

A Classification of Photochemical Reactions

William G. Dauben*

Department of Chemistry, University of California, Berkeley, California 94720

Lionel Salem*

Laboratoire de Chimie Théorique,[†] Université de Paris-Sud, 91405 Orsay, France

Nicholas J. Turro*

Department of Chemistry, Columbia University, New York, New York 10027

Received August 8, 1974

Classification has been the dream of chemists for centuries. We now propose a classification of photochemical reactions built on a single unifying concept.

Three striking features of photochemistry are the extreme variety of reactions which are known, the apparent haphazardness which governs the nature of the reactive state, and the lack of predictability of the consequences of slight modifications in reactant structural changes and/or experimental conditions. For instance, the photochemical cis-trans isomerization of dienes seems totally unrelated to the photodimerization of these same dienes to divinylcyclobutanes. Similarly there seems to be little relationship between the addition of an electron-rich olefin to a ketone and the photoreduction of pyridine.

One may therefore ask: is each photochemical reaction unique? A second question is: why does one reaction occur in the singlet state, another in the triplet state, and yet another in a different triplet state? Thus ketones generally photoabstract hydrogen atoms in n, π^* states, not π, π^* states, and again more efficiently in the triplet state than in the singlet state. A third typical question is: what effect does a

polar solvent have on the quantum yields of these reactions? Some answers have already been suggested for such questions, but no coherent framework has yet been provided to relate a plethora of different phenomena.

The first step in our procedure is to draw a *state correlation diagram* for each photochemical reaction. To do this, we assume a certain reaction coordinate and we use our knowledge of: (a) the four states characteristic of systems in which a bond is broken or made (*i.e.*, one which can be approximated by a diradical structure);¹ these four states are one triplet (diradical) state and three singlet (diradical and two zwitterionic) states; (b) symmetry; in certain photochemical processes the assumption of coplanar reaction geometry and the use of the molecular plane as a symmetry element allow for illustrative correlations between reactant and primary product states;^{2,3} (c) the shifting of the relative energetic positions of the diradical and zwitterionic surfaces as a function of environmental changes (*i.e.*, substitution at the reaction centers, solvation, etc.); (d) the mutual interaction of the four surfaces, particularly avoided crossings, which may result from environmental perturbations.⁴ Whatever is known about the primitive topology of the low-lying potential energy surfaces is also employed.

William G. Dauben is Professor of Chemistry at University of California, Berkeley. He received the B.A. degree from Ohio State University, and, in 1944, the Ph.D. from Harvard University. His research interests are in structural and mechanistic organic chemistry. He is a member of the National Academy of Sciences, and was recipient of the 1973 Ernest Guenther Award in the Chemistry of Essential Oils and Related Products sponsored by Fritzsche-Dodge and Olcott Incorporated.

Lionel Salem was born in 1937. He pursued his undergraduate studies at the Sorbonne where he received his Licence. He continued his studies in Cambridge, England, where he received his Ph.D in 1960. He then left for Cambridge, Mass., where he did postdoctoral work with E. B. Wilson and where he remained on the Harvard faculty until 1963 when he returned to his native France. He is presently a Professor at the Université de Paris-Sud, Orsay, France. His field of research is in theoretical chemistry.

Nicholas Turro received a B.A. degree from Wesleyan University in 1960, took his Ph.D. from Caltech, did a year's postdoctoral work at Harvard, and then joined the faculty at Columbia, where he is now Professor of Chemistry. He has research interests in many areas, including work on cyclopropanes and on molecular photochemistry of alkanones in solution. He is recipient of the 1974 ACS Award in Pure Chemistry sponsored by Alpha Chi Sigma Fraternity.

[†] The Laboratoire de Chimie Théorique is also associated with the CNRS.

(1) (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973); (c) J. Michl, *J. Mol. Photochem.*, **4**, 243 (1972).

(2) (a) L. Salem, W. G. Dauben, and N. J. Turro, *J. Chim. Phys. Phys.-Chim. Biol.*, **70**, 694 (1973); (b) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).

(3) Other examples of *state correlation diagrams* for photochemical reactions include (a) (pericyclic reactions) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2046 (1965); (b) (valence isomerizations of benzene) I. Haller, *J. Chem., Phys.*, **47**, 1117 (1967); D. Bryce-Smith, *Chem. Commun.* 806 (1969); (c) (photoadditions of oxygen) D. R. Kearns, *J. Am. Chem. Soc.*, **91**, 6554 (1969).

(4) (a) L. Salem, C. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975), have proposed a classification of avoided surface-crossing types in organic chemistry. See also the elegant reviews of: (b) T. F. O'Malley, *Adv. Atom. Mol. Phys.*, **7**, 223 (1971); (c) A. Devaquet, *Pure Appl. Chem.*, in press.

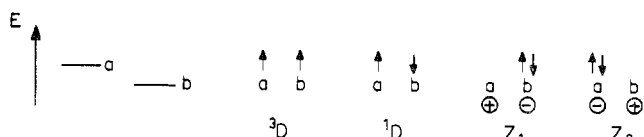


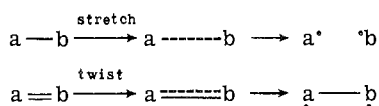
Figure 1. The four electronic states of a diradical (orbitals a and b are assumed to be localized and quasiorthogonal).

The major discriminating features which govern the pattern of correlation diagrams for different reactions are the total number and nature of available radical sites generated in the primary photochemical product. These features define the *topicity* of the reaction, a unifying concept introduced previously^{2b} and now generalized.

Having determined this major electronic characteristic for each photochemical reaction, we find that reactions which were hitherto apparently unrelated fall into families which share a common topicity. These families are shown in Table I. In this manner we can answer the preceding questions. The two reactions of the dienes are found to belong to the same family. Surprisingly, so do the addition of electron-rich olefins to ketones and the photoreduction of pyridine also belong to one family. The specific reactivities of particular excited states also stem naturally from consideration of the correlation diagrams: a reactant excited state which leads to a highly excited state of primary product can generally be ruled out as the photoreactive state, while a state correlating directly with primary product is a strong candidate to be the photoreactive state. Finally qualitative predictions can be made as to solvent effects by seeking out those states, in the correlation diagram, which will be stabilized or destabilized by the solvent. As such, the classification can serve as a useful guide to the photo-chemist.

The Description of Diradicals and of Their Electronic States

We first summarize briefly the important electronic properties of diradicals.¹ Imagine a chemical bond a-b which is being broken by either a stretching motion (*i.e.*, a σ bond) or a twisting motion (*i.e.*, a π bond). As the bond weakens the system takes on the characteristics of a diradical:



Chemists would normally expect diradical products as the result of these stretching or twisting motions. In fact, four different states may potentially be involved in the reaction mechanism corresponding to these motions. A simple description of these states, together with their labeling, is given in Figure 1. We assume that the energies of an electron on site a and site b are comparable, although not strictly equal. It is clear from the figure that two of the four electronic situations correspond to the standard notion of a diradical. These diradical states are labeled 3D and 1D according to their spin multiplicity. Furthermore, two states of ionic character, Z_1 and Z_2 ($Z_1 < Z_2$), occur. These zwitterionic states must be singlets because the two electrons are located in one orbital.

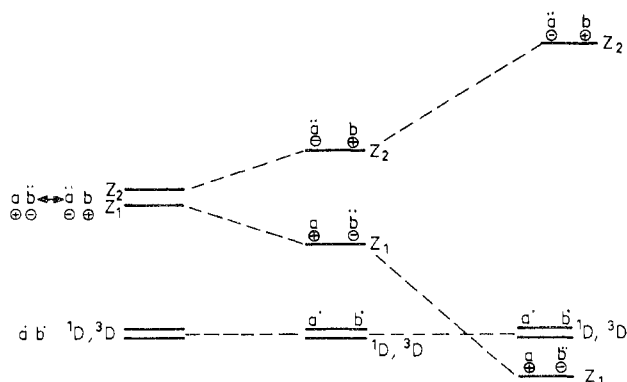


Figure 2. Ordering of the four states of a diradical as a function of the energy separation of a and b. In the limit where a and b have identical energies, Z_1 and Z_2 are properly represented by out-of-phase and in-phase combinations of a^+, b^- and a^-, b^+ . The dotted lines should not be construed as representing actual surfaces but only as a schematic connection between the states.

What is the energetic ordering of these four states? As long as sites a and b have comparable energies, the two diradical states fall below the two zwitterionic states. Either diradical state can be the ground state, depending on factors such as the relative orientation of the orbitals, the nature of the bonds which connect the sites, etc. The separation between the two zwitterionic states is very small if a and b have very similar energies. If the energy of site a is raised while that of site b is lowered (see Figure 2) a splitting of the two zwitterionic states occurs: Z_1 is lowered while Z_2 is raised. For moderate energy differences between a and b, the Z_1 state remains above the two diradical states. When b is strongly stabilized relative to a, the Z_1 state falls below the two D states and becomes the ground state of the system.

The same effect of reordering of states, as achieved by substitution, can also be reached by increasing the solvent polarity, a perturbation which specifically stabilizes the zwitterionic states relative to the diradical states. The only difference from Figure 2 would be a lowering of Z_2 relative to its initial energy, but the splitting of Z_1 and Z_2 would remain roughly constant.

Relationships between Potential Energy Surfaces

The pathway of a photochemical reaction may be determined by the manner in which the initial state connects with the final primary product. In order to make this connection properly, we must consider both the ordering of reactant low-lying excited states and of primary product D and Z states. The general kinds of interrelationships which will be found when these connections are carried out are (G refers to ground state, * refers to the lowest excited state of a given multiplicity, ** refers to an upper excited state; I and J are primary product states): (a) crossings, such as occur between electronic states of different spatial symmetry or different spin multiplicity;



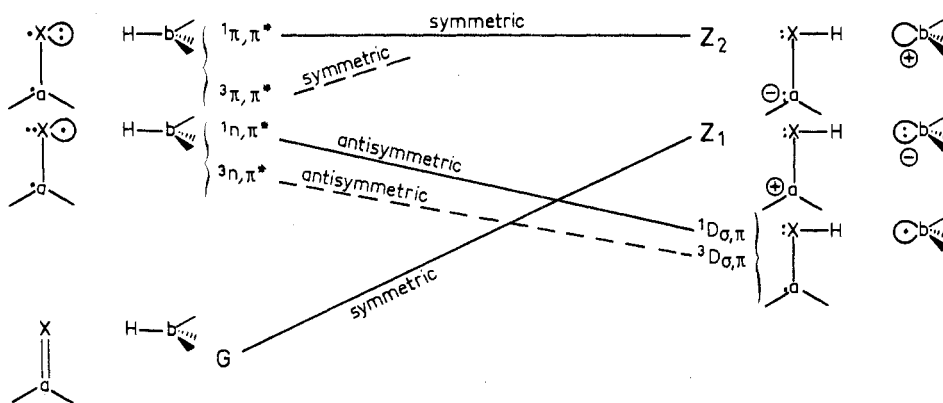
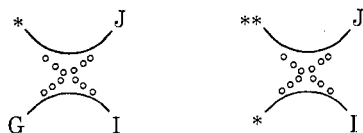


Figure 3. State correlation diagram for a hydrogen abstraction reaction.

