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Excited-State Intermediates in Solution Photochemistry

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Absorption of light by molecules can lead to the formation of several possible electronically excited states, depending on the energy of the light absorbed. Since selection rules require that the spin angular momentum of the ground state be conserved in this process, excitation of most substances leads initially to singlet excited states. Highly excited singlets (S_2, S_3...) formed with high-energy light are thought to decay extremely rapidly ($\sim 10^{12}$ sec^{-1}) to the lowest excited singlet state (S_1) which is usually depopulated within $\sim 10^{-8}$ sec by fluorescence or nonradiative internal conversion to the ground state (S_0), by chemical reaction, or by intersystem crossing to a triplet state (T_1, T_2....). Triplet states, on the other hand, are usually not formed during the initial act of light absorption, but once formed are relatively long-lived (10–10^{-4} sec). They likewise can decay by radiative (phosphorescence) and nonradiative intersystem crossing to the ground state or by chemical reaction.

The extensive current interest in photochemical reaction mechanisms stems largely from the introduction of powerful techniques for selective population and depopulation of specific excited states. Thus singlet and triplet excited states of photochemically reactive molecules may frequently be populated selectively by energy transfer from excited sensitizer molecules or depopulated by energy transfer to quencher molecules. These methods, together with several spectroscopic techniques, have permitted identification of chemically reactive excited states in many photochemical reactions and have allowed the photochemist to examine the details of "primary" processes by which these reactive excited states are transformed into ground-state products.

The interpretation of such experiments, as applied to complex molecules in solution, often must rest on assumptions derived from the behavior of far simpler molecules in the gas phase. Assumptions that are commonly made include the following. (1) Energy transfer from an electronically excited molecule to a ground-state molecule occurs so rapidly that there is no significant change in atomic positions (Franck–Condon principle). (2) Vibrationally excited ground states of reactant molecules do not survive long enough to be intermediates in photochemical reactions in solution. (3) Only the lowest excited singlet or triplet states of a reactant or sensitizer participate in chemical reactions or energy transfer in solution. Since doubts concerning the applicability of each of these concepts to complex molecules have been frequently expressed, we shall consider in this Account some recent evidence bearing on these assumptions that has provided new insight into the nature of excited-state intermediates.

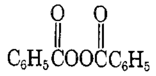
Energy-Transfer Processes

Three classical types of electronic energy-transfer processes in solution are recognized. The first of these is the so-called "trivial" process of reabsorption by a ground-state molecule of light emitted by a fluorescent donor. The second process results from dipolar or quadrupolar interactions between excited donor and ground-state acceptor molecules which can lead to energy transfer over relatively long distances (50–100 Å). Although, like the "trivial" process, this process always causes the acceptor to be excited to a singlet state, in a rigid matrix either excited singlet or triplet molecules may serve as donors. However in solution triplet lifetimes are generally much shorter, and the probability of energy transfer from donor triplets by this mechanism is correspondingly reduced. Because these processes involve strictly electronic transitions, they are not expected to be accompanied by changes in the geometries of the acceptor or donor (Franck–Condon principle).

The third energy-transfer mechanism operates over the very small distances required by direct orbital overlap. Hence, energy transfer is expected to occur only by direct collision of acceptor and donor molecules. Only those processes which conserve the total spin angular momentum are allowed. For example, energy transfer from a sensitizer triplet to a normal ground-state acceptor would lead to an acceptor triplet plus the singlet ground state of the sensitizer. Transfer from a triplet sensitizer to a ground-state triplet species such as oxygen would, on the other hand, lead to an excited singlet state of the acceptor. Careful studies of this process have suggested that the rate of energy transfer is close to diffusion controlled provided that the process is exothermic. Electronic energy of the donor in excess of that required to excite the acceptor appears as vibrational energy. Conversely, endothermic energy transfer occurs more slowly with an activation energy approximately equal to the excess energy requirement.

