

Hydride Affinities of Carbenium Ions in Acetonitrile and Dimethyl Sulfoxide Solution

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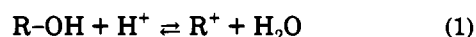
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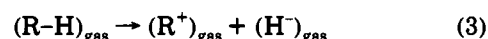
Abstract: Hydride affinities of organic cations in solution, defined as the free energy change for the reaction $(R^+)_s + (H^-)_s \rightleftharpoons (RH)_s$, where the subscript s refers to the solvent, can be determined using either of two equations (eqs 5 and 7) derived from thermochemical cycles. The degree of uncertainty in $\Delta G_{\text{hydride}}(R^+)_s$ depends primarily upon the errors associated with the determination of the reversible electrode potentials for the (R^+/R^-) and (R^+/R^*) couples. In this study, $\Delta G_{\text{hydride}}(R^+)_s$ values have been derived for a number of stable carbenium ions in dimethyl sulfoxide solution applying eq 7 with reversible electrode potentials. Values with a higher degree of uncertainty were also obtained from ring-substituted toluenes, 9-substituted fluorenes, and α - or 10-substituted 9-methylanthracenes, employing irreversible electrode potentials. The fact that the potentials for the (R^+/R^-) and (R^+/R^*) are summed in eq 7 gives rise to a partial cancellation of errors due to kinetic shifts of the experimental potentials from the reversible values. Structural effects on free energies of hydride transfer are discussed, comparisons with available gas-phase values are made, and ionic solvation energies are calculated in some cases.

Introduction

The influence of structure on the stabilities of carbenium ions has long been an important issue in many areas of organic chemistry. A number of approaches, including equilibrium measurements on reactions corresponding to eqs 1 and 2, were



developed to study the thermodynamic stabilities of carbenium ions in solution. Studies of the ionization of carbinols in acidic media (reaction 1) using the acidity function method allowed carbocation stability to be expressed in terms of the pK_{R^+} values. These studies³⁻⁷ were carried out in aqueous acid solutions and were applicable only to relatively stable cations. The calorimetric studies of reaction 2 by Arnett and co-workers, on the other hand, have provided the heat of reaction data in the nonnucleophilic solvent SO_2ClF which cover a much wider range of carbocation stability and were found to correspond quite well with the available gas-phase hydride affinity data.⁸⁻¹⁰ Gas-phase hydride affinity $[D(R^+H^-)]^{11}$ data for reaction 3 have been provided by several research groups¹²⁻¹⁵ over the past 15 years.



In solution, direct thermodynamic measurements on reaction 3 are not feasible since all such reactions have exceedingly small equilibrium constants and consequently hydride ion does not exist in any solvent in the presence of a cation. Thus, evaluation of the free energies of reaction 3 in solution requires indirect methods. In a preliminary communication of this study,¹⁶ it was suggested that reliable estimates of hydride affinities in solution can be obtained using thermochemical cycles in conjunction with pK_A and electrode potential measurements. For reactions in solution, we define the hydride affinity as the free energy change for reaction 4, $\Delta G_{\text{hydride}}(R^+)_s$, where the subscript s identifies the solvent.



The general approach, using electrode potentials to derive experimentally inaccessible thermochemical quantities, has recently been successfully applied to a wide range of problems.¹⁷⁻²⁴

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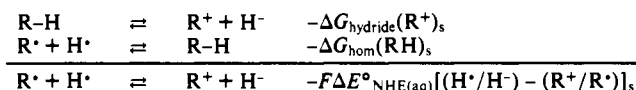
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In the present paper, we report $\Delta G_{\text{hydride}}(\text{R}^+)_s$ data thus obtained for a variety of stable carbocations and for less stable aromatic carbocations derived from substituted toluenes, fluorenes, and 9-methylanthracenes in acetonitrile (AN) and dimethyl sulfoxide (DMSO) solution.

Results and Discussion

Thermochemical Relationships. The free energy of R–H bond heterolytic dissociation can be derived from the isodesmic reaction relationship illustrated in Scheme I. The electrode potential

Scheme I



difference below the line is related to the difference in the free energy changes above the double line by eq 5. The data required

$$-\Delta G_{\text{hydride}}(\text{R}^+)_s = \Delta G_{\text{hom}}(\text{RH})_s - F\Delta E^\circ_{\text{NHE}(\text{aq})}[(\text{H}^+/\text{H}^-) - (\text{R}^+/\text{R}^*)]_s \quad (5)$$

to evaluate $\Delta G_{\text{hydride}}(\text{R}^+)_s$ include the free energy of homolytic bond dissociation, $\Delta G_{\text{hom}}(\text{RH})_s$ in solution, and the difference in potentials of the (H^+/H^-) and (R^+/R^*) couples in the solvent of interest as referenced to the normal hydrogen electrode [NHE(aq)].

