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Free Energy Halide Affinities of Carbenium Ions in the Gas Phase and in Solution

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Halide affinities [$\Delta G_{halide}(R^+)$] of simple carbenium ions ($R^+ + X^- \rightleftarrows RX$ $\Delta G_{halide}(R^+)$ (i)) in both the gas phase and in aqueous solution were obtained from the corresponding hydride affinities [$\Delta G_{hydride}(R^+)$] along with the differences in free energies of formation of RX and RH ($\Delta\Delta G^\circ_f[RX - RH]$) and the differences in free energies of formation of hydride and halide ions ($\Delta\Delta G^\circ_f[H^- - X^-]$) using eq ii ($\Delta G_{halide}(R+) - \Delta G_{hydride}(R+) = \Delta\Delta G^\circ_f[RX - RH] + \Delta\Delta G^\circ_f[H^- - X^-]$ (ii)). Equation ii, derived from a thermochemical cycle, does not incorporate any approximations. The significance of (ii) is that all of the quantities except $\Delta G_{halide}(R^+)$ are either available or readily obtained for simple alkyl halides and the corresponding hydrocarbons. Solvation energies [$\Delta G_{solv}(R^+)_{aq}$] of carbenium ions in water were estimated from known values of solvation energies of suitable model cations, and $\Delta G_{halide}(R^+)_{aq}$ were obtained from (iii) ($\Delta G_{halide}(R^+)_{aq} = \Delta G_{halide}(R^+)_{gas} - \Delta G_{solv}(R^+)_{aq} - \Delta G_{solv}(X^-)_{aq} + \Delta G_{solv}(RX)_{aq}$ (iii)). An analogous equation was used to calculate $\Delta G_{hydride}(R^+)_{aq}$. Linear relationships with near unit slope between hydride, electron, and halide affinities are demonstrated. Maximum possible values of first-order rate constants for the ionization of alkyl and benzyl halides in aqueous solution were estimated from the thermochemical data.

Introduction

The study of substitution reactions of alkyl halides and related compounds in solution has been central in the development of modern organic chemistry. The illuminating investigations by Hughes, Ingold, and co-workers more than a half century ago[1] established the existence of two kinetically distinct mechanisms of substitution at saturated carbon. The second-order mechanism (S_N2) involves a single step without the intervention of intermediates. The first-order mechanism (S_N1) consists of a rate determining ionization (1) followed by product-

$$RX \rightleftarrows R^+ + X^- \qquad (1)$$

$$R^+ + H_2O \rightleftarrows ROH + H^+ \qquad (2)$$

forming reactions of the resulting carbenium ion. Reactions (1) are commonly carried out in hydroxylic (water or alcohol) solvents and the overall result, eqs 1 + 2 (in water), is referred to as solvolysis.[2]

Direct observation of ionization reaction 1 in aqueous solvents is not possible. The pioneering calorimetric studies by Arnett and co-workers[3] provided quantitative measures of carbenium ion stability in non-nucleophilic solution. Free energies of activation of solvolysis reactions were observed to correlate linearly with heats of ionization reactions (3). Comparison of solvolysis with ionization

$$RX + SbF_5 \rightarrow R^+SbF_5X^- \qquad (3)$$

data resulted in estimates of the nucleophilic contributions to the free energies of activation of solvolysis reactions.

We have recently employed electrode potentials in thermochemical cycles to obtain free energy hydride affinities of carbenium ions (4)[4] and free radicals (5)[5] in

$$(R^+)_s + (H^-)_s \rightleftarrows (RH)_s \qquad \Delta G_{hydride}(R^+)_s \qquad (4)$$

$$(R^\bullet)_s + (H^-)_s \rightleftarrows (RH^{\bullet-})_s \qquad \Delta G_{hydride}(R^\bullet)_s \qquad (5)$$

acetonitrile and dimethyl sulfoxide solutions. Ionic solvation energies calculated from $\Delta G_{hydride}(R^+)_S$ along with gas-phase hydride affinities[6] were within 2 kcal/mol of those obtained from (6) in which the last term is the "absolute" potential of the NHE.[7]

$$\Delta G_{solv}(R^+) = E^\circ_{NHE}(R^+/R^\bullet) - IP(R^\bullet) + 4.44 \qquad (6)$$

In this paper a quantitative relationship is developed between free energy halide affinities of carbenium ions (7) and the corresponding hydride affinities (4) in both the gas phase and in solution.

$$(R^+)_s + (X^-)_s \rightleftarrows (RX)_s \qquad \Delta G_{halide}(R^+)_s \qquad (7)$$

