Theory of Photochemical Reactions

The theory is based on the four states (two diradical and two zwitterionic) of the primary intermediate.

L. Salem

A molecule in an electronically excited state has a personality entirely different from that of the same molecule in its ground state. This is particularly true of the intermediates or primary products that the molecule can form in the first step of a photochemical reaction. For instance a nonpolar ground-state intermediate may have highly polar excited states, and vice versa. Hence photochemical reaction mechanisms are often highly specific, with reaction products strikingly different from those obtained when the same system reacts thermally.

In the absorption of a photon by a molecule, two electrons, which were initially paired in a molecular orbital, generally become separated into different orbitals (only exceptionally are two electrons excited simultaneously). Hence the basic act of electronic excitation creates a species with two odd electrons. We can think of this vertically excited species as a diradical precursor; it will generate a primary product with the characteristics of a diradical. This idea is fairly old. In 1960 Kasha, who ten years previously had introduced n,π^* states into photochemistry, pointed out that the n,π^* excited state of a ketone "corresponds fairly closely to what a chemist describes as a diradical structure" (*1*). However, the essential implication of this idea—that the understanding of a photochemical reaction requires a detailed description of the electronic states of both reactant and diradical-like primary product—has only recently been grasped by photochemists.

Probably the first application of quantum mechanics to photochemistry dates back to 1932. Mulliken's paper entitled "Quantum theory of the double bond" (*2*) was a pioneering work in two respects. First, it gave a remarkable interpretation of the photochemical *cis-trans* isomerization of olefins and polyenes based on the form of the potential surface for the excited π,π^* state. This interpretation has remained unchallenged in essence, even though we now know that most such reactions occur in the triplet state. But Mulliken also pointed out that twisted ethylene has four low-lying valence states. This was the first qualitative description of the electronic states of a photochemical primary intermediate.

The electronic theory of photochemical reactions (*3–5*) is an attempt to describe the chemical behavior of electronically excited molecules in terms of the various electronic states of the primary intermediate, considered to have the characteristics of a diradical. The main feature is the existence of two centers ("radical sites"), each with a free residual valence, between which two electrons can be distributed; many examples of such intermediates are given in this article. Of particular importance are the ion-pair or "zwitterionic" excited states of intermediates with nonpolar ground states. The electronic structure of these states can give unusual chemical behavior to excited nonpolar organic molecules (*6*). It appears that zwitterionic states may also play an important role in the chemistry of vision (*7*).

The Four Electronic States of Diradicals

Diradicals have four chemically important electronic states with fundamentally different characteristics (*3*). These four different states may potentially be involved in the photochemical reaction mechanism. Figure 1 shows these states for a series of typical organic intermediates **1** to **8**, as would occur in common reaction processes such as double-bond twisting (**1**, **2**, and **6**), pericyclic reactions (**3**), two-step addition of double bonds (**4**), hydrogen atom transfer (**5**), single-bond breaking (**7**), and ring opening (**8**). The states are described by a single valence structure or a mixture of valence structures, with energies increasing from left to right. We have limited the examples to diradicals with only two available radical sites, each of which can accommodate one or two electrons. The ring-opened azirine **8** (a bent nitrile ylid) has an additional π site available, but we do not make use of it. All the systems have two "diradical" states, a triplet labeled ^3D and a singlet labeled ^1D. In these two states there is one electron on each radical site. There are also two states, which we call zwitterionic (*8*) and label Z_1 and Z_2, since they possess the electronic characteristics of organic zwitterions. In these two states the two electrons are paired on the same radical site. These zwitterionic states are therefore singlets. The nature and ordering of the four electronic states of molecules **1** to **8** in Fig. 1 can be discussed briefly by distinguishing two cases.

1) The radical sites are symmetry-equivalent (**1** to **4**). The sites therefore have equal energy. The cost of localizing two electrons on the same site is prohibitive, from the point of view of Coulombic energies, and the two diradical states ^1D and ^3D fall well below the two zwitterionic states in energy. The proper zwitterionic states Z_1 and Z_2 must be symmetrized. They are correctly represented, respectively, by the out-of-phase (–) and in-phase (+) combinations of two ionic resonance structures. We will see later the effect on the Z states of destroying the symmetry. The energy difference between these two ionic states is very small (of the order of 1 to 10 kcal/mole), as is the difference between the two diradical states. Furthermore, if the odd orbitals are orthogonal (**1**, **2**, and **3**), covalent wave functions and ionic wave functions have different symmetry. Hence ^1D is purely covalent and Z_1 and Z_2 are purely ionic. In the two-orbital, four-electron model, Hund's rule applies (*9*, footnote 15), with $^3D < {}^1D$ while $(-)Z_1 < (+)Z_2$. In practice, elaborate calculations show that the singlet diradical can fall below the triplet diradical, at least in **1** (*10*). Also, the (+) zwitterionic state Z_2 can borrow covalent character from higher excited states so as to fall below Z_1. This is the case of **1** (*10*) and **3** (*11*), and possibly also of **2**. If the odd orbitals are not orthogonal (**4**), covalent character and symmetrized (+) ionic character can mix. Then ^1D is only predominantly covalent and Z_2 predominantly ionic. Also, usually, $^1D < {}^3D$ (*9*).

2) The radical sites are not equivalent (**5** to **8**). The two sites therefore have different

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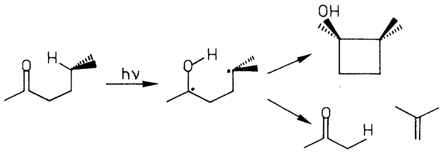
energies. In one of the zwitterionic states Z_1 the two electrons will tend to be localized on the more stable site, thereby lowering the energy of Z_1 relative to Z_2. If the site energies are still comparable, there will be some admixture of the other, less favorable, ionic resonance structure in Z_1; a similar situation holds for Z_2 (**5** and **6**). If one of the radical sites becomes very much more stable than the other (**7**), Z_1 can fall quite low in energy as one ionic structure is greatly favored over the other. Eventually Z_1 can become the ground electronic state ($Z_1 < {}^1D, {}^3D$), for instance in the presence of polar solvents. We will return to this effect later. Again, if the odd orbitals are orthogonal (**5** and **6**), the singlet states are pure (${}^1D$ covalent and Z_1 and Z_2 ionic). From Hund's rule, and with the reservations made above, ${}^3D$ lies slightly below ${}^1D$. If the odd orbitals are not orthogonal (**7** and **8**), covalent and ionic character will mix in all three singlet states. This is particularly true if the odd-orbital overlap is significant (**8**). The triplet diradical state ${}^3D$ then lies above the ground Z singlet, which is a covalent-ionic mixture.

In summary, intermediates with a pair of lowest-lying diradical states have two excited singlet zwitterionic states (**1** to **7**). On the other hand, an intermediate with a ground zwitterionic state has a (singlet, triplet) pair of excited diradical states (**8**). In short a diradical has excited zwitterionic states, while a zwitterion has excited diradical states.

We will now show how the concept of four states can be used to understand the mechanism of some basic photochemical reactions and to classify photochemical reactions, and finally how zwitterionic excited states behave.

