

Electron Affinities of Some Polycyclic Aromatic Hydrocarbons, Obtained from Electron-Transfer Equilibria

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Abstract: The gas-phase electron attachment free energies ΔG_a° , where $-\Delta G_a^\circ \approx EA$, were measured for several polycyclic aromatic hydrocarbons with the electron-transfer equilibria technique. The EA values in kcal/mol are as follow: anthracene, 13.2; benz[a]pyrene, 18.2; perylene, 22.3; tetracene, 23.9; and pentacene, 31.2. These results, when combined with the literature value for naphthalene, -4.4 kcal/mol, based on electron transmission spectroscopy, lead to an approximately linear correlation with the one-electron (polarographic) reduction potentials determined in solution. However, the slope of the line is not equal to 1 as previously assumed. The deviation from unity is probably due to decreases of the solvation exothermicity of the radical anions, expected because of the increasing charge delocalization for the negative ion with increasing electron affinity of the neutral precursor.

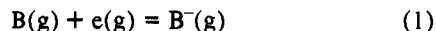
Introduction

The study of polycyclic aromatic hydrocarbons (PAHs) holds an important place in the history of applications of molecular orbital theory to organic chemistry. Within the context of the present work, it is worth recalling that Hückel himself showed, very early,¹ that the chemistry of the alkali addition compounds of aromatic hydrocarbons agrees with the simple MO picture in which an electron, released by the alkali atom, enters an available empty MO, i.e., the lowest antibonding π^* orbital of the unsaturated hydrocarbon. Following this suggestion, Maccoll² showed that the polarographic half-wave potentials, $\epsilon_{1/2}$, for the one-electron reduction of several unsaturated hydrocarbons give linear plots versus the relative HMO energy of the LUMO. This correlation was further extended and interpreted by Pullman,³ Lyons,⁴ and others.⁵ For a very good account and summary of data on the correlation between the reduction potentials $\epsilon_{1/2}$ and the energies of the HMO-evaluated LUMOs and PAHs, see Streitwieser.⁶

This early work¹⁻⁶ contributed significantly to the acceptance of MO theory by the body of organic chemists. Somewhat more recent comparisons of one-electron reduction potentials of PAHs with LUMO energies have involved somewhat more elaborate levels of theory such as the β -parametrized SCF-MO method, the method of Dewar,⁷ and a "self-consistent HMO" method, Wilcox.⁸

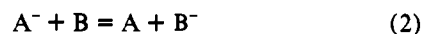
It is interesting that the above correlations, while essentially correct in the intended physical interpretation, depend on a number of approximations. The most important of these concerns the solvation of the PAH, called B in the subsequent discussion. The solvation free energy difference, $\Delta\Delta G_{sol}^\circ = \Delta G_{sol}^\circ(B^-) - \Delta G_{sol}^\circ(B)$, is assumed to be constant within the series of compounds examined. ΔG_{sol}° represents the free energy change for the transfer of B, respectively the radical anion B⁻, from the gas phase to the solvent, in which the $\epsilon_{1/2}$ is measured. For relevant

equations involving the reduction potentials, see Streitwieser⁶ and the Discussion section in the present work. Another assumption is that $EA(B) = -\Delta H_a^\circ(B) = -\Delta G_a^\circ$, where EA is the electron affinity of B, strictly defined as the zero-point energy difference between B and B⁻, while $\Delta H_a^\circ(B)$ and $\Delta G_a^\circ(B)$ refer to the enthalpy and free energy of electron attachment, i.e., of the formation of B⁻ from B and an electron at a given temperature, see eq 1:



A third assumption is that the electron affinity EA is equal to the (negative) energy of the LUMO rather than to the difference between the theoretically evaluated zero-point energies of B and B⁻.

Abundant experimental data on the energy changes, ΔH_a and ΔG_a° , for the electron attachment process, eq 1, became available^{9,10} only relatively recently. These were obtained from gas-phase electron-transfer equilibria, eq 2, where the relative



ion concentrations of A⁻ and B⁻ at equilibrium are determined with special mass spectrometric techniques.