(b) avoided crossings (indicated by circles),⁴ such as occur between electronic states of same spatial and spin symmetry. Approximate wave functions lead to intersecting surfaces; for the exact wave functions the intersection is avoided. The two surfaces are linked



dynamically by virtue of their intentional crossing; it may be easier for the nuclei to follow the circles along the intersecting surfaces because of the extensive electronic rearrangement required in keeping on the avoiding surfaces (full lines);^{4b} (c) matchings, in which the two surfaces remain well-separated throughout the reaction coordinate, with no dynamical link at the purely electronic level.

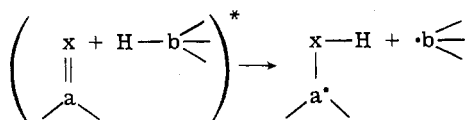


In these schemes I and J can be any of the four states 1D , 3D , Z_1 , Z_2 , although not all combinations apply (for instance, there cannot be, at the electronic level, an avoided crossing between 3D and a singlet state).

These pictures indicate that there are qualitatively different manners in which excited reactant can reach ground primary product. Each case will be discussed in detail as to its qualitative physical meaning and to its chemical implications.

Procedure for Analyzing a Specific Photochemical Reaction in Which Two Radical Sites Are Generated

(1) The procedure which serves as the basis of our classification is illustrated by considering a photochemical coplanar hydrogen abstraction reaction. It is important first to write the photochemical primary step—the first step in which a covalent bond is broken or formed—using standard structures to describe reactant and products:



Clearly, two radical centers are generated in the primary product(s).

(2) In such reactions the discriminating symmetry element is the *plane containing the pertinent reaction centers*, which is assumed to be conserved throughout the reaction. It is the plane $aXHb$ relative to which we locate the orientation of the odd-electron orbitals. The orbital on atom b remains in the symmetry plane at the end of the abstraction process and is therefore of σ symmetry. The electron on center a must be in an orbital of π nature relative to the reaction plane. We term such a process *bitopic*^{2b} because two radical centers are produced in the primary product. We also add the label σ,π to identify the symmetry of the newly generated odd-electron centers relative to the reaction plane.^{2b}

(3) The third step is to enumerate the states of the primary product, determine their symmetry, and dispose them in their probable energetic ordering. For two radical centers we have seen that the states are 3D , 1D , Z_1 , and Z_2 . The diradical states, with one odd σ electron and one odd π electron, are *antisymmetric* with respect to the molecular plane. They are labeled $D_{\sigma,\pi}$. The zwitterionic states, with a σ^2 or π^2 electron distribution, are *symmetric* with respect to the plane. Finally the ordering of the four states depends on the relative energies of centers a and b in exactly the manner discussed in Figure 2.

(4) We now turn to the relevant reactant states. In general only one or two starting-material states initiate the photochemistry. Of these states, the n,π^* *antisymmetric*, and π,π^* *symmetric* are the most commonly encountered. We must therefore concern ourselves usually with $^1n,\pi^*$, $^3n,\pi^*$, $^1\pi,\pi^*$, and $^3\pi,\pi^*$ states. We start by correlating as many reactant states, the ground state included, as we have available primary product states from our previous enumeration. In our hydrogen abstraction reaction, therefore, we can correlate the lowest antisymmetric and two lowest symmetric singlets of the reactants, as well as the lowest antisymmetric triplet. Any additional reactant state (e.g., $^3\pi,\pi^*$) must correlate with high-energy product states and will not always be shown.

(5) For specific correlation the usual procedure of joining states of the same symmetry, proceeding upwards in energy, is employed. This correlation² is shown in Figure 3. A convenient method for determining state symmetries and correlations is to count

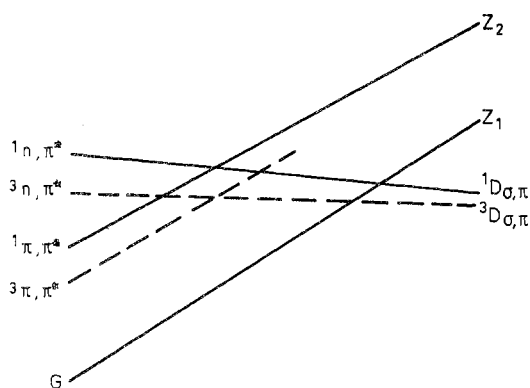


Figure 4. The new correlation diagram for hydrogen abstraction when the π, π^* manifold is lower than the n, π^* manifold.

σ and π electrons on the reaction centers. States with an even number of π electrons are symmetric while states with an odd number of π electrons are antisymmetric.

(6) The last step attempts to draw qualitative information by inspection of the diagram. The $^1n, \pi^*$ and $^3n, \pi^*$ states should both be reactive because they both correlate directly to diradical products. It is noteworthy that conversion of both these n, π^* states to primary products is an adiabatic process which does not involve an electronic deexcitation along the reaction pathway. Moreover the $^1\pi, \pi^*$ state is anticipated to be not only short-lived (as the second excited singlet of reactant) but also unreactive toward hydrogen abstraction. It correlates directly with an excited state, with high energy content, of the primary product. The same is true of the $^3\pi, \pi^*$ state, which correlates with some excited state of 3D .

(7) At this stage the essential features of any σ, π bitopic photochemical reaction are encompassed in the diagram of Figure 3. Environmental effects which would reverse the ordering of reactant ($^1n, \pi^*$ vs. $^1\pi, \pi^*$) or product (Z_1 vs. $^1D_{\sigma, \pi}$) states can now be easily evaluated. First, the situation in which the n, π^* and π, π^* manifolds are reordered. The appropriate correlation diagram is given in Figure 4. Inspection of the diagram shows that the two lowest excited states correlate with high-energy product states: $^1\pi, \pi^*$ with Z_2 , and $^3\pi, \pi^*$ with some excited state of 3D with an odd electron on b and one in a $\sigma^*(Xa)$ orbital. To a first approximation, both these states should react inefficiently. We cannot evaluate, however, how much efficiency might be gained if, instead of following the adiabatic pathways crossing the n, π^* surfaces, the molecule internally converts nonadiabatically to these surfaces which allow reaction to occur. To a first approximation, the n, π^* states remain the reactive states, but reaction from these states occurs inefficiently because of rapid internal conversion among reactant states.

(8) Finally we consider explicitly the case where the reactant state ordering is the original one but where the environmental polarity changes in such a way as to lower the energy of the zwitterionic state Z_1 relative to the diradical states. The resulting diagram is shown in Figure 5. In this case there is a matching, rather than a crossing, of surfaces, and the n, π^* states no longer correlate directly with primary products. This we interpret to mean that the reaction (to

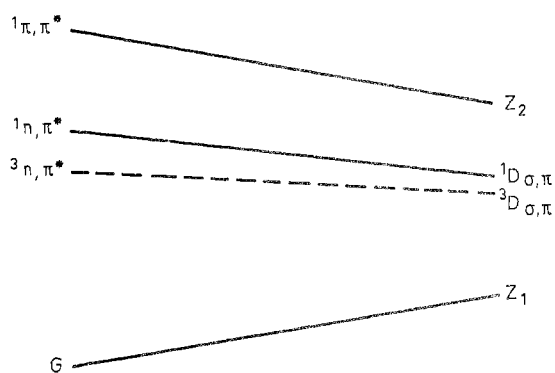


Figure 5. The new correlation diagram for hydrogen abstraction in highly polar solvent. The exact energy of Z_2 depends on the precise orientation of the solvent.

primary product Z_1) from n, π^* state now requires a radiationless transition and is thereby slowed down relative to the adiabatic pathway (to primary product $D_{\sigma, \pi}$) available in the nonpolar solvent (Figure 5). The quantum yield, albeit to a different product, should be smaller.

The reader will readily establish the correlation diagram in the case where both reactant and product states are shifted relative to our original model situation.

To summarize the qualitative features of our three diagrams: (i) in the first case (Figure 3), *crossing of reactant excited states downward toward products*, maximal reactivity is expected; (ii) in the second case (Figure 4), *crossing of reactant excited states upward toward high-energy product states*, we expect decreased reactivity; internal conversion at crossing points may allow residual reactivity; (iii) in the third case (Figure 5), *matching of surfaces*, the rate constant to reach primary diradical states (D) should not be affected but the requirement of a radiationless decay between well-separated surfaces should affect the quantum yields.

Experimental data on the hydrogen abstraction reaction of ketones ($X = \text{oxygen}$, $a = b = \text{carbon}$) provide numerous examples which illustrate the qualitative features of our correlation diagrams and the three major cases which they imply. First, a feature of Figure 3 is the occurrence of a "leakage" point as the result of the crossing of the $^1n, \pi^* \rightarrow ^1D_{\sigma, \pi}$ and $^3n, \pi^* \rightarrow ^3D_{\sigma, \pi}$ surfaces with that of the $G \rightarrow Z_1$ surface. In the Norrish type II hydrogen abstraction reaction, the $^1n, \pi^*$ state usually gives products less efficiently than the $^3n, \pi^*$ state even though the reactivities of the two states toward hydrogen abstraction are quite comparable.⁵ We can interpret these observations to mean that the rates of deactivation of $^1n, \pi^*$ and $^3n, \pi^*$ states are determined before the formation of primary products as the intersection is approached. However, the $^1n, \pi^*$ state has two spin-allowed channels for final "product" formation ($^1n, \pi^* \rightarrow ^1D_{\sigma, \pi}$ or G) but the $^3n, \pi^*$ state has only one ($^3n, \pi^* \rightarrow ^3D_{\sigma, \pi}$). This interpretation contrasts with the usual mechanism involved to explain singlet inefficiency ($^1n, \pi^* \rightarrow ^1D_{\sigma, \pi} \rightarrow G$) and suggests that an intermediate is not required to explain the inefficiency.

