364. *A Theoretical Treatment of the Diels–Alder Reaction. Part III.* Equilibria for Aromatic Hydrocarbons.*

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The localization theory of the Diels-Alder reaction, developed in Parts I and II (*J.*, 1950, 691, 2730), is applied to the equilibrium set up between some anthracene derivatives and maleic anhydride. It is shown that equilibria relative to a reference hydrocarbon can be predicted quantitatively for rigid, conjugated systems, energies being computed by the usual L.C.A.O. approximation including overlap. Neglect of overlap materially affects the agreement. The effect of some neglected factors upon the accuracy of the present theory is discussed.

In Parts I and II (*J.*, 1950, 691, 2730) the localization theory of organic reactions was used to discuss the Diels-Alder properties of polycyclic hydrocarbons and arylpolyenes. Particularly in the case of the former it was shown that the para-localization energies were in excellent accord with the observed reactivities, but attention was directed mainly to experimental data which probably indicated rates of reaction. It will now be shown that quantitative agreement with experiment is obtained for the Diels-Alder equilibria which are set up by many polycyclic aromatic hydrocarbons (Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 481).

The simplifying assumptions made when considering relative rates of reaction (Parts I and II) are equivalent to supposing that the entropy of activation remains constant. Similarly, for the present considerations of equilibria we may suppose, in the absence of more detailed information, that the entropy of reaction is substantially independent of the hydrocarbon involved, differences in the free energy of reaction for different hydrocarbons being predominantly due to differences in the heats of reaction. This is the more likely if the hydrocarbons have similar structures, which indeed is true of the compounds considered below.

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* Part II, *J.*, 1950, 2730.

In good approximation, the differences in the heats of reaction will be represented by differences in para-localization energies, so we may write

$$\Delta G - \Delta G_0 = P - P_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

which of course is equivalent to a description of the equilibria in terms of the changes in resonance energies. The validity of this equation, when P and P_0 are computed by the L.C.A.O. approximation, may be tested by use of Bachmann and Kloetzel's data (*loc. cit.*) for the % adduct in equilibrium with the hydrocarbon and maleic anhydride. Their experimental results are reproduced in Table I. The concentration, which enters into the equilibrium constant owing to the different numbers of reactant and product molecules, has been computed by assuming that all solutions were equimolar in the reactants and contained 0·1 g. of hydrocarbon in 2 ml. of solvent, as mentioned by Bachmann and Kloetzel. Unfortunately these authors give no indication of the precision with which the solutions were prepared.

TABLE I.

Hydrocarbon.	Molar concn., c.	Molar fraction of adduct at equilibrium, x.	d(ln K)/dx.*
Anthracene	0·28	0·99	95
1 : 2-Benzanthracene	0·22	0·84	13
1 : 2-5 : 6-Dibenzanthracene	0·18	0·30	6·2

T = ca. 140°; $\boldsymbol{R}T$ = 0·82 kcal.

* $K = \dfrac{x}{c(1-x)^2}$.

Dibenzanthracene was chosen as standard since for it d(ln K)/dx has the smallest value so that a given error in x_0 will produce the smallest relative error in K. Values of x for the other hydrocarbons were computed by use of equation (1) and the thermodynamic relation $\boldsymbol{R}T \ln (K/K_0) = \Delta G_0 - \Delta G$. The values of P and P' (for symbolism see Part I) were converted into kcals. by use of the values previously used (Part II), *i.e.*, $\beta = -17._1$ kcal., $\gamma = -33._6$ kcal.

The relevant values of the para-localization energies and the equilibrium molar fractions of adduct, $x(p)$, $x(p')$, calculated by using dibenzanthracene as standard are listed in Table II.

TABLE II.

Hydrocarbon.	p.	p'.	$x(p)$.	$x(p')$.	$x_{\text{exp.}}$.
Anthracene	3·3137	2·0744	$0{\cdot}87_3$	$0{\cdot}97_9$	0·99
Benzanthracene	3·4180	2·1729	$0{\cdot}65_5$	$0{\cdot}83_5$	0·84
1 : 2-5 : 6-Dibenzanthracene	3·5140	2·2630	(0·30)	(0·30)	0·30
1 : 2-3 : 4-Dibenzanthracene	—	2·2442	—	0·42	—
1 : 2-7 : 8-Dibenzanthracene	—	2·2618	—	0·31	—
Naphthalene	—	2·3964	—	$0{\cdot}005_6$	—

$p = -P/\beta$. $p' = -P'/\gamma$.