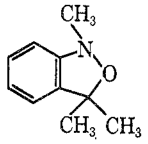
This direct orbital overlap process usually accounts for the frequently observed transfer of triplet energy in solution photochemistry. Although the mechanism is poorly understood, it is thought to involve an exchange interaction which, like the dipole coupling process, has frequently been considered to proceed nearly instantaneously without significant changes in geometry of acceptor or donor. The alternative view that donor and acceptor form covalently bound or charge-transfer complexes has been expressed, but it fails to explain the influence of sensitizer triplet energies on many photochemical reactions.[1] Nevertheless some observations suggest that in certain sensitized reactions complex formation and structural changes may accompany triplet energy transfer. Thus, sensitizers having lower triplet energies than that of *cis*-stilbene have been found to transfer triplet energy to this acceptor as shown by the formation of the *trans* isomer. The energy-transfer rates are less than diffusion controlled but appreciably greater than can be accounted for by endothermic energy-transfer processes in which the energy deficit is provided by thermal activation.[2] Energy transfer must therefore be less endothermic than implied by the acceptor and donor triplet energies, and it has been suggested that concurrent energy transfer and exothermic geometrical isomerization of *cis*-stilbene to give a low-energy triplet stilbene having a twisted or *trans* geometry may account for the energy deficit.

Other olefins as well as a variety of other compounds (**1–7**) have also been found to accept energy by this so-called "nonvertical" triplet energy-transfer mechanism. In each case there occurs apparent endothermic triplet energy transfer to compounds which, like *cis*-stilbene, might be expected to undergo facile transformations of their normal ("spectroscopic") triplets to geometrically modified lower energy triplet or diradical species. Thus the triplet states of peroxides (**1**),[3] substituted hydroxylamines (**2**),[4] cyclopropanes (**3**),[5] and azoalkanes (**4**)[6] apparently undergo efficient homolytic dissociation with spin conservation to give products derived from radical or diradical intermediates. Similarly, cyclobutanes **5**[5] and **6**[7] undergo cleavage of two σ bonds to give olefinic products; this presumably proceeds by initial homolytic cleavage of one bond to give triplet diradical intermediates. The final example, diphenylacetylene (**7**), is of some interest in that no photochemical reaction ensues even though there is apparent endothermic energy transfer in excess of 11 kcal. It has been suggested that facile exothermic rearrangement of the triplet again accompanies energy transfer, but that the product is an unstable nonlinear triplet acetylene which undergoes rapid intersystem crossing and vibrational relaxation to the linear singlet ground state.[8]



$C_6H_5\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}C_6H_5$

1



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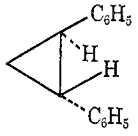

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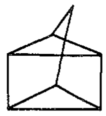
$(CH_3)_3CN{=}NC(CH_3)_3$

4



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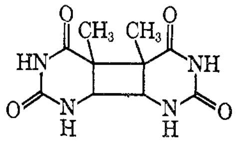

6

$C_6H_5C{\equiv}CC_6H_5$

7

Primary Processes

An important but poorly understood aspect of photochemistry concerns the details of the geometric and energetic changes that make up primary processes. Among the mechanisms that have been considered are (A) direct conversion of an electronically excited state of the reactant to an electronically excited state of the product followed by crossing to the ground state; (B) continuous reorganization of an electronically excited state of the reactant to the ground state of the product, or a similar but discontinuous process involving crossing between excited- and ground-state manifolds part way along the reaction coordinate; and (C) crossing of an electronically excited state of the reactant to a vibrationally excited ground state of the reactant which then undergoes an essentially thermal reaction to give ground-state product.

A. Reaction within an electronically excited-state manifold has been demonstrated relatively infrequently. The most firmly established examples are the photodeprotonation of weakly acidic compounds such as phenols.[9] In these cases fluorescence emission of the corresponding anions provides convincing evidence for the formation of the anion excited states. Similar results have been obtained for the protonation of the excited states of weak bases. Other probable examples are the geometrical isomerization of *cis*-stilbene triplet to give *trans*-stilbene triplet (discussed

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(1) (a) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); (b) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

(2) (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(3) C. Walling and M. J. Gibian, *ibid.*, **87**, 3413 (1965).

(4) N. A. LeBel, T. A. Lajiness, and D. B. Ledlie, *ibid.*, **89**, 3076 (1967).

(5) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

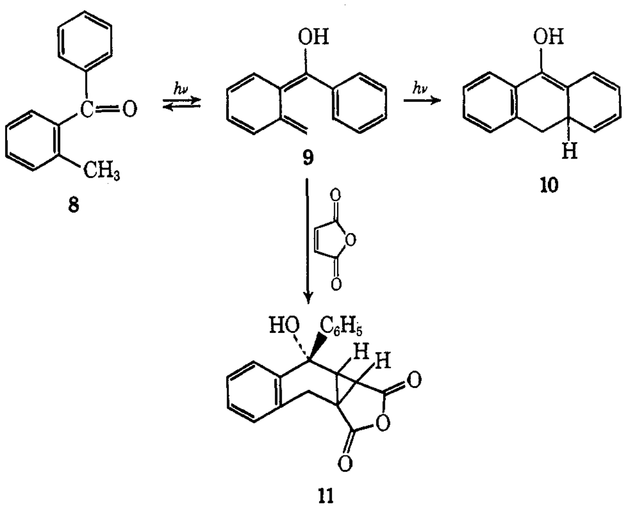
(6) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964).