Results and Discussion

Thermochemical Relationship between Halide and Hydride Affinities in the Gas Phase. The difference in halide and hydride affinities in the gas phase, $\Delta G_{halide}(R^+) - \Delta G_{hydride}(R^+)$, derived from the thermochemical cycle illustrated in Scheme I, is given by eq 8. The primary significance of (8) is that all of the quantities on the right-hand side of the equation are either known or readily

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Scheme I

	free energy change
$RH \rightleftharpoons R^+ + H^-$	$-\Delta G_{hydride}(R^+)$
$R^+ + X^- \rightleftharpoons RX$	$\Delta G_{halide}(R^+)$
$RH + X^- \rightleftharpoons RX + H^-$	$\Delta\Delta G^\circ_f[RX - RH] + \Delta\Delta G^\circ_f[H^- - X^-]$

Table I. Differences in Free Energies and Enthalpies of Formation of Hydride and Halide Ions in the Gas Phase[a]

anion	$\Delta H_f^\circ(X^-)$[b]	$S^\circ(X^-)$[b]	$\Delta G_f^\circ(X^-)$[c]	$\Delta\Delta H_f^\circ$-$[H^- - X^-]$[b]	$\Delta\Delta G_f^\circ$-$[H^- - X^-]$[b]
H^-	35.0	26.0	27.2		
Cl^-	−54.4	36.6	−65.3	89.4	92.5
Br^-	−50.9	39.1	−62.5	85.9	89.7
I^-	−45.0	40.4	−57.0	80.0	84.2

[a] Taken from ref 8. [b] At 298.15 K, in kcal/mol. [c] eu.

derived from existing thermochemical data for the simple alkyl halides and corresponding hydrocarbons. Pertinent thermochemical data[8] for use in eq 8 are gathered in Table

$$\Delta G_{halide}(R^+) - \Delta G_{hydride}(R^+) = \Delta\Delta G^\circ_f[RX - RH] + \Delta\Delta G^\circ_f[H^- - X^-] \quad (8)$$

I. It is of interest to note that the free energy difference, $\Delta\Delta G^\circ_f[H^- - X^-]$, is a relatively large positive quantity which decreases in value as the halide ion becomes larger with the quantity for chloride ion differing from that for iodide ion by 8 kcal/mol.

Ionization of Alkyl Halides in the Gas Phase. Standard enthalpies[9,10] and entropies[11] of formation of alkyl halides were used to calculate ΔG°_f(R-X) in the gas phase summarized in Table II. For those compounds for which standard entropies are not available, the parameters were estimated using Benson's additivity rules.[11] The appropriate additivity parameters are not available for the calculation of S°(*i*-PrBr). It was assumed that the difference between S°(*n*-Pr-Cl) and S°(*n*-PrBr), 2.8 eu, is the same for the corresponding *i*-PrX. No standard entropy of formation data are available for any $PhCH_2X$ while that for toluene is. The corresponding relative group values[11] for $C(X)(H_2)(C)$ were used along with S°-($PhCH_2H$) to estimate the other values. This approximation is not expected to cause serious error since, for a given R, the difference in high and low values of TS°(RX) are only about 4 kcal/mol and an error as much as 5 eu, which is highly unlikely, will give rise to a TS°(RX) contribution of only 1.5 kcal/mol.

With the exception of the methyl derivatives, the standard free energies of formation of RH are very close in value to ΔG°_f(RBr), and in all cases ΔG°_f(RCl) are significantly more negative than ΔG°_f(RH). Another noteworthy trend in the data is that the differences $\Delta\Delta G^\circ_f$-($RX_2 - RX_1$) are very similar for the alkyl halides with $\Delta\Delta G^\circ_f$(RI − RCl) equal to about 23 kcal/mol and $\Delta\Delta G^\circ_f$-(RI − RBr) amounting to close to 13 kcal/mol.

Table II. Thermochemical Data for the Ionization of Alkyl Halides in the Gas Phase

substrate	ΔG°_f(RX)/kcal mol^{-1}	ΔH°_f(RX)[a]	S°(RX)[b]
MeH	−31.2	−17.9(0.1)	44.48
MeCl	−36.3	−19.6(0.1)	56.00
MeBr	−26.1	−8.5(0.3)	58.87
MeI	−14.6	3.5(0.3)	60.71
EtH	−36.4	−20.0(0.1)	54.85
EtCl	−46.5	−26.8(0.3)	66.1
EtBr	−35.3	−14.8(0.4)	68.6
EtI	−22.9	−1.8(0.4)	70.7[c]
i-PrH	−44.2	−25.0(0.1)	64.51
i-PrCl	−56.7	−34.6(0.3)	74.1
i-PrBr	−47.0	−23.8(0.6)	77.9[d]
i-PrI	−33.1	−9.6(0.9)	78.7[c]
t-BuH	−53.1	−32.1(0.2)	70.42
t-BuCl	−66.5	−43.5(0.5)	77.0
t-BuBr	−55.6	−31.6(0.4)	80.5[c]
t-BuI	−41.8	−17.2(0.8)	82.5
$PhCH_2H$	−10.9	12.0(0.1)	76.64
$PhCH_2Cl$	−20.5	4.5(0.7)	84.0[e]
PhCHBr	−10.8	15.1(1.2)	87.0[e]
$PhCH_2I$	−1.6	25.0(1.4)	89.2[e]