Surface Crossings Between Electronic States

Let us consider first the photochemical γ-hydrogen abstraction by ketones which occurs in Norrish type II photoprocesses (*12, 13*). The reaction (reaction 1 below) has an extraordinarily puzzling feature. The primary product diradical is analogous to many familiar diradicals obtained as transition structures or intermediates in two-step thermal reactions. In principle, by simple heating or pyrolysis, the product cyclobutanol can yield this same diradical by simple ring opening and bond rotation. Yet the original ketone has been electronically excited. There is, at least in appearance, a flagrant contradiction.



1) Norrish II

The contradiction can be lifted by drawing a correlation diagram between the electronic states of the reactant and the electronic states of the di-yl intermediate. To construct such a diagram we use as discriminating symmetry element the plane containing the reaction centers—the carbonyl group and the γ carbon atom. We then draw out the resonance structures for ground and lowest excited states of both reactant and primary product (Fig. 2). Considering first the singlet manifold, we confidently expect the ground electronic state of primary product to be the diradical ${}^1D$ postulated by the organic chemists, while the excited state is the lowest (Z_1) of the two zwitterionic states (see **5** in Fig. 1). To find the resonance structure appropriate to each state we count the number of electrons with σ and π symmetry relative to the symmetry plane. The relevant electrons are the carbonyl π electrons, the oxygen n electrons (σ symmetry)—shown in a half p-lobe—and the two σ electrons that initially make up the CH σ bond.

The electron count yields directly the correlation between the two lowest singlet states of reactant and intermediate (solid lines in Fig. 2). The singlet n,π^* state correlates directly with the singlet diradical pri-

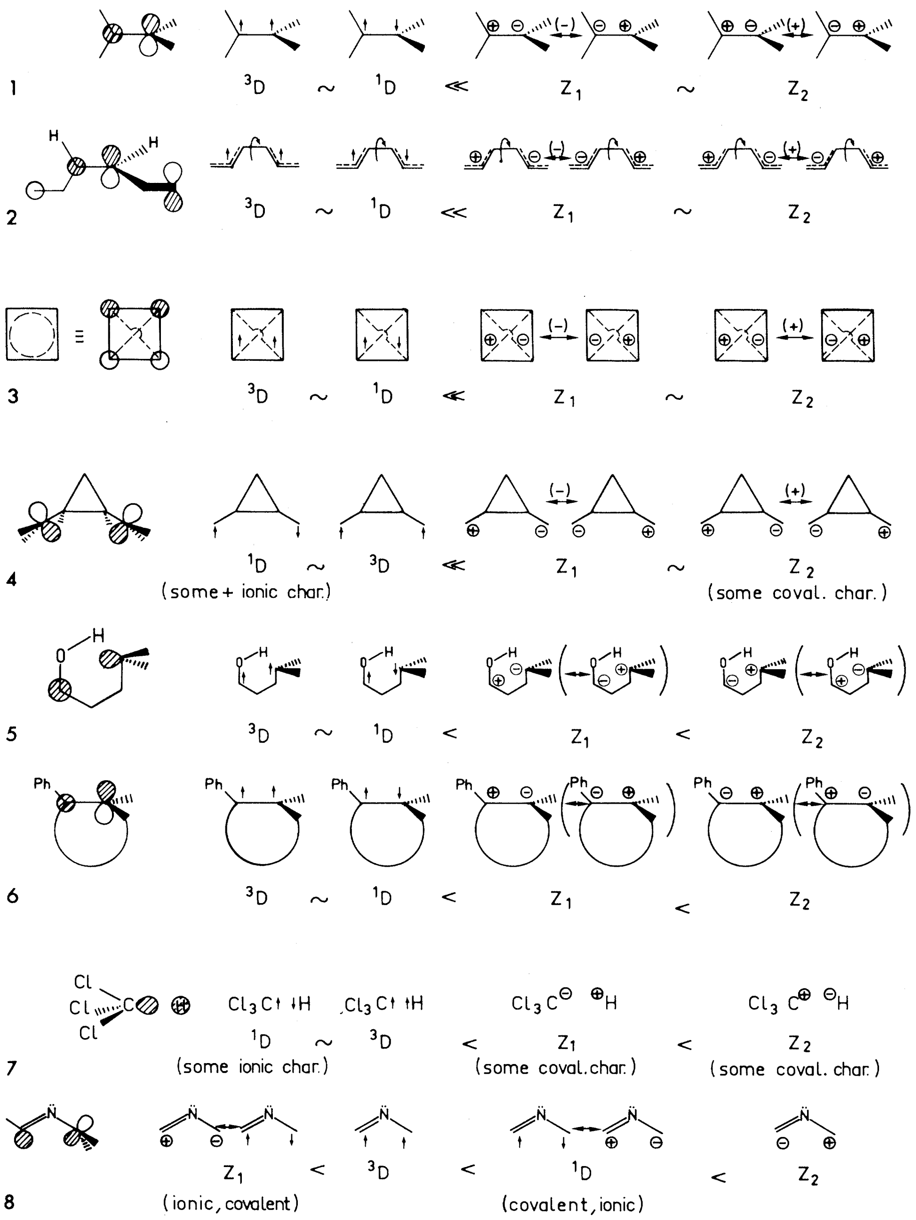


Fig. 1. Electronic states of various diradical intermediates. (**1**) Orthogonal twisted ethylene. (**2**) Orthogonal *s-cis, s-trans* diallyl. (**3**) Pericyclic transition state; Hückel array of four orbitals; the two radical sites are $\phi_1 - \phi_3$ and $\phi_2 - \phi_4$; orbitals belonging to the same radical site are linked by a dashed line. (**4**) 1,2-Cyclopropyldicarbinyl. (**5**) 1-Hydroxy-1,4-butane diyl. (**6**) Orthogonal phenylcycloalkene. (**7**) Dissociated chloroform. (**8**) Ring-opened azirine. The energies of the states increase from left to right. The sign ~ indicates nearly equal energies.

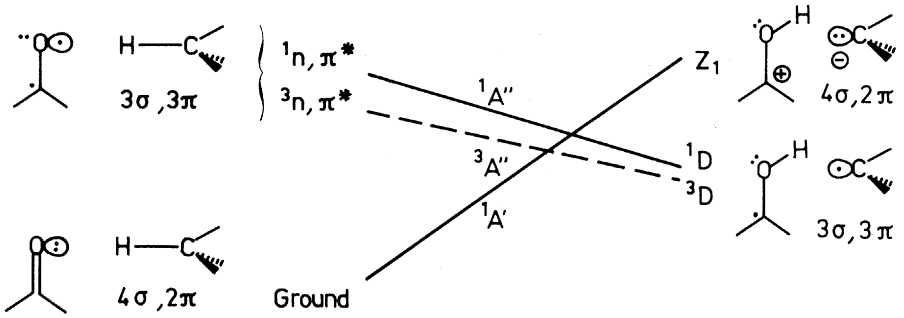


Fig. 2. State correlation diagram for hydrogen abstraction by a ketone (see reaction 1).

mary product ^1D. The excited molecule, in the billiard ball analogy, needs only to roll downhill to find itself on the ground surface of product. In practice, even on this single surface there is a slight activation energy. Conversely, the ground reactant correlates with the high-energy ionic excited state Z_1 of product (with implications for thermoluminescence). Hence the singlet-state surfaces intersect (*4*). The correlation diagram can be extended to include the triplet n,π^* state. Since the electron count is independent of multiplicity, this state correlates with ^3D—that is, also with a primary product state. The state symmetries ($^1A'$, $^1A''$, $^3A''$) have been included in Fig. 2.

