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The Relationship between the Electron Affinities and Half-Wave Reduction Potentials of Fullerenes, Aromatic Hydrocarbons, and Metal Complexes

Rodney S. Ruoff*

Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

Karl M. Kadish* and Pierre Boulas

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

E. C. M. Chen*

School of Natural and Applied Sciences, University of Houston Clear Lake, 2700 Bay Area Boulevard, Houston, Texas 77058

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Differences in energy for neutral molecule and negative ions upon going from the gas phase to solution, $-\Delta\Delta G_{\text{sol}}$, have been calculated from gas phase electron affinities and half-wave reduction potentials for a series of fullerenes, aromatic hydrocarbons, metalloporphyrins, and metal complexes in dimethylformamide (DMF). For those compounds with similar charge delocalization, the value of $-\Delta\Delta G_{\text{sol}}$ is constant and equal to 1.76 ± 0.06 eV for the fullerenes, 1.99 ± 0.05 eV for the aromatic hydrocarbons and the metalloporphyrins, and 2.19 ± 0.14 eV for the metal acetylacetonates. The fullerenes form a new class of molecules in which the charge is highly delocalized, and this is demonstrated by the relatively low value of $-\Delta\Delta G_{\text{sol}}$. A procedure for determining adiabatic electron affinities from reduction potentials, and vice versa, is established. This procedure is applied to benzene to give an electron affinity of -0.7 ± 0.14 eV, to La@C_{82} to give an electron affinity of 3.21 ± 0.06 eV, and to Y@C_{82} to give an electron affinity of 3.32 ± 0.06 eV. On the other hand, a value of $E_{1/2} = 0.09 \pm 0.14$ V vs SCE is predicted for the reduction of Ca@C_{60} in DMF based upon a reported electron affinity of 3.0 ± 0.1 eV.

Introduction

The discovery and isolation of fullerenes initiated a whole new area of research into the properties of this third form of carbon.¹ The molecule is related to a well-studied class of compounds, the aromatic hydrocarbons. Thus, it is important to compare data accumulated on aromatic hydrocarbons with data being obtained for fullerenes. Two especially important properties are the half-wave reduction potentials, $E_{1/2}$'s, and gas phase electron affinities, EA's.^{2,3} The gas phase electron affinities of several fullerenes are quite large, for example, 2.65 eV for C_{60} , 3.05 eV for C_{84} , and 4.06 eV for $\text{C}_{60}\text{F}_{48}$, one of the largest values for an organic molecule obtained to date.^{4–6} The half-wave potential for the first reduction of a given molecule is related to its gas phase electron affinity, and the two values can be used to determine the energy difference between the neutral molecule and the negative ion in the gas phase and in solution, $-\Delta\Delta G_{\text{sol}}$. Alternatively, if this energy difference can be estimated for a given molecule, then the gas phase electron affinity can be determined from the reversible reduction potential or vice versa. The establishment of this procedure is the ultimate objective of this paper.

The relationship between EA and $E_{1/2}$ is normally given as shown in eq 1,²

$$E_{1/2} = \text{EA} - \Delta\Delta G_{\text{sol}} + E_{\text{ref}} \quad (1)$$

where $E_{1/2}$ and EA are the experimental values of the reduction potential and the electron affinity for a given molecule and E_{ref} is the reference potential expressed in volts. For example, $E_{\text{ref}} = -4.71$ V if the potential is referenced to the SCE. The

quantity $\Delta\Delta G_{\text{sol}}$ depends on the solvent/supporting electrolyte system, which in this study is dimethylformamide (DMF) containing mainly 0.1 M tetraalkylammonium salt. An aqueous SCE is used as the reference electrode. Unless otherwise specified, the potentials refer to $E_{1/2}$ for the first reduction.

Various methods have been used to obtain experimental values for electron affinities of molecules. In the early 1960s, the first experimental determination of gas phase electron affinities for several aromatic hydrocarbons were reported based on the molar response of the electron capture detector (ECD).^{7,8} These values were obtained from measurements at a single temperature and assumed equilibrium. These values were later refined by measuring the temperature dependence of the molar response and applying a kinetic model to the reactions.⁹ Because no other experimental values of gas phase electron affinities were available at the time, the results were compared with $E_{1/2}$ for reduction of the same molecules in aprotic solvents. The temperature dependence of the abundance of the parent negative ions formed under thermal electron attachment in negative ion mass spectrometry can also be used to determine gas phase electron affinities and support the values obtained from the ECD.¹⁰ The ECD method has been applied to the determination of EA of about a hundred molecules.

In the 1980s, relative electron affinities of over a hundred molecules, including aromatic hydrocarbons, were obtained by measuring equilibrium constants for thermal charge transfer reactions (TCT).^{10–14} The reduction potentials measured for many of these molecules in aprotic solvents have been reported in the literature.¹⁵

Both gas phase EA's and $E_{1/2}$'s are needed to calculate $\Delta\Delta G_{\text{sol}}$ whose values primarily depend upon the degree of charge delocalization.³ For example, the series of mononitro

* Authors to whom correspondence should be addressed.

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compounds listed in group C in ref 2 have a localized anionic charge and are characterized by an average $-\Delta\Delta G_{\text{sol}}$ of about 2.5 eV. In contrast, the average $-\Delta\Delta G_{\text{sol}}$ for a series of aromatic hydrocarbons and other compounds for which the charge of the anion is delocalized (group A in ref 3) is about 2.0 eV. A third intermediate group of compounds (group B in ref 3) has an average $-\Delta\Delta G_{\text{sol}}$ of 2.29 eV. A specific description of the compounds in each group has been given elsewhere.³ The standard deviation in $-\Delta\Delta G_{\text{sol}}$ is about ± 0.1 eV, which is expected when one considers the combined errors in the experimental electron affinities and reduction potentials. Thus, by estimating the degree of charge delocalization, an estimate of the gas phase electron affinity can be made from the $E_{1/2}$ for the first reduction, as has been done for a series of chlorinated aromatic hydrocarbons,¹⁶ biologically significant purines and pyrimidines,¹⁷ and C_{60} .¹⁸

