= 1.223 g cm⁻³, μ = 5.54 cm⁻¹. Final R = 0.054 and R_w = 0.088 for 1698 reflections.

(b) Structure Analysis and Refinement. The structures were solved by direct methods (SHELXS)44 and refined by full-matrix least-squares treatments based upon F (SHELX).⁴⁵ The carboxylic hydrogens in the unsolvated host molecule 1, the carboxylic and alcoholic H atoms in structure 1.t-BuOH (1:1), and all hydrogens except those of the methyl group of the host in the 17-MeCN (1:1) clathrate were located from difference electron density calculations, and their positions were kept riding on their respective mother atoms during the refinements. The remaining, carbon-bonded H atoms in the free host molecule and in the inclusion compound with t-BuOH and the methyl hydrogens of the host in 17-MeCN (1:1) were given assumed positions, calculated after each cycle of the refinements. The C, O, and N atom positions were refined together with their anisotropic thermal parameters; an isotropic group temperature factor was refined for the H atoms in the unsolvated host molecule 1 and in the inclusion compound with t-BuOH, respectively, and individual temperature factors were refined for the non-methyl H positions in the structure of 17-MeCN (1:1). The methyl groups in this latter

(45) Sheldrick, G. M. SHELX 76: Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

structure, both of the host and of the guest, were treated as rigid groups with free rotation, and one isotropic group temperature factor was refined for each of them. Only data with $F > 6\sigma(F)$ were used in the refinement calculations. Final R values are included with the crystal data for each compound. Weights of the structure factors were calculated as w = $const/[\sigma^2(F) + g(F^2)]$ with const = 1.0, and the g value was refined to 0.06012 for unsolvated 1, 0.00982 for 1-t-BuOH (1:1), and 0.01507 for 17-MeCN (1:1). Final atomic coordinates and thermal parameters, observed bond distances, and bond angles are listed in Tables III-VI (supplementary material).

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Supplementary Material Available: Complete lists of isolated inclusion compounds including specification of solvents not allowing inclusion formation for each host (Table I) and of guest preferences (Table II) and crystallographic data for compounds 1, 1.t-BuOH (1:1), and 17.MeCN (1:1) such as fractional atomic coordinates of the non-hydrogen atoms, bond distances and bond angles, and anisotropic thermal parameters of the non-hydrogen atoms (Tables III-VI) (21 pages). Ordering information is given on any current masthead page.

Unifying the Solution Thermochemistry of Molecules, Radicals, and Ions¹

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Abstract: A general cycle was developed that defines the thermodynamics for all of the homolytic and heterolytic cleavage reactions of a hydrocarbon, R-R', in solution. Only seven experimental parameters were needed in order to define the energetics for all 11 of the possible cleavage reactions of R-R'. These parameters were the oxidation and reduction potentials of R-R'. R^{\bullet} , and R'^{\bullet} and the homolytic, R-R', bond energy. The utility of this approach was demonstrated for the case where R was an arylmethyl group and R' was hydrogen. The oxidation and reduction potentials of the arylmethyl radicals were measured by modulation voltammetry in acetonitrile, and the homolytic C-H bond energies of the corresponding hydrocarbons were measured by photoacoustic calorimetry. The cycle was also extended to a case where R-R' was a radical rather than a closed-shell molecule.

In the gas phase, the thermodynamic relationships between molecules and their related ions are easily understood and are well-defined in terms of familiar parameters. Homolytic bond dissociation enthalpies relate the thermochemical properties of molecules to those of radicals while ionization potentials and electron affinities tie the thermochemistry of neutral species to those of their corresponding ions. These properties have been studied extensively, and there is an abundant literature that describes them.²

The solution equivalents of ionization potentials and electron affinities are the electrochemical oxidation and reduction potentials. A number of thermochemical cycles have appeared in the literature in which combinations of homolytic bond energies and electrochemical potentials have been used to calculate other thermodynamic properties. These have included pK_a values for hydrocarbons^{3,4} and for radical cations^{5,6} and pK_R values for carbocations.7 Most of the recent activity has focused on the interplay between hydrocarbon acidities, carbanion oxidation potentials, and homolytic bond energies⁸ (eq 1-3).

