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Kinetics and Equilibria of Chloride Transfer Reactions. Stabilities of Carbocations Based on Chloride and Hydride Transfer Equilibria Measurements

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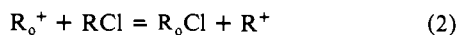
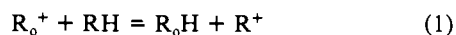
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Abstract: The kinetics of a number of gas-phase chloride transfer reactions $R_o^+ + RCl = R_oCl + R^+$ were measured with a pulsed electron high pressure mass spectrometer. Most of the reactions were found to occur near the collision limit, i.e., with rate constants $k \approx 10^{-9}$ molecules $^{-1}$ cm 3 s $^{-1}$. However, several reactions were much slower and were exhibiting negative temperature dependence, i.e., decreasing rate with increasing temperature. Hydride and chloride transfer equilibria were determined for various carbocations R^+ (R = isopropyl, cyclopentyl, *tert*-butyl, 1-methylcyclopentyl, substituted benzyls, norbornyl, 2-methyl-2-norbornyl, and adamantyl). Excellent agreement with earlier hydride transfer measurements of Solomon, Meot-Ner, and Field were observed. The chloride affinities generally support conclusions based on the hydride transfer data. Discussion of the data in connection with benzyl cation substituent effects, the norbornyl cation stability, and solvent effects on carbocation stability is presented. The data show that the 2-norbornyl cation is unusually stable. Significant differences between carbocation R^+ stabilities in gas phase and solution are found which suggest that both differential nucleophilic solvent stabilization and differential nonspecific solvation occur in solution.

Ion-molecule equilibria measurements in the gas phase¹ have become a prolific source of ion thermochemical data. For example, proton-transfer equilibria have provided gas-phase acidities, basicities, and associated ionic heats of formation for many hundreds of compounds.^{1,2}

Carbocation thermochemical data have been obtained from proton-transfer equilibria.^{2,3} For example, alkyl cations can be produced by protonation of the corresponding olefin (i.e., *t*-Bu⁺ from isobutene). However, some carbocations like benzyl⁺ cannot be obtained by this route. Also, often, proton-transfer equilibria involving olefins and polyunsaturates are accompanied by side reactions, like addition of the cations to the double bonds, which complicate the measurements.

The hydride transfer equilibria I represent another route to the carbocations.



Comprehensive studies of hydride-transfer kinetics and hydride-transfer equilibria have been performed by Meot-Ner, Field,

and co-workers.^{4,5} Hydride-transfer reactions are often quite slow. Meot-Ner and Field⁴ showed that the slow reactions have negative temperature dependence, i.e., the rate constants increase with temperature decrease, reaching the limiting collision rate at some low temperature. The exact cause for the negative temperature dependence of the hydride-transfer reactions has not been established.^{4,6} In spite of the slowness of hydride-transfer reactions, conditions for measurement of hydride-transfer equilibria could be established and thermochemical data for many carbocations of interest were obtained.⁵

The present work repeats some of the hydride equilibria measurements of Meot-Ner and Field.⁵ However, the major part is a study of the kinetics and equilibria of chloride-transfer reaction 2. The primary interest is in examining the usefulness of the chloride equilibria for the generation of carbocation thermochemical data and providing new data on the stability of carbocations. Chloride transfer has some advantages over hydride transfer. The position of reactive attack is well defined, while in hydride transfer to the position of the most reactive hydrogen has to be inferred from the chemical structure of RH. Also, chloride-transfer reactions are known⁷ to be generally much faster

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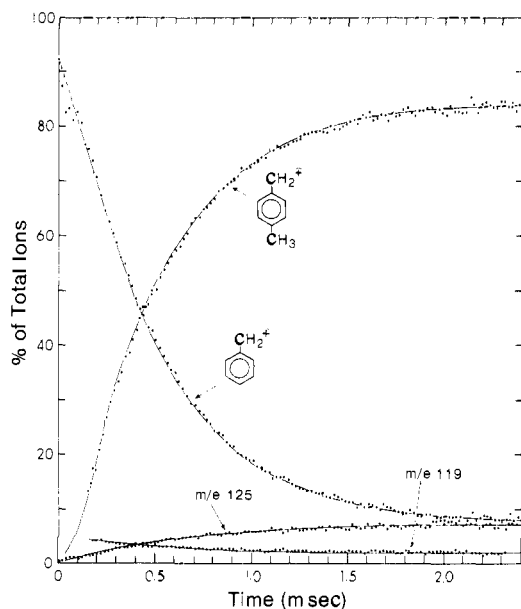


Figure 1. Time dependence of ion concentrations after the ionizing electron pulse. Decrease of benzyl⁺ and concomitant increase of *p*-methylbenzyl⁺ is due to the following chloride transfer reaction: $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{Cl} + \text{C}_6\text{H}_5\text{CH}_2^+ = p\text{-MeC}_6\text{H}_4\text{CH}_2^+ + \text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. Hydride abstraction by benzyl⁺ from benzyl chloride occurs also, and leads to $\text{C}_6\text{H}_5\text{CHCl}^+$ of mass 125. The rate constant for the hydride-transfer reaction is about 400 times smaller. Pressures: CH_4 , 4 torr (bath gas); benzyl chloride, 3.3 mtorr; α -chloro-*p*-xylene, 0.09 mtorr. Temperature = 302 °C. Duration of electron pulse = 15 μs .

than the corresponding hydride-transfer reactions and a faster approach to the equilibrium is desirable in the measurements. Measurements in the condensed phase practically never involve hydride removal, while chloride removal is quite common and Cl^- is closer to other leaving groups used in solution. It should be noted that hydride- (eq 1) and chloride- (eq 2) transfer energies are similar but not identical. One disadvantage of the chloride-transfer measurements is the much greater scarcity of $\Delta H_f(\text{RCl})$ data as compared to $\Delta H_f(\text{RH})$. The unavailability of RCl heats of formation particularly for the gas phase precludes the evaluation of the corresponding $\Delta H_f(\text{R}^+)$ from the ΔH_2 values.

Some understanding of the chloride-transfer kinetics was desirable for the successful execution of the equilibria measurements. The study of the chloride kinetics also is interesting from the standpoint of ion-molecule kinetics theory. For example, it is significant that the formally similar hydride- and chloride-transfer reactions should have such different rates. The question also arises whether all exothermic chloride transfer reactions proceed at collision rate and, if not, what properties of the reactants lead to low collision efficiencies?

The presentation of the results and discussion is organized as follows. The kinetic findings are in section a. This section is addressed primarily to gas-phase ion chemists. Section b deals with the actual equilibria measurements, and section c deals with the thermochemistry obtained from the hydride- and chloride-transfer measurements. The data obtained are of significance in these areas: substituent effects on the stability of benzyl cations (section d), stability of the norbornyl and methylnorbornyl cation (section e), and solvent effects on the stabilities of carbocations (section f).

Experimental Section

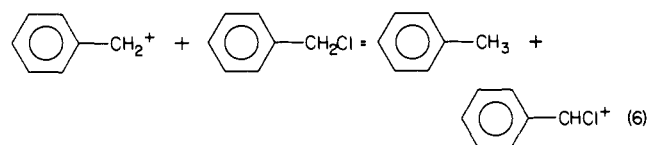
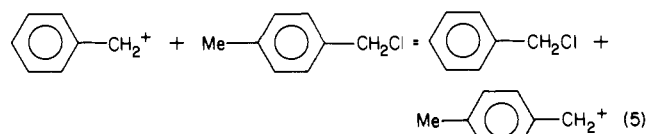
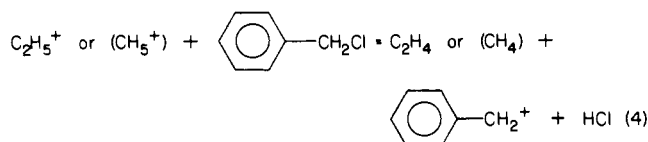
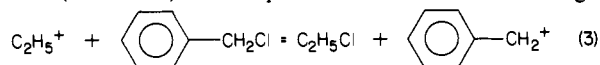
The measurements were performed with a pulsed electron beam high pressure mass spectrometer which was used in earlier work⁸ and has been described previously.⁹ The concentration conditions used will be de-

scribed in the subsequent section since their choice relates to the kinetics that were encountered.

Most of the compounds were purchased commercially and used as is. Checks of purity were made for the isomeric *o*-, *m*-, *p*-fluoro- and -chlorobenzyl chlorides. The meta compounds, which have the highest chloride affinities, contained some para and ortho impurities. The affinities quoted in the subsequent text were corrected for the presence of these impurities. We are indebted to Professor H. C. Brown for supplying us with samples of the norbornyl chlorides and Professor E. M. Arnett for a sample of 1-adamantyl chloride.

Results and Discussion

(a) Chloride Transfer Reaction Kinetics. The reactions occurring in a typical chloride-transfer experiment can be deduced from the time dependence of the observed ions⁹ (see Figure 1). Following the short electron pulse, rapid reactions in the major (bath) gas methane produce CH_5^+ and C_2H_5^+ as the two dominant reagent ions.⁸ These react very rapidly with the major component, benzyl chloride, producing almost exclusively the benzyl cation. Probably, chloride transfer (reaction 3) and dissociative proton transfer (reaction 4) are the processes involved. The changes



observed in Figure 1 show the decrease of the benzyl cation and the concomitant increase of the *p*-MePhCH₂⁺ due to the chloride transfer (reaction 5) which is the reaction that is to be studied. This chloride transfer is much slower than reaction 3 because of the much lower concentration of xylyl chloride relative to benzyl chloride. Reaction 5 is the dominant process observed in Figure 1.

The reaction frequency (pseudo-first-order rate constant) $\nu = kn$ for reaction 5 can be determined by plotting the logarithm of the reactant ion intensity (benzyl⁺), taken from Figure 1, vs. time, and the slope of such a plot should equal $\nu = kn$ where n is the concentration of the reactant neutral (*p*-xylyl chloride) present in vast excess over the reactant ion. Such plots are shown in Figure 2A, which includes the Figure 1 result and other determinations at the same temperature and different neutral reactant concentrations n . Good straight lines are observed. Plotting the ν_5 vs. the known n one obtains a straight line whose slope equals k_5 at the given reaction temperature (Figure 2B). Applying the same procedure at different temperatures one obtains the temperature dependence of k_5 . A plot of k_5 values vs. temperature is shown in Figure 3. The observed rate constants are close the collision limit k_{ADO} predicted by the average dipole orientation theory (ADO).¹¹ A small negative temperature dependence is observed.