The electron affinity of C_{60} has been determined by photo-detachment to be 2.65 ± 0.05 eV.⁴ Recently, gas phase electron affinities for a number of other fullerenes have been measured relative to that of C_{60} using the Knudsen mass spectrometric measurement of equilibrium constants of ion-molecule electron exchange reactions;^{5a} also, very accurate values for EA of C_{60} and C_{70} have been recently obtained by a new technique, laser photodetachment of C_{60}^- and C_{70}^- cooled in a heavy ion storage ring.^{5b} The gas phase electron affinity of $\text{C}_{60}\text{F}_{48}$ has been determined to be 4.06 ± 0.25 eV using the Fourier transform mass spectrometry (FTMS) bracketing method.⁶ Measurement of the $E_{1/2}$ values for fullerenes, as well as $E_{1/2}$ for derivatized fullerenes and endohedral fullerene complexes, were also recently carried out,¹⁸⁻²⁰ and these data make possible the calculation of $\Delta\Delta G_{\text{sol}}$ for those compounds where both EA and $E_{1/2}$ are known. If the $\Delta\Delta G_{\text{sol}}$ values are independent of the electron affinities of the molecules, then gas phase electron affinities can be obtained from electrochemical data of compounds where only $E_{1/2}$ is currently known (see eq 1), such as in the case of $\text{La}@\text{C}_{82}$ or $\text{Y}@\text{C}_{82}$.²¹ This would be significant because electrochemical techniques can determine $E_{1/2}$ with good precision (± 10 mV) for fullerene derived materials that might be present in quite small quantities, that is less than 1 mg. On the other hand, $E_{1/2}$ values can be predicted for compounds for which only the EA has been measured, such as in the case of $\text{Ca}@\text{C}_{60}$.²²

The large electron affinity of C_{60} plays a role in the stability of such solids as M_3C_{60} or M_6C_{60} where M is an alkali atom.²³ A determination of electron affinities for larger fullerenes would allow for a rapid estimation as to the stability of charge transfer complexes or ionic solids involving fullerene anions and one or more particular counteranions. The electrochemistry of fullerenes is useful for predicting their chemistry and will also be a guide to alternative synthetic routes which might be used in the synthesis of various solids.²⁴

The present paper has four objectives. The first is to provide an analysis of the energy differences between the fullerenes and their anions in the gas phase and in solution. The fullerenes are especially important because of their potential high degree of charge delocalization. Our analysis shows that the fullerenes form a new category of molecules for which $-\Delta\Delta G_{\text{sol}} = 1.76 \pm 0.06$ eV. The second purpose of this paper is to provide a selection of the "best" values for electron affinities of a series of aromatic hydrocarbons and the associated errors in these values.^{4,11,25} Using these results, an improved value for $-\Delta\Delta G_{\text{sol}}$, that is 1.99 ± 0.05 eV, is obtained for aromatic hydrocarbons. The third purpose is to analyze recently reported data on gas phase electron affinities and reduction potentials of a series of metal complexes^{26,27} and to determine $-\Delta\Delta G_{\text{sol}}$ for

TABLE 1: Electron Affinities (EA's), Reduction Potentials ($E_{1/2}$'s) and Solvation Energy Differences from Gas Phase to Solution between the Neutral Molecule and Its Anion ($-\Delta\Delta G_{\text{sol}}$'s) for Fullerenes

species	EA (eV)	$E_{1/2}$ (V vs SCE)	$-\Delta\Delta G_{\text{sol}}$ (eV)	ref	
				EA	$E_{1/2}$
$\text{C}_{60}\text{F}_{48}$	4.06 ± 0.25	1.04 ± 0.06	1.69 ± 0.25	6	19
C_{86}	3.14 ± 0.06	0.27 ± 0.06	1.84 ± 0.09	5a	18
C_{84}	3.07 ± 0.06	0.12 ± 0.06	1.76 ± 0.09	5a	18
C_{78}	3.05 ± 0.06	0.02 ± 0.06	1.68 ± 0.09	5a	18
C_{76}	2.86 ± 0.05	-0.15 ± 0.06	1.70 ± 0.08	5a	18
C_{70}	2.72 ± 0.05	-0.26 ± 0.06	1.73 ± 0.08	5a	18
C_{60}	2.65 ± 0.05	-0.26 ± 0.06	1.80 ± 0.05	4	18
av: 1.76 ± 0.06					

these compounds. It will be shown that $-\Delta\Delta G_{\text{sol}}$ for a series of porphyrin complexes is the same as for aromatic hydrocarbons, that is $-\Delta\Delta G_{\text{sol}} = 1.99 \pm 0.12$ eV. In contrast, a series of metal acetylacetonates has a $-\Delta\Delta G_{\text{sol}}$ of 2.19 ± 0.14 eV, which indicates an intermediate degree of delocalization between the aromatic hydrocarbons and the mononitro compounds. Finally, the fourth purpose of this paper is to predict values of electron affinities and first reduction potentials of yet to be characterized fullerenes.

Results and Discussion

Tables 1–3 summarize experimental data for the fullerenes, the aromatic hydrocarbons, and the metal complexes. The $-\Delta\Delta G_{\text{sol}}$ values given in Tables 1–3 were calculated using eq 1 and the appropriate $E_{1/2}$ and EA values. The errors in $-\Delta\Delta G_{\text{sol}}$ were calculated from errors in both EA and $E_{1/2}$. Because reduction potentials of the aromatic hydrocarbons and the metal complexes have been obtained from different sources, a value of ± 0.05 V has been assigned to the error. An error of ± 0.06 V has been assigned to the $E_{1/2}$ of the fullerenes. The average values of $-\Delta\Delta G_{\text{sol}}$ are weighted averages using the errors given in the tables as weighting factors. That is

$$\text{av} = \sum (x_i / s_i^2) / \sum (1 / s_i^2) \quad \sigma^2 = 1 / \sum (1 / s_i^2) \quad (2)$$

where x_i is the individual $\Delta\Delta G_{\text{sol}}$ of each compound and s_i is the error on this value, listed in Table 1, 2, or 3.

The errors in the average $-\Delta\Delta G_{\text{sol}}$ quoted in each table are the 2σ values. The only data point which is questionable in all of the tables is the value for stilbene where the deviation from the average is greater than 5 times the standard deviation and the individual error is about 2 times the standard deviation in the mean. This particular value for $\Delta\Delta G_{\text{sol}}$ of stilbene might indicate a lower degree of delocalization in this compound.