 $R-H \rightarrow R^- + H^+$ (1)

> $R^- \rightarrow R^{\bullet}$ (2)

$$R-H \rightarrow R^{\bullet} + H^{\bullet}$$
(3)

In this work, we have established a general scheme that links the thermochemical properties of a compound R-R' to those of

⁽⁴⁴⁾ Sheldrick, G. M. SHELXS 84: Program for Crystal Structure Solution; University of Göttingen: Göttingen, FRG, 1984; personal communication

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⁽¹⁾ Issued as NRCC publication No. 30484.

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 W. *Ibid.* 1973, 95, 411. (d) Breslow, R.; Goodin, R. *Ibid.* 1976, 98, 6076.
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(7) Breslow, R.; Mazur, S. J. Am. Chem. Soc. 1973, 95, 584.

$$\mathbf{R}^{\prime \bullet} \to \mathbf{R}^{\prime +} \tag{9}$$

$$\mathbf{R}^{\prime-} \to \mathbf{R}^{\prime\bullet} \tag{10}$$

which, by convention, are written in the direction of oxidation where appropriate. However, for a total definition of all of the thermochemistry, the scheme implicitly requires that the oxidation and reduction potentials of \mathbb{R}'^* be available (eq 9 and 10).

If all of these data can be assembled, the thermochemistry for the remaining six reactions can be calculated by applying Scheme I. The requisite expressions are listed formally in eq 11–16.

$$\Delta G^{\circ}_{11} = \Delta G^{\circ}_{4} + F[E^{\circ}_{5} - E^{\circ}_{7}]$$
(11)

$$\Delta G^{\circ}_{12} = \Delta G^{\circ}_{4} + F[E^{\circ}_{5} - E^{\circ}_{10}]$$
(12)

$$\Delta G^{\circ}_{13} = \Delta G^{\circ}_{4} + F[E^{\circ}_{9} - E^{\circ}_{7}]$$
(13)

$$\Delta G^{\circ}_{14} = \Delta G^{\circ}_{4} + F[E^{\circ}_{8} - E^{\circ}_{10}]$$
(14)

$$\Delta G^{\circ}_{15} = \Delta G^{\circ}_{4} + F[E^{\circ}_{9} - E^{\circ}_{6}]$$
(15)

$$\Delta G^{\circ}_{16} = \Delta G^{\circ}_{4} + F[E^{\circ}_{8} - E^{\circ}_{6}]$$
(16)

It is interesting to note that the Gibbs energies for bond dissociation in the radical cation and radical anion of R-R' (eq 11 and 16) are independent of the redox properties of R'^{\bullet} (eq 9 and 10). Simply stated, the relationship shows that the difference in bond dissociation energies of R-R' and its radical cation (or anion) is equal to the difference between the oxidation (or reduction) potentials of R-R' and of $R^{\cdot,5b}$ Other relationships that obviate the need to know the redox potentials of R'^{\bullet} are given in eq 17 and 18. These equations imply that Scheme I can be overdetermined if required.

$$\Delta G^{\circ}_{13} = \Delta G^{\circ}_{15} + F(E^{\circ}_{6} - E^{\circ}_{7})$$
(17)

$$\Delta G^{\circ}_{14} = \Delta G^{\circ}_{12} + F(E^{\circ}_{8} - E^{\circ}_{5}) \tag{18}$$

In practice, the complete set of experimental data required to determine all of the thermodynamic relationships defined in Scheme I may not be available. However, it should be recognized that even limited amounts of experimental data will often be sufficient to complete parts of the scheme and will allow some of the ion/neutral relationships to be quantified.

To summarize, the thermodynamic relationships between neutrals and their ions in solution can be unified by combining redox properties with the Gibbs energy for homolytic bond dissociation using the simple mnemonic described in Scheme I.