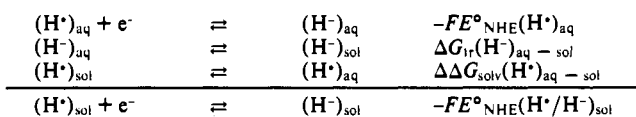
Bond dissociation free energies have recently been derived for a variety of R–H bonds using eq 6 based on a thermochemical cycle.²⁴ In order to apply eq 6 to determine $\Delta G_{\text{hom}}(\text{RH})_s$, it was

$$\Delta G_{\text{hom}}(\text{RH})_s = 2.303RTpK_A(\text{RH})_s + F\Delta E^\circ_{\text{NHE}(\text{aq})}[(\text{R}^+/\text{R}^-) - (\text{H}^+/\text{H}^*)]_s \quad (6)$$

necessary to evaluate the standard potential of the (H^+/H^*) couple. This was accomplished by showing that the free energies of solvation of the noble gases are linearly related to their van der Waals radii (r), and it was proposed that since r for H^+ (120 pm) is very close to that of He (122 pm), the solvation energies of the two gaseous atoms should be very nearly equal.^{24b}

Adopting a similar approach, the standard potential of the (H^+/H^-) couple in nonaqueous solvents can also be evaluated. The standard potential of the H^+/H^- couple in aqueous solution [$E^\circ_{\text{NHE}(\text{aq})}(\text{H}^+/\text{H}^-)$] has been estimated to be +0.18 V.²⁵ Since the hydride transfer reactions of interest generally take place in nonaqueous solvents, it was necessary to derive the standard potentials for the reduction of H^+ in these solvents.¹⁶ The thermochemical cycle relevant for the solvent change is illustrated in Scheme II. The free energy of transfer of hydride ion from

Scheme II



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Table I. Reversible Electrode Potentials for the (H^+/H^-) Couple and Hydride Ion Free Energies of Transfer from Water to Nonaqueous Solvents

solvent	$E^\circ_{\text{NHE}}(\text{H}^+/\text{H}^-)$, V	$\Delta G_{\text{tr}}(\text{H}^-)_{\text{aq} \rightarrow \text{sol}}$, kcal mol ⁻¹
water	+0.18 ^a	
AN	-0.60 ^b	17.2 ^c
DMSO	-0.55 ^b	16.7 ^c
DMF	-0.60 ^b	17.9 ^c

^a Value from ref 25 converted to the NHE. ^b Calculated with relationships in Scheme II. ^c From linear correlations described in the text.

water to a particular solvent ($\Delta G_{\text{tr}}(\text{H}^-)_{\text{aq} \rightarrow \text{sol}}$) and the difference in solvation energies of H^+ ($\Delta \Delta G_{\text{sol}}(\text{H}^+)_{\text{aq} \rightarrow \text{sol}}$) in water and the nonaqueous solvent are the quantities necessary to make the conversion. The former is experimentally inaccessible, while the latter has recently been evaluated for acetonitrile and DMSO solutions.^{24b}

Linear correlation of $\Delta G_{\text{tr}}(\text{X}^-)_{\text{aq} \rightarrow \text{sol}}$ for I^- , Br^- , and Cl^- ions in AN ($r = 0.98$), DMSO ($r = 0.996$), and *N,N*-dimethylformamide (DMF) ($r = 0.999$) with the corresponding free energies of hydration²⁵ provided relationships to calculate $\Delta G_{\text{tr}}(\text{H}^-)_{\text{aq} \rightarrow \text{sol}}$. These values are summarized in Table I along with the corresponding $E^\circ_{\text{NHE}}(\text{H}^+/\text{H}^-)$ evaluated using the relationships from Scheme II.

Substitution of the appropriate term derived from eq 6 for $\Delta G_{\text{hom}}(\text{RH})_s$ in eq 5 results in eq 7, where the last term is a constant. Thus, the evaluation of $\Delta G_{\text{hom}}(\text{RH})_s$ is not necessary

$$-\Delta G_{\text{hydride}}(\text{R}^+)_s = 2.303RTpK_A(\text{RH})_s + FE^\circ_{\text{NHE}}[(\text{R}^+/\text{R}^-) + (\text{R}^+/\text{R}^*)]_s - FE^\circ_{\text{NHE}}[(\text{H}^+/\text{H}^-) + (\text{H}^+/\text{H}^*)] \quad (7)$$

for evaluating $\Delta G_{\text{hydride}}(\text{R}^+)_s$, provided that the pK_A and the reduction potential of R^+ were experimentally determined.

Another quantity necessary in applying eq 5 or 7 is the potential of the (R^+/R^*) couple (see below). For stable carbocations, $E^\circ_{\text{NHE}}(\text{R}^+/\text{R}^*)$ can be obtained directly from measurements on the corresponding salts. For primary and most secondary species whose cations are not sufficiently stable to exist in solution, $E^{\text{ox}}(\text{R}^+)_s$ of the photochemically-generated radicals (see Experimental Section) were determined by photomodulation ac voltammetry^{22,26} to obtain the required electrode potential data. The hydride affinity data thus evaluated are summarized in Tables II–V.

Electrode Potentials and Thermochemical Cycles. Standard electrode potentials, i.e., reversible or thermodynamic electrode potentials referenced to the normal hydrogen electrode, are the quantities required in thermochemical cycles. These are designated as $E^\circ_{\text{NHE}}(\text{ox/red})$, where ox and red are the oxidized and reduced species of the couple, respectively. Experimental electrode potentials are often not reversible values. We will refer to electrode potentials derived from experimental measurements as either $E^{\text{ox}}(\text{red})$ or $E^{\text{red}}(\text{ox})$, depending upon which half-reaction is studied. When appropriate, $E^\circ_{\text{NHE}}(\text{ox/red})$ may be equated to $E^{\text{ox}}(\text{red})$ or $E^{\text{red}}(\text{ox})$. In some other cases, the latter may be corrected to the pertinent $E^\circ_{\text{NHE}}(\text{ox/red})$ by estimating the kinetic contributions associated with the experimental potentials.