In Figure 1, the calculated $-\Delta\Delta G_{\text{sol}}$ are plotted versus the EA's of the fullerenes, the aromatic hydrocarbons, and the metal complexes listed in Tables 1–3. Figure 2 shows a similar plot that uses the above data for the aromatic hydrocarbons and metal complexes and data previously used to classify the degree of delocalization.³ When available, these values have been recalculated from the consistent reduction potentials recently measured.² From Figure 2, it is clear that molecules with an electron affinity below ca. 2 eV have a $-\Delta\Delta G_{\text{sol}}$ which varies from 1.9 eV (43 kcal/mol) to 2.75 eV (63 kcal/mol) but that each molecule has an individual value and there is a continuum of energy differences.

Solvation energy differences for about 50 anions of organic acids in dimethyl sulfoxide (DMSO) have been reported.³² No correlation between solvation energy and electron affinity is apparent in the case of these anions of organic acids, and this

TABLE 2: Electron Affinities (EA's), Reduction Potentials (E_{red} 's), and Solvation Energy Differences from Gas Phase to Solution between the Neutral Molecule and Its Anion ($-\Delta\Delta G_{\text{sol}}$'s) for Aromatic Hydrocarbons (Group A)

species	EA (eV)	E_{red} (V)	$-\Delta\Delta G_{\text{sol}}$ (eV)	ref	
				EA	E_{red}
benzo(a)pyrene	0.83 ± 0.12	-1.99 ± 0.05	1.89 ± 0.13	tw, 8	15
benzanthracene	0.70 ± 0.05	-2.06 ± 0.05	1.95 ± 0.07	tw, 8	15
dibenz(a,j)anthracene	0.69 ± 0.16	-2.07 ± 0.05	1.95 ± 0.17	tw, 8	15
dibenz(a,h)anthracene	0.68 ± 0.12	-2.05 ± 0.05	1.98 ± 0.13	tw, 8	15
pyrene	0.56 ± 0.06	-2.10 ± 0.05	2.05 ± 0.08	tw, 8	15
anthracene	0.66 ± 0.08	-1.96 ± 0.05	2.09 ± 0.09	tw	15
benzo(c)phenanthracene	0.54 ± 0.04	-2.24 ± 0.05	1.93 ± 0.06	tw, 8	15
benzo(e)pyrene	0.49 ± 0.16	-2.17 ± 0.05	2.05 ± 0.17	tw, 8	15
chrysene	0.42 ± 0.04	-2.31 ± 0.05	1.98 ± 0.06	tw, 8	15
phenanthrene	0.31 ± 0.02	-2.46 ± 0.05	1.94 ± 0.05	tw, 8	15
triphenylene	0.29 ± 0.02	-2.46 ± 0.05	1.96 ± 0.05	tw, 8	15
naphthalene	0.15 ± 0.05	-2.51 ± 0.05	2.05 ± 0.07	tw, 8	15
pentacene	1.35 ± 0.05	-1.30 ± 0.05	2.06 ± 0.07	14	15
tetracene	1.07 ± 0.05	-1.64 ± 0.05	2.00 ± 0.07	14	15
perylene	0.97 ± 0.05	-1.67 ± 0.05	2.07 ± 0.07	14	15
benzo(a)pyrene	0.75 ± 0.05	-1.99 ± 0.05	1.97 ± 0.07	14	15
1,1-diphenylethylene	0.40 ± 0.06	-2.32 ± 0.05	1.99 ± 0.08	29	15
stilbene	0.35 ± 0.05	-2.21 ± 0.05	2.15 ± 0.07	29	15
styrene	0.15 ± 0.06	-2.65 ± 0.05	1.91 ± 0.08	29	15
biphenyl	0.13 ± 0.06	-2.60 ± 0.05	1.98 ± 0.08	29	15
benzene	-0.72	-3.42 ± 0.10		tw	33
av: 1.99 ± 0.05					

TABLE 3: Electron Affinities (EA's), Reduction Potentials (E_{red} 's), and Solvation Energy Differences from Gas Phase to Solution between the Neutral Molecule and Its Anion ($-\Delta\Delta G_{\text{sol}}$'s) for Metal Complexes

species ³⁶	EA (eV)	E_{red} (V)	$-\Delta\Delta G_{\text{sol}}$ (eV)	ref	
				EA	E_{red}
((TPP)F ₂₀ βCl ₈)FeCl	3.35 ± 0.20	0.45 ± 0.05	1.81 ± 0.21	26	ref in 26
((TPP)F ₂₀)FeCl	3.14 ± 0.20	0.25 ± 0.05	1.82 ± 0.21	26	ref in 26
(TPPo-Cl ₈ βCl ₈)FeCl	2.82 ± 0.11	0.27 ± 0.05	2.16 ± 0.12	26	ref in 26
(TPP-piv)Fe	2.07 ± 0.11	-0.65 ± 0.05	1.99 ± 0.12	26	ref in 26
(TPPo-Cl ₈)Fe	1.86 ± 0.11	-0.88 ± 0.05	1.97 ± 0.12	26	ref in 26
(TPP)Fe	1.87 ± 0.11	-0.83 ± 0.05	2.01 ± 0.12	26	ref in 26
((TPP)CHO)Ni	1.74 ± 0.11	-0.99 ± 0.05	1.98 ± 0.12	26	ref in 26
(TPP)H ₂	1.69 ± 0.11	-1.10 ± 0.05	1.92 ± 0.12	26	ref in 26
(TPP)Ni	1.51 ± 0.11	-1.19 ± 0.05	2.01 ± 0.12	26	ref in 26
av: 1.99 ± 0.12				26	ref in 26
Mn(acac) ₃	2.57 ± 0.22	-0.09 ± 0.05	2.05 ± 0.23	27	ref in 27
Co(acac) ₃	2.05 ± 0.18	-0.34 ± 0.05	2.32 ± 0.19	27	ref in 27
Fe(acac) ₃	1.87 ± 0.10	-0.67 ± 0.05	2.17 ± 0.11	27	ref in 27
Ru(acac) ₃	1.68 ± 0.10	-0.70 ± 0.05	2.33 ± 0.11	27	ref in 27
V(acac) ₃	1.08 ± 0.10	-1.48 ± 0.05	2.15 ± 0.11	27	ref in 27
Cr(acac) ₃	0.87 ± 0.10	-1.83 ± 0.05	2.01 ± 0.11	27	ref in 27
av: 2.19 ± 0.14				27	ref in 27