Limitations of the Data. The experimental data that are now available suffer from some limitations that are significant from the perspective of this work. The first limitation is if the electrochemical potentials are to be thermodynamically significant, they must be reversible.⁹ For simple molecules reversibility, or the lack of it, can be established experimentally by cyclic voltammetry. However, for radicals the situation is more difficult. This is because most radicals are transient species and cannot generally be investigated by simple voltammetry. Hence, to establish reversibility of a radical reduction, one needs to determine the half-wave potential for that reduction and, in a separate experiment, the oxidation potential of the corresponding anion. For a truely reversible system these values will be coincident. However, even when they are different, the experiments define an upper and a lower limit for $E^{\circ.10}$

The second limitation is that the entire scheme has to be defined in terms of Gibbs energies because electrochemical data define that property. Most homolytic bond strengths are reported in terms of enthalpy and must therefore be corrected for entropic contributions. However, this is not a severe problem because entropies are often available or are easily calculated.¹¹ In addition,

Scheme I



all of the related radicals, ions, and radical ions, i.e., R^{\bullet} , R^{+} , R^{+} , R^{-} , R^{-} , R^{-} , R^{-} , R^{-} , R^{-} , R^{-+} , and $R^{-}R'^{\bullet-}$. Seven pieces of experimental data are required to complete the entire scheme and to define 11 thermodynamic properties. The data required are the oxidation and reduction potentials of $R^{-}R'$, R^{\bullet} , and R'^{\bullet} as well as the homolytic bond dissociation energy in $R^{-}R'$. We describe several applications of this generalized thermochemical scheme with particular emphasis on cases where R is an arylmethyl group and R' is hydrogen. The examples include toluene, fluorene, 1-methylanthracene, 9,10-dihydronaphthalene, and 9,9-dimethyl-9,10-dihydroanthracene.

Photoacoustic calorimetry was used to measure the homolytic bond dissociation enthalpies, while cyclic voltammetry and photomodulation voltammetry were used to measure the electrochemical properties of the hydrocarbons and their radicals, respectively. As an aide memoire, we have presented the scheme in the form of a simple mnemonic.

Results and Discussion

General Scheme. Scheme I represents the relationships between a molecule, R-R', and its related ions. As we will see, it does not precisely define thermochemical cycles; rather it is a mnemonic and affords a simple way of establishing the experimental data required to obtain a chosen thermochemical property or heat of reaction in solution. The numbers in the scheme refer to equation numbers as they appear in the text (vide infra).

In the scheme, the horizontal arrows represent the electrochemical oxidation and reduction potentials, E° , of R-R' and R[•], while the vertical arrows defined homolytic cleavages. The central vertical arrow represents the Gibbs energy for homolytic cleavage of the R-R' bond. The fate of R' is not explicitly defined but is inferred from the reaction under review, and this is why the Scheme does not define true thermodynamic cycles. For example, along the vertical arrows R'• is formed as the product, while in the diagonal arrows that ascend from left to right it is the cation, R'+, that results. Similarly, the diagonal arrows that ascend from right to left imply that the anion, R'-, is the product of the reaction under consideration.

Seven pieces of experimental data are required to complete the entire scheme for a chosen compound. Five have been described above and are defined in Scheme I by the horizontal arrows and the central, vertical arrow. They are also given in eq 4-8,

$$\mathbf{R} - \mathbf{R}' \to \mathbf{R}^* + \mathbf{R}'^* \tag{4}$$

$$R^{\bullet} \rightarrow R^{+}$$
 (5)

$$R^- \rightarrow R^{\bullet}$$
 (6)

$$\mathbf{R} - \mathbf{R}' \to \mathbf{R} - \mathbf{R}'^{\bullet +} \tag{7}$$

$$\mathbf{R} - \mathbf{R}'^{\bullet-} \to \mathbf{R} - \mathbf{R}' \tag{8}$$

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⁽¹¹⁾ Benson, S. W. Thermochemical Kinetics; Wiley: New York, 1976. For the case where R' = H, ΔG°_{4} can be calculated from D(C-H) by assuming that the entropy of the radical and the hydrocarbon cancel, and therefore the entropy change is equal to $S^{\circ}(H^{\bullet}(g))$; i.e., $T\Delta S^{\circ} = 8 \text{ kcal mol}^{-1}$ at 298 K.

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Table I. Enthalpies for the Reaction $R-R'^{*+} \rightarrow R^+ + R'^*$ in Acetonitrile at 298 K

R	R′	$\frac{D(R^+-R'^{\bullet}),^{a,b}}{\text{kcal mol}^{-1}}$	
PhCH ₂	Н	50 (51)	
PhCH ₂	CH ₁	38 (39)	
PhCH,	PhCH,	24 (21)	
Ph ₂ CH	PhCH,	12°	
$PhC(CH_3)_2$	Ph ₂ CH	5°	
$(CH_3)_2NCH_2$	Н	34 (35)	
$(CH_3)_2NCH_2$	$(CH_3)_2NCH_2$	17 (13)	

^a Equation 11; uncertainty ± 2 kcal mol⁻¹. ^b Gas-phase values in parentheses. $D(R^+-R'^*) = D(R-R') - 23.06[IP(R-R') - IP(R^*)]$, where IP (in electronvolts) is the ionization potential.² ^c Reference 5b.

entropic contributions will often cancel in many of the thermodynamic calculations.