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(10) Expressing the ions in percent of the total ions as in Figure 1 removes the effect of ion loss due to diffusion of the ions to the wall of the ion source. This plot would correspond to the reactive concentration changes provided that all ion diffusion coefficients were the same. This is approximately true when the observed ions are of similar mass.

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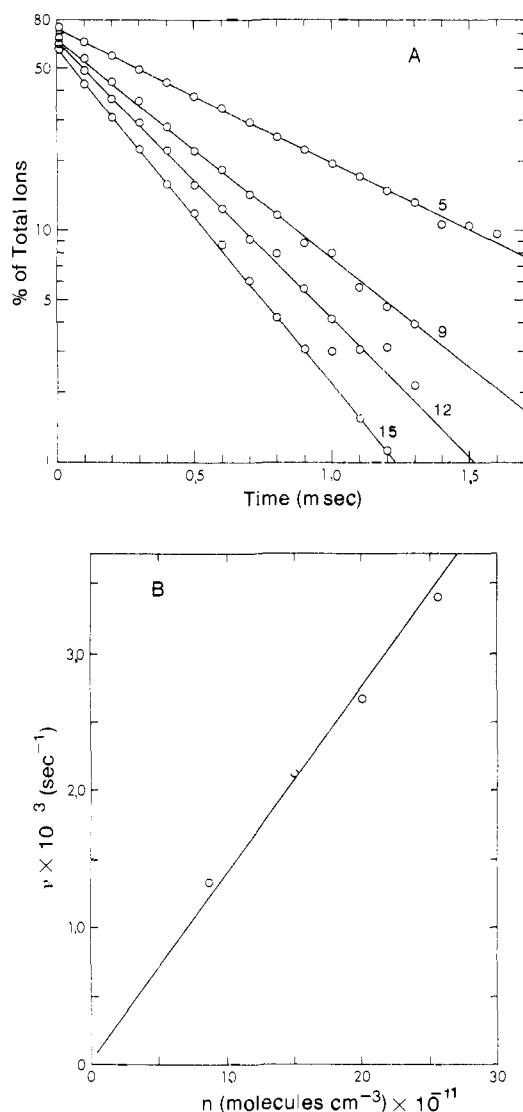


Figure 2. (A) Log plot of normalized ion intensity of benzyl⁺ vs. time in a reaction system like that shown in Figure 1 but at different concentrations n of the neutral reagent $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{Cl}$. Slope $\nu = kn$, where ν is pseudo-first-order rate constant. Numbers beside lines equal the pressure of neutral reagent $\times 10^5$ torr. (B) Plot of ν from part A vs. n . The slope equals the rate constant k (302 °C).

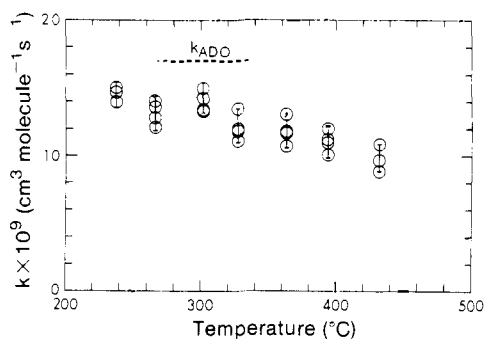


Figure 3. Temperature dependence of rate constant for the following chloride-transfer reaction: $\text{C}_6\text{H}_5\text{CH}_2^+ + p\text{-MeC}_6\text{H}_4\text{CH}_2\text{Cl} = \text{C}_6\text{H}_5\text{Cl} + p\text{-MeC}_6\text{H}_4\text{CH}_2^+$. The rate constant is close to the collision rate k_{ADO} . A weak negative temperature dependence is observed for the experimental rate constant.

This is somewhat larger than that predicted by the ADO theory. While the measured decrease of k with temperature is probably real, it should be noted that the method used (normalized ion intensities¹⁰) is not too well suited for determinations of very small changes of k with temperature.

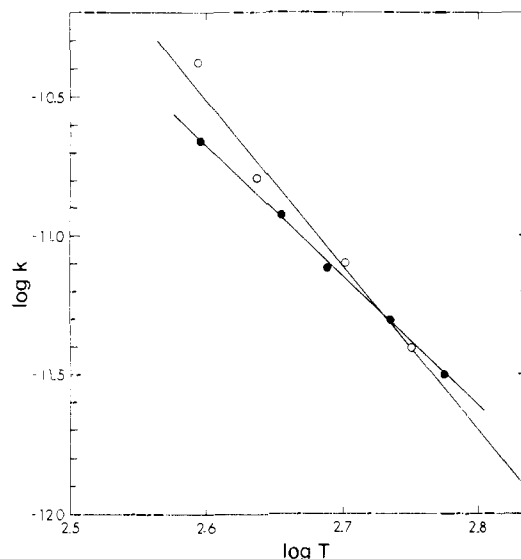


Figure 4. Chloride-transfer reactions $\text{R}_0^+ + \text{RCl} = \text{R}_0\text{Cl} + \text{R}^+$ with strong negative temperature dependence. $\log k$ vs. $\log T$ plots lead to approximate straight lines, i.e., $k = aT^{-b}$. $\text{R}_0^+ = p\text{-MeC}_6\text{H}_4\text{CH}_2^+$, $\text{RCl} = \text{C}_6\text{H}_5\text{CCl}_3$, $k = 1.9 T^{-4.6}$; $\text{R}_0^+ = p\text{-MeC}_6\text{H}_4\text{CH}_2^+$, $\text{RCl} = \text{MeOC}_6\text{H}_4\text{CH}_2\text{Cl}$, $k = 1.1 \times 10^5 T^{-6}$ (k in $\text{molecules}^{-1} \text{cm}^3 \text{s}^{-1}$).

Small yields of two other ions, of mass 125 and 199, are also observed in Figure 1. The 119, which is formed only at very short reaction times, is probably $\text{PhCHC}_2\text{H}_5^+$, presumably by a substitution reaction of C_2H_5^+ and benzyl chloride. The mass 125 ion had a satellite at 127 in the ^{35}Cl , ^{37}Cl ratio. This ion is almost certainly α -chlorobenzyl produced by the hydride abstraction (reaction 6), involving the benzyl cation and the major component—benzyl chloride. From Figure 1 one can deduce the ratio $\nu_5/\nu_6 \approx 12$, which combined with the known ratio of the neutral reactants leads to $k_5/k_6 \approx 400$. The α -chlorobenzyl cation produced in (6) is more stable than the benzyl cation (see the subsequent section on cation stabilities), and this means that reaction 6 is exothermic. As mentioned in the introduction, exothermic hydride-abstraction reactions often exhibit negative temperature dependence.^{4,7} This is obviously the case also for the hydride abstraction (reaction 6) whose rate constant at 300 °C is observed above to be at least two orders of magnitude lower than the collision rate constant.

The occurrence of hydride-transfer reactions like reaction 6 in the reaction mixtures set up for the measurements of chloride-transfer equilibria is unavoidable and presents a complication of the measurements. However, because in general the hydride-transfer reactions were much slower, it was possible to measure the chloride-transfer equilibrium in the presence of the slow hydride-transfer reactions. Chloride-transfer equilibria involving tertiary chlorides like *tert*-butyl chloride or adamantyl chloride cannot exhibit hydride-transfer side reactions, and generally with such systems one obtained the cleanest measurements.

At lower temperatures, $t < 100$ °C, various new side reactions were observed in the substituted benzyl chloride systems. These involved addition of the carbocations to the aromatic ring. Reactions of this type were described in an earlier study⁸ of the chloride-transfer equilibrium between $t\text{-C}_4\text{H}_9^+$ and benzyl⁺. To avoid the complications introduced by such reactions, all measurements were undertaken at higher temperatures.

A number of chloride-transfer reactions were studied in connection with the equilibria measurements. Generally, the neutral reactant concentrations chosen were higher than those used in Figure 5, in order to speed up the equilibria. These conditions were often not the best suited for kinetic measurements. However, in many cases semiquantitative rate measurements could be obtained. These results are shown in Table I. Only exothermic reactions are listed. The majority of the reactions, (5) and (7)–(13), have rate constants near $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with very weak negative temperature dependence, i.e., exhibit near ADO behavior. Reactions 14–18 are of intermediate behavior

Table I. Rate Constants for Exothermic Chloride-Transfer Equilibria 2: $R_o^+ + RCl = R_oCl + R^+$

eq no.	R_o	RCl^g	$k^a \times 10^9$	ΔH° ^e
5	PhCH ₂	<i>p</i> -MePhCH ₂ Cl	1.5 ^b (200), 1.0 (450)	6.5
7	<i>t</i> -Bu	<i>p</i> -MePhCH ₂ Cl	2 (135), ~1.5 (162)	7.0
8	<i>t</i> -Bu	<i>o</i> -MePhCH ₂ Cl	1 (135)	2.2
9	<i>t</i> -Bu	1-Cl- <i>c</i> -Pe	~1 (160) ^c to ~0.7 (233) ^c	3.0
10	<i>t</i> -Bu	AdCl	~2 (135) ^c	6.1
11	<i>t</i> -B	2-NbCl	~0.5 (120); ^c ~0.5 (202) ^c	2.4
12	<i>t</i> -Bu	2-Me-NbCl	~0.5 (120); ^c ca. 0.5 (202) ^c	11.1
13	<i>p</i> -FPhCH ₂	<i>p</i> -MePhCH ₂ Cl	~0.5 (323) ^c	6.4
14	adamantyl	2-Me-NbCl	~0.9 (87); ^c ~0.3 (226) ^c	5.0
15	<i>o</i> -MePhCH ₂	2-Me-NbCl	~0.3 (320) ^c	6.2
16	<i>p</i> -MePhCH ₂	2-Me-NbCl	~0.3 (166) ^c	4.1
17	norbornyl	2-Me-NbCl	~0.3 (136); ^c ~0.1 (222) ^c	8.7
18	PhCHCl	2-Me-NbCl	~0.1 (323) ^c	6.3
19	adamantyl	PhCCl ₃	~0.07 (162) ^c	4.8
20	<i>p</i> -MePhCH ₂	PhCCl ₃	0.02 (125); ^d 0.0025 (360) ^d	3.9
21	<i>p</i> -MePhCH ₂	<i>p</i> -MeOPhCH ₂ Cl	0.3 (125); ^d 0.002 (360) ^d	~15 ^f

^aIn cm³ molecules⁻¹ s⁻¹. Temperatures (°C) given in parentheses. ^bSee Figures 1–3. ^cSemiquantitative determination, can be in error by a factor of 3. ^dSee Figure 4. ^eEnthalpy change for reaction 2. From Table V. ^fFrom Harrison,²⁷ assuming that bond-dissociation energies of the two chlorides are the same. ^g*c*-Pe = cyclopentyl. Ad = adamantyl.