Thus the apparent contradiction in the simple mechanistic scheme for the Norrish type II reaction is lifted. The scheme is inherently correct. Furthermore much information can be gleaned from even such a simple diagram:

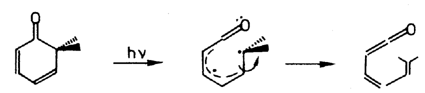
1) The rates for triplet and singlet reactions should be similar, since the surfaces are parallel, but the quantum yields should be different, since the leakage path for singlet to return to ground reactant (internal conversion at the crossing point) seems to be more important than that for triplet (intersystem crossing).

2) The $^1\pi,\pi^*$ state must correlate with Z_2 and must therefore be unreactive.

3) In polar solvents Z_1 falls below the pair ^1D,^3D. For both singlet and triplet one expects a decreased quantum yield, insofar as the excited molecule must undergo an additional radiationless transition.

4) For noncoplanar abstraction, the singlet quantum yield should decrease (the crossing is avoided; see Fig. 5A), but the triplet quantum yield should remain constant.

We now apply the same technique to the cleavage of a carbon-carbon bond alpha to the keto group in a Norrish type I photoprocess (*12, 14*). The example of cyclohexadienone is given in reaction 2. Again an intermediate diradical is postulated [this particular reaction was illustrated by Quinkert (*15*)]. To simplify matters, we construct the state correlation diagram for the α-cleavage of a saturated ketone. The result is shown in Fig. 3. For the primary product state there is a major distinction from the previous case. If, for instance, R = H, the formyl radical has two available low-lying states: a bent $^2A'$ state with an unpaired σ electron, and a linear $^2A''$ (or $^2\pi$) state with an unpaired π electron, lying roughly 1 electron volt above. The same is true for the acetyl radical (R = CH_3) or higher acyl radicals. As a consequence, when we include the departing methyl radical, there are two pairs of primary product diradical states. We label the lower pair D_σ, according to the nature of the two odd electrons, and the higher pair $D_{\sigma,\pi}$.



2) Norrish I

In contrast to the previous example, the singlet surfaces do not cross. They stay apart, or touch in certain geometries. Both $^1n,\pi^*$ and $^3n,\pi^*$ states lead to excited primary product. However, one excited state does lead to ground primary product: the lowest symmetric triplet state, which must have essentially $^3\pi,\pi^*$ character with some $^3n,\sigma^*$ admixture. We have here a simple justification for the purely triplet nature of photochemical α-cleavage. The most likely reaction pathway is that where the $^3n,\pi^*$ state reacts by internal conversion to the descending $^3\pi,\pi^*$ state. However, if the ketone is conjugated as in reaction 2, the σ,π diradical product may be sufficiently stabilized to bring about a surface crossing (*15*).

The two preceding examples illustrate the electronic control of photochemical reactions, as demonstrated by state correlation diagrams. For adiabatic motions at least, the excited molecule converts inexorably to the primary product that is on the same potential energy surface. Probably the first demonstration of electronic control in a photochemical reaction was that given by Woodward and Hoffmann (*16*) in their theory of pericyclic reactions.

Classification of Photochemical Reactions: Topicity

Several other photochemical reactions, such as the photoreduction of aza-aromatics, which proceeds through a hydrogen abstraction, have a state correlation diagram similar to that for the Norrish type II reaction. This is also true of the addition of ketones, through their *n* orbitals, to electron-rich olefins. On the other hand, the photochemical ring opening of azirines, through a $\sigma(n),\pi^*$ state (*17*), and that of furans to cyclopropenylketones, through a σ,π^* state (*18*), have correlation diagrams qualitatively similar to that of Fig. 3 for the Norrish type I reaction. What, then, is the critical feature that leads, for the reactants, to a singlet surface crossing (Fig. 2) or to singlets that remain apart (Fig. 3)? This essential feature is the total number of available radical sites created in the two reactions.

In the hydrogen abstraction reaction, two distinct radical sites are created: one on the carbonyl carbon and one on the γ carbon. Therefore in the primary product a pair of *D* states competes with the lowest zwitterionic state Z_1. In the α-cleavage reaction one fragment carries two radical sites (the acyl fragment can accommodate the odd electron in either the σ orbital or in the low-lying π^* orbital), and three radical sites are created altogether. Combining the two acyl sites with the methyl radical site leads to two pairs of competing *D* states. The available radical sites are shown in Fig. 4, together with the nomenclature which we adopt. We label the first type of reaction σ,π bitopic, while the second family is called σ(σ,π) tritopic (*4*). The parentheses include the alternatives for a single electron on one fragment.

Then for any reaction we can define the topicity (*5*) as the total number and nature of available radical sites generated in the primary process. The topicity number ranges from 2 to 6. The topicity label has the general form

$$(i,j,k)(i',j',k')$$

where *i,j*, . . . are usually symmetry labels, but may also indicate a type (donor or acceptor) of orbital. With some practice one can rapidly write out the topicity for most photochemical reactions. It is necessary only to be familiar with the number of sites of some typical radicals, such as hydrogen (one site), acyl RCO˙ (two), alkoxy RO˙ (two), phenyl (two), and halogen (three). In collaboration with Dauben and Turro, I have established a classification of photochemical reactions (*5*), based on the respective topicities of different families. This classification has two useful features.

First, it allows the photochemist to construct a single energy diagram along the entire assumed reaction coordinate. Indeed, knowledge of the number of radical sites in each fragment leads directly to the number of diradical states ^1D,^3D, zwitterionic states Z, and "diradical ion pair" states $^1D_\pm$,$^3D_\pm$ (in which distinct radical sites are occupied, with the creation of an ion pair) (*19*). Second, it delineates the minimum requirements which must be met by any reaction mechanism, by producing a set of natural pathways on the electronic surfaces for the system. The partitioning of the system between the different possible pathways is then a problem of dynamics.

Avoided Surface Crossings

Let us first summarize the different types of avoided crossings (Fig. 5). There appear to be four distinct families (*4*).

Type A. The avoided crossing in the neighborhood of a symmetry-allowed crossing, created by destruction of the symmetry element. In multidimensional space we are near a true crossing of electronic states. Such an avoided crossing occurs, for instance, for slightly noncoplanar hydrogen abstraction by ketones. The intersection itself is conical (*20*).

Type B. The avoided crossing between an ionic configuration and a covalent configuration, as in the famous case of sodium chloride.

Type C. The avoided crossing between two molecular orbital configurations at a molecular orbital intersection. The most familiar case in organic chemistry (*21*) occurs at the symmetry-allowed orbital crossing in Woodward-Hoffmann thermally forbidden pericyclic reactions. The description of the states as single configurations becomes incorrect in the region where the ground and doubly excited configurations have nearly equal energies. The type C avoided crossing is to molecular orbital theory what the type B one is to valence bond theory.

