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CORRELATION BETWEEN POLAROGRAPHIC HALF-WAVE POTENTIALS AND ELECTRONIC ABSORPTION SPECTRA OF CONJUGATED AROMATIC HYDROCARBONS

By

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Abstract

The absolute values of the polarographic half-wave potentials for the conjugated aromatic hydrocarbons have been estimated on the basis of 4.42 v for the standard potential of the hydrogen electrode in aqueous medium obtained by Randles. From the comparison of these absolute potentials with $h\nu$ of the $\pi-\pi^*$ transition spectra of these molecules, it has been found that the oxidation and reduction potentials change linearly with $h\nu$ with gradient $+1/2$ and $-1/2$ respectively with limiting approach to the value close to the work function of graphite with decreasing $h\nu$, suggesting that they correspond respectively to the energy levels of the highest occupied and the lowest unoccupied molecular orbitals (**HOMO** and **LUMO**) of the π -electrons which are disposed symmetrically about the Fermi-level of graphite.

Introduction

Many attempts have been made to determine the energy levels of the **HOMO** and **LUMO** of the π -electrons of the conjugated aromatic hydrocarbons from the polarographic half-wave potentials of these molecules.¹⁻²³⁾ However, in order to answer this problem it is essential to determine the half-wave potentials referred to the standard state of the gaseous electron, *i. e.*, the absolute values of these potentials. The absolute half-wave potentials of the conjugated hydrocarbons can be estimated if the absolute potentials of the reference electrodes used for the polarographic measurements are known.

On the other hand, the absolute electrode potentials of the redox systems of monoatomic ions have been estimated in aqueous and some non-aqueous media,^{21,24-26)} on which basis it may be possible to estimate the absolute

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potentials of the reference electrodes and consequently the absolute half-wave potentials. Comparing the absolute half-wave potentials estimated in this way with the $h\nu$ -values of the p -band which is associated with the $\pi-\pi^*$ transition¹⁴⁾ for a number of compounds collected in the work of Bergmann¹³⁾ and others,^{5,6)} an attempt will be made in the present work to probe the correlation between the standard potentials of the redox systems of the conjugated aromatic hydrocarbons and the energy levels of the π -electrons of these molecules. The solvation free energies of the intermediate radical ions of the aromatic hydrocarbons will also be discussed in connection with the ionization potentials and the electron affinities of these molecules in the gas phase.

Estimation of the absolute potentials of the reference electrodes

The half-wave potentials of the conjugated hydrocarbons can be regarded as the standard potentials of the redox systems, the difference of the activity coefficients and the diffusion constants between the molecules and radical ions being neglected. These half-wave potentials for a number of hydrocarbons have been systematically determined in a variety of non-aqueous solvents referred to some fixed reference electrodes, *i. e.*, the aqueous saturated calomel electrode **SCE(aq)**, **Hg-pool**, **Ag/Ag⁺** and **Sb/SbCl₃** electrodes in the same non-aqueous test solution, as listed in Table 1.

TABLE 1. The absolute potentials of the reference electrodes used for the measurement of the half-wave redox potentials.

Solvent	Reference electrode	Absolute potential (v)	Ref.
2-methoxyethanol	Hg-pool	4.19	13
CH₃CN	SCE(aq)	4.66	6, 20
CH₃CN	Ag/Ag⁺ (0.1 N)	4.96	12
Dioxane	SCE(aq)	4.66	2
CH₃CN	SCE(aq)	4.66	22, 19
CH₂Cl₂	SCE(aq)	4.66	23
Dimethylformamide	SCE(aq)	4.66	20
SbCl₃	Sb/Sb³⁺	5.28	28
CH₃CN	Ag/Ag⁺ (0.001 N)	4.70	21

Correlation between Polarographic Half-wave Potentials and Spectra for Aromatic Compounds

The estimation of the absolute potential values of these reference electrodes will be described in what follows.

i) The aqueous saturated calomel electrode

The electrode potential of the **SCE (aq)** against the standard hydrogen electrode **SHE (aq)** in aqueous medium is given to be 0.24 v and the absolute potential of the SHE (aq) $\phi_{\text{H}^+/\text{H}_2, \text{aq}}^0$ is given as 4.42 v using the Randles' value 11.30 ev for the standard real free energy of hydration of proton.²⁴⁾ The absolute potential $\phi_{\text{SCE}(\text{aq})}$ of the **SCE (aq)** is therefore estimated to be 4.66v. Gomer and Tryson,²⁵⁾ however, have recently reported 4.73 v for $\phi_{\text{H}^+/\text{H}_2, \text{aq}}^0$. If we use the latter value, we should have $\phi_{\text{SCE}(\text{aq})} = 4.97$ v. The present work, however, will be based on the Randles' value for convenience.

ii) The mercury pool electrode in 2-methoxyethanol

From the comparison of the half-wave reduction potentials of the conjugated aromatic hydrocarbons in 2-methoxyethanol referred to the mercury pool in the same solution with those in 75% dioxane measured against the **SCE (aq)**, it is found that the former is less negative than the latter by 0.47 v within an accuracy of ± 0.06 v for 17 aromatic compounds as pointed out by Bergmann.¹³⁾ The absolute potential of the mercury pool in 2-methoxyethanol may therefore be estimated to be 4.19 v, assuming that the difference of the absolute half-wave potentials in 2-methoxyethanol and 75% dioxane is negligible.

iii) The Ag^+/Ag (0.1 N) electrode in acetonitrile

The absolute potential $\phi_{\text{Ag}^+/\text{Ag}}(0.1\text{N})$ in **acetonitrile** may be estimated to be 4.96 v by adding 0.3 v to $\phi_{\text{SCE}(\text{aq})}$ according to Pysh and Yang⁶⁾ and Larson *et al.*²⁷⁾

iv) The Ag^+/Ag (0.001 M) electrode in acetonitrile

The absolute potential of this electrode has been determined by Case *et al.*²¹⁾ as 4.70 v.

v) The Sb/SbCl_3 electrode

It is found that the half-wave oxidation potentials of aromatic hydrocarbons in SbCl_3 measured against Sb/SbCl_3 at 99°C ²⁸⁾ are more negative than those in acetonitrile measured against the **SCE (aq)** by 0.62 v with the standard deviation ± 0.14 v for eight compounds. The absolute potential of Sb/SbCl_3 electrode may therefore be estimated to be 5.28 v, assuming that the difference in the absolute half-wave potentials in SbCl_3 and acetonitrile is negligible.