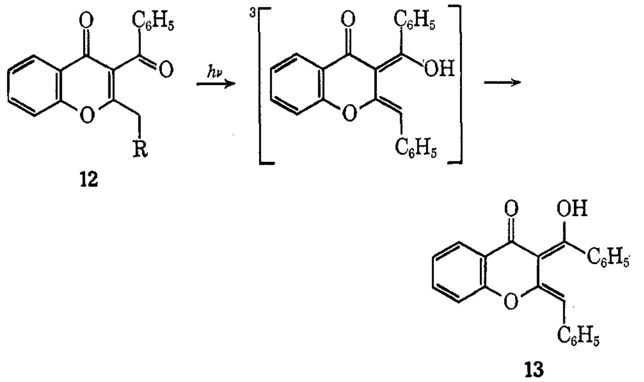
(7) A. A. Lamola, *ibid.*, **88**, 813 (1966).

(8) E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **89**, 4390 (1967).

(9) A. Weller, *Progr. Reaction Kinetics*, **1**, 199 (1961).

above) and the photoenolization of unsaturated ketones. The occurrence of this mechanism in the photoenolization of *o*-methylbenzophenone (**8**)[10,11] is suggested from the geometry of the photoenol product **9** which is opposite to that required for internal abstraction of a methyl hydrogen atom by the carbonyl oxygen in **8**. The geometry shown in **9** is suggested by the ability of **9** to undergo photocyclization to give **10**[11] and by the stereochemistry of its maleic anhydride adduct **11**.[12] Since the photoenol **9** appears to be formed in one photochemical step through a triplet of the ketone **8**, the reaction must lead directly to an excited (presumably triplet) photoenol capable of subsequent geometrical isomerization to **9**.[13] Similarly, the chromone **12** ($R = C_6H_5$) reacts through its triplet state to give a geometrically rearranged photoenol, **13**, which again suggests the formation of an intermediate triplet photoenol.[14]





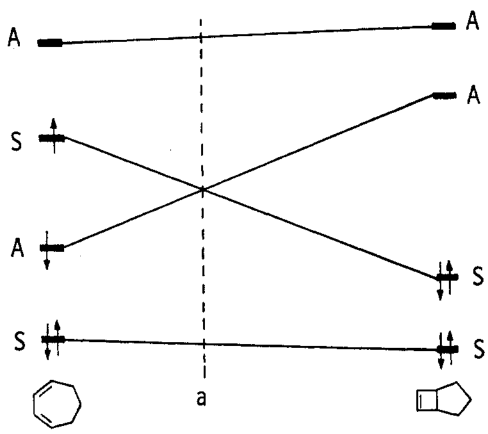


Figure 1. Orbital symmetry correlation diagram for interconversion of 1,3-cycloheptadiene and 6-bicyclo[3.2.0]heptene.

B. Reorganization of a reactant excited state directly to a product ground state is even less well documented. Such processes may be quite common and can be envisioned as proceeding through dissociative states which may be subject to control by spin and orbital symmetry conservation. For example, reactions leading to homolytic bond rupture such as C–X cleavage of halides, C–CO cleavage of ketones (type I process), O–NO cleavage of nitrites (Barton reaction), O–O cleavage of peroxides, etc., might be expected to proceed directly from both singlet and triplet states since spin conservation restrictions would be absent due to the formation of radicals. In one reaction of this type that has been carefully studied, 1-iodonaphthalene was, in fact, found to undergo C–I bond cleavage through both its singlet and triplet states.[15] In heterolytic dissociation processes, on the other hand, spin conservation would seem to require a singlet-state reaction. Although few reactions of this type are known, heterolytic ring opening of 2,2-paracyclophane[16] and 1,2-diphenylcyclopropane (**3**)[17] and C–N cleavage of aryldiazonium salts[18] are believed to occur exclusively *via* the singlet states, in agreement with this assumption.