Substituent Effects on Hydride Affinities. Consideration of the hydride affinity equilibrium 4 shows that substituent effects are expected for both (R^+) and (RH) . In the following discussion we attribute differences in $\Delta G_{\text{hydride}}(\text{R}^+)_s$ associated with a substituent change to changes in stabilities of the corresponding cations. This is probably a safe practice in a qualitative sense in view of the increased electron demand on going from R–H to R^+ . However, substituent effects in R–H cannot always be

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Table II. Hydride Affinities [$\Delta G_{\text{hydride}}(\text{R}^+)$] of Stable Carbenium Ions in DMSO Solution

substrate	pK_A^a	$E^{\circ}_{\text{NHE}}(\text{R}^+/\text{R}^-)_s^b$	$E^{\circ}_{\text{NHE}}(\text{R}^+/\text{R}^-)_{s,c}^{b,c}$	$-\Delta G_{\text{hydride}}(\text{R}^+)^d$
Ph ₃ CH	30.6	-0.949 ^e	0.280	96
(4-Me ₂ NC ₆ H ₄) ₃ CH	39.4 ^f	-1.51 ^e	-0.572	76
(4-ClC ₆ H ₄) ₃ CH	27.0	-0.731	0.367 ^h	98
4-PhC ₆ H ₄ CHPh ₂	29.4	-0.879	0.256 ^h	96
xanthene	30.0	-1.148 ^{e,i}	0.244	90
9-phenylxanthene	27.9	-0.994 ^{e,i}	0.171	89
9-phenylthioxanthene	27.3	-0.889	0.165 ^j	90
cycloheptatriene	35.1 ^f	-1.418 ^{e,i}	-0.08	83
1,2,3-triphenylcyclopropene	47 ^f	-1.508 ^{e,i}	-0.386	90

^a Values from Bordwell's laboratories (ref 41) unless otherwise specified. ^b Reversible electrode potential in volts unless noted otherwise. ^c $E^{\text{red}}(\text{R}^+)$ of carbocations measured in DMSO/Bu₄NPF₆ (0.1 M) at a Pt electrode using cyclic voltammetry (unless otherwise noted) with a sweep rate equal to 1 V/s and a substrate concentration equal to 1.5 mM. ^d Evaluated using eq 7 in kcal/mol. ^e Data from ref 19n. ^f Data from ref 17c adjusted by subtracting 0.9. ^g Value from ref 17c adjusted to NHE. ^h From second oxidative wave of the carbanion for the 1 e⁻ process of R⁻ → R[•]. ⁱ Irreversible electrode potential. ^j The second oxidative wave of the carbanion gave an $E^{\text{ox}}(\text{R}^- \rightarrow \text{R}^{\bullet}) = 0.164$ V.

Table III. Hydride Affinities of Benzyl Cations Derived from Toluenes in Acetonitrile

substrate	pK_A^a	$E^{\text{red}}_{\text{NHE}}(\text{R}^+)_s^b$ V	$E^{\text{ox}}_{\text{NHE}}(\text{R}^+)_s^c$ V	$-\Delta G_{\text{hydride}}(\text{R}^+)_s^d$ kcal/mol
HC ₆ H ₄ CH ₃	50.3	-1.19	0.97 ^e	118
<i>p</i> -MeC ₆ H ₄ CH ₃	53.0	-1.38	0.74 ^f	112
<i>p</i> -MeOC ₆ H ₄ CH ₃	54.4	-1.51	0.54 ^e	107
<i>p</i> -ClC ₆ H ₄ CH ₃	50.0	-1.16	1.15 ^f	123
<i>p</i> -FC ₆ H ₄ CH ₃	51.4	-1.26	1.16 ^f	123
<i>p</i> -MeCOC ₆ H ₄ CH ₃	39.2	-0.47	1.14 ^e	124
<i>m</i> -NCC ₆ H ₄ CH ₃	46.0	-0.87	1.35 ^e	129
<i>p</i> -NCC ₆ H ₄ CH ₃	40.4	-0.53	1.07 ^f	122
<i>p</i> -O ₂ NC ₆ H ₄ CH ₃	~29 ^g	0.12 ^h	1.40 ⁱ	129

^a The pK_A for toluene in acetonitrile was calculated using eq 6 and $\Delta G_{\text{hom}}(\text{RH})_s$ equal to 82 kcal/mol (BDE = 88 kcal/mol⁴³). Gas-phase BDEs have been observed to exceed $\Delta G_{\text{hom}}(\text{RH})_s$ by 6 kcal/mol in acetonitrile.^{24b,c} Relative pK_A values from ref 22d were adjusted to the toluene value. ^b From ref 22d and converted to vs NHE. ^c Measured by photomodulation ac voltammetry (see Experimental Section) in 0.1 M Bu₄NPF₆/MeCN at a platinum electrode in a UV cell; sweep rate, 50 mV/s; counter electrode, thin Au film; substrate concentration, 0.1–0.5 M; uncertainty, ±50 mV. ^d Evaluated from eq 7. ^e From ref 22a and converted to vs NHE. ^f Relative values obtained in this work adjusted to $E^{\text{ox}}(\text{PhCH}_2^{\bullet})$ from ref 22a. ^g Derived from Bordwell's value⁴¹ of 20.4 in DMSO by adding 9. ^h This work. ⁱ Value obtained in DMSO.