It should be noted that the values of the absolute half-wave potentials depend on the value of $\phi_{\text{H}^+/\text{H}_2, \text{aq}}^0$ used, and furthermore the junction potentials

between aqueous KCl solution in **SCE(aq)** and the non-aqueous test solutions are neglected in the present treatment. Therefore the absolute potentials of the reference electrodes used in the present work may include an uncertainty of some hundreds millivolts.

Results and Discussion

Table 2 shows the absolute half-wave reduction and oxidation potentials ϕ_r^0 and ϕ_{ox}^0 of the first polarographic maxima for the conjugated aromatic hydrocarbons in some non-aqueous media. The values of $h\nu$ of the p-band classified by Clar¹⁴⁾ and the ionization potentials (**IP**) and the electron affinities (**EA**) for these compounds are also shown in Table 2.

The $h\nu$ -dependence of ϕ_r^0 in 2-methoxyethanol and ϕ_{ox}^0 in acetonitrile is shown in Fig. 1 as a typical example. As seen from the figure, ϕ_r^0 increases linearly with decreasing $h\nu$ with gradient $-1/2$, while ϕ_{ox}^0 increases linearly with increasing $h\nu$ with gradient $1/2$, and the limiting value of ϕ_r^0 or ϕ_{ox}^0 at $h\nu \rightarrow 0$ is close to the work function of graphite $\phi_{gr} = 4.39$ eV, as pointed out by Matsen⁷⁾ and Hammerich and Parker,¹⁹⁾ i. e., the $h\nu$ -dependence of ϕ_r^0 and ϕ_{ox}^0 can be expressed by the following equations within an accuracy of the absolute potentials of the reference electrodes estimated in the present treatment

$$\phi_{ox}^0 = \Phi_{gr} + \frac{1}{2} h\nu, \text{ eV} \quad (1)$$

$$\phi_r^0 = \Phi_{gr} - \frac{1}{2} h\nu, \text{ eV} \quad (2)$$

and the difference $\phi_{ox}^0 - \phi_r^0$ and the sum $\phi_{ox}^0 + \phi_r^0$ for a given molecule equal respectively $h\nu$ and $2\Phi_{gr}$.

We obtain the same trend of $h\nu$ -dependence as that in Fig. 1 for ϕ_r^0 in dioxane and **DMF** and for ϕ_{ox}^0 in SbCl_3 in Table 2 and Fig. 2, and Eqs. (1) and (2) hold in the relation between ϕ_r^0 or ϕ_{ox}^0 and $h\nu$ in any solvent described in Table 2, and consequently the difference $\phi_{ox}^0 - \phi_r^0$ and the sum $\phi_{ox}^0 + \phi_r^0$ for a given molecule are close to $h\nu$ and $2\Phi_{gr}$ respectively in any case of combination of the solvents in Table 2. The values of ϕ_{ox}^0 and ϕ_r^0 for some conjugated aromatic hydrocarbons in acetonitrile obtained by Case *et al.*²¹⁾ and Parker *et al.*¹⁹⁾ are also found to be in the straight line given by Eqs. (1) and (2) respectively. It may be concluded from these facts that the oxidation and reduction potentials of the conjugated aromatic hydrocarbons correspond respectively to the energy levels of the **HOMO** and **LUMO** of the molecules and they are disposed symmetrically about the Fermi-level of graphite, as predicted by Hush and Pople.²⁰⁾

TABLE 2. The absolute half-wave redox potentials ϕ_r^0 and ϕ_{ox}^0 of the conjugated aromatic hydrocarbons in non-aqueous media, and their electronic absorption spectra $h\nu$ of the p -band, and ionization potentials **IP** and electron affinities **EA** in the gas phase.























No.	Compound	$h\nu$, ev ^{a)}	I. P., ³⁷⁾ ev	E. A., ev	2-Methoxy ethanol	CH ₃ CN		Dioxane	DMF	SbCl ₃	CH ₂ Cl ₂	
					ϕ_r , v ¹³⁾	ϕ_r , v ²²⁾	ϕ_{ox} , v ^{b)}	ϕ_r , v ^{c)}	ϕ_r , v ^{d)}	ϕ_{ox} , v ³⁰⁾	ϕ_r , v	ϕ_{ox} , v
Orthofused Polycyclic Hydrocarbons												
1	 Naphthalene	4.35	8.15	0.65 ³⁸⁾ , 0.67 ⁴⁾ , -0.20 ³⁹⁾	2.21		6.20	2.16	2.13			
2	 Anthracene	3.31	7.41	1.19 ³⁸⁾ , 1.38 ⁴⁾ , 0.42 ⁴⁰⁾ , 0.61 ⁴¹⁾	2.73		5.75	2.70	2.71	5.79		
3	 Tetracene	2.63	7.01		3.05		5.43	3.08	3.08	5.49		
4	 Pentacene	2.15	6.64		3.33* ¹⁾							
5	 Phenanthrene	4.24	7.92	0.69 ³⁸⁾ , 0.20 ⁴⁰⁾ , 0.25 ⁴¹⁾	2.25		6.16	2.20	2.22			
6	 Tetraphene	3.45	7.42	0.46 ⁴⁰⁾	2.66		5.84	2.66		5.91		
7	 1,2-Benzotetracene	2.74			3.00							
8	 1,2-Benzpentacene	2.25			3.24							
9	 Triphenylene	4.36	7.84	0.14 ⁴⁰⁾	2.22		6.21	2.17				
10	 1,2:3,4-Dibenzanthracene	3.55	7.43		2.65		5.91					

Table 2 (Continued)

