

methods<sup>9-12</sup>, given in Table 1, shows that the values obtained by us are very close to those obtained by Dewar *et al.*<sup>9</sup> and using IOC- $\omega$  technique<sup>11</sup>, but generally lower than those obtained using semi-empirical SCF-MO method<sup>10</sup> and simplified version of IOC- $\omega$  technique<sup>12</sup>. For molecules for which experimental values of vertical ionization potentials are available the first two methods give very encouraging results, while the latter two generally give high values. Since, in the calculations molecular geometry has been assumed to remain unchanged, these values are the so called vertical ionization potentials and therefore, should be essentially higher than the spectroscopic values<sup>13-15</sup>.

Table 2 reports the heats of formation of some nitrogen containing heterocyclic molecules. Our results are in fair agreement with the experimental values<sup>16</sup> although these are not as good as those obtained by Dewar and Harget<sup>17</sup>.

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### An Improved IOC- $\omega$ Technique: Oxidation & Reduction Potentials & Charge Transfer Energies of Some Conjugated Hydrocarbons

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The polarographic half-wave oxidation and reduction potentials of conjugated hydrocarbons and charge transfer energies of their complexes with iodine have been calculated from the values of ionization potentials and electron affinities calculated using a recently described improved IOC- $\omega$  technique. The results are compared and found to be in good agreement with the experimental values.

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**CORRELATIONS** between the polarographic half-wave reduction potentials ( $-E_{1/2}$  red.) of conjugated hydrocarbons and the lowest unoccupied HMO energies have been described by various workers<sup>1-3</sup>. Similar correlations have also been observed<sup>4-6</sup> between polarographic half-wave oxidation potentials ( $E_{1/2}$  ox.) and energies of highest occupied HMOs. Dewar *et al.*<sup>7,8</sup> have obtained excellent correlations between reduction potentials and electron affinities and oxidation potentials and ionization potentials using a variable  $\beta$ -semi-empirical SCFMO method for hydrocarbons as well as hetero-molecules. Pysh and Yang<sup>6</sup> have calculated ionization potentials of some aromatic hydrocarbons from these correlations and measured values of oxidation potentials. The following relations can be derived theoretically between oxidation and reduction potentials and ionization potentials ( $I$ ) and electron affinities ( $A$ )<sup>6,7</sup>:

$$E_{1/2}(\text{ox.}) = mI + C \quad \dots(1)$$

and

$$-E_{1/2}(\text{red.}) = m'A + C' \quad \dots(2)$$

In a series of charge transfer complexes between a single acceptor and a series of polynuclear hydrocarbons if the interactions between the donor and acceptor are small, the transition energy,  $\Delta E_{CT}$  for the first charge transfer (CT) band should be given by<sup>6</sup>,

$$\Delta E_{CT} = I - A + \text{const.} \quad \dots(3)$$

$I$  is the ionization potential of hydrocarbon and  $A$ , the electron affinity of acceptor molecule. For a given acceptor molecule Eq. (3) becomes:

$$\Delta E_{TC} = I + \text{const.} \quad \dots(4)$$

and a linear plot can be obtained between  $\Delta E_{CT}$  and  $I$ :

$$\Delta E_{CT} = m''I + C'' \quad \dots(5)$$

On the basis of above correlations, we have calculated, in the present paper polarographic half-wave oxidation and reduction potentials of some conjugated molecules and charge transfer transition energies of some iodine-hydrocarbon complexes from the values of ionization potentials and electron affinities, obtained using an improved IOC- $\omega$  technique<sup>9</sup>. Method of calculation and some of the results have already been reported<sup>9,10</sup>. The parameters  $m$  and  $C$  have been obtained by theoretically calculating the slope and intercept respectively of a plot between  $E_{1/2}(\text{ox.})$  (on  $Y$ -axis) and  $I$  (on  $X$ -axis). Similarly parameters  $m'$ ,  $C'$ ,  $m''$  and  $C''$  can also be obtained. Here, we have obtained,  $m = 0.90$ ,  $C = -5.88$ ,  $m' = -0.86$ ,  $C' = 2.07$ ,  $m'' = 1.032$  and  $C'' = -5.098$ .