[a] All data in kcal/mol from ref 10; numbers in parentheses are the uncertainties reported in ref 10. [b] Data in eu from ref 11. [c] Calculated using parameters given in ref 11. [d] Additivity parameters are not available. The difference between S°(*n*-PrCl) and S°(*n*-PrBr), 2.8 eu, taken to be the same for this series. [e] Estimated from $S^\circ(PhCH_2H)$ and relative group values (ref 11) for $C(H_3)(C)$, $C(Cl)(H_2)(C)$, $C(Br)(H_2)(C)$, and $C(I)(H_2)(C)$.

Table III. Differences in Free Energy Hydride Affinities and Halide Affinities of Carbenium Ions in the Gas Phase[a]

RX	$[\Delta G_{halide}(R^+) - \Delta G_{hydride}(R^+)]$[b]	$[T\Delta S^\circ(RX) - T\Delta S(RH)]$
MeCl	87.4	3.4
MeBr	94.8	4.3
MeI	100.8	4.9
EtCl	82.4	3.4
EtBr	90.8	4.1
EtI	97.7	4.7
i-PrCl	80.0	2.9
i-PrBr	86.9	4.0
i-PrI	95.3	4.2
t-BuCl	79.1	2.0
t-BuBr	87.2	3.1
t-BuI	95.5	3.7
$PhCH_2Cl$	82.9	2.2
$PhCH_2Br$	89.8	3.1
$PhCH_2I$	93.5	3.7

[a] All values in kcal/mol. [b] Calculated using eq 8.

Differences in Hydride and Halide Affinities of Carbenium Ions in the Gas Phase. The differences, $\Delta G_{halide}(R^+) - \Delta G_{hydride}(R^+)$, for alkyl and benzyl carbenium ions listed in Table III were calculated using data found in Tables I and II. The last column in Table III gives the entropy contribution to the differences, the mean value of which is 3.6 ± 0.9 kcal/mol. This suggests that enthalpy values for the halide and hydride affinities could be used and a correction of 3.6 kcal/mol applied without causing excessive error. The entropy contribution arises from the fact that S°(RX), in Table II, are on the average 12.5 eu greater when X are halogen as compared to hydrogen for a particular R group.

Considering only the data for the alkylcarbenium ions we find that $\Delta G_{halide}(R^+) - \Delta G_{hydride}(R^+)$ increases in a similar fashion for all of the series with the quantity for RI exceeding that for RCl by about 15 kcal/mol. For a particular X, the quantity decreases as the R group becomes larger. The values of $\Delta G_{halide}(R^+) - \Delta G_{hydride}$-$(R^+)$ are not of particular interest in themselves. However, it would be of considerable interest and importance to derive $\Delta G_{halide}(R^+)$ from the differences making use of known hydride affinities.

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Table IV. Calculated Enthalpy Chloride Affinities of Carbenium Ions Compared with Experimental Values[a]

carbenium ion	$-\Delta H_{hydride}(R^+)$[b]	$\Delta\Delta H_f$[RX − RH][c]	$-\Delta H_{chloride}(R^+)$ eq 9	$-\Delta H_{chloride}(R^+)$ ref 14	ΔΔ[d]
2-propyl	250.7	−9.6	170.9	170.5	0.4
tert-butyl	233.8	−11.4	155.8	155.9	−0.1
benzyl	237.5	−7.9	155.6	155.4	0.2

[a] At 298.15 K, in kcal/mol. [b] Data quoted in Table IV of ref 19. [c] From data in Table II. [d] The difference in $-\Delta H_{chloride}(R^+)$ obtained using eq 9 and those reported in Table IV of ref 19.

Table V. Free Energy Hydride Affinities in the Gas Phase and Water and Free Energies of Hydration of Carbenium Ions[a]

R^+	$-\Delta G_{hydride}(R^+)$[b]	$-\Delta G_{solv}(R^+)_{aq}$[c]	model[c]	$-\Delta G_{hydride}(R^+)_{aq}$
CH_3^+	308.1	96	$NH_3^{\bullet+}$	125
$CH_3CH_2^+$	270.2	78	$CH_3NH_3NH_2^{\bullet+}$	105
$(CH_3)_2CH^+$	244.2	59	$(CH_3)_2NH^{\bullet+}$	97
$(CH_3)_3C^+$	227.3	54	$(CH_3)_3NH^+$	84
$PhCH_2^+$	231.0	59	$C_6H_7^+$	86

[a] All data in kcal/mol. [b] $D(R^+H^-)$ data from ref 6c minus 6.5 kcal/mol as discussed in the text. [c] Solvation energy data for model ions from ref 23.