Another broad class of reactions which might be of the type which undergo direct reorganization from reactant excited state to ground-state product are electrocyclic processes that proceed through π,π^* excited states and are formally allowed by the Woodward–Hoffmann orbital symmetry rules.[19] For example, the orbital symmetry correlation diagram for the ring closure of cycloheptadiene to bicycloheptene (Figure 1) implies that the excited singlet state of the diene should rearrange through an intermediate geometry (a) which is electronically degenerate with an extremely distorted

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[10] (a) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961); (b) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *ibid.*, **85**, 2671 (1963); (c) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

[11] E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1863 (1965).

[12] F. Nerdel and W. Brodowski, *Ber.*, **101**, 1398 (1968).

[13] Further support for this viewpoint is found in the observed fluorescence emission of methyl *o*-hydroxysalicylate which appears to arise from a "photoenol" in which the hydroxy proton is transferred to the carbonyl oxygen; *cf.* ref. 9.

[14] (a) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5417 (1965); (b) W. A. Henderson, Jr., and E. F. Ullman, *ibid.*, **87**, 5424 (1965).

[15] F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

[16] R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

[17] C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *ibid.*, **88**, 5675 (1966).

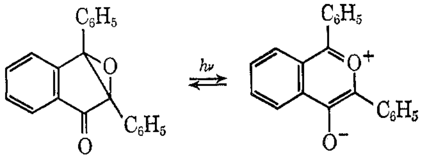
[18] D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys Chem.*, **66**, 2486 (1962).

[19] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

vibrationally excited ground state of the product. On the other hand, the rearrangement of triplets to singlet products must involve a discontinuity, and thus we might expect that allowed photochemical processes would normally occur only through the singlet state. This has frequently been found to be the case in electrocyclic processes involving allowed cycloadditions, ring–chain tautomerization of polyenes, and sigmatropic rearrangements. The most common exceptions are among cycloaddition reactions of olefins to form cyclobutanes where there is evidence for diradical intermediates.[20]

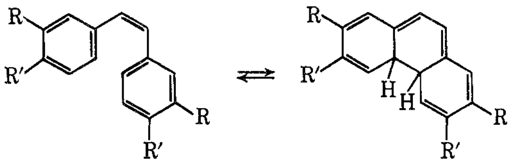
C. Vibrationally excited ground states in gas-phase photochemical reactions at sufficiently low pressures are well-accepted intermediates. However, theoretical difficulties with this concept arise in solution photochemistry. Even molecules that have sufficient vibrational energy to surmount a thermal activation energy barrier are predicted by unimolecular rate theory to react at a limited rate that is controlled by the probability of sufficient vibrational energy becoming concentrated at the reaction site. This probability drops with increasing degrees of freedom and hence size of the molecule, and it also drops upon decreasing the available vibrational energy in excess of that required to surmount the activation energy barrier. These requirements permit only very small vibrationally excited molecules to react in solution at a rate competitive with deactivation by the solvent, and thus it has been argued that vibrationally excited ground states of reactants are not important in solution photochemistry.[21] Nevertheless, certain photochemical reactions behave in solution very much as though vibrationally excited ground-state intermediates might be involved.

Studies of the indenone oxide **14**[22] show that interconversion with **15** occurs both photochemically and thermally. Low activation energies measured for the two processes should favor reaction through vibrationally excited ground states, although **14** and **15** seem to be too large to quantitatively accommodate this mechanism. Nevertheless solvent changes which would effect an increase in the energy of vibrationally excited **14** relative to the thermal activation energy were found to increase the quantum yields of **15** as predicted qualitatively by unimolecular rate theory. Also as predicted, the energetically similar S_1 and T_1 states of **14** ($\Delta E \sim 10$ kcal), which might cross to isoenergetic vibrationally excited ground states, rearrange with nearly equal probabilities, whereas singlet **15** rearranges much more efficiently than its much lower energy triplet. Vibrationally excited ground-state intermediates are also suggested by evidence that excludes alternative mechanisms in which excited states of **14** might rearrange through excited states of **15** and *vice versa*. Thus, formation of excited states of **14** by rearrangement of excited states of **15** are energetically forbidden, and the reverse process is excluded by the failure to observe a characteristic photochemical reaction and emission of **15** upon excitation of **14**.



