COGITATIONES

# The Specificity of Reactions of Polycyclic Aromatics

## II. Polarographic Reductions[1]

By F. T. Wallenberger[*]

Polarographic reductions of polycyclic aromatic hydrocarbons have been studied extensively by Wawzonek[2,3] and by Bergman[4]. Wawzonek was primarily interested in the mechanism of the reduction of conjugated and aromatic systems at the dropping mercury electrode and has related[3] polarography to addition of alkali metals to polycyclic aromatics. Bergman[4] has reported half-wave potentials ($E_{1/2}$) of 75 polycyclic aromatic hydrocarbons. In the quest for a theoretical assessment of his extensive experimental study he has attempted to correlate graphically the number of $\pi$-electrons per molecule and the wave lengths of para-bands[5] in the UV spectra with the half-wave potentials.

While Wawzonek's mechanism studies and Bergman's experimental contributions are of extreme significance to the chemistry of polycyclic aromatics, it appears that Bergman's theoretical correlation is of limited validity and open to criticism.

The para-bands (also known as *p*-, group II-, primary, and $L_a$-bands)[6] as classified and defined by Clar[4,5] have been attributed to meso-C-atoms or, in other words, to excitations of para positions of these molecules in the UV spectra. Assuming this being so, Bergman's correlations should not have included data derived from 1,2-(bond) reactions (phenanthrene, chrysene, etc.) but only compounds which are clearly reduced by 1,4-(conjugate) addition. There is furthermore also a certain ambiguity about the band assignments themselves.

Thus it appears that a general and comparative correlation of polarographic reductions of polycyclic aromatics has to be attempted on a different basis.

*Table I*
Specificity of Polarographic Reductions of Polycyclic Aromatics

| Hydrocarbon in C. A. numbering and nomenclature | Reduction[a] Potential $E_{1/2}$ |  | Diffusion[b] Current $i_d$ |  | Resonance[c] Energy |  | Positions of Preferred Reduction |
|---|---|---|---|---|---|---|---|
|  | 1st | 2nd | 1st | 2nd | Positions | kcal. |  |
| Naphthalene | 1·98 |  | 5·5 |  | 1,2 | 20·0 | 1,2; 1,4[2–4, e] |
|  |  |  |  |  | 1,4 | 27·6 |  |
| Anthracene | 1·46 |  | 3·3 |  | 1,2 | 20·0 | 9,10[3,4] |
|  |  |  |  |  | 1,4 | 25·6 |  |
|  |  |  |  |  | 9,10 | 15·6 |  |
| Naphthacene | 1·135 | 2·02 | 1·51 | 1·47 | 1,2 | 19·5 | 5,12[4] |
|  |  |  |  |  | 1,4 | 24·6 |  |
|  |  |  |  |  | 5,12 | 13·6 |  |
| Pentacene | 0·86 | 1·92 | 0·053 | 0·094 | 1,2 | 19·4 | 6,13[4] |
|  |  |  |  |  | 1,4 | 24·6 |  |
|  |  |  |  |  | 5,14 | 13·6 |  |
|  |  |  |  |  | 6,13 | 11·6 |  |
| Phenanthrene | 1·935 | 2·125 | 3·4 | 3·9 | 1,2 | 23·9 | 9,10[2–4] |
|  |  |  |  |  | 3,4 | 24·4 |  |
|  |  |  |  |  | 1,4 | 29·6 |  |
|  |  |  |  |  | 9,10 | 16·2 |  |
| Chrysene | 1·805 | 2·165 | 5·5 | 2·9 | 1,2 | 23·6 | 5,6[2,4] |
|  |  |  |  |  | 3,4 | 23·3 |  |
|  |  |  |  |  | 5,6 | 18·1 |  |
|  |  |  |  |  | 1,4 | 28·6 |  |
| Dibenz(a, h)anthracene | 1·545 | 1·97 | 1·85 | 4·3 | 5,6 | 15·7 | 5,6[4] |
|  |  |  |  |  | 7,12 | 22·6 |  |
| Pyrene | 1·61 | 1·70 | 3·25 | 3·3 | 4,5 | 16·0 | 4,5[3,4] |
|  |  | (1·80)[d] |  |  |  |  |  |
| Benz(a)pyrene | 1·36 | 1·59 | 2·15 | 2·35 | 1,2 | 17·6 | 6,7[3,4, f] |
|  |  | (1·89)[d] | (1.45)[d] |  | 6,7 | 14·8 |  |
| Triphenylene | 1·97 |  | 8·84 |  | 1,2 | 25·8 | 1,2[4] |
|  |  |  |  |  | 2,3 | 32·1 |  |
|  |  |  |  |  | 1,4 | 30·0 |  |

[a] From reference [4]; [b] from reference [4] ($i_d = I_d/\mathrm{cm}^{2/3}\, t^{1/6}$); [c] obtained or calculated from data contained in references [8,9], and [10]; [d] third wave; [e] the 1,2-dihydro T. S. is theoretically favored; [f] the possibility of 1,6-additions in polarographic reductions is under consideration.