The electron-transfer equilibria data provide only the energy differences, $\Delta G_a^\circ(B^-) - \Delta G_a^\circ(A^-)$ and $\Delta H_a^\circ(B^-) - \Delta H_a^\circ(A^-)$, but the individual (absolute) values can be obtained by calibration to the absolute value for one standard compound (SO₂) whose electron affinity was determined by a photodetachment technique¹¹ and for which $\Delta H_a^\circ(SO_2)$ and $\Delta G_a^\circ(SO_2)$ can be evaluated^{10c} from available vibrational frequencies of SO₂ and SO₂⁻. Due to similarities in the geometries and vibrational frequencies for the neutral and the negative species for many compounds, the approximate equality $-EA(B) \approx \Delta H_a^\circ(B) \approx \Delta G_a^\circ(B)$ is found to hold when the stationary electron convention is used.^{10c}

Plots of the reduction potential $\epsilon^\circ(B)$ versus $-\Delta G_a^\circ(B) \approx EA(B)$ gave approximate straight lines for some series of compounds;^{10,12} however, the slope was not equal to 1 but was smaller for

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substituted nitrobenzenes, naphthalenes, anthracenes, and quinones, showing that the reduction potentials change less than the electron affinities. This difference was attributed^{10,12} to a failure of the assumption that the solvation energy difference $\Delta\Delta G_{\text{sol}}^{\circ}(\text{B})$ is constant. Such a failure can be expected since increases in electron affinities in a substituted series are often correlated with increasing charge delocalization in the negative ion, and increased charge delocalization leads to a decrease of solvation exothermicity for the negative ion.^{10,12}

For the PAHs, the presence of a similar effect may be expected, and therefore it is of interest to compare the correlation between the gas-phase electron attachment energies, $\text{EA}(\text{PAH}) \approx -\Delta G_{\text{a}}^{\circ}(\text{PAH})$, with the theoretical values based on MO theory and with the reduction potentials $\epsilon^{\circ}(\text{PAH})$. To achieve such a comparison, the $-\Delta G_{\text{a}}^{\circ} \approx \text{EA}$ for several larger PAHs had to be determined since they were not available in the literature.

Experimental Section

(a) Apparatus and Methodology of Equilibria Determinations. The electron-transfer equilibria measurements were carried out with a pulsed high-pressure mass spectrometer (PHPMS), which has been described in detail.¹³ Methane bath gas containing the neutral reactants was allowed to flow through the ion source of the mass spectrometer. Short pulses (10–50 μs) of electrons accelerated by a 2000-V potential entered the ion source through a very narrow slit at 10-ms intervals. Each pulse produced predominantly positive ions and secondary electrons from methane. The secondary electrons became thermalized by successive collisions with methane molecules. Some of the slow electrons were captured by the neutral reactants A and B, which have positive electron affinities. As the A^{-} and B^{-} ions diffused toward the walls of the source, they were thermalized and also reached the electron-transfer equilibrium, eq 2. A small fraction of the ions that came to the vicinity of a very small sampling slit at the wall of the source escaped into the vacuum of the mass analysis system, where they were separated by mass. The time-resolved ion counts for ions of a given mass were recorded in a multichannel scaler.

The time for ion diffusion to the walls of the ion source was several milliseconds. This was also the limiting time available for reaction. The electron transfer equilibria should be established in a much shorter time, and this sets a lower limit to the concentrations of neutral reactants that must be supplied. For the reaction in the exoergic direction, which generally proceeds at collision rates $k \approx 10^{-9}$ molecules⁻¹ cm³ s⁻¹, this corresponds to a concentration of ~ 0.05 mTorr. In the apparatus used, the neutral reaction mixture was usually prepared^{10,13} using 1 atm of CH_4 bath gas in a 5-L storage vessel at 50 °C and then bled by means of a control valve in and out of the ion source, which was maintained at ~ 3 Torr total pressure. The desired partial pressures of the reactants were usually obtained by injecting known quantities of the reactants into the 2-L storage vessel, where the reactants evaporated. For the very nonvolatile PAHs this technique cannot be applied. Therefore, these compounds were evaporated directly into the 3-Torr methane stream. The methane passed over a stainless steel boat which contained the neutral solid. The temperature of the boat was maintained at least 10 °C lower than the rest of the flow system and ion source, to prevent condensation of the PAH compound.

The temperature of the boat and the rate of methane flow were adjusted to obtain a pressure of the PAH = B, with which the rate of electron transfer from A^{-} to B can be conveniently measured. A is a volatile reference compound with known electron affinity which is present at known partial pressure in the methane stream originating from the 5-L storage vessel.

Since the concentrations of the neutrals A and B vastly exceed those of the ions A^{-} and B^{-} , the rates in the forward and reverse direction for the electron-transfer reaction, eq 2, are first order, and the pseudo-first-order rate constant (reaction frequency) $\nu_f = k_f[\text{B}]$ is easily determined. Using a calculated (Langevin) rate constant k_f , the concentration of the PAH = [B] can be determined from ν_f .

