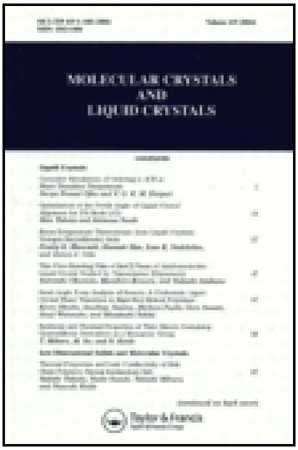

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Experimental Determination of Electron Affinities of Organic Molecules

E. C. M. Chen [a] & W. E. Wentworth [b]
[a] School of Natural and Applied Sciences, University of Houston CL, Houston, Texas, 77058
[b] Chemistry Department, University of Houston, Houston, Texas, 77004

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Experimental Determination of Electron Affinities of Organic Molecules

E. C. M. CHEN
School of Natural and Applied Sciences, University of Houston CL, Houston, Texas 77058

and

W. E. WENTWORTH
Chemistry Department, University of Houston, Houston, Texas 77004

The electron affinity of a molecule is the definitive measure of its ability to act as an electron acceptor. During the past twenty years, experimental methods for the determination of this quantity have been developed. While the magnetron procedure and the electron capture detector method were introduced in the 1960s, only recently have confirmatory gas phase measurements been made. In this review, the experimental procedures and their limitations will be summarized, the available experimental results (about 200 values) will be critically evaluated, and the gas phase measurements will be compared with half wave reduction potentials. A method for estimating electron affinities from substituent effects will be presented.

INTRODUCTION

The Electron Affinity (EA) is the fundamental thermodynamic property of atoms and molecules which governs reactions of thermal electrons in gases, liquids and solids. Its importance to charge transfer complexes was first recognized by Mulliken[1] in the 1950s. In a book published in 1961, Briegleb[2] introduced the terminology electron donor acceptor complexes (EDA) and emphasized the role of the EA as follows. "The electron affinity is the unequivocal measure of acceptor strengths. Unfortunately, there are no universal methods for determining the adiabatic electron affinity of organic compounds. Thus, the frequency of the EDA absorption maxima can be used to obtain relative values of the EAs."

In the 1960s, the magnetron (MT)[3] and the electron capture detector (ECD)[4] procedures were developed for measuring adiabatic electron affinities in the gas phase. Since the experimental range for these two methods do not overlap, confirmatory measurements could not be made. In the 1970s, the alkali metal beam (AMB) procedure[5] was applied to several charge transfer acceptors. Recently, the determination of relative electron affinities in the gas phase by thermal charge transfer (TCT) measurements was applied extensively to charge transfer acceptors.[6] These relative values have been anchored to the electron affinity of sulfur dioxide[7] to give absolute values which overlap the ECD, MT and AMB values, making it timely to critically review the electron affinities obtained for organic molecules in the gas phase and to establish guidelines for the accuracy and precision of the various methods.

In this review, the experimental electron affinities of atoms, "small" molecules and free radicals[7] will not be discussed. A procedure for calculating electron affinities from half wave reduction potentials will be presented, but calculations from the available electrochemical data will not be carried out.

The adiabatic electron affinity is defined as the energy released when a species reacts with thermal electrons to form the negative ion in the gas phase at 0°K.

$$AB(g) + e^-(g) \rightleftharpoons AB^- \tag{1}$$

By convention, this quantity is positive if the negative ion is more stable than the neutral. In the case of atoms, metastable negative ions which involve electronic excitation have been observed and the corresponding excited state EAs defined. However, for molecules two other energy quantities involving the ground electronic

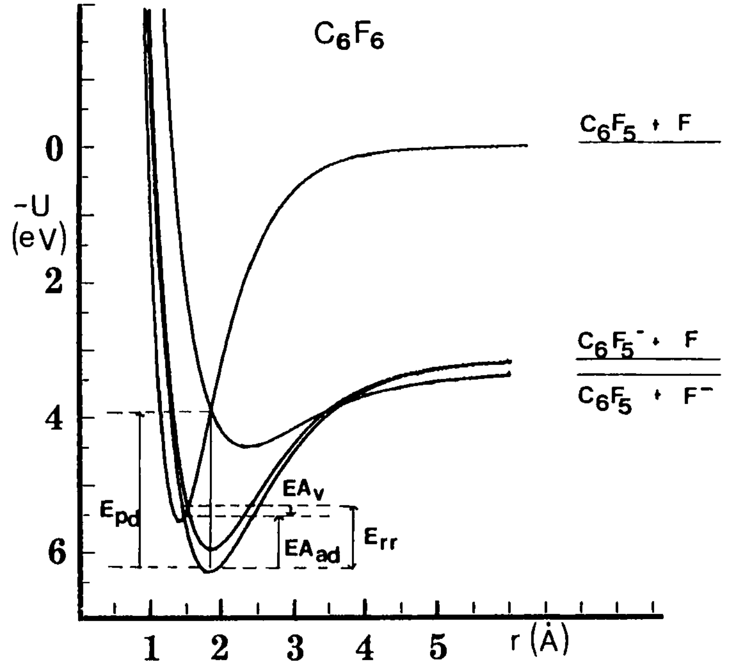

FIGURE 1 Morse potential energy curves for C_6F_6 and $C_6F_6^-$.