It is evident that $x(p)$ is only qualitatively in agreement with experiment. On the other hand $x(p')$ is in good *quantitative* accord with $x_{\text{exp.}}$, the experimental uncertainty in the latter, according to Bachmann and Kloetzel, being 0·01—0·02.

Further corroborative evidence for the surprising precision of the L.C.A.O. approximation for the ground states of conjugated hydrocarbons, the overlap integral being retained for nearest neighbours, is found in a study of the relative rates of addition of osmium tetroxide to aromatic hydrocarbons (Brown, *J.*, 1950, 3249).

It would of course be desirable to extend the comparison with experiment to further polycyclic hydrocarbons. With this in view values of $x(p')$ for naphthalene and two additional dibenzanthracenes are given in Table II, the results applying to the experimental conditions employed by Bachmann and Kloetzel. As mentioned below, naphthalene may not prove as satisfactory as the other hydrocarbons because the adduct will contain an isolated double bond in place of an aromatic system in the other adducts.

The Effects of Errors in x_0 *and* $p_0' - p'$.—The calculated values of $x(p')$ in Table II will of course be affected by errors in the theoretical calculation of $p_0' - p'$, and by any error involved in taking x_0 as 0·30. Values of dx/dx_0 and dx/d($p_0' - p'$) are given in Table III for the compounds listed in Table II.

TABLE III.

Hydrocarbon.	dx/dx_0.	dx/d($p_0' - p'$).	Hydrocarbon.	dx/dx_0.	dx/d($p_0' - p'$).
Anthracene	$0{\cdot}06_5$	0·43	1 : 2-3 : 4-Dibenzanthracene	1·1	7·0
Benzanthracene	$0{\cdot}4_7$	3·1	1 : 2-7 : 8-Dibenzanthracene	1·0	6·7
Naphthalene	0·03	0·23			

It is seen from Table III that in order to obtain agreement between $x(p')$ and $x_{\text{exp.}}$ to 0·01, the quantity $p_0' - p'$ must be correct to 0·02 for anthracene and 0·003 for benzanthracene. When it is recalled that p_0' and p' are calculated as differences in π-electron energies, which for dibenzanthracene are of the order of 20 (in units of γ), the self-consistency of the L.C.A.O. calculations required to obtain the agreement found in Table II seems quite extraordinary.

Factors Neglected in the Present Treatment.—The localization treatment of the Diels–Alder reaction does not distinguish between *endo*- and *exo*-forms of the adduct with respect to equilibrium concentrations (or rates of formation). However, it is often the case that one stereoisomer is formed exclusively, indicating that factors not so far taken into account in the localization theory can be decisive in determining the relative rates of formation of the two possible products. It seems certain that the difference in stability of the two stereoisomers is due to induction forces of the type responsible for molecular binding between aromatic compounds and polynitro-compounds (Briegleb, "Zwischenmolekulare Kräfte und Molekülstrüktur," Enke, 1937).

When the diene is a polycyclic hydrocarbon the relative stabilities of the two stereoisomers will be determined by the difference in interaction energy of the maleic anhydride multipole and the two smaller cyclic systems on either side of the ring undergoing addition. Since induction forces fall off very rapidly with distance the interactions will be very similar even when the cyclic systems are rather different (*e.g.* benzene and anthracene). The present results and the qualitative success of the theory for polycyclic systems (Part I) support this conclusion.

However, in the case of 1 : 4-addition to naphthalene, for example, in the *endo*-form the interaction is between the maleic anhydride residue and benzene, whilst in the *exo*-form it is between the maleic anhydride residue and ethylene. Here some difference in energy might be expected. For this reason naphthalene may not prove as useful a test of the quantitative agreement between theory and experiment as larger polycyclic hydrocarbons. The variation in induction forces may also be important in arylpolyenes, such as those considered in Part II, and for this reason the localization theory may not prove so successful for these compounds even when the difficulties associated with partial rotation about bonds of low mobile order are resolved.

Another factor neglected in the present treatment is the variation of the resonance integral with bond order. In the case of polycyclic hydrocarbons this variation is not so important because the variation in mobile order is not very great, but in the case of polyenes and arylpolyenes the variation is greater. The allowance for this variation in the calculation of π-electron energies is very tedious and it seems important to establish first how reliable are the present simplified molecular-orbital calculations by further quantitative investigations of equilibria before introducing further refinements into the theoretical treatment.

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