can be illustrated by the following examples: $-\Delta\Delta G_{\text{sol}}$ for the *p*-nitrophenoxide ion and the acetate ion are respectively +45 kcal/mol (1.95 eV) and -63.7 kcal/mol (-2.75 eV) despite the fact that the electron affinities of both species are about the same. However, the values measured for $-\Delta\Delta G_{\text{sol}}$ correlate well with the amount of charge delocalization, and this is illustrated as follows. For the eight acids that give the most delocalized anions and contain no heteroatoms, fluorene, 1,3-diphenylindene, 2,5-diphenylcyclopentadiene, 9-phenylfluorene, 9-neopentylfluorene, 9-isopropylfluorene, 9-*ter*-butylfluorene, and triphenylmethane, the value of $-\Delta\Delta G_{\text{sol}}$ is 50 ± 5 kcal/mol (2.16 ± 0.2 eV). Since there is a solvent shift of about 0.05 eV upon going from DMSO to DMF, the anions of these eight organic acids have $-\Delta\Delta G_{\text{sol}}$ similar to that of the aromatic hydrocarbons or the metalloporphyrins, within experimental error (see Tables 2 and 3). In the same report,³² the anion with the lowest solvation energy difference is the octafluorofluorenyl anion. For this compound, $-\Delta\Delta G_{\text{sol}}$ is 41.4 kcal/mol (1.8 eV), which is comparable to the value for the fullerenes.

Thus, as seen in Figures 1 and 2, the molecules can be placed into four separate groups on the basis of charge delocalization and the values for $\Delta\Delta G_{\text{sol}}$. The aromatic hydrocarbons and

metalloporphyrins form one group for which $\Delta\Delta G_{\text{sol}} = -1.99 \pm 0.05$ eV. The error in the combined group cannot be larger than the error in the more precise value when taking the weighted average of the values which are measures of the same quantity. The metal acetylacetonates can be placed in an intermediate category with a value of -2.19 ± 0.14 eV, while compounds with localized charge form the third category with a value of -2.5 ± 0.1 eV. The fullerenes form a unique class of compounds with the smallest solvation energy, that is -1.76 ± 0.06 eV.

In Figure 3, the corrected $E_{1/2}$ so that $-\Delta\Delta G_{\text{sol}} = 2.0$ eV are plotted against the EA's for the metal complexes, the fullerenes, the aromatic hydrocarbons, and the metalloporphyrins. The $-\Delta\Delta G_{\text{sol}}$ of 2.0 eV was arbitrarily chosen because it is close to the $-\Delta\Delta G_{\text{sol}}$ value of the aromatic hydrocarbons (1.99 eV) which represents the most extensively studied group of compounds. Three adjustable parameters are used to correlate about 50 data points which fit on a straight line with a slope of 1.0. In Figure 4, these data are combined with values for the compounds shown in Figure 2. Here, four adjustable parameters are used to fit about 150 data points on a straight line with a slope of 1.0; that is, $\Delta E_{1/2} = \Delta EA$. These results clearly show

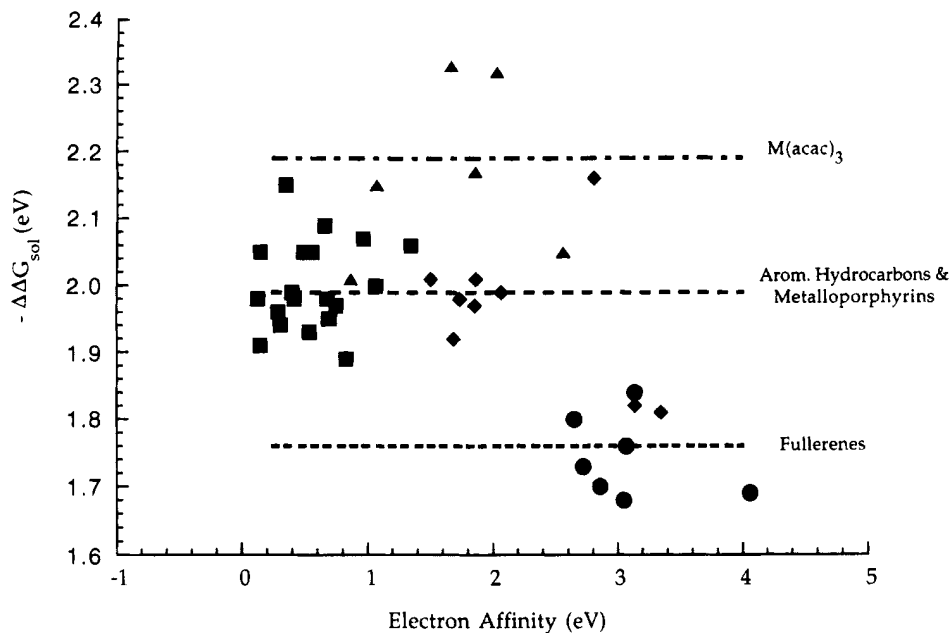


Figure 1. Solvation energy difference from the gas phase to solution between the neutral molecule and its anion ($-\Delta\Delta G_{\text{sol}}$) versus gas phase adiabatic electron affinity for aromatic hydrocarbons (■), fullerenes (●), metalloporphyrins (◆), and metal acetylacetonates (▲) listed in Tables 1–3.

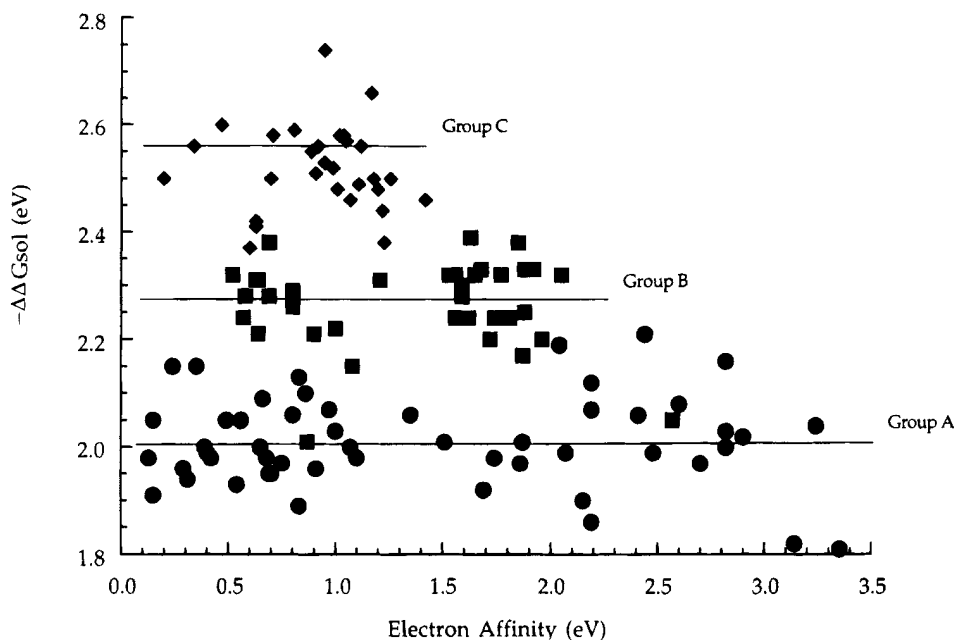


Figure 2. Solvation energy difference from the gas phase to solution between the neutral molecule and its anion ($-\Delta\Delta G_{\text{sol}}$) versus gas phase adiabatic electron affinity for molecules with localized charge (group C) (◆), partially localized charge (group B) (■), and delocalized charge (group A) (●).

a procedure for obtaining intrinsic gas phase electron affinities from reduction potentials.

