
**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY.
PHOTOCHEMICAL AND FREE RADICAL REACTIONS**

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Recently proposed method of the so called overlap determinant is extended in this study to free radical and photochemical reactions. In comparison with existing alternative procedures the advantage of this generalised formalism consists not only in its simplicity but above all in its universality allowing to analyse in a unified manner all types of chemical reactions.

In a previous study¹ a simple mathematical formalism was proposed allowing to classify the nature of chemical reactions. The wide applicability of the method was demonstrated on a number of examples involving sigmatropic, cheletropic, electrocyclic and cycloaddition reactions, valence isomerisations *etc.* In all these cases only the ground state reactivity of closed shell molecules was considered¹. The formalism of the method is, however, general enough to be extended also to reactions of free radicals and excited molecular species. In this paper such generalisation is described.

THEORETICAL*Photochemical Reactivity*

The extension of the original formalism of the overlap determinant method to photochemical reactions can be the most simply demonstrated on pericyclic reactions the stereochemical course of which is governed by the Woodward–Hoffmann (W–H) rules². The most important feature of the generalised formalism consists, in this case, in reproducing the inversed stereochemical course of photoreactions. As an example let us analyse in details the photocyclisation of 1,3-butadiene to cyclobutene. The principal modification of the formalism appears at the level of the construction of the irreducible core. As it has been shown previously¹ the butadiene cyclisation can be, in the ground state, characterised as a transformation of the type $2\pi \rightarrow \pi + \Sigma$ with the irreducible core containing the set of π_{12} and π_{34} butadiene bonds and the set of π_{23} and σ_{14} cyclobutene bonds. The fact that in photochemical

reaction the butadiene reacts not in the ground but in the excited* state is formally respected by replacing one of its π bonds from the irreducible core of ground state reaction by what can be called the "virtual" π^* bond. The exact definition of this term is not at this stage necessary and will be given later. Here it is sufficient to indicate only the analogy with the corresponding antibonding orbital. Having in mind the equivalency of butadiene π bonds it is of no importance which of them is actually replaced by its virtual counterpart and both alternatives can be considered. Let it be *e.g.* the bond π_{34} which is replaced by the virtual bond π_{34}^* . The irreducible core of butadiene photocyclisation is then formed by the set of the bonds π_{12} , π_{34}^* , π_{23} , σ_{14} and the reaction is characterised as a transformation of the type $\pi + \pi^* \rightarrow \pi + \Sigma$. This specification is of course only very crude and says nothing about *e.g.* the exact nature of photoreactive states but as suggests the usefulness of closely related W-H rules such a detailed characterisation is not necessary.

After having determined the irreducible core the corresponding bonds have to be specified. Similarly as in the original study¹ we use for this purpose the familiar linear combinations of certain orbitals χ and χ' where the primes again denote the orbitals in the product (Eq. 1)

$$\begin{aligned} \pi_{12} &= \chi_1 + \chi_2 & \pi_{23} &= \chi'_2 + \chi'_3 \\ \pi_{34}^* &= \chi_3 - \chi_4 & \sigma_{14} &= \chi'_1 + \chi'_4 \end{aligned} \quad (1)$$

In accordance with the above indicated analogy the virtual bond is described by the antibonding combination of orbitals χ_3 and χ_4 characterised by the presence of the node between the corresponding centers. The structure of the "excited" butadiene is now characterised in terms of the bonds π_{12} , π_{34}^* by the "excited" bonding function Φ_R^* (Eq. 2)

$$\Phi_R^* = |\pi_{12}\bar{\pi}_{12}\pi_{34}^*\bar{\pi}_{34}^*| \quad (2)$$

and the structure of the cyclobutene by the function Φ_P (Eq. 3) the form of which is just the same as for the ground state reaction¹.

$$\Phi_P = |\pi_{23}\bar{\pi}_{23}\sigma_{14}\bar{\sigma}_{14}| \quad (3)$$

Despite the function Φ_R^* is not entirely satisfactory from the quantum chemical point of view (it does not describe, even approximately, any of the observed "spectroscopic" butadiene excited states) it is nevertheless useful as a simple heuristic aid allowing to reproduce the photochemical selection rules. Here it is probably interesting to mention that the specific "closed shell" form of this function suggests,

* Similarly as W-H rules the overlap determinant method does not require the exact specification of photoreactive states.

in analogy with the results of Van der Lugt and Oesterhoff³ the crucial role of bi-excited configurations in governing the stereochemical course of the cyclisation.

