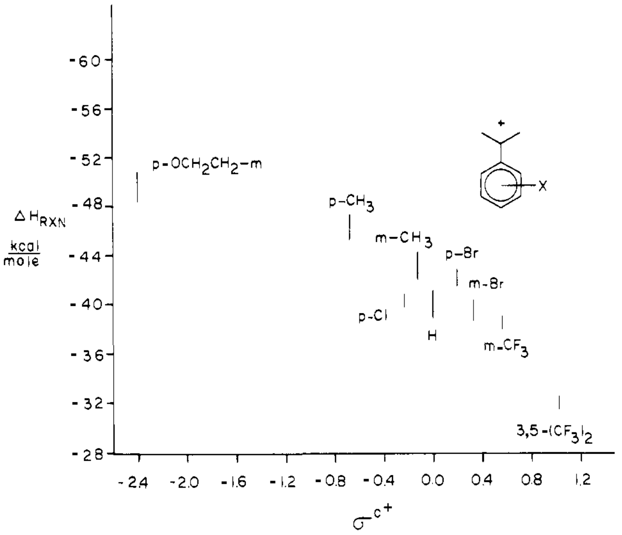


Figure 2. Correlation of ΔH_{rxn} of substituted *tert*-cumyl (and coumaranyl) alcohols with $SbF_5/FSO_{\Delta}H/SO_2ClF$ at −40 °C vs. σ^+ values for the same substituents.[26]

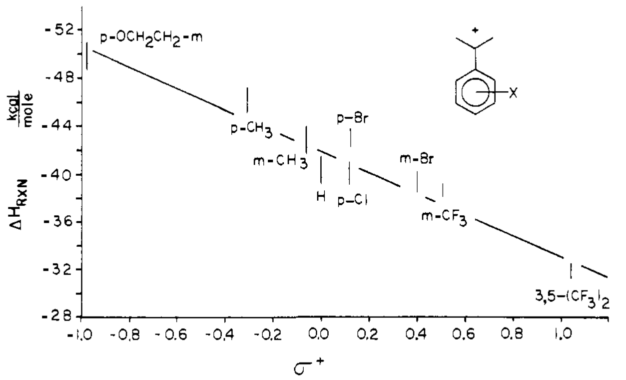


Figure 3. Correlation of ΔH_{rxn} of substituted *tert*-cumyl (and coumaranyl) alcohols in $SbF_5/FSO_2H/SO_2ClF$ at −40 °C vs. σ^{C^+} values for the same substituents.[19,20]

heats of association in the present system are small enough to be obscured within the experimental errors (±1 kcal/mol) for many of these heats of ionization.

Correlation with pK_R's and Substituent Constants. Figure 1 compares the effects of structural change on heats of ionization of carbinols in $SbF_5/HSO_3F/SO_3ClF$ at −40 °C with available pK_R's for the same compounds in aqueous sulfuric acids at 25 °C. The latter properties are convertible into standard free energies of ionization in water simply by multiplication by 1.36 (i.e., 2.303*RT*), a factor which compensates for half of the difference between the observed slope and unity. Considering that we are comparing different properties at widely different temperatures in media of drastically different types, there is no reason at all to expect a unit slope. We had hoped to populate this line more heavily but were thwarted repeatedly by poor solubility of the carbinols in SO_2ClF at −40 °C. Even when samples eventually dissolved, the process was often so slow that poor precision resulted from heat leaks and thermal drifts during the period of ionization in the calorimeter. Figure 1 provides a means for estimating the pK_R's for several cations derived from saturated alcohols. Although attempts have been made to observe *tert*-butyl cation in aqueous H_2SO_4,[4,25] they have all failed, apparently because of rapid polymerization. Again strong sulfuric acid oxidizes 1-adamantanol to adamantanone so there has been no means to tell directly whether or not this alcohol could be ionized significantly in aqueous acid in the absence of oxidation. Using ΔH_{rxn}'s for ionization of *tert*-butyl alcohol, 1-adamantanol, and 2-norbornanol, one may interpolate pK_R's which would be expected for their cations if they could be maintained in equilibrium with their alcohols in aqueous acid. This relationship predicts that all three alcohols should be half-ionized within the range of *85* to *98%* aqueous sulfuric acid if escape through other channels would be prevented.

Using the correlation equation for Figure 1, we estimate hypothetical pK_R's for *tert*-butyl cation = −14.7, 2-norbornyl = −15.3, and 1-adamantyl = −17.5.