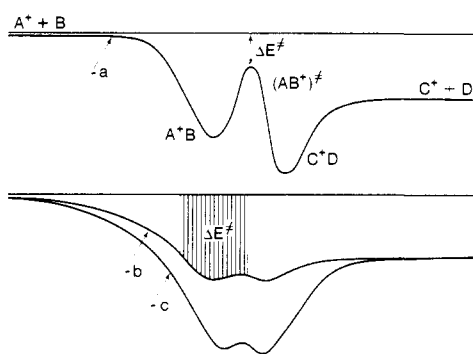


Figure 5. Reaction coordinates for exothermic bimolecular ion-molecule reactions: $A^+ + B = B^+ + C$. Reaction coordinate (a) has a large internal barrier associated with the formation of the transition state. It occurs in S_N2 reactions^{12–16} and leads to a decrease of rate constant with temperature (negative temperature dependence). (b) Reaction coordinate which can lead to reaction inefficiency (negative temperature dependence) in the absence of a large internal barrier. This occurs when the stability of adduct A^+B is low and the exothermicity of the reaction is not too high. MO ab initio calculations indicate such a reaction coordinate for hydride-transfer reactions.¹⁶ (c) Reaction coordinate model for chloride-transfer reactions proceeding with near collision efficiency.¹⁶

while reactions 19 and particularly 20 and 21 exhibit strong negative temperature dependence and are some 3 orders of magnitude below the collision limit at the highest, 360 °C, temperature used in the measurements. The two slowest reactions (reactions 20 and 21) were subjected to special kinetic study similar to that used for (5). The resulting temperature dependence of k_{20} and k_{21} is shown in Figure 4. These results demonstrate the observed strong negative temperature dependence, i.e., a rapid decrease of collision efficiency with increasing temperature.

Olmstead and Brauman^{12,13} have shown that exothermic bimolecular reactions of low collision efficiency can result from a reaction coordinate in which a substantial internal barrier associated with the formation of the transition state leads to a $-\Delta E^\ddagger$ which is small (0–10 kcal/mol) (see Figure 5, case a). Magnera and Kebarle⁶ have pointed out that the Brauman model case a leads to negative temperature dependence. The observed kinetics of nucleophilic substitution reactions (S_N2) involving positive¹⁴ and negative¹⁵ reactant ions were found to fit this model. Reaction inefficiency and negative temperature dependence can occur also in the absence of a large internal barrier, if loss of external ro-

tations of the collision partners in the complex AB^+ (locked rotors) occurs at a position where $-\Delta E^\ddagger$ is small⁶ (see Figure 5 case b). This case occurs when the adduct A^+B is very weakly bonded. Weak bonding is expected for the R_o^+HR adducts occurring in the hydride-transfer reactions 1. The inefficiency and negative temperature dependence of the hydride-transfer reactions is probably due to a reaction coordinate like b (see Magnera⁶ and Sunner¹⁶).

The adduct R_o^+ClR occurring in the chloride-transfer reactions 2 is a chloronium ion, and chloronium ions are known^{14,17} to be much more strongly bonded than the corresponding R_o^+HR species. This stronger bonding leads to a deeper well in the reaction coordinate as shown for the case c in Figure 5. The absence of a significant internal barrier as shown in case b for hydride transfer and case c for chloride transfer is indicated by molecular orbital calculations of the respective reaction coordinates.¹⁶ The high collision efficiency and lack of strong negative temperature dependence for most chloride transfer reactions can be explained on the basis of reaction coordinate type c.

While the chloride-transfer kinetics data provided in Table I are fairly comprehensive, still they are insufficient to provide clear indication to the structural features that lead to reaction inefficiency in chloride transfer. Clearly (see Table I) there is no obvious direct correlation with reaction exothermicity. One factor that seems common to all inefficient reactions is the fact that both R_o^+ and R^+ are highly stabilized cations. Inspection of Figure 12, given in the next section, shows that the carbocations involved in the inefficient reactions 14–17 of Table I have the lowest chloride affinities, i.e., the highest stabilities. A study¹⁷ of the binding energies of chloronium ions $RCIR^+$ and R_oClR^+ has shown that the binding energy defined by ΔH_7 , see eq 7, decreases with

$$R_o^+ClR = R_o^+ + ClR \quad (7)$$

increasing stability of R_o^+ . This means that the adducts R_o^+ClR occurring in the inefficient reactions 14–17, Table I, lead to shallow minima, i.e., to case b rather than case c. Clearly a wider range of reactions should be studied before this point can be considered as proven. We plan to report in the near future¹⁶ studies of the kinetics of inefficient hydride- and chloride-transfer reactions.

The low rate observed for reaction 21, where $RCl = p$ -methoxybenzyl chloride, may be due to a different reason. The formation of the oxonium ion adduct provides a much deeper minimum than that for the chloronium adduct. This deflection of the reagent ion into a deeper minimum might be reducing the efficiency of the chloride transfer.

(b) Measurements of the Hydride- and Chloride-Transfer Equilibria $R_o^+ + RH = R_oH + R^+$. Several hydride-transfer

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 (15) Caldwell, G.; Magnera, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959.

(16) Sunner, J.; Magnera, T. B.; Hirao, K.; Chowdhury, S., in preparation.
 (17) Sen Sharma, D. K.; Hojer-Mesa, S.; Kebarle, P. *J. Am. Chem. Soc.*, following paper in this issue.

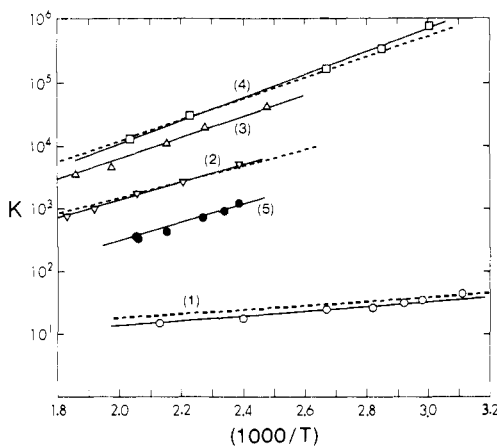
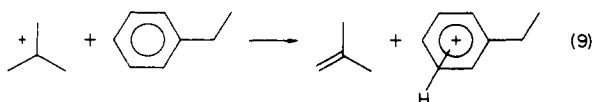


Figure 6. van't Hoff plots of equilibrium constants for hydride-transfer reactions: $R_0^+ + RH = R_0H + R^+$. Numbers beside plots correspond to reactions given in Table II: —, present work; ---, Field et al.⁵ Excellent agreement with the earlier work of Field et al. is observed.

equilibria were determined. Each measurement was performed at several different temperatures so that van't Hoff plots of the equilibrium constants could be obtained. The van't Hoff plots are shown in Figure 6. The equilibrium constants K_1 were determined at a given temperature and several different neutrals concentration ratios R_0H/RH . In general this ratio was varied by a factor of 2 to 5 with the equilibrium constant remaining constant within $\pm 20\%$. The equilibrium constants were found also to be independent of the total pressure which was varied from 2 to 5 torr. On the whole, the reactions were very clean. It will be noted from Figure 6 that it was possible to measure some very large equilibrium constants, i.e., K_1 in the order of 10^6 . These reactions involved $R_0^+ = t\text{-Bu}^+$ produced from $R_0H = \text{isobutane}$. The isobutane available was very pure, and it was possible to work with R_0H in the 5-torr range, while RH was in the 1- to 10-mtorr range. This leads to the R_0H/RH ratio of ~ 500 , which combined with our ability to measure R^+/R_0^+ equilibrium ratios as large as 2000 leads to measurable equilibrium constants K_1 in the 10^6 range. An example of such a run is given in Figure 7. The ability to measure large equilibrium constants makes it possible to measure hydride affinity differences which are as large as 9 kcal/mol.

The results from the hydride transfer van't Hoff plots are given in Table II. Three of the equilibria and the corresponding hydride affinity differences were measured previously by Solomon, Meot-Ner, and Field.⁵ These results are shown in Figure 6 and in Table II. Excellent agreement between the two sets of determinations is observed. The only equilibrium measurement which was affected by some problems was reaction 5, Table II, involving hydride transfer from ethylbenzene to $t\text{-Bu}^+$. In this reaction system the formation of protonated ethylbenzene (i.e., an ion at mass 107) was observed also. The protonation was four to five times slower than the hydride-transfer reaction and should not have affected the equilibrium measurements. However, the equilibrium constant was found to depend on the pressure of the isobutane gas, which as also the major gas (~ 4 torr). The equilibrium constants shown in Figure 6 and Table II were obtained at different temperatures with a constant isobutane pressure (4 torr). Probably the proton-transfer reaction 9 was responsible for the production of protonated ethylbenzene. Reaction 9 is



endoergic by about 3 kcal/mol.¹⁸ This endoergicity must have been responsible in slowing the proton-transfer reaction 9 down and permitting the (approximate) hydride equilibrium measure-

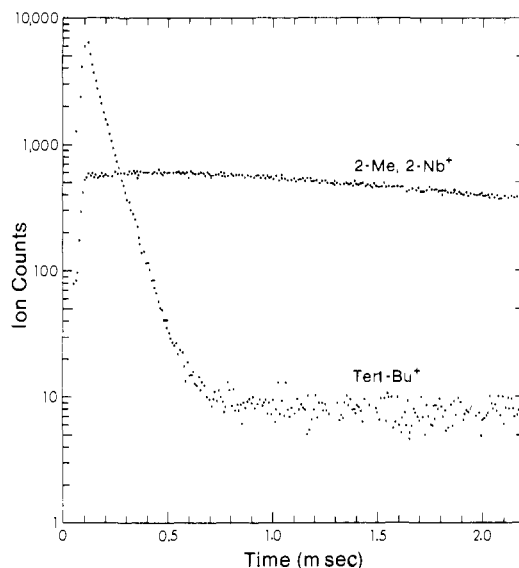


Figure 7. log (ion intensity) vs. time plots, obtained in hydride-transfer equilibrium measurement: $t\text{-Bu}^+ + 2\text{-methyl-norbornane} = \text{isobutane} + 2\text{-methyl-2-norbornyl}^+$. Achievement of equilibrium occurs where log (ion intensity) plots become equidistant. This occurs, for the present case, some 0.6 ms after the electron pulse. Most other reactions were measured under conditions where the equilibrium did establish much faster. $p(\text{isobutane}) = 4.22$ torr, $p(2\text{-methyl-norbornane}) = 8.0$ mtorr. MeNB^+ was collected for 10 s while $t\text{-Bu}^+$ was collected for 200 s. Ion ratio $\text{MeNB}^+ : t\text{-Bu}^+ = 1420$ and the neutral ratio $1/527.3$ leads to the equilibrium constant $K = 7.5 \times 10^5$ (temp 60°C). The present example illustrates that measurements of very large K are possible with the method used. Decrease of ion intensity after equilibrium has been achieved, i.e., after log plots become parallel, and is due to ion diffusion to the wall and possible ion-molecule side reactions involving either of the two ions.