No.	Compound	$h\nu$, ev ^{a)}	I. P., ³⁷⁾ ev	E. A., ev	2-Methoxy ethanol	CH ₃ CN		Dioxane	DMF	SbCl ₃	CH ₂ Cl ₂	
					ϕ_r , v ¹³⁾	ϕ_r , v ²²⁾	ϕ_{ox} , v ^{b)}	ϕ_r , v ^{c)}	ϕ_r , v ^{d)}	ϕ_{ox} , v ³⁰⁾	ϕ_r , v	ϕ_{ox} , v
11	 1,2:3,4-Dibenzotetracene	2.81			2.98							
12	 1,2:3,4-Dibenzopentacene	2.30			3.26							
13	 1,2:5,6-Dibenzanthracene	3.53	7.42		2.64		5.85	2.63				
14	 1,2:7,8-Dibenzotetracene	2.83			2.94							
15	 1,2:8,9-Dibenzopentacene	2.37			ca 3.34*1							
16	 Chrysene	3.89	7.61	0.33 ⁴⁰⁾	2.38		6.01	2.36				
17	 3,4-Benzotetraphene	3.38			2.75		5.67					
18	 2,3:8,9-Dibenzchrysene	2.95			2.86*1							
19	 3,4-Benzphenanthrene	3.94	7.62	0.33 ⁴⁰⁾	2.44							
20	 1,2:7,8-Dibenzanthracene	3.53	7.42		2.62		5.92					
21	 1,2:3,4:7,8-Tribenznaphthalene	3.71			2.54							
22	 1,2:3,4:7,8-Tribenzanthracene	3.59			2.62							

























23		Tetrabenzonaphthalene	3.53			2.60							
24		1,2:5,6-Dibenzophenanthrene	3.87			2.46							
25		1,2-Benzotetraphene	3.17			2.79							
26		Picene	3.77			2.40		5.99					
27		Pentaphene	3.45	7.35		2.66							
28		Hexaphene	2.82			2.97							
29		3,4-Benzopentaphene	3.37			2.69							
30		3,4:9,10-Dibenzopentaphene	3.37			2.67'							
31		Naphtho(2',3':3,4)-pentaphene	3.20			2.72'							
Perylene and its derivatives													
32		Perylene	2.86	6.90		2.94		5.51	2.99	2.99 ²⁾	5.52		
33		1,2-Benzperylene	2.47			3.22							
34		1,2:7,8-Dibenzperylene	2.27			3.31							
35		1,2:10,11-Dibenzperylene	2.47			3.19							

Table 2 (Continued)

No.	Compound	$h\nu$, ev ^{a)}	I.P., ³⁷⁾ ev	E. A., ev	2-Methoxy ethanol	CH ₃ CN		Dioxane	DMF	SbCl ₃	CH ₂ Cl ₂	
					$\phi_{r, v^{13}}$	$\phi_{r, v^{22}}$	$\phi_{ox, v^b)}$	$\phi_{r, v^c)}$	$\phi_{r, v^d)}$	$\phi_{ox, v^{30}}$	$\phi_{r, v}$	$\phi_{ox, v}$
36	 1,12-benzoperylene	3.20	7.13		2.70		5.67					
37	 1,12:2,3-Dibenzoperylene	3.28			2.67							
38	 1,12:2,3:8,9-Tribenzoperylene	3.08			2.84'							
39	 Coronene	3.63	7.34		2.55		5.89	2.62	2.59	5.92		
40	 2,3:8,9-Dibenzoperylene	2.86			2.91							
41	 1,14-Benzobisanthene	2.31			3.27*1							
42	 7,8-Benzoterrylene	1.93			3.51'							
43	 1,9:5,10-Di-(perinaphthylene)-Anthracene	1.97			3.49'							
Pyrene and it's derivatives												
44	 Pyrene	3.27	7.41	1.16 ⁴⁾ , 0.39 ⁴⁰⁾ , 0.55 ⁴¹⁾	2.58		5.82	2.55		5.87		
45	 4,5-Benzpyrene	3.47	7.39		2.52		5.93			5.94		
46	 1,2-Benzpyrene	3.22			2.83		5.60	2.66		5.72		

























47		2,3:4,5-Dibenzpyrene	3.08			1st 3.11 2nd 2.89		5.67						
48		1,2:4,5-Dibenzpyrene	3.28			2.74		5.81						
49		4,5:9,10-Dibenzpyrene	3.77			2.50								
50		1,2:6,7-Dibenzpyrene	2.75			3.03								
51		1,2:7,8-Dibenzpyrene	3.12			2.87								
52		Naphtho-(2',3':4,5)-pyrene	3.59			1st 2.68 2nd 2.57								
53		Naphtho-(2',3':1,2)-pyrene	2.71			3.04								
54		Dinaphtho-(2'',3'':1,2);(2',3':6,7)-pyrene	2.15			3.41*1								
55		Dinaphtho-(2'',3'':1,2);(2',3':7,8)-pyrene	2.74			3.04*1								
56		1,2:4,5:7,8-Tribenzpyrene	3.25			2.85								
57		Peropyrene	2.84			3.01'								
58		4,5:11,12-Dibenzperopyrene	2.79			3.04'								
59		Anthanthrene	2.86			3.00								

Table 2 (Continued)

No.	Compound	$h\nu$, ev ^{a)}	I.P., ³⁷⁾ ev	E. A., ev	2-Methoxy ethanol	CH ₃ CN		Dioxane	DMF	SbCl ₃	CH ₂ Cl ₂	
					ϕ_r , v ¹³⁾	ϕ_r , v ²²⁾	ϕ_{ox} , v ^{b)}	ϕ_r , v ^{c)}	ϕ_r , v ^{d)}	ϕ_{ox} , v ³⁰⁾	ϕ_r , v	ϕ_{ox} , v
60	 Pyranthrene	2.68			3.13*1							
61	 2,3:8,9-Dibenzanthanthrene	2.10			3.39*1							
Fluoranthene and it's derivatives												
62	 Fluoranthene	3.46	7.8		1st 2.84 2nd 2.55		6.11	1st 2.90 2nd 2.55				
63	 1,2-Benzfluoranthene	2.90			1st 3.21 2nd 2.93							
64	 1,2:5,6-Dibenzfluoranthene	2.17			1st 3.54 2nd 3.34							
65	 3,4-Benzfluoranthene	3.54			2.81							
66	 7,8-Benzfluoranthene	3.24			1st 3.02 2nd 2.74							
67	 8,9-Benzfluoranthene	3.10			2.80							
68	 Naphtho-(2',3':7,8)-fluoranthene	3.04			1st 3.13 2nd 2.84							
69	 Naphtho-(2',3':8,9)-fluoranthene	2.83			2.81							
70	 3,4-peri-Phenylene-fluoranthene	3.02			1st 3.29 2nd 2.90							