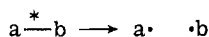
(5) (a) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, 21, 499 (1974); (b) the authors are grateful to F. D. Lewis for a discussion of singlet quantum yields in Norrish type II reactions.

Referring now to our discussion of Figure 4, numerous cases have been reported for which a decrease of ${}^3\pi, \pi^*$ relative to ${}^3n, \pi^*$ reactivity has been observed in hydrogen abstraction reactions.⁶ In a recent study, it was found that, when measured under comparable conditions, the rate constant for hydrogen abstraction from 2-propanol by 4-methylacetophenone (${}^3\pi, \pi^*$) is an order of magnitude smaller than that for acetophenone (${}^3n, \pi^*$). The rate constant for acetophenone triplets decreases as solvent polarity increases ($20 \times 10^5 M^{-1} \text{ sec}^{-1}$ in benzene, $5 \times 10^5 M^{-1} \text{ sec}^{-1}$ in 2-propanol, $0.5 \times 10^5 M^{-1} \text{ sec}^{-1}$ in water).^{7a} This reduced reactivity is attributed to a higher π, π^* character of the initial acetophenone triplet in polar solvents.

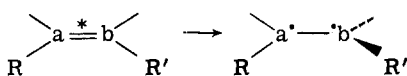
We consider finally the behavior of hydrogen abstraction in polar solvent. The rate constant for hydrogen abstraction from 2-propanol by benzophenone n, π^* triplets is insensitive to solvent,^{7b} as expected from Figure 5, since benzophenone still possesses lowest n, π^* state, even in polar solvents. The lowering of energy of Z relative to $D_{\sigma, \pi}$ (Figure 5) may, however, be the origin of the strong dependence of type II hydrogen abstraction quantum yields on solvent polarity.^{7c}

Further Examples of the Procedure in the Case of Generation of Two Radical Sites

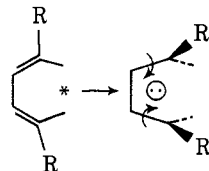
There are other photochemical reactions in which two radical sites are created but where the primitive topology of the energy surfaces is fundamentally different from those in examples discussed above. Such reactions include the rupture of a bond:



and concerted pericyclic photochemical reactions.⁸



the cis-trans isomerization of olefins:



We choose the isomerization of olefins as a second example to illustrate the procedure for analyzing photochemical reactions. We rapidly proceed through the same steps as in the previous analysis.

(6) For example, see N. C. Yang and R. L. Dusenberry, *J. Am. Chem. Soc.*, **90**, 5899 (1968); N. C. Yang and R. L. Dusenberry, *Mol. Photochem.*, **1**, 159 (1969); P. J. Wagner and G. Copen, *ibid.*, **1**, 173 (1969).

(7) (a) H. Lutz, M. C. Duval, E. Breheret, and L. Lindqvist, *J. Phys. Chem.*, **76**, 821 (1972); (b) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974); (c) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970; N. T. Anh, "Les Règles de Woodward-Hoffmann," Ediscience, Paris, 1970. The primary product of a pericyclic photochemical allowed reaction, whose structure corresponds to the minimum along the excited-state surface, is an antiaromatic skeleton with a diradical ground-state (M. J. S. Dewar, *Angew. Chem., Int. Ed., Engl.*, **10**, 761 (1971); H. E. Zimmermann, *Acc. Chem. Res.*, **4**, 272 (1971)). The two radical sites are delocalized, but the odd electrons occupy distinct atoms of the cyclobutadienoid skeleton (see further, ref 36).

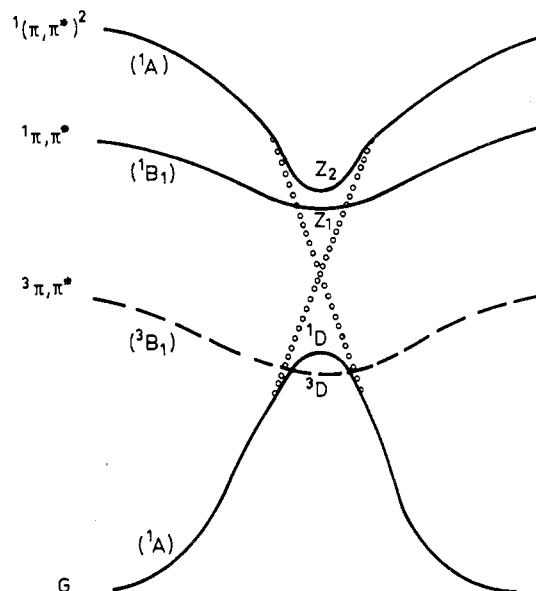
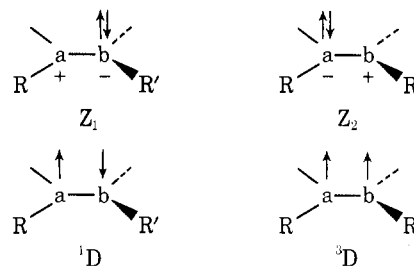


Figure 6. State correlation diagram for olefin twist (circles indicate avoided crossing). The symmetry notation of the states in the D_2 point group is given in parentheses.

(1) We write out the reaction in the classical manner as above.

(2) Two radical centers, in orthogonal orbitals, are generated in this reaction. The reaction, although formally bitopic because of the generation of the two radical sites, cannot be given the same label as in the abstraction reaction, since the orbital directions of a and b are orthogonal only at a single point along the reaction coordinate (*i.e.*, 90° twist) rather than throughout the reaction. The appropriate labeling for these types of systems is discussed on p 52.

(3) The states of the primary intermediate are a ${}^1D, {}^3D$ pair of diradical states and two zwitterionic states Z_1 and Z_2 described by the classical formulas



(4) In the reactant olefin only π, π^* states need be considered. Specifically we include ${}^3\pi, \pi^*$ state, ${}^1\pi, \pi^*$ state,⁹ and formally "doubly excited" ${}^1(\pi, \pi^*)^2$ state.¹⁰ Together with the ground state, we have precisely three singlets and one triplet to correlate with the three singlets and triplet states of the primary product.

(5) The proper correlations are well known^{1,9,11} and are shown in Figure 6. This figure shows several

(9) There is a lower, Rydberg, singlet state, but the ${}^1\pi, \pi^*$ state still correlates with Z_1 via a weakly avoided crossing with this Rydberg state (S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **27**, 243 (1972); R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971)).

(10) This "doubly excited" state, which in dienes lies near the ${}^1\pi, \pi^*$ state, is a mixture of several configurations (K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972); T. H. Dunning, R. P. Hosteny, and J. Shavitt, *J. Am. Chem. Soc.*, **95**, 5067 (1973)).

(11) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968); A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

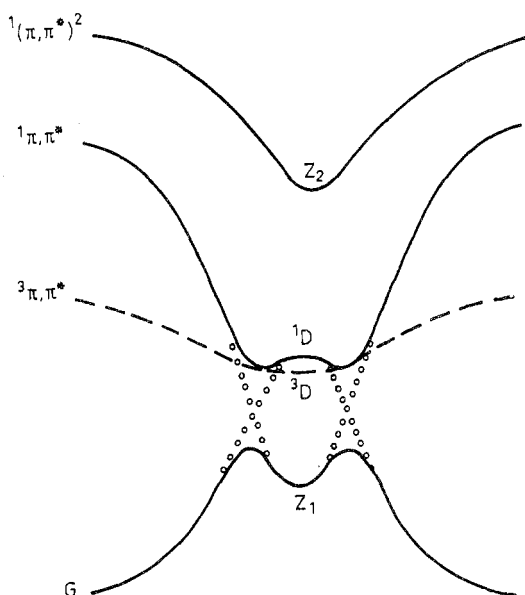


Figure 7. State correlation diagram for olefin twist in highly polar solvent (circles indicate avoided crossing).¹³

interesting features: (a) an avoided crossing between doubly excited state (near Z_2) and ground state (near 1D), which finds its origin in the crossing of π and π^* molecular orbitals of ethylene as the molecule undergoes a 180° twist;⁴ (b) a matching of ${}^1\pi, \pi^*$ state and ground-state surfaces; and (c) a crossing between ${}^3\pi, \pi^*$ state and ground-state surfaces.

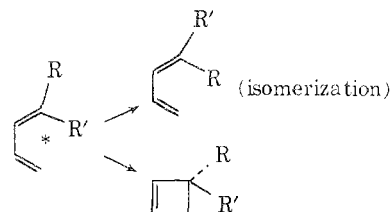
(6) We now draw qualitative conclusions from this diagram. The first is that the *triplet* should undergo efficient *cis-trans* isomerization because its surface crosses slightly that of the ground primary product. The intersystem crossing rate between 3D and 1D is not expected to be particularly fast,^{1a} but, since the triplet is in a minimum, intersystem crossing is still an efficient process. For the lowest singlet, it would appear that the most efficient pathway to 1D requires prior internal conversion to Z_2 ; Z_2 can in turn convert to 1D via the dynamical link between the two surfaces. For this same reason the reaction would appear to be more facile in the *higher* ${}^1(\pi, \pi^*)^2$ state.

(7) The final step is to deduce the surface pattern when Z_1 lies below D . This would occur under conditions of strong polar solvation of an olefin or in extremely polar olefins.¹² The first excited ${}^1\pi, \pi^*$ state of the olefin still tends to correlate with Z_1 while the ground state tends to correlate with 1D . Since 1D now lies above Z_1 there is an *intended* crossing, similar to the crossing of ionic and covalent surfaces in alkali halides.⁴ In practice this crossing will be avoided: the ionic and covalent characters mix in the crossing region, giving a "type B" avoided crossing.^{4a} The avoided crossing should be reflected by a potential barrier in the ground surface and by a *secondary minimum* for Z_1 (Figure 7).¹³ Here is a case in which the ground state and *lowest* excited singlet surface, though separated throughout the reaction path, are linked dynamically by virtue of their intentional crossing. An additional feature is that decay from the excited singlet, which was originally most likely to occur at the position of 90° twist (Figure 6), is now predicted to occur more effectively at some earlier stage of the

torsional motion. One consequence is a faster decay to ground surface but a reduced efficiency in isomerization. Another is the formation of a zwitterionic intermediate which corresponds to a highly twisted olefin (*vide infra*).

