$AlCl_3$ and β-chloropropiophenone which was obtained from benzene, β-chloropropionyl chloride, and $AlCl_3$.[8] These samples were purified either by recrystallization from ethanol–methylcyclohexane mixture or by steam distillation followed by chromatography using a column of alumina and/or silica gel. 1-Tetralone was obtained from Eastman Distillation Products and it was purified through steam distillation and recrystallization from water. 2,2-Dimethyl-1-indanone and 2,2-dimethyl-1-tetralone were prepared from their respective benzocyclonones following the procedure of Haller and Bauer.[9] All derivatives of 1-indanone were obtained from Norman L. Allinger of Wayne State University and they were purified by vacuum sublimation or distillation. The solvents used for the emission studies were 3MP (3-methylpentane), EPA (5:5:2 by volume of ether, isopentane, and alcohol), EP (1:9, 3:7, and 1:1 by volume of ether and isopentane), MCH (methylcyclohexane), TP (1:1 by volume of triethylamine and isopentane), MTF (2-methyltetrahydrofuran), PA (1:1 by volume of isopentane and ethanol), and ME (1:1 by volume of methanol and ethanol).

The polarization and excitation spectra of phosphorescence were obtained using Aminco-Bowman and Aminco SPF-1000 spectrophotofluorometers, while higher resolution phosphorescence spectra were obtained using a Jarrell-Ash 0.5-m Ebert scanning spectrometer. Recording electronics for the last instrument consisted of an EMI 6255B photomultiplier tube and a Sargent MR recorder. The phosphorescence mean lifetimes were determined using a GE BH-6 mercury arc lamp operating as a flash lamp.

Acknowledgments. We wish to thank Professors Normal Allinger, Carl Johnson, and Harvey Posvic for helpful discussions.

---

[8] B. Amagat, *Bull. Soc. Chim.*, **41**, 940 (1927).

[9] A. Haller and E. Bauer, *Compt. Rend.*, **150**, 1475 (1910).

A Comparison of the Photodimerizations of 2-Cyclopentenone and of 2-Cyclohexenone in Acetonitrile[1a]

Peter J. Wagner[1b] and David J. Bucheck[1c]

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48823.

Received March 27, 1969

Abstract: In acetonitrile, head-to-head:head-to-tail photodimer ratios are independent of ketone concentration, being 4:5 for cyclopentenone and 2:1 for cyclohexenone. The variation in dimer quantum yields as a function of ketone concentration indicates k_i/k_a ratios of 0.06 and 2.7, respectively, where k_a is the bimolecular rate constant for reaction of triplet ketone with ground-state ketone and k_i is the rate of unimolecular triplet decay. Stern–Volmer quenching studies with conjugated dienes yield measures of triplet lifetimes as a function of ketone concentration. These studies indicate k_a values of 6.9×10^8 and 1.1×10^8 M^{-1} sec^{-1} and k_i values of 4×10^7 and 3×10^8 sec^{-1}, respectively, for cyclopentenone and cyclohexenone. For both ketones dimerization occurs from the lowest triplet; the more rapid decay rate of the reactive cyclohexenone triplet probably reflects a greater ease of twisting. The maximum efficiency of dimerization is only 36% for cyclopentenone and 74% for cyclohexenone. Since intersystem crossing is 100% efficient for both ketones, these results indicate that both dimerizations proceed through metastable dimeric species, significant percentages of which revert to two ground-state monomers. A comparison of these results with others in the literature suggests that dimerization occurs from π,π^* triplet states.

Photodimerization of α,β-unsaturated cyclic ketones is a well-known process.[2] Although the reaction is general for many cyclopentenones and cyclohexenones,[3] detailed studies have been made only of cyclopentenone (CP),[4,5] cyclohexenone (CH),[6] and isophorone.[7] For all three ketones, *cis-anti*-fused head-to-head and head-to-tail cyclodimers are the principal products and arise solely from the excited triplet states of the ketones. de Mayo and coworkers have suggested that the cycloaddition reactions of cyclopentenone involve the *second* excited triplet, the lowest triplet apparently undergoing only photoreduction.[8,9] Hammond and coworkers suggest that cyclohexenone dimerizes from its lowest triplet.[6] Chapman and coworkers, however, have suggested that isophorone undergoes cycloadditions from two distinct triplets.[7,10]

The HH/HT dimer ratios increase significantly with solvent polarity for all three ketones. This fact complicates mechanistic studies, since the enones are polar enough that product distributions and thus relative rates are a function of ketone concentration.

