

# TOWARDS A UNIFIED THEORETICAL TREATMENT OF THE TRANSITION STATE IN THE REACTIONS OF UNSATURATED MOLECULES—III A STUDY OF TWO PHOTOCHEMICAL REACTIONS

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**Abstract**—The experimental results concerning the photodeuteration of various benzene derivatives and the photooxidation of a series of acenes are found to be explicable by means of the delocalized transition state model.

SURPRISINGLY little work has been done to apply theoretical chemistry to the chemical reactivity of aromatic molecules in their excited states. Most of these attempts have been based upon the same static and dynamic indices used to predict the chemical reactivity of aromatic molecules in their ground states.<sup>1</sup> However, the only dynamic index used so far has been the Wheland model of the transition state. In this paper, we wish to report the application of the delocalized model of the transition state developed in part I<sup>2</sup> to the problem of photodeuteration and photooxidation of aromatic molecules.

## I. Photodeuteration

De Bie and Havinga<sup>3,4</sup> studied experimentally and theoretically the photodeuteration of nitrobenzene, anisole, and *m*- and *p*-nitroanisole in various deuterating media such as CH<sub>3</sub>CO<sub>2</sub>D, CF<sub>3</sub>CO<sub>2</sub>D and CF<sub>3</sub>CO<sub>2</sub>D + H<sub>2</sub>SO<sub>4</sub>. The deuterium content of the products was determined by NMR. To distinguish between the *ortho*, *meta* and *para* positions in the deuterated product, anisole was converted into 2,4-dibromoanisole and nitrobenzene into *m*-dinitrobenzene.

In the reaction in the dark, nitrobenzene is unreactive while the other compounds exhibit the classic electrophilic substitution pattern of *ortho/para* activation by the OMe group. For this reaction De Bie and Havinga found that calculations based on the Wheland model or the  $\pi$ -electronic charges, using the appropriate phenol rather than the anisoles as a model, both gave good agreement with the experimental results.

The situation is very different in the case of the smooth reaction which takes place in the presence of light. Here only the  $\pi$ -electronic charges are in agreement with the experimental results. Consequently we are led to the conclusion that the Wheland

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model does not correspond to a good description of the transition state in the photo-deuteration reaction. Therefore it seemed worthwhile to see if the delocalized model is a better description of the transition state in this photochemical reaction.

The use of the delocalized model to represent the transition state involves the introduction of molecular orbitals of the type:

$$\Phi = \lambda\gamma + \sum_1 u_1 \phi\pi_1$$

where  $\gamma$  denotes the electronic distribution near the attacking reagent which in this case is a deuteron. Obviously this function depends upon the position of the reagent with respect to the conjugated molecule and also on the position of the various molecules of solvent surrounding the site of reaction. Therefore the integral:

$$\alpha_D = \langle \gamma | H^{SCF'} | \gamma \rangle$$

will vary continuously during the course of the reaction.

Since the aromatic molecule is assumed to be in first excited state, it is usually represented in the MO approximation by determinants containing the lowest unoccupied MO of the ground state. The delocalized electron energy calculated from these determinants is the initial state energy  $E_1$ . In the transition state of the photo-deuteration reaction, the activated complex is also assumed to be in its first excited state and consequently it too can be represented by determinants containing the lowest unoccupied MO's of the activated complex. The delocalized electron energy calculated from these determinants is the energy of the transition state  $E_{TS}$ .

The difference in energy,  $\Delta E^{\ddagger}(r)$ , between the electron energy of the transition state  $E_{TS}$  and  $E_1$ , the energy of the initial state, is the stabilization energy resulting from the extension of delocalization on to the attacking reagent. This stabilization energy  $\Delta E^{\ddagger}(r)$  will be particularly great when  $\alpha_D$  has a value identical to that associated with the lowest unoccupied MO of the ground state of the conjugated molecule.<sup>5</sup> When these values are identical the resonance phenomenon is at a maximum. The corresponding value of  $\Delta E^{\ddagger}(r)$  can be considered as a dynamic index. It is not necessarily associated with a potential barrier but it can give an idea of the negative of the slope of the energy surface at the beginning of the reaction path.

Since De Bie and Havinga used phenol, *p*-nitro and *o*-nitrophenol as model compounds to calculate  $\pi$ -electronic charges, calculations of  $\Delta E^{\ddagger}(r)$  were carried out on these three compounds to make our results comparable.