The general forms of the surfaces in Figures 6 and 7 are also pertinent to the analysis of pericyclic photochemically allowed processes.⁸ Not only is the topology of ground surface and lowest excited surfaces qualitatively the same,¹⁴ but the relevant excited states in the pericyclic reactions are precisely those which we have just examined, and their correlation with the (D, Z) manifold is identical with that of Figure 6. In particular, Z_2 remains linked dynamically to 1D via an avoided crossing.^{3a}

Indications are, however, that the surfaces for pericyclic reactions have certain features which discriminate these reactions from simple olefin isomerizations (Figure 8).¹⁴ Such differences, which appear by comparing Figure 8 with Figure 6, can be important in determining the partitioning of products in competing reactions such as:



Essentially: (a) in the singlet manifold of pericyclization, Z_2 drops below Z_1 . This should help the previously mentioned $Z_1 \rightarrow Z_2$ internal conversion from ${}^1\pi, \pi^*$ state to ${}^1(\pi, \pi^*)^2$ state. It also brings Z_2 closer to 1D at 58 kcal/mol^{14e} compared with 88 kcal/mol,⁹ and should thereby facilitate $Z_2 \rightarrow {}^1D$. Let us now follow an excited ${}^1\pi, \pi^*$ butadiene molecule along the two *distinct* pathways which lead it above the two *distinct* ground surface 1D maxima related respectively to cyclobutene and to its *cis,trans*-butadiene isomer. To make this comparison we compare Figures 6 and 8. The $Z_1 \rightarrow Z_2$ conversion, and the $Z_2 \rightarrow {}^1D$ decay, can occur above either maximum in two different regions of hyperspace. The overall decay process $Z_1 \rightarrow {}^1D$, however, should be more efficient above the cyclobutene peak and in this simple picture singlet butadiene should prefer the pericyclic reaction to the isomerization reaction. (b) The triplet ${}^3\pi, \pi^*$ surface seems to remain *above* (but close to) ground singlet surface throughout the reaction path and also not to show a significant minimum.¹⁴ Again, if we follow ${}^3\pi, \pi^*$ butadiene along two distinct pathways dealing respectively with cyclobutene and to the *cis,trans*-butadiene isomer, intersystem crossing ${}^3D \rightarrow {}^1D$ should be more efficient near the isomer maximum than near the cyclobutene maximum. In contrast to the singlet, the triplet state should prefer isomerization to pericyclic reaction.^{14f}

(12) H. O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973).

(13) L. Salem and W. D. Stohrer, *Chem. Commun.*, in press.

(14) (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969); (b) J. Langlet and J. P. Malrieu, *ibid.*, **94**, 7254 (1972); (c) O. Kikuchi, *Bull. Chem. Soc. Jpn.*, **47**, 1551 (1974); (d) J. Michl, *Pure Appl. Chem.*, in press; (e) D. Grimbert, G. Segal, and A. Devaquet, *J. Am. Chem. Soc.*, submitted for publication; for a detailed discussion of pericyclic minima ("funnels") and their open-chain counterparts, see J. Michl, *Fortschr. Chem. Forsch.*, **46**, 1 (1974), Section F.

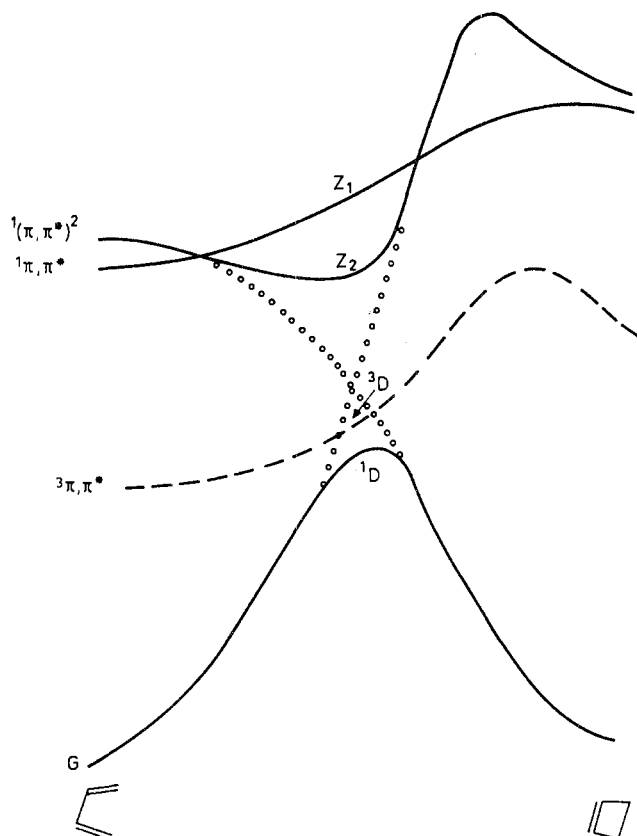
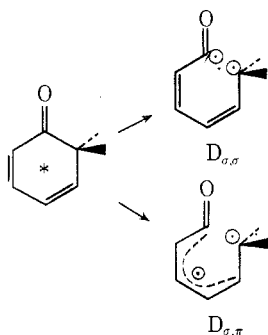


Figure 8. Potential energy surfaces for a photochemical pericyclic reaction adapted from Grimbert, Segal, and Devaquet.^{14c}

Examination of *cis-trans* isomerization of olefins has revealed a new pattern of relationships between potential-energy surfaces (Figures 6, 7), *avoided crossing between ground and excited singlet states*, with enhanced radiationless transition to ground state (relative to matching of surfaces with a similar energy gap). A final type, *avoided crossing between excited-state surfaces*, will be encountered shortly (see Figure 13).

Procedure for Analyzing Photochemical Reactions in Which Three or More Available Radical Sites Are Generated

(1) The α cleavage of 2,4-cyclohexadienones illustrates a feature of certain photochemical reactions in which more than two radical sites are generated in the primary photochemical product.



(2) In this example the electron on the quaternary carbon remains in a σ orbital in the plane of the molecule as cleavage occurs (assumedly in a coplanar fashion). However, the other electron of the bond

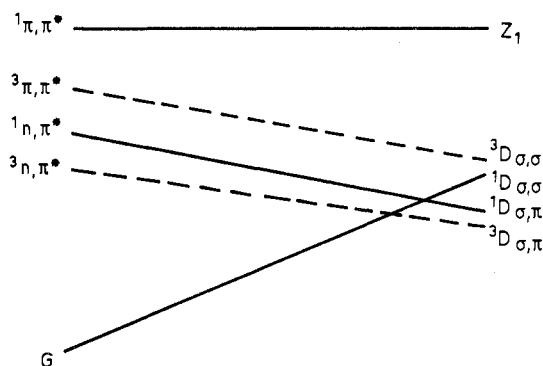


Figure 9. State correlation diagram for α cleavage of 2,4-cyclohexadienones.¹⁵ We have placed triplet ${}^3D_{\sigma,\pi}$ below singlet ${}^1D_{\sigma,\pi}$ in accordance with Hund's rule for orthogonal orbitals. The relative ordering of $D_{\sigma,\sigma}$ singlet and triplet—shown here as in the cleavage of a σ bond—is uncertain and will depend on nonorthogonality, through-bond interactions, etc.

cleaved has a choice, in the fragment formed, between occupancy of a σ orbital on the acyl carbon or of a delocalized pentadienylic π orbital perpendicular to the molecular plane. All together *three* available radical sites are generated by the cleavage of the bond. Since one of the radical sites remains σ in the two primary products formed, and since the other site can have either σ or π symmetry, we term such a process $\sigma(\sigma,\pi)$ *tritopic*.^{2b} The parentheses include the alternatives for a single electron.

(3) Enumeration of the possible electronic states of primary product requires distribution of the two electrons, in all allowable combinations, in the three radical sites. There are clearly *two* diradical pairs of states (1D , 3D) corresponding to the two classical structures illustrated. One of these diradicals, which we label $D_{\sigma,\pi}$, is a σ,π diradical whose singlet and triplet states are antisymmetric with respect to the molecular plane. The other diradical, which we label $D_{\sigma,\sigma}$, is a σ,σ diradical with symmetric state wave functions. There are a number (three) of singlet zwitterionic states in which a pair of electrons enters respectively into any one of the three radical sites. These states are all symmetric. Finally, there is a pair (singlet, triplet) of "mixed" states with simultaneous diradical and ionic character in which one electron occupies the acyl carbon σ orbital and a second electron (with antiparallel or parallel spin) the odd π delocalized orbital. Of these nine states we only keep those (five) required to correlate the pertinent reactant states.

(4) The reactant states are the usual ground, n,π^* , and π,π^* singlet and triplet pairs.

(5) Figure 9 shows the correlation diagram for the α -cleavage of 2,4-cyclohexadienones when the n,π^* manifold of states lies below the π,π^* manifold. In this figure we have placed the σ,π diradical states below the σ,σ diradical states, thanks to the additional energy accrued from π delocalization in the former.¹⁵

(15) A word of caution concerns the possible occurrence of maxima between the initial state and final state even when they are correlated by a surface of decreasing slope in our analysis. Such maxima may arise (a) for states with same symmetry but with a different electron count (i.e., ${}^1\pi,\pi^* \rightarrow Z_2$ with $4\sigma,2\pi \rightarrow 2\sigma,4\pi$ in σ,π bitopic reactions), or (b) for states with same symmetry but where a change occurs in the (σ,π) nature of a pair of radical sites (i.e., ${}^3\pi,\pi^* \rightarrow {}^3D_{\sigma,\sigma}$). Both cases involve a change in the occupancy of individual MO's. (In the second example the singly occupied π and π^* reactant

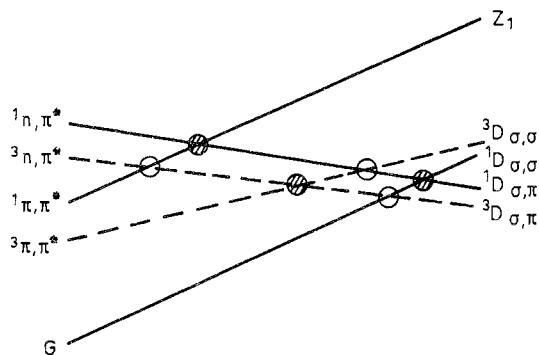


Figure 10. State correlation diagram for α cleavage of 2,4-cyclohexadienones when the π, π^* manifold lies below the n, π^* manifold. Circles indicate favorable intersystem-crossing points. Shaded circles indicate internal-conversion points.