After having specified the bonding functions all the subsequent analysis is just the same as in the case of ground state reaction. It consists in calculating the overlap integral of the function Φ_R^* with the function Φ_P modified with the aid of the assigning tables. Since these tables are completely identical as for the ground state reactions it is not necessary to repeat the whole procedure of their construction. We shall restrict ourselves therefore only to the presentation of the final assignment which has in the case of conrotatory reaction the following form¹ (Eq. 4)

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 & \chi'_3 &\rightarrow \chi_3 \\ \chi'_2 &\rightarrow \chi_2 & \chi'_4 &\rightarrow -\chi_4 \end{aligned} \quad (4)$$

Using these tables the bonds in the product can be rewritten in the basis of unprimed orbitals χ (Eq. 5)

$$\begin{aligned} \pi_{23} &= \chi'_2 + \chi'_3 \xrightarrow{f_{\text{con}}} \chi_2 + \chi_3 \\ \sigma_{14} &= \chi'_1 + \chi'_4 \xrightarrow{f_{\text{con}}} \chi_1 - \chi_4 \end{aligned} \quad (5)$$

The overlap determinant constructed by the usual way then confirms the inversed stereochemical course of the cyclisation and the reaction is forbidden (Eq. 6)

$$D_{\text{con}}^* = \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}^2 = 0 \quad (6)$$

Similarly it can be shown that the analogous disrotatory reaction characterised by the assignment (7) leads to nonzero value of

$$\begin{aligned} \chi'_1 &\rightarrow \chi_1 & \chi'_3 &\rightarrow \chi_3 \\ \chi'_2 &\rightarrow \chi_2 & \chi'_4 &\rightarrow \chi_4 \end{aligned} \quad (7)$$

the corresponding overlap determinant indicating the allowed nature of the reaction (Eq. 8)

$$D_{\text{dis}}^* = \begin{vmatrix} 1 & 1 \\ 1 & -1 \end{vmatrix}^2 \neq 0 \quad (8)$$

The same procedure can be analogously applied to the analysis of any other photo-reaction governed by the W-H rules. For all these cases is typical the "closed shell" form of the "excited" bonding function. A number of examples presented below demonstrates the wide applicability of the proposed formalism.

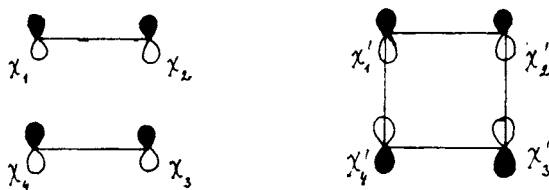
RESULTS AND DISCUSSION

Cycloaddition reaction. The simple and the most typical representative of the whole class of these reactions is the 2 + 2 dimerisation of ethene. In the ground state the irreducible core of this reaction is formed by the set of two disappearing π bonds and two newly formed σ bonds. The fact that we do not analyse the thermal but photochemical reaction will be again respected by formally replacing one of the reactant π bonds by the corresponding virtual bond. The reaction can be then characterised as a transformation of the type $\pi + \pi^* \rightarrow 2\Sigma$. (The reversed fragmentation of the cyclobutane is to be analogously characterised as a transformation of the type $\Sigma + \Sigma^* \rightarrow 2\pi$). Let the replaced bond be *e.g.* the bond π_{12} . Bonds forming the irreducible core of the forward photoreaction are then described by the familiar linear combinations of atomic orbitals (Eq. 9)

$$\begin{aligned} \pi_{12}^* &= \chi_1 - \chi_2 & \sigma_{14} &= \chi'_1 + \chi'_4 \\ \pi_{34} &= \chi_3 + \chi_4 & \sigma_{23} &= \chi'_2 + \chi'_3. \end{aligned} \quad (9)$$

The transformation of the product bonds from the basis of primed orbitals χ' into the basis of orbitals χ requires the use of assigning tables the actual form of which is given, for the case of supra-supra mechanism by Eq. (10) (Scheme 1)

$$\begin{aligned} \sigma_{14} &= \chi'_1 + \chi'_4 & \xrightarrow{f_{s,s}} & \chi_1 - \chi_4 \\ \sigma_{23} &= \chi'_2 + \chi'_3 & \xrightarrow{f_{s,s}} & \chi_2 - \chi_3 \end{aligned} \quad (10)$$



SCHEME 1

The nonzero value of the corresponding overlap determinant (11) demonstrates that in contrast to ground state reaction the 2 s + 2 s photoaddition is allowed.

$$D_{s,s}^* = \begin{vmatrix} 1 & -1 \\ -1 & -1 \end{vmatrix}^2 \neq 0 \quad (11)$$

On the other hand the $2s + 2a$ mechanism characterised by the assignment (12) is forbidden.

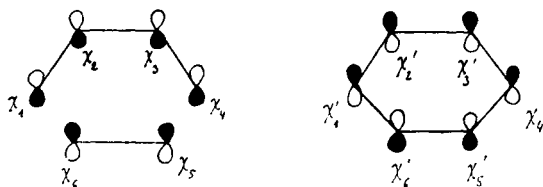
$$\begin{aligned}\sigma_{14} &= \chi'_1 + \chi'_4 \xrightarrow{f_{s,u}} \chi_1 - \chi_4 \\ \sigma_{23} &= \chi'_2 + \chi'_3 \xrightarrow{f_{s,a}} \chi_2 + \chi_3\end{aligned}\quad (12)$$