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


















71		Isorubicene	2.42			1st 3.59 2nd 3.22						
72		5,6:11,12-Di-periphenylenetetracene	2.03			1st 3.85' 2nd 3.49'						
Non-fused polycyclic compounds												
73		Biphenyl	4.96		0.41 ³⁸⁾ , 0.70 ⁴⁾ , -0.37 ²⁹⁾	2.11		6.44 ¹²⁾	1.96	2.08		
74		p-Terphenyl	4.49			1st 2.28 2nd 2.06			2.33			
75		p-Quaterphenyl	4.25			1st 2.42 2nd 2.29			2.46			
Fluorene series												
76		Fluorene	4.75			2.07						
77		2,3-Benzfluorene	3.92			2.43						
78		Zethrene	2.69			3.73						
79		Benzene	5.96	9.24	-0.54 ³⁸⁾ , -0.36 ⁴⁾ , -1.14 ³⁹⁾			6.96 ¹²⁾				
Aliphatic alkenes and it's α, ω -Diphenyl derivatives												
80	$\text{H}_2\text{C} : \text{CH}_2$	Ethylene	7.63 ³¹⁾	10.50				7.80 ³²⁾				
81	$\text{H}_2\text{C} : \text{CH} \cdot \text{CH} : \text{CH}_2$	1,3-Butadiene	5.71 ²⁸⁾	9.07				6.99 ⁸⁾	2.00			

Table 2 (Continued)

No.	Compound	$h\nu, \text{ev}^{\text{a}}$	I. P., ³⁷⁾ ev	E. A., ev	2-Methoxy ethanol	CH ₃ CN		Dioxane	DMF	SbCl ₃	CH ₂ Cl ₂	
					$\phi_{\text{r}}, \text{v}^{\text{13}}$	$\phi_{\text{r}}, \text{v}^{\text{22}}$	$\phi_{\text{ox}}, \text{v}^{\text{b}}$	$\phi_{\text{r}}, \text{v}^{\text{c}}$	$\phi_{\text{r}}, \text{v}^{\text{d}}$	$\phi_{\text{ox}}, \text{v}^{\text{30}}$	$\phi_{\text{r}}, \text{v}$	$\phi_{\text{ox}}, \text{v}$
82	$\text{H}_2\text{C}=(\text{CH}=\text{CH})_3=\text{CH}_2$ Octatetraene	4.08 ³³⁾						2.64				
83	$\text{O}-\text{CH}=\text{CH}-\text{O}$ Stilbene	3.89		1.33 ⁴⁾				2.50 ³⁵⁾	2.45 ²⁾			
84	$\text{O}-(\text{CH}=\text{CH})_2-\text{O}$ 1,4-Diphenylbutadiene	3.52		1.47 ⁴⁾				2.75				
85	$\text{O}-(\text{CH}=\text{CH})_3-\text{O}$ 1,6-Diphenylhexatriene	3.29						2.90				
86	$\text{O}-(\text{CH}=\text{CH})_4-\text{O}$ 1,8-Diphenyl- octatetraene	3.07						3.04				
87	$\text{O}-(\text{CH}=\text{CH})_5-\text{O}$ 1,10-Diphenyl- decapentaene	2.92						3.12				
88	$\text{O}-(\text{CH}=\text{CH})_6-\text{O}$ 1,12-Diphenyl- dodecahexaene	2.79						3.21				
Heterocyclic hydrocarbons												
89	$\text{O}^{\text{N}=\text{O}}$ Pyridine N-oxide	4.40				2.36	6.46					
90	N^{O} Pyridine mono-N-oxide	4.53				2.82	6.97					
91	$\text{O}^{\text{O}^{\text{N}=\text{O}}}$ Pyridine di-N-oxide	3.87				3.04	6.40					

92		Quinoline N-oxide	3.54					2.82	6.20				
93		Isoquinoline N-oxide	3.95					2.71	6.26				
94		Quinoxaline mono-N-oxide	3.75					3.20	6.63				
95		Quinoxaline di-N-oxide	3.02					3.41	6.26				
96		Phenanthridine N-oxide	3.62					2.85	6.14				
97		Acridine N-oxide	2.73					3.30	5.94				
98		Phenazine mono-N-oxide	2.94					3.64	6.41				
99		Phenazine di-N-oxide	2.51					3.81	6.00				
Thiochromone and it's derivative													
100		Thiochroman-4-one	3.62 ²³⁾									2.76 ²³⁾	6.41 ²³⁾
101		Thiochromone	3.71 ²³⁾									2.83 ²³⁾	6.62 ²³⁾

- a) The $h\nu$ -values of No. 1—No. 79, No. 83—No. 88 and No. 89—No. 99 are taken from ref.s 14), 34) and 22) respectively.
- b) The ϕ_{ox} -values in acetonitrile of No. 1—No. 62 and No. 89—No. 99 are calculated from $E_{\ddagger,ox}$ quoted from ref.s 6) and 22) respectively.
- c) The ϕ_r -values in dioxane of No. 1—No. 88 except No. 83 are calculated from $E_{\ddagger,r}$ quoted from ref. 2)
- d) The ϕ_r -values in DMF of No. 1—No. 37 except No. 32 are calculated from $E_{\ddagger,r}$ quoted from ref. 20).
- ') means that the solubility is very low (ref. 13).
- *) means that benzen is added to the solution in order to increase the solubility (ref. 13).
- 1st and 2nd in the column of 2-methoxyethanol mean the ϕ_r -values calculated from 1st and 2nd polarographic maxima (ref. 13).