Table II. Thermochemical Data^a from van't Hoff Plots of Hydride-Transfer Equilibrium Constants for Reaction 1: $R_0^+ + RH = R_0H + R^+$

	R_0^+	R^+	$-\Delta G_1^\circ$ (300), kcal/mol	$-\Delta H_1^\circ$ kcal/mol	ΔS_1° cal T^{-1} (eu)
(1)			6.9 (6.7)	6.5 (5.9)	1.4 (2.6)
(2)			2.3 (2.3)	1.5 (1.6)	2.1 (2.8)
(3)			8.2	7.6	2.1
(4)			8.8 (8.6)	7.8 (7.5)	3.6 (3.6)
(5)			6.4	7.7	4.3
(6)			(5.5)	(6.4)	(2.9)

^a Experimental data for hydride-transfer reactions from van't Hoff plots, Figure 6. Values in parentheses are from Solomon, Meot-Ner, and Field.⁵

ments. When a measurement of the hydride-transfer equilibrium between p -xylene and $t\text{-Bu}^+$ was attempted, rapid protonation of the xylene was observed, presumably due to a reaction analogous to (9). This result is to be expected since p -xylene is known to have a higher proton affinity than ethyl benzene,³ which makes the protonation exoergic.

The chloride-transfer kinetics and side reactions occurring in the equilibria measurements were described in the preceding section. Two types of equilibrium measurements were performed. A select group of reactions were measured at different temper-

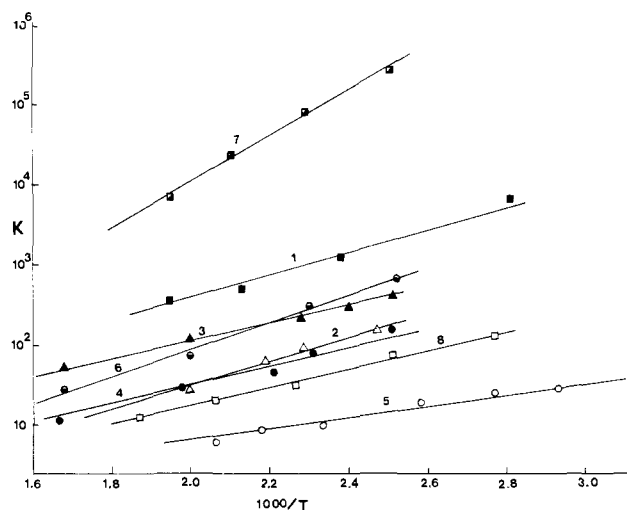


Figure 8. van't Hoff plots of the following chloride-transfer equilibria: $R_0^+ + RCl = R_0Cl + R^+$. Numbers correspond to reactions given in Table III.

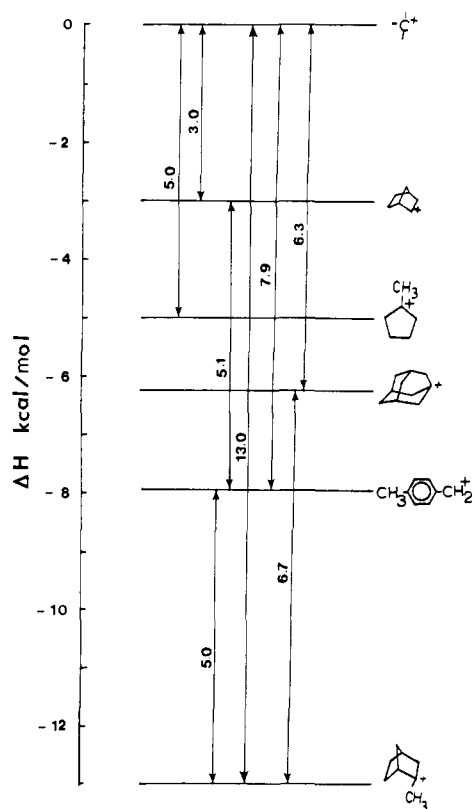


Figure 9. Ladder of ΔH_2° values for chloride-transfer equilibria based on van't Hoff plots in Figure 8 and Table III. Chloride affinity decreases and stability of R^+ increases from top to bottom. Chloride affinities relative to $R_0^+ = t\text{-Bu}^+$ are given on the ordinate.

atures so that van't Hoff plots could be obtained. The van't Hoff plots obtained are shown in Figure 8. The ΔH_2° obtained from the plots in Figure 8 are shown in the ladder of ΔH_2° values (Figure 9). As is evident, multiple thermodynamic cycles are occurring in Figure 9 which serve as a check on the consistency of the data. On the whole, consistency within less than 1 kcal/mol is observed (see Figure 9).

In order to be able to cover a wider range of compounds, determinations of the chloride-transfer equilibria at a single temperature (600 K) also were performed. The results are shown in the ΔG° ladder Figure 10. The resulting thermodynamic data are summarized in Figure 10 and Tables III and IV.

(c) Thermochemical Data, Hydride Affinities, Chloride Affinities, and Heats of Formation of R^+ . The hydride and chloride

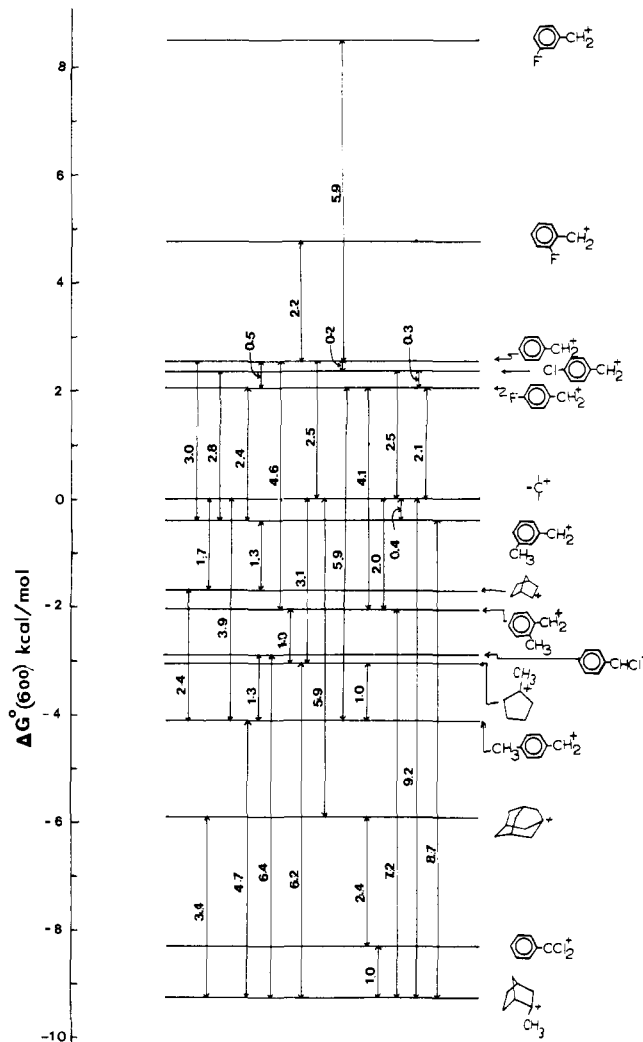
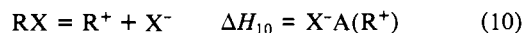
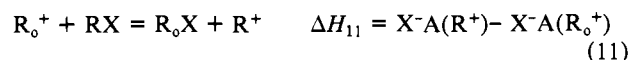


Figure 10. Ladder of ΔG°_{600} values for chloride transfer equilibria 2 measured at 600 K. Chloride affinity decreases and stability of R^+ increases from top to bottom. Chloride affinities (ΔG°_{600}) relative to $t\text{-Bu}^+$ are given on the ordinate. For ΔG°_{300} and ΔH° estimated from these data see Table V.

affinity of R^+ , $H^-A(R^+)$ and $Cl^-A(R^+)$, are defined in eq 10 where X^- may be H^- or Cl^- . The hydride- and chloride-transfer equilibria 1 and 2 provide relative hydride



and chloride affinities as shown in eq 11



Absolute affinities can be obtained from (11) if the affinity of one ion (R_0^+), taken as standard, is known. A single standard is sufficient when a continuous ladder as in Figure 9 or 10 is available. For the hydride affinities a continuous ladder connecting the secondary and tertiary carbocations is not available (see Table II). Therefore, in the construction of the absolute hydride affinities given in Table IV, two external standards, $i\text{-C}_3\text{H}_7^+$, $t\text{-C}_4\text{H}_9^+$, were used. The literature data¹⁹⁻²⁴ for heats of formation of the standard

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



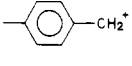






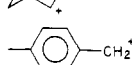



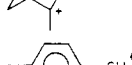
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Table III. Thermodynamic Data from Chloride-Transfer Equilibria van't Hoff Plots^a $R_0^+ + R = R_0 + R^+$

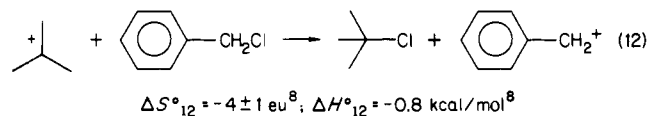
	R_0^+	R^+	ΔH , kcal/ mol	ΔG_{600} , kcal/ mol	ΔS eu
1.			-6.3	-5.9	0.6
2.			-6.7	-3.4	-6.6
3.			-5.0	-4.7	-0.5
4.			-5.0	-3.1	-3.2
5.			-3.0	-1.7	-2.3
6.			-7.9	-3.8	-6.9
7.			-13.1	-9.2	-7.7
8.			-5.1	-2.4	-4.5

^a From van't Hoff plots, Figure 8, see also ΔH ladder, Figure 9.

ions and the associated data on the heats of formation of the neutral reactants are given in Table IV.