As a next example of cycloadditions let us analyse now the well known Diels–Alder reaction. This reaction is known to proceed in the ground state as $4s + 2s$ process and on the basis of irreducible core can be characterised as a transformation of the type $3\pi \rightarrow \pi + 2\Sigma$. This specification is again modified for the case of photoreaction by replacing one of the reactant π bonds by its virtual counterpart. The photoaddition is thus to be considered as a transformation of the type $2\pi + \pi^* \rightarrow \pi + 2\Sigma$. Such a specification is not, however, in this case entirely unambiguous since it does not distinguish which of the reacting components is excited (butadiene or ethene). The detailed analysis however shows that the value of the overlap determinants corresponding to both these alternatives does not depend on which of them is actually considered. Let for example the excited component be the ethene. The irreducible core can be then described in a usual way by Eq. (13)

$$\begin{aligned}\pi_{12} &= \chi_1 + \chi_2 & \sigma_{16} &= \chi'_1 + \chi'_6 \\ \pi_{34} &= \chi_3 + \chi_4 & \sigma'_{45} &= \chi'_4 + \chi'_5 \\ \pi_{56}^* &= \chi_5 - \chi_6 & \pi'_{23} &= \chi'_2 + \chi'_3.\end{aligned}\quad (13)$$

The assignment table of supra-supra mechanism the form of which follows from the Scheme 2 allows to transform the product bonds from the basis of primed orbitals χ' into the basis χ in the following way (Eq. 14) (Scheme 2)

$$\begin{aligned}\sigma_{16} &= \chi'_1 + \chi'_6 \xrightarrow{f_{s,s}} \chi_1 - \chi_6 \\ \sigma_{45} &= \chi'_4 + \chi'_5 \xrightarrow{f_{s,s}} \chi_4 - \chi_5 \\ \pi_{23} &= \chi'_2 + \chi'_3 \xrightarrow{f_{s,s}} \chi_2 + \chi_3\end{aligned}\quad (14)$$



SCHEME 2

The overlap determinant (15) confirms the expected result that the 4 s + 2 s mechanism is photochemically forbidden.

$$D_{s,s}^* = \begin{vmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & -1 & 0 \end{vmatrix}^2 = 0 \quad (15)$$

The next example of 4 + 2 photocycloaddition of allylanion to ethene is analysed as an example of the reaction in which the structure of the reacting molecules cannot be described by only one classical structural formula. Similarly as for the ground state reaction it is not in this case possible to construct the overlap determinant using classically localised bonds but one has to use directly the delocalised molecular orbitals¹. Thus the ground state of allylanion is characterised by the set of two functions φ_1, φ_2 the nodal structure of which is identical with the nodal structure of occupied molecular orbitals (Eq. (16))

$$\varphi_1 = \chi_1 + \chi_2 + \chi_3 \quad (16)$$

$$\varphi_2 = \chi_1 - \chi_3 .$$

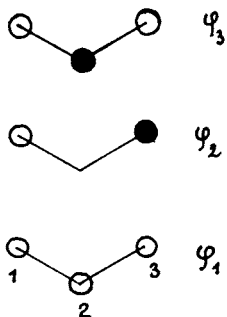
The remaining ethene double bonds as well as all newly formed σ bonds in the product are already classically localised and can be described in a usual way (Eq. (17))

$$\begin{aligned} \pi_{45} &= \chi_4 + \chi_5 \\ \sigma_{15} &= \chi'_1 + \chi'_5 \xrightarrow{f_{s,s}} \chi_1 - \chi_5 \\ \sigma_{34} &= \chi'_3 + \chi'_4 \xrightarrow{f_{s,s}} \chi_3 - \chi_4 \\ n &= \chi'_2 \xrightarrow{f_{s,s}} \chi_2 . \end{aligned} \quad (17)$$

The set of bonds $\varphi_1, \varphi_2, \pi_{45}, \sigma_{15}, \sigma_{34}, n$ then serves to construct the overlap determinant of thermally initiated reaction. If we want to analyse the photochemical reaction it is again necessary to replace one of the reactant bonds by the corresponding virtual counterpart. Similarly as in the above example of Diels–Alder reaction it is of no importance whether the excitation takes place at the ethene or allylanion fragment. The case where the excited component is ethene is entirely analogous to already discussed examples and will not be considered. (The π_{45} bond is replaced by the virtual π_{45}^* bond). More interesting to analyse is the second case in which the formally excited component is the allylanion. To describe this excitation properly, the function φ_2 (representing the analogy of HOMO) has to be replaced by the function φ_3 the nodal structure of which reproduces the orbital LUMO (Eq. 18)

(Scheme 3)

$$\varphi_3 = \chi_1 - \chi_2 + \chi_3 \quad (18)$$



SCHEME 3

The bonding function of excited reactants (Eq. 19) then corresponds to HOMO \rightarrow \rightarrow LUMO biexcited configuration.

$$\Phi_R^* = |\varphi_1 \bar{\varphi}_1 \varphi_3 \bar{\varphi}_3 \pi_{45} \bar{\pi}_{45}| \quad (19)$$

The overlap determinant for the supra-supra addition then shows (Eq. 20) that the reaction is forbidden. (In agreement with W-H rules).

$$D_{S,S}^* = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \\ -1 & -1 & 0 \end{vmatrix}^2 = 0 \quad (20)$$

On the other hand the corresponding supra-antara addition is allowed (Eq. (21))

$$D_{S,a}^* = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \\ -1 & 1 & 0 \end{vmatrix}^2 \neq 0 \quad (21)$$