state can be defined. The vertical electron affinity EA(v) is the energy difference between the negative ion and the neutral retaining the geometry of the neutral. EA(v) is measured in electron beam and/or transmission experiments. The vertical attachment energy has been defined as the negative of the EA(v). The difference is defined as the rearrangement energy, E(rr). i.e. EA(ad) = EA(v) + E(rr). Theoretical calculations are often made for the geometry of the neutral so that the result is EA(v). The vertical detachment energy, E(pd), measured in photodetachment experiments is the difference between the neutral and the negative ion retaining the geometry of the negative ion. These quantities are shown in the "pseudo two dimensional" Morse potential energy curves in Figures 1–3.

Potential energy curves such as these which have been used to describe the negative ion states of the diatomic halogens[8] and SF_6[9] are a convenient way of consolidating diverse data on negative ions. The use of the Morse potentials for the negative ions leads to properties which have not been measured. For example, using ECD data and electron beam and/or transmission data, the vibrational frequency and the internuclear distance of the negative ion can be calculated.

In 1953, the experimental data for the EA's of atoms, molecules and radicals were critically reviewed by Pritchard.[10] Interestingly, only the calculated electron affinity of the hydrogen atom currently survives as the "best" value. In 1966, Chen[11] updated this list and added the molecular electron affinities obtained using the magnetron and ECD methods. In 1963, Briegleb[12] summarized the EA values of

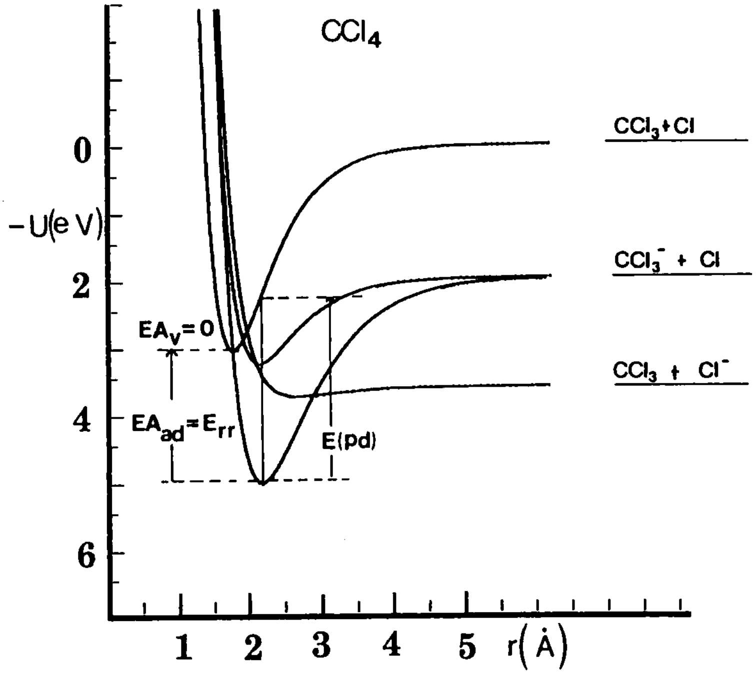

FIGURE 2 Morse potential energy curves for CCl_4 and CCl_4^-.

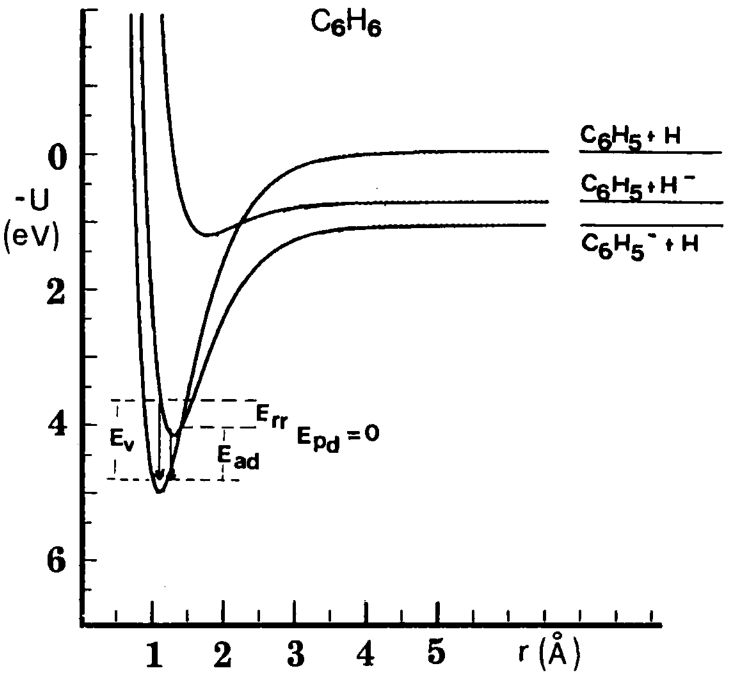

FIGURE 3 Morse potential energy curves for C_6H_6 and $C_6H_6^-$.

many organic compounds including values obtained from empirical correlations. Christophorou[13,14] has provided extensive tabulations of electron affinities of atoms, molecules and radicals but has not critically evaluated these results. Chen and Wentworth[15] provided a critical evaluation of the electron affinities of pi charge transfer complex acceptors in 1975. Janousek and Brauman[16] have reviewed the electron affinities of molecules and radicals determined using photodetachment (PD), photoelectron spectroscopy (PES), endothermic charge transfer (ECT), and alkali metal beam procedures. The most comprehensive and critical list of electron affinities is one prepared by Bartmess[16] which is available on request. Gutsev and Boldyrev[18] have reviewed theoretical methods of obtaining electron affinities.