The calculated values of  $\Delta E^{\ddagger}(r)$  are compared with the experimental results reported by De Bie and Havinga in Table 1 for phenol, *p*-nitrophenol and *o*-nitrophenol using the Hückel approximation with the following parameters:

$$\beta_{C-D} = 0.2\beta^{\circ}$$

$$\beta_{C-O} \text{ (phenol)} = 0.5\beta^{\circ}$$

$$\beta_{C-N} \text{ (nitro)} = 0.61\beta^{\circ}$$

$$\beta_{N-O} \text{ (nitro)} = 1.26\beta^{\circ}$$

$$\alpha_O \text{ (nitro)} = \alpha^{\circ} + 1.14\beta^{\circ}$$

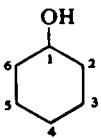
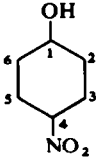
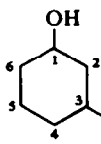
$$\alpha_N \text{ (nitro)} = \alpha^{\circ} + 0.68\beta^{\circ}$$

$$\alpha_O \text{ (phenol)} = \alpha^{\circ} + 1.7\beta^{\circ}$$

The accord between  $\Delta E^{\ddagger}(r)$  and the experimental results is satisfactory, indicating that the delocalized model is a good one to represent the transition state of photo-deuteration.

It can be seen from the results in Table 1 that  $\Delta E^{\ddagger}(r)$  and the  $\pi$ -electron charge of the first excited state predict the same results except in the case of the 4-position of *m*-nitrophenol where an inversion occurs. Unfortunately, a choice between the two models cannot be made due to the experimental difficulties involved in determining the percent deuterium uptake in the 2, 5 and 4-positions of *m*-nitroanisole.<sup>3</sup>

TABLE 1. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS OF THE PHOTODEUTERATION OF PHENOL, *m*- AND *p*-NITROPHENOL

Compound	Position	$\Delta E^{\ddagger}(r)$	$\pi$ -electron charge <sup>a</sup> in first excited state	Wheland localization Energies <sup>a</sup>	Percent deuterium uptake after 4 h <sup>a</sup>
	2	0.125	-0.093	-0.078	7.5
	3	0.127	-0.087	-0.136	8.0
	4	0.110	+0.051	-0.182	<1.0
	2	0.065	-0.025		6
	3	0.090	-0.007		6
	6	0.1	-0.014		9
	2	0.09	-0.009		small
	5	0.07	+0.027		small
	4	0.08	+0.108		small

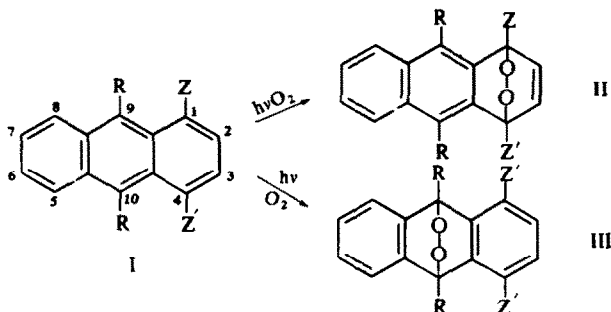
It is interesting to note that an approximate expression of  $\Delta E^{\ddagger}(r)$  can be calculated by an extension of the perturbation method suggested by Dewar<sup>6</sup> and Longuet-Higgins.<sup>7</sup> It can readily be shown<sup>8</sup> that:

$$\Delta E^{\ddagger}(r) = |C_r| \beta_{C-D}$$

where  $C_r$  is the coefficient of the atomic orbital at the position of attack in the lowest unoccupied orbital in the ground state of the molecule. This formula shows that as a first approximation the order of the  $\Delta E^{\ddagger}(r)$  is independent of the choice of the parameter  $\beta_{C-D}$ .

## II. Photooxidation

It is well known that certain aromatic compounds containing a naphthalene or an anthracene nucleus when irradiated add a molecule of oxygen.<sup>9</sup> In particular the photooxidation of substituted anthracenes has been extensively studied<sup>10</sup> and it has been found that the addition of oxygen can take place to give the 1,4-adduct (II), the 9,10-adduct (III) or both depending upon the nature of the substituents.