Electrocyclic reactions. Since the cyclisation of 1,3-butadiene to cyclobutene has been already analysed above let us discuss as a next example of this type of reactions the cyclisation of 1,3,5-hexatriene to 1,3-cyclohexadiene. Irreducible core characterises the parent ground state reaction as the transformation of the type $3\pi \rightarrow 2\pi + \Sigma$. Excitation of the hexatriene as a reactant manifests itself in the modification of the irreducible core to the type $2\pi + \pi^* \rightarrow 2\pi + \Sigma$. Similarly as in the previous case of Diels-Alder reaction it is not again important which of the three reactant π

bonds is replaced by the virtual one. Let it be *e.g.* the bond π_{12} . The bonds forming the irreducible core can be then described by Eq. (22)

$$\begin{aligned}\pi_{12}^* &= \chi_1 - \chi_2 & \pi_{23} &= \chi_2' + \chi_3' \\ \pi_{34} &= \chi_3 + \chi_4 & \pi_{45} &= \chi_4' + \chi_5' \\ \pi_{56} &= \chi_5 + \chi_6 & \sigma_{16} &= \chi_1' + \chi_6'\end{aligned}\quad (22)$$

Using the assignment tables for the disrotatory reaction¹ the product bonds can be expressed in the basis of unprimed orbitals (Eq. 23) (Scheme 4)

$$\begin{aligned}\pi_{23} &= \chi_2' + \chi_3' & \xrightarrow{f_{dis}} & \chi_2 + \chi_3 \\ \pi_{45} &= \chi_4' + \chi_5' & \xrightarrow{f_{dis}} & \chi_4 + \chi_5 \\ \sigma_{16} &= \chi_1' + \chi_6' & \xrightarrow{f_{dis}} & \chi_1 + \chi_6\end{aligned}\quad (23)$$



SCHEME 4

The zero values of the corresponding overlap determinant (24) demonstrates, in accordance with W-H rules, that the reaction is forbidden.

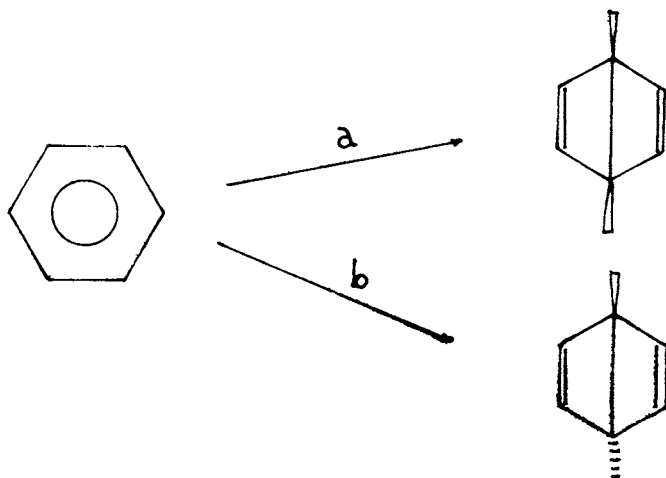
$$D_{dis}^* = \begin{vmatrix} -1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{vmatrix}^2 = 0 \quad (24)$$

On the other hand the conrotatory cyclisation has to be regarded on the basis of the determinant (25) as allowed.

$$D_{con}^* = \begin{vmatrix} -1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \end{vmatrix}^2 \quad (25)$$

Valence isomerisations. This type of reactions is represented *e.g.* by the rearrangement of benzene to [2,2,0]cyclohexadiene (Dewar benzene), the mechanism of which was analysed for the case of ground state reaction in the previous paper¹. The analogy

of this reaction to the cyclisation of 1,3-butadiene was stressed there (both reactions have the same irreducible core). This analogy can be extended also to photoreaction which is thus characterised as a transformation of the type $\pi + \pi^* \rightarrow \pi + \Sigma$. We can thus expect the rearrangement to proceed by the disrotatory mechanism (reaction a, Scheme 5) whereas the analogous conrotatory transformation leading to the product b) is forbidden.



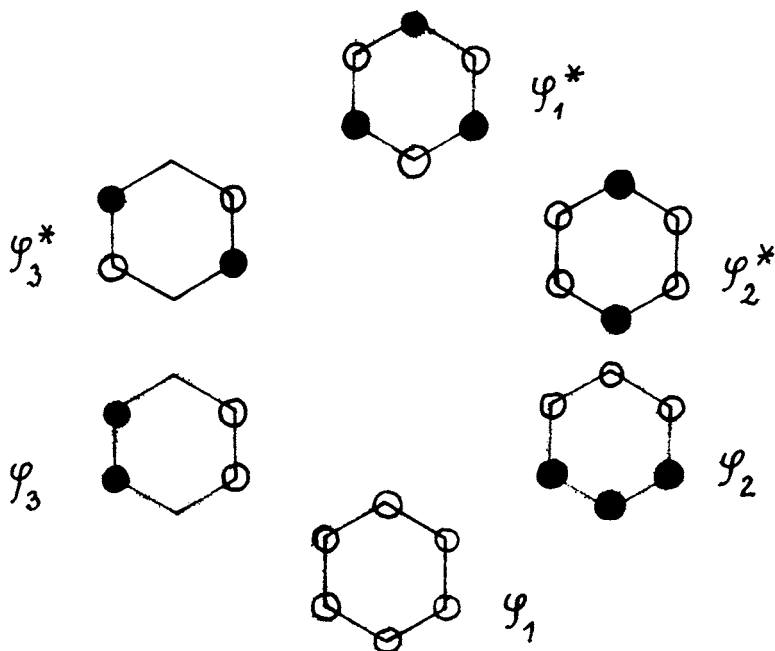
SCHEME 5

As a next example of this type of reaction let us analyse in details the photoinitiated rearrangement of benzene to prismane (Scheme 6). As demonstrated in the previous study¹ the reaction can be in the ground state described as a transformation of the