Substituent Constants. Figures 2 and 3 compare ΔH_{rxn} with *meta*- and *para*-substituent constants derived from solvolysis of cumyl chlorides, σ^+,[26] or ^{13}C NMR chemical shifts at the cationic carbon, σ^{C^+}.[27] Obviously, a better linear fit is obtained using σ^+ even if the heavily weighted point for the coumaranyl ion is disregarded. The question of how best to interpret ^{13}C chemical shifts in terms of charge delocalization is presently controversial,[27,28] but has no direct relation to our results. We simply note that σ^+ is a reaction constant derived from the free-energy changes for converting the *tert*-cumyl chlorides to their solvolysis transition states in 90% aqueous acetone. It seems only reasonable that such energy terms would correlate better with enthalpies of reaction, ΔH_{rxn}, than do chemical shifts σ^{C^+} which refer to a ground-state property of the ions alone.[28]

It is interesting to compare the response of substitution on the *tert*-cumyl nucleus for activation to a solvolysis transition state in ethanol with that for the various aliphatic and alicyclic cations (which we examined previously[11c]) in terms of charge development. A plot of the free energies of activation for chloride solvolysis in ethanol at 25 °C vs. ΔH_i for the same chlorides in SbF_5/SO_2ClF at −55 °C gave a slope of 0.89[11c] which may be taken as the percent of charge development toward a fully formed ion or ion pair in the ethanolysis transition state.

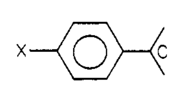
For the substituted *tert*-cumyl compounds listed in Table I, a correlation with σ^+,[26] for solvolysis (Figure 2) yields the equation

$$\Delta H_{rxn} = 8.68\sigma^+ - 42.2$$

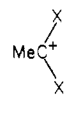
with $r = 0.96$ for 9 points.

A factor of 4.67 is required to convert σ^+ to $\log k/k_H$ in ethanol,[26] and 1.36 is required to convert this log ratio to relative free energies of activation. Dividing by 6.35 (4.67 × 1.36) brings the correlation slope to 1.37 so that the demand on substituents for reaching the solvolysis transition state is about 75% that required for ionization of the *tert*-cumyl alcohols in $SbF_5/HSO_3F/SO_2ClF$. In view of the many interpolations required to compare the two sets of numbers and the differences in leaving group and superacid media, we believe that there is reasonable agreement concerning the degree of ionization required for limiting solvolysis and that interpretation of the modest difference (75 vs. 89%) is inappropriate.

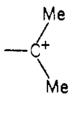
Effects of Cyclopropyl, Phenyl, Methyl, and Hydrogen Substituents. Table I shows that within the series X_3C^+ the effect of these four groups on the driving force to produce the trisubstituted cation is cyclopropyl > phenyl > methyl >> hydrogen (obviously, not shown) in agreement with many other studies using pK_R's of these carbinols,[4] solvolysis of the *para*-substituted *tert*-cumyl chlorides[26]



and also formation of the ions in the gas phase by protonation


$\mathrm{MeC^{+}X_2}$

and


$\mathrm{-C^{+}Me_2}$

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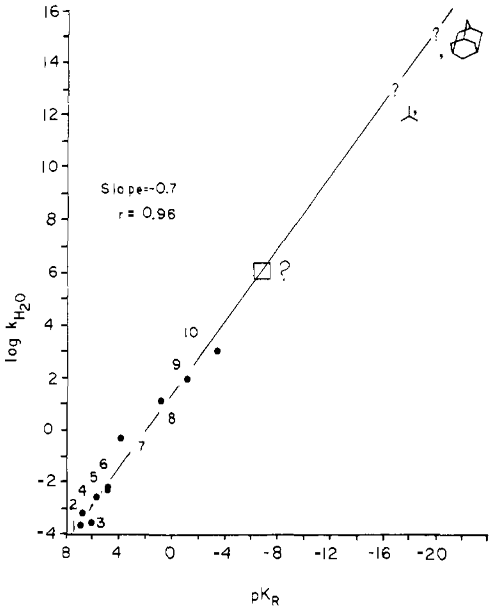

