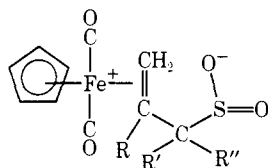
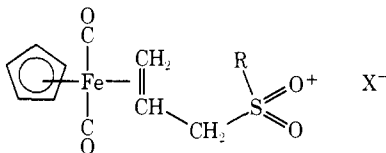


mmol).¹⁵ **4a**¹⁶ was isolated in 70% yield as a yellow solid, mp 130° dec. Similarly prepared, by treatment of **3a** with (C₆H₅)₃CCl and addition of NH₄PF₆, was **5a**,¹⁸ mp 135–136° dec. In contrast, treatment of **3a**



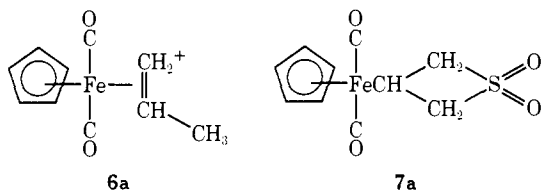
- 3a**, R = R' = R'' = H
b, R = R' = H; R'' = CH₃
c, R = H; R' = R'' = CH₃
d, R = CH₃; R' = R'' = H



- 4a**, R = CH₃; X = BF₄
5a, R = (C₆H₅)₃C; X = PF₆

with CH₃OSO₂F (or HCl gas) unexpectedly affords known⁶ **6a**.

Whereas rapid removal of the SO₂ from freshly prepared (or aged) solutions of **1b–d** yields only **2b–d**, respectively, similar treatment of the SO₂ solution of **1a** affords some (5%) **2a** and another 1:1 adduct of **1a** and SO₂, **7a**. **7a**, a yellow solid, mp 62–65°, is



monomeric¹⁹ and the suggested structure receives support from the ir and nmr data.²⁰ Surprisingly, **7a** polymerizes on storage in SO₂, CHCl₃, or CH₂Cl₂. Initially, soluble dimeric and/or trimeric species can be isolated,²¹ mp 150–160° dec. They show a new C₅H₅ ¹H nmr signal,²² a richer ν_{SO} ir region,²³ but vir-

(15) The same synthesis of **4a** was mentioned in a recent review.^{2d}

(16) *Anal.* Calcd for C₁₁H₁₃FeO₃SBF₄: C, 34.42; H, 3.41; S, 8.34. Found: C, 34.17; H, 3.31; S, 8.22. Δ_M = 111 ohm⁻¹ cm² (~5 × 10⁻⁴ M, acetone),¹⁷ ir ν_{C=O} 2072, 2041, ν_{SO} 1302, 1139 cm⁻¹ (Nujol); ¹H nmr (PF₆⁻ derivative of **4a**) C₅H₅ τ 4.00 s, CH₃ 6.95 s (deuterioacetone).

(17) Molar conductivities of ~1 × 10⁻³ M solutions of 1:1 electrolytes in acetone fall in the range of 100–150 ohm⁻¹ cm²; see M. B. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948).

(18) *Anal.* Calcd for C₂₉H₂₈FeO₄SPF₆: C, 51.96; H, 3.76; S, 4.77. Found: C, 51.80; H, 3.76; S, 4.57. Δ_M = 134 ohm⁻¹ cm² (~5 × 10⁻⁴ M, acetone), ir ν_{C=O} 2081, 2039, ν_{SO} 1296, 1127 cm⁻¹ (Nujol); ¹H nmr C₅H₅ τ 4.10 s (deuterioacetone).

(19) Calcd molecular weight for C₁₀H₁₀FeO₄S: 282. Found: 285–288 (CHCl₃, osmometric). The compound is hygroscopic and was handled accordingly in a drybox for this and other measurements.

(20) Ir ν_{C=O} 2012, 1957, ν_{SO} 1302, 1109 cm⁻¹ (KBr), ¹H nmr τ 5.03 s (5 H), 6.5 complex (4 H), 7.8 complex (~1 H) (CDCl₃), τ 5.00 s (5 H) (SO₂).