Table I. Polarizabilities of PAH and Evaluated Langevin Rate Constants

neutrals	polarizability of PAH (10 ⁻²⁴ cm ³)	k_{Langevin} (10 ⁻⁹ cm ³ /molecule s)
tetracene, <i>m</i> -nitrotoluene ^c	32.3 ^a	1.44
tetracene, <i>p</i> -CF ₃ -benzonitrile ^c	32.3 ^a	1.34
pentacene, <i>p</i> -F-nitrobenzene ^c	41.22 ^b	1.55
pentacene, <i>p</i> -CN-benzaldehyde ^c	41.22 ^b	1.59
benz[<i>a</i>]pyrene, <i>o</i> - or <i>m</i> -CF ₃ -benzonitrile ^c	33.51 ^b	1.34
perylene, <i>p</i> -CF ₃ -benzonitrile ^c	33.51 ^b	1.34
perylene, 2,3-dimethylnitrobenzene ^c	33.51 ^b	1.39

^a Experimental values compiled by Miller and Savchik.¹⁷ ^b Estimated values using method of Miller and Savchik.¹⁷ ^c Molecule of negative ion A^{-} involved in electron transfer to PAH and whose mass was used in reduced mass required for evaluation of rate constant k_{Langevin} .

The use of calculated rate constants (Langevin) to evaluate the concentration of a neutral reactant is a procedure used earlier by Meot-Ner et al.¹⁴ The electron-transfer reactions proceeded with Langevin rates when the geometry changes for A to A^{-} and B to B^{-} are small and when the reactions are exoergic by about 2 kcal/mol or more.^{10,15} In the present work, all determinations involved exoergicities of 2–6 kcal/mol. The calculated Langevin rate constants¹⁶ $k_{\text{L}} = 2\pi\epsilon(\alpha/\mu)^{1/2}$ for the PAHs used in the present work are given in Table I. Also given are the polarizabilities α for the respective PAHs. The polarizability for tetracene has been determined experimentally.¹⁷ The other values were estimated with the method of Miller and Savchik.¹⁷

Errors in the concentration of the PAH due to the rate constant not being equal to k_{L} are estimated^{10,15} to be less than a factor of 2, and errors due to the polarizability being estimated are much less than a factor of 2. A factor of 2 leads to errors in $\Delta G_{\text{a}}^{\circ}$ of ~ 0.6 kcal/mol.

The time dependence of the reactant ion intensities obtained in a typical determination of an electron-transfer equilibrium is shown in Figure 1. The standard compound A with known $\Delta G_{\text{a}}^{\circ}$ is 3-nitrotoluene, and the PAH is tetracene = B. Compound A is present at a higher pressure (0.26 mTorr) and captures initially more electrons, leading to A^{-} . Electron transfer ($\text{A}^{-} + \text{B} = \text{A} + \text{B}^{-}$) gradually leads to equilibrium. The kinetic stage, where the relative concentrations change, is over in 1 ms, and the ion concentration ratio becomes constant for longer reaction times. In the logarithmic plot, a constant ratio corresponds to a constant distance between A^{-} and B^{-} intensities. The gradual decrease of both intensities is due to diffusion of the ions to the wall.

(b) Determinations of Equilibria When Compounds of Very Low EA Are Involved. Experiments Involving Naphthalene. The electron affinity of naphthalene is important for the discussion in the present work, vide infra. Because there is a significant disagreement between determinations in the literature, $\text{EA} = -4.4$ kcal/mol by electron transmission spectroscopy (ETS)¹⁸ and the electron capture detector (ECD) method,^{19,20} but $\text{EA} = +3.5$ kcal/mol, vide infra, attempts were made to obtain the EA of naphthalene via the present electron-transfer equilibria (ETE) method. The earlier determination of the electron affinity of anthracene, $\text{EA} \approx 13.2$ kcal/mol, with the ETE method²¹ had shown that thermal electron detachment (autodetachment), eq 3, occurs for this compound:



To avoid rapid autodetachment one needed to work at lower temperatures, i.e., at ~ 100 °C rather than the 150 °C used for the other compounds.^{12d}

