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Energetics of Electrode Reactions. III.[1] The Dependence of the Magnitude of Substituent Effects upon the Absolute Potential of Electrode Processes

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Dedicated to Professor K. A. Jensen on his 70th birthday

Linear correlations were obtained from plots of electrode potentials *vs.* σ_p for the oxidation of substituted anthracenes, the reduction of methyl substituted anthracenes as well as the reduction of methyl substituted naphthalenes. A relationship was found by which the absolute potential for an electrode reaction involving alternant aromatic hydrocarbons can be estimated from the measured potential difference ($\Delta E_{1,2}$) for two different electrode processes involving parent aromatic compounds and the slopes of E *vs.* σp (ϱ_1 and ϱ_2) for the two series of substituted alternant aromatic hydrocarbons. The

$$E^1_{\text{abs}} = \Delta E_{1,2}/(1-\varrho_2/\varrho_1)$$

equation results from the observation that the magnitudes of the slopes, ϱ_1 and ϱ_2, were found to depend upon the magnitudes of E_1 and E_2 measured on an arbitrary scale. The assumption that a zero substituent effect ($\varrho = 0$) would imply zero energy of the parent alternant aromatic hydrocarbon electrode process, allowed for the scaling of a plot of ϱ *vs.* E to pass through the origin and thus convert the arbitrary scale of electrode potentials to the absolute scale. The absolute potential for the oxidation of anthracene was estimated to be equal to 5.42 V while the absolute potentials for the oxidation of the anthracene and naphthalene anion radicals were estimated to be equal to 2.08 and 1.56 V. respectively.

Linear free energy relationships are often found in comparisons of rates and equilibria of reactions belonging to a closely related series and such relationships have had a profound effect upon the development of modern organic chemistry.[2] A number of linear free energy relationships have been found upon examination of oxidation and reduction potentials of organic compounds.[3] Electrode potentials, measured on an arbitrary scale, can be substituted into the form of the Hammett equation [2] which applies to equilibria (1) to give (2) where E_x is the potential for the substituted compound and

$$\log K_x/K_0 = \varrho\sigma_x \tag{1}$$

$$E_x - E_0 = \varrho\sigma_x \tag{2}$$

E_0 is that for the parent in the series.

We have found that redox reactions of alternant aromatic hydrocarbons (AAH) and substituted AAH constitute a family of reaction series which give linear plots of electrode potentials *vs.* σ constants. The electrode reaction of the unsubstituted compound is the parent reaction for each series. That is, each AAH can belong to two different electrode reaction series, one series being the oxidation and the other the reduction of the compounds. The various series of reactions investigated in this study, written in the direction of oxidation are illustrated in eqns. (3)–(5) where the symbols AN and NA refer to anthracenes and naphthalenes, respectively. The oxidation of

Table 1. Oxidation potentials of 9- and 9,10-substituted anthracenes.

Substituents	$\sum\sigma_p$[a]	Acetonitrile[b]	Dichloromethane[b]
9,10-Dimethoxy	-0.54	0.56	0.65
9-Ethoxy-10-ethyl	-0.42	0.60	0.67
9,10-Dimethyl	-0.34	0.65	0.72
9,10-Diethyl	-0.30	0.67	0.73
9-Methyl	-0.17	0.79	0.82
Unsubstituted	0.00	–[c]	0.91
9-Bromo	$+0.23$	0.94	1.01
9,10-Dibromo	$+0.46$	1.02	1.10
9,10-Dichloro	$+0.46$	1.01	1.09
9-Nitro	$+0.78$	1.20	1.29
Slope (mV)		473	485
Correlation coefficient		0.994	0.997

[a] Values taken from Ref. 2. [b] All potentials reported in this study are formal potentials in V *vs.* SCE measured at the potential midway between the oxidation and reduction peaks from reversible cyclic voltammograms. Supporting electrolyte: Bu_4NBF_4 (0.1 M). [c] Oxidation irreversible due to the reaction of the cation radical with acetonitrile.[4]

naphthalenes, eqn. (6), is not suitable for linear free energy

$$AN \rightleftharpoons AN^{+} + e^{-} \quad (3)$$

$$AN^{-} \rightleftharpoons AN + e^{-} \quad (4)$$

$$NA^{-} \rightleftharpoons NA + e^{-} \quad (5)$$

$$NA \rightleftharpoons NA^{+} + e^{-} \quad (6)$$

studies since naphthalene cation radicals are very reactive and it has not been possible to measure reversible electrode potentials for this series.