(6) One remarkable conclusion is that the diagram is fundamentally analogous to that for hydrogen abstraction (Figure 3), in that surface crossings occur between the n, π^* reactant states and the ground state during the cleavage of the σ bond. Facile reaction from the n, π^* manifold, as has been observed,¹⁶ follows immediately. A novel feature is the possible reactivity of $^3\pi, \pi^*$ state^{2b} even though it is the second excited triplet, suggesting the possibility of wavelength-dependent photochemistry. Indeed this triplet state correlates directly with the σ, σ diradical,¹⁵ which cannot lie more than a few kcal/mol above the ground σ, π diradical (see footnote 55 of ref 2b).

(7) We now reverse the relative energetic order of n, π^* and π, π^* manifolds (there are intermediate cases in which these manifolds are interspersed, which we leave as an intellectual exercise for the reader to explore). Figure 10 shows the appropriate correlation diagram. The form of the patterns for both $^3\pi, \pi^*$ and $^1\pi, \pi^*$ involves an energetically unfavorable "upwards" crossing with a higher (n, π^*) state of the same spin multiplicity and also a higher (n, π^*) state of different multiplicity and different spatial symmetry. This latter situation is extremely favorable for intersystem crossing^{1a} between states and is indicated in the diagram by circles at important intersections. Depending on the surface slopes and intersystem-crossing probabilities, some reactivity may be expected.^{2b} The most likely reaction path is that where the $^3\pi, \pi^*$ state reacts *via* internal conversion to the descending $^3n, \pi^*$ state.

This allows us to emphasize two features hitherto neglected in the interpretation of photochemical reactions: (a) the reactivity of a state is not necessarily related to its spectroscopic classification whenever an upward crossing to a state of different spatial or spin symmetry occurs; (b) the changeover, at such a crossing point, from one state to another, *via* internal conversion or intersystem crossing, requires vibronic

orbitals do not correlate with the two primary product singly occupied σ orbitals). In both cases the *total* symmetry is conserved but the *individual* orbital symmetries are not (D. M. Silver, *J. Am. Chem. Soc.*, **96**, 5959 (1974)). Since the correlations are possible because of increasing admixture of foreign configurations ($^1n, \pi^* \rightarrow ^1\pi, \pi^*$; or $^3\sigma, \sigma^* \rightarrow ^3\pi, \pi^*$) into the major configurations of the reactant excited state, the size of the barrier will depend (inversely) on the extent to which such secondary components are already mixed-in at the starting geometry. Further studies of these cases are in progress (L. Salem, unpublished results); see also the lucid account of J. Michl, *Fortschr. Chem. Forsch.*, **46**, 1 (1974), in particular pp 51–52.

(16) G. Quinkert, *Pure Appl. Chem.*, **33**, 285 (1973).

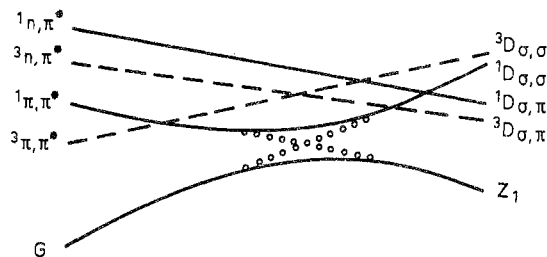
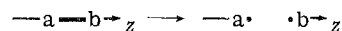


Figure 11. State correlation diagram for α cleavage of 2,4-cyclohexadienone with ground Z_1 primary product (π, π^* manifold below n, π^* manifold).

mixing of the two states, but this phenomenon is *not the same* as the generally invoked mixing of states, at the equilibrium geometry of the reactant, *via* vibrations which are totally unrelated to the reaction coordinate.

(8) In the usual manner we now envisage the case where system or solvent polarity pushes Z_1 below diradical pairs of states. The result is shown in Figure 11, in which the π, π^* manifold is kept *below* the n, π^* manifold. The new characteristic is the ("type B")⁴ avoided crossing between a ground surface, which tends covalently toward $^1D_{\sigma, \sigma}$, and an excited $^1\pi, \pi^*$ surface, which tends ionically toward ground primary product Z_1 . Compared to the situation in nonpolar solvent represented in Figure 9, reactivity of the $^1\pi, \pi^*$ state should be considerably enhanced.¹⁷

Bond cleavage can generate more than three available radical sites, indeed as many as six distinct sites. In the process



atoms a or b can in principle carry their odd electron in a σ orbital coaxial with the a–b direction or in π_x, π_y orbitals perpendicular to it. This is true if a or b is a halogen atom, which therefore carries *three* radical sites (2P state). This number is reduced to *two* (σ , one π) for alkoxy oxygen or amino nitrogen. The general label of such a reaction, or "topicity label," is

$$(i, j, \dots)(i', j', \dots)$$

where i, j , etc., refer to the available radical sites generated on center a and i', j' to those generated on center b. The total number of sites is equal to the total number of labels in the two parentheses.

Examples of such photochemical reactions are: (a) *Four sites* (tetratopic): $\sigma(\sigma, \pi_x, \pi_y)$: the photolysis of alkyl halides. There are three pairs of primary product diradical states, depending on the orientation of the odd-electron orbital in the departing halogen atom. Figure 12 shows a simplified correlation diagram concerning only the three singlet diradical states. The relevant excited states are from the pair of n orbitals on halogen to σ^* in the halogen–carbon bond.

$(\sigma, \pi)(\sigma, \pi)$: photocleavage of the central bond of an α -diketone. Two tetratopic reactions deserve special attention: the cleavage of 1,2-dioxetanes¹⁸ and photochemical electron-transfer reactions. We consider the latter reaction in some detail below.

(17) H. Hart, *Pure Appl. Chem.*, **33**, 247 (1973).

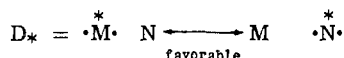
(18) N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, submitted for publication, and references therein.

(b) *Five sites* (pentatopic): $(\sigma, \pi)(\sigma, \pi_x, \pi_y)$: photocleavage of acyl halides; photodissociation of aromatic halides. The labels π_x and π_y refer respectively to an *in-plane* p orbital and an out-of-plane p orbital both perpendicular to the axis of bond cleavage. An alternative but less explicit notation would be $(\sigma, \pi)(\sigma_1, \sigma_2, \pi)$.

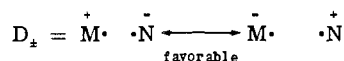
(c) *Six sites* (hexatopic): $(\sigma, \pi_x, \pi_y)(\sigma, \pi_x, \pi_y)$: photodissociation of halogens X_2 and interhalogens. There are nine diradical pairs of states which correlate with ground, singly excited, and doubly excited molecular states.

Another Example of the Procedure in the Case of Generation of More than Two Radical Sites

Photochemical electron transfer is an important reaction-initiating process occurring in many photoassociation reactions between donor (M) and acceptor (N) molecules. We view such photoassociation reactions as tetratopic in nature because excitation in *either* partner leads to *two* half-vacant orbitals. Photoassociation reactions which form exciplexes¹⁹ are characterized by (a) a repulsive ground surface (interaction of 1M with 1N); (b) a bound singlet surface in which a locally excited state (LE) leads to an exciplex



(note the four available radical sites); in this exciplex the "diradical" character switches back and forth between M and N. We label this diradical 1D_* , because excitation transfer stabilizes the species; a triplet surface, leading to a triplet exciplex 3D_* , parallels the behavior of the singlet surface; (c) a higher pair of surfaces in which a charge-transfer state (CT) of the aggregate leads to a radical-ion pair



in either a singlet or a triplet state. The temptation might be to label the singlet state Z_1 because of the + or - charges which appear in the notation. However, the *key characteristic of a zwitterion*, for the purposes of our analysis, is the *presence of paired electrons in orbitals* rather than polar character. We therefore label these states $^1D_{\pm}$, $^3D_{\pm}$ according to their stabilization by charge resonance.^{20,21}

The relative energetic disposition of D_* and D_{\pm} will depend on the polarity of the solvent and ability of the components of the aggregate to stabilize positive and negative charges. In particular, along a *solvation coordinate* which stabilizes D_{\pm} , the radical-ion pair can fall below exciplex, *i.e.* $D_{\pm} < D_*$. As a re-

(19) See J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, London, 1970.

(20) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963.

(21) (a) Since the reaction is formally tetratopic we should have *four pairs* of diradical states. However, two of these pairs of states correspond to similar resonance schemes as above, but with *unfavorable* resonance interaction. If M and N are similar molecules, these four additional states may be close by. *Often, however, only one of the two molecules (the acceptor) has an available vacant orbital j as radical site: for all practical purposes the reaction becomes tritopic with two pairs of low-lying diradical states.* (b) Symmetry does not preclude interaction between the resonance structures shown in b and the resonance structures shown in c, in which case the locally excited states can lead to "dipolar exciplexes."

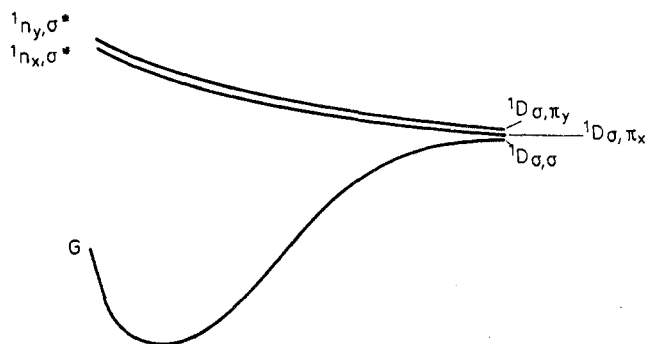


Figure 12. Correlation diagram for photolysis of alkyl halides (singlet states only).

sult the neutral LE states correlate with ionic intermediates D_{\pm} while the ionic CT states correlate with the covalent intermediates D_* . There is an avoided crossing between excited states²²—the fifth fundamental pattern which we have encountered. The surface schemes for both $D_* < D_{\pm}$ and $D_* > D_{\pm}$ cases are shown in Figure 13. On the left-hand side the gap between 1D_* and ground surface is ideal for a long lifetime of the intermediate and observation of excimer or exciplex fluorescence. On the right-hand side excitation to the lowest singlet 1LE of the aggregate leads to transfer of an electron and formation of $^1D_{\pm}$. The reaction coordinate is mixed, involving approach of the molecules simultaneously with rearrangement of the polar solvent. An "electron jump" occurs in the intended crossing region of the two excited singlet surfaces. This corresponds to the physical mechanism of photochemical electron transfer described by Weller.²³ The diagram on the right-hand side of Figure 13 suggests, however, that as a result of the avoided crossing and dynamical connection between the two excited singlet surfaces the yield of radical-ion pair $^1D_{\pm}$ and of electron transfer may be reduced by leakage into the exciplex 1D_* . The lifetime of $^1D_{\pm}$ itself depends on the energy gap between ground surface and first-excited singlet surface. An electron jump also occurs in the triplet manifold (*vide infra*).