This reaction is believed to be a photosensitized autooxidation in which anthracene acts as a sensitizer to produce a singlet oxygen which adds to the anthracene in its ground state. Thus the photooxidation of anthracene A can be summarized by the following set of equations:



This last step in the photooxidation mechanism is considered to be a diene synthesis in which the singlet oxygen acts like a dienophile.<sup>11</sup>

Attempts to interpret the effect of substituents upon the position of addition of oxygen to anthracene using the Wheland model or an intermediate complex similar to the initial state, gives unsatisfactory results.<sup>12</sup> The use of the delocalized model, on the other hand, provides an excellent agreement between theory and experiment. In this paper, we wish to report the extension of this model to other substituted anthracenes and naphthalenes.

Since the photooxidation reaction is believed to occur between singlet oxygen, whose electrons are paired and a molecule of anthracene in the ground state, with all electrons paired, it follows that in the activated complex all electrons must also be paired. Thus the electron energy of the activated complex is obtained by summing the energies of all the doubly occupied orbitals. This differs from the photodeuteration where the activated complex and the initial molecule contain unpaired electrons. Thus while this oxidation is photo induced, the simple Hückel method used here treats the reaction as though it were a ground state reaction.

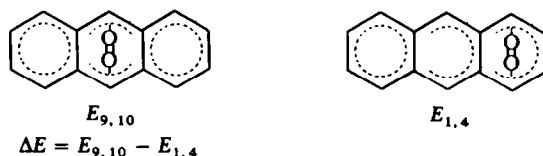
It is assumed that the products are formed by kinetic control and as a result the amounts of each isomer are proportional to the difference in the delocalized electron energies of the transition state leading to each isomer. The delocalized electron energies of the transition states of the isomers were calculated using the Hückel approximation as described in Part I<sup>1</sup> with the following parameters:

$$\begin{aligned} \alpha_O &= \alpha^\circ + \beta^\circ & \beta_{OO} &= 0.8\beta^\circ & \beta_{O-C} &= 0.3\beta^\circ \\ \alpha_{O-CH_3} &= \alpha^\circ + 1.2\beta^\circ & \beta_{C-OCH_3} &= \beta^\circ \\ \alpha_{N(CH_3)_2} &= \alpha^\circ + 0.50\beta^\circ & \beta_{CN} &= 1.2\beta^\circ \end{aligned}$$

The calculated value  $\Delta E^*$  is the difference between the electron energies (in units of  $\beta$ )

\* This  $\Delta E$  is related to the  $\Delta E_i^\ddagger$  of Ref 12 in the following way:  $\Delta E = \Delta E_i^\ddagger(9, 10) - \Delta E_i^\ddagger(1, 4)$ . The values of  $\Delta E_i^\ddagger$  for anthracene and 1,4-dimethoxyanthracene reported in Ref 12 are incorrect due to typographical errors.

of the delocalized model of the transition state of the 9, 10-adduct and the 1,4-adduct. In the case of the naphthalene derivatives,  $\Delta E$  is the difference between the electron energies of the transition state of the 5,8-adduct and the 1,4-adduct.



Thus, if  $\Delta E$  is positive the 9,10-adduct (or the 5,8-adduct in the case of the naphthalene derivatives) is predicted to be the product while if  $\Delta E$  is negative, the 1,4-adduct is the predicted product.

The theoretical and experimental results of the photooxidation of substituted anthracenes and naphthalenes are given in Table 2 and 3. The agreement between

TABLE 2. EXPERIMENTAL AND THEORETICAL RESULTS OF THE PHOTOOXIDATION OF SUBSTITUTED ANTHRACENES

R	Z	Z'	Y	Y'	$\Delta E$ (in units of $\beta$ )	% 9, 10	% 1, 4
H	H	H	H	H	+0.054	100	0
C <sub>6</sub> H <sub>5</sub>	H	H	H	H	+0.058	100	0
H	OCH <sub>3</sub>	OCH <sub>3</sub>	H	H	-0.030	0	100
C <sub>6</sub> H <sub>5</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	H	H	-0.040	0	100
C <sub>6</sub> H <sub>5</sub>	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	+0.026	100	0
C <sub>6</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	H	H	H	-0.024	0	100
C <sub>6</sub> H <sub>5</sub>	Cl	Cl	H	H	+0.050	100	0

\* Full details of this reaction will be the subject of a future publication.