Finally, most homolytic bond strengths have been determined in the gas phase, and, therefore, solvation effects have to be considered. However, recent studies have shown that differences in the solvation energies of organic radicals and their parent molecules tend to be very small¹² even in solvents as polar as water.¹³

While all of these effects need to be considered, it is probably fair to say that the greatest uncertainties are generally associated with the electrochemical data and the question of reversibility.

Some Simple Examples. We calculated bond dissociation enthalpies for a series of dimer radical cations by using eq 11, i.e., by taking the differences between the oxidation potentials of R-R'and R^{\bullet} and by introducing the bond dissociation enthalpy for R-R'.¹⁴ Formally, the Gibbs energy for dissociation in R-R'should have been used. However, we made the assumption that the entropy changes for the dissociation of R-R' and of $R-R'^{*+}$ would be similar (i.e., they would cancel) and therefore used ΔH_4 to obtain ΔH_{11} . The results are reported in Table I together with the corresponding gas-phase data. Interestingly, the gas- and solution-phase values are the same within experimental error and imply that the solvation enthalpies of R^+ and $R-R'^{*+}$ are essentially the same.

Breslow and his colleagues³ made use of elements of Scheme I to determine pK_a values in hydrocarbons, i.e., ΔG°_{15} for the case where R' was hydrogen. They measured E°_{6} by studying the oxidations of a series of anions, R⁻, and applied literature values for ΔG°_{4} . However, they circumvented the need to know E°_{9} , the oxidation of hydrogen in the solvent of interest, by establishing a scale of relative pK_a values from the electrochemical data. This was then put on an absolute basis by linking the scale to the pK_a of triphenylmethane that had been determined independently.

Bordwell and his co-workers⁸ have employed a variation of this approach and combined measured hydrocarbon acidities, ΔG°_{15} , with anion oxidation potentials, E°_{6} , to determine Gibbs energies for bond dissociation, ΔG°_{4} . Again, the need to determine E°_{9} was circumvented by establishing a scale of relative bond dissociation enthalpies. This work has focused on fluorene and its derivatives where acidities have been measured in equilibrium studies and where anion oxidation potentials have been determined in electrochemical studies of the appropriate lithium salts. The scale of relative bond dissociation enthalpies was put on an absolute basis by using the C-H bond dissociation methalpy for fluorene itself. The Gibbs energies for bond dissociation were converted to enthalpies by assuming that the entropy differences between the substituted fluorenes and their corresponding radicals were independent of substituent.

We have recently measured the reduction potentials for a series of substituted benzyl radicals⁴ and have shown that the pK_a values for the toluenes in acetonitrile can be determined directly, without the need to anchor the data to a reference compound with a well-defined pK_a or bond dissociation enthalpy. To do this, we took advantage of the approach taken by Nicholas and Arnold^{5a} and estimated a value for the missing ingredient of the cycle, i.e., the oxidation potential of the hydrogen atom in acetonitrile.

Nicholas and Arnold^{5a} and Bordwell and his coworkers⁶ have used to different elements of Scheme I (eq 13 and 17) to calculate the pK_a value for radical cations. The method chosen reflected the availability of the requisite experimental data. It was found that the acidity of hydrocarbons was greatly enhanced by the removal of an electron. For example, the pK_a of toluene was found to be 51 in acetonitrile⁴ while that of toluene radical cation was -13 in the same solvent.^{5a}

New Results. It is clear from the examples cited above that various researchers have independently made use of elements of Scheme I to link the thermodynamic properties of radicals and ions. However, the development of this approach has often been thwarted by the experimental difficulties associated with the determination of the redox properties of transient radicals and of homolytic bond dissociation enthalpies.

