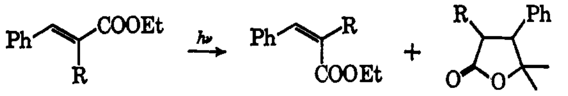
On irradiation of V with 2537-Å light, diminution of all the ultraviolet bands again occurred, and a hydrogen abstraction process again appeared to be involved. In addition to polymer and pinacol, a mixture of four lactones was isolated in about 30% yield. One of these, VII, crystallized after chromatography and distillation: $\nu_{C=O}$ 1760 cm^{-1}; nmr τ 6.30 (CH_2O, quartet sharpened by D_2O), 6.71 (2CH, m), 7.49 (OH), 8.16 (CH_2, m), and 8.50 and 8.91 ($2CH_3$); m/e 234 (M), 176 (M − $(CH_3)_2CO$), and 148 (M − CO − $(CH_3)_2CO$). The remaining products appeared to be closely related structural and geometrical isomers.

Like the above esters, ethyl *trans*-cinnamate (VIII) and ethyl *trans*-α-methylcinnamate (IX) on irradiation in isopropyl alcohol with 2537-Å light yielded their geometrical isomers together with a multiplicity of products, including low yields (3 and 8%) of the respective lactones X [$\nu_{C=O}$ 1755 cm^{-1}; τ 2.73 (5ArH), 6.48 (1CH, t, J = 9 Hz), 7.10 (CH_2, d, J = 9 Hz), 8.49 (CH_3), and 9.00 (CH_3); m/e 190 (M), 162 (M − CO), 104 (M − CO − $(CH_3)_2CO$)] and XI [stereoisomeric mixture, $\nu_{C=O}$ 1750 cm^{-1}; m/e 204 (M), 176 (M − CO), and 118 (M − CO − $(CH_3)_2CO$)]. However, VIII and IX failed to show wavelength dependence, and both the isomerization and hydrogen abstraction reactions were induced with the longest wavelengths of light (3103 Å) that could be absorbed.



VIII, R = H
IX, R = CH_3

X, R = H
XI, R = CH_3

Although products derived from hydrogen abstraction by several photochemically excited α,β-unsaturated esters have been reported, wavelength dependence of these reactions remains largely unstudied.[4,5] The present examples of hydrogen abstraction by the unsaturated lactones with only short wavelengths suggest that a reactive upper excited state is populated which has sufficient lifetime to undergo a bimolecular reaction. Based on analogy with the photochemistry of ketones, this behaves like an n,π^* state. On the other hand the wavelength-insensitive geometrical isomerization reactions probably proceed through π,π^* states since both reactive states of I and V probably have triplet character, and their reactivity difference most likely rests, therefore, in factors other than multiplicity.[6]

A particularly interesting aspect of the present data is the failure of the reactions of the acyclic esters to display similar wavelength dependence. Although the acyclic esters may exist predominately in their *s-trans* conformations as opposed to the enforced *s-cis* conformations of the lactones, it seems unlikely that differences between the very closely related *s-cis* and *s-trans* chromophores could alone be responsible for the observed behavior. On the other hand, molecular orbital calculations imply that a significant lowering of n,π^* relative to π,π^* levels results from a 90° twisting about the carbonyl-to-oxygen single bond of the acyclic esters. Provided the n,π^* triplets of these compounds are of higher energy than the π,π^* triplets (as implied in the above discussion), internal conversion of an initially formed planar n,π^* triplet of an acyclic ester will be facilitated by the mixing of states resulting from rotation about the carbonyl-to-oxygen single bond. Reactions characteristic of both excited states might therefore be expected with all wavelengths of light, as is, in fact, observed.

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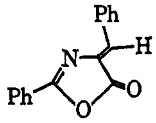
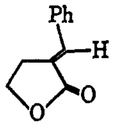
Photosensitization of Wavelength-Dependent Lactones. Influence of Orbital Symmetries on Triplet Energy Transfer

Sir:

The preceding communication[1] describes two lactones, I and II, that were shown to undergo wavelength-dependent photochemical reactions. Although both compounds were found to undergo geometrical isomerization with all absorbed wavelengths, hydrogen abstraction from solvent was found to proceed only at relatively short wavelengths. We report here evidence concerning the multiplicity of the reactive excited states involved in these reactions which may provide some insight into the general problem of energy-transfer mechanisms.