EXPERIMENTAL

The two basic strategies for the determination of electron affinities are the determination of the equilibrium constants for the formation of negative ions from electrons or other negative ions and the observation of the formation or destruction of negative ions by interaction with atoms, ions, electrons or photons. The thermodynamic methods are the magnetron,[3] electron capture detector[4] and the thermal charge transfer[6] methods. The ECD and MT methods give absolute values since they require only the experimental measurements and fundamental constants to give the adiabatic electron affinity. The TCT method gives relative values. The methods involving the alternate strategy are the photon methods,[16] the electron beam[14] and/or transmission[19] studies, the endothermic charge transfer,[16] and the alkali metal beam[16] procedures. All of these have been reviewed extensively so that the experimental details and the original references are readily available. However, some discussion will be devoted to the experimental limitations and problems of each method.

In the PD and PES experiments photons interact with negative ions. These have produced the most accurate and precise electron affinities for atoms and small molecules. However, they have not been successfully applied to large organic molecules, such as tetracyanoethylene and sulfur hexafluoride.[6,9]

In the EB and ET experiments negative ion resonances are observed with monochromatic electrons impacting on molecules. These experiments give EA(v). To obtain the adiabatic EA, an extrapolation or an estimate of E(rr) is required. The transmission experiments only give the vertical position of the resonance. The EB studies give the cross sections for negative ion formation as a function of electron energy. Recently these measurements[20] have been combined in a single instrument. The formation of the molecular ion at zero energy implies a positive electron affinity.

In the endothermic charge transfer experiment, negative ion beams react with a neutral molecule to form another negative ion. The electron affinity of the original negative ion must be known. These experiments have given accurate values for the diatomic halogens but values for some organic fluorocompounds which are too large.

The threshold for ion pair formation with an alkali metal beam has been successfully used to determine adiabatic electron affinities. Since the ionization potential of the alkali metal is well known, the error in the measurement (±0.2 eV) is primarily in the determination of the threshold and corrections to this quantity.

In the magnetron method thermal electrons generated at a heated filament react with a known concentration of the neutral molecule. The electron and ion concentrations are measured by the application of a magnetic field. The temperature is measured with an optical pyrometer. The apparent electron affinity is obtained by plotting Ln K vs. 1/T. There are many reactions that can take place, but the direct capture process is the only one which has an equilibrium constant which decreases with increasing temperature. In addition, the entropy for the reaction can be calculated and generally is consistent with the experimental value. The apparent electron affinity is corrected to 0K by subtracting 2RT. The method is only applicable to molecules with electron affinities greater than 0.8 eV.

In the ECD method, thermal electrons are generated in an Ar/Methane mixture by beta particles from a radioactive foil. The electron concentration, monitored with and without the test sample, is measured by the application of a brief pulsed voltage. A small, highly purified amount of the test sample is introduced via a gas chromatograph. The temperature is then changed and the process repeated. From the data, an electron capture coefficient K can be obtained. In certain cases, this quantity is equal to the equilibrium constant times a constant. From a plot of $\mathrm{Ln}(KT^{3/2})$ vs. 1/T the electron affinity can be determined directly. For some compounds, dissociation of the negative ion occurs while for other compounds, recombination competes with electron detachment so that the equilibrium constant is not obtained. However, the only process in which K decreases significantly with increasing temperature is the attachment/detachment one. In addition, the intercept can be estimated from fundamental constants and a rate constant and is consistent with experimental results. For molecules with very low (< 0.1 eV) electron affinities, electron scattering is a problem. In this case, the measured electron affinity is an upper limit. This is especially critical when the "constant potential" mode is used.[21] Another variation which has been used but does not give accurate electron affinities is the direct current mode of operation because of hyperthermal electrons.[22] Lyons, Morris and Warren[23] have used a static method of introducing the sample. We prefer the use of the chromatographic method because of its ability to instantaneously purify the sample. The range of accurately measured EAs using the ECD is 0.1–0.9 eV. The upper limit is due to the maximum temperature of the detector.

The thermal charge transfer determinations use the measurement of the equilibrium constants for the reaction

$$A^- + B \rightleftharpoons A + B^- \tag{2}$$

If equilibrium is established, the determination of the ion ratio and the concentrations of the neutrals give the equilibrium constant, K_{et}. Two systems, the "high pressure" mass spectrometer and the ICR[24] have been used. The measurement of K_{et} as a function of temperature gives both the entropy and energy for this reaction. If the measurements are made at a single temperature, estimates of the entropy must be made to obtain the energy. In addition, the absolute electron affinity of at least one compound must be known. Kebarle has used SO_2[7] as the reference compound. A better procedure would be to use multiple reference compounds. Electron detachment may present a problem with measuring lower values of electron affinities. The demonstrated range is 0.5–3.0 eV.