(21) *Anal.* Calcd for (C₁₀H₁₀FeO₄S)₂ or ₃: C, 42.58; H, 3.57; O, 22.69; mol wt, 564 (dimer), 846 (trimer). Found: C, 42.33, 42.41; H, 3.63, 3.76; O, 22.65; mol wt, 571–577, 604–660 (CHCl₃, osmometric). The closely agreeing oxygen analysis is particularly important as it mitigates the possibility of a sulfonate formulation, (C₁₀H₁₀FeO₄S)_n (calcd O for C₁₀H₁₀FeO₄S: 26.85).

(22) At τ 5.03 (SO₂) or 5.08 (CDCl₃). The rest of the nmr spectrum is ill resolved but qualitatively similar to that of the monomer.

(23) 1324, 1298, 1126, 1109 cm⁻¹ (KBr).

tually unchanged in ν_{C=O} band positions. The mass spectra (70 eV, 100°) of these associated species contain peaks at *m/e* 190 (C₅H₅Fe(CO)₂CH⁺ and/or C₅H₅-Fe(CO)C₃H₅⁺, intensity 11.7), 162 (C₅H₅Fe(CO)CH⁺ and/or C₅H₅FeC₃H₅⁺, intensity 30.2), and 134 (C₅H₅-FeCH⁺, intensity 10.8),²⁴ thus suggesting the presence of an Fe–C σ-bond therein. However, the structure of the (C₅H₅SO₂)₂ or ₃ sulfone moiety is not evident from these data.²⁵ Prolonged storage of **7a** in solution yields insoluble, presumably more highly associated species. It is not obvious to us why **7a** should undergo this unusual behavior.²⁶

Two important conclusions emerge from this work. (1) It has been demonstrated unequivocally for the first time that reactions of η⁵-C₅H₅Fe(CO)₂(η¹-allyl) with SO₂, and very likely also with other electrophilic molecules such as (CN)₂C=C(CN)₂, ClSO₂NCO, and CF₃-COCF₃, *inter alia*,⁵ proceed *via* zwitterionic iron-olefin intermediates. Our observation that η⁵-C₅H₅Mo(CO)₃-CH₂CH=CH₂ interacts similarly to **1a** with SO₂ suggests that such behavior is general of transition metal-η¹-allyl complexes. (2) It is noteworthy that the rates of the rearrangement of the iron-olefin intermediates (**3a–d**) to the *S*-sulfinato products (**2a–d**, respectively) tend to increase with the increasing extent of alkyl substitution in the olefin fragment. This trend is consistent with transition metal-olefin bonding being destabilized by such alkyl substitution,²⁷ thus rendering the olefin more labile toward SN1 or SN2 displacement. Significantly, the least alkyl-substituted zwitterionic iron-olefin intermediate, **3a**, is the slowest to dissociate to yield **2a**. It is also the only intermediate which rearranges *via* cycloaddition, very likely because the iron binds this olefin most strongly and hence activates it best toward nucleophilic attack by the sulfinate oxygen or sulfur.

Acknowledgments. The financial support of this research by the National Science Foundation is gratefully acknowledged. We thank Professors Giering and Rosenblum for helpful comments.

(24) Intensity of C₅H₅Fe⁺ = 100. The *m/e* 134 peak may alternatively be assigned to C₆H₆Fe⁺, as suggested by a referee. However, we consider the presence of such an ion very improbable, especially since C₆H₆⁺ is not observed in the spectrum.

(25) Attempts are now being made to elucidate the structures of **7a** and its dimer by X-ray crystallography.

(26) η⁵-C₅H₅Fe(CO)₂CHCH₂CH₂S(O)₂CH₂, a homolog of **7a**, does not exhibit this behavior; instead it is converted to η⁵-C₅H₅Fe(CO)₂S(O)₂-CH₂CH₂CH=CH₂ on heating.^{2a} We find that the dimer or trimer of **7a** yields only a trace amount of **2a** on heating at 110–125° for 48 hr.

(27) For example, M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 21, and M. Herberhold, "Metal π-Complexes," Vol. II, Elsevier, New York, N. Y., 1974, pp 130–134.