Equilibrium studies of hydride exchange reactions of secondary and tertiary alkyl carbenium ions have provided relative free energy hydride affinities.[12,13] There are some experimental values of gas phase enthalpy halide affinities[14–19] of carbenium ions available. These have been obtained using pulsed electron high pressure mass spectrometry or ion cyclotron resonance spectroscopy and are believed to be accurate to ±1–2 kcal/mol. These data provide an excellent basis for testing data derived from the thermochemical cycle (Scheme I).

Comparison of Halide Affinities Derived from Hydride Affinities with Experimental Values. The thermochemical cycle (Scheme I) can also be used to derive (9) in which the energies are expressed as enthalpies. The

$$\Delta H_{halide}(R^+) - \Delta H_{hydride}(R^+) = \Delta\Delta H^\circ_f[RX - RH] + \Delta\Delta H^\circ_f[H^- - X^-] \quad (9)$$

left hand side of (9) is the difference in the heterolytic bond dissociation energies of the R-H [$D(R^+X^-)$] and the R-X [$D(R^+X^-)$] bonds. These quantities are referred to in (9) as enthalpy halide and hydride affinities to be consistent with the free energy terms derived from (8).

Halide affinities derived using (9) are compared to the values obtained by pulsed electron high pressure mass spectrometry[19] in Table IV. The differences in the heats of formation $\Delta\Delta H^\circ_f$[RX − RH] are from the data in Table II, and $\Delta H_{hydride}(R^+)$ are those quoted in Table IV of ref 19. The only other data necessary to derive $\Delta H_{halide}(R^+)$ using (9) is $\Delta\Delta H^\circ_f[H^- - X^-]$, the difference in standard enthalpies of formation of hydride ion and halide ion. When X^- is chloride this is equal to 89.4 kcal/mol (Table I).

Table VI. Free Energy Halide Affinities of Carbenium Ions[a]

RX	$-\Delta G_{halide}(R^+)_{gas}$[b]	$\Delta G_{solv}(R\text{-}X)_{aq}$[c]	$\Delta G_{solv}(R^+)_{aq}$[d]	$-\Delta G_{halide}(R^+)_{aq}$[e]
MeCl	220.7	1.4	96	48
MeBr	213.8	1.1		47
MeI	207.3	1.0		49
EtCl	187.8	1.3	78	34
EtBr	179.4	1.2		30
EtI	172.5	1.2		32
i-PrCl	164.2	1.7	59	29
i-PrBr	157.3	1.4		27
i-PrI	148.9	1.4		28
t-BuCl	148.2	2[f]	54	17
t-BuBr	140.1	2[f]		14
t-BuI	131.8	2[f]		15
$PhCH_2Cl$	148.1	1[g]	59	13
$PhCH_2Br$	141.2	1[g]		11
$PhCH_2I$	137.5	1[g]		17

[a] All values in kcal/mol. [b] Calculated from data in Tables IV and V. [c] Calculated from data in ref 28. [d] Data from Table V. [e] Calculated using eq 14. [f] Estimated using data in Table I of ref 28. [g] Estimated from data for similar compounds in ref 28.

The average difference between the experimental value of $-\Delta H_{chloride}(R^+)$ and that obtained using (9) is 0.2 kcal/mol. This is well within the estimated[19] experimental error and would appear to indicate that halide affinities estimated using eq 9 can be expected to be reliable with an uncertainty of the order of ±1 kcal/mol.

A check on the reliability of data obtained using eq 8 can also be carried out using experimental data from ref 19. Equilibrium measurements on (10) resulted in ΔG_{10},

$$(CH_3)_3C^+ + PhCH_2Cl \rightleftarrows (CH_3)_3CCl + PhCH_2^+ \quad (10)$$

$$\Delta G_{10} = \Delta G_{chloride}[(CH_3)_3C^+] - \Delta G_{chloride}(PhCH_2^+) \quad (11)$$

at 300 K, equal to 0.0 ± 0.3 kcal/mol. Since ΔG_{10} is simply the difference in chloride affinities of the two cations (11), this result can be compared with data obtained using (8). The pertinent data (see following section), $\Delta G_{chloride}[(CH_3)_3C^+] = -148.2$ kcal/mol and $\Delta G_{chloride}(PhCH_2^+) = -148.1$ kcal/mol, are listed in Table VI. Thus, ΔG_{10} is predicted to be equal to −0.1 kcal/mol. The discrepancy between the experimental value of ΔG_{10} and that predicted from (8), −0.1 kcal/mol, is well within the expected errors for the halide affinities.