If the EA of a molecule is to be determined from $E_{1/2}$, the first reduction potential of reference compounds with similar charge distributions should be measured. These compounds should have measured electron affinities which closely bracket the estimated electron affinity. In this manner, systematic errors can be eliminated. Also, when multiple reference compounds are used, then the average value of the solvation energy difference can be determined. If one is to determine the gas phase electron affinity of a molecule from data in the literature, then the solvation energy difference must be estimated. The values given in this paper can be used as guidelines.

Fullerenes. The electron affinities for the fullerenes have been taken from the literature. The ultimate reference compound is C_{60} , and the error in the value obtained by photode-

tachment is ± 0.05 eV,⁵ which has been added to the random errors. The reduction potentials for the fullerenes are also taken from the literature or from recent values measured in our laboratory. It was necessary to “adjust” the $E_{1/2}$'s of higher fullerenes to what their values would be in DMF. This leads to an estimated error of ± 60 mV in $E_{1/2}$ based on the fact that, upon varying the solvent, the difference in $E_{1/2}$ between C_{60} and higher fullerenes does not differ by more than 60 mV as calculated from literature data. This allows one to predict, within ± 60 mV, the $E_{1/2}$'s of the higher fullerene in any solvent. This approach, when applied to obtain the $E_{1/2}$ in DMF listed in Table 1, is valid unless a very specific but yet unknown effect of DMF on the electrochemistry of one of the higher fullerenes is seen.

The fullerenes have relatively large molecular volumes and surface areas. Because they are rigid molecules, there are no

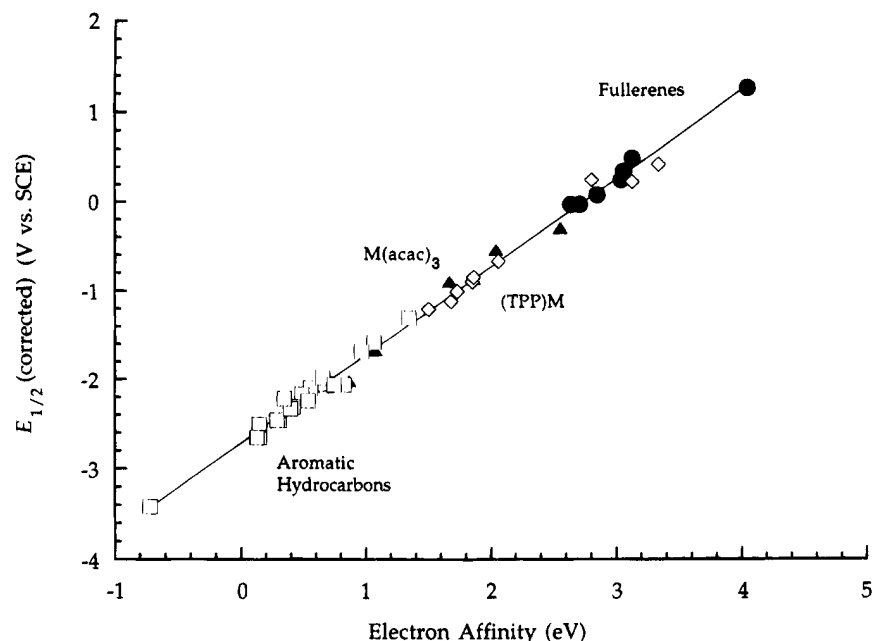


Figure 3. Corrected reduction potential, so that $\Delta\Delta G_{\text{sol}} = -2$ eV, versus gas phase adiabatic electron affinity for aromatic hydrocarbons (\square), fullerenes (\bullet), metalloporphyrins (\diamond), and metal complexes (\blacktriangle) listed in Tables 1–3. The value at $(-3.4, -0.7)$ is for benzene, which is estimated in this paper.

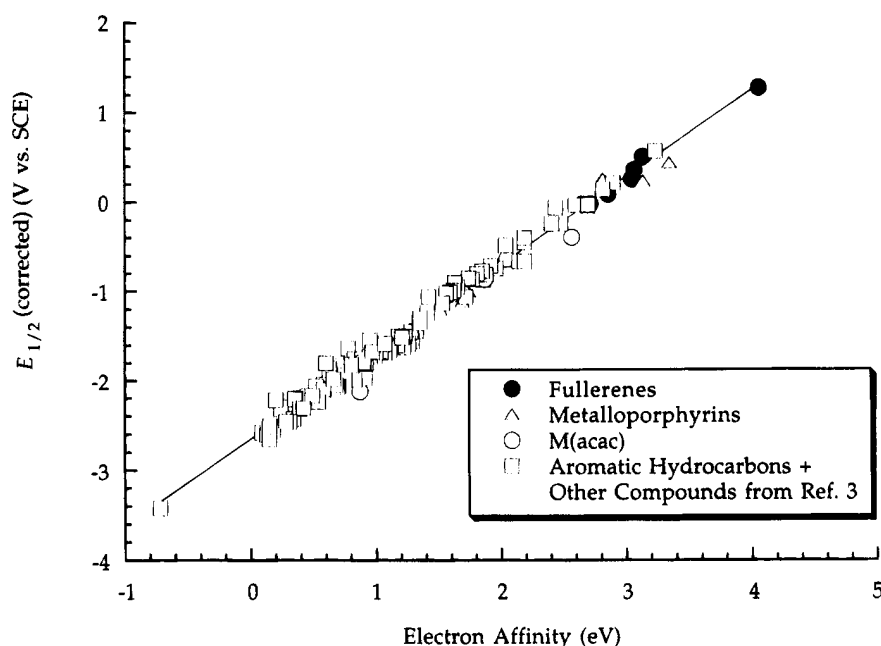


Figure 4. Corrected reduction potential, so that $\Delta\Delta G_{\text{sol}} = -2$ eV, versus gas phase adiabatic electron affinity for fullerenes (\bullet), metalloporphyrins (\triangle), metal complexes (\circ), aromatic hydrocarbons and compounds from ref 3 (\square). The value at $(-3.4, -0.7)$ is for benzene, which is estimated in this paper.