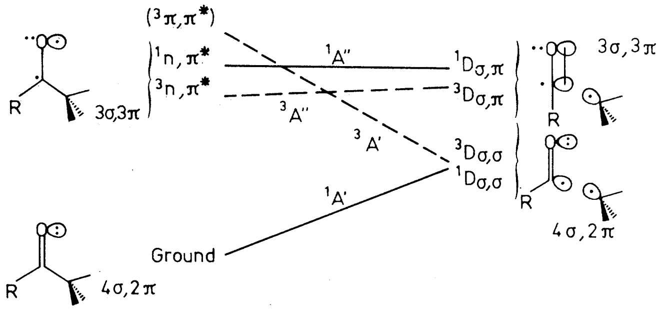
Type D. The avoided crossing between two one-electron molecular orbital levels. Such avoided crossings generally occur between a Rydberg orbital and a valence orbital, for instance in the twisting of ethylene (*22*). They carry over directly to the electronic states. Figure 5 also shows the main characteristic of each avoided-crossing region.

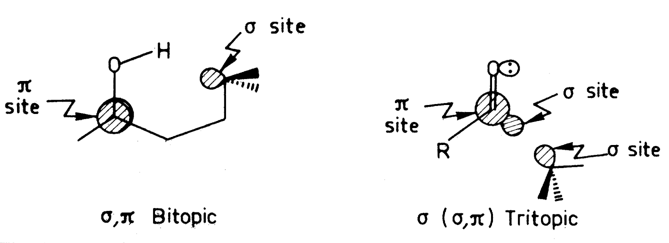
Recently, our attention has been drawn to a fifth type of avoided crossing, which we might call type E. This avoided crossing is characterized by migration of an electronic state from one fragment of a molecule to another. An example occurs in styrene, where the first excited π,π^* singlet migrates from the phenyl ring to the double bond during rotation to the perpendicular conformation (*23*). For a starting model with wave functions localized on one or the other of the separate fragments, the surfaces for excitation on the phenyl and excitation on the double bond intersect; allowance for interaction between the two fragments destroys the intersection.

Michl (*24*) has underlined the importance of avoided-crossing regions, or "funnels," in the radiationless decay of excited molecules. The geometries corresponding to avoided crossings should be particularly favorable for internal conversion because of the Landau-Zener law for the probability of dropping from one surface to the other.

Photochemical Electron Transfer Reactions

Photochemical electron transfer reactions illustrate the interplay between covalent and ionic surfaces, generally involving a type B avoided crossing or sometimes an allowed intersection (*5*, *25*). In these reactions, a nonpolar excited state of a (donor, acceptor) pair leads directly, through an electron jump, to an ionic intermediate. Such electron transfer reactions can occur by direct encounter in nonpolar solvents (such as hexane) of an appropriate donor (diethylaniline) and an appropriate acceptor (anthracene) (*26*). The electron transfer is characterized by a new emission band, to the red of the acceptor's spectrum. In these direct reactions, the reaction coordinate is the intermolecular distance. The behavior with intermolecular distance of the three lowest singlet states of a donor, acceptor pair is shown in Fig. 6. The stable excited ionic intermediate $^1D_\pm$ corresponds to an excited charge transfer complex ^{1}(acceptor$^{\cdot-}$, donor$^+$)*. It is a radical-ion pair and therefore has the characteristics of a dirad-





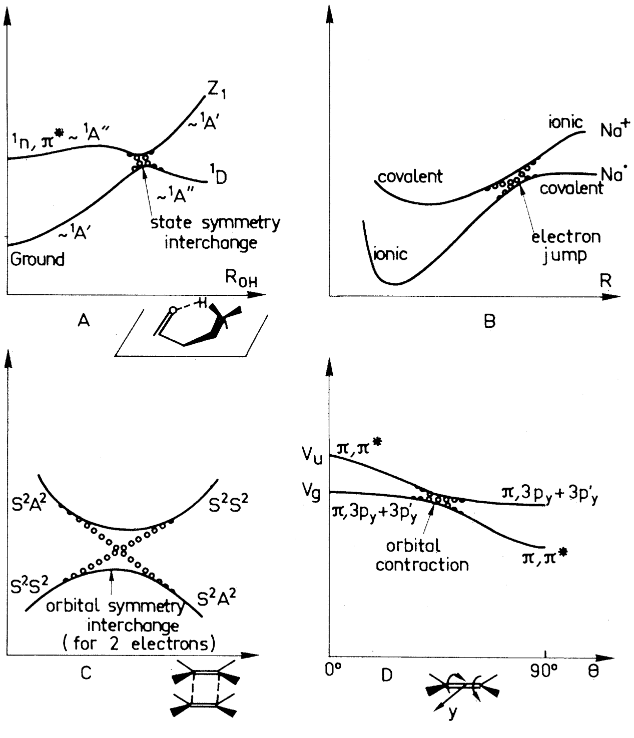


Fig. 3 (top left). State correlation diagram for α-cleavage of a saturated ketone (compare reaction 2). Fig. 4 (bottom left). Radical sites in primary products for hydrogen abstraction and α-cleavage. Fig. 5 (right). Different classes of avoided surface crossings. Lines built with circular dots indicate avoided crossing. In case D the two electronic configurations have different symmetries at 0° (D_{2h} group) but mix for twisted geometries (D_2 group).

ical, but one that carries net charges—hence the specific notation $D_{\pm}$. Normally the locally excited (LE) state would lead to a covalent exciplex D_*, (acceptor*, donor), also with the characteristics of a diradical, while the charge transfer (CT) excited state would correlate with $D_{\pm}$. This is true in both spin manifolds. Actually, an avoided crossing leads to a direct correlation between the LE state and $D_{\pm}$, with concomitant electron transfer.

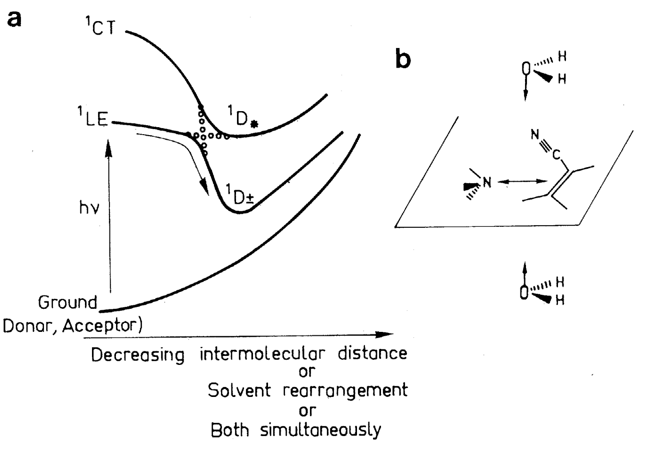
It is possible to mimic the electron transfer in a calculation. One can choose a system in which the CT and LE states have different spatial symmetries so that an actual surface crossing, rather than an avoided crossing, occurs. In a model calculation, Ramunni and Salem (*25*) have obtained a crossing of an $n(NH_3)$, π^*(olefin) CT singlet state and a π(olefin), π^*(olefin) LE singlet state by allowing an ammonia molecule to approach cyanoethylene (Fig. 6) at a distance of ~ 4 Å.