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In pursuit of an earlier suggestion of MACCOLL[7] involving relationships with the coefficient of the molecular orbital resonance energy integral, it will now be attempted to correlate the specificity and ease of polarographic reductions of polycyclic aromatics with theoretical resonance energy decreases accompanying the reaction.

Having found that the reactions proceed by 1,2-(bond) and 1,4-(conjugate) addition, it appears that the preferred type of reaction, like in ozonizations of polycyclic aromatics[1], depends upon the relative stability of various possible ortho and para dihydroaromatic intermediates and products. These relative stabilities can be assessed from resonance energies which have been calculated[8] for ortho positions of a large number of polycyclics and which are easily computed for para positions of these compounds from para-localization energies[9] according to a suggestion of WHELAND[10].

Table I comprises such a correlation of resonance energies, first half-wave potentials, and preferred course of polarographic reduction of a representative number of individual hydrocarbons.

In general it can be seen that reaction occurs preferentially at positions of lowest resonance energy values. References indicate wherever products have been studied experimentally[2] or where the significance of first and subsequent waves has been rigorously assessed in terms of first reaction step and further reduction of the primary reaction products[3].

The course of the preferred polarographic reduction with naphthalene is not entirely clear. Alkali metals are added predominantly by 1,4-addition, and electrolytic reduction in the presence of $CO_2$ gave reportedly both 1,2- and 1,4-dicarboxylic acid; only the latter was definitely isolated[2]. It seems that electronic repulsion and steric substituent effects favor 1,4-addition despite the more stable 1,2-dihydro transition state. This assumption is substantiated by the ease of rearrangement of 1,4- into 1,2-dihydronaphthalene[11].

In more complex polycyclic aromatic hydrocarbons (e.g. benz(a)pyrene, perylene, etc.) it was found that 1,6-oxidations occur readily with various oxidants[5] as well as with oxygen, catalyzed by 2–4% ozone[12]. This suggests that the 1,6-quinoid (dihydro) structures of these compounds are relatively more stable under given conditions than their 1,4- and 1,2-quinoid (dihydro) structures. Correspondingly one might also expect 1,6-reactions from polarographic reductions. The resonance energies (if calculated to apply to such conditions) then likewise are lower than the resonance energy decreases calculated for the most favored 1,4- and 1,2-positions.

The presented correlation for the first time explains why polarographic reductions proceed predominantly by 1,2-(bond) addition with some polycyclic aromatics and by 1,4-(conjugate) addition with others. The resonance energy correlation can be extended to compounds[4,8–10] not listed in this communications.

Furthermore, it is now also possible to assess the order of relative reactivity towards reduction (Table II) of the polycyclic aromatics listed in Table I, with pentacene as most reactive and triphenylene as least reactive. There is a linear relationship for para-reductions while the relationship for ortho-reductions rapidly levels off to a constant value 2·00 ± 20.

*Table II*

Reactivity of Polycyclic Aromatic towards Polarographic Reduction

| Hydrocarbon in C. A. numbering and nomenclature | Reactive Positions | | Resonance[a] Energy | | Reduction[b] Potential | |
|---|---|---|---|---|---|---|
| | para | ortho | para | ortho | para | ortho |
| Pentacene . . | 6,13 | | 11·6 | | 0·86 | |
| Naphthacene . | 5,12 | | 13·6 | | 1·135 | |
| Benz(a)pyrene . | | 6,7[c] | | 14·8 | | 1·36 |
| Anthracene . . | 9,10 | | 15·6 | | 1·46 | |
| Dibenz(a,h) anthracene . | | 5,6 | | 15·7 | | 1·545 |
| Pyrene . . . . | | 4,5 | | 16·0 | | 1·61 |
| Phenanthrene . | | 9,10 | | 16·2 | | 1·935 |
| Chrysene . . . | | 5,6 | | 18·6 | | 2·165 |
| Naphthalene . | | 1,2[d] | | 20·0 | | 1·98 |
| Triphenylene . | | 1,2 | | 25·8 | | 1·97 |

[a] Obtained or calculated from data contained in references [8,9] and [10]. – [b] From reference[4]; [c] see footnote b in Table I; [d] the 1,2-dihydro T. S. is theoretically favored.

Thus it has been shown that it is possible to predict the specificity of polarographic reductions and to account for the relative reactivity of polycyclic aromatics towards reactions at the dropping mercury electrode.

## *Zusammenfassung*

Die polarographische Reduktion polyzyklischer aro matischer Verbindungen kann als 1,2-, 1,4- oder 1,6 Addition erfolgen. Der Verlauf der Reaktionen lässt sic aus der Abnahme der Resonanzenergie ableiten.

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