Entropy Corrections Necessary To Calculate $\Delta G_{halide}(R^+)$ Using Eq 8 and $D(R^+H^-)$ Values. Gas-phase hydride affinities are enthalpies for reaction 12.[6] These must be corrected for the entropy contributions which are given by (13). However, it has been shown in

$$RH \rightleftarrows R^+ + H^- \qquad D(R^+H^-) \quad (12)$$

$$\Delta S^\circ(R^+H^-) = S^\circ(R^+) + S^\circ(H^-) - S^\circ(RH) \quad (13)$$

related gas-phase proton transfer reactions that the entropy contributions of R^- and RH tend to offset one another for large molecules.[20,21] The degree to which the two terms cancel would be expected to depend upon the extent of structural change in going from RH to R^-. That this is the case is evident from the tabulation of $\Delta S^\circ(R^-H^+)$ for acids of widely differing structure.[21] For example,

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$\Delta S^\circ(\mathrm{R^-H^+})$ for the proton affinity (PA) of anions derived from acetylenes (RC≡CH) is equal to 26.3 ± 0.6 eu [$T\Delta S^\circ(\mathrm{R^-H^+})$ equal 7.85 kcal/mol at 298.15 K] which is very close to $S^\circ(\mathrm{H^+})$. At the other extreme, where there is an sp^3 to sp^2 hybridization change in going from RH to $\mathrm{R^-}$, $\Delta S^\circ(\mathrm{R^-H^+})$ is significantly lower; for example, the average value of $\Delta S^\circ(\mathrm{R^-H^+})$ for ionizations of alkyl nitro compounds ($\mathrm{RCH_2NO_2}$) is equal to 21.5 ± 0.9 eu [$T\Delta S^\circ(\mathrm{R^-H^+})$ equal 6.41 kcal/mol at 298.15 K].

During the reaction of a carbenium ion with an anion, the carbon atom undergoing bond change goes from sp^2 to sp^3 hybridization. Thus, the contributions of $S^\circ(\mathrm{R^+})$ and $S^\circ(\mathrm{R\text{-}H})$ to $\Delta S^\circ(\mathrm{R^+H^-})$ are not expected to cancel. In order to obtain a "best estimate" of $\Delta S^\circ(\mathrm{R^+H^-})$ all of the $\Delta S^\circ(\mathrm{R^-H^+})$ values in Table III of ref 20 for ionizations in which a carbon atom changes hybridization from sp^2 to sp^3 were averaged (21.9 ± 1.1 eu). This corresponds to an entropy contribution of 6.5 kcal/mol. The $\Delta G_{\mathrm{hydride}}(\mathrm{R^+})$ applicable in eq 8 are $-D(\mathrm{R^+H^-})$ data[6c] which must be corrected by 6.5 kcal/mol to account for $T\Delta S^\circ(\mathrm{R^+H^-})$.

Solvation Energies of Carbenium Ions in Water. The hydride and halide affinities of carbenium ions in the gas phase are of interest in that they are related both to the intrinsic stabilities of the carbenium ions as well as to those of the anions in the absence of solvation effects. However, in terms of reaction chemistry, the energetics in solution are of paramount importance. In order to evaluate the anion affinities of carbenium ions in solution, solvation energies must be estimated.

Solvation energies cannot be rigorously calculated. Following Ritchie,[22] Pearson has discussed reliable methods of estimating hydration energies of $\mathrm{B^{\cdot+}}$ (radical cations), $\Delta G_{\mathrm{solv}}(\mathrm{B^{\cdot+}})_{\mathrm{aq}}$, from known values of $\Delta G_{\mathrm{solv}}(\mathrm{BH^+})_{\mathrm{aq}}$ for the corresponding onium ions.[23] The procedure apparently works well for ions of large molecules but not for small ions such as $\mathrm{NH_3^{\cdot+}}$. The problem with the procedure for the latter case is that $\mathrm{NH_3^{\cdot+}}$ has a significant dipole moment while $\mathrm{NH_4^+}$ does not. Fortunately, the discrepancy between $\Delta G_{\mathrm{solv}}(\mathrm{B^{\cdot+}})_{\mathrm{aq}}$ and $\Delta G_{\mathrm{solv}}(\mathrm{BH^+})_{\mathrm{aq}}$ diminishes upon substitution of $\mathrm{CH_3}$ for H in $\mathrm{NH_3}$ and the values for $\mathrm{(CH_3)_2NH^{\cdot+}}$ and $\mathrm{(CH_3)_2NH_2^+}$ are nearly the same.