RESULTS

Gas Phase Determinations

The MT, ECD, and AMB experiments have been used to directly determine adiabatic electron affinities of about 100 organic compounds. More than 130 relative electron affinities have been determined using the TCT method. However, fewer than 50 have been measured by more than one method. Thus an important tool for evaluating the reliability of the gas phase data is the half wave reduction potential data.[15] In Table I the EA's for compounds which have been studied by more than one technique are tabulated and a "most representative" value selected.

The standard deviation of the magnetron values from the selected values is about ±0.2 eV and the average deviation is −0.03 eV. The standard deviation is larger than the average precision (±0.13 eV) quoted for individual values. However, most significantly for EDA studies, the MT value for TCNQ has been determined by two different groups[14,17] and has been verified by the AMB method. It was observed earlier that the values for benzoquinone and anthraquinone were low.[15] Subsequent measurements for these compounds using the AMB method and the TCT methods show that the MT results are extremely low. Possibly, the negative

TABLE I

Electron affinities (electron volts)

Compound	EA(MT)	EA(AMB)	EA(TCT)	EA(ECD)	Selected
Hexacyanobutadiene	3.24 ± 0.07				3.24 ± 0.07
TCNE	2.88 ± 0.05		3.17 ± 0.2		2.90 ± 0.1
TCNQ	2.80 ± 0.1	2.80 ± 0.1			
	2.83 ± 0.18	2.80 ± 0.3			2.82 ± 0.1
Hexacyanobenzene	2.48 ± 0.13				2.48 ± 0.13
Chloranil	2.40 ± 0.26	2.76 ± 0.2	2.78 ± 0.1		
			2.77 ± 0.1		2.7 ± 0.1
Fluoranil	2.27	2.92 ± 0.2	2.70 ± 0.1		
			2.45 ± 0.1		2.6 ± 0.1
Bromanil		2.44 ± 0.2			2.44 ± 0.2
F-Benzoquinone	2.16				2.16 ± 0.15
Tetracyanobenzene	2.15 ± 0.22				2.15 ± 0.22
Tetracyanopyridine	2.12 ± 0.17				2.12 ± 0.17
p-Benzoquinone	1.34 ± 0.09	1.89 ± 0.2	1.91 ± 0.1		
			1.92 ± 0.1		1.91 ± 0.1
9-10 Anthraquinone	1.15 ± 0.1		1.59 ± 0.1		1.59 ± 0.1
t-Dicyanoethylene	0.78 ± 0.1		1.24 ± 0.1		1.0 ± 0.2
o-Dicyanobenzene	1.04 ± 0.1		0.95 ± 0.1		1.0 ± 0.1
Hexafluorobenzene	1.20 ± 0.08		0.52 ± 0.1	0.86 ± 0.03	0.86 ± 0.03
CCl_4	2.06 ± 0.1		2.0 ± 0.2		
			2.08 ± 0.2		2.06 ± 0.1
$CHCl_3$	1.70 ± 0.05				1.70 ± 0.05
CH_2Cl_2	1.31 ± 0.05				1.31 ± 0.05
SF_6	1.4 ± 0.4	0.5 – 0.8	1.05 ± 0.1	1.15 ± 0.15	1.10 ± 0.1
Maleic Anhydride		1.40 ± 0.2	1.44 ± 0.1		1.42 ± 0.1
CS_2		0.62 ± 0.2	0.51 ± 0.1	0.6 ± 0.1	
		1.0 ± 0.2			0.6 ± 0.1
COS		0.46 ± 0.2		>0.4 ± 0.1	0.46 ± 0.2
CH_3NO_2		0.44 ± 0.2	0.48 ± 0.1	0.45 ± 0.1	0.45 ± 0.1
Cl_2		2.40 ± 0.2			
		2.45 ± 0.05			2.45 ± 0.1
Br_2		2.60 ± 0.2			
		2.55 ± 0.1			2.57 ± 0.1
I_2		2.58 ± 0.1			
		2.55 ± 0.1			2.56 ± 0.1
NO				0.1 ± 0.10	0.024 ± 0.01
O_2				0.46 ± 0.05	0.440 ± 0.008
Benzophenone (BP)			0.65 ± 0.1	0.64 ± 0.05	0.64 ± 0.1
4-F-BP			0.66 ± 0.1	0.64 ± 0.05	0.65 ± 0.05
4-Cl-BP			0.84 ± 0.1	0.8 ± 0.1	0.84 ± 0.1
1-Naphthaldehyde			0.70 ± 0.1	0.68 ± 0.03	0.69 ± 0.03
2-Naphthaldehyde			0.65 ± 0.1	0.62 ± 0.03	0.63 ± 0.03
Anthracene			0.60 ± 0.1	0.56 ± 0.05	0.57 ± 0.05
Azulene			0.69 ± 0.1	0.69 ± 0.05	0.69 ± 0.05
Nitrobenzene			1.01 ± 0.1	>0.9 ± 0.1	1.01 ± 0.1
m-Nitrotoluene			0.99 ± 0.1	0.8 ± 0.2	0.99 ± 0.1

ions are in an excited electronic state. It must be emphasized that only molecular electron affinities are considered. Nothing concerning the accuracy of magnetron results for radicals is implied.