Table IV. Hydride Affinities in DMSO for Cations Derived from 9-Substituted Fluorenes

substrate	pK_A^a	$E^{\text{ox}}_{\text{NHE}}(\text{R}^+)_s^b$ V	$E^{\text{ox}}_{\text{NHE}}(\text{R}^+)_s^{c,d}$ V	$-\Delta G_{\text{hydride}}(\text{R}^+)_s^e$ kcal/mol
fluorene	22.6	-0.532	0.87	109
9-Me ₂ N-fluorene	22.5	-0.845	0.30	88
9-MeO-fluorene	22.1	-0.787	0.29	89
9- <i>tert</i> -butylfluorene	24.3	-0.580	0.79	108
9-Ph-fluorene	17.9	-0.491	0.59	97
9-(3-ClC ₆ H ₄)-fluorene	16.8	-0.401	0.80	102
9-PhS-fluorene	15.4	-0.312	0.59	97
9-CO ₂ Me-fluorene	10.3	0.045	1.24	114
Ph ₂ CH ₂	32.2	-1.003	0.60	105

^a See footnote a in Table II. ^b Values from ref 44. ^c See footnote c in Table III. ^d $E_{1/2}$ data obtained in acetonitrile are listed. This is expected, on the basis of comparison of data available in both solvents, to result in an error of no more than about 60 mV. ^e Evaluated from eq 7.

ignored and may sometimes make significant contributions to $\Delta G_{\text{hydride}}(\text{R}^+)_s$.

An analogous situation arises when considering substituent effects on homolytic bond dissociation energies, BDE (eq 8).



Relative BDEs are frequently used as a measure of relative radical stability. However, evidence has been presented to show that there are pitfalls to this approach.^{27,28} Relative C–Br BDEs of

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Table V. Hydride Affinities for Cations Derived from 10-Substituted 9-Methylanthracenes in DMSO

substituent		$pK_A^{a,b}$	$E^{\text{red}}_{\text{NHE}}(\text{R}^+)_s^b$ V	$E^{\text{ox}}_{\text{NHE}}(\text{R}^+)_s^c$ V	$\Delta G_{\text{hydride}}(\text{R}^+)_s^d$ kcal/mol
10-	9-				
H	CH ₃	31.1	-0.952	0.33	98
CH ₃	CH ₃	31.8	-0.978	0.17	95
CH ₃ O	CH ₃	31.8	-1.000	0.05	91
H	CH ₂ OCH ₃	30.6	-1.098 ^e	0.69	102
H	CH ₂ OPh	30.2	-0.976	0.96	111
H	CH ₂ SPh	28.6	-0.825	0.82	109
Cl	CH ₃	28.2	-0.810	0.66	105
NO ₂	CH ₃	13.2	0.158	1.25	120

^a See footnote a in Table II. ^b Values from ref 45. ^c See footnote c in Table III. ^d Evaluated using eq 7. ^e Value from ref 46.

a number of 4-substituted benzyl bromides were found to differ substantially from the relative C–H BDEs of the corresponding toluenes.²⁸

Stable Carbenium Ions. Table II presents the hydride affinity values for a number of stable cations along with the necessary data required in the evaluation. The $E^{\text{red}}(\text{R}^+)$ values were obtained directly by linear sweep voltammetry. The reduction potentials of the corresponding carbocations were measured for most of the substrates with the exception of (4-ClC₆H₄)₃CH and (4-PhC₆H₄)CHPh₂, for which $E^{\text{ox}}(\text{R}^-)$, from the second oxidation wave of the anion, was obtained. This measurement strategy is not expected to be associated with a significant error since the second oxidation wave of the 9-phenylthioxanthene anion (both waves were reversible) was observed at 0.164 V, which is identical to the reduction potential of the corresponding cation [$E^{\text{red}}(\text{R}^+) = 0.165$ V].

An inspection of the table shows that the stability order of these carbenium ions ($\Delta G_{\text{hydride}}(\text{R}^+)$ in parentheses) is tropylium (83) > 1,2,3-triphenylcyclopropenium (90) ~ 9-phenylxanthene (89) > xanthene (90) ~ 9-phenylthioxanthene (90) > Ph₃C⁺ (96). The trityl cation is slightly stabilized by a 4-phenyl group but is destabilized by a 4-Cl substituent, as expected. The dramatic stabilization observed upon the introduction of the 4-NMe₂ groups in trityl (20 kcal/mol) agrees remarkably well with the free energy difference of the carbinol ionizations ($\Delta\Delta G = 21.8$ kcal mol⁻¹) by the same structural variation in aqueous sulfuric acid, as indicated by a change in the pK_{R^+} values from -6.6 to +9.4.³