14 **15**

Photocyclization of *cis*-stilbenes **16** to dihydrophenanthrenes **17** show similar correlations.[23] The reactions proceed exclusively through singlet states which would yield higher energy and more reactive vibrationally excited ground states than the relatively low-energy stilbene triplets, and the quantum yields of cyclization of the *para*-substituted derivatives **16** (R = H) correlate well with the stilbene singlet energies and hence the energies of the derived vibrationally excited states. Moreover, the *meta*-substituted derivatives **16** (R′ = H), all of which have similar singlet energies, react with quantum yields that correlate directly with the *ground*-state electron densities at the two *ortho* carbon atoms of **16** that enter into new bond formation.



16 **17**

Other photochemical reactions which behave as though they were controlled by the activation energy of parallel thermal reactions include the photoelimination of sulfur dioxide from cyclic sulfones related to **18**.[24] Thus analogs of **18** having high ground-state activation energies require excitation with short-wavelength light and react only through high-energy singlet states, while analogs which undergo facile thermal reactions react from their lowest singlet or triplet states. Similarly, the considerably higher thermal activation energy barrier for ring opening of **19** (R = Ac) over that of the isoelectronic alcohol **19** (R = H) appears to be reflected in the much higher quantum yield for ring opening of the latter compound.[25]

Since these data seem to fit the qualitative picture

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(20) (a) R. S. H. Liu, *Tetrahedron Letters*, 2159 (1966); (b) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

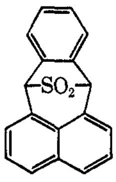
(21) (a) G. Zimmerman, L. Chow, and U. Paik, *ibid.*, **80**, 3528 (1958); (b) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

(22) E. F. Ullman and W. A. Henderson, Jr., *ibid.*, **86**, 5050 (1964); *ibid.*, **88**, 4942 (1966).

(23) (a) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964); (b) H. Güsten and L. Klasinc, *Tetrahedron*, **24**, 5499 (1968).

(24) M. P. Cava, R. H. Schlessinger, and V. P. Van Meter, *J. Am. Chem. Soc.*, **86**, 3173 (1964).

(25) (a) K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *Tetrahedron Letters*, 931 (1967); (b) E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman; *ibid.*, 935 (1967).



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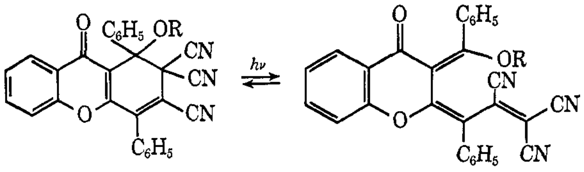

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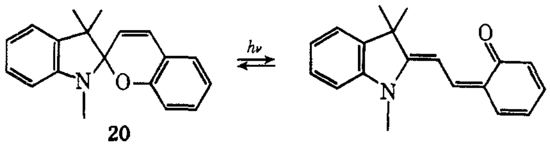
depicted by unimolecular rate theory for vibrationally excited ground-state reactions, it is worth reexamining the quantitative argument used to eliminate this mechanism. This argument begins with the assumption that a vibrationally excited ground-state molecule derived by crossing from an electronically excited state will have its vibrational energy randomly distributed as if it had been excited through thermal activation. Collisional deactivation in solution is then predicted to compete effectively with any redistribution of the energy that would permit a reaction to occur. However, the vibrational energy in a species derived by isoenergetic crossing from an electronically excited state may initially be concentrated in those bonds which are most strongly affected by the change in electronic state. Thus, the largest single factor controlling the efficiency of such a reaction and even its direction may be the changes in bonding associated with specific electronic states, and factors such as the number of degrees of freedom may be of secondary importance.

It is noteworthy that each of these reactions which display behavior suggestive of vibrationally excited ground-state intermediates are photochemically allowed electrocyclic processes. Thus possibly our picture of a vibrationally excited ground-state mechanism is not functionally distinct from the model depicted by orbital-symmetry correlation diagrams. Indeed, it seems probable that symmetry-allowed photochemical processes are strongly affected by the ground-state energy surface, and the failure of many of these reactions to proceed through triplet states may be due to the high energies of the thermal transition states relative to the triplet energies. This idea is supported by observations that allowed photochemical processes having exceptionally low thermal activation energy barriers have been found to proceed through triplet states. Included in this group are the sulfone **18**[24] and the easily thermally activated photochromic compounds **14**,[22] **19**,[25] and **20**.[26]

Reactions from Upper Excited States

One common assumption concerning photochemical reactions in solution is that chemical reactions generally proceed through the lowest excited singlet and triplet states.[27] This assumption is based on the absence of fluorescence emission from excited states other than S_1 in most compounds and also by theory, which predicts that an important factor controlling the rate of radiationless crossing between states is the magnitude of the energy difference between the states. Thus the normally large spacing between the ground and lowest excited singlet and triplet states is thought to account for the long lifetimes of these states relative to the more closely spaced upper excited states. Although several exceptions to the rule that fluorescence occurs only from S_1 have been claimed, only the reported fluorescence emission from S_2 of azulene has survived critical examination. This observation seems in agreement with theory in that the energy difference between S_1 and S_2 of azulene is exceptionally large.