The AMB procedure is important because it acts as a bridge for the two absolute procedures and as indicated earlier only requires the ionization potential of the alkali metal to give absolute values. The accuracy of the AMB results is quoted at ±0.2 eV. The results shown in Table I indicate this is a conservative estimate of the standard deviation since the greatest deviation from the selected value is ±0.22 eV. In some cases, the AMB method has given low values for the electron affinity such as for SF_6. The determinations for carbon disulfide and nitromethane are especially significant since there are multiple determinations of the values.

The molecular electron affinities determined with the ECD and the TCT method are also given in Table I. The precision of the TCT values is given as ±0.1 eV except for the value for TCNE which is ±0.2 eV. If there is a sufficiently large temperature range for the determination of the equilibrium constant, the ECD method has a nominal precision of ±0.05 eV. Indeed for some compounds, this can be reduced to ±0.02 eV. In order to determine EA's for compounds with a limited temperature range, we have used a "fixed" intercept. These values are lower limits. In our earlier work, we calculated electron affinities using a fixed intercept and cited a correspondingly better precision of ±0.01 eV. We feel that the best values are those which are determined directly from the slope.

The ECD results for NO and O_2 are especially important since they link the thermodynamic values to the spectroscopic determinations which are generally more precise. These results are also important to the TCT values since the relative scale is placed on an absolute one by reference to the spectroscopic value for the electron affinity of SO_2. Indeed, the determination of the electron affinity of molecular oxygen has been carried out by so many methods that it could be used as a "litmus" test for any new procedure. The ECD method has been applied to the study of dissociative electron capture and successfully yields determinations of the electron affinities of radicals if the corresponding bond dissociation energy is known. Examples of this are the acetate radical, nitrogen dioxide, and SF_5. The use of the ECD in conjunction with a mass spectrometer has yielded the electron affinity of SF_6 in good agreement with other methods. These other applications support the model of the ECD processes and hence the reliability of the direct capture results.

There are some ECD values in the literature which seem suspicious. First are those reported by Briegleb without regard to the dissociative or non-dissociative nature of the electron capture process.[12] Second are those reported by Kuhn and Levy[24] for a single temperature. Third are electron affinities reported using a constant potential.[22] Finally, the electron affinities of the methyl benzenes reported by Wojnarovits and Foldiak[23] are upper limits. The electron affinity of benzene is negative and the substitution of methyl groups on benzene should lower the electron affinity. These electron affinities are close to zero and some other processes might be taking place or the ECD response may be due to an impurity.

The general agreement between the ECD and TCT results is very good except for hexafluorobenzene. The difference of 0.33 eV is outside the expected error limits. We have interpreted this in terms of an excited state of the negative ion as shown in Figure 1. The TCT value for TCNE is 0.23 eV higher than the selected value but is within the error. The lower value is supported by the relative values of the half wave reduction potentials of TCNE and TCNQ. The TCT method has been used very successfully to determine gas phase acidities which can lead to electron affinities of radicals supporting the overall mechanism and the values for molecules.

In conclusion, the molecular electron affinities determined in the gas phase are in good agreement with each other with a few minor exceptions which could be due to the formation of excited states. The nominal values of the standard deviations are ±0.2 eV for the magnetron method, ±0.15 eV for the alkali metal beam method, ±0.05 eV for the electron capture detector method and ±0.1 eV for the TCT method. At the outer limits of the accessible range of electron affinities, these can be larger.

HALF WAVE REDUCTION POTENTIALS AND ADIABATIC ELECTRON AFFINITIES

For molecules in which the reaction is reversible; half wave reduction potentials, $E_{1/2}$, in aprotic solvents can be related to the adiabatic electron affinity of the molecule. The relationship is generally given as

$$E_{1/2} = a\,\mathrm{EA} - \mathrm{C}$$

where EA is the electron affinity, $E_{1/2}$ is the reversible potential in an aprotic solvent referenced to SCE and a and C are constants. The exact nature of this relationship has not been rigorously examined for lack of sufficient EA data. With the recent data, a least squares procedure can be used to determine the slope and intercept. The EA data are gas phase data and the reduction potentials are taken from the literature.[25-27] Data obtained in all aprotic solvents and all supporting electrolytes were used. Multiple EA values were used. The slope was found to be 0.97 ± 0.02 and the intercept 2.45 ± 0.03 eV. Previously it had been assumed that the slope is unity. The least squares value is close to one but this does not mean that there are no variations in C for different compounds. The value of C is directly related to the solvation energy difference between the neutral and negative ion. In order to determine whether the value of C could be related to the structure of the molecule, the slope was taken to be unity and C calculated for each data point. The mononitro compounds form a class of compounds with a smaller value of $C = 2.19 \pm 0.1$ which implies a larger than average solvation energy. The aromatic hydrocarbons, haloquinones, cyanocarbons, and other compounds, where the electron is not localized form, another class which has a high value of $C = 2.65 \pm 0.1$ which implies a low solvation energy. Finally, there is a group of compounds with an intermediate value of $C = 2.42 \pm 0.1$ eV. The average value for all data points is 2.48 ± 0.2 eV. Thus with a value of C, the EA can be determined directly from the half wave reduction potential. If the molecule can be placed into a specific category, then the EA value can be more precisely determined.