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On the Problem of Assigning Values to Energy Changes of Electrode Reactions

Sir:

Unlike ionization potential or electron affinity measurements, the energy change during an electrode reaction is never assigned a real value but rather it is always necessary to refer the potential to that of a reference

Table I

	$(E_p + 30)$ mV _{red} ^a	$(E_p - 30)$ mV _{ox} ^a	Midpoint	$\pm E^b$	IP ^c	$(-\Delta G^{\circ}_{\text{soln}})^{\pm}$ + ϕ^d
Anthracene (II)	-1.97	+1.29	-0.34	1.63	7.97	6.34
1,2-Benzanthracene (VI)	-2.02	+1.30	-0.36	1.66	8.04	6.37
Chrysene (XVI)	-2.27	+1.57	-0.35	1.92	8.19	6.38
Perylene (XXXII)	-1.66	+1.06	-0.30	1.36	7.72	6.36

^a Potential in volts measured vs. saturated aqueous calomel (sce) reference. ^b The potential in volts for oxidation or reduction in acetonitrile measured vs. midpoint potentials. ^c Data from ref 3. ^d Value calculated from: $IP - \Delta E^{\circ} = -(\Delta G^{\circ}_{\text{soln}} + \phi)$.

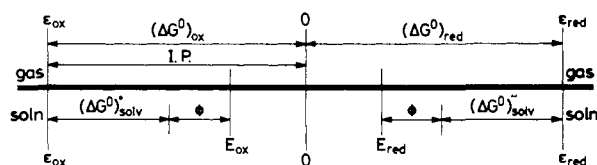
electrode. The latter fact seriously limits the use of electrode potentials in estimating energetics of reactions. Recently, significant advances have been made on the latter problem by the estimation of the medium activity coefficient for the transfer of silver ion from acetonitrile to water.^{1,2} In this communication the observation of a symmetry point on the potential scale between the oxidation and reduction potentials of several even alternate aromatic hydrocarbons (AAH) is reported. It is suggested that this point of symmetry should be considered the zero reference potential for electrode reactions.

Molecular orbital (MO) theory indicates that the MO's of AAH occur in pairs of bonding and antibonding orbitals of energy $-\epsilon$ and $+\epsilon$. Thus, the potential required to reduce (e added to antibonding orbital) should be equal but opposite in sign to that required to oxidize (e removed from bonding orbital) an AAH provided that the potentials are referred to the zero reference potential and the solvation energies of the resulting anion and cation radical are equal.³ The change in free energy for the oxidation, which for the AAH is equal to that for the reduction, is given by eq 1.⁴ The

$$\Delta G^{\circ} = (G^{\circ}_{\text{R}})_{\text{gas}} - (G^{\circ}_{\text{R}^+})_{\text{gas}} + (\Delta G^{\circ})_{\text{soln}} - \phi \quad (1)$$

energies involved are shown in Scheme I. If we ne-

Scheme I



glect entropy effects, which is customary for this type of analysis,⁵ the difference in free energy of R and R⁺ in the gas phase can be equated to the ionization potential of the aromatic hydrocarbon, R.

In order to test the hypothesis of a symmetry point on the potential scale between the oxidation and reduction potentials of AAH, it was necessary to measure reversible redox potentials for both processes in the same solvent vs. the same reference electrode at the same indicator electrode. It has recently been shown that reversible electrode potentials can be measured in most aprotic electrochemical solvents by conducting the measurements in the presence of suspended neutral alumina which very effectively scavenges impurities

that normally preclude the observation of reversible voltammograms.⁶ Using the latter technique, reversible or nearly reversible⁷ voltammograms for both the oxidation and reduction of anthracene, 1,2-benzanthracene, chrysene, and perylene were obtained. The data referred to the saturated aqueous calomel electrode (SCE) are summarized in Table I. It was gratifying to note that the midpoints for the redox potentials were very nearly constant (average = -0.34 V) which supports the idea that the midpoint potential may indeed be the zero reference potential.