significant conformational changes between the neutral species and the monoanion, and it is therefore possible to calculate the nuclear framework and van der Waals surface, surface areas, and volumes.²⁹ When an anion of a fullerene is formed, the extra charge can be delocalized over the π -bonding network. One might expect that, for a relatively small change in surface area (as occurs upon going from C_{60} to the slightly larger C_{84}), the polarizing power of a fullerene anion would be essentially constant and weak because the charge is spread over a large volume. It is likely that the fullerenes have the smallest $-\Delta\Delta G_{\text{sol}}$ among the four groups assessed here because the extra charge is not concentrated in a small volume in the molecule. Consequently, contributions to $-\Delta\Delta G_{\text{sol}}$, such as counteraction effects or solvent reorganization effects, are minimized.

Recently, very accurate values for the EA of C_{60} and C_{70} have become available from a new technique where molecular anions are cooled in a heavy ion storage ring, and the minimum photon energy for electron photodetachment is measured.^{5b} It is well-known that the electrochemical reduction potentials of C_{60} and C_{70} are very similar,¹⁸ more similar than the nominal $2.72 - 2.65 = 0.070$ eV difference predicted from the EA values determined in ref 5a. Thus, this new set of data obtained on C_{60} and C_{70} , for which a difference of only $2.666 - 2.676 = 0.01$ eV in the EA is reported, agrees well with the similarity in the $E_{1/2}$ measured for each species. We chose not to list these new data in Table 1 for clarity and because it is important to compare data that are obtained using a similar technique and, if possible, in the same laboratory. However, further measure-

ments using the laser electron photodetachment of fullerene or organofullerene monoanions cooled in a heavy ion storage would probably allow a more precise determination of $\Delta\Delta G_{\text{sol}}$ for these species.

The adiabatic electron affinity of La@C_{82} has not been measured. However, the first reduction potential of this compound was measured and found to be 0.70 V more positive than that of C_{60} .^{21a} Thus, the EA of La@C_{82} can be estimated as $\text{EA}(\text{C}_{60}) + 0.70 = 3.35 \pm 0.06$ eV using the relationship $\Delta\text{EA} = \Delta E_{1/2}$. This can be compared with a theoretical estimate of 3.22 eV reported by Nagase.³⁵ Similarly, the EA of Y@C_{82} can be calculated as 3.43 ± 0.06 eV based upon a $E_{1/2}$ of 0.78 V more positive than the one of C_{60} .^{21b} On the other hand, the calculation of the $E_{1/2}$ from a measured EA can be illustrated in the case of Ca@C_{60} , where the EA has been measured as 3.0 ± 0.1 eV.²² Thus, the $E_{1/2}$ in DMF should be 0.35 V greater than that of C_{60} ; that is, $-0.26 + 0.35 = 0.09 \pm 0.14$ V vs SCE. To calculate $E_{1/2}$ or EA on an absolute basis, the appropriate $\Delta\Delta G_{\text{sol}}$ must be used. The 230-mV negative potential shift observed for the first reduction of C_{60} upon going from DMF to DCM leads to a value of $-1.76 + 0.23$ V = -1.53 ± 0.06 eV for $\Delta\Delta G_{\text{sol}}$ of fullerenes in dichloromethane (DCM). Thus, the calculated potential for the first reduction of Ca@C_{60} in DCM is $E_{1/2} = \text{EA} - \Delta\Delta G_{\text{sol}} + E_{\text{ref}} = 3.0 + 1.53 - 4.71 = -0.18 \pm 0.14$ V vs SCE. This value has yet to be experimentally measured.

Aromatic Hydrocarbons. The EA of aromatic hydrocarbons which have been determined using ECD were earlier reported, but two different data reduction procedures were used. In one, the electron affinity of the compound was obtained from the temperature dependence of the equilibrium constant by determining both a slope and an intercept of a plot of $\ln(KT^{3/2})$ vs $1/T$ where K is the molar ECD response, expressed in liters per mole.⁹ At high temperatures, K is equal to the equilibrium constant for the reaction of thermal electrons with the molecule. The other procedure used a fixed value for the intercept and only determined one parameter, the slope.⁷⁻⁹ The latter procedure is equivalent to assuming a constant entropy value for the reaction of thermal electrons with the molecule. We are convinced that the more accurate values are those obtained from both the slope and the intercept. In this paper we have chosen the best values for the electron affinities to be included in Table 2, and more importantly, we present some realistic errors in the values.⁷⁻⁹ We have only included the aromatic hydrocarbons in Table 2 in which the charge is delocalized.

In restudying the data, another potential difficulty in obtaining electron affinities from ECD data was noted. Lyons et al. reported a value of 0.88 eV for the electron affinity of tetracene using the ECD method.²⁸ However, the recent value obtained from TCT measurements, which we will show is supported by $E_{1/2}$ data, is 1.07 ± 0.05 eV.¹⁴ The difference between the two values can be explained by noting that, in the ECD data, there is a transition at about 473 K from a positive slope to a negative slope in the plot of $\ln(KT^{3/2})$ vs $1/T$. This can be interpreted as a transition from one electronic state of the negative ion to another. The existence of excited states for the chloroethylenes in these experiments has been clearly established.²⁹ It was noted by Szwarc and Jaqur-Grodzinski³⁰ that the electron affinity of anthracene measured in the gas phase did not agree with the value obtained in solution. This led us to reconsider the electron affinity reported for anthracene.¹⁰ We have analyzed the data for anthracene using a four parameter nonlinear least squares procedure to determine a "new" electron affinity, and this value is included in Table 2.