I



II

During the investigation of the above lactones, the photoefficiency of the hydrogen abstraction process was found to be exceptionally sensitive to the lactone concentration. Increasing the concentration of I from 10^{-5} to 10^{-4} M in isopropyl alcohol resulted in a sharply reduced rate of lactone disappearance (hydrogen abstraction) while leaving the geometrical isomerization rate nearly unaffected. The lactone II displayed similar behavior, and quantitative measurements yielded a linear Stern–Volmer relationship if the lactone was assumed to act as a self-quencher.[2] A quantum efficiency for hydrogen abstraction at infinite dilution of 0.4–1.0 and a lifetime of the reactive species of τ = $(4 \pm 2) \times 10^{-4}$ sec (assuming $k_{dif} = 2.7 \times 10^9$ sec^{-1}) were estimated. This long lifetime is clearly consistent with a triplet rather than a singlet excited state. If the excited state is in fact a triplet, the existence of the self-quenching process then raises the question of how

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(4) (a) M. J. Jorgenson, *Chem. Commun.*, 137 (1965); (b) M. Pereyre, G. Colin, and J. Valade, *Tetrahedron Letters*, 4805 (1967).

(5) A report that diethyl maleate reacts with dioxane only with <300-mμ light is of uncertain significance since wavelength dependence was not found with tetrahydrofuran: I. Rosenthal and D. Elad, *Tetrahedron*, 23, 3193 (1967).

(6) Although proof of a triplet intermediate for the direct light-induced isomerization is lacking, sensitization studies show that the reaction can proceed through a triplet state. Since hydrogen abstraction resulting from direct or sensitized irradiation occurs through a triplet state which differs from that leading to isomerization, these excited-state symmetry assignments appear to be reasonable at least in the sensitized reactions: E. F. Ullman and N. Baumann, *J. Am. Chem. Soc.*, **90**, 4158 (1968).

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

(2) Probable traces of a radical scavenger (oxygen?) interfered with quantitative studies of the direct photolyses of I.

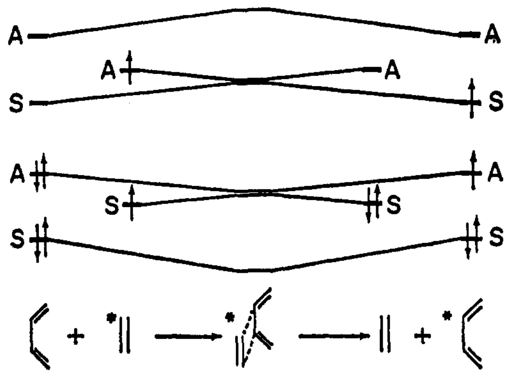


Figure 1. Allowed energy-transfer correlation diagram.

spin conservation is obeyed. An attractive explanation is that the long-lived reactive species is a higher triplet, $^3\mathrm{II}_2$, which may enter into exothermic energy transfer to ground-state II_0 leading to a lower unreactive triplet, $^3\mathrm{II}_1$ (eq 1).[3]

$$\mathrm{II}_0 + {}^3\mathrm{II}_2 \longrightarrow {}^3\mathrm{II}_1 + \mathrm{II}_0 \qquad (1)$$

A triplet intermediate in the hydrogen abstraction process is further supported by the observation that 10^{-3} *M* piperylene also quenched the disappearance of I or II (3130 Å). On the other hand, the isomerization reactions must proceed by way of excited states other than $^3\mathrm{I}_2$ or $^3\mathrm{II}_2$ since neither piperylene nor self-quenching affected their rates. Nevertheless, sensitization studies on I (Table I) suggest that both the isomerization and hydrogen abstraction reactions are susceptible to triplet sensitization (the low concentrations used exclude singlet energy transfer) and that isomerization must be able to proceed through some other triplet intermediate, presumably $^3\mathrm{I}_1$ or $^3\mathrm{II}_1$. Thus, while all sensitizers were found to initiate isomerization, only certain sensitizers initiated hydrogen abstraction.

Table I. Photosensitization of I[a]

Sensitizer	E_T, kcal	Isomerization	H abstracn, quantum yield[b]
Benzene	85	+	3×10^{-2}
Fluorene	68	+	1×10^{-2}
Triphenylene	67	+	$<1 \times 10^{-4}$
Biphenyl	66	+	0.6×10^{-2}
Phenanthrene	62	+	$<1 \times 10^{-4}$
Naphthalene	61	+	0.4×10^{-2}
α-Naphthaldehyde	56	+	Inefficient[c]
Pyrene	49	+	$<1 \times 10^{-4}$

[a] 4×10^{-5} *M* in degassed isopropyl alcohol. [b] Uncorrected for sensitizer intersystem-crossing efficiencies and triplet lifetimes. [c] 3130-Å light absorbed partially by I. Much less efficient than without sensitizer.

The ability of a given sensitizer to initiate hydrogen abstraction was clearly related to some factor other than merely its triplet energy (Table I).[4] In this regard it is of interest to compare orbital symmetries at each atom of I with those of the various sensitizers. Assuming a face-to-face collision during energy transfer, it is found that isomerization is the exclusive reaction only when there is close atom-for-atom matching of the highest filled (HFMO) and lowest vacant (LVMO) orbitals of the sensitizer and acceptor, respectively. By contrast, both processes occur with the remaining sensitizers, none of which have even two properly spaced atoms capable of matching the termini of the exocyclic unsaturated carbonyl chromophore.