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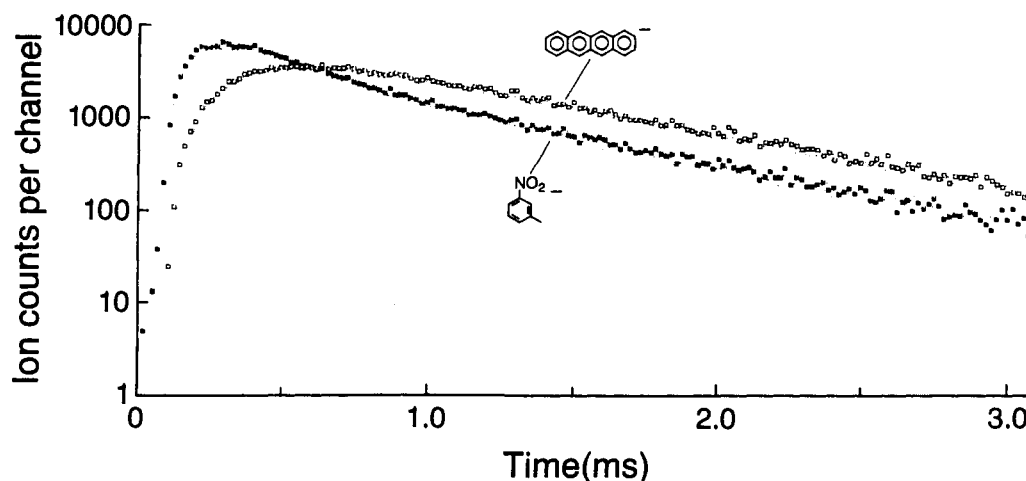


Figure 1. Ion counts per channel versus time after electron pulse observed for reaction system: 3-nitrotoluene + tetracene = 3-nitrotoluene + tetracene⁻. The nitrotoluene which is present at a higher partial pressure (0.26 mTorr) relative to tetracene (0.06 mTorr) attaches electrons more rapidly, and the initial concentration of the nitrotoluene⁻ is higher than that of tetracene⁻. The electron transfer from the nitrotoluene⁻ to tetracene, which has a higher EA, leads to electron-transfer equilibrium. Equilibrium is achieved after ~1.5 ms, when the ion concentration ratio becomes constant. In the logarithmic plot used, a constant ratio corresponds to a constant vertical distance between the plots. The slow decreases of the ion intensities of both ions are due to diffusion to the wall. $T = 458$ K, total pressure 3.2 Torr.

In the present work with naphthalene, the presence of a naphthalene negative ion could not be observed, even at 30 °C. An estimate of the negative ion to electron concentration at 30 °C can be made. The autodetachment rate constants k_d for azulene²³ and hexafluorobenzene²⁴ have the Arrhenius form

$$k_d = A \exp(-EA/RT) \quad (4)$$

where, $A \approx 10^{11} \text{ s}^{-1}$ at 300 K. Using the ECD value for naphthalene, EA = 3.5 kcal/mol, and eq 4, one evaluates a $k_d \approx 3 \times 10^8 \text{ s}^{-1}$ at 300 K. The electron attachment rate constant to naphthalene is not known, but assuming^{25,26} a $k_a \approx 10^{-9} \text{ particle}^{-1} \text{ cm}^3 \text{ s}^{-1}$, one can estimate the ion B⁻ to electron concentration ratio:

$$\begin{aligned} k_a[e][B] &= k_d[B^-] \\ [B^-]/[e] &= \frac{k_a[B]}{k_d} \end{aligned} \quad (5)$$

Equation 5 governs the concentration ratio, since the major mechanism for charge loss, ambipolar diffusion to the wall, is much slower, $k_{\text{diff}} \approx 10^3 \text{ s}^{-1}$ (at 300 K and 3 Torr total pressure²³). From eq 5 and $[B] = 3 \times 10^{13} \text{ molecules/cm}^3$ (at 1 mTorr naphthalene) one obtains

$$[B^-]/[e] \approx 10^{-4}$$

Since in the absence of thermal detachment, the free electrons will have been converted to negative ions, a decrease of ion intensity by a factor of $\sim 10^4$ is predicted for naphthalene, relative to the normal high EA compounds observed with our PHPMS. A smaller k_a will lead to an even larger loss. A dynamic range of 10^4 is available in the PHPMS but as an upper limit, and therefore our inability to observe the naphthalene negative ion does not invalidate the positive EA for naphthalene determined by ECD.