Solvation energies of carbenium ions $\Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}}$ estimated taking into account Pearson's discussion[23] are listed in Table V. The ammonia radical cation was taken as a model for $\mathrm{CH_3^+}$. Methylamine radical cation was selected as a model for $\mathrm{CH_3CH_2^+}$, and 10 kcal/mol was added to $\Delta G_{\mathrm{solv}}(\mathrm{CH_3NH_3^+})_{\mathrm{aq}}$ as suggested by Pearson for the estimation of primary amine radical cation solvation energies. The solvation energy estimates for isopropyl and *tert*-butyl cations were straightforward. It is interesting to note that solvation energies of larger ions have very nearly the same values. For example, we have observed that the solvation energies of $\mathrm{Ph_3C^+}$, $\mathrm{Ph_2CH^+}$, and $\mathrm{PhCH_2^+}$ in acetonitrile are the same within experimental error with a value of 41 ± 1 kcal/mol.[4]

The estimation of $\Delta G_{\mathrm{solv}}(\mathrm{PhCH_2^+})_{\mathrm{aq}}$ must account for another factor. The charge on the alkyl carbenium ions is localized on a single carbon atom while extensive charge delocalization is expected for $\mathrm{PhCH_2^+}$. The anilinium ion ($\mathrm{PhNH_3^+}$), in which the charge is localized on N, is thus not expected to be an adequate model for the estimation of $\Delta G_{\mathrm{solv}}(\mathrm{PhCH_2^+})_{\mathrm{aq}}$. The effect of charge delocalization on $\Delta G_{\mathrm{solv}}(\mathrm{R^-})_{\mathrm{aq}}$ is apparent in comparing the hydration free energies of $\mathrm{PhCH_2^-}$ (−57 kcal/mol) with that of $\mathrm{Ph^-}$ (−72 kcal/mol). The charge on $\mathrm{Ph^-}$ is localized on a single carbon while that of $\mathrm{PhCH_2^-}$ is delocalized over the π-system. Therefore, the conjugate acid of benzene ($\mathrm{C_6H_7^+}$) in which the charge is delocalized is expected to be a better model for the estimation of $\Delta G_{\mathrm{solv}}(\mathrm{PhCH_2^+})_{\mathrm{aq}}$. The hydration free energy of $\mathrm{C_6H_7^+}$ has been estimated to be equal to −61 kcal/mol.[23] Pyridinium ion ($\mathrm{C_5H_5NH^+}$) is an alternative possibility to use as a model. The latter has a hydration energy of −57 kcal/mol which is the same as that estimated for $\mathrm{PhCH_2^-}$. It appears reasonable to expect the hydration free energies of $\mathrm{PhCH_2^-}$ and $\mathrm{PhCH_2^+}$ to be close in magnitude.[24] For these reasons, $\Delta G_{\mathrm{solv}}(\mathrm{PhCH_2^+})_{\mathrm{aq}}$ was taken to be the average of that for $\mathrm{C_6H_7^+}$ and $\mathrm{C_5H_5NH^+}$, *i.e.*, −59 kcal/mol.

Hydride Affinities of Carbenium Ions in Water. Solution hydride affinities of carbenium ions [$\Delta G_{\mathrm{hydride}}(\mathrm{R^+})_{\mathrm{aq}}$] were calculated using eq 14 with $\Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}}$ and

$$\Delta G_{\mathrm{hydride}}(\mathrm{R^+})_{\mathrm{aq}} = \Delta G_{\mathrm{hydride}}(\mathrm{R^+})_{\mathrm{gas}} - \Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}} - \Delta G_{\mathrm{solv}}(\mathrm{H^-})_{\mathrm{aq}} + \Delta G_{\mathrm{solv}}(\mathrm{RH})_{\mathrm{aq}} \quad (14)$$

$\Delta G_{\mathrm{solv}}(\mathrm{RH})_{\mathrm{aq}}$ listed in Table V along with $\Delta G_{\mathrm{solv}}(\mathrm{H^-})_{\mathrm{aq}}$ equal to −87 kcal/mol.[23] The free energies of solvation of neutral RH [$\Delta G_{\mathrm{solv}}(\mathrm{RH})_{\mathrm{aq}}$] were calculated using data reported by Hine.[28] The gas phase values were obtained from $-D(\mathrm{R^+H^-})$[6c] with a 6.5 kcal/mol correction for $T\Delta S^\circ(\mathrm{R^+H^-})$ as discussed in a previous section.

The principal source of error in $\Delta G_{\mathrm{hydride}}(\mathrm{R^+})_{\mathrm{aq}}$ is associated with the estimation of $\Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}}$. Because of the fact that solvation energies of ions tend toward a common value as the ion becomes larger, it is proposed that the error in the estimation of the hydration free energies of the last three ions in Table V is of the order of ±2 kcal/mol. The degree of uncertainty is much greater for $\Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}}$ of the smaller ions, $\mathrm{CH_3^+}$ and $\mathrm{CH_3CH_2^+}$, and an error of ±5 kcal/mol appears reasonable.