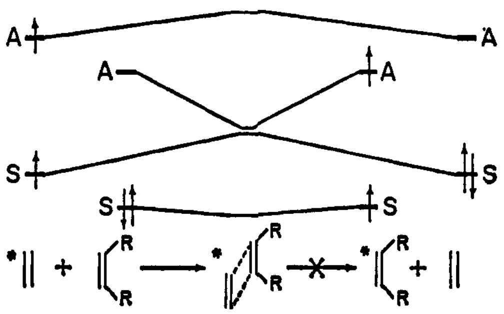
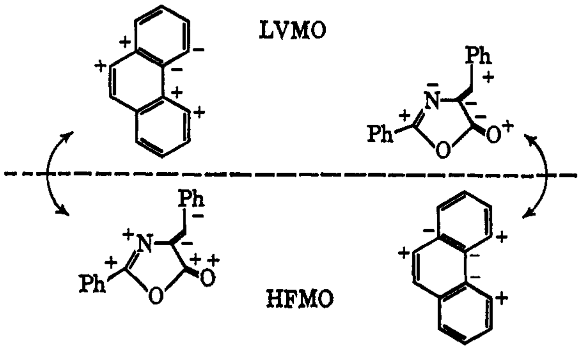


Figure 2. Forbidden energy-transfer correlation diagram.



These relationships are probably not fortuitous. Most likely the hydrogen abstraction intermediate ($^3\mathrm{I}_2$) is an n,π* triplet and the isomerization intermediate ($^3\mathrm{I}_1$) is a π,π* triplet.[1,5] Energy transfer to I, if exothermic, could in principle populate both triplets in a ratio dependent on their respective energies.[6] However, the presumed π,π* triplet ($^3\mathrm{I}_1$) is instead populated selectively when orbital symmetry matching is possible. Selection rules based on orbital symmetry may therefore be applicable to intermolecular energy transfer processes involving π,π* excitation. Correlation diagrams related to those used in the interpretation of electrocyclic reactions[7] serve to rationalize the present results. Simple models are given in Figures 1 and 2. On moving from left to right in these diagrams a face-to-face interaction between the sensitizer and acceptor is assumed to increase until the perturbation is sufficient to cause crossing of the energy levels. At this point degenerate states are formed, and crossing between these states by redistribution of the electrons in degenerate orbitals should be very rapid. In allowed processes, crossing leads to electronic configurations

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(3) An alternative explanation involving self-quenching through triplet eximer formation is less economical since two triplet states are still required by the sensitization data (*vide infra*).

(4) An assumption of energy transfer from upper triplets of naphthalene and biphenyl would permit a correlation with sensitizer triplet energies, but double-sensitizer experiments eliminate this possibility. Thus, for example, addition of naphthalene to a triphenylene-sensitized reaction greatly increased the rate of hydrogen abstraction.

(5) Although $^3\mathrm{I}_2$ seems to have n,π* character, its long lifetime suggests the occurrence of some stabilizing distortion of the spectroscopic $^3\mathrm{I}_2$ state to account for its slow crossing to $^3\mathrm{I}_1$.

(6) Selective sensitized excitation of oxygen to the $^1\Sigma_g$ and $^1\Delta_g$ state is an example of such a process: D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Am. Chem. Soc.*, **89**, 5455 (1967).

(7) R. Hoffman and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited.

which permit over-all energy transfer as the molecules separate (progression from center to far right of Figure 1). On the other hand, crossing between degenerate states in forbidden processes results in configurations which cannot lead to energy transfer (Figure 2).

Although these considerations appear to be useful in explaining the present results as well as recent results of others,[8] we wish to emphasize that orbital symmetry will generally be secondary in importance to energy in determining the rate of energy-transfer processes. Thus exothermic energy transfer is expected to occur in general with or without orbital symmetry conservation, and control by orbital symmetry is expected only when there is a competition between different energy-transfer processes.

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(8) Orbital symmetry requirements in fluorescence quenching have recently been reported (G. S. Hammond, 20th National Organic Chemical Symposium, Burlington, Vt., June 18-22, 1967).

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Electron Paramagnetic Resonance of ${}^1\Delta$ Oxygen from a Phosphite–Ozone Complex

Sir:

The identification of electronically excited oxygen as a product of organic chemical reactions is usually based on its subsequent reaction with unsaturated organic molecules.[1-3] The evidence is usually the observation of products which have also been obtained with photosensitized oxidations or with microwave discharged oxygen.[4,5] While the physical evidence is unequivocal for both ${}^1\Delta$ and ${}^1\Sigma$ oxygen in the discharge,[6] similar support for the chemical production of these states has been confined to their electronic emission spectra arising with some inorganic reactions.[7] To determine if excited oxygen is, in fact, produced in one of the organic reactions which had been suggested as a source, we have examined the epr spectrum of the oxygen produced by the decomposition of a triphenyl phosphite–ozone complex.[3] The presence of ${}^1\Delta$ oxygen has been demonstrated by its characteristic absorptions.