An attempt to obtain the EA of naphthalene on the basis of a substituent effect correlation was also made. It was shown in previous work, dealing with substituted nitrobenzenes,²⁷ that very good correlations between substituent constants and electron affinities can be obtained. Electron affinities for naphthalenes substituted with NO₂, CN, and CHO groups are available;²¹ however, in order to obtain a correlation which might

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predict the value for the unsubstituted naphthalene, values with other substituents such as F and Cl would be required. These substituents are expected to increase the EA by only a few kcal/mol and thus could lead to measurable electron-transfer equilibria. It was found in the present work that the radical anions for 1-F naphthalene and 1-Cl naphthalene could be detected but only at low temperature (30 °C) and when very low pressures, $p \leq 0.1$ mTorr, of these compounds were used. However, the intensities obtained were so low that electron-transfer equilibria could not be measured. Evidently, thermal electron detachment from these compounds is still very rapid and affects adversely the anion concentrations. The requirement of low pressure for the neutrals ($p < 0.1$ mTorr) was traced to the presence of impurities in the fluoro- and chloronaphthalene. Cl-containing impurities which have large electron-capture cross sections for dissociative electron capture were particularly troublesome, even at concentrations as low as 0.1%. Presumably the high electron concentration due to autodetachment led to large electron loss to these impurities.

It is possible that ETE measurements with these compounds at temperatures much below 30 °C would have been successful, but such experiments were not performed.

Results and Discussion

(a) Electron Affinities of Polycyclic Aromatic Hydrocarbons.

The equilibrium constants K_2 for the electron-transfer equilibria, eq 2, involving different reference compounds A with known $\Delta G_a^\circ(A)$, reacting with given PAH, were obtained from the ion ratios at equilibrium. For a typical result see Figure 1. The corresponding $\Delta G_2^\circ = -RT \ln K_2$ are shown on the scale given in Figure 2. The ΔG_2° combined with the known $\Delta G_a^\circ(A)$ leads to $\Delta G_a^\circ(B)$ values as shown in Figure 2.

Two different reference compounds A were used for each PAH, and the average $\Delta G_a^\circ(B)$ resulting from these determinations is also shown in Figure 2. In general, the two determinations with two reference compounds are seen to be consistent to within less than 0.5 kcal/mol.

The ΔG_a° for the PAHs obtained in this manner are summarized in Table II. Also included in Table II is the ΔG_a° value for anthracene, previous work obtained from this laboratory,²¹ and available EA values for the other PAHs from the literature.^{19–22}

The agreement between the $-\Delta G^\circ(B)$ from electron-transfer equilibria and the electron-capture detector technique for anthracene, benz[a]pyrene, and tetracene is good to fair, the values being within ~ 2 kcal/mol of each other.

The EAs obtained by Dewar with the parametrized SCF-MO method⁷ are seen to be very close to the equilibria results for anthracene and all the higher PAHs, see Table II.

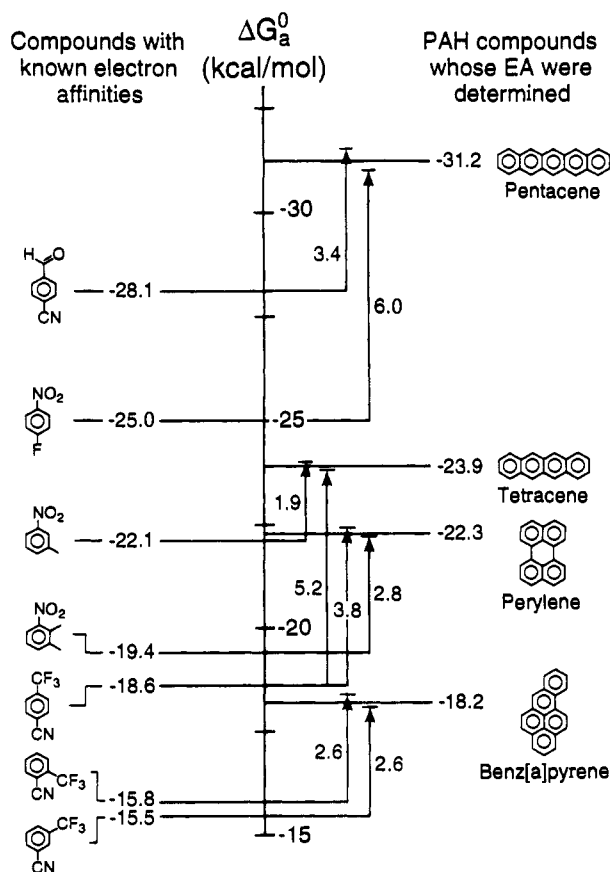


Figure 2. Summary of results for electron-transfer equilibria, eq 2: $A^- + B = A + B^-$. Compounds A shown in the left column have known electron affinities ($-\Delta G_a^0$). Compounds B are the PAHs indicated on the right. The ΔG_2^0 measured, shown as vertical distances tipped with an arrow, combined with known ΔG_a^0 (A), lead to ΔG_a^0 of the PAHs. Two different standard compounds A were used for each PAH determination. All values in kcal/mol.