From the scheme, we can define the relationship between the ionization potential and the real potential for oxidation or reduction of AAH (eq 2). Assuming

$$IP = \Delta E^{\circ} - (\Delta G^{\circ})_{\text{soln}} + \phi \quad (2)$$

that the reversible potentials measured vs. the midpoint potential between oxidation and reduction of AAH (Table I) are indeed the real potentials, the quantity $\phi - (\Delta G^{\circ})_{\text{soln}}$ can be calculated. The calculated values of the latter quantity were identical within experimental error of the measurements for the four compounds tested. Since ϕ is a constant associated with the energy of the electron in the electrode, the solvation energies for the four compounds must be nearly identical. The latter being the case, it seemed reasonable to assume that $(\Delta G^{\circ})_{\text{soln}}$ for the entire series of AAH should be very nearly identical which leads to the following relationship between ionization and electrode potentials (eq 3).

$$\Delta E^{\circ} = IP - 6.36 \text{ eV} \quad (3)$$

In order to test the applicability of eq 3, the half-wave potentials⁹ previously correlated³ were adjusted to refer to (sce - 0.34 V).¹⁰ The latter potentials along with those calculated from eq 3 and the differences are summarized in Table II. The experimental and calculated potentials agree within ± 0.04 V. Furthermore, the largest deviations are probably a consequence of the fact that the potentials were measured under conditions where many of them are not reversible. For example, both benzene and naphthalene gave irreversible oxidation peaks during voltammetry in acetonitrile even when the measurements were conducted in the presence of neutral alumina. However, under the

(6) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).

(7) It was not possible to obtain a reversible voltammogram for the oxidation of anthracene in acetonitrile. However, the rate constant for the reaction of anthracene cation radical with acetonitrile has recently been measured to be equal to 125 sec^{-1} which is not great enough to cause a significant shift in the peak potential for the oxidation.⁸

(8) O. Hammerich and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, in press.

(9) E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

(10) This was accomplished by using the four compounds tested as standards which resulted in adding 0.51 V to the published³ potentials.

(1) B. G. Cox and A. J. Parker, *J. Amer. Chem. Soc.*, **94**, 3674 (1972).
 (2) I. M. Kolthoff and M. K. Chantooni, *Anal. Chem.*, **44**, 194 (1972).
 (3) The Born equation, $-\Delta G^{\circ}_{\text{soln}} = Ne^2(1 - 1/D)/2r$, in which the symbols have their usual significance, predicts the latter to be the case. The solvation energies referred to are the differences in solvation energy of the ions and the substrate.
 (4) ϕ is the work function of the electrode.
 (5) M. J. S. Dewar, J. A. Hashmall, and N. Triajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

Table II. Electrode and Ionization Potentials of Aromatic Compounds



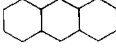
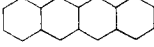
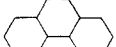
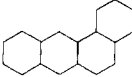
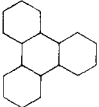
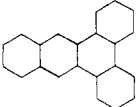
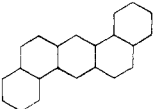
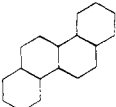
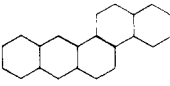
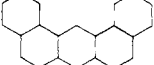
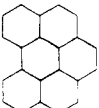
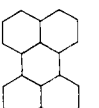
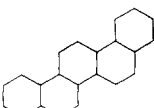

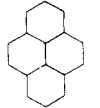
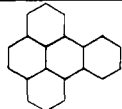
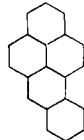
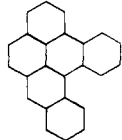
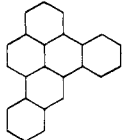
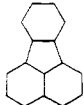
Compound ^a		m^a	E^b	IP ^a	E_{enl}^c	ΔE^d
	O	1.0000	2.81 (2.94) ^e	9.368	3.01	+0.20 (+0.07)
	I	0.6180	2.05 (2.11) ^e	8.541	2.18	+0.11 (+0.05)
	II	0.4142	1.60	7.972	1.61	+0.01
	III	0.2950	1.28	7.597	1.24	-0.04
	V	0.6052	2.01	8.434	2.02	+0.01
	VI	0.4523	1.69	8.037	1.68	-0.01
	IX	0.6840	2.06	8.454	2.09	+0.03
	X	0.4991	1.76	8.098	1.74	-0.02
	XIII	0.4735	1.70	8.070	1.71	+0.01
	XVI	0.5201	1.86	8.193	1.83	-0.03
	XVII	0.4048	1.52	7.875	1.52	0.00
	XX	0.4917	1.77	8.095	1.74	-0.03
	XXXVI	0.4393	1.52	7.846	1.49	-0.03
	XXXII	0.3473	1.36	7.724	1.36	0.00
	XXVI	0.5019	1.84	8.157	1.80	-0.04
	XXXIX	0.5392	1.74	7.976	1.62	-0.12
	XLIV	0.4450	1.67	7.951	1.59	-0.08