Primary and Secondary Benzylic Carbenium Ions. Since stable cations cannot be obtained in solution for any of the substrates listed in Tables III–V, linear sweep voltammetry is not suitable for the potential measurements. The method of choice for measurements of redox potentials of transient species is photomodulation ac voltammetry (PACV) developed by Wayner²² (see Experimental Section for details). PACV was applied to determine the redox potentials for the R⁺/R[•] couples which are necessary for applying eq 5 or 7 to evaluate the hydride affinity data. The $E^{\text{ox}}(\text{R}^+)_s$ for four of the toluenes in Table III have

Table VI. Comparison of Solution Hydride Affinities with Other Measures of Carbenium Ion Stability and Calculated Ionic Solvation Energies

substrate	$-\Delta G_{\text{hydride}}(\text{R}^+)$, ^a kcal/mol (solvent)	$\text{p}K_{\text{R}^+}$ ^b	$D(\text{R}^+\text{H}^-)$, ^c kcal/mol	$-\Delta G_{\text{solv}}(\text{R}^+)$, ^d kcal/mol
triphenylmethane (TPM)	96 (DMSO)	-6.6	(215)	(41)
4,4',4''-tris(dimethylamino)TPM	76 (DMSO)	9.4	(193)	(39)
4,4',4''-trichloroTPM	98 (DMSO)	-7.7	(218)	(42)
xanthene	90 (DMSO)	-0.85	210.2	42 (41)
9-phenylxanthene	89 (DMSO)	1.1	(208)	(41)
cycloheptatriene	83 (DMSO)	4.7	(201)	(40)
Ph_2CH_2	105 (DMSO)	-13.3	222.3	40 (42)
fluorene	109 (DMSO)	-16.6	(229)	(42)
PhCH_3	118 (MeCN)	(-23.8)	237.7	42 (44)
4-MeOC ₆ H ₄ CH ₃	106 (MeCN)	(-14.1)	226.6	43 (43)
4-MeC ₆ H ₄ CH ₃	112 (MeCN)	(-19.0)	236.0	46 (43)
4-FC ₆ H ₄ CH ₃	122 (MeCN)	(-27.1)	240.9	41 (44)
4-ClC ₆ H ₄ CH ₃	121 (MeCN)	(-26.3)	243.0	44 (44)
4-COMeC ₆ H ₄ CH ₃	123 (MeCN)	(-27.9)	245.2	44 (44)
4-CNC ₆ H ₄ CH ₃	122 (MeCN)	(-27.1)	246.6	47 (44)

^a Hydride affinity (ΔG) in solution obtained in this work. ^b $\text{p}K_{\text{R}^+}$ values from ref 5. Values in parentheses were derived using eq 10. ^c Gas-phase hydride affinity (ΔH) derived from MNDO calculations from ref 15. Values in parentheses were calculated using eq 9. ^d Obtained from the relationship expressed in eq 11; those in parentheses were derived using $D(\text{R}^+\text{H}^-)$ from eq 9.

previously been reported by Wayner and co-workers using the same experimental method.^{22,26} The $E^{\text{ox}}(\text{R}^{\bullet})$ s obtained in this study agree quite well with Wayner's results. The hydride affinities of benzyl cations in MeCN are listed in Table III. The benzyl cation, derived from the parent compound toluene, has a $-\Delta G_{\text{hydride}}$ of 118 kcal/mol, indicating a 22 kcal/mol increase in the heterolytic bond cleavage energy as compared to triphenylmethane. Note that a 4-methoxy group causes a 12 kcal/mol stabilization on the benzyl cation, whereas the strong electron-withdrawing substituents *m*-cyano and *p*-nitro decrease the stability of the benzyl cation by 10 and 11 kcal/mol, respectively. The 3 and 4 kcal/mol cation-destabilizing effects brought about by the *p*-chloro and *p*-fluoro groups, respectively, are in line with the destabilization on the benzhydryl cation by the same substitution (3.8 and 3.7 kcal/mol, respectively), as reflected by the heats of ionization of the corresponding carbinols measured in $\text{SbF}_5/\text{FSO}_3\text{H}$.^{10a}

Table IV includes the relevant data for 9-substituted fluorenes and for diphenylmethane. An examination of the table again shows that the Me_2N group has a very strong stabilizing effect on the fluorenyl cation (21 kcal/mol), which is as large as the total effect caused by the three Me_2N groups in (4- $\text{Me}_2\text{NC}_6\text{H}_4$)₃ C^+ (20 kcal/mol). This can be interpreted as a reflection of the fact that the antiaromatic structure of the fluorenyl cation creates a greater demand for stabilization from the electron-releasing substituent. Other electron-donating groups (EDG) and electron-withdrawing groups (EWG) show a similar trend in affecting the stability of the fluorenyl cation as found in the benzyl series.