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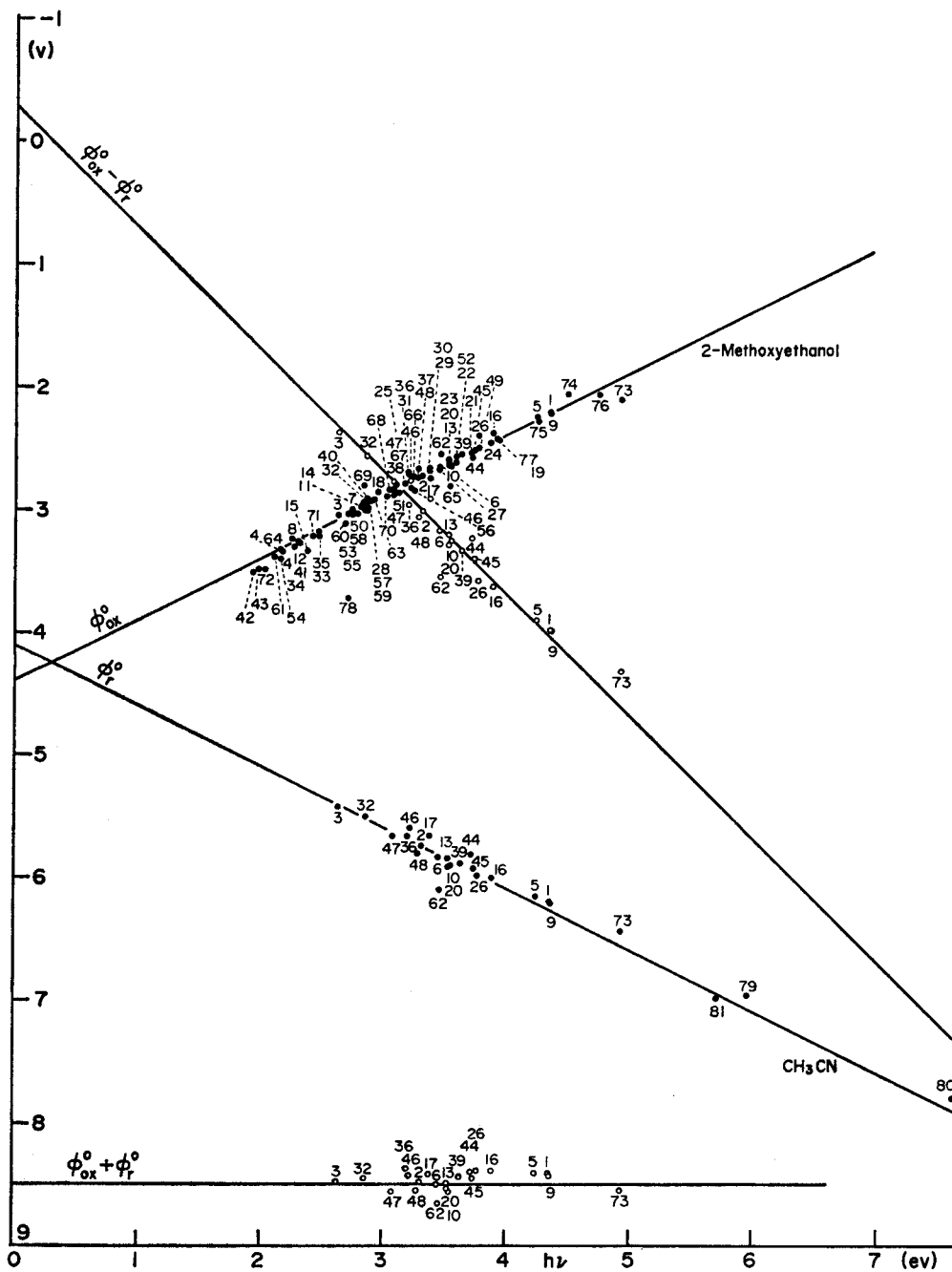


Fig. 1. The $h\nu$ -dependence of ϕ_r^0 in 2-methoxyethanol (\bullet), ϕ_{ox}^0 in acetonitrile (\bullet), $\phi_{ox}^0 - \phi_r^0$ (\circ) and $\phi_{ox}^0 + \phi_r^0$ (\circ) for the conjugated aromatic hydrocarbons. The standard deviations σ_r and σ_{ox} of ϕ_r^0 and ϕ_{ox}^0 values of each compound from ϕ_r^0 , $\phi_{ox}^0 - h\nu$ -lines are 0.06 v, and 0.08 v respectively.

Correlation between Polarographic Half-wave Potentials and Spectra for Aromatic Compounds