The electron transfer can also be induced in polar solvents (such as acetonitrile), where it is considerably enhanced by rearrangement of the solvent (*27*). Here the appropriate reaction coordinate is essentially the solvent motion that stabilizes the CT state. In our model we can induce the same surface crossing by keeping the ammonia and cyanoethylene partners at a fixed distance (5 Å), where the exciplex $^1D_*$ normally lies below the CT complex $^1D_{\pm}$, and then bringing up two water molecules with their planes parallel to the olefinic plane (Fig. 6). The stabilized $^1D_{\pm}$ minimum now represents a "solvent-surrounded" excited charge transfer complex, which can ultimately lead, through some additional solvent rearrangement and a slight conformational barrier, to a "solvent-separated" ion pair. Figure 7 shows the overall potential surfaces in three dimensions for our model system (the ^{3}LE state has been included; although the ^{3}CT state comes down close by the ^{1}CT state, it does not come down low enough to cross the ^{3}LE state). The intersection between the two excited singlets, which defines the region of electron transfer, now appears as a curve in three-dimensional space.

The case just discussed constitutes a solvent-assisted surface crossing (or avoided crossing), as the polar solvent simply facilitates the electron transfer, which would otherwise occur if the molecules came close enough together. In other cases photochemical electron transfer occurs only in presence of a polar solvent. The rearrangement of solvent becomes the crucial nuclear coordinate since it alone can create the surface crossing ($^1D_{\pm} < {}^1D_*$); the exciplex $^1D_*$ remains below the ionic intermediate $^1D\pm$ in nonpolar solvents. A nice example, due to Libman (*28*), is that of photoexcited cyanonaphthalene which, in the presence of carboxylic acids, deactivates preferentially by exciplex emission in benzene but by electron transfer followed by chemical reactions in acetonitrile (*29*). In this case we have a solvent-induced surface crossing or avoided crossing, depending on the symmetry [see also figure 13 in (*5*)].

Photochemistry of Excited Zwitterionic States

I now wish to discuss the remarkable photochemical properties of excited zwitterionic states. Figure 8 illustrates the ground singlet ^1D and excited zwitterionic singlets Z_1 and Z_2 of 90°-twisted ethylene. As discussed previously (Fig. 1, **1**) these two states are symmetrized combinations of two ionic resonance structures, with the out-of-phase [or antiresonance (*9*)] combination lying lowest in the two-orbital model. The existence of the Z states as resonance mixtures with nearly equal energies has two important consequences. First, the lower Z state may be stabilized by appropriate substitution. Unsymmetrical substitution destroys the energy equivalence of the $+\leftrightarrow-$ and $-\leftrightarrow+$ resonance structures; Z_1 increases its percentage of the more favorable resonance structure and is stabilized. The other Z state is left with the unfavorable ion-pairing character and rises in energy. (This is true irrespective of the actual ordering of the $-$ and $+$ states.) Second, the two Z states have a large polarizability (*30*). Indeed, the two Z states are separated by only a few kilocalories per mole, and each one is a 50 percent mixture of two highly polarized structures. Hence a



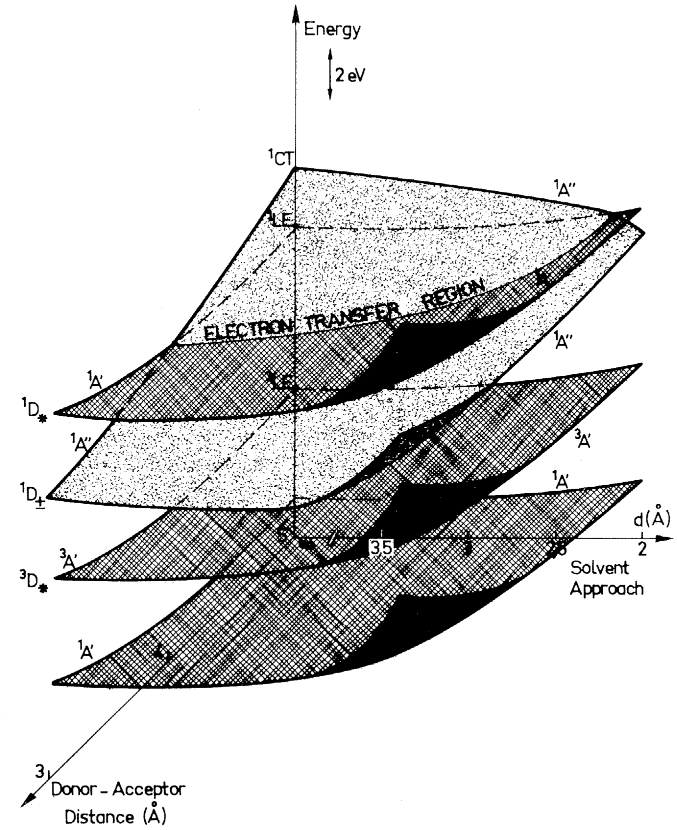


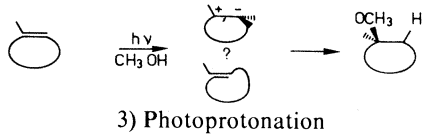
Fig. 6 (left). (a) Singlet state surfaces for photochemical electron transfer. Arrows show photochemical electron transfer process. Nomenclature: ^{1}CT, charge transfer singlet; ^{1}LE, locally excited singlet; $^1D_*$, nonpolar exciplex; $^1D_{\pm}$, charge transfer complex or solvated ion pair. (b) Model system with symmetry plane (see Fig. 7). Fig. 7 (right). Three-dimensional surfaces (including lowest triplet) for the system in Fig. 6. The CT state is represented by the $n(NH_3)$, π^*(olefin) transition while the LE states are represented by the π(olefin), π^*(olefin) transition. The distance d is that from the oxygen atoms to the symmetry plane (Fig. 6b).

very small perturbation can mix Z_1 and Z_2. One state, by "borrowing" from the other, acquires nearly 100 percent of one ionic structure, the other state nearly 100 percent of the second ionic structure; and each state acquires a strong polarization. The effect is analogous to an internal Stark effect and can be induced by simple substitution, destruction of molecular symmetry, and so forth. We study these two chemically important phenomena in turn.

1) Olefin isomerization in polar solvents (*31*). We first ask what happens if the lower zwitterionic state of a photochemical intermediate is stabilized to such an extent that it actually falls below the diradical states. There seem to be dire consequences, at least for the simple case of olefin isomerization. It has been realized for some time now (*32*) that strongly heteropolar olefins should have a rather stable orthogonal (90°-twisted) conformation, and efforts have been made to isolate such compounds. Normally, for an unsymmetrically substituted olefin $A_2C = CB_2$, the ground state (mainly covalent) leads to the ^1D state of the orthogonal form, while the singly excited $^1\pi,\pi^*$ state (mainly ionic) correlates with state Z_1 (Fig. 9a). If the unsymmetrical olefin is now introduced into a highly polar solvent—or substituted by extremely polar substituents—the zwitterionic state should be strongly stabilized, so as to create a situation where Z_1 lies below D. In this approximate picture we obtain the crossing indicated in Fig. 9b. However, since the states have the same symmetry in the crossing region, their intersection will be avoided as the ionic and covalent characters mix in the crossing region. A type B avoided crossing is created (*4*), which should be reflected by a potential barrier on the ground surface and a secondary minimum for Z_1, with an overall double-well potential.