In this work, we have used the techniques of photomodulation voltammetry¹⁵ and photoacoustic calorimetry^{13,16} to make the necessary measurements of radical oxidation potentials and of bond strengths. By focusing on cases where R' = H, we have been able to complete Scheme I in several cases and have thus been able to unify the thermodynamic properties of a number of hydrocarbons, in solution, with all of their related ions. The compounds investigated were toluene, fluorene, 1-methylnaphthalene, 9,10-dihydroanthracene, and 9,9-dimethyl-9,10-dihydroanthracene.

The C-H bond enthalpies of toluene, fluorene, and 1methylnaphthalene were available in the literature.¹⁷ Those for 9,10-dihydroanthracene¹⁷ and 9,9-dimethyl-9,10-dihydroanthracene were determined in solution by using photoacoustic calorimetry. This technique has been described in detail elsewhere.^{13,16a} Briefly, a benzene solution containing di-*tert*-butyl peroxide was photolyzed in a standard UV flow cell with a nitrogen laser (337.1 nm) to generate *tert*-butoxyl radicals, which then abstracted hydrogen from the hydrocarbon of interest (eq 19 and 20).

$$t$$
-BuO-OBu- $t \xrightarrow{h\nu} 2 t$ -BuO* (19)

$$2t - BuO^{\bullet} + 2R - H \rightarrow 2t - BuOH + 2R^{\bullet}$$
(20)

The enthalpy change associated with reactions 19 and 20, ΔH_r , was smaller than the energy delivered by the laser pulse (84.8 kcal mol⁻¹). The difference, ΔH_{obs} , was released into the solution as heat, producing a shock wave that was detected by a piezoelectric transducer attached to the bottom of the cell. The signal was amplified, averaged over 256 laser shots, and stored in an oscilloscope. The slope, a_r , of a plot of the wave amplitudes versus the optical densities of the solutions at several concentrations of *t*-BuO-OBu-*t* was related to ΔH_r through eq 21 and 22, where

$$\Delta H_{\rm r} = (84.8 - \Delta H_{\rm obs}) / \Phi \,(\rm kcal \ mol^{-1}) \tag{21}$$

$$= (84.8/\Phi)(1 - a_{\rm r}/a_{\rm s}) \tag{22}$$

 Φ is the quantum yield for di-*tert*-butyl peroxide dissociation in benzene ($\Phi = 0.85$)^{16b} and a_s is a calibration constant. The latter was obtained by plotting the wave amplitudes for benzene solutions containing variable amounts of *o*-hydroxybenzophenone against the respective optical densities. This compound converts all of the absorbed radiation into heat.^{16a}

Reliable measurements of reaction enthalpies by the photoacoustic technique require that the heat release (ΔH_{obs}) be faster than the transducer response (2 µs). The rate of hydrogen ab-

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hydrocarbon	ΔG°_{4} , kcal mol ⁻¹	<i>E</i> °5 ^{<i>b</i>}	E°6 ^b	E°7 ^c	E°8 ^c
toluene	80 ^d	0.73	-1.45	2.43 ^e	-3.50
fluorene	728	0.76	-0.76	1.75	-2.70
1-methylnaphthalene	77 ^d	0.47	-1.27	1.53	-2.58 ^h
9,10-dihydroanthracene	70 ⁱ	0.10	-1.23	1.62	j
9,9-dimethyl-9,10-	69 ⁱ	0.22	-1.26	1.77	j
dihydroanthracene					•

^a Bond enthalpies in solution were measured by photoacoustic calorimetry. The Gibbs energies for homolytic cleavage (ΔG°_{4}) include a contribution for the entropy of the hydrogen atom.¹¹ The bond energies have an uncertainty of ± 2 kcal mol⁻¹ and the redox potentials have an uncertainty of ± 0.05 eV. In our system, E° for the oxidation of ferrocene was measured to be 0.408 V vs SCE in acetonitrile containing 0.1 M TBAP. ^b Measured by photomodulation voltammetry.¹⁵ In volts vs SCE. CMeasured by cyclic voltammetry. In volts vs SCE. All values are irreversible unless otherwise indicated. ^dReference 17. ^eReference 10. ^fData from: Eberson, L. Electron Transfer in Organic Chemistry; Springer-Verlag: Berlin, 1987. ^gReference 8b. *Reversible potential. 'This work. 'Not available.

straction from 9,10-dihydroanthracene¹⁸ meets that requirement since $k_{20} = 8.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and the concentrations used were 0.2-0.3 M. It was assumed that the rate constant for abstraction at the dimethyl analogue would be a factor of 2 less, and since similar concentrations were used in that case the kinetic limitation must have been satisfied.

