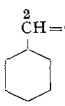
Half-Wave Potentials of Phenyl-substituted Ethylenes

The ethylenic double bonds are not reducible at the dropping mercury electrodes. The phenyl-substituted ethylenes, however, are smoothly reduced, the half-wave potentials are independent of p_H and the mechanism following from the logarithmic analysis of the reduction wave has been suggested for the process:

$$R + e \rightarrow R^{-} \quad \text{(reversible, potential determining)}$$
$$R^{-} + e \rightarrow R^{=} \quad \text{(irreversible, fast).}$$

From the point of view advocated by the authors[1),2)], the half-wave potentials for these systems may be related to the π-electron energy change associated with the localisation of an electron on one of the carbon atoms of the ethylenic double bond. Thus in the case of styrene the localisation may take



place either at carbon atom 1 or at 2. Free radical attack leading to the polymerisation of styrene, usually takes place at position 1. However, SCHLENK and BERGMANN[3)] have shown that in ether medium phenyl-substituted ethylenes react with metallic sodium by the following mechanism:

$$2\,(C_6H_5)_2{-}C{=}CH_2 + 2\,Na \rightarrow 2\,(C_6H_5)_2{-}\underset{\displaystyle Na}{\overset{\displaystyle \cdot}{C}}{-}CH_2\,,$$

where the sodium atom attacks the carbon atom at position 2. As no polymerisation has been reported in the polarographic reduction and as the process simulates the reduction by moist sodium in ether medium, it may be assumed that in the potential determining step electron addition takes place at carbon atom 2. In the Table 1 are summarized the localisation energy calculated by M. O. method for a number of phenyl-substituted ethylenes along with their half-wave potentials.

In styrene $L(-\beta)$ refers to energy necessary to localize an electron at carbon atom 2, in stilbene at either of the carbon atoms 1 or 2 and in diphenyl butadiene at the carbon atom 1 or 4. From the table it is evident that there is a good parallelism between $E_{\frac{1}{2}}$ and $L(-\beta)$ for styrene-stilbene-diphenyl butadiene systems as expected from the localisation theory. For 1,1-diphenyl ethylene-triphenyl ethylene-tetraphenyl ethylene systems also a parallelism exists between $E_{\frac{1}{2}}$ and $L(-\beta)$, but the two systems are not comparable as regards the absolute magnitude of $L(-\beta)$. In fact this is not very unexpected. In the M. O. calculation for the second series of compounds we have assumed the molecule to be planar which they cannot possibly be due to steric restriction. The calculation therefore refers to certain hypothetical molecules and although the variation of $L(-\beta)$ may be in the right sequence, their absolute magnitude cannot be taken too seriously.

In the last column of the Table 1 are given the energy values, E_m, of the first empty M. O. which according to

Table 1. *Localisation energy and half-wave potentials of substituted ethylenes*

Compounds	$E_{\frac{1}{2}}$ (S.C.E.)[5)]	$L(-\beta)$	$E_m\,[(\alpha+\alpha_c)/\beta]$
Styrene	2·35	2·42	0·662
Stilbene	2·26	2·16	0·504
1—4 diphenyl butadiene	1·98	2·02	0·386
1—1 diphenyl ethylene	2·14	2·81	0·565
Triphenyl ethylene	2·11	2·57	0·437
Tetraphenyl ethylene	2·05	2·42	0·368

MACCOLL[4)] should be related to $E_{\frac{1}{2}}$ of the respective compound. It is evident that the parallelism between $E_{\frac{1}{2}}$ and E_m is equally good for these systems.

It seems therefore that for most of the systems analysed by us[1),2)], the localisation method and MACCOLL's method lead to the same conclusion. The two methods are therefore not antagonistic as they appear at first sight.

Department of Chemistry, University College of Science, 92 Upper Circular Road, Calcutta-9, India

(Miss) RAMA BHATTACHARYA and SADHAN BASU

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