SCHEME 6

type $3\pi \rightarrow 3\Sigma$. Since again the benzene π bonds entering into the irreducible core cannot be described in a usual way in terms of localised pairs the set of functions $\varphi_1, \varphi_2, \varphi_3$ reproducing the nodal structure of occupied π molecular orbitals has to be used (Scheme 7). In the case of photochemical transformation the original irreducible core has again to be modified by formally replacing one of these functions



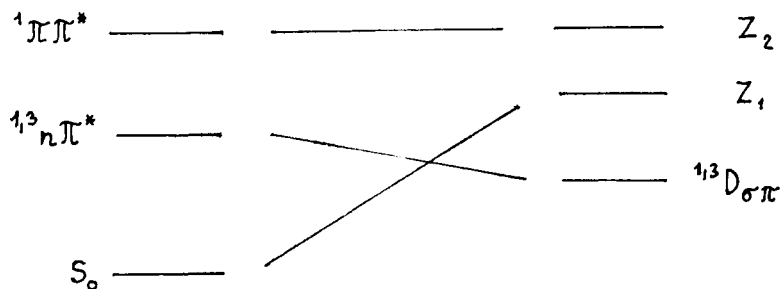
SCHEME 7

by the corresponding functions φ_1^* , φ_2^* , φ_3^* characterising the nodal structure of anti-bonding molecular orbitals. In contrast to the addition of ethene to allylanion, where such modification was trivial (HOMO→LUMO excitation) in this case the situation is much more complex because of degeneracy in both the highest occupied and the lowest virtual orbitals. Formal HOMO→LUMO excitation can be now described by several different ways leading to several alternatives in the construction of the bonding function Φ_R^* (Eq. 26)

$$\begin{aligned}
 \Phi_1^* &= |\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2 \varphi_3^* \bar{\varphi}_3^*| \\
 \Phi_2^* &= |\varphi_1 \bar{\varphi}_1 \varphi_3 \bar{\varphi}_3 \varphi_2^* \bar{\varphi}_2^*| \\
 \Phi_3^* &= |\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2 \varphi_2^* \bar{\varphi}_2^*| \\
 \Phi_4^* &= |\varphi_1 \bar{\varphi}_1 \varphi_3 \bar{\varphi}_3 \varphi_3^* \bar{\varphi}_3^*|.
 \end{aligned}
 \tag{26}$$

From the four possible overlap determinants constructed using this set of "excited" bonding functions only the alternative based on the function Φ_3^* leads to the correct result that the reaction is allowed (expected on the basis of inversion of W-H rules). This specific limitation restricting the choice of bonding functions has probably some deeper physical reasons (manifesting themselves *e.g.* in the specific require-

ments on the symmetry of the photoreactive state⁴) but our aim is not to analyse such questions in details. A simple qualitative rationalisation of this restriction would be nevertheless useful. For this purpose it is important to realize that the function Φ_3^* considering the excitation $\varphi_3 \rightarrow \varphi_2^*$ is the only alternative excluding from the participation on the irreducible core the functions φ_3 and φ_3^* which both have zero overlap with any of the product σ bonds.* This criterion can be of course

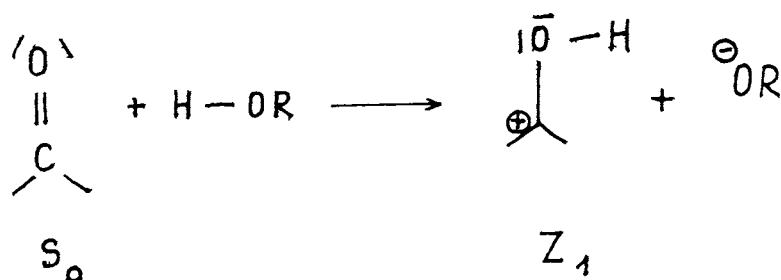


SCHEME 8

considered as nothing but a simple empirical recipe the only aim of which is to resolve the ambiguity in the selection to the bonding functions. Fortunately such complications arising from the necessity of certain selection of bonding functions are exceptional and in majority of cases the problem of selecting the proper bonding function is trivial. In a number of the above examples the wide applicability of the formalism of overlap determinant method was clearly demonstrated. In all these cases, however, the new formalism only reproduces, even if perhaps in a more simple way, the classical W-H rules. Its advantage consists, however, not only in the simplicity but above all in a great universality allowing to employ it for the analysis of reactions exceeding the scope of applicability of W-H approach. This aspect becomes especially important in photochemistry where such reactions are quite frequent. As an example let us mention *e.g.* the dissociation of toluene to hydrogen and benzylradical, the H-abstraction by $^3n\pi^*$ excited ketones, α -cleavage of alkanones *etc.* The theoretical interpretation of these important photoreactions was the subject of numerous studies⁵⁻⁹. The most general approach proposed by Salem and Michl is based on the construction of the specific type of correlation diagrams^{5,6,9}. The example of such diagram is visualised, for the case of H-abstraction reaction in Scheme 8. This diagram naturally explains all the experimental observations according to which the reaction requires the specific $^3n\pi^*$ excitation of the ketone component and does not proceed in the ground state. The requirement of the specific ketone excitation is rationalised on the