Plots of E *vs.* σ_p for reaction series (3)–(5) were observed to be linear. Early in this investigation, we noted that the slopes of the correlation lines, *i.e.* ϱ values, varied over a wide range and appeared to be dependent upon the relative potentials for the parent reactions in the series. In this paper, we present the results of a detailed investigation of the Hammet plots of reactions (3)–(5) which lead to the conclusion that a direct relationship exists between ϱ and the potential of the parent electrode processes.

RESULTS

Reversible oxidation potentials for several 9- and 9,10-substituted anthracenes along with those for the unsubstituted compound in both acetonitrile and dichloromethane are summarized in Table 1. The potentials were measured from cyclic voltammograms under conditions where the cation radicals were stable on the time scale of cyclic voltammetry. The latter was accomplished by making voltammetric measurement on solutions containing suspended neutral alumina, a technique which has recently been used to advantage in observing reactive intermediates generated at electrodes.[5] The potentials measured in dichloromethane are on the average about 80 mV more positive than those in acetonitrile. This potential shift is most likely connected with the reference electrode since both the oxidation and reduction potentials of anthracenes and related compounds have been shown to be nearly independent of the solvent.[6–8] The slopes given at the end of the table are the least squares values from plots of E *vs.* $\sum\sigma_p$.

Both oxidation and reduction potentials for a number of anthracenes substituted only with methyl groups are tabulated in Table 2. Here again, only reversible potentials are reported and they were obtained in the manner described previously for the oxidation of substituted anthracenes.

The reduction potentials for a large number of methyl substituted naphthalenes[9] and anthracenes[10] have been reported by Klemm.

Table 2. Redox potentials of methyl substituted anthracenes.

Substituents	Oxidation [a]	Reduction [b]
Unsubstituted	1.340	−2.035
2-Methyl	1.278	−2.076
9-Methyl	1.224	−2.042
2,3-Dimethyl	1.210	−2.128
2,6-Dimethyl	1.201	−2.117
2,7-Dimethyl	1.189	−2.121
9,10-Dimethyl	1.125	−2.044
2,3,9-Trimethyl	1.088	−2.129
2,6,9-Trimethyl	1.090	−2.121

[a] Potential in V *vs.* SCE measured midway between the oxidation and reduction peaks of reversible cyclic voltammograms. Solvent: dichloromethane, supporting electrolyte: Bu_4NBF_4 (0.1 M). [b] Potential in V *vs.* SCE measured midway between the oxidation and reduction peaks of reversible cyclic voltammograms. Solvent: dimethylformamide, supporting electrolyte: Bu_4NBF_4 (0.1 M).

In the latter studies, the effect of methyl substitution was observed to depend upon the position of the substituent. For naphthalene there are two unique positions, 1 and 2, for mono substitution, while for anthracene there are three, 1, 2 and 9. Thus, in order to account for the effect of methyl substitution it was necessary to average the effect over two positions for naphthalenes and over three positions for anthracenes. In Table 3, the averaged reduction potentials for methyl substituted naphthalenes [9] and anthracenes [10] measured in 75 % dioxane-water are tabulated along with the averaged values for the reduction of methyl anthracenes in anhydrous dimethylformamide (DMF) and the oxidation potentials for the same compounds in dichloromethane, the latter two sets of potentials were derived from the data in Table 2. The naphthalene potentials were averaged from two monomethyl values, ten dimethyl values and four trimethyl values. In the case of the anthracenes, potentials are from three monomethyl values, four dimethyl values, two trimethyl and two tetramethyl values.

The slopes recorded at the bottom of Table 3 refer to plots of the averaged potentials *vs.* $\sum\sigma_p$. It is of particular interest to note that the slopes for the reductions of the anthracenes in anhydrous DMF and in 75 % dioxane-water are identical at 185 mV. We certainly do not claim that the precision in the measurements and the linear relationships are so high so as to expect equal slopes for the two sets of experiments. We do believe, however, that it is significant that the slopes are equal or nearly so in that it shows the absence or near absence of a solvent effect. The latter also indicated that reduction potentials of AAH measured in aqueous dioxane compare very favorably with those in anhydrous media where the processes are known to be reversible. Exactly the same conclusion was recently arrived at in comparing Bergmans [11] potentials for AAH reduction in aqueous dioxane with reversible potentials measured in anhydrous

Table 3. The effect of methyl substitution on redox potentials of anthracene and naphthalene.