The values for reduction potentials of aromatic hydrocarbons have been taken directly from a compilation by Mann and Barnes.¹⁵ An average value was taken when more than one determination was reported. Due concern for solvents, reference electrodes, and supporting electrolytes was taken in obtaining the average value. The procedure for determining electron affinities from reduction potentials can be illustrated as follows. The experimental value for the reduction potential value for benzene has been determined to be -3.42 ± 0.1 eV.³³ This gives

$$\text{EA} = E_{1/2} + \Delta\Delta G_{\text{sol}} - E_{\text{ref}} = -3.42 - 1.99 + 4.71 = -0.7 \pm 0.14 \text{ eV}$$

This is the best value of the adiabatic electron affinity of benzene. The error in the value is due to the error in the reported $E_{1/2}$ value. The vertical electron affinity has been measured and is -1 eV.³⁴ This data point has been included in Figures 3 and 4 to illustrate the possibility of obtaining negative EA's by using $E_{1/2}$.

Metal Complexes. The electron affinities of the metal complexes have been taken from the literature. These EA's are relative to a given "standard", and therefore, the errors in these quantities must also include any error in the electron affinity of the reference compound. The electron affinities of the porphyrins (Table 3) have been determined using TCT relative to multiple standards. The random errors have been reported in earlier papers, but errors in the standard values have not previously been considered. Therefore, errors in the reference compounds have now been included in the values given in Table 3. The errors in the electron affinities of the metal acetylacetonates (also in Table 3) are those given in the original paper²⁷ and include any error in the values of the reference compound.

The reduction potential data for the metalloporphyrins have been obtained from ref 26 and have been adjusted to DMF as a solvent by shifting the measured values by the difference in $E_{1/2}$ between the reduction of C_{60} in DMF and in CH_2Cl_2 , benzonitrile, or dichloroethane, that is approximately 0.2 V.²⁰

The original logic in defining the groups of compounds was to empirically select those compounds which fell closest to the midpoint between the extremes of -2.06 and -2.52 eV to define the intermediate group.² The average value of $\Delta\Delta G_{\text{sol}}$ for the compounds in group B is -2.29 eV (see Figure 2). The extreme values now fall closer to -1.76 and -2.52 eV; thus, -2.25 eV is an intermediate value between groups A and B. Metal acetylacetonates clearly belong to that intermediate group. The authors of the original work, Sharpe and Richardson,²⁷ found that the $\Delta\Delta G_{\text{sol}}$ values for the metal acetylacetonates are about -2.16 ± 0.2 eV.

The relationship established in this paper is important for metal complexes. Only recently have gas phase electron affinities been measured for these types of compounds, although reduction potential data are quite common. The above procedure can be used to predict the electron affinities of metal complexes by using known reduction potentials. However, the metal complexes have the greatest possibility for $\Delta\Delta G_{\text{sol}}$ variations so that caution must be taken. This can be illustrated by data for the porphyrins. We have excluded from the current analysis data for two Fe(III) complexes, namely, $(\text{TPP})\text{FeCl}$ and $(\text{TPPO-Cl}_8)\text{FeCl}$. The electron affinities of these two compounds are 2.15 ± 0.15 and 2.10 ± 0.19 eV, respectively, while the reduction potential for both is -0.04 V. The calculated value of $-\Delta\Delta G_{\text{sol}}$ is then 2.5 ± 0.2 eV, which can be compared with an average of 1.99 eV for the $-\Delta\Delta G_{\text{sol}}$ of porphyrins listed in

Table 3. This indicates that the charge is more localized on (TPP)FeCl³⁶ and (TPPo-Cl₈)FeCl³⁶ than on the other porphyrins.

Another precaution for metal complexes and indeed for the fullerenes is that these analyses only apply to the first reduction. Indeed, it may be valuable to compare the second and/or third reductions of a given series of compounds to better understand the processes that take place as more electrons are added to a system.

Conclusions

Within the experimental error, the solvation energy differences for neutrals and anions in going from the gas phase to solution in DMF are constant for molecules with similar charge distributions. The average $-\Delta\Delta G_{\text{sol}}$ is 1.99 ± 0.05 eV for a series of aromatic hydrocarbons and metalloporphyrins. For the fullerenes, $-\Delta\Delta G_{\text{sol}} = 1.76 \pm 0.06$ eV. Such a small value suggests extensive charge delocalization over a large volume. For a series of metal acetylacetonates, $-\Delta\Delta G_{\text{sol}} = 2.19 \pm 0.14$ eV, which indicates an intermediate degree of delocalization between the aromatic hydrocarbons and compounds with localized charges such as the mononitro derivatives for which $-\Delta\Delta G_{\text{sol}}$ is ca. 2.5 eV. The $\Delta\Delta G_{\text{sol}}$ values for aromatic hydrocarbons are in agreement with previous analyses and indicate that delocalization of charge in the anion is an important factor in determining the solvation energy. The fullerenes have the smallest value of $-\Delta\Delta G_{\text{sol}}$ because the extra charge in the monoanion is spread over the π -network; the large volume means that the charge is very diffuse and the polarizing power is minimized. When the charge is less delocalized over the molecular volume, the polarizing power is greater, and solvent-based contributions (such as solvent reorganization in response to concentrated charge) will be larger so that the absolute value of $-\Delta\Delta G_{\text{sol}}$ is also larger.

On the basis of these results, a procedure for obtaining electron affinities from reduction potentials and vice versa can be established for similar compounds. This has been applied to benzene to give an electron affinity of -0.7 ± 0.14 eV, to La@C₈₂ to give an electron affinity of $+3.21 \pm 0.06$ eV, and to Y@C₈₂ to give an electron affinity of $+3.32 \pm 0.06$ eV. On the other hand, the $E_{1/2}$ of Ca@C₆₀ is predicted to occur at $+0.09 \pm 0.14$ V vs SCE in DMF and at -0.28 ± 0.14 V vs SCE in DCM based upon a measured electron affinity of $+3.0 \pm 0.1$ eV. The basis of our approach relies on establishing the degree of charge delocalization for a given compound. For the fullerenes, it can be assumed (and the data agree) that the charge is delocalized to the greatest extent so that $-\Delta\Delta G_{\text{sol}}$ is constant. A $-\Delta\Delta G_{\text{sol}}$ value of $+1.76 \pm 0.06$ eV is proposed for the fullerenes in DMF and $+1.58 \pm 0.06$ eV in DCM. For other molecules, theoretical calculations of charge distributions may be used to test the placement of each molecule in a specific group.