Figure 4. Correlation and extrapolation for the hydrolysis reaction of carbocations with water vs. their measured or interpolated (Figure 1) hydrolysis equilibria in aqueous H_2SO_4 (pK_R). Numbers correspond to trityl cations with following substituents: (1) (p-DMA)$_2$, (2) (p-NO$_2$)(p-DMA)$_2$, (3) (p-CF$_3$)(p-DMA)$_2$, (4) (p-OCH$_3$)$_2$(p-DMA), (5) (p-OCH$_3$)(p-DMA)$_2$, (6) (p-CH$_3$)(p-DMA), (7) (p-O-di-OCH$_3$)$_3$, (8) (p-OCH$_3$)$_3$, (9) (p-OCH$_3$)$_2$, (10) (p-OCH$_3$). DMA = dimethylamino, □ is interpolated position for unsubstituted trityl cation; see text.

of the olefins.[23] In contrast the order phenyl > cyclopropyl > hydrogen > methyl is seen in Table I for creating the $(C_6H_5)_2C^+$–X ions from the alcohols in $SbF_5/HSO_3F/SO_2Cl_2$ at −40 °C. This is, to the best of our knowledge, the first time this order has been seen for tertiary carbocations. The phenyl > cyclopropyl > methyl > hydrogen order has been seen many times for the ^{13}C spectra of carbocations and a carbocation such as protonated ketones[28,29] where the shifts may be related more directly to charge delocalization without reference to contributions of electronic, steric, or solvation factors from the initial state. Olah[28] and Sommer[29] both emphasize that no simple order of phenyl vs. cyclopropyl may be expected to hold for delocalizing effects in carbocations of widely varied types. In fact, for producing the following types of ions from alkene, ketone, or ester precursors by proton transfer in the gas phase, the order is phenyl > cyclopropyl > methyl > hydrogen.[23,24] Larsen, Bouis, and Riddle[30] examined a variety of results for the energetics of creating different types of carbocations in strong acids and noted a persistent order of methyl > phenyl. After considerable discussion of possible reasons for this order (which is the reverse of that expected on the grounds of charge stabilization by delocalization) they concluded that inductive withdrawal by phenyl or ion solvation factors might be responsible. The ICR results[24] cited above, which clearly place phenyl > methyl for gas-phase protonation of ketones and esters, decide the issue definitively in favor of solvation. However, the resolution of this problem merely raises the new question of why the phenyl group is relatively more effective than methyl in the gas phase but less so in solution. We propose the fairly obvious (but somewhat tautological) answer that the greater polarizability of the phenyl group is called into play in the gas phase, but solvent polarization reduces demand on it in solution.

Whatever else may be said, our results and those reviewed above emphasize the utter failure of any regular order for the effects of these groups. Clearly, inversions representing large energy changes are produced by changing the type of cation to which the group is attached, the process being observed, and the medium surrounding the ion. The effects are large enough to provide a delightful challenge to theoretical chemistry.

Rates of Reaction with Water. A frequent consideration in the enormous literature on solvolysis is the rate of reaction of various putative carbocation intermediates with water. Taft[31] and Ritchie[32] and their co-workers were able to measure directly the rates of nucleophilic attack of water on a number of para-substituted triarylmethyl cations over a range of 10^8, well into the stopped-flow region. A linear relation (with some dispersion into families[31]) was found for a plot of log k_{H_2O} vs. pK_R. If we use the estimates for pK_R of *tert*-butyl, adamantyl, or 2-norbornyl cations from Figure 1, estimates of hydrolysis rates for these ions can be made. Figure 4 suggests rates far above the usual diffusion-controlled level of 10^{10}–10^{11} if a linear extropolation is used. Alternatively, points 7–10 suggest either a line or curve which would place the *tert*-butyl and adamantyl points closer to the diffusion-controlled limit. By either extrapolation the mechanism for hydrolysis of the unstable aliphatic ions may be expected to differ from the long-lived triarylmethyl ones. Jencks[33] has proposed that solvolysis mechanisms for very unstable intermediates may be "enforced" by involvement of properly oriented solvent molecules; more specifically, he suggests that the *tert*-butyl cation may be too unstable to exist as a diffusionally equilibrated "free" ion in the presence of a nucleophilic solvent.[34] Taken at face value, Figure 4 lends strong support to this view. The positions of *tert*-butyl and adamantyl cations on this plot are derived from their thermodynamic properties for complete ionization in superacids. We would consider that if, in fact, these ions are truly intermediates during hydrolysis, rather than transition states, then they must be stabilized either by close proximity of the counterion leaving group, polarization of the attacking nucleophilic water molecule, intense polarization of the entire nearby solvent shell, or, more probably, all three. In any event, Figure 4 makes the existence of anything like a free *tert*-butyl cation in water seem quite improbable.