Number of methyls	$\sum\sigma_p$	$NA \rightarrow NA^-$ Diox$-H_2O$ [a]	$AN \rightarrow AN^-$ Diox$-H_2O$ [b]	$AN \rightarrow AN^-$ DMF [c]	$AN \rightarrow AN^+$ Dichloromethane [c]
0	0.00	−2.437	−1.924	−2.035	1.340
1	0.17	−2.459	−1.944	−2.059	1.246
2	0.34	−2.484	−1.987	−2.103	1.181
3	0.51	−2.516	−2.005	−2.125	1.089
4	0.68	—	−2.049	—	—
6	1.02	—	−2.109	—	—
Slope (mV) [d]		138	185	185	481
Correlation coefficient		0.999	0.996	0.991	0.998

[a] Potentials averaged from Ref. 7. [b] Potentials averaged from Ref. 8. [c] Potentials averaged from Table 2. [d] All slopes are positive when referring to the reaction series in the oxidation direction.

media.[12] These observations are reasonable in view of the fact that the protonation of the anion radicals of both naphthalene and anthracene have been observed to be very slow in aqueous DMF, second order rate constants of 4.6×10^{-3} and 2.0×10^{-4} M^{-1} s^{-1}, respectively.[13] Thus, if the protonation rate constants are of the same order of magnitude in 75 % dioxane-water the measured potentials in that medium would be expected to be very close to the reversible values.

The slopes reported in the tables are values obtained from the least squares procedure. The slope resulting from the reduction potentials of naphthalenes in dioxane-water, was derived neglecting the point with $\sum\sigma_p = -0.51$ which deviates significantly from the line passing through the other three points. Including the latter point changes the slope from 138 to 154 mV and the correlation coefficient from 0.999 to 0.996.

DISCUSSION

The Hammet ϱ value represents the relative sensitivity of a series of rates or equilibria to substituent effects.[2] Both reaction series (3) and (4) have identical or nearly identical ϱ values in two different solvents which show that the substituent effects for AAH redox reactions are nearly solvent independent. Relative potentials for these processes change little with solvent indicating that the solvation energy differences between the ions and the neutral compounds are also nearly independent of the solvent.[6] The only variable changing in going from one series to the next appears to be the electrode potential of the reaction of the parent in the series. A plot of ϱ for series (3)−(5) *vs.* the parent AAH redox potential on a relative scale gives a good linear correlation. This indicates that a unique value of ϱ is associated with each and every value of the electrode potential, on every reference scale, for the reaction of the parent AAH in the series.

The discussion in the previous paragraph has a very important consequence. Since the value of ϱ is directly proportional to the free energy of the parent electrode process, it is reasonable to assume that ϱ equals zero when the free energy of the standard reaction in the series equals zero. This corresponds to the assumption that a plot of E, on the absolute scale, *vs.* ϱ passes through the origin. Given this additional reference point, eqn. (7) can

Table 4. Absolute potential for the oxidation of anthracene calculated from correlation slopes.

	AN+ (MeCN)[a] 9,10 pos.	AN+ (CH_2Cl_2)[b] 9,10 pos.	AN+ (CH_2Cl_2)[c] methyl	AN⁻ (DMF)[d] methyl	AN⁻ (diox)[e] methyl	NA⁻ (diox)[f] methyl
AN+ (acetonitrile)[a] 9,10 positions		–	–	5.48	5.48	5.45
AN+ (dichloromethane)[b] 9,10 positions	–		–	5.40	5.40	5.40
AN+ (dichloromethane)[c] methyl substituents	–	–		5.43	5.43	5.41
AN⁻ (dimethylformamide)[d] methyl substituents	5.48	5.40	5.43		–	5.39
AN⁻ (dioxane-water)[e] methyl substituents	5.48	5.40	5.43	–		5.39
NA⁻ (dioxane-water)[f] methyl substituents	5.45	5.40	5.41	5.39	5.39	

$\varrho =$ [a] 473, [b] 485, [c] 481, [d] 185, [e] 185, and [f] 138 mV.

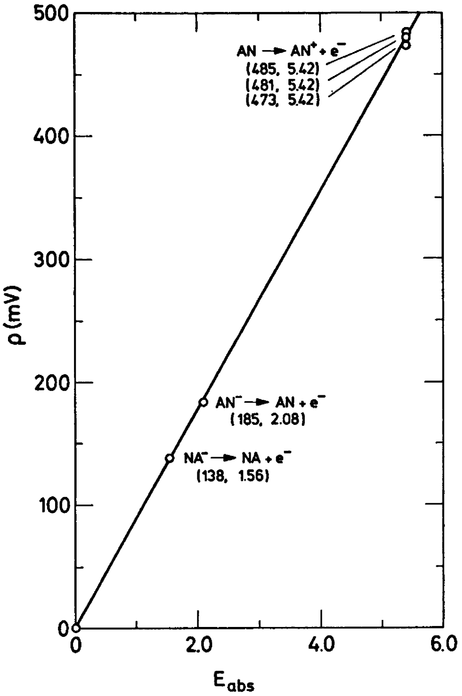

Fig. 1. Plot of ϱ *vs.* E_{abs} for AAH redox reactions. Correlation coefficient: 0.9998.