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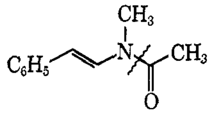
Short-Lived Upper Excited States. Despite these considerations, a number of reports have appeared of qualitative changes in the photochemistry of compounds in solution on varying the wavelength of the exciting light. Some of these observations do not, however, require long-lived upper excited states since the short-wavelength reactions are dissociative processes which might occur virtually instantaneously upon excitation. Among the compounds which appear to selectively undergo dissociative reactions, only with shorter wavelengths than necessary to ensure light absorption, are **21**–**23**.[28–30] The enamide **21** has been carefully studied and shown to undergo cleavage of the OC–N bond with short-wavelength light, whereas longer wavelengths ($>$300 mμ) produce exclusive geometrical isomerization.[28] The reported evidence suggests a singlet precursor in the dissociative short-wavelength process and a triplet intermediate in the long-wavelength isomerization process. Presumably, therefore, population of the S_1 state with long-wavelength light fails to produce dissociation, and the state survives long enough to cross to T_1 which subsequently isomerizes. With shorter wavelengths the initially formed species must dissociate so rapidly that crossing to T_1 is largely prevented.



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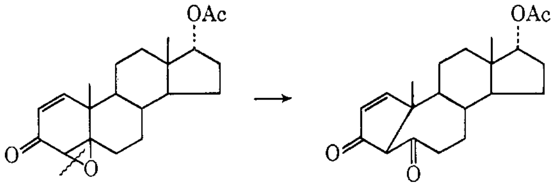
(26) T. Bercovici and E. Fischer, *J. Am. Chem. Soc.*, **86,** 5687 (1964).

(27) See, for example, N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 5.

(28) R. W. Hoffmann and K. R. Eicken, *Tetrahedron Letters*, 1759 (1968).

(29) H. Wehrli, C. Lehmann, P. Keller, J. J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49,** 2218 (1966).

(30) J. Streith and J. M. Cassal, *Compt. Rend., Ser. C*, **264,** 1307 (1967).



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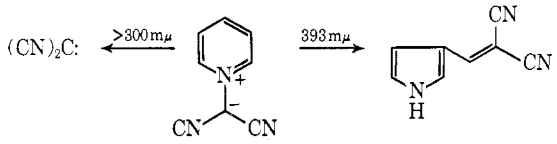

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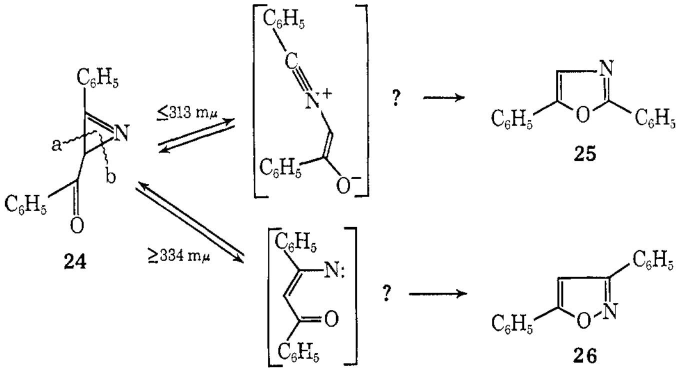
The azirine **24** shows particularly dramatic wavelength dependence of a similar type.[31] This compound rearranges nearly quantitatively to the oxazole **25** with 313-mμ light and to the isoxazole **26** with 334-mμ light. Despite the small energy difference between the two exciting wavelengths (5.5 kcal/mol), each wavelength selectively induces a different process in high quantum yield (~0.3). The formation of **25** can be neither sensitized nor quenched and might proceed through a singlet state which undergoes dissociative cleavage at bond a with spin conservation to give a zwitterionic intermediate. The formation of **26**, on the other hand, can proceed through a triplet state. Again, dissociation with spin conservation can be envisioned, in this case by bond scission at b with possible formation of a triplet nitrene.