* The presence of these functions in the irreducible core automatically leads to the zero value of the overlap determinant.

basis of the direct correlation of $^3n\pi^*$ excited state of the ketone component with the $^3D_{\sigma\pi}$ biradical representing the most favourable arrangement of primary product of the reaction. On the other hand the ground state initiated abstraction correlates the ground state of the reactants with the zwitterionic state Z_1 . The straightforward correlation of these states suggests that the reaction should be considered as allowed but the high energy of the zwitterionic state makes the reaction unfavourable thermodynamically. The remaining zwitterionic state Z_2 the energy of which is even higher than the energy of the Z_1 state (owing to its reversed unfavourable polarisation) then correlates with the singlet $^1\pi\pi^*$ state of the ketone. In the following part we shall demonstrate that all these conclusions resulting from the Salem diagrams can be reproduced also in the framework of the overlap determinant method. Let us consider the ground state reaction first (Scheme 9).



SCHEME 9

Since all the components participating in the reaction are of the closed shell type the irreducible core can be determined by the standard procedure consisting in mutual comparing of the sets of the bonds in the reactant and in the product. Applying this procedure we find the irreducible core to contain the free σ electron pair of carbonyl oxygen n_0 , carbonyl π_{12} bond and σ_{OH} bond of alcohol (from the part of the reactant) and from the part of the product the newly formed σ_{OH} bond, the free electron pair n_0^π of the π type at the carbonyl oxygen and the free σ_{OR} pair of the alkoxide ion. The set of these bonds is described in a usual way by the linear combination of atomic orbitals (Eq. 27)

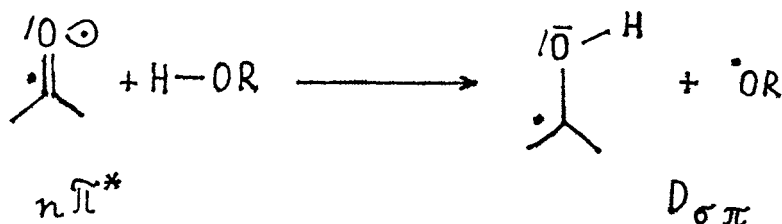
$$\begin{array}{l}
 \sigma_0 = n_0 \quad \sigma_{\text{OR}} = \chi'_0 \rightarrow \chi_0 \\
 \pi_{12} = \chi_1^\pi + \chi_2^\pi \quad \sigma_{\text{OH}} = n'_0 + h \rightarrow n_0 + h \\
 \sigma_{\text{OH}} = \chi_0 + h \quad n_0^\pi = \chi_2^{\pi'} \rightarrow \chi_2^\pi
 \end{array} \quad (27)$$

The assignment simultaneously presented in these equations expresses the elementary fact that the reaction proceeds as a simple migration of hydrogen in the plane

$C=O\dots O$ (which is the only conserved symmetry element) without the change of the nodal properties of participating orbitals. The corresponding overlap determinant confirms the direct correlation of S_0 and Z_1 states suggested by the Salem diagram (Eq. (28))

$$D_{S_0} = \begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix}^2 \neq 0. \quad (28)$$

Let us analyse now the reaction initiated by the ${}^3n\pi^*$ excitation of the carbonyl component (Scheme 10). The specific feature of this reaction is that both the reactant



SCHEME 10

and the product are the open shell species. As a consequence of this specificity the standard procedure of constructing the irreducible core has to be modified. This modification consists in the necessity of separately considering of α and β spin bonding orbitals (at least there where the excitation formally destroys the pairing of electrons in the bonds). In our case the irreducible core includes from the part of the reactant the electron pair of σ_{OH} alcohol bond, the electron pair of carbonyl π_{12} bond together with the unpaired electron with α spin localised at the n_0 orbital of the carbonyl oxygen. The second unpaired electron with the α spin is placed in the carbonyl antibonding π_{12}^* orbital. From the part of the products the irreducible core contains the electron pair in the orbital χ_2^π at the carbonyl oxygen, the free electron pair of the newly formed σ_{OH} bond and two unpaired electrons (with α spin) localised at the χ_0 orbital of the alkoxide fragment and in the χ_1^π orbital at carbonyl carbon. The structure of the reacting components is then characterised, using the above set of bonds and orbitals in term of bonding functions (29) the form of which clearly suggests the analogy with the corresponding configurations of photoreactive states

$$\begin{aligned}
 \Phi_R^* &= |\sigma_{OH}^R \bar{\sigma}_{OH}^R \pi_{12} \bar{\pi}_{12} n_0 \pi_{12}^*| \\
 \Phi_P &= |\sigma_{OH}^P \bar{\sigma}_{OH}^P \chi_2^\pi \bar{\chi}_2^\pi \chi_0 \chi_1^\pi|
 \end{aligned} \quad (29)$$