It is also interesting to note that the open-chain analog of fluorene, i.e., diphenylmethane, has a $-\Delta G_{\text{hydride}}$ of 105 kcal/mol, which is 4 kcal/mol lower than the value for fluorene, which possesses a planar structure. This again can be understood on the basis of the greater instability of the fluorenyl cation caused by its antiaromatic character. Similar phenomena were observed in both the equilibrium and the heat of ionization measurements of the carbinols in acidic media. The $\text{p}K_{\text{R}^+}$ of -16.6 for 9-fluorenyl indicates a 4.5 kcal/mol destabilization of the cation as compared to the benzhydryl cation ($\text{p}K_{\text{R}^+} = -13.3$), whereas a 2.1 kcal/mol destabilization is reflected from their heats of ionization (-35.4 vs -37.5 kcal/mol).^{10a} The 9 kcal/mol difference in hydride affinities between diphenylmethane and triphenylmethane (105 vs 96 kcal/mol) can also be corroborated by the 9.7 kcal/mol difference in heats of ionization of the corresponding alcohols measured in super acid (-39.3 vs -49.0 kcal/mol).^{10a}

It is obvious from the above discussion that when a structural variation is capable of providing an increase in delocalization of the positive charge in a cation, a decrease in the heterolytic bond energy [i.e., $-\Delta G_{\text{hydride}}(\text{R}^+)$] is expected, and vice versa. This is

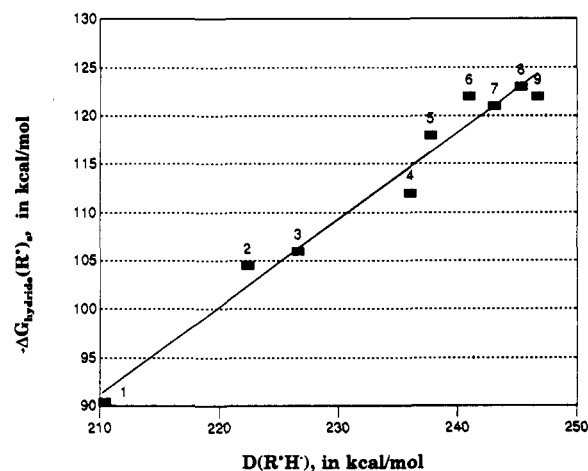


Figure 1. Plot of free energy hydride affinities in solution [$-\Delta G_{\text{hydride}}(\text{R}^+)$]_s versus gas-phase hydride affinities [$D(\text{R}^+\text{H}^-)$]. 1. Xanthene. 2. Ph_2CH_2 . 3. 4-MeOC₆H₄CH₃. 4. 4-MeC₆H₄CH₃. 5. PhCH_3 . 6. 4-FC₆H₄CH₃. 7. 4-ClC₆H₄CH₃. 8. 4-COMeC₆H₄CH₃. 9. 4-CNC₆H₄CH₃.

further supported by the data in Table V which summarize the hydride affinities of the 10- or α -substituted 9-methylanthracenes. The free energy hydride affinity for 9-methylanthracene is found to be 98 kcal/mol, which is significantly less positive (by 20 kcal/mol) than that for toluene, as a result of the increased delocalization of the positive charge in the cation. Thus, the following decreasing order of the carbocation stability is found as expected (in kcal/mol): trityl (96) > 9-methylanthryl (98) > diphenylmethyl (105) > fluorenyl (109) > benzyl (118).

Correlations of the Solution Hydride Affinities with Data from Other Sources. The early¹²⁻¹⁴ gas-phase determination of the hydride affinities was restricted to cations derived from small molecules. Far fewer data have been reported for aromatic molecules which are obviously of great importance in organic chemistry. More recently, Karaman and co-workers have reported theoretical calculations which provide reasonably good estimates of $D(\text{R}^+\text{H}^-)$ for toluene derivatives and other aromatic compounds.¹⁵ These data, together with their solution counterparts obtained in this study and the $\text{p}K_{\text{R}^+}$ values, are collected in Table VI for comparison.

The data in Table VI reveal a remarkably good correspondence of the $-\Delta G_{\text{hydride}}(\text{R}^+)$ s, with both the gas-phase $D(\text{R}^+\text{H}^-)$ and with the $\text{p}K_{\text{R}^+}$ values in aqueous sulfuric acid (whenever available), even though the media are dramatically different. A plot of $-\Delta G_{\text{hydride}}(\text{R}^+)$ s vs the gas-phase $D(\text{R}^+\text{H}^-)$ (Figure 1) is linear with a regression coefficient of 0.986(9). The slope of 0.904 indicates a small attenuation of the substituent effect in the

$$-\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}} = 0.904D(\text{R}^+\text{H}^-) - 98.7 \quad (9)$$

condensed phase as compared to that in the gas phase. Similar trends were also observed when the heats of ionizations of halides or carbinols in super acids were compared with the corresponding gas-phase hydride affinity data.^{10a} This implies that these carbocations are solvated to more or less the same degree in those media or that their solvation energies are linearly correlated to those of the neutral substrates. The recent linear correlation of the solution- vs gas-phase $\text{p}K_{\text{HA}^+\text{s}}$ for a variety of radical cations reported by Bordwell and Cheng^{19b} and the earlier work on the correlation of electrode potentials with gas-phase ionization potentials and electron affinities²⁹ provide ample precedent for similar trends in solvation energies of charged organic ions.