TABLE 3. EXPERIMENTAL AND THEORETICAL RESULTS OF THE PHOTOOXIDATION OF SUBSTITUTED NAPHTHALENES

R	Z	Z'	$\Delta E$ (in units of $\beta$ )	% 5, 8	% 1, 4
H	OCH <sub>3</sub>	OCH <sub>3</sub>	-0.092	0	100
C <sub>6</sub> H <sub>5</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	-0.040	0	100
H	CH <sub>3</sub>	CH <sub>3</sub>	-0.061	0	100

\* Full details of this reaction will be the subject of a future publication.

experiment and theory is excellent. It seems, therefore, that the delocalized model is a good description of the transition state of the photooxidation of substituted anthracenes and naphthalenes.

In an empirical method such as the Hückel method, there is always a danger that the parameters chosen may be the unique set which provides good agreement between the theoretical and experimental results. In order to rule out this possibility, calculations were carried out on a 1-substituted anthracene (IV) and a 1,4-disubstituted anthracene (V) in order to determine how a variation of  $h$  in the Coulomb integral  $\alpha_x$  and  $k$  of the resonance integral  $\beta_x$  between the substituent X and the adjacent

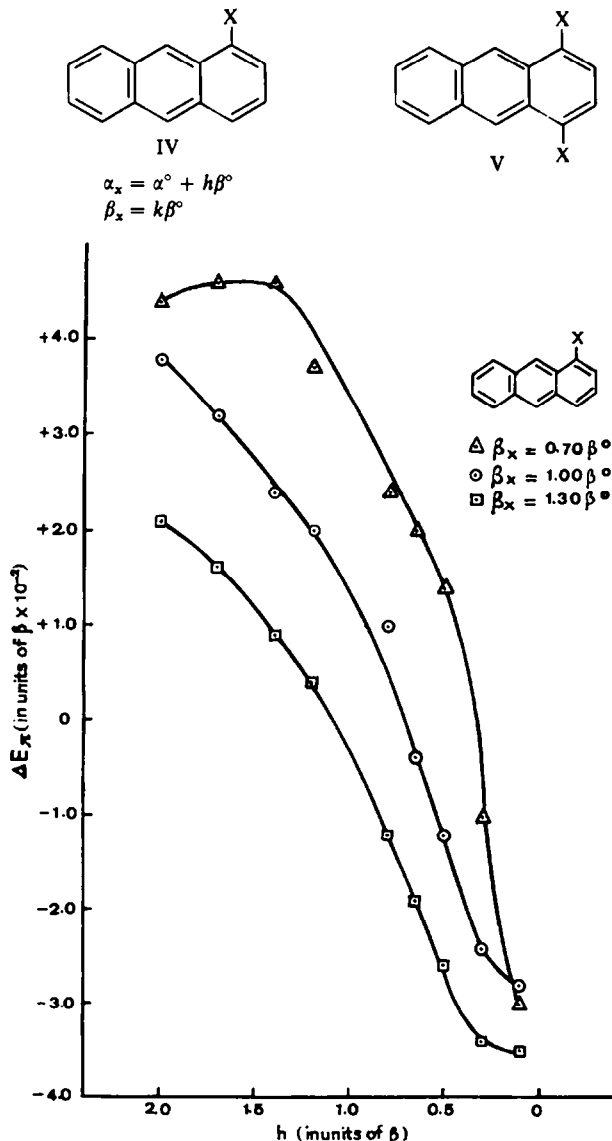


FIG. 1 The effect on  $\Delta E$  of variations of  $h$  and  $k$  in the Coulomb integral  $\alpha_x$  and the resonance integral  $\beta_x$  respectively of 1-X-anthracene.