This is especially important for EDA acceptors since the electrochemical experiment is much easier to perform than the determination of the EA in the gas phase.

The selected values for the EA (Table I) and average values for the reduction potentials are tabulated in Tables II, III, and IV. The calculated values of the electron affinity are obtained by using a fixed value for C. As an example of the use of these tables, consider the determination of the electron affinity of tetrafluortetracyanoquinodimethane (TFTCNQ). The half wave reduction potential is

TABLE II

Half-wave reduction potentials and electron affinities Group A

Compound	C[a] (eV)	$E_{1/2}$[b] (eV)	EA(Gas Phase)[c] (eV)	EA(calc from $E_{1/2}$)[d] (eV)
Hexacyanobutadiene	2.61	0.57	3.24	3.32
Tetracyanoethylene	2.64	0.21	2.90	2.86
Tetracyanoquinodimethane	2.66	0.14	2.82	2.79
p-Fluoranil	2.63	−0.03	2.60	2.63
p-Chloranil	2.74	−0.04	2.70	2.61
p-Bromanil	2.50	−0.06	2.44	2.59
2,6-Cl_2Benzoquinone	2.72	−0.24	2.48	2.47
2,5-Cl_3Benzoquinone	2.65	−0.24	2.41	2.47
2,3-Cl_2Naphthoquinone	2.64	−0.45	2.19	2.20
Phenyl-*p*-Benzoquinone	2.43	−0.39	2.04	2.26
s-Tetracyanobenzene	2.81	−0.66	2.15	2.02
t-Dicyanoethylene	2.46	−1.36	1.0	1.29
o-Dicyanobenzene	2.72	−1.68	1.00	0.97
Tetracene	2.56	−1.58	0.88	1.07
9-Cl-Anthracene	2.61	−1.75	0.86	0.90
1-Cl-Anthracene	2.53	−1.75	0.78	0.90
2-Cl-Anthracene	2.60	−1.85	0.75	0.80
1,2-Benzpyrene	2.72	−2.06	0.67	0.59
1,2-Benzanthracene	2.73	−2.06	0.64	0.59
Dibenz[a,j]anthracene	2.71	−2.07	0.64	0.58
Dibenz[a,h]anthracene	2.69	−2.05	0.64	0.60
Pyrene	2.66	−2.10	0.56	0.55
Anthracene	2.51	−1.95	0.56	0.70
Benzo[c]phenanthrene	2.78	−2.24	0.54	0.41
3,4-Benzpyrene	2.68	−2.17	0.51	0.48
s-Tetrachlorobenzene	2.62	−2.17	0.45	0.48
Chrysene	2.72	−2.31	0.41	0.34
s-Trichlorobenzene	2.69	−2.35	0.34	0.30
Phenanthrene	2.77	−2.46	0.31	0.29
Triphenylene	2.78	−2.49	0.29	0.16
1-Chloronaphthalene	2.58	−2.30	0.28	0.35
Benzonitrile	2.58	−2.32	0.24	0.33
p-Dichlorobenzene	2.74	−2.56	0.18	0.09
Naphthalene	2.65	−2.51	0.15	0.14
o-Dichlorobenzene	2.67	−2.58	0.09	0.07
C(avg)	2.65 ± 0.1			

[a] C = EA − $E_{1/2}$.

[b] References 25–27.

[c] References 3–6, 14.

[d] Calculated by using the average value of C = 2.65 ± 0.1.

0.73 eV. Since TCNQ has a high value of C, TFTCNQ would also have a high value giving EA = 2.65 + 0.73 = 3.38 ± 0.1 eV. To obtain the most precise values, the electrochemical studies should be performed on compounds with known EA's and the unknown values interpolated using a unit slope.