24 25 26

The strong wavelength sensitivity and high quantum yields of the azirine reactions are somewhat puzzling since selective excitation of different strongly overlapping absorption bonds within the wavelength-sensitive region does not seem possible. One interpretation is that both reactions proceed through initial excitation to the S_1 state. Higher vibrational levels of S_1 produced with short wavelengths might then undergo dissociation at bond a within a single vibration and thus fail to undergo vibrational cascade to the ground vibrational level of S_1. On the other hand, lower energy nondissociative levels of S_1 produced with longer wavelengths might survive sufficiently long to cross to T_1 which could dissociate at bond b. The high selectivity and quantum yields could then be accounted for by asuming that an exceptionally large proportion of the light energy is accumulated in the azirine C–C bond at the instant of formation of the S_1 state. Singlet molecules born with sufficient energy to overcome a small activation energy for bond cleavage would then always react, whereas singlet molecules with only slightly less energy would survive sufficiently long for the vibrational energy to become redistributed.

An alternative explanation is that the short-wavelength process proceeds through S_2. Although the wavelength sensitivity is then more readily accommodated by ascribing different reactivities to the S_2 and S_1 levels, an unusual assumption is still required. The large overlap of the azirine absorption bands in the 313–334-mμ region demands that 313-mμ light populate vibrationally excited levels of S_1 as well as S_2. The observed selectivity of the reactions then requires that crossing from an initially formed hot S_1 level to an isoenergetic lower vibrational level of a dissociative S_2 state must compete effectively with vibrational relaxation of S_1. At present no choice between this mechanism and reaction through a vibrationally excited S_1 state can be made, though possibly such distinctions have no real physical significance.

Long-Lived Upper Excited States. The most puzzling observations regarding reactions of upper excited states in solution concern the photochemistry of carbonyl-containing compounds since the theoretical restriction on the upper excited-state lifetimes often seems to be disobeyed. In one example, the reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene to give an oxetane,[32] quenching studies have demonstrated the intermediacy of two excited states. The data seem to require that at least one of these intermediates must be an upper triplet, although the interpretation is complicated by the possible formation of excited states of an olefin–anthraldehyde charge-transfer complex. The relatively long lifetime of this species (1×10^{-9} or 3×10^{-10} sec) may be accounted for by the normally large energy difference (~32 kcal)[33] between the T_1 and T_2 states of anthracene derivatives. For example, 9,10-dibromoanthracene has an unusually long-lived T_2 state (1.3×10^{-10} sec), as demonstrated by the ability of this compound to sensitize reactions that would not be susceptible to sensitization by energy transfer from the low-energy T_1 state.[34]

In other aromatic ketones the energy gaps between the T_1 and T_2 states are much less, yet two types of phosphorescence emission from glassy solutions are often observed.[35] Presumably the emitting species are the lowest n,π* and π,π* triplets, but it is not obvious why radiationless decay to the lowest triplet does not compete effectively with emission. Conceiv-

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[31] (a) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); (b) B. Singh and E. F. Ullman, *ibid.*, **89**, 6911 (1967).

[32] N. C. Yang and B. L. Loeschen, *Tetrahedron Letters*, 2571, 3701 (*errata*) (1968).

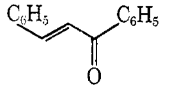
[33] R. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

[34] (a) R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968); (b) R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968).

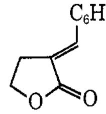
[35] (a) N. C. Yang and S. Murov, *J. Chem. Phys.*, **45**, 4358 (1966); (b) R. D. Rauh and P. A. Leermakers, *J. Am. Chem. Soc.*, **90**, 2246 (1968); (c) R. N. Griffith, *Photochem. Photobiol.*, **7**, 159 (1968).

ably there are several populations of molecules in the frozen matrices which have different lowest excited states due to differences in their microscopic environments. However, there is a growing body of evidence which suggests that species that behave like upper triplet states of carbonyl compounds may frequently survive long enough even in liquid solution to undergo bimolecular reactions. For example, 2-cyclopenten-1-one has been found to undergo triplet-sensitized cycloaddition to cyclohexene provided that the triplet energy of the sensitizer is at least 73 kcal.[36] This implies that an upper triplet level of the cyclopentenone must be involved, since the T_1 energy of cyclopentenone is only about 61 kcal. Moreover, 3,5,5-trimethylcyclohex-2-en-1-one (isophorone) appears to give different cycloaddition products depending on which of two triplet states has been populated, and quenching data imply that the lifetime of even the shorter lived reactive state is relatively long, 10^{-7}–10^{-8} sec.[37]