Calculations by Salem and Stohrer (*31*), using an intermediate Hamiltonian that optimizes the orbitals in an average field seen by the closed-shell ^1Z and open-shell ^1D states (*4*), seem to confirm these predicted shapes, although the secondary minimum is small (6 kcal/mole) (*33*). If the starting olefin is already too ionic, the ground surface will go smoothly to Z_1 and the secondary minimum will disappear. It would, of course, be interesting to capture such a zwitterionic intermediate in a polar solvent.

These results may be relevant to another important photochemical reaction, photoprotonation, shown as reaction 3 (*34*).



3) Photoprotonation

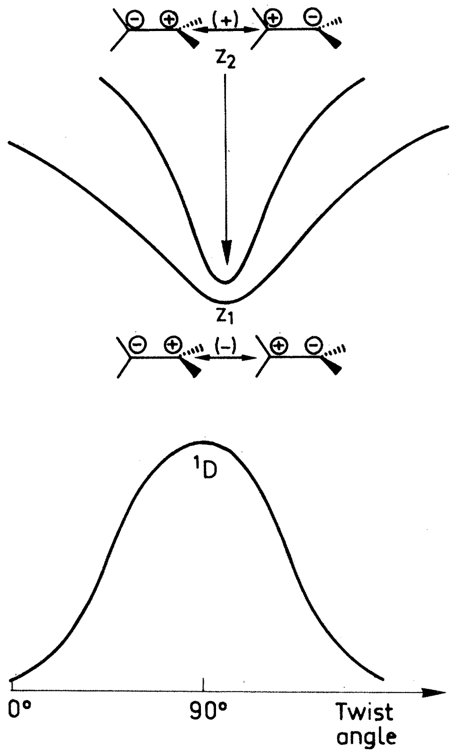
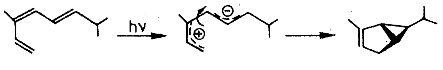


Fig. 8. Potential surfaces (singlet manifold) for olefin twist (*cis-trans* isomerization).

One possibility is that this reaction occurs through a short-lived *trans*-cycloalkene (upper route). However, there is another possible route. If we accept the reasonable postulate of an ionic intermediate Z_1, it is doubtful that Z_1 is an excited zwitterionic singlet since the reaction, by sensitization, can be made to occur in the triplet state. Most likely, in the polar solvent, Z_1, has fallen below the ^1D, ^3D pair of diradical states (compare with **6** in Fig. 1), and the observed protonation could be that of the ground metastable zwitterionic intermediate, reached from either of the two excited diradical states. Since the chemical behavior of the strained *trans*-olefin and that of Z_1 should be similar, it is difficult to distinguish between these two pathways.

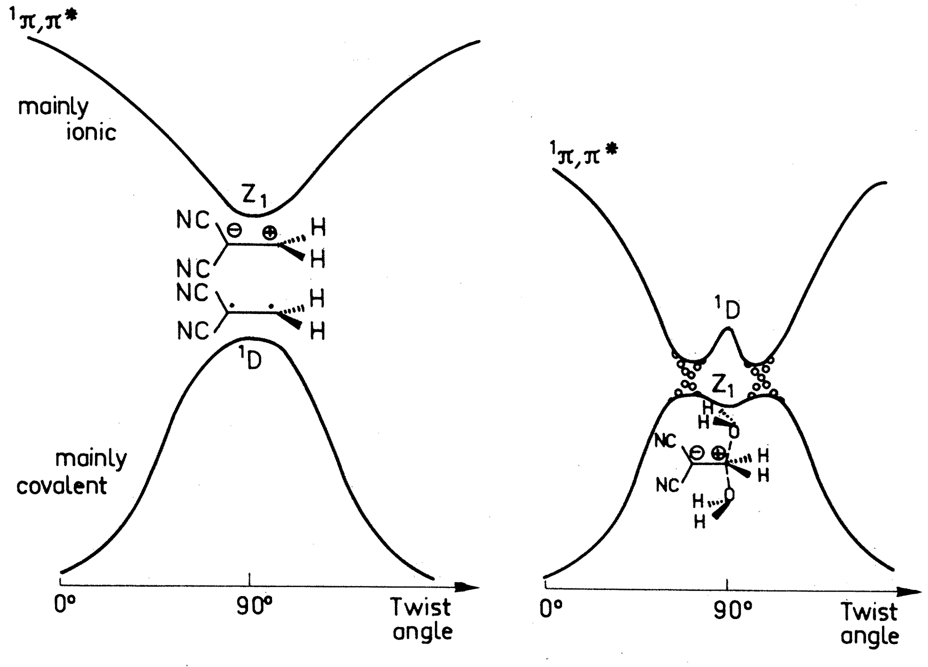
2) The sudden polarization effect (*6*). Let us now consider one final photochemical reaction, the photocyclization of dienes and trienes.

Reaction 4 shows the photocyclization



4) Cyclization of trienes, dienes

of hexatriene, which owes much to the pioneering work of Dauben *et al.* (*35*) and Havinga and co-workers (*36*). The zwitterionic mechanism invoked by Dauben *et al.* seems reasonable, since whenever it is possible to obtain stereochemical information on the closure of the three-membered ring, it is shown to occur in a conrotatory manner, as from a (ground) allyl anion. Yet it is surprising to think of a strongly nonpolar molecule behaving ionically. The problem is, can one justify a strongly ionic excited state with anionic character in the *s-trans* position of the molecule? The answer to this question lies in the extraordinary polarizability of states Z_1 and Z_2 when they are quasi-degenerate. As pre-



(a) in vacuum or in non-polar solvent

(b) in strongly polar solvent

Fig. 9. Lowest pair of singlet surfaces for the *cis-trans* isomerization of unsymmetrical olefins. Lines built with circular dots indicate avoided crossing.

dicted by Wulfman and Kumei (*30*), very small perturbations will mix Z_1 and Z_2, thereby localizing the charge on one radical site and creating a large charge separation. Calculations in our laboratory have shown that a slight chemical dissymmetry between the two odd-electron sites is sufficient to cause a large separation of charge. This is shown in Fig. 10a for the case where one CH_2 group is pyramidal in 90°-twisted ethylene. Clearly, one should not rely on ordinary chemical intuition to estimate the extent of charge separation in excited Z_1 states.

For the *s-cis*, *s-trans* diallyl intermediate (Fig. 10b) a similar calculation does not yield any charge separation—the system keeps resonating between the two alternative ionic forms—except in the very narrow interval $89° < \theta < 91°$ (θ is the twist angle around the central bond). Near 90°, as in the twisted olefin, an abrupt charge separation occurs as the *cis* moiety becomes positive and the *trans* moiety negative. Hence the *trans*-linked nature of one allylic group suffices to make it chemically totally different from the *cis*-linked allyl group in the excited state. The charge separation occurs only in the narrow two-degree region of twist angles. Thus closure to a cyclopropane ring must occur as the molecule passes through the $\theta = 90°$ region. In other cases (for example, trimethylene) the region is much broader.