Table II (Continued)

Compound ^a	<i>m</i> ^a	<i>E</i> ^b	IP ^a	<i>E</i> _{calcd} ^d	Δ <i>E</i> ^c	
	XLV	0.4970	1.78	8.028	1.67	-0.11
	XLVI	0.3711	1.45	7.747	1.39	-0.06
	XLVII	0.3983	1.56	7.777	1.42	-0.14
	XLVIII	0.4216	1.52	7.841	1.48	-0.04
	LXII	0.6180	1.96	8.337	1.98	+0.02

^a Reference 3. ^b Values in ref 3 + 0.51 V. ^c IP - 6.36 = *E*_{calcd}. ^d *E*_{calcd} - *E* = Δ*E*. ^e Measurements made in the presence of neutral alumina.

latter conditions the respective potentials were found to be 2.94 and 2.11, both differing only +0.07 V from the calculated values. One other compound for which a deviation was observed, coronene (XXXIX), was reinvestigated. The oxidation was so irreversible in the latter case that a distinct peak was not observed. Thus, excellent agreement was observed between the calculated and experimental electrode potentials.

Since the ionization potential is related to the HMO parameters by eq 4, a combination of eq 3 and 4 gives

$$\text{IP} = \alpha + \beta m \quad (4)$$

the relationship between the HMO parameters and electrode potential (eq 5). A plot of the IP data³ gave

$$\Delta E^\circ = \alpha + \beta m - 6.36 \text{ eV} \quad (5)$$

a value of 6.69 for α and 2.88 for β . Thus, a plot of ΔE° vs. m should have a slope of 2.88 and an intercept of 0.33 eV. A plot of the data in Table I is shown in Figure 1. Actually, the best line with that slope has an intercept of 0.39 eV.

In arriving at the zero potential of the electrode, we have made only one assumption; namely, $(\Delta G^\circ)_{\text{solv}}^+ = (\Delta G^\circ)_{\text{solv}}^-$ as predicted by the simple Born expression. The Born equation also indicates that $(\Delta G^\circ)_{\text{solv}}^{2+} = (\Delta G^\circ)_{\text{solv}}^{2-} = 4(\Delta G^\circ)_{\text{solv}}^{\pm}$. Thus for AAH, $(E^\circ_2 - E^\circ_1)_{\text{ox}} = (E^\circ_2 - E^\circ_1)_{\text{red}}$. For perylene it was possible to measure all four potentials in acetonitrile. The differences in potentials for the first and second charge transfers were found to be equal to 525 (oxidation) and 530 (reduction) mV. Any error in the original assumption, $(\Delta G^\circ)_{\text{solv}}^+ = (\Delta G^\circ)_{\text{solv}}^-$, would have been magnified by a factor of 4 in this experiment. It seems

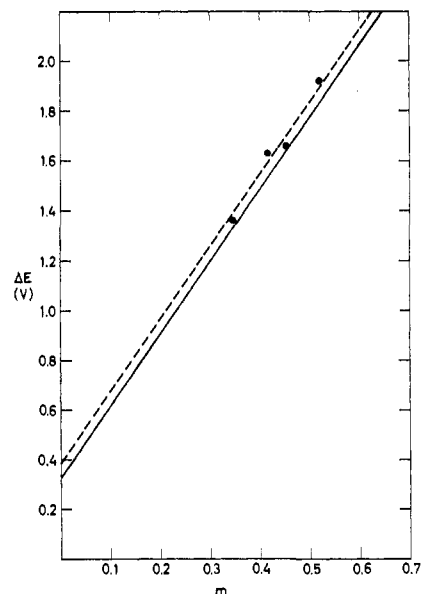


Figure 1. Plot of reversible redox potentials vs. energy of the highest occupied MO: calculated intercept, —; observed intercept, - - -.

reasonable to conclude that the potential of the saturated calomel electrode in acetonitrile is $+0.34 \pm 0.04$ V.

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