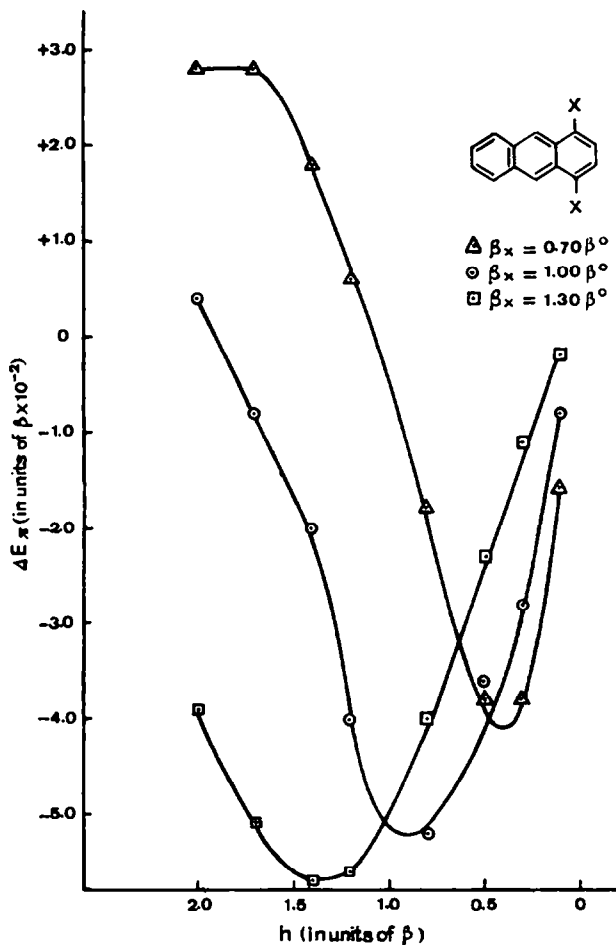


FIG 2 The effect on  $\Delta E$  of variations of  $h$  and  $k$  in the Coulomb integral  $\alpha_x$  and the resonance integral  $\beta_x$  respectively of 1,4-Di-X-anthracene.

carbon would affect  $\Delta E$ . The results of these calculations are shown in Figs 1 and 2. In all these calculations, it is assumed that the group X contributes two electrons to the  $\pi$ -system. Consider first the monosubstituted anthracene. As the value of  $h$  decreases from 2 to 0.10,  $\Delta E$  becomes more negative predicting that the 1,4-photoadduct will be the preferred product. Decreasing the value of  $h$  from 2 to 0.10 corresponds to making the group X less electronegative and as a result a better electron donating group.<sup>13</sup> Thus these calculations predict that as the group X becomes a better electron donor, the 1,4-photoadduct will be the dominant product. This is exactly in accord with experiment.<sup>10</sup> Figure I also shows that small variations in the choice of  $h(\pm 0.20\beta)$  and  $k(\pm 0.30\beta)$  for any group (e.g. —Me) have little effect upon a qualitative description of the effect of that substituent.

While similar conclusions are evident from Fig. 2, there is one major difference. As the two groups X become very strong electron donors ( $b < 1.0$ ) the values of  $\Delta E$  become more positive rather than more negative as in the case of the monosubstituted

anthracene. This predicts that products of the photooxidation reaction of an anthracene molecule containing two strong electron donating groups in the 1-, 4-position should be a mixture of the 9,10 and 1,4-adducts. This prediction has yet to be tested experimentally.

Another test of parameters was carried out by varying the value of  $h$  in the Coulomb integral  $\alpha$  assigned to the oxygen molecule in its reaction with 1,4-dimethoxyanthracene. The value of  $h$  was varied from +2.00 to -1.50 and the results are given in Table 4. It is clear that an inversion occurs in the position of attack as the electronegativity

TABLE 4. VARIATION OF  $\Delta E$  WITH CHANGE OF  $h$  IN THE COULOMB INTEGRAL ASSIGNED TO THE DIENOPHILE IN ITS ADDITION REACTION TO 1,4-DIMETHOXYANTHRACENE

$h$	$\Delta E$ (in units of $\beta$ )
-1.50	+0.161
-1.00	+0.098
-0.50	+0.042
+0.10	+0.022
+0.30	+0.018
+0.50	+0.011
+0.70	-0.002
+0.90	-0.026
+1.10	-0.040
+1.30	-0.032
+1.50	-0.024
+1.70	-0.019
+2.00	-0.014

of the atoms of the dieneophile change. Thus for a dieneophile which has been given a value of  $h < +0.10$  the 9,10-adduct is the preferred product while for a dieneophile which has been given a value of  $h > +0.70$  the 1,4-isomer is preferred. A dieneophile such as maleic anhydride would be assigned a value of  $h = 0$  ( $\pm 0.30$ ) and as a result, the Diels-Alder reaction of maleic anhydride with 1,4-dimethoxyanthracene, would be expected to give the 9,10-adduct. This is found to be the case.<sup>10</sup>

It can be concluded that the values of the parameters chosen in this study are not a unique set. Rather they provide a good qualitative description of the transition state of the photooxidation and photodeuteration of a series of scenes.

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