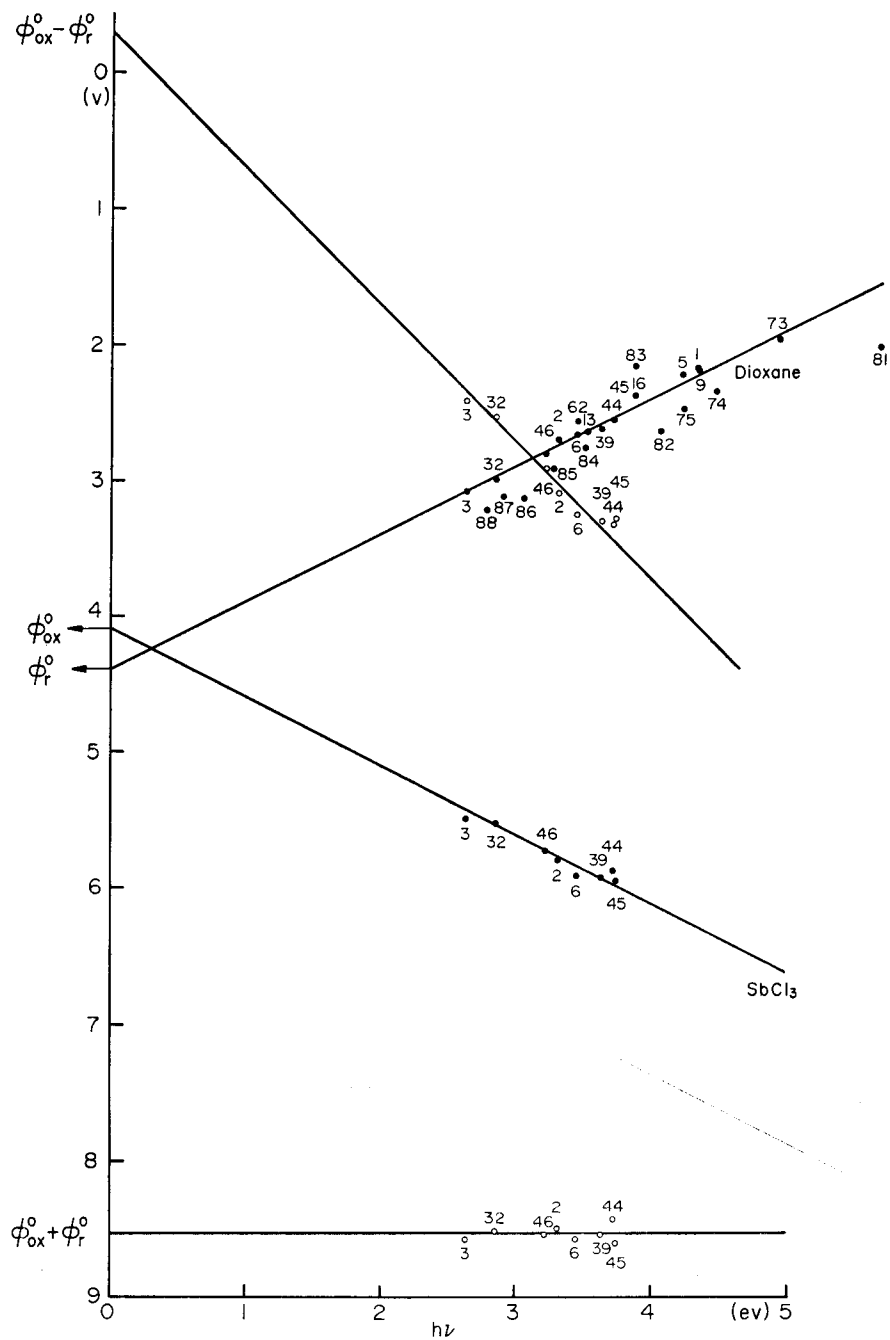


Fig. 2. The $h\nu$ -dependence of ϕ_r^0 in dioxane (\bullet), ϕ_{ox}^0 in $SbCl_3$ (99°C) (\bullet), $\phi_{ox}^0 - \phi_r^0$ (\circ) and $\phi_{ox}^0 + \phi_r^0$ (\circ) for the conjugated aromatic hydrocarbons. $\sigma_r = 0.16$ v, $\sigma_{ox} = 0.05$ v.

However, for some compounds of the perylene, pyrene and fluorane groups and most of fluoranthene group compounds the values of ϕ_r^0 in 2-methoxyethanol for the first polarographic maximum are lower than those in the straight line in Fig. 1. In this case, however, the values of ϕ_r^0 for the second polarographic maximum are found to be in the straight line as shown in Fig. 3. It is noted from Fig. 1 that the values of ϕ_{ox}^0 for ethylene (No. 80) and 1, 3-butadiene (No. 81) in acetonitrile are also found to be in the straight line in Fig. 1.

On the other hand, ϕ_r^0 and ϕ_{ox}^0 for the heterocyclic compounds²²⁾ such as pyridine N-oxide in acetonitrile are rather scattered around the straight lines given by Eqs. (1) and (2), but the difference $\phi_{ox}^0 - \phi_r^0$ practically coincides with $h\nu$ of the p-band of these molecules as seen from Fig. 4. These facts suggest that ϕ_{ox}^0 and ϕ_r^0 correspond respectively to the energy levels of the **HOMO** and **LUMO** of the molecules, but they are not symmetric about the Fermi-level of graphite. It is also found that Eqs. (1) and (2) hold in the case of thiocromone derivatives in methylene chloride, but the sum $\phi_{ox}^0 + \phi_r^0$ is higher than $2\Phi_{gr}$.

The experimental values of **IP** and **EA** in Table 2 are plotted against

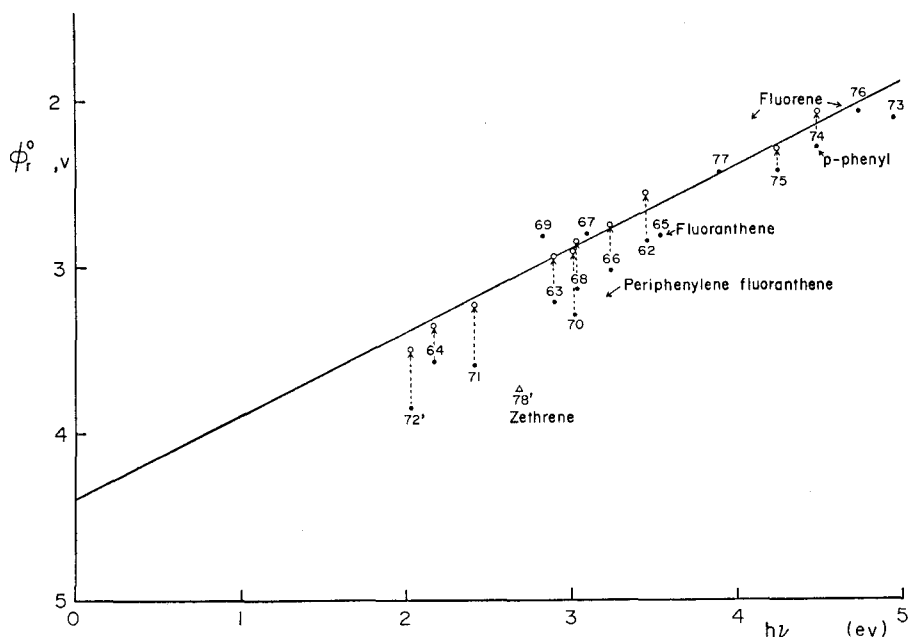


Fig. 3. The $h\nu$ -dependence of ϕ_r^0 in 2-methoxyethanol for fluorene and fluoranthene group compounds. The vertical arrows show the displacement of ϕ_r^0 from the first to the second polarographic maximum.

Correlation between Polarographic Half-wave Potentials and Spectra for Aromatic Compounds