In solution, the differential solvation caused by changes in the media is expected to be even smaller, and this is exactly what is suggested by the excellent linear correlation between the $-\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ in DMSO solution and the $\text{p}K_{\text{R}}$ values in aqueous sulfuric acid (Figure 2). The regression equation 10 gives a r of 0.997 and a slope of 1.23. Conversion of the $\text{p}K_{\text{R}}$ values to kcal/

$$-\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}} = -1.23\text{p}K_{\text{R}} + 88.7 \quad (10)$$

mol units (by multiplying $2.303RT$) results in a slope very close to 1 (0.90). Although it is not yet ruled out that this very close match of the free energy changes for these two largely different processes is not fortuitous, eq 10 can certainly serve as a most effective way to estimate the new $\text{p}K_{\text{R}^+}$ values from the $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ data, or vice versa. Using this equation, we estimate a $\text{p}K_{\text{R}^+}$ value of -23.8 for the benzyl cation, in reasonable agreement with the recent estimate of about -20 .³⁰ It should be pointed out that there is evidence that correlations of hydride affinity with $\text{p}K_{\text{R}^+}$ are not perfect³¹ and that these imperfections could be responsible for the less than 1 slope.

Estimation of Ionic Solvation Energies.³² The solution $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ and the corresponding gas-phase $D(\text{R}^+\text{H}^-)$ data are interrelated by eq 11. The last term in (11), $\Delta G_{\text{solv}}(\text{H}^-)$, was

$$-\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}} = D(\text{R}^+\text{H}^-) - T\Delta S^\circ(\text{R}^+\text{H}^-) + \Delta G_{\text{solv}}(\text{R}^+) + \Delta G_{\text{solv}}(\text{H}^-) \quad (11)$$

estimated to be -70 kcal/mol from the free energy of hydration²⁵ along with the free energy of transfer of hydride ion from water to dimethyl sulfoxide (Table I). The entropy change for gas-phase reaction 3 can be equated to the difference in absolute entropies of reactant and products as shown in (12). Arguments

$$\Delta S^\circ(\text{R}^+\text{H}^-) = S^\circ(\text{R}^+) + S^\circ(\text{H}^-) - S^\circ(\text{RH}) \quad (12)$$

have previously been presented³³ for the near equality of $S^\circ(\text{R}^-)$ and $S^\circ(\text{RH})$ in the related ionization of acids in the gas phase. We suggest, in analogy, that the $S^\circ(\text{R}^+)$ and $S^\circ(\text{RH})$ contributions in (12) are expected to cancel and $\Delta S^\circ(\text{R}^+\text{H}^-)$ is equal to $S^\circ(\text{H}^-)$, a known³⁴ quantity (26.015 eu). Thus, $T\Delta S^\circ(\text{R}^+\text{H}^-)$ is equal to 8 kcal/mol at 298.14 K. In cases where the gas-phase $D(\text{R}^+\text{H}^-)$ are available, $\Delta G_{\text{solv}}(\text{R}^+)$ values were calculated and are collected in the last column of Table VI. The values in parentheses were derived from $D(\text{R}^+\text{H}^-)$ estimated from linear

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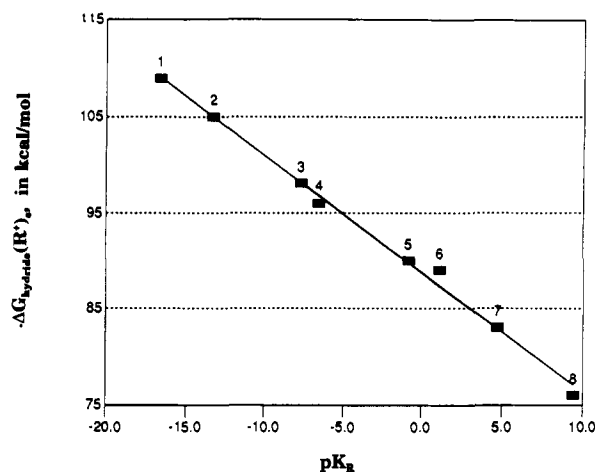


Figure 2. Plot of solution hydride affinities $[-\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$] versus $\text{p}K_{\text{R}}$ values. 1. Fluorene. 2. Ph_2CH_2 . 3. $(4\text{-ClC}_6\text{H}_4)_3\text{CH}$. 4. Ph_3CH . 5. Xanthene. 6. 9-Phenylxanthene. 7. Cycloheptatriene. 8. $(4\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$.

regressions eq 9. It is of interest to compare $\Delta G_{\text{solv}}(\text{R}^+)$ for tropylium ion in DMSO (-40 kcal/mol) with the value previously estimated in acetonitrile (-43 kcal/mol)³⁵ from the gas-phase ionization potential (IP) of the radical using eq 13, where the last term is the "absolute" potential of the NHE. Applying eqs 11

$$\Delta G_{\text{solv}}(\text{R}^+) = E^\circ(\text{R}^+/\text{R}^\bullet) - \text{IP}(\text{R}^\bullet) + 4.44 \quad (13)$$

and 13 to estimate $\Delta G_{\text{solv}}(\text{PhCH}_2^+)$ results in values of -42 kcal/mol in both cases. This suggests that the values for $\Delta G_{\text{solv}}(\text{R}^+)$ calculated using eq 11 are very close to those obtained using eq 13. In any event, we feel that the solvation energies in Table VI can be considered to be reasonably good estimates.