There is a large difference between the two literature values for the EA of naphthalene: -4.4 kcal/mol obtained with electron transmission spectroscopy (ETS), Jordan et al.,¹⁸ and $+3.5$ kcal/mol, with the electron capture detector (ECD), Chen and Wentworth,¹⁹ see Table II.

The ETS results can be considered to lead to vertical electron affinity values,¹⁸ and the difference between the ETS and ECD value could then be attributed to a difference between the vertical (ETS) and adiabatic (ECD) electron affinity. However, the resonance observed by Jordan et al.^{18b} for naphthalene contains vibrational structure which indicates that the lowest energy transition at -4.4 kcal/mol is the 0-0 transition and thus corresponds to the adiabatic EA of naphthalene.²⁸

A disagreement between ETS and ECD appears to exist also for benzene. Jordan et al.^{18b} expect that their vertical EA value of -25.8 kcal/mol for benzene corresponds fairly closely to the adiabatic value. On the other hand, Wojnarovits and Foldiak,²⁰ who have measured with ECD the EA for a series of aromatic hydrocarbons, see Table II, find a positive EA of 2 kcal/mol for 1,2,3,5-tetramethylbenzene and higher values for more highly methylated benzenes. This is a surprising result because it is generally observed that methyl substitution on sp^2 hybridized carbon leads to a destabilization of the anion.^{10c} For example, successive substitution of methyl into benzoquinone decreases the EA by ~ 1.7 kcal/mol per methyl, leading to a total decrease

(28) The resonance observed by Jordan et al. shows vibrational progressions involving two normal vibrations in the anion. The intensity changes indicate that the lowest energy transitions for both correspond to the zero vibrational level. Assuming that transitions to other vibrational modes are not present, which is likely, one concludes that the lowest energy transition at -4.4 kcal/mol is the 0-0 transition and thus the adiabatic EA. We are indebted to Dr. K. D. Jordan for this more detailed interpretation.

of 6.4 kcal/mol for tetramethylbenzoquinone.^{12a} The anion destabilization by methyl substitution on sp^2 hybridized carbon is a general effect observed also for even electron anions such as deprotonated acetylenes,²⁹ carboxylic acids,³⁰ and phenols.³¹ Wojnarovits and Foldiak²⁰ observed an ECD response for benzene, but the signal was too weak to permit temperature-dependence measurements.

It is very difficult to understand how substitution with four methyl groups can raise the EA of benzene from around -25 kcal/mol (ETS) to $+2$ kcal/mol in tetramethylbenzene. We consider it quite possible that the ECD method does not provide reliable values for compounds whose EA is less than a few kcal/mol. The theory behind the ECD method and the actual processes involved is quite complex, and the method suffers from the drawback that the actual negative ions present are not detected.

The adiabatic value of the EA of naphthalene is of importance for the full utilization of the present data since it extends significantly the range of EA and the range of PAH structure types, vide infra. Therefore, in an effort to resolve the discrepancy between the ETS and ECD values, we attempted in the present work to determine the EA of naphthalene with the electron transfer equilibrium method. As described in the Experimental Section, this work was unsuccessful because of problems created by the rapid thermal electron detachment which occurs when compounds with very low positive electron affinities are involved. In the subsequent discussion we will consider both EA values for naphthalene, but we will give greater weight to the negative ETS value, which we consider more likely to correspond to the adiabatic EA.

A plot of the $-\Delta G_a^0 = EA$ versus the Hückel LUMO coefficient is shown in Figure 3. In the early correlations of reduction potentials with electron affinities,^{2,3,6} it was assumed that the $\epsilon_{LUMO} = \alpha + m\beta$, evaluated with simple HMO, is proportional to $-EA$. The plot in Figure 3 confirms this assumption. The slope provides a value of -3.8 eV for β , which is close to the value of -3.14 eV used by Compton et al.³² The linear correlation between the simple HMO ϵ_{LUMO} and the electron affinity does not extend to benzene. Compton et al. have shown that a linear correlation including a large variety of aromatic hydrocarbons and benzene can be obtained when the LUMO energy is evaluated with the semiempirical Pariser-Parr-Pople approximation.

(b) **Correlations with Reduction Potentials in Solution.** Plots of the reduction potentials ϵ_0 of the PAH, where the ϵ^0 are taken equal to the polarographic halfwave potential $\epsilon_{1/2}$, versus $-\Delta G_a^0 \approx EA$ are shown in Figure 4. Two sets of $\epsilon_{1/2}$ values, obtained for two different solvents, 25% dioxane and 75% water, from literature sources compiled by Streitwieser,⁶ and 2-methoxyethanol, Bergman,³³ are used in the plots.