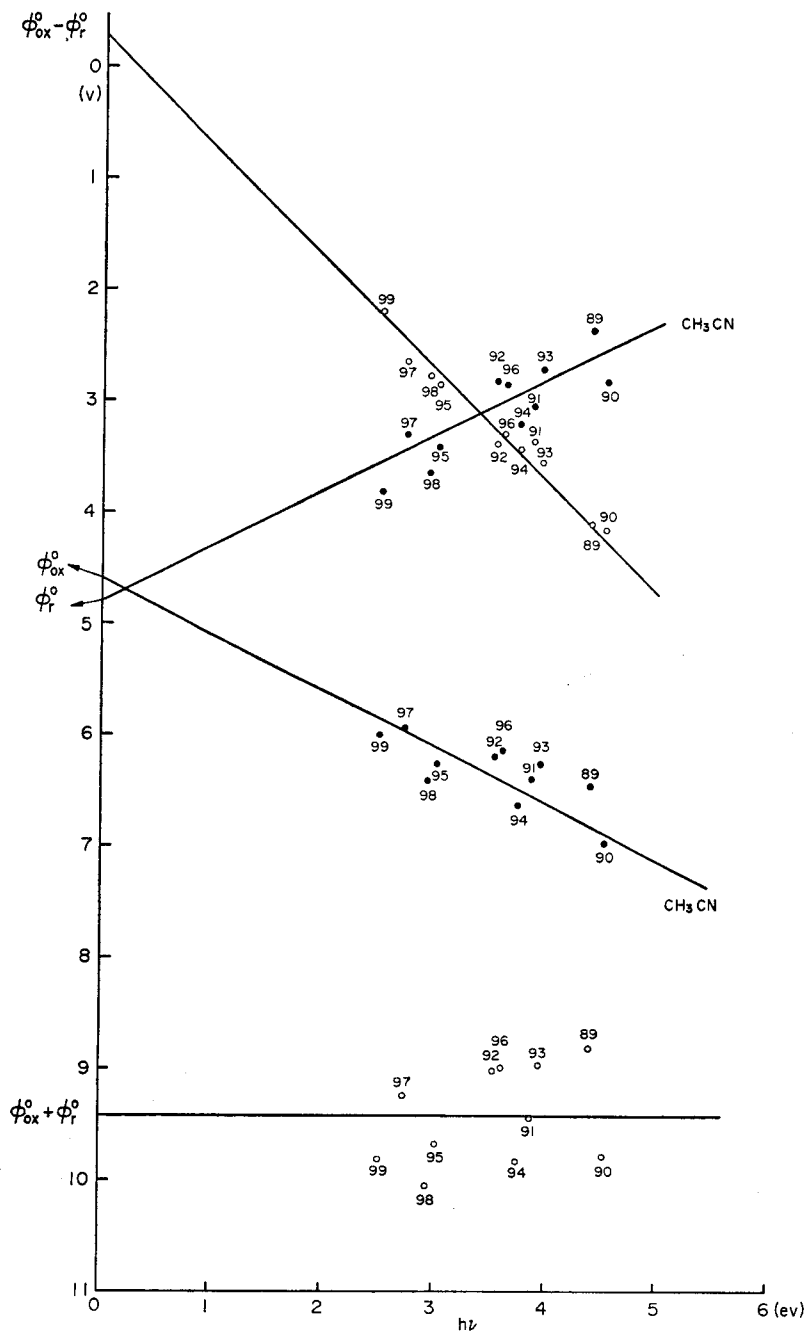


Fig. 4. The $h\nu$ -dependence of ϕ_r^0 (●), ϕ_{ox}^0 (●), $\phi_{ox}^0 - \phi_r^0$ (○) and $\phi_{ox}^0 + \phi_r^0$ (○) for heterocyclic amine N-oxides in acetonitrile²².

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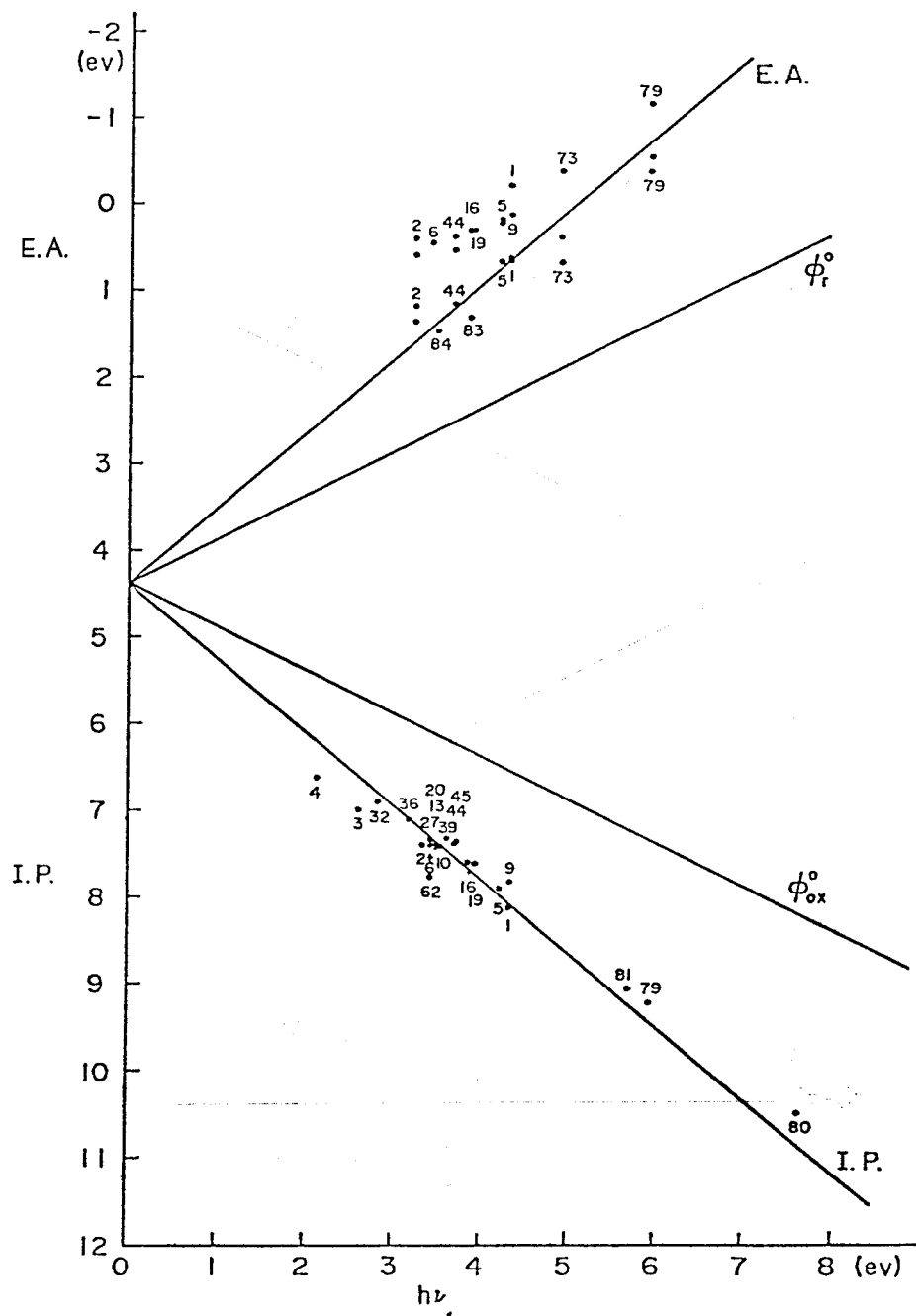


Fig. 5. The $h\nu$ -dependence of the ionization potential and the electron affinity for the conjugated aromatic hydrocarbons.