TABLE III

Half-wave reduction potentials and electron affinities Group B

Compound	C^a (eV)	$E_{1/2}{}^b$ (eV)	EA(Gas Phase)^c (eV)	EA(calc from $E_{1/2}$)^d (eV)
p-Dinitrobenzene	2.51	−0.55	1.96	1.87
p-Benzoquinone	2.44	−0.52	1.92	1.90
t-butyl-Benzoquinone	2.35	−0.62	1.88	1.80
2,6-Di-*t*-butyl-Benzoquinone	2.50	−0.62	1.88	1.80
Methyl-benzoquinone	2.43	−0.58	1.85	1.84
1,4-Naphthoquinone	2.42	−0.61	1.81	1.81
2,5-Dimethylbenzoquinone	2.44	−0.67	1.77	1.75
2-Methyl-1,4-Naphthoquinone	2.50	−0.66	1.74	1.86
p-Cyanonitrobenzene	2.59	−0.87	1.72	1.55
o-Dinitrobenzene	2.41	−0.76	1.65	1.60
Trimethylbenzoquinone	2.32	−0.69	1.63	1.73
m-Dinitrobenzene	2.40	−0.78	1.62	1.66
Tetramethylbenzoquinone	2.43	−0.84	1.59	1.58
9,10-Anthraquinone	2.41	−0.82	1.59	1.60
2-*t*-Butyl-9,10-Anthraquinone	2.39	−0.83	1.56	1.59
2-Ethyl-9,10 Anthraquinone	2.39	−0.83	1.56	1.59
m-cyanonitrobenzene	2.47	−0.94	1.53	1.58
Maleic anhydride	2.29	−0.87	1.42	1.58
Phthalic anhydride	2.53	−1.32	1.21	1.10
4-I-Benzophenone	2.49	−1.49	1.00	0.93
4-Br-Benzphenone	2.50	−1.60	0.90	0.82
4-Cl-Benzophenone	2.42	−1.62	0.80	0.90
Acenaphthalene	2.45	−1.65	0.80	0.77
Cinnamaldehyde	2.44	−1.64	0.80	0.78
1-Naphthaldehyde	2.43	−1.64	0.69	0.78
Azulene	2.33	−1.64	0.69	0.78
4-F-Benzophenone	2.43	−1.74	0.69	0.71
Benzophenone	2.40	−1.76	0.64	0.66
4-Methoxybenzophenone	2.50	−1.86	0.64	0.56
2-Naphthaldehyde	2.30	−1.67	0.63	0.75
Fluoranthene	2.40	−1.77	0.63	0.65
Biacetyl	2.34	−1.71	0.63	0.71
Cyclooctatetraene	2.21	−1.61	0.60	0.81
3-Cl-Acetophenone	2.43	−1.85	0.58	0.55
4-Cl-Acetophenone	2.47	−1.90	0.57	0.52
Diethylphthalate	2.39	−1.87	0.52	0.55
Methylbenzoate	2.43	−2.23	0.20	0.19
C(avg)	2.42 ± 0.1			

[a] $C = EA - E_{1/2}$.

[b] References 25–27.

[c] References 3–6, 14.

[d] Calculated by using the average value of C = 2.42 ± 0.1.

TABLE IV

Half-wave reduction potentials and electron affinities Group C

Compound	C[a] (eV)	$E_{1/2}$[b] (eV)	EA(Gas Phase)[c] (eV)	EA(calc from $E_{1/2}$)[d] (eV)
m-CF_3-Nitrobenzene	2.13	−0.72	1.41	1.47
m-Br-Nitrobenzene	2.24	−0.92	1.32	1.27
p-Br-Nitrobenzene	2.32	−1.03	1.29	1.16
m-Cl-Nitrobenzene	2.21	−0.93	1.28	1.26
p-Cl-Nitrobenzene	2.32	−1.06	1.26	1.13
l-Nitronaphthalene	2.22	−0.98	1.23	1.21
p-Nitrobiphenyl	2.26	−1.06	1.20	1.13
m-F-Nitrobenzene	2.32	−1.10	1.22	1.09
2-Nitronaphthalene	2.16	−0.98	1.18	1.21
o-Br-Nitrobenzene	2.26	−1.09	1.17	1.20
o-Cl-Nitrobenzene	2.22	−1.10	1.12	1.09
p-F-Nitrobenzene	2.25	−1.13	1.11	1.06
O-Nitrobiphenyl	2.23	−1.16	1.07	1.03
Nitrobenzene	2.13	−1.10	1.01	1.09
m-Methoxy-Nitrobenzene	2.19	−1.15	1.04	1.03
m-Nitrotoluene	2.18	−1.19	0.99	1.01
N,*N*-dimethyl-3-Nitroaniline	1.97	−1.02	0.95	1.17
p-Nitrotoluene	2.15	−1.20	0.95	0.99
o-Nitrotoluene	2.20	−1.28	0.92	0.91
p-Methoxy-Nitrobenzene	2.16	−1.25	0.91	0.94
3,4-Dimethylnitrobenzene	2.12	−1.23	0.89	0.96
2,3-Dimethylnitrobenzene	2.13	−1.32	0.81	0.87
2,6-Dimethylnitrobenzene	2.11	−1.40	0.71	0.79
Nitromethane	2.15	−1.68	0.47	0.41
Benzaldehyde	2.22	−1.81	0.41	0.38
Acetophenone	2.25	−1.91	0.34	0.28
C(avg)	2.19 ± 0.1			

[a] $C = EA - E_{1/2}$.

[b] Ref. 25–27.

[c] References 3–6, and 14.

[d] Calculated by using the average value of $C = 2.19 \pm 0.1$.