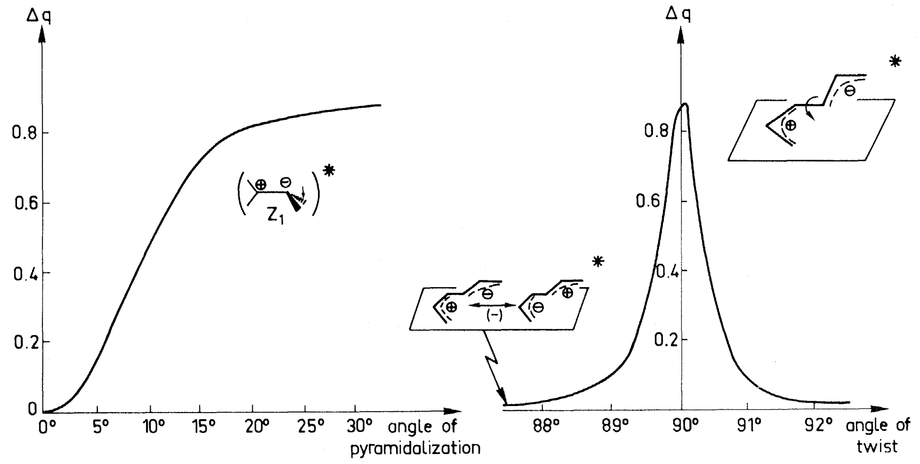
We have described here a novel effect, which can discriminate sharply between the different conformations available to excited reactant species. The sudden flow of charge into a portion of the molecule must play a crucial role in the outcome of certain photochemical reactions. We might call this the sudden polarization effect. Requirements for sudden polarization are (i) some element of dissymmetry and (ii) very small overlap between the two odd orbitals. The dissymmetry need only be very slight: the charge distribution is uniform in the Z states of orthogonal *s-trans*, *s-trans* diallyl (Fig. 1, **2**) but not in orthogonal *s-cis*, *s-trans* diallyl. A similar polarization occurs if one of the methylene groups in **4** is rotated by 90° from the bisected to the perpendicular conformation (*37*). This may be relevant to the mechanism of the di-π methane rearrangement or Zimmerman reaction (*38*). The second condition—a small overlap—is easy to understand. The two-electron energy of the symmetrized (–) Z state is

$$\tfrac{1}{2}(J_{aa} + J_{bb}) - K_{ab}$$

where a and b are the two odd radical sites, K_{ab} is the exchange integral, and J_{aa} and J_{bb} are the two self-repulsion Coulomb integrals. The two-electron energy of a polarized Z state is simply J_{bb}. Hence an approximate condition for charge separation is

$$K_{ab} < \tfrac{1}{2}(J_{aa} - J_{bb})$$

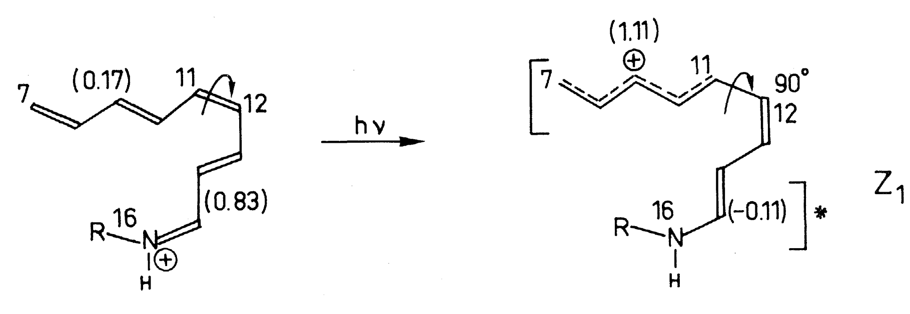
More generally, one can require that the mixing between the two localized polarized states, K_{ab}, be small compared to their energy difference $J_{aa} - J_{bb}$.) Since the two sites (*s-trans* allyl, *s-cis* allyl) have nearly identical self-repulsion integrals, K_{ab} (and hence the overlap) must be very small. However, in cases where more than two atomic orbitals are involved in the radical sites—especially if they are all sufficiently close to overlap significantly as in pericyclic transition states (**3**)—the (+) Z_2 state may acquire partial covalent character from higher excited states and become the lowest excited state (*10, 11*). It is then Z_2 which borrows the favorable polarization; however, its polarization may be less significant because of its covalent character. In other cases, such as that of diallyl, the separation between Z_2 and Z_1 becomes so small at the geometries where charge separation occurs that the "oppositely polarized" Z_2 state will be partially populated, thereby decreasing the overall polarization on a macroscopic level (*39*).



(a) zero overlap

(b) non-zero overlap except near 90°

Fig. 10. Sudden polarization in pyramidal orthogonal twisted ethylene and orthogonal *s-cis*, *s-trans* diallyl.



a) 11-cis, 12-s-cis

b) 11-orthogonal, 12-s-cis

Fig. 11. Sudden polarization in *N*-retinylidene chromophore. The indicated net charges correspond to a calculation for R = CH_3. [Reproduced with permission from (*7*)]

Sudden Polarization in the *N*-Retinylidene Visual Chromophore

One of the major unresolved problems in the chemistry of vision is the detailed mechanism whereby absorption of a photon by rhodopsin can ultimately change the permeability of the rod plasma membrane to positive sodium ions (*40*–*42*). A realistic model of the chromophoric part of rhodopsin is the nonatetraenylidene-methyliminium ion in its 11-*cis*, 12-*s-cis* conformation (Fig. 11a; R = CH_3; for convenience the atoms are numbered as in the full retinylidene skeleton). This model molecule has the important protonated Schiff base characteristic of rhodopsin (*43*). Another possibility is that the chromophore of rhodopsin exists as a weakly hydrogen-bonded but nonprotonated Schiff base (*44*). Whatever the case, the primary photoprocess involves isomerization around the 11-12 double bond, with ultimate formation of the all-*trans* form. A crucial feature of the molecule is the nonequivalent nature of the two pentadienylic fragments 7-11 and 12-16. From what we have seen, the presence of the nitrogen atom should create a sudden polarization effect as the twist angle reaches 90° (*7*). This is confirmed by ab initio calculations: the negative charge in the polarized Z_1 state cancels the positive charge on the nitrogen atom, leaving a now neutral amino group on the 12-16 fragment and a newly positively charged 7-11 pentadienyl moiety. Figure 11b shows the net charge on the two fragments (the results are very similar for the neutral Schiff base, in which Z_1 at 90° resembles Fig. 10b). The change in dipole moment upon excitation and twist can be estimated to be in the range of 35 to 40 debyes and constitutes a large electrical signal. We have suggested (*7*) that this electrical signal acts as a trigger on the medium, either by direct, electrostatic interaction on neighboring "pores" or by inducing a conformational change in the protein. Whatever the case, this system presents a fascinating example of conversion of a photon into an electrical signal (*7*).

Other Considerations: Dynamics, Rydberg States, Feasible Forbidden Reactions

Many topics of importance to the electronic theory of photochemical reactions have not been dealt with in this article. We have stated that dynamics is the crucial factor in the selection, by an excited molecule, of its preferred pathway. The pioneering work on two-surface dynamics of organic molecules is due to Warshel and Karplus (*45*). Many calculations will have to be performed on simple photochemical systems to determine the exact probabilities for a molecule to jump from excited to ground surface in or around avoided-crossing regions (*24*). The relative importance of internal conversion processes and intersystem crossing processes must be assessed. The theory of radiationless transitions (*46*) will be essential for a coherent and comprehensive picture.