readily be derived.* The absolute potential for the standard reaction in series 1 is equal to the measured potential difference between the two standard reactions ($\Delta E_{1,2}$) divided by 1.0 minus the ratio of ϱ values for series 2 and 1.

$$E^1_{abs} = \Delta E_{1,2}/(1 - \varrho_2/\varrho_1) \tag{7}$$

The absolute potential for the oxidation of anthracene was calculated from eqn. (7) using all possible combinations of the data and the values obtained are gathered in Table 4. The average value is 5.42 ± 0.02 V and the largest deviation from the average is equal to only 0.06 V. The excellent linear correlation of all of the data, passing through the origin is illustrated by the plot of ϱ *vs.* absolute electrode potential in Fig. 1.

There is no need to emphasize the importance of the determination of an absolute electrode potential. Once that one such potential is available, the absolute values of all measured reversible potentials will be known. This in turn allows for the evaluation of the energies of single ions in solution, the goal of a large volume of research in physical chemistry.

In order to place the present work in context, we can refer to some recent work on attempts to calculate the absolute potential of the hydrogen electrode. Calculation of the latter ultimately involves the chemical free energy for the hydration of the proton ($\mu_{H^+}^{H_2O,0}$).[14] Two approaches have been taken, both involving approximate non-thermodynamic procedures, to evaluate the hydration energy of the proton. In the first, conventional hydration energies referred to an arbitrary scale are plotted against a suitable function of the ionic radius based on models and finally extrapolation to radius equal to zero gives the chemical free energy of hydration of the proton. The second approach[15] makes use of the real free energy of hydration of the proton ($\alpha_{H^+}^{H_2O,0}$), which is a measureable quantity, and equation (8). The drawback to this method is that χ,

$$\alpha_{H^+}^{H_2O,0} = \mu_{H^+}^{H_2O,0} + F\chi^{H_2O} \tag{8}$$

the surface potential of water, cannot be measured and must be estimated. Values for the absolute potential of the hydrogen electrode equal to 4.63[16] and 4.813[17] using the first procedure while values of 4.31[14] and 4.78[15] have been reported using the second approach.

It can be seen from the preceding paragraph that a great deal of uncertainty exists in the absolute potential of the hydrogen electrode. In comparison, the variation in the calculated values of the absolute potential for the oxidation of anthracene listed in Table 4 are indeed small. However, at this point we must stress, in spite of the excellent agreement of the values in Table 4, that the amount of data is too limited to place a high level of confidence on 5.42 ± 0.02 V as the absolute potential of the anthracene-anthracene cation radical half reaction.

In the previous paper of this series another approach was taken to arrive at the values of absolute potentials of AAH redox reactions.[1b] The sums of the solvation energies of an AAH⁺ and the corresponding AAH⁻ were calculated

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* For two electrode potentials, we have two equations $E^1_{abs} = m\varrho_1$ and $E^2_{abs} = m\varrho_2$, where m is the slope of the potentials *vs.* ϱ line, which passes through the origin. Substracting the second equation from the first and rearranging gives: $E/m\varrho_1 = 1 - \varrho_2/\varrho_1$, which after the appropriate substitution gives eqn. 7.

according to eqn. (9). The derivation of eqn. (9) did not require the value of the potential of a reference electrode since E°_{sum} is the difference in potential for the oxidation and reduction

$$2(\Delta G^\circ_{\text{solv}})^{\pm} = (\Delta G^\circ_{\text{solv}})^{-} + (\Delta G^\circ_{\text{solv}})^{+} = E^\circ_{\text{sum}} + \text{EA} - \text{IP} \qquad (9)$$