Conclusions

The estimates of $E^\circ_{\text{NHE}}(\text{H}^\bullet/\text{H}^-)_{\text{s}}$ in nonaqueous solvents (Table I) allow $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ for a wide variety of organic cations to be calculated from redox potentials and $\text{p}K_{\text{s}}(\text{RH})$ values using either eq 5 or eq 7. For example, relative $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ have been reported for a series of NADH model compounds.^{36,37} Electrode potentials $E^{\text{red}}(\text{R}^+)$ and $E^{\text{ox}}(\text{R}^-)$ have been reported for this series of compounds³⁸ and have been used to determine relative C-H bond dissociation energies of the NADH model compounds. Neither the pertinent $\Delta G_{\text{hom}}(\text{RH})_{\text{s}}$ nor the $\text{p}K_{\text{s}}$ have been reported, which rules out the use of eqs 5 or 7 to calculate $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ until these data are available. However, we have recently observed a linear correlation between $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ and solution electron affinities of a wide range of hydride acceptors including cations and radicals.³⁹ Using a relationship based on this, $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ of 10-methylacridinium ion in acetonitrile [$E^\circ_{\text{NHE}}(\text{R}^+/\text{R}^\bullet) = -0.17$ V³⁸] was estimated to be equal to -83 ± 2 kcal/mol. Comparison of gas-phase $D(\text{R}^+\text{H}^-)$ with $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ provides a convenient means for evaluating ionic solvation energies of the cations when both quantities are available. The excellent correlation between $\Delta G_{\text{hydride}}(\text{R}^+)_{\text{s}}$ and $\text{p}K_{\text{R}^+}$ of the corresponding carbinols allows for the convenient estimation of either of the quantities, providing that the other is known.

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Experimental Section

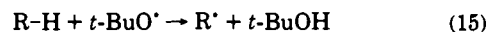
General. NMR spectra were obtained on a Varian XL 300 or a JEOL 270 spectrometer. Mass spectra were measured using a Finnigan MAT ITD GC/MS system. Gas chromatography was performed on a Varian 3700 instrument equipped with a flame ionization detector. Reagent grade acetonitrile was distilled from P₂O₅ under N₂ and stored over activated alumina. The purification of DMSO and the preparation of the dimsyl base were carried out according to a literature procedure.⁴⁰

Materials. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from CH₂Cl₂/Et₂O and vacuum-dried at 110 °C for 10 h before use. Trityl fluoroborate, tropylium fluoroborate, crystal violet, fluorene, 9-methylanthracene, 9,10-dimethylanthracene, diphenylmethane, toluene, *p*-xylene, 4-methylanisole, 4-chlorotoluene, 4-fluorotoluene, 4-methylacetophenone, 3-tolunitrile, 4-tolunitrile, and 4-nitrotoluene were obtained from Aldrich and used as received. All other compounds were prepared using published or modifications of published procedures. The purity of all compounds was verified by melting point determination and spectral analysis.

Electrochemical Measurements (General). The instrumentation for the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments was the same as described in a previous paper.^{24a} A standard three-electrode electrochemical cell equipped with a Teflon-brand top was used throughout the LSV and CV measurements. The working electrode was a 0.2-mm-diameter Pt disk and was reconditioned by polishing with a 0.05- μ m alumina suspension (Struers, Denmark) between runs. The potentials were measured at a sweep rate of 1 V/s vs a 0.1 M AgClO₄/Ag reference electrode with the ferrocenium/ferrocene redox couple as the internal standard. The counter electrode was a Pt wire. In a typical experiment, the substrate (1.0 mM) in a stock solution of 0.1 M tetrabutylammonium hexafluorophosphate was placed in a carefully dried electrochemical cell which was purged with Ar for several minutes before beginning to make measurements. In the cases where the redox potentials of less stable cationic species were determined, higher concentrations (up to 5 mM) of the substrate were sometimes used and small amounts of activated alumina were added to the solutions in order

to remove the last traces of water. The carbanions were generated in situ by addition of a stock dimsyl solution, and voltammograms were recorded immediately after generation.

Photomodulation ac Voltammetric Measurements. The method of Wayner and co-workers^{22,26} was adopted with minor modifications. Transient radicals were generated by modulated photolysis (eqs 14 and 15) in a quartz UV cell fitted with a Pt working electrode ($d = 0.2$ mm),



a AgClO₄ (0.01 M)/Ag reference electrode, and a Au film auxiliary electrode. The contents of the cell were continually stirred using a stream of argon. In order to limit depletion of reagents, the light entering the cell was restricted to a small area around the electrode. The solution contained the radical precursor ([RH] 0.1–0.5 M), *tert*-butylperoxide (0.2–0.5 M), and tetrabutylammonium hexafluorophosphate (0.1 M) in the appropriate solvent. The light source was a 300-W Hg/Xe lamp (Oriel Model 6183) and was modulated using a mechanical light chopper (PAR Model 125) at a frequency of 104 Hz which was also the reference signal for the lock-in amplifier (EG&G PAR Model 5210). The voltammogram of the photochemically-generated radical was obtained using a JAS Model J-1600-B potentiostat driven by a Hewlett-Packard 3314A function generator controlled by a PC/AT via an IEEE interface. The output of the lock-in amplifier was recorded on a Nicolet Model 310 digital oscilloscope and subsequently relayed to the computer for processing. The current–potential curves were recorded at a sweep rate of 50 mV/s. The potentials in Tables III–V were obtained after averaging 5 scans and are half-wave potentials measured at ambient temperature of 23 \pm 1 °C.

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