Our discussion has been confined to the photochemistry of valence excited states. But in many small molecules the lowest excited singlet states are Rydberg states. This is the case for ethylene, where both $\pi,3p_y + 3p'_y$ and $\pi,3s + 3s'$ Rydberg states lie below the vertical valence π,π^* state (*22*). It has been suggested, however, that "even if absorption of a photon initially populates a state which is largely Rydberg in character, as the molecule relaxes along the reaction coordinate, that state is likely to become or intersect a state which is strongly valence in character" (*47*). This is certainly true for the photodissociation of water (*48*) and the photoisomerization of ethylene (*22*). Hence the photochemistry of such systems would generally be governed by an avoided crossing of type D (Fig. 5D).

A final and intriguing feature is the form of the excited state potential surface and the extent to which its behavior carries a "memory" of orbital symmetry requirements. It is known that a ground state surface that involves nonconservation of orbital symmetry has a large potential barrier (*16*). Now several allowed excited state correlations that we have already considered, such as ${}^3\pi,\pi^* \rightarrow {}^3\mathrm{D}_{\sigma,\sigma}$ (Fig. 3) and ${}^1\pi,\pi^* \rightarrow Z_2$ (discussed with reaction 1), involve violation of orbital symmetry. For instance, in Fig. 3 a $\sigma^2\pi^1\pi^1$ configuration correlates with a $\pi^2\sigma^1\sigma^1$ configuration. In practice this is possible only through monotonically increasing mixing of the initial ${}^3\pi,\pi^*$ configuration with ${}^3\sigma,\sigma^*$ configurations along the reaction coordinate. Michl (*49*) first pointed out that even when an excited state correlates directly with a low-energy primary product, such a violation of orbital symmetry conservation will entail a potential barrier at the outset. Silver (*50*) has called such reactions "[state] feasible [orbitally] forbidden." Calculations by Grimbert (*51*) in our laboratory have confirmed the existence of a sizable barrier (20 to 30 kcal/mole) in the ${}^3\pi,\pi^*$ state for α-cleavage of formaldehyde and an even larger one for β-cleavage of acetaldehyde. It is probable that the ${}^1\pi,\pi^*$ $(4\sigma,2\pi) \rightarrow Z_2$ $(4\pi,2\sigma)$ surface in the Norrish type II reaction (reaction 1) also has an initial barrier. Now that photochemistry of higher excited states has been clearly demonstrated (*52*), such barriers should be important in interpreting the mechanism of certain photochemical reactions.

Summary and Conclusions

Although the great number of electronic states available to an excited molecule might seem to preclude a coherent picture of photochemical reaction mechanisms, it is possible to bring out some basic features common to a great many reactions. The electronic states of the primary diradical intermediates, surface crossings, topicity, and avoided surface crossings have been shown to be essential components of the electronic theory of photochemical reactions.

Diradicals have four important electronic states. Knowing these states, and making a simple electron count, it is possible to draw state correlation diagrams. Some diagrams show a typical surface crossing of the ground singlet state with the lowest (singlet, triplet) pair of excited states, with clear-cut consequences for quantum yields under various conditions. In other reactions the surfaces stay apart. The critical discriminating feature that determines the type of correlation diagram is the topicity. Photochemical reactions can be classified according to topicity, which is useful in interpreting their mechanisms (*53*). Avoided surface crossings can also be classified into different types. Figure 7, which illustrates the interplay of a covalent and an ionic surface responsible for photochemical electron transfer, is a typical multidimensional representation of a photochemical reaction.

The chemical behavior of the excited zwitterionic states of common intermediates, such as twisted ethylene or diallyl, reflects the quantum mechanical nature of photochemical processes. In these states, for perfectly symmetric systems, charge oscillates back and forth between two symmetry-equivalent sites. Slight geometric perturbations can create a sudden polarization of the excited molecule, with localization of almost a full charge at one end of the molecule. A photon is transformed into an electrical signal thanks to an appropriate molecular distortion. Nature may have used this simple process in the *N*-retinylidene visual chromophore to trigger an electrical response to vision.

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NEWS AND COMMENT

National Science Foundation: Criticism from Conlan, GAO

The scene on 10 February could have been a flashback to last summer when Representative John B. Conlan (R–Ariz.) accused National Science Foundation (NSF) officials of misrepresenting the views of peer reviewers. The difference at the 10 February hearings before a House Committee on Science and Technology subcommittee was that in the interim a General Accounting Office (GAO) report had substantiated Conlan's main contention. Also, NSF director H. Guyford Stever had written subcommittee chairman James Symington (D–Mo.) that "we regret these mistakes" and had pledged more strenuous efforts to remedy them.

Conlan testified on 10 February at an authorization hearing devoted to a discussion of NSF's science education program. He charged that there was a "scandal of deceit and corruption of the NSF grant award process" in the foundation's curriculum improvement program. The essence of Conlan's charge was that NSF staff members had misrepresented peer reviewer's comments in a summary of reviews provided to the National Science Board. The NSB is responsible for giving formal approval to major NSF programs. Conlan also accused NSF officials of a "cover-up" and urged that Congress suspend funding of NSF curriculum development activities for a year.

Although Stever and other top NSF officials were on hand for the session, they were not grilled on the Conlan accusations. An investigation by committee staff of the issues raised by Conlan and by the GAO report is now in progress and Stever has promised Symington that he will conduct his own thorough examination of the situation, so an inquest has been at least delayed.

Conlan's ire was concentrated on an NSF-supported interdisciplinary high school science course called Individualized Science Instructional Systems (ISIS) currently being developed at Florida State University. Conlan emerged about a year ago as a resolute critic of NSF curriculum programs (*Science*, 2 May 1975), when he objected not only to content but to contracting and course-implementation practices associated with an elementary school behavioral science course titled Man: A Course of Study (MACOS). In the peer review hearings last summer Conlan shifted his main fire to ISIS and insisted that evaluations of outside reviewers had been misrepresented. At the time, he was denied access to the reviewers' original comments on the grounds of NSF policies protecting the confidentiality of verbatim peer review documents. (Under the system of mail peer review prevailing at NSF, reviewers have been asked individually for their opinions and seldom learned whether their suggestions influenced NSF decisions on programs, were brought to the attention of those involved in projects, or were incorporated into the projects.) Subsequently, the material Conlan had sought as background to a 5 September 1972 staff memorandum recommending support of the ISIS project became available as a result of the GAO study, requested by Symington in October.

The GAO report is not a wholesale condemnation of the ISIS transaction. The report notes, for instance, that the staff memorandum in question was only one part of the package of documentation on which the National Science Board based its decision on ISIS. But a major conclusion of the GAO investigators is that "In our opinion, however, the memorandum recommending support of the Florida State University proposal was not a totally complete and accurate representation of peer reviewers' comments."

The cover letter accompanying the report says that, to the extent that the comments of 11 reviewers were summarized in the memo, "they are accurately represent-