Similarly as in the above cases the feasibility of the reaction is analysed in terms of the overlap integral of the function Φ_R^* with the modified function Φ_P . Since, however, these functions are no longer of the "closed shell" type, their overlap cannot be calculated in a usual way in terms of only one overlap determinant. Instead, one has to use the generalised formula (30) requiring the separate calculation of determinants for α and β spin.*

$$\int \Phi_R^* \Phi_P \, d\tau = D_\alpha \cdot D_\beta \quad (30)$$

The corresponding determinant D_α and D_β are given, in our case by Eq. (31)

$$D_\beta = \begin{vmatrix} \int \sigma_{OH}^R \sigma_{OH}^P \, d\tau & \int \sigma_{OH}^R \chi_2^\pi \, d\tau \\ \int \pi_{12} \sigma_{OH}^P \, d\tau & \int \pi_{12} \chi_2^\pi \, d\tau \end{vmatrix} \quad (31a)$$

$$D_\alpha = \begin{vmatrix} \int \sigma_{OH}^R \sigma_{OH}^P \, d\tau & \int \sigma_{OH}^R \chi_2^\pi \, d\tau & \int \sigma_{OH}^R \chi_0 \, d\tau & \int \sigma_{OH}^R \chi_1^\pi \, d\tau \\ \int \pi_{12} \sigma_{OH}^P \, d\tau & \int \pi_{12} \chi_2^\pi \, d\tau & \int \pi_{12} \chi_0 \, d\tau & \int \pi_{12} \chi_1^\pi \, d\tau \\ \int n_0 \sigma_{OH}^P \, d\tau & \int n_0 \chi_2^\pi \, d\tau & \int n_0 \chi_0 \, d\tau & \int n_0 \chi_1^\pi \, d\tau \\ \int \pi_{12}^* \sigma_{OH}^P \, d\tau & \int \pi_{12}^* \chi_2^\pi \, d\tau & \int \pi_{12}^* \chi_0 \, d\tau & \int \pi_{12}^* \chi_1^\pi \, d\tau \end{vmatrix} \quad (31b)$$

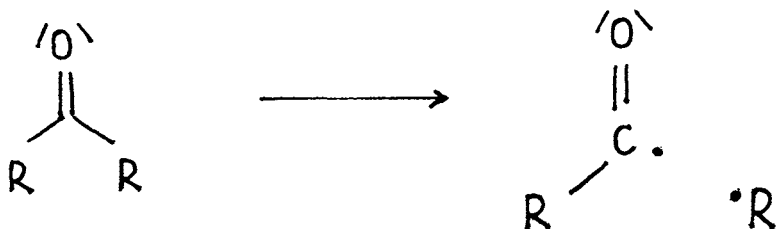
Substituting the actual values of the individual orbital overlap integrals these equations obtain the following final form (Eq. (32)) confirming the direct correlation of photoreactive states required by Salem diagram.

$$D_\alpha = \begin{vmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 \end{vmatrix} \neq 0 \quad (32)$$

$$D_\beta = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} \neq 0$$

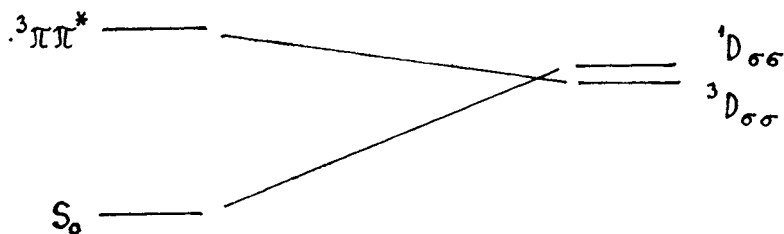
* If both of the bonding functions are of the closed shell type $D_\alpha = D_\beta = D$ and the overlap integral is simply equal to the square of the corresponding overlap determinant.

The same procedure can be also used to analyse the remaining types of mentioned photochemical reactions. Such analysis demonstrates that the proposed formalism correctly depicts the mutual assignment of photoreactive states even in the cases where the construction of Salem diagrams has to be complemented by the concept of the so called natural MO correlations⁹ (feasible forbidden reactions)¹⁰. As an example of such reaction may serve *e.g.* the α -cleavage of alkanones (Scheme 11).



SCHEME 11

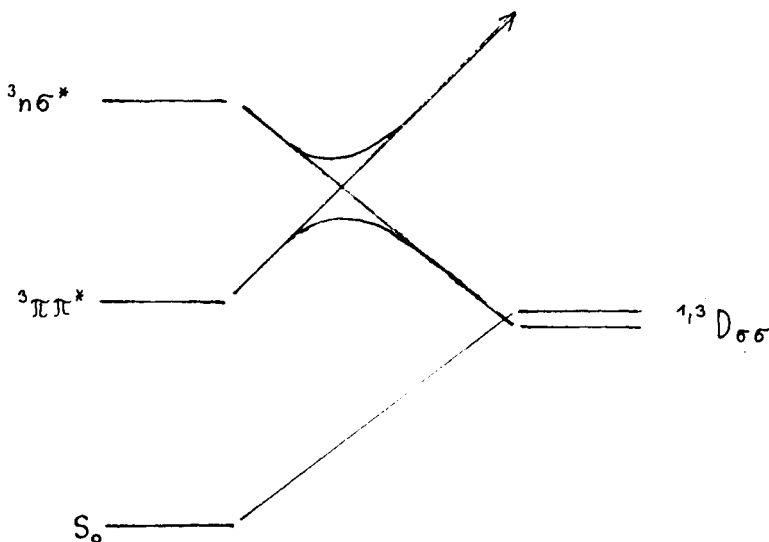
The simplified correlation diagram depicting the correlation of primary photo-reactive states is taken from the Salem review⁶ (Scheme 12). This diagram based on simple symmetry arguments relates the ${}^3D_{\sigma\sigma}$ biradical state of the dissociated