Case Histories

We now discuss a few well-known photochemical reactions of wide scope, providing interpretation according to the procedure which we have outlined.

Heterolytic Photosubstitution Reactions of Aromatic Compounds.^{24,25} As recently as 9 years ago this reaction attracted considerable discussion at the Thirteenth Solvay Conference.²⁶ The analysis was

(22) A symmetry-allowed crossing may occur. Such a crossing may be responsible for the sharp discontinuities observed in excimer fluorescence as a function of solvent polarity: F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **72**, 1155 (1968); **74**, 624 (1970).

(23) (a) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); (b) H. Knibbe, K. Röllig, F. P. Schäfer, and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967); (c) D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).

(24) E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); G. P. de Gunst and E. Havinga, *Tetrahedron*, **29**, 2167 (1973), and references therein; J. Mulder, Thesis, University of Leiden, 1972, Part 2, Section 5; J. G. Lammers, Thesis, University of Leiden, 1974; J. G. Lammers and J. Lugtenburg, *Tetrahedron Lett.*, 1777 (1973).

(25) H. E. Zimmermann and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963).

(26) (a) See, in particular, E. Havinga, in "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N.Y., 1967, p. 201, the discussion on p 219 ff, and the general discussion on p 302 ff. (b) A more recent attempt at drawing potential surfaces is due to P. Seiler and J. Winz, *Helv. Chim. Acta*, **55**, 2693 (1972).

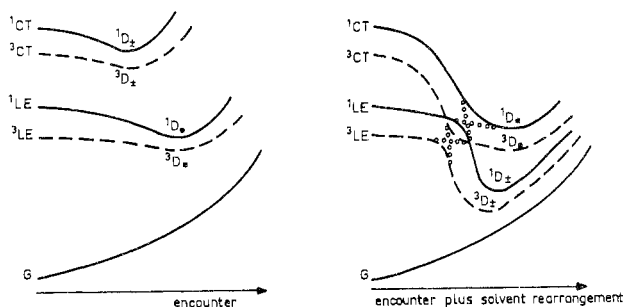
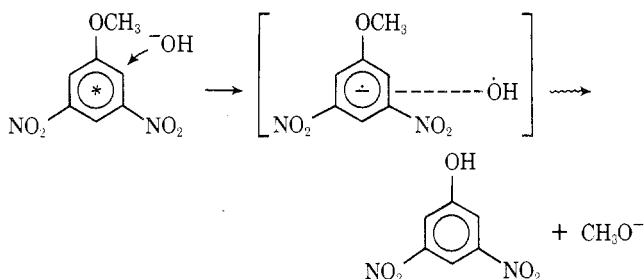


Figure 13. State correlation diagrams for photoassociation and photochemical electron transfer (circles indicate avoided crossing). Left-hand side: nonpolar solvent; right-hand side: polar solvent.

generally couched in terms of a single excited surface and a ground-state surface between which excitation first, and radiationless decay next, were assumed to occur. As with many other reactions, little attention was paid to the possible role of state symmetries and electronic characteristics of reactants and primary products in determining the photochemical pathway.

Heterolytic photosubstitution reactions constitute an interesting case because the element of symmetry present in most of our previous examples does not occur. Thus we must seek to correlate the general electronic characteristics of the reaction, which appear in the classical resonance structures for reactant and primary product, with one of our previously discussed reaction types. A typical primary reaction step (for nucleophilic substitution of methoxybenzenes)²⁴ can be written as



The system within the brackets corresponds to Havinga's "aromate-nucleophile-complex" between the triplet excited aromatic compound and the nucleophile. Since we do not know the detailed structure of this complex, we are purposely vague about the nature of the bonding between the interacting partners. However, since the radical anion of the starting material is found to originate from this complex, we assume that the structure indicated, with the negative charge on the highly electrophilic dinitrobenzene ring, is the proper primary product to which to make a correlation.

Looking back to a previous example we see that the primary step is fundamentally photochemical electron transfer between a donor and an excited acceptor molecule. Even though the molecular plane of the aromatic molecule cannot remain a symmetry element along the reaction coordinate, the correlation diagram can be constructed by analogy with Figure 12. We identify the aromatic acceptor with molecule M and the hydroxide anion with molecule N. The reaction is tritopic.²¹ The locally excited states, and 1D_* , 3D_* states, involve π, π^* excitation on the ar-

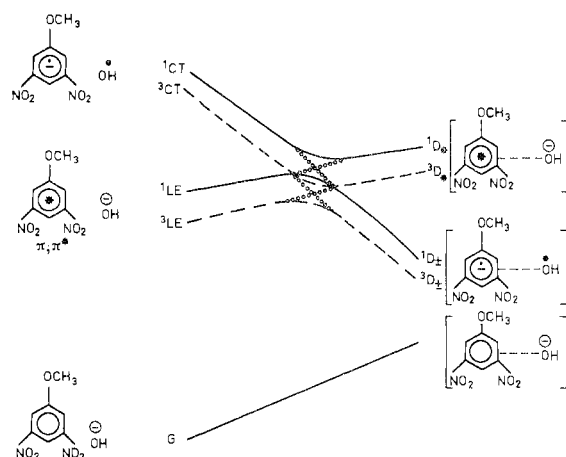


Figure 14. State correlation diagram for nucleophilic aromatic photosubstitution (circles indicate avoided crossings). Compare also with ref 26b.

omatic nucleus. The charge-transfer states, and $^1D_{\pm}$, $^3D_{\pm}$ states, involve charge transfer from ^-OH to neutral aromatic, to form hydroxyl radical and aromatic anion radical.

The correlation diagram for states is shown in Figure 14. (The nomenclature in Figure 14 is extrapolated from systems which bear no overall net charge. The reader may find the correspondence with previous cases by formally subtracting a negative charge from the hydroxyl group without changing the number of electrons.) The $^1D_{\pm}$, $^3D_{\pm}$ states have been placed below the 1D_* , 3D_* states because of the incipient stabilization which results from partial covalent bond formation between the two odd-electron sites. The D* pair may lie above LE because there is no matching of orbitals allowing for stabilization by excitation transfer. Inspection of the diagram shows that there is a direct path from 3LE to $^3D_{\pm}$, via an electron jump which occurs in the region of the avoided crossing between charge-transfer triplet and locally excited triplet. Indeed experimentally it is found that the $^3\pi, \pi^*$ state is the reactive state in this photosubstitution. We have now shown that this $^3\pi, \pi^*$ state, in the presence of hydroxide anion, can form Havinga's "aromate-nucleophile-complex" in the triplet state via a simple electron transfer reaction along a single adiabatic surface. The 0.5- μ sec lifetime observed for this intermediate agrees well with its triplet character. Without this energy diagram it would not be apparent that the complex is still on an excited surface.

Photo-Fries Rearrangements²⁷ and α Cleavage of Alkanones. The Photo-Fries rearrangement is an interesting case because it apparently involves the cleavage of a σ bond in the singlet state as an efficient process.²⁸ The singlet state, according to available evidence,^{27,28} may be of either n, π^* or π, π^* configuration. This situation offers a contrast to the α cleavage of alkanones, for which the triplet state is clearly more reactive than the singlet.^{5a,29} We can ascribe

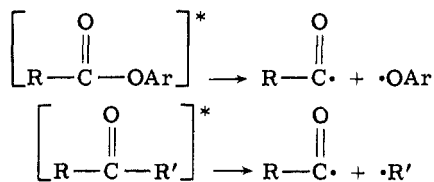
(27) (a) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc., London*, 217 (1960); (b) D. Bellus, *Adv. Photochem.*, 8, 109 (1971).

(28) (a) C. E. Kalmus and D. M. Hercules, *J. Am. Chem. Soc.*, 96, 449 (1974); (b) W. Adam, *Chem. Commun.*, 289 (1974).

(29) (a) R. G. W. Norrish, *Trans. Faraday Soc.*, 33, 1521 (1937); (b) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, 5, 92 (1972).

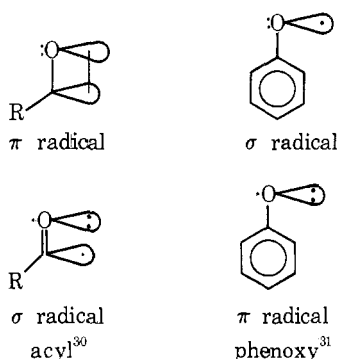
this contrasting behavior to the existence of an additional low-lying product state which results from the higher topicity (4 vs. 3) of the Photo-Fries reaction.

The photochemical primary steps of these reactions are:



In spite of the seemingly identical chemical behavior exhibited in the two reactions, a fundamental difference exists in the total number of radical sites generated by them. In the first case *both* fragments have two (σ, π) available radical sites, and therefore the reaction is (σ, π)(σ, π) tetratopic with *four* primary product diradical pairs of states available. In the second case two radical sites are available on the acyl fragment, but only one on the alkyl fragment. The reaction is $\sigma(\sigma, \pi)$ tritopic with two pairs of product diradical states.

Figure 15 presents state-correlation diagrams for both reactions. The ordering of primary product states is based on the following ordering of states for the radical fragments:



Although there are no calculations on the excited states of the phenoxy radical, and only fragmentary ones^{2b} on the acyl radical, the energy differences between ground and excited radical in both system are probably comparable, and close to 0.5–1.0 eV. The diradical states of the (acyl, phenoxy) pair required in the Photo-Fries reaction are then ordered as follows: a ground $\sigma_{\text{acyl}}, \pi_{\text{phenoxy}}$ $1,^3D_{\sigma, \pi}$ pair of states; two excited diradical pairs of states of comparable energy, corresponding to the $\pi_{\text{acyl}}, \pi_{\text{phenoxy}}$ configuration and to the $\sigma_{\text{acyl}}, \sigma_{\text{phenoxy}}$ configuration. We label these neighboring states $1,^3D_{\pi, \pi}$ and $1,^3D_{\sigma, \sigma}$. If the π, π and σ, σ configurations have extremely close energies there will be resonance mixing between them. In any case the two pairs of states remain very close, since the splitting between the “in-phase” and “out-of-phase” resonance states is easily shown to be small.