The ΔH_2 values for the chloride-transfer reaction 2 measured in the van't Hoff plots were given in the ladder Figure 9. This ladder was anchored to *t*-Bu⁺ as standard. The ladder does not connect to the isopropyl and cyclopentyl cations. The chloride affinity of *i*-Pr⁺ given in Table IV was thermochemically evaluated from the standard $\Delta H_f(i\text{-Pr}^+)$ and the ΔH_f of isopropyl chloride. The same procedure was used also for *c*-Pe⁺.

The most extensive ladder of chloride-transfer data (Figure 10) gives experimental ΔG_2° values at 600 K. Approximate ΔH_2° values were obtained for all compounds but the substituted benzyli, by estimating the entropy ΔS_2° on basis of symmetry numbers only. For the benzyli ions R^+ , apart from symmetry numbers, it was also assumed that the change $RCl \rightarrow R^+$ is accompanied by a loss of entropy due to restricted internal rotation in the benzyli cation. This is loss of rotation between the C_6H_5 and CH_2^+ groups, introduced by the stiffening of the C-C bond due to π donation from phenyl to the CH_2^+ group. We chose $\Delta S = -3$ eu for this change; the total loss of internal rotation corresponds to about -6 eu (see Benson).²⁵ This choice leads to a $\Delta S_{12} = -4.4$ eu for reaction 12

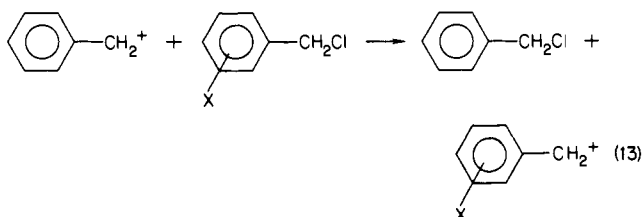


$\Delta S_{12}^\circ = -4 \pm 1$ eu;⁸ $\Delta H_{12}^\circ = -0.8$ kcal/mol⁸ which is essentially the same as the $\Delta S_{12}^\circ = -4$ eu determined from a van't Hoff plot of reaction 12 from the earlier study in our laboratory.⁸ The ΔH_2° values obtained from Figure 10 and estimated ΔS_2° are given in Table V. For five cases comparison can be made with the ΔH_2 value deduced from van't Hoff plots (see Figure 9 and Table V). In general, agreement within ± 1 kcal/mol is observed, which is within the estimated error. An exception is the case for 2-methyl-2-norbornyl⁺ for which the two determinations differ by some 3 kcal/mol. The ΔH_2 values from the van't Hoff plots need not be the more accurate result. While they are direct

experimental determinations of ΔH_2° , an error in the van't Hoff plots of ± 1 kcal/mol is quite common and in unfavorable cases can be even larger. The uncertainty of the ΔH_2° values derived from the $\Delta G_2^\circ(600)$ ladder comes from the ΔS_2° estimates which may be in error by as much as 3 eu. This corresponds to a $T\Delta S$ error of ~ 2 kcal/mol at 600 K. On the other hand, the $\Delta G_2^\circ(600)$ values are better documented due to the greater number of multiple thermodynamic cycles present in these data (see Figure 10).

Comparisons between hydride affinity differences ΔH_1 and chloride affinity differences ΔH_2 for a given pair of ions will be made in the subsequent discussion. It is generally found that $\Delta H_1 \approx \Delta H_2$. However, differences between ΔH_1 and ΔH_2 of a few kcal/mol can be expected. An equality between the two values would require that $\Delta H_f(RH) - \Delta H_f(R_0H) = \Delta H_f(RCl) - \Delta H_f(R_0Cl)$. An examination of available heats of formation (see, for example, Table IV) reveals that the $\Delta\Delta H_f(RH)$ and $\Delta\Delta H_f(RCl)$ generally differ by one to a few kcal/mol.

(d) **Substituent Effects in Benzyli Cations.** The chloride affinities of substituted benzyli cations based on data from Figure 10 and Table IV are given in Table VI. The enthalpy changes shown correspond to reaction 13. Thus a negative ΔH in Table IV indicates that the substituted cation has a lower chloride affinity,



i.e., is more stable than benzyli⁺. Also given in the table are results for the hydride-transfer reactions, obtained from molecular orbital (STO-3G) calculations by Hehre et al.²⁶ Relatively good agreement is observed between the two sets of data. The only case with an appreciable difference is *p*-fluoro, for which the present results give only 0.5-kcal/mol stabilization relative to benzyli while the calculation²⁶ gives 4 kcal/mol. On the basis of Figure 10, we believe that our result cannot be in error by more than 1 kcal/mol, i.e., the stabilization of *p*-F-Bz⁺ cannot be larger than 1.5 kcal/mol.

Also given in Table V are ΔI_p results which correspond to the difference between the ionization potential of the substituted and unsubstituted benzyli radical. These are from the early radical ionization potential measurements of Lossing²⁷ and also represent early work on carbocation stabilities by one of the present authors (P.K.). The ΔI_p would be identical with ΔE for reaction 13 provided that the bond-dissociation energies R-Cl do not change with substitution on the benzene ring. Since the bond dissociation energy changes are relatively small,²⁸ the ΔI_p 's should correspond approximately to ΔH_{13} . Fair agreement is observed between these data and the present results (Table V).

The effect of fluoro and methyl substitution in different positions on the ring on the chloride affinities (present work) is shown below.

<i>m</i> -F	<i>m</i> -Me	<i>o</i> -F	<i>o</i> -Me	<i>p</i> -F	<i>p</i> -Me
+6.5	-2.2	+3.0	-3.9	-0.5	-6.1

The results for the fluoro substituent are consistent with the role of fluorine as π donor stabilizing the cation and σ acceptor (electron-withdrawing field-inductive effect) destabilizing the cation. In the meta position the π donor effect is absent and one observes maximum destabilization of the cation. Methyl is both a (pseudo) π donor and exerts a stabilizing field-inductive effect, thus its substitution leads to stabilization in all positions, with the meta position, due to lack of π donation, being the least stabilizing.

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Table IV. Hydride and Chloride Affinities and Associated Thermochemistry, from Hydride- and Chloride-Transfer Reactions

R ⁺	$\Delta H_f(R^+)$	H ⁻ A(R ⁺) ^a	$\Delta H_f(RH)$	Cl ⁻ A(R ⁺) ^h	$\Delta H_f(RCl)$	$[\delta(H^+Cl^-A)]^j$
<i>i</i> -Pr ⁺	191 ^b	250.7 ^e	-25.0 ^c	170.5 ^e	-33 ^c	80.2
<i>c</i> -Pe ⁺	191.4 ^f	244.5 ^f	-18.4 ^c	164.9 ^e	-27.6 ^k	81.2
Nb ⁺	184.7 ^g (185.8) ^l	231.8 ^g	-12.4 ^d	153.5 ⁱ	-21.8 ^k	78.9
<i>t</i> -Bu ⁺	166.5 ^b	233.8 ^e	-32.1 ^c	155.9 ^e	-43.5 ^c	77.9
Me- <i>c</i> -Pe ⁺	166.9 ^g	226.9 ^g	-25.3 ^c	151.9 ⁱ	-36.8 ^k	75
Bz ⁺	214.8 ^b	237.5 ^e	12.0 ^c	155.4 ^b	4.1 ^b	
α -MeBz ⁺	198.6 ^g	226.1 ^g	7.2 ^c			
1-Ad ⁺		225.7 ^g		149.8		76
2-MeNb ⁺	171.3 ^g (170.0) ^l	225.6 ^g	-19.6	144.8 ⁱ	-28.9 ^k	81

^aHydride affinity H⁻A(R⁺) equals ΔH° in kcal/mol for the gas-phase reaction RH = R⁺ + H⁻, H⁻A(R⁺) = $\Delta H_f(H^-) + \Delta H_f(R^+) - \Delta H_f(RH)$, $\Delta H_f(H^-) = 34.7$ kcal/mol, Rosenstock.¹⁹ ΔH_1 and ΔH_2 used in the present table are taken from van't Hoff plot data, Table II (ΔH_1), and Figure 10 (ΔH_2). Accuracy of hydride affinities estimated at ± 1 kcal/mol. ^bT. Baer,²² Rosenstock,²³ Lias,²¹ ^cCox and Pilcher,²⁰ ^dReference 24. ^eFrom $\Delta H_f(R^+)$. ^fFrom H⁻A(*i*-Pr⁺) - H⁻A(R⁺), Table II, and $\Delta H_f(*i*-Pr^+)$. ^gFrom H⁻A(*t*-Bu⁺) - HA(R⁺), Table II, and $\Delta H_f(*t*-Bu^+)$. ^hChloride affinity of R⁺, Cl⁻A(R⁺) equal ΔH for reaction RCl = R⁺ + Cl⁻. $\Delta H_f(Cl^-) = -54.1$ kcal/mol, Rosenstock.¹⁹ Accuracy of chloride affinities estimated as ± 1 kcal/mol and ± 2 kcal/mol in less favorable cases, like 2-Me-2-Nb⁺. See Table V. ⁱFrom Cl⁻A(R⁺) - Cl⁻A(*t*-Bu⁺) see Figure 10 and Table V. ^j $\delta(H^+Cl^-A) = H^+A(R^+) - Cl^-A(R^+)$. This value should be constant provided that hydride and chloride affinities gave identical account of carbocation stabilities. Lack of constancy may be caused by experimental error but more likely is a true effect. ^kSchleyer and Allinger,²⁰ from MM2 force field calculations. ^lFrom Cl⁻A(R⁺) (Table V) and $\Delta H_f(RCl)$.