The epr of ${}^1\Delta$ O_2 in a discharge was first observed and characterized by Falick, *et al.*[8] We may regard these absorptions as arising from the magnetic moment due to the orbital motion of the two π^* electrons. In a corresponding ${}^1D$ state of an atom, the pure orbital motion produces a $g = 1$, and epr absorption would be near 6000 G at 9 Gc. In the ${}^1\Delta$ O_2 the component of orbital angular momentum along the internuclear axis is $2\hbar$. This knowledge of one component of the total angular momentum J implies, by the uncertainty principle, that the direction of J is off the axis. We may view the internuclear axis as tumbling about J so that, on the average, only the component of the orbital magnetic moment parallel to J remains to interact with the external magnetic field. The reduced moment is equivalent to $g = 4/(J(J + 1))$.[8,9] For the lowest rotational state of the molecule $J = 2$, a value which arises from the orbital motion. For this state $g = {}^2/_3$ and absorption is expected at ~9000 G. The higher rotational states have a smaller g factor, and resonance will occur only at fields beyond the upper limit of the magnet (15 kG). Consequently we see only the four $\Delta m_J = 1$ transitions of $J = 2$. These transitions are split by a second-order interaction, and four absorptions at intervals of ~100 G are observed.[8]

In a typical run, 0.01 mol of the solid triphenyl phosphite–ozone complex,[3] diluted with sand to moderate the decomposition,[10] was allowed to decompose at ~−20°. The oxygen produced traversed a quartz tube which passed through a Varian V-4535 large-access cavity. Large diameters (~20 mm) were used in the system to minimize the time interval between the production of the O_2 and its entrance into the cavity. The oxygen pressure in the tube was kept in the range of 0.2–2 mm. The higher pressure was associated with collisional broadening, and most experiments were done at 0.3–0.6 mm. The intensity of the absorptions paralleled the rate of oxygen evolution by the complex. The strong signals characteristic of ${}^3\Sigma$ O_2 were easily detected. In addition, the weaker absorptions of the ${}^1\Delta$ O_2 were observed. These were identified by comparison with the spectrum observed with oxygen which had experienced a microwave discharge and then passed through the same cavity. The positions of the lines agreed within 1 G. For both the chemically and electrically produced ${}^1\Delta$ O_2 the inner two lines are about 50% stronger than the outer, as expected for a ${}^1\Delta$ state.[9]

The relative intensities of the ${}^3\Sigma$ and ${}^1\Delta$ were also measured for discharged and for chemically produced oxygen. Assuming that the discharge contains 10% ${}^1\Delta$,[8,11] the gas from the complex contained ~1% ${}^1\Delta$ when it was in the cavity. Implicit in this determination is the assumption that both sources of ${}^1\Delta$ have the same relative amount of the $J = 2$ state, the one rotational state observed in the resonance experiments. At 300°K, in thermal equilibrium, some 3% of the oxygen is in $J = 2$. Significant departures from equilibrium in one sample could invalidate the comparison, but we do not feel that large differences are likely.

Although the ${}^1\Delta$ is observed, we do not wish to imply that this must be the state originally produced on decomposition of the complex. Another possibility is that ${}^1\Sigma$ is the first product, but would, of course, not be detectable in the epr experiment. Relaxation to the ${}^1\Delta$ and also to the ${}^3\Sigma$ state would then allow their observation. Relaxation of the original excited state could occur as it diffuses out of the reaction mixture and travels to the cavity, although direct production of ${}^3\Sigma$ in the decomposition is also possible.

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(1) H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 3073 (1967).

(2) J. A. Howard and K. U. Ingold, *ibid.*, **90**, 1956 (1968).

(3) R. W. Murray and M. L. Kaplan, *ibid.*, **90**, 537 (1968).

(4) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *ibid.*, **90**, 975 (1968), and references cited therein.

(5) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3882 (1964).

(6) L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964).

(7) J. S. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, **4**, 963 (1965).

(8) A. M. Falick, B. H. Mahan, and R. J. Meyers, *J. Chem. Phys.*, **42**, 1837 (1965).

(9) A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc.*, (London), **B293**, 108 (1966).

(10) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, 90, 4161 (1968).

(11) In our experiments the concentration of ${}^1\Delta$ in the discharge was largely independent of the microwave discharge power except at the lowest power levels. A decrease of the ${}^3\Sigma$ signal of 7–8% was observed with the initiation of the discharge.