of an AAH. By making a single assumption, *i.e.* that the solvation energies of AAH^- $(\Delta G^\circ_{\text{solv}})^-$ and AAH+ $(\Delta G^\circ_{\text{solv}})^+$ are equal, the oxidation and reduction potentials of AAH could be referred to an absolute energy scale. Thus, eqn. (10) gives the absolute potential for the oxidation of an AAH for which $(\Delta G^\circ_{\text{solv}})^{\pm}$ is known from eqn. (9). For AN, EA has been determined to be equal to 0.55 eV [18] and the photoelectron ionization potential has been reported to be equal to 7.47 eV.[19] Since the latter IP value is for the vertical ionization of AN, it is somewhat higher than the adiabatic value, needed for eqn. (9). The calculated vertical IP values reported by Dewar [20] are on the average 0.17 eV higher than the corresponding adiabatic values. Therefore, a reasonable estimate of the adiabatic IP for AN can be arrived at by subtracting 0.17 eV from the photoelectron value resulting in an estimate of 7.30 eV. Thus, we arrive at a value of −1.71 V for $(\Delta G^\circ_{\text{solv}})^{\pm}$ according to (9).* The absolute potential for the oxidation of anthracene can then be estimated from eqn. (10) to be equal to 5.59 V. It has previously been proposed that although the

$$E_{\text{abs}} = \text{IP} + (\Delta G^\circ_{\text{solv}})^{+} \qquad (10)$$

chemical solvation energies of AAH+ and AAH^- should be equal, the real free energies of solvation should differ by twice the surface potential of the solvent. The value of $\varkappa$ for acetonitrile was estimated to be equal to -0.10 ± 0.06 V.[21] Taking the latter into account, values of −1.81 and −1.61 V, respectively, are obtained for $(\Delta G^\circ_{\text{solv}})^+$ and $(\Delta G^\circ_{\text{solv}})^-$. This value for the solvation energy of AAH+ leads to a value of 5.49 for the absolute potential of the anthracene-anthracene cation radical redox couple according to eqn. (10).

The agreement between E_{abs} for the oxidation of anthracene from Table 4 and the value estimated from eqn. (9) and eqn. (10) is remarkable in view of the large discrepancies which arise from the different approaches in estimating the absolute potential of the hydrogen electrode. The method employing eqns. (9) and (10) might be considered a more conventional approach than the use of linear free energy relationships as in this paper. However, the uncertainty in adiabatic IP values, experimental error in measuring EA values, the uncertainty in the value of surface potentials, as well as the assumption that the solvation energies of AAH^- and AAH+ are equal allows for the possibility of much greater error by the former procedure. On the other hand, the fact that the two methods give almost identical values for the absolute potential for the oxidation of anthracene suggests that the Hammett ϱ *vs.* absolute potential relationship is indeed legitimate.

In conclusion, we once again emphasize the completely empirical manner in which the data in Table 4 were arrived at. One assumption is involved in this treatment, *i.e.* a ϱ value of zero corresponds to a free energy change of zero for the standard electrode process. Stated still another way, the assumption is that since there is only one value of ϱ for each value of E_{abs} of the standard electrode process, the value of E_{abs} is zero when ϱ is zero. One might inquire as to what further data might be obtained to strengthen the arguments presented here and make the absolute potential scale so defined more precise. Obviously, more experimental points would be highly desirable. If a series of substituted tetracenes (TE) were available, predicted absolute potentials for the oxidation and reduction of TE are 4.95 and 2.55 V, respectively, the gap between the oxidation and reduction of anthracene in Fig. 1 would be filled and these extra points would greatly increase the reliability of the treatment. However, when one considers the structure of TE it becomes obvious that to obtain the necessary methyl substituted compound would be an enormous exercise in organic synthesis. Just considering the mono and disubstituted derivatives we find that there are three possible of the former and twelve of the latter. In spite of the complexity of the tetracene series and in view of the importance of the definition of the absolute potential scale, work is planned on that series.

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* A somewhat larger value, −1.97 V, was obtained using calculated vertical IP values.[1b]

EXPERIMENTAL

The equipment used for voltammetric measurements has been described earlier.[22] Acetonitrile (Fluka, *purum*) and dimethylformamide (Fluka, *puriss.*) were purified as recommended by Moe.[23] Dichloromethane (Merck, *pro analysi*) was used as obtained All solvents were predried by passing through neutral alumina (ICN Pharmaceuticals W 200) prior to use. Supporting electrolyte was in all cases Bu_4NBF_4 prepared from Bu_4NHSO_4 (Hässle, Göteborg, Sweden) and HBF_4 (50 % aqueous solution, Riedel-de Haën AG). 9-Substituted and 9,10-disubstituted anthracenes were reagent grade and recrystallized from ethanol or acetic acid. Methyl substituted anthracenes [10] were not further purified. Voltammetry was conducted under nitrogen in the presence of neutral alumina. This technique has been described in detail previously.[5a] The temperature was controlled to 20.0 ± 0.1°.

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