Table V. Chloride Affinities from Chloride-Transfer Equilibria Measurements at a Single Temperature^a

R ^c	ΔG°_{600} ^b	($\sigma_{RCl}/\sigma_{R^+}$) ^d	ΔS° ^e	ΔG°_{300} ^e	ΔH° ^{e,f}	ΔH°_{av} ^g	Cl ⁻ A(R ⁺) ^h
<i>m</i> -FBz	+8.2	1	3	7.3	6.4	6.4	162.3
<i>o</i> -FBz	+4.7	1	3	3.9	2.9	2.9	158.8
Bz	+2.5	1/2	4.4	1.2	-0.1	-0.5	155.4
					(-0.8)		
<i>p</i> -ClBz	+2.3	1/2	4.4	1.0	-0.3	-0.3	155.6
<i>p</i> -FBz	+2.0	1/2	4.4	0.7	0.6	-0.6	155.3
<i>t</i> -Bu ⁱ	0.0	1	0	0	0	0	155.9 ⁱ
<i>m</i> -MeBz	-0.4	1	0	-1.2	-2.2	2.2	153.7
2-Nb	-1.7	1	0	-1.7	1.7	-2.4	153.5
					(-3.0)		
<i>o</i> -MeBz	-2.1	1	3	-3.0	-3.9	-3.9	152.0
α -ClBz	-2.9	1	3	-3.8	-4.8	-4.8	151.1
1-Me- <i>c</i> -Pe	-3.0	1	0	-3.0	-3.0	-4.0	151.9
					(-5.0)		
<i>p</i> -MeBz	-4.1	1	3	-5.0	-6.1	-7.0	148.9
					(-7.9)		
Ad	-5.9	1	0	-5.9	-5.9	-6.1	149.8
					(-6.2)		
α,α -Cl ₂ Bz	-8.3	1/2	4.4	-9.6	-10.9	10.9	145.0
2-MeNb	-9.2	1	0	-9.2	-9.2	-11.1	144.8
					(-12.9)		

^aBased on equilibria measurements ladder Figure 10. ^b ΔG° at 600 K for the reaction *t*-Bu⁺ + RCl = *t*-BuCl + R⁺ from Figure 10. ^cIdentity of R can be deduced from Figure 10. Bz = benzyl, Nb = 2-norbornyl, Ad = 1-adamantyl, *c*-Pe = cyclopentyl. ^dSymmetry number ratio used to correct for rotational symmetry change. ^e ΔS° estimated from rotational symmetry changes alone except for all benzyl compounds for which also a $\Delta S^\circ = -3$ eu was added to take into account loss of internal rotation, see text. ^f ΔH values in brackets from van't Hoff plots, Table III. ^gAverage between ΔH from estimated ΔS and ΔH from van't Hoff plot. These averages are considered best values. ^hChloride affinities of R⁺. Estimated error ± 1 kcal/mol except for 2-MeNb⁺ where the estimated error is ± 2 kcal/mol. ⁱAnchoring standard, see Table IV.

Table VI. Relative Stabilities of Substituted Benzyl Cations from Chloride-Transfer Equilibria

X	$\Delta G^\circ_2(600)$ ^a	ΔH_2 ^a	ΔE_2 ^b	ΔI_p
<i>m</i> -F	+5.7	6.5	6.7	9.6
<i>o</i> -F	+2.2	3.0		
H	0	0		
<i>p</i> -Cl	-0.2	-0.2	4.4	
<i>p</i> -F	-0.5	-0.5	-4.0	0.1
<i>m</i> -Me	-3.0	-2.2	-1.7	-2.5
<i>o</i> -Me	-4.6	-3.9		
α -Cl	-5.4	-4.8		
<i>p</i> -Me	-6.6	-6.1	-6.6	-6.9
α,α -Cl ₂	-10.8	-10.8		
α -Me			$\sim(-11.9)$ ^d	

^aFor reaction Bz⁺ + X-BzCl = BzCl + XBz⁺ where Bz = benzyl. Data from Table V in kcal/mol. ^b ΔE_1 for hydride-transfer reaction evaluated by Hehre et al.,²⁶ using STO-3G. ^cIonization potential difference $I_p(XBz) - I_p(Bz)$. Early work on radical I_p by Harrison, Kebablar, and Lossing.²⁷ ^dHydride affinity difference, Table VI.

The 2 kcal/mol stronger stabilization by Me in the para relative to the ortho position is interesting, since one might have expected that the ortho position would be more stabilizing due to a stronger

field-inductive effect. The weaker stabilization in the ortho position might be due to a through space repulsion and thus destabilization between the methyl and the CH₂⁺ group of benzyl. The methyl group should be acquiring positive charge by both π and σ donation, and this charge should lead to the suggested repulsion.

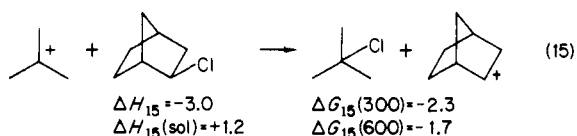
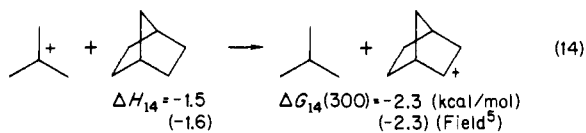
The effect of chlorine substitution on the ring and on the methylene group of benzyl is shown below.

<i>p</i> -Cl	<i>a</i> -Cl	α,α -dichloro
-0.2	-5	-10

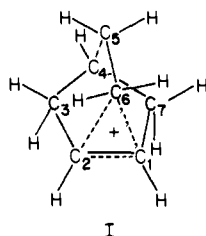
Chloride is much more stabilizing in the α position. The much greater polarizability of Cl relative to H is probably the largest contributing factor to this effect. It should be noted that the α position is also the most strongly stabilizing one for methyl substitution (see Table V). Substitution of a second chlorine in the α position leads to as large a change of the chloride affinity as for the first chlorine. A weakening of the stabilization by the second chlorine would be expected if polarizability and π donation were the only major sources of stabilization. What must be involved here is an additional effect, i.e., a weakening of the C-Cl bond with cumulative α -Cl substitution. Such weakening is predicted from thermochemical data available for related cases.²⁹

We had hoped to obtain chloride affinities of benzyl cations carrying a much wider range of substituents. However, difficulties were encountered due to side reactions. Also, substituents like methoxy which could form oxonium ions with R_o^+ led to slow chloride-transfer kinetics (see section a), and this increased the adverse effect of side reactions on the equilibria measurement.

(e) **Stability of Norbornyl Cations in the Gas Phase.** Results from the gas-phase hydride- (Table II) and chloride- (Table IV) transfer equilibria unequivocally show that reactions 14 and 15 are exothermic, which means that the 2-norbornyl cation (Nb^+) has a lower hydride and chloride affinity than $t\text{-Bu}^+$. Thus Nb^+ , if considered formally as a secondary cation, has unusual stability.

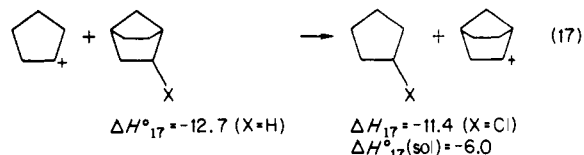
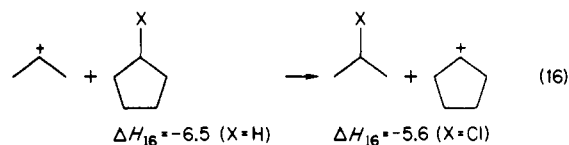


The above results make an important contribution toward the resolution of the norbornyl controversy,³⁰ which in spite of shifting positions³¹ has at its heart two questions: (a) is the Nb^+ unusually stable and (b) is this unusual stability due to the σ bridged (non-classical) structure I?

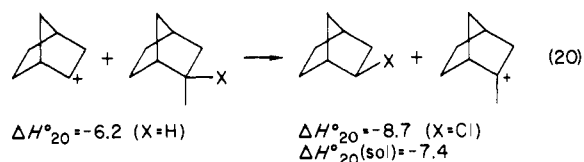
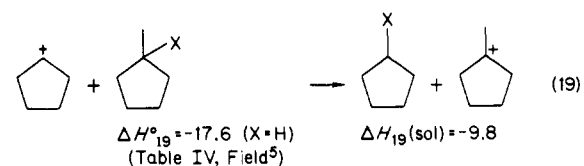
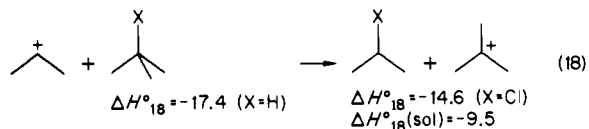


The Nb^+ energetics can be elaborated further on the basis of the available data. Reaction 16 shows the increase of stability from $i\text{-Pr}^+$ to $c\text{-Pe}^+$, i.e., when $i\text{-Pr}^+$ is extended into $c\text{-Pe}^+$ by the introduction of a CH_2CH_2 group. Reaction 17 gives the increase of stability when $c\text{-Pe}^+$ is extended by the introduction of another CH_2CH_2 group to become the Nb^+ ion. The exothermicity of (17) is nearly twice that of (16). This result also clearly demonstrates the unusual properties of the Nb^+ structure. Had Nb^+ not been special one would have expected an exothermicity for the introduction of the second CH_2CH_2 bridge (i.e., $-\Delta H_{17}$) which is less than that observed for the introduction of the first bridge (i.e., $-\Delta H_{16}$).

Reactions 18–20 illustrate the methyl-substituent effects on the three formally secondary ions, $i\text{-Pr}^+$, $c\text{-Pe}^+$, and Nb^+ . Both hydride- and chloride-transfer energetics are available for (18) and



(20). The Me-substitution effect on the stability of Nb^+ is seen to be considerably smaller than that for the other two secondary ions. This again indicates special stabilization for Nb^+ .



The $\Delta H(\text{sol})$ values given for eq 16–20 are for the corresponding chloride transfer in SO_2ClF solution. These values, which are based on calorimetric measurements of Arnett et al.,³⁹ will be discussed in the next section which deals with solvent effects.

The thermochemical arguments for the special stability of Nb^+ embodied in eq 14, 15, 18–20 are the same as those used by Solomon and Field.^{5b} New in the present work is the fact that Field's hydride results could be so well reproduced by the present work and that the thermochemistry could be extended to the corresponding chloride-transfer reactions. In particular the results in Figure 10 provide a very graphic description of the position of Nb^+ and MeNb^+ chloride affinities relative to those of other stabilized carbocations. The arguments presented through eq 16 and 17 were used earlier, in work from this laboratory³² which provided thermochemical information on Nb^+ via the protonation of 2-norbornene (see also Beauchamp³³). The evaluation of hydride affinities involved in (16) and (17) from these data^{32,33} required the heats of formation of 2-norbornene and norbornane. The heats of formation of these neutral compounds, used earlier,³² lead to results in close agreement³⁴ with the present results.