The relationship between the reduction potential $\epsilon^0(B)$ and the electron attachment free energy $\Delta G_a^0(B)$ is given below:

$$\mathcal{F}\epsilon^0(B) = -\Delta G_a^0(B) - (\Delta G_{sol}^0(B^-) - \Delta G_{sol}^0(B)) + C \quad (6)$$

\mathcal{F} is the Faraday constant, equal to the charge of one mole of electrons, and C is a constant that depends on the absolute reduction potential of the reference electrode used. For the derivation of eq 6 see Matsen.³⁴ Recent comparisons of ΔG_a^0 and $\epsilon_{1/2}$ on the basis of eq 6 were made by Heinis et al.,^{12a} Kebarle et al.,^{12b} and Shalev and Evans.³⁵

According to eq 6, a straight line relationship with slope = 1 will be obtained only if $\Delta\Delta G^0$ is constant. In earlier work for

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Table II. Summary of Electron Affinities and Electron Attachment Free Energies

compd	$-\Delta G_a^{\circ a}$ (kcal/mol)	T (K)	EA (lit.) (kcal/mol)	Dewar ^b	$\epsilon_{1/2}^c$ (V)	$\epsilon_{1/2}^d$ (V)	$-m_{(m+1)}^e$
naphthalene			-4.4, ^g 3.5 ^{h,i}	1.7	2.50	1.98	0.618
anthracene	13.2 ^f	423	11.1, ^f 13.1, ^f 12.8 ^h	15.0	1.96	1.46	0.414
benz[a]pyrene	18.2	420	15.7 ^h	21.4	1.85	1.36	0.365
perylene	22.3	425		22.0	1.67	1.25	0.347
tetracene	23.9	458	20.3 ^f	24.4	1.58	1.14	0.295
pentacene	31.2	584		30.9		0.86	0.220

^a Free energy of electron attachment at temperature T , using stationary electron convention. Estimated error in $\Delta G_a^{\circ} \pm 1$ kcal/mol. ^b Calculated from Dewar,⁷ parametrized SCF-MO method. ^c Polarographic half-wave reduction potentials in 25% dioxane, 75% water versus SCE, compiled by Streitwieser.⁶ ^d Same as *c*, but in 2-methoxyethanol versus mercury pool electrode, Bergman.³³ ^e Simple HMO coefficients for LUMO in units of β .⁶ ^f From electron-transfer equilibria, Chowdhury.²¹ ^g Jordan and Burrow,¹⁸ electron transmission spectroscopy. ^h Wentworth and Chen,¹⁹ ECD method. ⁱ Wójciszewski²⁰ ECD method. ^j Lyons²¹ ECD method.

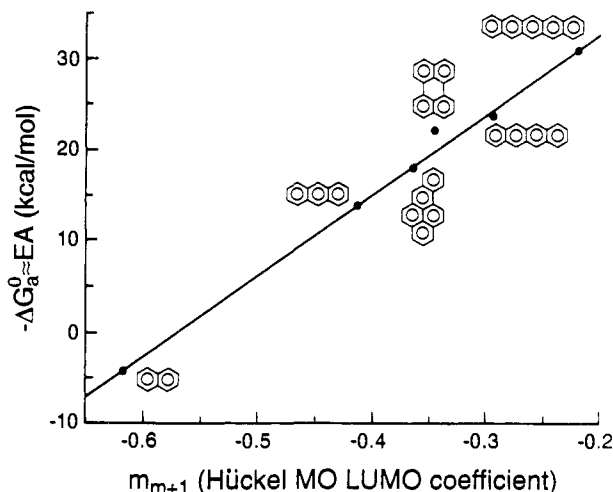


Figure 3. Plot of gas-phase electron attachment free energies versus value of HMO coefficient of LUMO, m_{m+1} .