The results obtained for ΔH_r , -15.6 ± 1.8 and -17.5 ± 1.8 kcal mol⁻¹ for 9,10-dihydroanthracene and 9,9'-dimethyl-9,10-dihydroanthracene, respectively, were obtained at room temperature $(298 \pm 2 \text{ K})$ and represent the average of four independent experiments. The uncertainties are twice the standard deviation of the means. The values of ΔH_r lead to carbon-hydrogen bond dissociation enthalpies $D(R-H) = 78.3 \pm 1.5$ and 77.3 ± 1.5 kcal mol⁻¹, respectively, when combined with literature values¹⁷ for $D(t-BuO-OBu-t) = 38.0 \pm 1.0$ and $D(t-BuO-H) = 105.1 \pm 1.0$ kcal mol^{-1} (eq 23).

$$D(R-H) = \Delta H_r / 2 - D(t-BuO-OBu-t) / 2 + D(t-BuO-H)$$
(23)

The oxidation and reduction potentials of the hydrocarbons (Table II) were measured by cyclic voltammetry on a glassycarbon electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP). With the exception of the 1methylnaphthalene reduction all of the potentials were irreversible.

Oxidation and reduction potentials of the radicals (Table II) were measured using photomodulation voltammetry. This technique has been described in detail elsewhere.¹⁵ Basically, radicals were generated photochemically and their concentrations were modulated by using a mechanical light copper in the photolysis beam. Phase-sensitive voltammetric detection then provided the necessary sensitivity enhancement so that signals due to the radical could be detected even though the concentrations were only ca. 10^{-7} M and lifetimes were ca. 1 ms.

In order to apply eq 11-16 to a hydrocarbon, R-H, the E° values for the oxidation and reduction of the hydrogen atom in acetonitrile are required (eq 9 and 10). Estimating these values (vs SCE) in water is straightforward since all of the necessary thermochemical data are available¹⁹ (eq 24 and 25). In these

$$E^{\circ}(H^{\bullet}/H^{+})_{water} = E^{\circ}(\frac{1}{2}H_{2}/H^{+}) - \Delta G^{\circ}_{f}(H^{\bullet}(aq)) = -2.35 \text{ V vs SCE} (24)$$

$$E^{\circ}(H^{-}/H^{\bullet})_{water} = E^{\circ}(H^{-}/l_{2}H_{2}) + \Delta G^{\circ}_{f}(H^{\bullet}(aq)) = -0.36 \text{ V vs SCE} (25)$$

equations,
$$E^{\circ}(1/_{2}H_{2}/H^{+}) = -0.2412 \text{ V}, E^{\circ}(H^{-}/1/_{2}H_{2}) = -2.47$$

Scheme II⁴



^aRedox potentials in V vs SCE. Bond energies in kcal mol⁻¹.

V, and $\Delta G^{\circ}_{f}(H^{\bullet}(aq)) = \Delta G^{\circ}_{f}(H^{\bullet}(g)) = 2.11 \text{ eV}$. The value of $E^{\circ}(H^{\bullet}/H^{+})_{MeCN}$ (eq 26) can then be determined from the known free energy change for the transfer of a proton from water into acetonitrile,²⁰ $\Delta G^{\circ}_{tr}(H^+) = 0.48 \text{ eV}.$

> $E^{\circ}(H^{\circ}/H^{+})_{MeCN} = -1.87 \text{ V vs SCE}$ (26)

The value for $\Delta G^{\circ}_{tr}(H^{-})$ between water and acetonitrile is not, to our knowledge, available. However, we note that the absolute solvation energy of the proton is ca. -258 kcal mol⁻¹ in water while that for hydride is only -84 kcal mol^{-1,21} Since the heat of transfer of the proton to acetonitrile is only 0.48 eV and the solvation energy of hydride in water is only a fraction of that for the proton, we have made the assumption that the value of $\Delta G^{\circ}_{tr}(H^{-})$ is negligibly small and hence that $E^{\circ}(H^{-}/H^{\circ})_{MeCN} \approx -0.36$ V.