Polarographic half-wave oxidation and reduction potentials of some conjugated hydrocarbons and charge transfer transition energies of some iodine-hydrocarbon complexes have been compared with respective experimental values<sup>6,11,12</sup> in Table 1. For comparison we have used the values which refer to measurements done under identical experimental conditions for a large number of hydrocarbons, since, although the relative values of oxidation and

TABLE 1 — POLAROGRAPHIC HALF-WAVE OXIDATION AND REDUCTION POTENTIALS OF SOME HYDROCARBONS AND TRANSITION ENERGIES OF THEIR COMPLEXES WITH IODINE

Molecule	I (eV)	A (eV)	$E_{\frac{1}{2}}$ (ox) (V)		$-E_{\frac{1}{2}}$ (red) (V)		$\Delta E_{CT}$ (eV)	
			Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Benzene	9.03	—	2.25	2.30	—	—	4.221	4.184
Naphthalene	8.26	0.27	1.55	1.54	1.84	1.98	3.426	3.452
Anthracene	7.81	0.78	1.15	1.09	1.40	1.46	2.962	2.890
Phenanthrene	8.19	0.28	1.49	1.50	1.83	1.94	3.354	3.288
Chrysene	7.96	0.45	1.28	1.35	1.68	1.81	3.117	3.154
Triphenylene	8.18	0.05	1.48	1.55	2.03	1.97	3.344	3.154
Pyrene	7.86	0.63	1.19	1.16	1.53	1.61	3.014	2.959
Biphenyl	8.29	0.01	—	—	2.06	2.08	3.457	3.654
Stilbene	8.01	—	—	—	—	—	3.168	3.331
Naphthacene	7.52	1.10	0.89	0.77	1.12	1.14	—	—
3,4-Benzphenanthrene	—	0.34	—	—	1.78	1.75	—	—
1,2-Benzanthracene	7.79	0.56	1.13	1.18	1.59	1.53	—	—
Pentacene	—	1.32	—	—	0.93	0.86	—	—
Dibenz-(1,2:5,6)-anthracene	7.87	0.57	1.20	1.19	1.58	1.55	—	—
Dibenz(1,2:7,8)anthracene	7.93	0.61	1.26	1.26	1.55	1.57	—	—
Dibenz(1,2:3,4)anthracene	7.94	0.48	1.27	1.33	1.66	1.54	—	—
Pentaphene	—	0.69	—	—	1.48	1.53	—	—
Perylene	7.55	0.89	0.92	0.85	1.31	1.25	—	—
Benz(4,5)pyrene	7.87	0.51	1.20	1.27	1.63	1.67	—	—
Benz(1,2)pyrene	7.64	0.84	1.00	0.94	1.35	1.36	—	—
Benz(1,12)pyrene	7.71	—	1.06	1.01	—	—	—	—
Coronene	7.88	0.40	1.21	1.23	1.73	1.64	—	—
Anthanthrene	—	1.08	—	—	1.14	1.19	—	—
Benz(1,2:4,5)pyrene	7.69	0.69	1.04	1.01	1.58	1.45	—	—
Dibenz(1,2:6,7)pyrene	—	1.01	—	—	1.20	1.16	—	—
Dibenz(1,2:7,8)pyrene	—	0.90	—	—	1.30	1.32	—	—
Dibenz(4,5:9,10)pyrene	—	0.34	—	—	1.78	1.69	—	—
p-Terphenyl	—	0.23	—	—	1.87	1.91	—	—
p,p'-Diphenyl-biphenyl	—	0.35	—	—	1.77	1.77	—	—
Azulene	7.31	—	0.70	0.71	—	—	—	—
Fluoranthene	8.15	0.87	1.46	1.45	1.32	1.35	—	—
Benz(8,9)fluoranthene	—	0.73	—	—	1.44	1.39	—	—

reduction potentials, etc. seem to be same in different solvents, their absolute values vary<sup>13</sup>. From the table it is clear that our calculated values are in excellent agreement with experimental values.

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#### Exchange of Metal Ions on Dowex A-1(H<sup>+</sup>)

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**Distribution of about forty metal ions between Dowex A-1(H<sup>+</sup>) and aqueous solutions (pH 1.0 to 6.0) in the presence and absence of 1,10-phenanthroline is reported. The data are compared with the results of similar experiments with a carboxylic acid exchanger (Zeo-Karb-226, H<sup>+</sup>).**

**S**ORPTION characteristics of metal ions on Dowex A-1 as a function of pH have been reported<sup>1-4</sup>, employing the exchanger in acid or salt form and adjusting the pH with or without buffers. The pH of decomplexation of some metal ions from the exchanger is also available<sup>5-7</sup>.

Recently, sorption characteristics of about forty cations on a carboxylic acid exchanger (ZeoKarb-226, H<sup>+</sup>) as a function of pH (1.0 to 6.0 without buffers) have been studied in our laboratory<sup>8</sup>. For comparison, the study of sorption of metal ions on Dowex A-1 as a function of pH (ref. 4) has been extended to other cations and the results are reported