Halide Affinities of Carbenium Ions in Water. The corresponding halide affinities of carbenium ions in aqueous solution summarized in Table VI were obtained using eq 15 with halide hydration energies, $\Delta G_{\mathrm{solv}}(\mathrm{X^-})_{\mathrm{aq}}$,

$$\Delta G_{\mathrm{halide}}(\mathrm{R^+})_{\mathrm{aq}} = \Delta G_{\mathrm{halide}}(\mathrm{R^+})_{\mathrm{gas}} - \Delta G_{\mathrm{solv}}(\mathrm{R^+})_{\mathrm{aq}} - \Delta G_{\mathrm{solv}}(\mathrm{X^-})_{\mathrm{aq}} + \Delta G_{\mathrm{solv}}(\mathrm{RX})_{\mathrm{aq}} \quad (15)$$

equal to −75 ($\mathrm{Cl^-}$), −70 ($\mathrm{Br^-}$), and −61 ($\mathrm{I^-}$) kcal/mol from the literature.[23] Solvation energies of neutral RX were derived from data in ref 28. The gas-phase values listed in Table VI were derived using the data in Tables IV and V. Again, the greatest uncertainty associated with the anion affinities in solution lies in the estimation of the hydration energies as discussed in the previous section.

Relationships between Hydride, Halide, and Electron Affinities. We have recently observed an excellent correlation of hydride affinities of substituted benzyl cations and radicals with the corresponding electron

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(22) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313.

(23) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(24) For large charge-delocalized ions, it is commonly assumed that the solvation energies of anions and cations of similar structure should be very nearly the same. This is the basis for estimating solvation energies of alternant aromatic hydrocarbon radical anions and cations.[25,26] The tetraphenyl borate assumption,[27] *i.e.*, that the solvation energy of $\mathrm{(Ph_4As^+)(Ph_4B^-)}$ can be attributed to equal contributions of the two ions, is another example of similar reasoning.

(25) Case, B.; Hush, N. S.; Parsons, R.; Peover, M. E. *J. Electroanal. Chem.* **1965**, *10*, 360.

(26) (a) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656.

(27) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(28) Hine, J.; Mookerjee, P. K. *J. Org. Chem.* **1975**, *40*, 292.

Table VII. Linear Relationships between Gas-Phase Free Energy Hydride Affinities and Free Energy Halide and Electron Affinities of Alkyl Carbenium Ions

	$-\Delta G_{\text{anion}}(X^-)_{\text{gas}}$ (kcal/mol)				
R^+	H^-	e^{-a}	Cl^-	Br^-	I^-
CH_3^+	308.1	226.9	221	214	207
$CH_3CH_2^+$	270.2	193.3	188	179	173
$(CH_3)_2CH^+$	244.2	174.1	164	157	149
$(CH_3)_3C^+$	277.3	154.5	148	140	132
slope		1.14	1.11	1.10	1.08
r^2		0.996	1.000	0.999	1.000

[a] Electron affinity equal –IP from ref 19.

affinities of $ArCH_2^+$ and $ArCH_2H$.[5] The correlation encompassed a range of free energy hydride affinities from –19 to –129 kcal/mol with a correlation coefficient of 0.999. It was suggested that a general relationship exists between hydride affinities and electron affinities. In this study, there are a number of possible relationships to test for linearity. The anion and electron affinities of alkyl carbenium ions are gathered in Table VII. Linear regression analyses with $\Delta G_{\text{hydride}}(R^+)$ as the dependent variable resulted in the following equations:

$$\Delta G_{\text{hydride}}(R^+) = 1.14\Delta G_{\text{electron}}(R^+) - 42.8 \qquad (r^2 = 0.996) \tag{16}$$

$$\Delta G_{\text{hydride}}(R^+) = 1.11\Delta G_{\text{chloride}}(R^+) - 67.2 \qquad (r^2 = 1.000) \tag{17}$$

$$\Delta G_{\text{hydride}}(R^+) = 1.10\Delta G_{\text{bromide}}(R^+) - 76.0 \qquad (r^2 = 0.999) \tag{18}$$

$$\Delta G_{\text{hydride}}(R^+) = 1.08\Delta G_{\text{iodide}}(R^+) - 86.6 \qquad (r^2 = 1.000) \tag{19}$$

The fact that all of the slopes in eqs 16–19 are similar in value suggests that correlation of any of the anion or electron affinities with each other would result in a linear correlation with near unit slope. This is the case.