The experimental values that we have obtained for ΔG°_{4} and E°_{5} to E°_{8} are given in Table II for several hydrocarbons and the derived thermodynamic values, ΔG°_{11} to ΔG°_{16} , are given in Table

The data in Table III provide some interesting insights into the thermochemical properties of radicals and ions in solution vis-a-vis the gas phase. Loss of a proton from R-H (ΔG°_{15}) or from $R-H^{+}(\Delta G^{\circ}_{13})$ is more favorable than the loss of hydrogen atom $(\Delta G^{\circ}_{4} \text{ or } \Delta G^{\circ}_{11})$ in solution, although the converse is generally true in the gas phase. The difference is due to the fact that the solvation energy for the proton dominates the thermochemistry and is far greater than solvation energies of the organic cations.¹⁵ By contrast, hydride loss from radical anions (ΔG°_{14}) or neutrals (ΔG°_{12}) is generally not as favorable as hydrogen atom loss because the solvation energies of H⁻ and the organic anions¹⁵ are similar. In these cases, there is little difference between the gasand solution-phase thermochemistry. Finally, the extent to which carbon-hydrogen bonds are weakened by oxidation or reduction of R-R', i.e., $\Delta G^{\circ}_{4} - \Delta G^{\circ}_{11}$ and $\Delta G^{\circ}_{4} - \Delta G^{\circ}_{16}$, is similar. We presume that this is due to the fact that adding an electron to an antibonding orbital or removing one from a bonding orbital has much the same effect and creates a bond order of ca. 0.5.

Extended Calculations. Equations 11-16 are not restricted to chemical systems in which R-R' is a simple molecule. They are quite general and can be applied in other cases. Scheme II illustrates their application to the case where R-R' is the 9,10dihydroanthracen-9-yl radical. In this instance, ΔG°_{4} is the Gibbs energy for fragmentation of the radical to give anthracene and

⁽¹⁸⁾ Measured by laser flash photolysis. We thank Dr. J. C. Scaiano for the use of the instrument.

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⁽²¹⁾ The standard Gibbs energy of formation of H⁺ and H⁻ in the gas phase were derived as 362.2 and 31.2 kcal mol⁻¹, respectively, by using data from ref 22a and the Sakur-Tetrode^{22b} equation (plus a R ln 2 term) to calculate the entropy of the electron. The equivalent quantities in water were obtained as +103.8 and -52.3 kcal mol⁻¹, respectively, by assuming an absolute blance as +103.6 and -32.3 kcall hold, respectively, by assuming an absolute energy of 4.74 eV for the SCE²³ and using the values for $\mathcal{E}^{\circ}(1/_2H_2/H^+)$ and $\mathcal{E}^{\circ}(H^-/_2H_2)$ given in the text. (22) (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. J. Phys. Chem. Ref.

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Table III. Calculated Thermodynamic Data^a

hydrocarbon	ΔG°_{11}	ΔG°_{12}	ΔG°_{13}	ΔG°_{14}	ΔG°_{15}	$\Delta G^{\circ}{}_{16}$
toluene	40.8	105.1	-19.2	7.6	70.3	32.7
fluorene	49.2	97.8	-11.5	18.0	46.4	27.3
1-methylnaphthalene	52.6	96.1	-1.4	25.8	63.2	46.8
9,10-dihydroanthracene	35.0	80.6	-10.5	b	55.2	Ь
9,9-dimethyl-9,10-dihydroanthracene	33.3	82.4	-14.9	b	54.9	ь

^aSee equations in text and Scheme I. All values $\pm 2 \text{ kcal mol}^{-1}$. ^b E°_{8} not available.

a hydrogen atom (35 kcal mol⁻¹),^{11,24} E°_{5} and E°_{6} are the oxidation and reduction potentials of anthracene (1.19 and -2.07 V vs SCE, respectively), and E°_{7} and E°_{8} are the oxidation and reduction potentials of 9,10-dihydroanthracen-9-yl (Table II). Now, ΔG°_{13} defines the p K_{a} of the protonated aromatic hydrocarbon (-7.6) while ΔG°_{15} establishes the basicity of the radical anion (28.4).

It is interesting to note that loss of hydrogen from the 9,10dihydroanthracen-9-yl cation, ΔG°_{11} , is less favorable than loss of hydrogen from the radical itself, ΔG°_{4} . By contrast, the data in Table III shows that hydrogen loss from *radical* cations was more facile than that from the parent hydrocarbon.