(29) $D(\text{CH}_3\text{-Cl}) \approx 84$ kcal/mol while $D(\text{CCl}_3\text{-Cl}) \approx 73$ kcal/mol can be evaluated from available thermochemical data, see Handbook of Chemistry and Physics and Cox and Pilcher.²⁰

(30) A compact modern summary on the "norbornyl controversy" can be found in a set of four articles in *Accounts of Chemical Research*: Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432. Olah, G. A.; Pankash, G. K. S.; Saunders, M. *Ibid.* **1983**, *16*, 440. Walling C. *Ibid.* **1983**, *16*, 448. Grob, C. A. *Ibid.* **1983**, *16*, 455.

(31) One of the present authors (P.K.) in connection with the present and earlier³² measurements concerning Nb^+ has spent many hours familiarizing himself with the Nb^+ literature. His "innocent bystanders" view is that the two central questions in the Nb^+ controversy were the following: (a) is Nb^+ unusually stable and (b) is this unusual stability due to σ bridging? H. C. Brown now³⁰ considers the explanation of the observed high *exo*- to *endo*-norbornyl solvolysis rates as the central point. While the *exo*-endo rates were the starting point and the experimental battleground, the "theory" behind the explanations dealt with questions (a) and (b). This is clear from the position of H.C.B. which contended that the *exo* rate is not particularly fast (as it would have been had Nb^+ been stabilized by σ bridging) but that the *endo* rate is unusually slow (due to steric hindrance to nucleophilic stabilization of the *endo* transition state).³⁰

(32) Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1084.

(33) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964.

(34) The Kebarle and Saluja³² and the Beauchamp³³ determinations lead to $t\text{-Bu}^+ + 2\text{-norbornene} = \text{isobutene} + 2\text{-Nb}^+$; $\Delta H_{\text{a}} = -4.5$ kcal/mol. Straightforward thermochemistry leads to the expression $\Delta H_{14} = \Delta H_{\text{a}} + \Delta H_f(\text{norbornene}) - \Delta H_f(\text{isobutene}) - \Delta H_f(\text{norbornane}) + \Delta H_f(\text{isobutane})$. Using the well-established ΔH_f for the C4 compounds one obtains $\Delta H_{14} = -32.64 + A$, where $A = \Delta H_f(\text{norbornene}) - \Delta H_f(\text{norbornane})$. The value for $A = 31.5$ kcal/mol used in the previous work^{32,33} was based on data available at the time and leads to $\Delta H_{14} = -1.14$ kcal/mol in close agreement with Field's and the present value from direct measurement of hydride transfer $\Delta H_{14} = -1.5$ kcal/mol. It is also consistent with the observation that the analogous chloride transfer reaction 15 is $\Delta H_{15} = -3.0$ kcal/mol. However, recent work by Steele (Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 919) gives $A = 36.5$ and thus a $\Delta H_{14} = +3.9$ kcal/mol which is in disagreement with the direct measurements of ΔH_{14} (and ΔH_{15}). Since we believe that the direct measurements are correct, either ΔH_{a} from the proton transfer^{32,33} equilibria or Steele's data are incorrect. An error of 5 kcal/mol in ΔH_{a} appears highly improbable. The discrepancy with the Steele data thus remains unexplained.

Table VII. Comparison of Chloride Affinities in Gas Phase and SO₂ClF Solution^a

R ⁺	ΔH ₂ (g) ^a	ΔH ₂ (s) ^{a,b}	δΔH ₂ (s) (R ⁺ s) ^c	δΔH _{sol} ⁻ (R ⁺) ^d
<i>i</i> -Pr	+14.6	+9.5	-5.1	-5.4
<i>t</i> -Bu ⁺	0	0	0	0
2-Nb ⁺	-2.4	1.2	+3.6	+2.1
Me-c-Pe ⁺	-4.0	-2.3	+1.7	-0.2
1-Ad ⁺	-6.1	+3.2	+9.3	
2-Me-2-Nb ⁺	-11.1	-6.2	+4.9	

^a ΔH₂(g) and ΔH₂(s) are gas phase and solution values in kcal/mol for the reaction *t*-Bu⁺ + RCl = *t*-BuCl + R⁺. ^b For SO₂ClF solution, Arnett et al.³⁹ ^c δΔH₂(R⁺,s) = ΔH₂(s) - ΔH₂(g) = ΔH_{sol}(R⁺) - ΔH_{sol}(*t*-Bu⁺) + ΔH_{sol}(*t*-BuCl) - ΔH_{sol}(RCl), where sol stands for solvation energy of species on transfer from gas phase to solution. Assuming that ΔH_{sol}(RCl) - ΔH_{sol}(*t*-BuCl) is considerably smaller than ΔH_{sol}(R⁺) - ΔH_{sol}(*t*-Bu⁺) values given correspond to a solvation energy of R⁺ relative to that of *t*-Bu⁺ where a positive value means that R⁺ is less well solvated than *t*-Bu⁺. ^d δΔH_{sol}(R⁺) = ΔH_s(R⁺) - ΔH_s(*t*-Bu⁺), solvation energy of R⁺ relative to that of *t*-Bu⁺.

However, newer and different values for the ΔH_f of norbornane and norbornene due to Steele³⁴ remove this agreement.³⁴

The question whether the cause for the unusual stability of Nb⁺ is the σ bridged structure I can be answered by theoretical computation. The best and most recent theoretical calculations^{35,36} predict that the σ bridged structure is the only true minimum.³⁷ As pointed out earlier,³² gas-phase thermochemical data can be of utility also in the theoretical search. For example, the energy change ΔE for the isodesmic reaction 17 provides a good test for the energies obtained in the theoretical calculations, when energies *E* for all the reactants are calculated with the same level basis sets (and electron correlation). Thus, as pointed out earlier,³² MINDO/3 (Dewar³⁸) predicts a -ΔE₁₇ of only 4.2 kcal vs. the -ΔH₁₇ of 12.7 kcal/mol and is thus unreliable. Unfortunately, ΔE₁₇ changes from the most recent calculations^{35,36} are not available.

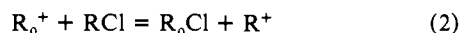
Much of the Nb⁺ controversy³⁰ concerns solvolysis rates and solvolysis transition states. This is an area where the understanding of the basic factors involved is very imperfect. One has to deal not only with the (gas phase) reaction coordinates of the respective transition states but also with the solvent effect on the reaction coordinate. The next section, which compares the stabilities of carbocations in gas phase and solution, indicates some of the difficulties encountered in accounting properly for the ion solvation effects.

(f) Stabilities of Carbocations in the Gas Phase and Solution. Arnett et al.³⁹ in a recent series of papers have reported measurements of the heats of ionization of RCl in solution. The calorimetric measurements of reaction 21 were performed in SO₂ClF. Using these data (Table I^{39f}) one can obtain relative



chloride affinities (i.e., ΔH₂) in SO₂ClF solution as shown in the equation²²

$$\Delta H_f(\text{RCl}) - \Delta H_f(\text{R}_0\text{Cl}) = \Delta H_2(\text{R}^+, \text{sol}) \quad (22)$$



Given in Table VII are the ΔH₂ values obtained from (22) for R₀⁺ = *t*-Bu⁺ and several key ions R⁺, together with the corre-

sponding gas-phase ΔH₂ obtained in the present work. Inspection of the numbers reveals significant differences between the two media. For example, ΔH₂(1-adamantyl⁺,sol) = +3 kcal/mol while ΔH₂(1-adamantyl⁺,g) = -6 kcal/mol, which corresponds to a difference ΔH₂(s) - ΔH₂(g) of a whole 9 kcal/mol. The analogous difference for 2-MeNb⁺ is 5 kcal/mol and Nb⁺ 4 kcal/mol. Had *i*-Pr⁺ been used for R₀⁺ rather than *t*-Bu⁺, the differences would have increased by another 5 kcal/mol, i.e., to 14 kcal/mol for adamantyl⁺ (see Table VII). The difference expressed in (23) can be also expressed by (24). Thus eq 23 will give the relative

$$\delta\Delta H_2(\text{R}^+, \text{s}) = \Delta H_2(\text{R}^+, \text{sol}) - \Delta H_2(\text{R}^+, \text{g}) \quad (23)$$

$$\delta\Delta H_2(\text{R}^+, \text{s}) =$$

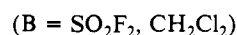
$$\Delta H_{\text{sol}}(\text{R}^+) - \Delta H_{\text{sol}}(\textit{t}\text{-Bu}^+) - \Delta H_{\text{sol}}(\text{RCl}) + \Delta H_{\text{sol}}(\textit{t}\text{-BuCl}) \quad (24)$$

solvation energy of R⁺ provided that δΔH_{sol}(RCl) is relatively small, which is often the case. An accurate evaluation of

$$\delta\Delta H_{\text{sol}}(\text{R}^+) = \Delta H_{\text{sol}}(\text{R}^+) - \Delta H_{\text{sol}}(\textit{t}\text{-Bu}^+) \quad (25)$$

δΔH_{sol}(R⁺) can be obtained from the heats of formation of the ions R⁺ and *t*-Bu⁺ in the gas phase and in solution. The few values which can be evaluated from Arnett and Pienta's data³⁹ and the present results for ΔH_f(R⁺) are given in Table VII. This evaluation suffers from cumulative errors in the ΔH₂ values and the heats of formation of the neutrals. Comparison with the δΔH₂(R,s) indicates that the δΔH₂ results reflect the solvation energy differences δΔH_{sol}(R⁺). The further discussion is based on this assumption.

In comparing their solution data with some available gas-phase hydride affinity differences, Arnett et al.³⁹ concluded that the solvent effects were small. The present data show that this generalization is not justified. The difference between the gas-phase and solution results could be due to differential: ion pairing, specific, i.e., nucleophilic solvation and general solvation, of R⁺. By specific nucleophilic solvation we mean the stabilization of R⁺ by (transient) formation of oxonium, fluoronium, or chloronium ions R⁺SO₂ClF, while the general (non specific) solvation corresponds to the stabilization of the ion by the solvent dielectric medium. One expects that the ion pairing and nucleophilic stabilization will decrease as the (gas phase) stability of R⁺ increases.⁴⁰ Measurements of the complexing energies of R⁺ with one solvent molecule based on equilibria 26 determinations in the gas phase¹⁷



lead to the finding that -ΔG^o₂₆ and -ΔH^o₂₆ decrease with decreasing chloride affinity of R⁺, i.e., confirm that the nucleophilic stabilization by a solvent molecule decreases with increasing stability of R⁺. However, the changes of ΔG^o₂₆ and ΔH^o₂₆ are significant only for large changes in R⁺, i.e., from Me⁺ to Et⁺ to *i*-Pr⁺, the changes for tertiary R⁺ and Nb⁺ are found to be very small, indicating that for the more stable R⁺ there is little differential nucleophilic solvent stabilization. There can be little doubt that a similar trend will be followed also in the ion pairing stabilization.