This interpretation of Figure 4 also supports a suggestion of Rappoport's[35] which harmonizes the well-known failure of the reactivity–selectivity principle (RSP) when applied to nucleophilic attack on stable carbocations with its successful application to competitive capture of solvolytically generated cations by azide ion and water. If the stable cations react with similar selectivity toward N_3^- and water, the Ritchie N_+ relationship is found. If unstable ions react at a constant diffusion-controlled rate with N_3^- and then follow Hammond postulate behavior in their reaction with water, RSP behavior will be produced. Rappoport estimates a k_{H_2O} = 10^6 − 10^7 for trityl cation; based on this reasoning, it should lie on the extrapolation line in Figure 4 based on its pK_R = −6.6.

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Registry No. Tricyclo[3.3.1.1^{3,7}]decan-1-ol, 768-95-6; bicyclo[2.2.1]heptan-2-ol, 1632-68-4; 2-methyl-2-propanol, 75-65-0; 1-methyl-1-cyclopentanol, 1462-03-9; 1-methyl-1-cyclohexanol, 590-67-0; 2-methyl-2-butanol, 75-85-4; 3-methyl-3-pentanol, 77-74-7; 2-methylbicyclo[2.2.1]heptan-2-ol, 5240-73-3; α,α-dimethylbenzenemethanol, 617-94-7; α,α,3-trimethylbenzenemethanol, 5208-37-7; α,α,4-trimethylbenzenemethanol, 1197-01-9; 3-bromo-α,α-dimethylbenzenemethanol, 30951-66-7; 4-bromo-α,α-dimethylbenzenemethanol, 2077-19-2; 4-chloro-α,α-dimethylbenzenemethanol, 1989-25-9; α,α-dimethyl-3-(trifluoromethyl)benzenemethanol, 618-11-1; α,α-dimethyl-3,5-bis(trifluoromethyl)benzenemethanol, 67570-38-1; 2,3-dihydro-α,α-dimethyl-5-benzofuranmethanol, 82954-97-0; triphenylmethanol, 76-84-6; (p-methylphenyl)diphenylmethanol, 5440-76-6; bis(p-methylphenyl)phenylmethanol, 6266-56-4; tris(p-methylphenyl)methanol, 3247-00-5;

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tris(*o*-methylphenyl)methanol, 6922-86-7; bis(*o*-methylphenyl)methanol, 2845-91-2; diphenylmethanol, 91-01-0; bis(*p*-methylphenyl)methanol, 885-77-8; 1,1-diphenyl-1-ethanol, 599-67-7; α,α-diphenylcyclopropanemethanol, 5785-66-0; α,α-dicyclopropylcyclopropanemethanol, 23719-88-2; 9-methyl-9-fluorenol, 6311-22-4; bis(*p*-chlorophenyl)methanol, 90-97-1; bis(*p*-fluorophenyl)methanol, 365-24-2; tricyclo[3.3.1.1^{3,7}]dec-1-ylium, 19740-18-2; bicyclo[2.2.1]hept-2-ylium, 24321-81-1; 1,1-dimethylethylium, 14804-25-2; 1-methylcyclopentylium, 17106-22-8; 1-methylcyclohexylium, 26378-05-2; 1,1-dimethylpropylium, 17603-15-5; 1-ethyl-1-methylpropylium, 17603-16-6; 2-methylbicyclo[2.2.1]hept-2-ylium, 3197-78-2; 1-methyl-1-phenylethylium, 16804-70-9; 1-methyl-1-(3-methylphenyl)ethylium, 20605-65-6; 1-methyl-1-(4-methylphenyl)ethylium, 20605-66-7; 1-(3-bromophenyl)-1-methylethylium, 77826-66-5; 1-(4-bromophenyl)-1-methylethylium, 67595-62-4; 1-(4-chlorophenyl)-1-methylethylium, 41912-29-2; 1-methyl-1-[3-(trifluoromethyl)phenyl]ethylium, 77826-67-6; 1-[3,5-bis(trifluoromethyl)phenyl]-1-methylethylium, 67595-63-5; 1-(2,3-dihydrobenzofuran-5-yl)-1-methylethylium, 82955-09-7; triphenylmethylium, 13948-08-8; (4-methylphenyl)diphenylmethylium, 13947-74-5; bis(4-methylphenyl)phenylmethylium, 34073-85-3; tris(4-methylphenyl)methylium, 14039-17-9; tris(2-methylphenyl)methylium, 84988-00-1; bis(2-methylphenyl)methylium, 84988-01-2; diphenylmethylium, 709-82-0; bis(4-methylphenyl)methylium, 58493-75-7; 1,1-diphenylethylium, 16805-85-9; cyclopropyldiphenylmethylium, 38252-94-7; tricyclopropylmethylium, 25940-78-7; 9-methylfluoren-9-ylium, 20685-25-0; bis(4-chlorophenyl)methylium, 15876-05-8; bis(4-fluorophenyl)methylium, 39769-55-6.