Conclusions

The results described in this paper demonstrate that electrochemical redox potentials can be combined with homolytic bond dissociation energies to give a unified description of the thermodynamic properties of radicals and their related ions. The methods for combination can be formally expressed in equations or can be represented in the form of a handy mnemonic. Among the properties that can be derived are the energies for all of the possible cleavages of R-R', $R-R'^{*+}$, and $R-R'^{--}$.

The cycles described in eq 11–16 are quite general and can be extended to cases where R-R' is a radical, an ion, or a radical ion. This means that other properties such as the acidities of carbocations, dications,²⁵ etc., and the basicities of radical anions, dianions,²⁶ etc., can be defined by applying Scheme I. The usefulness of the approach is only limited by the availability and quality of the necessary bond energy and redox data.

Experimental Section

Benzene (spectroscopic grade) was used as received. Di-*tert*-butyl peroxide was purified according to a literature procedure.²⁷ Acetonitrile (HPLC grade) was refluxed over calcium hydride (2 g/L) for 12 h in an inert (Ar) atmosphere and then fractionally distilled just before it was used.

Tetrabutylammonium perchlorate (TBAP) was recrystallized three times from ethylacetate/hexane (9:1, v/v) and then dried at 45 °C in a vacuum oven. 9,10-Dihydroanthracene (Aldrich) was purified by recrystallization (five times from ethanol) prior to use. 9,9-Dimethyl-9,10-dihydroanthracene was prepared according to a literature procedure²⁸ and was purified by recrystallization (three times from pentane) prior to use.

Photoacoustic Calorimetry. The photoacoustic apparatus used in these experiments has been described in detail elsewhere¹⁶ and was similar to the one described by Peters.²⁹ Solutions were photolyzed by a Molectron UV 24 pulsed nitrogen laser ($\lambda = 337.1$ nm, pulse width 10 ns, 5 Hz), and the resulting shock waves were detected by a Panametrics V101 transducer (2-µs response) amplified by a Panametrics Model 5670 ultrasonic preamplifier and signal-averaged with a Tektronix 7D20 digitizer. Optical densities were measured with a Hewlett-Packard Model 8450A diode array spectrophotometer.

Cyclic Voltammetry. The cyclic voltammetry was performed with a PAR Model 173 potentiostat equipped with a Model 175 universal programmer. A standard three-electrode cell that was fully *iR* compensated was used for all measurements. Voltammograms were recorded on an HP 7045B X-Y recorder. Solutions (acetonitrile, 0.1 M TBAP) were deoxygenated with a stream of dry argon. The carbon working electrode was cleaned, before each measurement, with a fine polishing powder and a soft cloth. All potentials are reported with respect to the saturated calomel electrode (SCE).

Photomodulation Voltammetry. The instrument has been described in detail elsewhere. Radicals were generated in the electrochemical cell by photolysis, through an optically transparent gold electrode, of a solution of di-*tert*-butyl peroxide in acetonitrile (1:9, v/v) containing TBAP (0.1 M) and the hydrocarbon (0.5 M). The output from the lamp was modulated with a light chopper so the light intensity (and therefore the radical concentration) rose and fell as a sine wave. The electrochemical cell was fully *iR* compensated and was controlled with a PAR Model 174 polarographic analyzer. The AC component of the faradaic current was detected with an Ithaco Model 391A lock-in amplifier and plots of the AC current, as a function of potential, were recorded on a HP 7045B X-Y recorder. All measurements were made at 53-Hz modulation with detection of the quadrature component of the signal. Values of half-wave potentials are reported with respect to the SCE.

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⁽²⁴⁾ The enthalpies of formation of anthracene and 9,10-dihydroanthracene in the gas phase, 55.2 ± 0.5 and 38.2 ± 1.1 kcal mol⁻¹, respectively, lead to 121.2 ± 1.2 kcal mol⁻¹ for the sum of the first and the second C-H bond dissociation enthalpies for 9,10-dihydroanthracene: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data for Organic Compounds*; Chapman and Hall: London, 1986. Using the photoacoustic value given in this paper, $D_1 = 78.3 \pm 1.5$ kcal mol⁻¹, $D_2 = 42.9 \pm 1.9$ kcal mol⁻¹ is derived.

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