Correlation between Polarographic Half-wave Potentials and Spectra for Aromatic Compounds

$h\nu$ of the p -band in Fig. 5. As seen from this figure, **IP** vs. $h\nu$ plots can be expressed by the following equation

$$\mathbf{IP} = \Phi_{\text{gr}} + 0.85 h\nu, \text{ ev} \quad (3)$$

while the **EA** vs. $h\nu$ plots are rather scattered as compared with that of the ionization potential. However, it may be reasonable to assume the following relation for the electron affinity of the gaseous conjugated hydrocarbons

$$\mathbf{EA} = \Phi_{\text{gr}} - 0.85 h\nu, \text{ ev} \quad (4)$$

insofar as **IP** and **EA** can be regarded as the energy levels of the **HOMO** and **LUMO** of the gaseous molecule which may be symmetrical about the Fermi-level of graphite.

It may be possible to estimate the standard free energies of solvation of the radical ions of the conjugated aromatic hydrocarbons from the following equations²⁶⁾ together with Eqs. (1)-(4)

$$\mathbf{IP} = \Delta\bar{\alpha}^0 + \phi_{\text{ox}}^0, \text{ ev} \quad (5)$$

$$\mathbf{EA} = -\Delta\bar{\alpha}^0 + \phi_{\text{r}}^0, \text{ ev} \quad (6)$$

where $\Delta\bar{\alpha}^0$ is the difference of the solvation free energies between the radical ion and the neutral molecule of the conjugated aromatic hydrocarbon. It follows from Eqs. (1)-(6) that $\Delta\bar{\alpha}^0$ can be related to $h\nu$ by the equation

$$\Delta\bar{\alpha}^0 = 0.35 h\nu, \text{ ev} \quad (7)$$

independent of the solvent for both cations and anions. The values of $\Delta\bar{\alpha}^0$ estimated in this way are found to be in the range from 0.68 ev for 7, 8-benzoterrylene (No. 42) to 2.68 ev for ethylene (No. 80).

Therefore we can expect that the absolute oxidation and reduction potentials of a given compound of the conjugated aromatic hydrocarbon are independent of the solvent within an accuracy of the present treatment.

References

- 1) A. Maccoll, *Nature*, **163**, 178 (1949).
- 2) G. J. Hoijtink and J. van Schooten, *Rec. Trav. Chem.*, **71**, 1089 (1951) and **72**, 691 (1953); G. J. Hoijtink, J. van Schooten, E. de Boer and W. I. Aalbesberg, *ibid.*, **73**, 355 (1954); G. J. Hoijtink, *ibid.*, **73**, 895 (1954); A. C. Aten, C. Buthker and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959) and A. C. Aten and G. J. Hoijtink, *Z. Phys. Chem.*, **21**, 192 (1959).
- 3) A. Pullman, B. Pullman and G. Berthier, *Bull. Soc. Chim.*, **17**, 591 (1950).
- 4) L. E. Lyons, *Nature*, **166**, 193 (1953).
- 5) A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, J. Wiley and Sons, Inc., New York, 1961.
- 6) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).
- 7) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

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- 8) W. E. Neikam, G. R. Dimeler and H. H. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).
- 9) M. J. S. Dewar, J. A. Hashmall and N. Trinajstic, *J. Am. Chem. Soc.*, **92**, 5555 (1970).
- 10) L. L. Miller, G. D. Noldblom and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972).
- 11) A. T. Watson and F. A. Matsen, *J. Chem. Phys.*, **18**, 1305 (1950).
- 12) H. Lund, *Acta. Chem. Scand.*, **11**, 1323 (1957).
- 13) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).
- 14) E. Clar, *Aromatische Kohlenwasserstoff*, 2nd Ed., Springer-Verlag, Berlin-Göttingen-Heidelberg, 1952.
- 15) Latimer and Slansky, *J. Chem. Phys.*, **7**, 108 (1939).
- 16) A. Braun and G. Bush, *Helv. Phys. Acta*, **20**, 33 (1947).
- 17) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
- 18) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).
- 19) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973); V. D. Parker, *J. Am. Chem. Soc.*, **98**, 98 (1976), **96**, 5656 (1974).
- 20) C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Non-aqueous Systems*, Marcel Dekker, Inc., New York, 1970.
- 21) B. Case, N. S. Hush, R. Parsons and M. E. Peover, *J. Electroanal. Chem.*, **10**, 360 (1965).
- 22) H. Miyazaki, T. Kubota and M. Yamakawa, *Bull. Chem. Soc. Japan*, **45**, 780 (1972).
- 23) R. O. Loutfy, W. J. Still, M. Thompson and T. S. Leong, *Canad. J. Chem.*, **57**, 538 (1979).
- 24) J. E. B. Randles, *Trans. Faraday Soc.*, **52**, 1573 (1956).
- 25) R. Gomer and G. Tryson, *J. Chem. Phys.*, **66**, 4413 (1977).
- 26) A. Matsuda, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **27**, 101 and 167 (1979).
A. Matsuda and R. Notoya, *ibid.*, **28**, 67 (1980).
R. Notoya and A. Matsuda, *ibid.*, **28**, 1 (1980).
- 27) R. C. Rarson, R. T. Iwamoto and R. N. Adams, *Anal. Chim. Acta*, **25**, 371 (1961).
- 28) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, **A174**, 220 (1940).
- 29) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).
- 30) D. Bauer, J. P. Beck and P. Texier, *Collection Czechoslov. Chem. Commun.*, **36**, 940 (1971).
- 31) J. R. Platt, H. B. Klevens and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949).
- 32) M. Fleischmann and D. Pletcher, *Tetrahedron lett.*, **60**, 6255 (1968).
- 33) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **71**, 1396 (1949).
- 34) K. W. Hausser, R. Kuhn and A. Smakula, *J. Physik. Chem.*, **B29**, 384 (1935).
- 35) R. Pointeau, *Ann. Chim.*, **7**, 669 (1962).
- 36) L. Everson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).
- 37) K. Siegbahn and D. A. Allison, *CRC Handbook of Spectroscopy Vol. 1*, Ed. by J. W. Robinson, Section B, *ESCA-Photoelectron Spectroscopy*, CRC Press, Cleveland, 1974.
- 38) N. S. Buchel'nikova, *Usp. Fiz. Nauk*, **65**, 351 (1958).
- 39) I. Nenner and G. J. Schulz, *J. Chem. Phys.*, **62**, 1747 (1975).
- 40) W. Wentworth and R. S. Becker, *J. Am. Chem. Soc.*, **84**, 4263 (1962).
- 41) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 21 (1962).