Communications to the Editor

Molecular Structure of Silicon Dichloride and Silicon Dibromide from Electron Diffraction Combined with Mass Spectrometry

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Direct information on the structure and reactivity of carbene analogues and their derivatives is of great importance.[1,2] Experimental determination of the molecular structure of the carbene analogues is usually hindered, however, by their high reactivity and polymerization at ordinary temperatures. The recently developed combined electron diffraction/mass spectrometric technique with a high-temperature reactor nozzle system[3,4] has opened new possibilities in this respect. Recently, the molecular structures of germanium dichloride[4] and germanium dibromide[5] have been communicated. On the basis of available experimental structural data, the geometries for several other carbene analogues have been predicted,[5] among them silicon dichloride and silicon dibromide. Here we report the molecular structures of these two molecules.

Parallel quadrupole mass spectrometric and electron diffraction experiments were carried out on the products of the reactions.

$$\mathrm{Si(solid)} + \mathrm{Si_2Cl_6(gas)} \rightarrow \mathrm{SiCl_2(gas)}$$

$$\mathrm{Si(solid)} + \mathrm{SiBr_4(gas)} \rightarrow \mathrm{SiBr_2(gas)}$$

The former reaction has been found to produce higher $SiCl_2$ yield than the reduction of $SiCl_4$ with Si. The optimum experimental conditions were reached in both cases at a temperature of about 1200 °C of the molybdenum reactor nozzle.[3,4] The other experimental conditions as well as the data treatment were similar to those employed earlier.[4,5] The molecular intensities and radial distributions are presented in Figures 1–4. The two principal maxima on the radial distribution curves correspond to the silicon–halogen and halogen–halogen contributions. The experimental data on silicon dibromide could be well approximated by $SiBr_2$ species only. The somewhat poorer agreement for silicon dichloride necessitated that the possible presence of other species also be considered, viz., Si_2Cl_6, $SiCl_4$, and Si_2Cl_4. Some improvement in the agreement with reasonable structural implications could be achieved by supposing a small amount of Si_2Cl_4 species, The molecular parameters obtained from the electron diffraction analysis are presented in Table I. The Cl–Si–Cl angle is in good

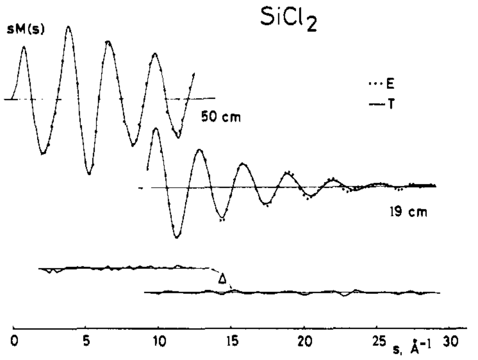

Figure 1. Experimental (E) and theoretical (T; cf. Table I) molecular intensities and their differences for silicon dichloride; 50 and 19 cm are the two camera ranges.

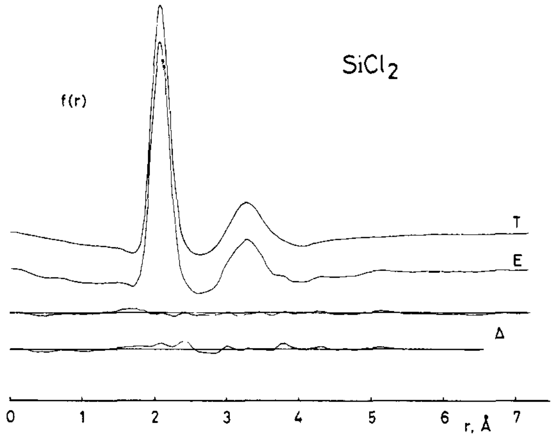

Figure 2. Experimental (E) and theoretical (T) radial distributions and difference curves for silicon dichloride. The first three curves correspond to those in Figure 1. The lower difference curve refers to a model with $SiCl_2$ monomeric species only.

[†] Hungarian Academy of Sciences.

[‡] Academy of Sciences of the USSR.

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