Had ion pairing and nucleophilic stabilization been the dominant solvation interactions, δΔH₂(R⁺,s) would have increased linearly with an increase of the gas-phase stability of R⁺. While such a trend may be partially present, it is clearly not dominant. Nb⁺ is only about 2-3 kcal/mol more stable in the gas phase than *t*-Bu⁺ (see eq 14 and 15) but has a δΔH₂(Nb⁺,s) of 4 kcal/mol (Table VII). Furthermore, the largest δΔH₂(R⁺,s) is not for the most stable R⁺ = 2-MeNb⁺ but for 1-adamantyl⁺. This indicates clearly that nonspecific solvation plays an important role. Obviously the solvation of adamantyl is the poorest because the large hydrocarbon cage of this ion excludes solvent molecules from the

(35) Yoshimine, M.; McLean, A. D.; Lin, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185.

(36) Raghurachari, K.; Haddon, R. C.; Scheyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 5915.

(37) The theoretical work does not involve geometry optimization at the highest level of computation.

(38) Dewar, M. J. S.; Haddon, R. C.; Kormornicki, A.; Rzepa, H. J. *Am. Chem. Soc.* **1977**, *99*, 377.

(39) (a) Arnett, E. M.; Petro, S. C. *J. Am. Chem. Soc.* **1978**, *100*, 2563. (b) Arnett, E. M.; Petro, S. C. *Ibid.* **1978**, *100*, 5402, 5408. (c) Arnett, E. M.; Petro, S. C.; Schleyer, P. v. R. *Ibid.* **1979**, *101*, 3329. (d) Arnett, E. M.; Pienta, N. J. *Ibid.* **1980**, *102*, 3329. (e) Arnett, E. M.; Hofelich, T. C. *Ibid.* **1982**, *104*, 3522. (f) Arnett, E. M.; Hofelich, T. C. *Ibid.* **1983**, *105*, 2889.

(40) For an elegant series of papers examining the decrease of ion-solvent molecule interactions with increasing stability of the carbocation (increasing energy of the LUMO carbocation orbital) see: Cournoyer, M. E.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 5104 and references therein.

vicinity of the positive charge and this solvent exclusion reduces the nonspecific solvation. The same should be true for Nb^+ (relative to $t\text{-Bu}^+$ or $c\text{-Pe}^+$).

The above observations have some bearing on the Nb^+ controversy (see preceding section). The $\Delta H_2(\text{sol})$ changes based on Arnett's data³⁹ for reactions 15-20 were given in the preceding section. Clearly the solution data appear to present a less dramatic case for the special stability of Nb^+ . Thus Nb^+ is less stable than $t\text{-Bu}^+$ in solution reaction 15, while the opposite is true in the gas phase. For the change $i\text{-Pr}^+$, $c\text{-Pe}^+$, Nb^+ , reactions 16 and 17, one observes also a reduced trend in solution. Thus the change $c\text{-Pe}^+$ to Nb^+ is only ~ 4 kcal/mol more exothermic than the change $i\text{-Pr}^+$ to $c\text{-Pe}^+$ while in the gas phase the value is ~ 6 kcal/mol. Also the changes in the methyl substituent series reactions 18-20 are less pronounced in solution.

When one considers the above ΔH changes in solution one must remind oneself that they are used as models to the stability of Nb^+ in connection with the exo-endo solvolysis rate differences.³⁰ The experimental solvolysis rates establish a difference of about 6 kcal/mol between the exo and endo transition states (R^+-X^-)^{*} in solution.³⁰ In the nonclassical view only the exo transition state is significantly stabilized by σ bridging. Since the exo state is electronically more stabilized one expects that the nucleophilic solvent stabilization will be somewhat less for that state than for the endo state. As was pointed out above some differential nucleophilic stabilization is probably affecting the Arnett solution data. Thus, in this respect these data may be suitable models for

the exo-endo norbornyl transition states. However, it was seen that Arnett's data are much more strongly affected by differential nonspecific solvation, i.e., solvent exclusion by bulky hydrocarbon structures that lead to poorer solvation. This change of general solvation present in the Arnett results makes the energy changes in eq 16-20 in solution not suitable for modeling of the exo-endo transition-states energies. No gross changes of the size of ion occur for the exo relative to the endo transition state, and thus no significant changes of nonspecific solvation for these transition states can be expected. Thus Arnett's solution data, if they are to be applied for modeling energy changes of exo-endo transition states, should be corrected for the presence of nonspecific solvation. The corrections, which cannot be quantitatively assessed, will be in the direction of greater agreement with the gas-phase results and increased support of reactions 16-20 energy change models for the unusual stability of Nb^+ and by implication also of the exo- Nb^+-X^- transition state in solution.

Registry No. Cl^- , 16887-00-6; H^- , 12184-88-2; PhCH_2^+ , 6711-19-9; $t\text{-Bu}^+$, 14804-25-2; $p\text{-FPhCH}_2^+$, 29180-23-2; $o\text{-MePhCH}_2^+$, 63246-55-9; $p\text{-MePhCH}_2^+$, 57669-14-4; PhCHCl^+ , 56683-65-9; $o\text{-MePhCH}_2\text{Cl}$, 552-45-4; $p\text{-MePhCH}_2\text{Cl}$, 104-82-5; PhCCl_3 , 98-07-7; $p\text{-MeOPhCH}_2\text{Cl}$, 824-94-2; PhCHCH_3^+ , 25414-93-1; $(\text{CH}_3)_2\text{CH}^+$, 19252-53-0; $m\text{-FPhCH}_2^+$, 65108-06-7; $o\text{-FPhCH}_2^+$, 65108-14-7; $p\text{-ClPhCH}_2^+$, 29180-24-3; $m\text{-MePhCH}_2^+$, 60154-94-1; PhCCl_2^+ , 24154-22-1; AdCl , 935-56-8; 2-NbCl , 29342-53-8; Ad^+ , 19740-18-2; Nb^+ , 24321-81-1; $1\text{-Cl-}c\text{-Pe}$, 930-28-9; 2-Me-NbCl , 96246-73-0; $1\text{-Me-}c\text{-Pe}^+$, 17106-22-8; $c\text{-Pe}^+$, 25076-72-6.

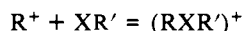
Stabilities of Halonium Ions from a Study of Gas-Phase Equilibria $\text{R}^+ + \text{XR}' = (\text{RXR}')^+$

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Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received December 11, 1984

Abstract: The gas-phase ion equilibria $\text{R}^+ + \text{B} = \text{RB}^+$, where $\text{R}^+ = \text{Et}^+$, $i\text{-Pr}^+$, $c\text{-Pe}^+$, $t\text{-Bu}^+$, $2\text{-Me-}2\text{-Bu}^+$, and 2-Nb^+ and $\text{B} = \text{CH}_3\text{Cl}$, CH_2Cl_2 , CHCl_2 , CHCl_3 , SO_2F_2 , CF_3H , and CF_4 were determined in a pulsed electron beam high pressure mass spectrometer. van't Hoff plots provide ΔG°_{300} , ΔH° , and ΔS° . For the chloronium ions the following trends were observed. The bond energy $D(\text{R}^+-\text{ClR}_0)$, where R^+ changes and R_0 is constant, decreases with increasing electronic stabilization of R^+ , i.e., in the order Me^+ , Et^+ , $i\text{-Pr}^+$, $c\text{-Pe}^+$, $t\text{-Bu}^+$, Nb^+ . The same order was observed earlier in this laboratory for $D(\text{R}^+-\text{Cl}^-)$, i.e., the chloride affinity of R^+ . However, the changes of $D(\text{R}^+-\text{ClR}_0)$ for $\text{R}^+ = 2\text{-Me-}2\text{-Bu}^+$, Nb^+ , and $t\text{-Bu}^+$ are very small. This means that little differential, specific nucleophilic solvation of these ions in solution is to be expected when solvents of low nucleophilicity like CH_2Cl_2 and SO_2ClF are used. The bond energies $D(\text{Me}^+-\text{ClR})$ increase in the order $\text{R} = \text{Me}$, Et , $i\text{-Pr}$, $t\text{-Bu}$. The bond energies $D(t\text{-Bu}^+-\text{B})$ decrease in the order $\text{B} = \text{C}_2\text{H}_5\text{Cl}$, $\text{CH}_2\text{Cl}_2 \approx \text{CH}_3\text{Cl}$, CCl_3H , SO_2F_2 , CF_3H , CF_4 . The significance of these trends is discussed.

Measurements of ion equilibria in the gas phase¹ include acceptor-donor (Lewis acid-base) equilibria of the type in eq 1,



where R^+ is a carbocation and B a σ , π , or n donor base. Determination of the equilibrium constant K_1 with a pulsed electron beam high pressure mass spectrometer leads via van't Hoff plots to the corresponding ΔG°_1 , ΔH°_1 , and ΔS°_1 .

The present work describes results for systems where $\text{R} = \text{ethyl}$ (Et), isopropyl ($i\text{-Pr}$), *tert*-butyl ($t\text{-Bu}$), 2-methyl-2-butyl ($t\text{-Pe}$), cyclopentyl ($c\text{-Pe}$), and 2-norbornyl (Nb), while $\text{B} = \text{XR}' = \text{CH}_3\text{Cl}$, CH_2Cl_2 , CHCl_3 , $\text{C}_2\text{H}_5\text{Cl}$, CHF_3 , CF_4 , and SO_2F_2 . The

work is an extension of measurements described in an earlier publication² in which reactions involving Et^+ , $i\text{-Pr}^+$, and MeCl were studied. The present results allow one to observe the change of bonding in R^+-B with increasing stabilization of the carbocation R^+ . They also give the bonding changes for a given R^+ with changing donor character (nucleophilicity) of B . Chloronium ions are important alkylating agents in solution.³ Their usefulness as alkylating agents in the gas phase was pointed out recently.⁴ Thus, the dimethylchloronium ion can be used⁴ for the clean gas-phase preparation of tertiary oxonium and quaternary ammonium ions as shown in reaction 2. The product ions can then

(1) Kebarle, P. *Annu. Rev. Phys. Chem.* 1977, 28, 455.

(2) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* 1978, 100, 5826.

(3) Olah, G. A. "Halonium Ions"; Wiley: New York, 1975.

(4) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* 1982, 104, 19.

[†] Permanent address: Chemistry Department, University of Mexico, Mexico City, Mexico.