Relevance of the Thermochemical Data to Substitution Reactions in Solution. The first-order rate constants (k_1) of limiting S_N1 reactions, *i.e.*, those in which the ionization reaction (1) is rate limiting and the recombination of ions is slow relative to trapping of the carbenium ion by water (2), can readily be estimated from the equilibrium constants derived from $\Delta G_{\text{halide}}(R^+)_{\text{aq}}$. The estimation of the forward rate constant depends upon the assumption of a value for k_{-1}, the rate constant for reverse reaction 1. The most straightforward procedure is to assume that for an endergonic equilibrium the reverse reaction is diffusion controlled which then gives rise to the maximum possible value, $(k_1)_{\text{max}}$. The results of an analysis using the latter assumption are summarized in Table VIII.

The value of $(k_1)_{\text{max}}$ predicted for the ionization of CH_3Br in water at 298 K is 10^{-24} s^{-1} which corresponds to a half-life of about 10^{16} years. The energetics of S_N1 ionization of CH_3CH_2Br are somewhat more favorable, but the reaction is not predicted to take place on a measurable time scale ($t_{1/2} = 10^5$ years). The predicted minimum half-lives for the ionization of $(CH_3)_2CHBr$ is 220 years. On the other hand, the minimum half-life calculated for the ionization of both $(CH_3)_3CBr$ and $PhCH_2Br$ are exceedingly short, 0.7 s and 7 ms, respectively. It must be kept in mind that the calculated half-lives are minimum values, and it is likely that ion recombination in the latter two cases would not be diffusion controlled. The uncertainty in $\Delta G_{\text{halide}}(R^+)_{\text{aq}}$ for $(CH_3)_3C^+$ and $PhCH_2^+$ is believed to be of the order of ±2 kcal/mol which corresponds to an error of ±1.5 in log $(k_1)_{\text{max}}$.

Table VIII. Estimated Maximum Possible First-Order Rate Constants for the Ionization of Alkyl Bromides in Water at 298 K[a]

substrate	$-\Delta G_{\text{bromide}}(R^+)_{\text{aq}}$	$-\log [K_1(RBr)/M]$	$\log [(k_1)_{\text{max}}{}^b/s^{-1}]$
CH_3Br	47 ● 5	34 ± 4	–24 ± 4
CH_3CH_2Br	31 ± 5	23 ± 4	–13 ± 4
$(CH_3)_2CHBr$	27 ± 2	20 ± 2	–10 ± 2
$(CH_3)_3CBr$	14 ● 2	10 ± 2	0 ± 2
$PhCH_2Br$	11 ± 2	8 ± 2	2 ± 2

[a] $\Delta G_{\text{bromide}}(R^+)_{\text{aq}}$ from Table VI. Estimated uncertainty based upon $\Delta G_{\text{solv}}(R^+)_{\text{aq}}$ as described in the text. [b] The maximum possible rate constant for ionization of RBr calculated assuming the recombination reaction of ions to be diffusion controlled.

The trend in rate constants for ionization of RBr in Table VIII and the estimated minimum half-lives in water reflect the general order of reactivity expected on the basis of the extensive body of knowledge about substitution reactions.[2] However, predictions of the nature of those in the previous paragraph have not been possible earlier because of the absence of thermochemical data. Work in progress is aimed at gathering a thermochemical database for the ionization of alkyl halides and derivatives in solution which will be of use in the analysis of substitution kinetic data.

Conclusions. The thermochemical cycle illustrated in Scheme I resulted in eq 8 which allows the free energy difference, $\Delta G_{\text{halide}}(R^+) - \Delta G_{\text{hydride}}(R^+)$, in the gas phase to be calculated from well-known thermochemical quantities. There are no approximations in the derivation of eq 8 which allows reliable values of halide affinities of simple carbenium ions to be calculated in the gas phase. The uncertainties in the halide affinities are expected to be of the same magnitude as those of the corresponding hydride affinities. In order to relate these values to the energetics of the very important ionization reactions of alkyl halides and related compounds in solution, solvation energies of the carbenium ions must be estimated. This was accomplished using analyses[22,23] previously developed for other cations. Reliable values of $\Delta G_{\text{solv}}(R^+)_{\text{aq}}$ were estimated using either amine radical cations ($B^{\cdot+}$) or onium ions (BH^+) as models for R^+. The error in $\Delta G_{\text{halide}}(R^+)$ expected due to uncertainties in $\Delta G_{\text{solv}}(R^+)_{\text{aq}}$ diminishes as the size of R^+ increases, and it is concluded that the error from this source is of the order of ±2 kcal/mol for $(CH_3)_2CH^+$ and larger ions.

Linear relationships were observed between all anion (including hydride, chloride, bromide, and iodide) and electron affinities of alkylcarbenium ions in the gas phase. These observations suggest that the number of carbenium ions for which anion affinities are available can be expected to increase markedly with the publication of work now in progress.

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