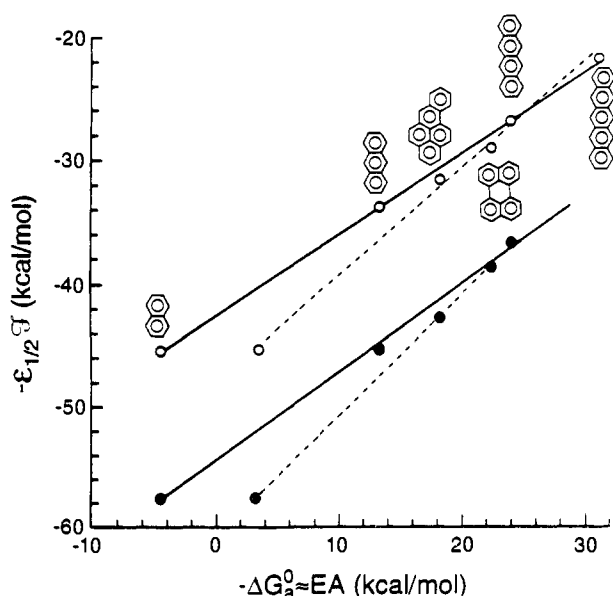


Figure 4. Plot of gas-phase electron attachment free energies ΔG_a° versus one-electron reduction free energies based on polarographic half-wave potentials $\epsilon_{1/2}$. \mathcal{F} is Faraday's constant (electron charge per mole); \circ , polarographic potentials determined in 75% aqueous dioxane and aqueous SCE as reference electrode;⁶ \bullet , 2-methoxyethanol solvent and Hg pool counter electrode.³³ Depending on the literature values for naphthalene, -4.4 kcal/mol ETS and +3.5 kcal/mol ECD, two different slopes, 0.72 ETS¹⁸ (—) and ~ 1.0 ECD¹⁹ (- -), are indicated.

substituted nitrobenzenes, approximate straight lines were obtained with slopes ≈ 0.35 (methanol)³⁵ and 0.5 (tetrahydrofuran),³⁵ while for substituted quinones there was much more scatter and slopes less well defined but still less than 1.^{12a,35} An approximate linear relationship with slope less than 1 can be expected for the cases where increase of electron affinity is

accompanied by increased charge delocalization. This is the case for the substituted nitrobenzenes and quinones where increases of the electron affinity are obtained with electronegative substituents to which the charge is delocalized. Since charge delocalization decreases solvation exothermicity, an approximately linear relationship with slope less than 1 can result.

The results for the PAH shown in Figure 4 are compatible with two slopes. A slope of approximately 1 is obtained when the high 3.5 kcal/mol ECD value¹⁹ for naphthalene is used, while a somewhat better straight line correlation with a slope of ~ 0.72 is obtained with the -4.4 kcal/mol ETS value.¹⁸ Considering the results for the quinones and nitrobenzenes discussed above, one could assume that the lower slope, 0.72, is the correct one, and this would also indicate that the ETS value for naphthalene is the correct one. However, the situation is more complicated. Abundant information of $\Delta \Delta G_{sol}^{\circ}$ (anions) is available from comparisons of gas-phase and solution-phase acidities.^{30,31} With substituted phenols and benzoic acids one obtains^{30,31} plots of solution versus gas phase acidities which have much less than unit slopes and indicate a decreasing $\Delta \Delta G_{sol}^{\circ}$ (anion) with increasing acidity—a behavior analogous to that for the nitrobenzenes and quinones discussed above. All of these systems have strongly electronegative heteroatoms (primarily oxygen) in which most of the negative charge is concentrated. On the other hand, Taft and Bordwell³⁷ have found that carbon acids with no heterosubstituents, which lead to highly delocalized anions (acids such as fluorenes, diphenylcyclopentadiene, and triphenylmethane), lead to a slope = 1 correlation of solution- (dimethyl sulfoxide) versus gas-phase acidity.

The PAH radical anions represented in Figure 4 are more closely related to the carbanions of Taft and Bordwell than to anions of the heterosubstituted systems. However, there is an important difference. For the series naphthalene, anthracene, tetracene, pentacene there is a regular progression. The charge of the single electrons as indicated by the squares of the LUMO coefficients becomes progressively delocalized, and this corresponds to an effective increase of the size of the anion. Estimates of the $\Delta \Delta G_{sol}^{\circ}$ on the basis of the Born equation and the charge delocalization based on the LUMO coefficients can be found in Hedges and Matsen:³⁸ $-\Delta \Delta G_{sol}^{\circ}$ (kcal/mol) benzene ≈ 42 , naphthalene ≈ 25 , and anthracene ≈ 18 . Further but smaller decreases are expected for tetracene and pentacene. Therefore, a slope less than 1 is expected for the plot in Figure 4. Considering the uncertainties of the solvation energy estimates, it is not possible to establish whether the expected slope should be closer to the ~ 0.72 value indicated by the ETS result for naphthalene or the 1.0 value based on the ECD result. Furthermore, because the expected changes of solvation energies are largest for the first few members, i.e., benzene, naphthalene, and anthracene, a curve with increasing slope approaching 1 for the high PAHs should be expected rather than a straight line. Unfortunately, suitable reduction potential data for benzene are not available. The data points in Figure 4 are compatible with such a gently curved line but much more so if the lower (ETS) value for naphthalene is used.

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