

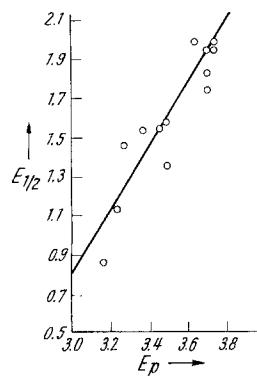
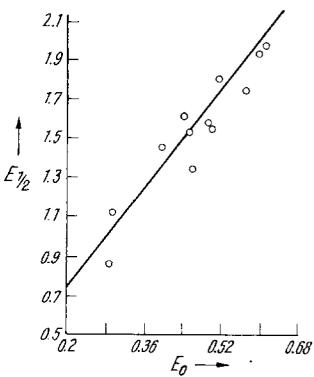
**Reduction Potentials of Conjugated Systems**

In the recent times attempts have been made by various workers to correlate the reduction potentials, especially the polarographic half-wave potentials,  $E_{1/2}$ , of aromatic compounds with their  $\pi$ -electronic energy. Thus MACCOLL<sup>1)</sup> suggested that

Table 1. Half-wave potentials and energy indices of aromatic compounds

Compound	$E_{1/2}$ (volt)	$E_p (\beta)$	$E_0 [(\alpha - \alpha_c)/\beta]$
Naphthalene . . . . .	1.98	3.68 (1—4)	0.618
Anthracene . . . . .	1.46	3.31 (9—10)	0.414
Tetracene . . . . .	1.14	3.25 (5—12)	0.294
Pentacene . . . . .	0.86	3.18 (6—13)	0.219
Phenanthrene . . . . .	1.94	3.77 (1—4)	0.605
3—4 Benzophenanthrene . . . . .	1.75	3.74 (1—4)	0.567
Chrysene . . . . .	1.81	3.74 (1—4)	0.520
1—2 Benzoanthracene . . . . .	1.53	3.41 (7—12)	0.452
Pyrene . . . . .	1.61	4.38 (1—13)	0.445
Triphenylene . . . . .	1.97	3.79 (1—4)	0.684
1:2—3:4 Dibenzanthracene . . . . .	1.54	3.49 (9—14)	0.499
1:2—5:6 Dibenzanthracene . . . . .	1.35	3.51 (7—14)	0.473
1:2—7:8 Dibenzanthracene . . . . .	1.57	3.51 (7—14)	0.491

$E_{1/2}$  should be directly proportional to the energy of the lowest unoccupied orbital of the molecule, while BASU and BHATTACHARYA<sup>2)</sup> noticed a linear relationship between  $E_{1/2}$  and para-localisation energy of a number of aromatic hydrocarbons. MACCOLL's suggestions get support from the fact that in tetrahydro furan mono- and di-negative ions of aromatic compounds are formed in presence of metallic sodium<sup>3)</sup>. It is also equally well established that in the reduction of aromatic hydrocarbons by sodium and alcohol hydrogen addition takes place at the para positions<sup>4)</sup>. KOLTHOFF and LINGANE<sup>5)</sup>

Fig. 1. Para-localisation energy  $E_p$  vs. half-wave potential  $E_{1/2}$ Fig. 2. Lowest empty orbital energy  $E_0$  vs.  $E_{1/2}$ 

have noticed a similarity between sodium-alcohol reduction and polarographic reduction of aromatic hydrocarbons. It is therefore evident that the suggestions of MACCOLL and of BASU and BHATTACHARYA are reasonably justified by experimental facts. Recent publication of the Dictionary of Molecular Constants by COULSON and DAUDEL and the experimental data of the half-wave potentials of a large number of aromatic hydrocarbons<sup>6)</sup> inspired us to analyse the effectiveness of the two methods over a larger number of compounds than has been done so far. In the table 1 are given the half-wave potentials,  $E_{1/2}$ , minimum para localisation energy,  $E_p$ , and the energy of the lowest unoccupied orbital  $E_0$ , for a number of aromatic hydrocarbons. The plot of  $E_{1/2}$  vs  $E_p$  as well as of  $E_{1/2}$  vs  $E_0$  are given in Figs. 1 and 2.

It is evident that only an average linear plot is obtained in both cases and the points are rather widely scattered. As these hydrocarbons undergo irreversible reduction at the dropping mercury electrode, the potential is not associated with a well defined thermodynamic quantity. We can not therefore expect any better agreement between the experimental and theoretical quantity and none of the suggestions can describe the actual situation exactly. MACCOLL's method, however, is applicable to any  $\pi$ -electron system but BASU and BHATTACHARYA's method is possible if and only if the reduction takes place by the para addition of protons. The latter method is an outcome of the attempt to visualise the reduction process as a chemical reaction between molecules and electrons.

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<sup>3)</sup> CHU, T., and S. YU: J. Amer. Chem. Soc. 76, 3367 (1954). — <sup>4)</sup> CLAR, E.: Aromatische Kohlenwasserstoffe. Berlin: Springer 1948. — <sup>5)</sup> KOLTHOFF, I., and J. LINGANE: Polarography, Vol. 2. New York: Interscience Inc. 1952. — <sup>6)</sup> BERGMEN, E.: Trans. Faraday Soc. 50, 829 (1954).