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References and Notes

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. Krättschmer, W.; Lamb, L. D.; Fostiropoulos, R.; Huffman, D. R. *Nature* **1990**, *347*, 354.
- (2) Shalev, H.; Evans, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 2667.
- (3) Chen, E. C. M.; Wentworth, W. E. *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 271.
- (4) (a) Wang, L. S.; Conceicao, J.; Changming, C.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *182*, 5. (b) Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017. (c) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Chesnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.
- (5) (a) Boltalina, O. V.; Sidorov, L. N.; Borschchevsky, A. Y.; Sukhanova, E. V.; Skokan, E. V. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 1009. (b) Brink, C.; Andersen, L. H.; Hvplund, P.; Mathur, D.; Voldstad, J. D. *Chem. Phys. Lett.* **1995**, *233*, 52.
- (6) (a) Haufli, R. E.; Jin, C.; Hettich, R. L.; Huang, R.; Plummer, E. W.; Compton, R. N. The Electrochemical Society, 184th Meeting, Abstract 639, New Orleans, LA, Oct 10–15, 1993. (b) Jin, C.; Hettich, R. L.; Compton, R. N.; Tuinman, A.; Derecskei-Kovacs, A.; Marynick, D. S.; Dunlap, B. I. *Phys. Rev. Lett.* **1994**, *73*, 2821. (c) Hettich, R. L.; Jin, C.; Compton, R. N. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 263.
- (7) Wentworth, W. E.; Becker, R. S. *J. Am. Chem. Soc.* **1962**, *84*, 4263.
- (8) Becker, R. S.; Wentworth, W. E. *J. Am. Chem. Soc.* **1963**, *85*, 2210.
- (9) Wentworth, W. E.; Chen, E. C. M.; Lovelock, J. E. *J. Phys. Chem.* **1966**, *70*, 445.
- (10) Chen, E. C. M.; Wiley, J. R.; Batten, C. F.; Wentworth, W. E. *J. Phys. Chem.* **1994**, *98*, 88.
- (11) Fukada, E. K.; McIver, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 2291.
- (12) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627.
- (13) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513.
- (14) Crocker, L.; Wang, T.; Kebarle, P. *J. Am. Chem. Soc.* **1993**, *115*, 7818.
- (15) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-aqueous Systems*; Dekker: New York, 1970.
- (16) Wiley, J. R.; Chen, E. C. M.; Chen, E. S. D.; Richardson, P.; Reed, W. R.; Wentworth, W. E. *J. Electroanal. Chem.* **1989**, *307*, 1.
- (17) Wiley, J. R.; Robinson, J. M.; Ehdia, S.; Chen, E. C. M.; Chen, E. S. D.; Wentworth, W. E. *Biochem. Biophys. Res. Commun.* **1991**, *180*, 841.
- (18) (a) Lerke, S. A.; Parkinson, B. A.; Evans, D. E.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807. (b) Boulas, P.; Jones, M. T.; Kadish, K. M.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R.; Tse, D. T. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society Proceedings Series; Electrochemical Society: Pennington, NJ, 1994; pp 1221–1233. (c) Selegue, J. P.; Shaw, J. P.; Guarr, T. F.; Meier, M. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society Proceedings Series; Electrochemical Society: Pennington, NJ, 1994; pp 1274–1292. (d) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society Proceedings Series; Electrochemical Society: Pennington, NJ, 1994; pp 1300–1320.
- (19) Zhou, F.; Van Berkel, G. J.; Donovan, B. T. *J. Am. Chem. Soc.* **1994**, *116*, 5485.
- (20) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.
- (21) (a) Suzuki, T.; Mayurama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006. (b) Kikuchi, K.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Suzuki, T.; Maruyama, Y. *J. Am. Chem. Soc.* **1994**, *116*, 9367.
- (22) Wang, L. S.; Alford, J. M.; Vhai, Y.; Diener, M.; Zhang, J.; McClure, S. M.; Guo, T.; Scuseria, G. E.; Smalley, R. E. *Chem. Phys. Lett.* **1993**, *207*, 354.
- (23) Wang, Y.; Tomanek, D.; Bertsch, G.; Ruoff, R. S. *Phys. Rev.* **1993**, *B47*, 6711.
- (24) (a) Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505. (b) Boulas, P.; Subramanian, R.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Electrochem. Soc.* **1993**, *140*, L130. (c) Koh, W.; Dubois, D.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 6871. (d) Jones, M. T.; Kadish, K. M.; Subramanian, R.; Boulas, P.; Vijayashree, M. N. *Synth. Met.*, submitted for publication. (e) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2780. (f) Penicaud, A.; Perez-Benitez, A.; Gleason, R. V.; Munoz, E. P.; Escudero, R. *J. Am. Chem. Soc.* **1993**, *115*, 10392.
- (25) Wojnarovits, L.; Foldiak, G. *J. Chromatogr.* **1981**, *206*, 511.
- (26) Chen, H. L.; Ellis, P. E.; Wijesekera, T.; Hagan, T. E.; Grob, S. E.; Lyons, J. E.; Ridge, D. P. *J. Am. Chem. Soc.* **1994**, *116*, 1086.

- (27) Sharpe, P.; Richardson, D. E. *J. Am. Chem. Soc.* **1991**, *113*, 8339.
(28) Lyons, L. E.; Morris, G. C.; Warren, L. J. *J. Phys. Chem.* **1968**, *72*, 3677.
(29) Wiley, J. R.; Chen, E. C. M.; Wentworth, W. E. *J. Phys. Chem.* **1993**, *97*, 1256.
(30) Szwarc, M.; Jagur-Grodzinski In *Ions and Ion Pairs in Organic Chemistry*; Wiley: New York, 1972.
(31) Adams, G. B.; O'Keeffe, M.; Ruoff, R. S. *J. Phys. Chem.* **1994**, *98*, 9465.
(32) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.
(33) Mortensen, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 84.
(34) Doering, J. P. *J. Chem. Phys.* **1969**, *68*, 2866.
(35) Nagase, S.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1837.
(36) (TPP) is the dianion (5,10,15,20-tetraphenylporphyrin); (TPPoCl₈) is the dianion of (5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin); (TP-PF₂₀) is the dianion of (5,10,15,20-tetrakis(pentafluorophenyl)porphyrin); (TPPCHO) is the dianion of (2-CHO-5,10,15,20-tetraphenylporphyrin); (TPP-piv) is the dianion of (5,10,15,20-tetrakis(2-(NHCOC(CH₃)₃)phenyl)porphyrin); (TPPoCl₈βCl₈) is the dianion of ((2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin); (TPPF₂₀βCl₈) is the dianion of ((2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin).

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