The major difference in the correlation diagrams is the availability in the Photo-Fries arrangement of a low-lying primary product singlet diradical state cor-

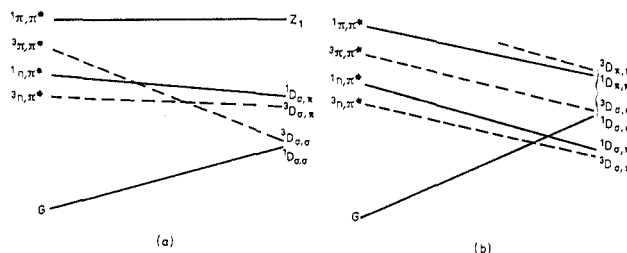
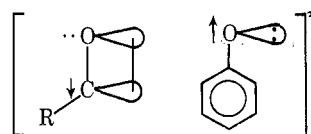


Figure 15. State correlation diagrams¹⁵ for (a) α cleavage of alkanones; (b) photo-Fries rearrangement (first subscript under D refers to acyl radical).

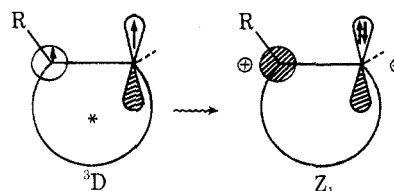
relating with the $1\pi, \pi^*$ state of reactant. Most likely, even if there is a slight avoided crossing of σ, σ and π, π configurations at the very end of the reaction path (*i.e.*, if $D_{\pi, \pi}$ lies slightly below $1D_{\sigma, \sigma}$),¹⁵ the correlation occurs to an excited primary product singlet radical pair:



Internal conversion in the acyl radical should allow the system to relax easily to its overall ground singlet state.

The formation of a π phenoxy radical agrees with the nature of the observed products, whether from intramolecular (cage) reactions to lead to 1,3 or 1,5 acyl shifts or from intermolecular reactions such as hydrogen abstraction or dimerization. However Figure 15b shows that the singlet and triplet n, π^* states should also react in a facile manner and also lead to the appropriate π phenoxy radical. It is also noteworthy that the $1n, \pi^*$ state in the case of the Photo-Fries reaction has a direct correlation with the lowest energy primary diradical whereas in alkanones (Figure 15a) this is not the case. *In alkanones an intersystem crossing to $3\pi, \pi^*$ may be required for $1n, \pi^*$ reactivity.*

Photoprotonation of Olefins³² The photoprotonation of olefins in hydroxylic media occurs under direct or sensitized irradiation for monosubstituted cyclohexenes and cycloheptenes. Although the involvement of a strained-ground state trans double bond has been postulated,³² it has never been unambiguously established. Our previous study of olefin isomerization demonstrated the importance of the polar Z_1 state, and of its susceptibility to the stabilizing effect of polar solvents (see Figures 2, 6, and 7). In the case where Z_1 falls below the $1D, ^3D$ pair of diradical states, an alternate mechanism becomes obvious by inspection of Figure 7. Excitation to $1\pi, \pi^*$ state can



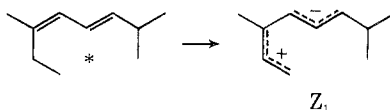
(30) For the analogous formyl radical, see (a) G. Herzberg, “Electronic Spectra and Electronic Structure of Polyatomic Molecules,” Van Nostrand, Princeton, N.J., 1966, p 496; (b) G. Herzberg “The Spectra and Structures of Simple Free Radicals,” Cornell University Press, Ithaca, N. Y., 1971, p 186.

(31) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

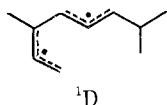
(32) (a) P. J. Kropp, E. J. Reardon, Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, *J. Am. Chem. Soc.*, **95**, 7058 (1973), and references therein; (b) J. A. Marshall, *Science*, **170**, 137 (1970); (c) R. Noyori and M. Kato, *Bull. Chem. Soc. Jpn.*, **47**, 1460 (1974).

lead to ground Z_1 via the dynamical link between the two singlet surfaces. Excitation to ${}^3\pi,\pi^*$ state can also lead to ground Z_1 for a 90° twist configuration. Indeed intersystem crossing should occur with much greater facility than in a ${}^3D \rightarrow {}^1D$ process. The geometry of Z_1 and its ionicity are in fact *optimal* for such intersystem crossing.^{1a} In this new mechanism the process leading to the key carbonium ion intermediate would be the *protonation of Z_1* rather than either the protonation of a covalent triplet state or of a trans double bond.

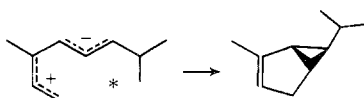
Photocyclization of 1,3,5-Hexatrienes to Bicyclo[3.1.0]hexenes.³³ This reaction illustrates the fate of a relatively stable but still excited zwitterionic intermediate Z_1 . The primary process starting from an s-cis,s-trans conformation of the triene can be written³⁴



If the Z_1 state is stabilized by the conformation of the triene and/or the substituents, it should lie well below the companion zwitterion Z_2 . Internal conversion to Z_2 is ruled out. At the same time Z_1 should still lie well above the singlet diradical.



The situation is somewhat akin to Figure 6, but with a much larger Z_1 - Z_2 separation. Since Z_1 lies in a comfortable minimum and has no dynamical link to 1D , it has time to rearrange further before collapsing on the ground surface:

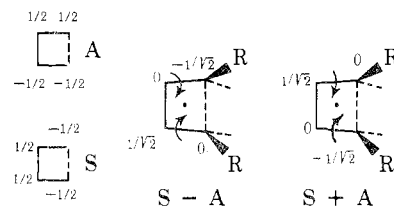


The significant novel feature of our analysis is the *excited* character of the ionic intermediate.

Classification of Photoreactions

Based upon the foregoing discussion of the role of potential energy surfaces in photoreactions, and on the total number of distinct radical sites generated in the primary photochemical process, we can now organize a wide variety of photochemical reactions (Table I). The major discriminating feature is the *topicity* of the reaction, which is defined by the *total number and nature of available radical sites generated in the primary process*. The "topicity number" ranges from 2 to 6. Reactions are also differentiated by the "topicity label" which enumerates all the available sites and specifies their symmetry or their nature. Reactions already encountered include σ,π bitopic, $\sigma(\sigma,\pi)$ tritopic and $(\sigma,\pi)(\sigma,\pi)$ tetratopic. Such symmetry labels can be used *only* if the molecular symmetry plane has been conserved *throughout* the reaction.

Attention is now given to certain reactions for which the foregoing symmetry labels do not hold, because they do not proceed in a coplanar fashion. Two important examples are (a) olefin isomerization and pericyclic reactions and (b) photoassociation and electron-transfer reactions. In pericyclic reactions or in olefin isomerization the system as a whole does not remain coplanar, but certain internal symmetry elements (C_s plane, C_2 axis) are conserved. In spite of this difference, the reactions have been analyzed as having a topicity number of two. Woodward and Hoffmann have shown that in concerted photochemical pericyclic reactions there is an (S,A) pair of nonbonding orbitals available for the two odd electrons.⁸ In their notation S and A refer to symmetries relative to the internal symmetry element. The *diradical* state of the intermediate skeleton is obtained, however, not by ascribing one electron to S and one electron to A³⁵ but by assigning them respectively to the orbitals S + A and S - A. This is exemplified below for a cyclobutadienoid skeleton, as would occur in the photochemical electrocyclic closure of butadiene:



The two odd orbitals are degenerate, with the additional characteristic that they are confined to *different* atoms (but not to the termini of the bonding process). It is a general feature that the two nonbonding molecular orbitals which are the correct sites for the diradical ground state of a photochemical concerted pericyclic transition structure can be confined to different sets of atoms.³⁶ These two sets are respectively the well-known "starred" (\star) and "unstarred" (\circ) atoms of conjugated hydrocarbons. We therefore label such a bitopic intermediate (e^\star , e°), where the letter e refers to the general notation for a pair of symmetry degenerate orbitals. This labeling convention can be carried over to the olefin isomerization reaction, since again at 90° twist angles the proper diradical sites are the combinations $\pi + \pi^*$ and $\pi - \pi^*$ which are localized on the two reaction centers.

In bimolecular photoassociation reactions there is no symmetry. Under these conditions a label must be found to specify the molecular orbitals involved in the LE and CT states of both partners. Since the interactions in these states are of the excitation-exchange and charge-resonance type, we use the notation d (*donor*) and a (*acceptor*) to characterize respectively the orbitals of the donor and of the acceptor. The four relevant radical sites become d,d* on the donor and a,a* on the acceptor. A further special feature is that *four electrons are involved* in the significant reactant states and primary product states. In such cases a prefix 4 has been utilized to call attention to this situation. Thus the general tetratopic

(33) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973), and references therein.

(34) J. Meinwald, A. Eckell, and K. L. Erickson, *J. Am. Chem. Soc.*, **87**, 3532 (1965).

(35) The SA configuration yields the Z_1 zwitterionic state.

(36) For a discussion of this point, see W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973), in particular ref 10.