TABLE V

Electron affinities for substituent effects (eV)

Compound	H	CF_3	CN	(C=O)CH_3	(C=O)H	NO_2
Benzene	(−0.73)	—	0.26	0.33	0.41	1.01
Naphthalene	(0.15)	—	0.68(1) 0.65(2)	0.61	0.69(1) 0.63(2)	1.23(1) 1.18(2)
Anthracene	0.57	—	1.27	0.97	1.31	1.43
F-Benzene	(−0.35)	—	(0.38)	0.44(o) 0.58(m) 0.40(p)	0.64(o) 0.67(m) 0.48(p)	1.07(o) 1.23(m) 1.12(p)
Cl-Benzene	(−0.15)		(0.62)	0.58(m) 0.57(p)	— —	1.14(o) 1.28(m) 1.26(p)
Br-Benzene	(0.2)	—	—	(0.9)	—	1.16(o) 1.32(m) 1.29(p)
Pentafluorobenzene	0.73	0.94	1.1	0.94	—	—
Benzonitrile	0.26	0.70(o) 0.67(m) 0.76(p)	0.95(o) 0.91(m) 1.10(p)	1.13 — —	1.00(m) 1.22(p) —	1.61(o) 1.56(m) 1.72(p)
Acetophenone	0.33	0.64(o) 0.66(m) 0.64(p)	1.13(p)	1.08	—	1.38(o) 1.31(m) 1.55(p)
Nitrobenzene	1.01	1.33(o) 1.41(m) 1.47(p)	1.61(o) 1.56(m) 1.72(p)	1.38(o) 1.38(m) 1.55(p)	1.51(o) 1.41(m) 1.67(p)	1.63(o) 1.65(m) 1.96(p)
Benzoquinone	1.92	(2.26)	(2.37)	(2.18)	—	(2.63)

SUBSTITUENT EFFECTS

The effect of substituting a functional group for a hydrogen atom can be established by examining Table V where the electron affinities are listed for substituents on different molecules. The values of the electron affinities determined from half wave reduction potentials are given in parentheses. The increments for a given functional group can be obtained by subtracting the appropriate entries. For example, the substitution of Cl for H in nitrobenzene gives an increase of .13 to .27 eV.

The adiabatic electron affinity of benzene has been estimated to be −0.72 eV based on half wave reduction potential data. This is consistent with the vertical electron affinity of −1.15 eV determined in electron transmission experiments. The corresponding potential energy curves in the C-H dimension are shown in Figure 3. For comparison purposes, the curves for hexafluorobenzene, a molecule which forms a stable negative ion, and carbon tetrachloride, a molecule which dissociates are given in Figures 1 and 2.

The effects of an alkyl group, the methoxy group and the amino group are not listed because these all consistently cause a decrease in the value of about 0.1–0.2 eV. From the data for the parent molecules in the first column, it can be seen that the greatest change is for the substitution on benzene. For the nitro group there is an increase of 1.7 eV while the increase for the F substitution is 0.4 eV. For most of the other functional groups, except for CN, the order is consistent. The CN group is more effective than the acetyl group for anthracene but less effective for benzene. There is also a decrease in the magnitude of the effect with an increase in the electron affinity of the parent molecule. For example, the second nitro group on nitrobenzene only increases the electron affinity by 1 eV. This is evidenced in multiple substitution in the cyanobenzene series. For example, the last two CN groups only contribute about 0.25 eV each while the addition of a second CN group to benzonitrile contributes about 0.8 eV.

By using Table V, the electron affinity of other molecules can be predicted. For example, trifluoromethyl anthracene should have an electron affinity of about 0.9 eV while that of trifluoromethylnaphthalene should be 0.5 eV. Table V can be used to rationalize the experimental electron affinities of the cyanoethylenes. The vertical electron affinity of ethylene has been determined to be -1.7 eV. If the rearrangement energy is about the same for benzene and ethylene, then the adiabatic electron affinity is about -1.3 eV. The first CN group would raise this to about -0.1 eV and a second CN group would raise this to 1.0 eV while the third CN would add another 1.0 eV to give 2.0 eV for tricyanoethylene and finally the fourth CN group would bring the value up to 2.9 eV. This analysis is consistent with the experimental data.

This table can also be used to evaluate experimental data. One prime example are the electron affinities of the haloanils. The electrochemical results for fluoranil, chloranil, and bromanil are the same. Noting the effect of the nitro group on the halobenzenes, it is clear that if anything, the order should be bromanil > chloranil > fluoranil not as indicated by the AMB data. However, if the values are considered to be the same and the individual values are averaged, then the AMB average is 2.71 ± 0.25 eV which agrees with the electrochemical value of 2.61 ± 0.1. Note also that the EA of tetrafluorodicyanobenzene is 1.89 eV as opposed to the value of 1.10 eV for the dicyanobenzene.

In addition to the change in the substituent effect with the magnitude of the EA of the parent and the leveling effect of the substituents, there are other factors which must be taken into consideration in using substituent effects. One of these is the effect of the position of the substituent. The increment for the fluorine substitution is 0.08 eV for the para position while that for the meta position is 0.25 eV. Another consideration is the substitution on different rings. For example, in the case of perfluorobiphenyl, the last five fluorine on the second ring contributes less than 0.18 eV or 0.03 eV/F. This is estimated from the EA perfluorbiphenyl = 0.91 eV while the EA of pentafluorobenzene is 0.73 eV. Finally, there are steric effects which can even change the direction of the effect. The prime example here is the EA of trimethylacetophenone which is greater than that of acetophenone because of a release of strain in the negative ion.

Thus in conclusion, the substituent effects should only be used as qualitative guidelines to the EAs of new acceptors. The electron affinities should at least be determined using electrochemical data. If the properties of the acceptor prove to be very valuable, then gas phase determinations of the acceptors should be made.

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