SCHEME 12

products with the ${}^3\pi\pi^*$ excited state of alkanone. This correlation despite of being formally correct is not, however, confirmed by the detailed quantum chemical calculations indicating a considerable energetic barrier separating on the corresponding hypersurface the ${}^3\pi\pi^*$ and ${}^3D_{\sigma\sigma}$ states¹⁰. The detailed analysis performed by Salem himself explains this barrier as a consequence of the so called "avoided crossing" of original ${}^3A'({}^3\pi\pi^*)$ hypersurface of the alkanone excited state with the hypersurface of the high lying ${}^3n\sigma^*$ state of the same symmetry (Scheme 13). The formal assignment taking into consideration only the requirement of the correlation of the lowest states of the same symmetry is thus in this case misleading and has to be corrected

by invoking the concept of natural MO correlations⁹. In contrast, the overlap determinant method, the formalism of which automatically includes the criterion of the conservation of electronic configurations¹⁰⁻¹³ leads even in this case directly to the correct assignment without the necessity of invoking any auxiliary concepts.



SCHEME 13

Free Radical Reactivity

The reason why these in principle ground state reactions are treated together with the photochemical reactions originates from the specific open shell character of the reacting components manifesting itself in the modification of the formalism at the level of the construction of the bonding function. The whole procedure can be the most easily demonstrated on a typical example of free radical reaction as *e.g.* the addition to C=C bond (Scheme 14). After the reduction the aim of which is to elimi-



SCHEME 14

nate the bonds not directly participating in the reaction the irreducible core contains the ethene π_{12} bond, the χ_X orbital carrying the unpaired radical in the attacking radical χ , the σ_{CX} bond in the product and the orbital χ_2 containing the unpaired electron in the product $\dot{C}H_2CH_2X$. The bonding function of the reactants is now constructed in the form of RHF determinant (Eq. 33)

$$\Phi_R = |\pi\bar{\pi}\chi_X|. \quad (33)$$

Analogously the bonding function of the product is given by Eq. (34)

$$\Phi_P = |\Sigma_{CX}\bar{\Sigma}_{CX}\chi_2|. \quad (34)$$

Participating bonds are again expressed using the familiar linear combinations of orbitals χ and χ' (Eq. (35))

$$\begin{aligned} \pi &= \chi_1 + \chi_2 (\alpha + \beta) & \Sigma_{CX} &= \chi'_1 + \chi'_X (\alpha + \beta) \\ \chi_X &= \chi_X (\alpha) & \chi_2 &= \chi'_2 (\alpha). \end{aligned} \quad (35)$$

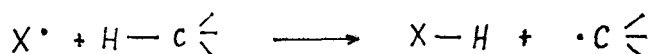
The assignment tables the construction of which assumes the reaction to proceed by a single step one-end mechanism then allows to express the product bonds in the unprimed basis of orbitals (Eq. (36))

$$\begin{aligned} \Sigma_{CX} &= \chi'_1 + \chi'_X \rightarrow \chi_1 + \chi_X \\ \chi_2 &= \chi'_2 \rightarrow \chi_2 \end{aligned} \quad (36)$$

The calculation of the overlap integral requires to take into the consideration the open shell character of the function ϕ_R and ϕ_P . Consequently one has to use the general Eq. (30) which in our case leads to the final result given by Eq. (37)

$$D = \begin{vmatrix} 1 & 1 \\ 1 & 0 \end{vmatrix}_\alpha \cdot 1_\beta \neq 0 \quad (37)$$

This result confirms the conclusion of earlier theoretical study¹⁴ demonstrating the allowed nature of one-end addition. The formalism of the method can be analogously applied to the analysis of any other free radical reaction. Thus for example applying such approach to the analysis of metathetic reactions (represented *e.g.* by the hydrogen abstraction from the CH bonds) the overlap determinant method confirms the allowed nature of the linear reaction mechanism (Scheme 15)



SCHEME 15

CONCLUSIONS

In the above example the applicability of the new formalism was clearly demonstrated. In summarising these encouraging results it should be emphasized that the proposed topological approach is not intended to substitute the more sophisticated quantum chemical description in terms of states and potential energy hypersurfaces. Our aim was rather to propose a simple and sufficiently efficient procedure allowing to help in empirical rationalisation and classification of photochemical reactions. Besides the simplicity the most valuable contribution of the proposed formalism consists in its universality allowing to analyse in a unified manner all types of reaction irrespective of whether and which symmetry element is conserved during the reaction. In this respect thus the overlap determinant method can be regarded as an alternative formulation of earlier Goddard "orbital phase continuity principle"¹⁵.

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