Table I

Topicity		Number			Examples
Number	Label	Number of D states	Number of $D_{\text{ion-pair}}$ states	of Z states	
2	σ, π	1 pair		2	Coplanar H abstraction by ketones, carbenes, etc. from RH; ketones plus electron-rich olefins
	σ, σ	1 pair		2	Cleavage of alkanes
	$e\sigma^*, e\sigma^*$	1 pair		2	Olefin twist; concerted pericyclic
	n, a^*		1 pair (D_{\pm})	2 ^a	Polar pericyclic; nucleophile plus electron-poor unsaturated system
3	$\sigma(\sigma, \pi)$	2 pairs	1 pair	3	α cleavage of ketones; furans to cyclopropenyl ketones; ring opening of azirines; ketones (n, π^*) + electron-poor olefins; cleavage of saturated ethers
	4: $\pi(\sigma, \pi)$	2 pairs	1 pair	3	Coplanar H abstraction by ketones from aldehydes and phenols
	4: $n(a, a^*)$ (d, d^*) a^*	1 pair (D_*) 1 pair (D_*)	2 pairs (D_{\pm}) 2 pairs (D_{\pm})	3 ^{b,c} 3 ^{b,d}	Heterolytic nucleophilic substitution Heterolytic electrophilic substitution
4	$\sigma(\sigma, \pi_x, \pi_y)$ (σ, π)(σ, π)	3 pairs 4 pairs	3 pairs 2 pairs	4 4	Cleavage of alkyl halides Photo-Fries; cleavage of α -diketones, dioxetanes, peroxides and α -pyrones ^e
	4: (d, d^*)(a, a^*)	2 pairs (D_*)	4 pairs (D_{\pm})	4 ^b	Exciplex formation; electron transfer
5	(σ, π)(σ, π_x, π_y)	6 pairs	4 pairs	5	Cleavage of aryl halides, acyl halides, hypohalites
6	(σ, π_x, π_y)(σ, π_x, π_y)	9 pairs	6 pairs	6	Cleavage of interhalogens

^a The $D_{\text{ion-pair}}$ states correspond to the electronic configuration na^* and the Z states to the electronic configurations $(a^*)^2$ and n^2 . ^b See ref 39. ^c The D states correspond to n^2aa^* , the $D_{\text{ion-pair}}$ states to na^2a^* and $na(a^*)^2$, and the Z states to $a^2(a^*)^2$, n^2a^2 , and $n^2(a^*)^2$. ^d The D states correspond to dd^* , the $D_{\text{ion-pair}}$ states to da^* and d^*a^* , and the Z states to $(a^*)^2$, d^2 , and $(d^*)^2$. ^e There are two distinct, orthogonal π sites in the cleavage of an α -pyrone in spite of the apparent delocalization of any odd π electron over the entire skeleton. Indeed the odd electron can occupy the ether oxygen O-1 (and C-3, C-5, O-7) or the acyl carbon C-6 (and C-4, C-2).

photoassociation reaction is labeled 4:(d, d^*)(a, a^*). We have also seen that one reaction partner may bring only a single radical site into the association process. This was the case in our study of the nucleophilic photosubstitution reactions, where the donor nucleophile has no readily available empty orbital but has a readily available radical site in the form of its top occupied nonbonding n orbital. In such cases the pertinent donor orbital is identified with the label n . The previous reaction becomes 4: $n(a, a^*)$ tritopic. If the acceptor a -orbital electrons are too stable to become involved in the reaction, site a can be neglected and the appropriate reaction label is n, a^* (bitopic). Polar pericyclic reactions may be an example of such a photochemical process.³⁷

Besides topicity number and label, Table I provides the total number of states of different nature which are appropriate for primary reaction products. There are actually three different types of states: (a) *diradical pairs of states* $^1D, ^3D$, in which two *distinct* radical sites are occupied each by a single electron; (b) "*diradical ion pair*" states, $^1D_{\text{ion-pair}} ^3D_{\text{ion-pair}}$,³⁸ in which such occupancy is accompanied by the creation of an ion pair in the system; this can occur either for electrons localized on different fragments but which originally belonged to the same fragment (e.g., the n, a^* bitopic case) or for electrons on the same fragment but which were originally shared between the two (e.g., the diradical ion pair states of $\sigma(\sigma, \pi)$

tritopic processes); (c) *zwitterionic states*, Z, which are singlet states in which two electrons occupy the *same* radical site.³⁹

For reactions for which a single electron pair, shared originally by two different fragments, is cleaved the number of D pairs of states is equal to the total number of pairwise combinations of radical sites belonging to different fragments. The number of $D_{\text{ion-pair}}$ pairs of states is equal to the total number of pairwise combinations of sites belonging to a same fragment.^{39b} The number of Z states is equal to the topicity number. Devaquet has shown⁴⁰ that the *total* number of states is equal to the square of the topicity number!

Finally, Table I lists typical photochemical reactions within each class of topicity.⁴¹

Discussion and Warning

In the foregoing development of a unitary concept,

(39) (a) The name "zwitterionic" for such states is a natural one only insofar as the two electrons were originally shared by two sites belonging to *different* fragments. For reactions in which the two electrons belong originally to the *same* fragment—such as donor-acceptor reactions (see previously, and in Table I, the heterolytic substitution reactions) or bond cleavages of inorganic complexes $[\text{Cr}^{\text{II}}(\text{CO})_5\text{Cl}_2]^* \rightarrow \text{Cr}^{\text{II}}(\text{CO})_5\text{Cl}_2 + \text{CO}$ —the ground state of primary product has two electrons on the same site but carries no charge separation because of the dative nature of the initial bonding. The authors are grateful to W. D. Stohrer and A. Devaquet for a discussion of this point. (b) For such reactions, in which the electron pair belongs originally to the *same* fragment, the numbers of D and $D_{\text{ion-pair}}$ states are interchanged (see Table I).

(40) A. Devaquet, private communication to the authors (1974).

(41) The lumi rearrangements of α, β -unsaturated ketones and cross-conjugated dienones, and the intramolecular di- π -methane and oxa-di- π -methane rearrangements, upon preliminary study, have not found a place in the present classification. Further study is being devoted to extension of the present guidelines to such reactions, for which it is difficult to choose the controlling symmetry element(s).

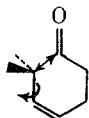
(37) N. D. Epiotis has made the interesting suggestion that polar cycloadditions proceed first *via* an excited charge-transfer complex (N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, 13, 751 (1974)).

(38) In our previous discussion these states were labeled $^1D_{\pm}, ^3D_{\pm}$ for the sake of simplicity.

the premise of the reaction occurring *in a symmetry plane* has been utilized to construct correlation diagrams for all the reactions in Table I in which the electrons involved have σ or π symmetry. It can be argued that we have arbitrarily introduced this symmetry operator and that many photochemical reactions do not possess such a symmetry element. To discuss this criticism two cases should be considered: (1) reactions in which the real pathway may not have a symmetry plane but in which a *model*, neighboring reaction pathway does possess this plane—for instance hydrogen abstraction by ketones; (2) reactions in which *no* reasonable reaction coordinate conserves a symmetry plane or other symmetry element.

(1) Cases in which the reaction path deviates from the model, coplanar case are easily handled by the theory. As the reaction centers deviate from this planar symmetry, previously allowed surface crossings become weakly avoided, and gradually more and more so. Although in the extreme (for instance hydrogen abstraction in a direction perpendicular to the carbonyl plane) the crossing, or intention thereof, is totally lost, for moderate deviations, the intention to cross remains a dominant feature and the molecule retains memory of its original intended course in the coplanar system. Available evidence points to a rather strong memory of such crossings.^{2b} Furthermore, in bimolecular reactions where the coplanar or nonplanar approaches do not differ too significantly in energy, the *dynamics* of the reaction must sample the coplanar and neighboring situations. Thereby, quantum yields will partially reflect the properties of the coplanar reaction path and of our predictions for this path.

(2) In reactions in which *composite motions*, such as stretching and twisting, accompany the primary creation of the radical sites, no symmetry element is conserved along the reaction coordinate. Take, for example, α cleavage of a β,γ -unsaturated ketone in which the stretching of the bond is concomitant with a twisting motion of the methylene group

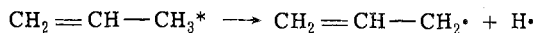


so as to lead to allylic conjugation. If the bond breaking were occurring alone, the horizontal plane would be conserved as the symmetry element for the reaction centers. If, on the other hand, the methylene group were to rotate by 90° , there would be a local C_2 axis, as in olefin twist. The potential-energy surfaces for the actual reaction process will borrow controlling factors from both symmetry elements. The degree as to which one or the other symmetry elements controls the process cannot be determined at this time, although clearly in the early stages of the reaction the symmetry plane has more weight while in the later stages the C_2 -like axis should predominate.

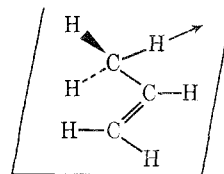
A warning⁴² concerns the danger of the "imposi-

(42) G. S. Hammond (private communication to the authors, 1974) writes: "Where you may get yourself into bad problems is by analyzing a symmetric model, because it can be analyzed and then fooling yourself into believing that the analytically derived reactant and product states of the system must be the real states."

tion of unnatural restraints" by the chemist who would wish, at all cost, to analyze a reaction of the second family in terms of a coplanar model. Consider for instance the reaction



If a coplanar reaction coordinate is chosen for the purpose of analysis, the primary product allyl radical is generated in a high-energy twisted form:



Surely chemical common sense must dominate in the analysis of any reaction, and the choice of proper reaction coordinate.

We emphasize, furthermore, that symmetry is not a prerequisite for drawing state-correlation diagrams (see, for instance, Figures 7 and 12). *Topicity exists for any photochemical reaction irrespective of whether or not there is an element of symmetry.* The topicity number can always be specified, and sometimes also topicity labels (d, a, n, etc., in the photochemical electron-transfer reactions and heterolytic substitution reactions). Since, in the absence of symmetry, these topicity labels are not symmetry labels which would allow for a facile description of the electronic states of primary product, the analysis of the reaction is more difficult. Such an analysis is a challenge for future theoretical work.

Conclusion

The underlying assumption in our classification is that *all photochemical processes are controlled by generation of primary products which have the characteristics of diradicals.* The generality of such a phenomenon might seem unexpected until one notes that it relates to the physical fact that in the initial (single-excitation) photoprocess two electrons of a pair are separated into two distinct orbitals.

The utility of this classification is that (1) it allows the photochemist to construct a single *energy diagram* along the entire assumed reaction coordinate; (2) in so doing, it delineates the *minimum requirements* that any mechanistic suggestion must meet by defining those *electronic surfaces* which the molecule can explore along the coordinate, and by providing a set of *natural pathways* on these surfaces; (3) it enables prediction of the effect, on the course of reaction, of changes in solvent polarity and of structural variations in the reactive system. What remains to be solved is a definitive set of rules which govern the partitioning of the system between the possible pathways along the reaction coordinate.

The authors are indebted to numerous colleagues for stimulating discussions. Special acknowledgment is due to A. Devaquet, G. S. Hammond, E. Havinga, O. Kahn, P. de Mayo, M. Raban, D. Rehm, and A. Weller. N.J.T. is grateful to the University of Paris-Sud for an Exchange Professorship, and to the Air Force Office of Scientific Research and the National Science Foundation for their generous support.