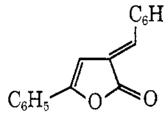
A recent study of chalcone (**31**) suggests that upper excited states of acyclic ketones also are reactive and relatively long lived.[38] With >220-mμ light **31** dimerizes to a cyclobutane, whereas >320-mμ light produces only geometrical isomerization. The lactones **32**–**34** show related behavior.[39] Products isolated from **32** and **34** suggest that the reactions at short wavelengths (254 mμ) are initiated by hydrogen abstraction from the solvent, while long-wavelength light only causes geometrical isomerization. By contrast, acyclic unsaturated esters, such as ethyl cinnamate and ethyl α-methylcinnamate, undergo both reactions independent of wavelength.



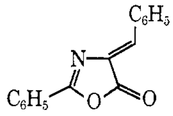
31



32



33



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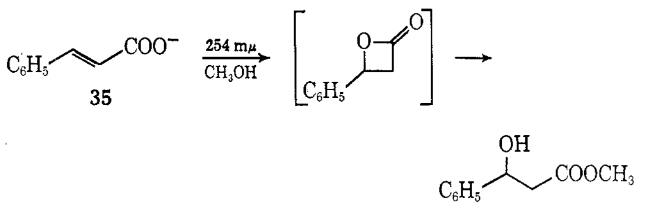
The evidence concerning the excited states of the lactones **32**–**34** again suggests that two reactive triplet states may be involved.[38,40] Thus, with certain triplet sensitizers the lactones **33** and **34** undergo both reactions, while other sensitizers produce only geometrical isomerization. Quenching studies on **32** and **33** suggest further that the upper excited states produced with short wavelengths are unusually long-lived (~10^{-4} sec). In analogy with ketone photochemistry, the hydrogen-abstraction reaction of these long-lived triplets suggests an n,π^* electronic configuration, whereas the geometrical isomerization of the lower energy triplets is characteristic of π,π^* states.

Although these observations suggest that upper excited states of carbonyl compounds may often have very substantial lifetimes, the reason for these long lifetimes remains unknown. Possibly upper n,π^* triplets of carbonyl compounds undergo rather large geometrical deformations which introduce a barrier for crossing to lower states. Whatever the explanation, a possible mechanism for depopulation of these states is suggested by the failure of the cinnamic esters to show wavelength dependence. Thus the apparently slow crossing between the upper n,π^* and the lower π,π^* triplets in the lactone **32** may be accelerated in the corresponding acyclic ester, ethyl α-methylcinnamate, by rotation about the carbonyl–oxygen single bond. The resulting nonplanar conformation should have a lower n,π^* and higher π,π^* energy, and thus the energy difference between these states would be decreased. This should facilitate crossing between the states and account for the failure to observe wavelength dependence in the reactions of the cinnamate esters. In partial confirmation of this hypothesis, it has been found that the cinnamate anion **35**, which cannot undergo a similar rotation about a carbonyl–oxygen bond, displays primarily geometrical isomerizaton with >300-mμ light but appears to form a β-lactone with 254-mμ light.[38]



In conclusion, it is evident that many of the important questions concerning photochemical processes in solution remain incompletely answered, and the interpretations presented here can be considered as little more than working hypotheses. Recent studies of energy-transfer processes suggest that factors influencing the rates of both singlet and triplet energy transfer may be far more complex than indicated above. Orbital symmetry relationships between the donor and acceptor may influence the rate of energy transfer,[40] and singlet energy may sometimes be transferred in a manner akin to triplet nonvertical energy-transfer processes.[41] Further, the full significance of vibrationally excited ground states in solution still remains to be delineated, and the recent discovery of numerous wavelength-dependent reactions suggests that many reactions that have already been carefully studied may now require reexamination using different wavelengths of light.

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(36) P. DeMayo, J. P. Pete, and M. Tehir, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

(37) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968).

(38) E. F. Ullman, N. Baumann, M. Sung, and R. J. Weinkam, unpublished observations.

(39) N. Baumann, M. Sung, and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 4157 (1968).

(40) E. F. Ullman and N. Baumann, *ibid.*, **90**, 4158 (1968).

(41) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).