Relatively few results have been reported which afford values of the rate constants for the primary reactions of the excited enone triplets. A bimolecular rate constant of 10^6 M^{-1} sec^{-1} has been estimated for the addition of triplet isophorone to ground-state isophorone.[7] However, quenching studies indicate triplet-state lifetimes of only a few nanoseconds for 3 M cyclopentenone[4b] and for 1 M cyclohexenone.[6] Eaton has shown that cycloheptenone and cyclooctenone do not dimerize

---

[1] (a) Preliminary report: P. J. Wagner and D. J. Bucheck, *Can. J. Chem.*, 47, 713 (1969); (b) Alfred P. Sloan Fellow, 1968–1970; (c) National Institutes of Health Predoctoral Fellow, 1966–1969.

[2] For a review, see O. L. Chapman and G. Lenz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 283.

[3] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, 33, 4060 (1968).

[4] (a) P. E. Eaton, *J. Am. Chem. Soc.*, 84, 2344 (1962); (b) P. E. Eaton and W. S. Hurt, *ibid.*, 88, 5038 (1966).

[5] J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967).

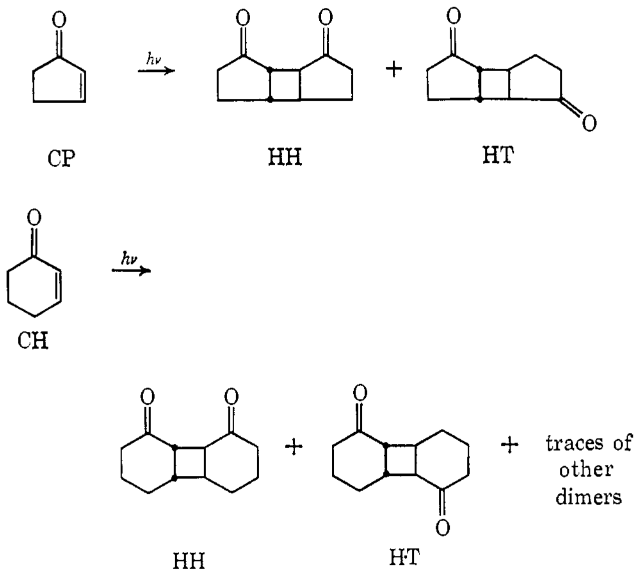
[6] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

[7] O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswald, *Record Chem. Progr.*, 28, 167 (1967).

[8] P. de Mayo, J.-P. Pete, and M. Tchir, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

[9] P. de Mayo, J-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968).

[10] O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Am. Chem. Soc.*, **90**, 1657 (1968).



from their triplet states but rather undergo twisting about their double bonds.[11] His work suggests that increased ring size permits radiationless decay of the triplet to compete better with cycloaddition. This paper reports our detailed studies which confirm this hypothesis and which provide estimates of the primary triplet-state rate constants for cyclopentenone and cyclohexenone.

Results

Product Distribution. In acetonitrile, the HH/HT dimer ratios are independent of enone concentration. Over a range of 0.1 to 3.0 *M* ketone, the HH/HT ratio is 4:5 for cyclopentenone and 2:1 for cyclohexenone. These values compare favorably with those in the literature.[4-6] A third product peak, amounting to only 4% of the total, appears just before the two major cyclohexenone dimer peaks on glpc traces and probably corresponds to a dimer with a *trans*-6/4 ring junction.

Quantum Yields. Quantum yields of dimerization as a function of enone concentration were determined by parallel irradiation at 3130 Å of degassed samples containing various concentrations of ketone and fixed concentrations of internal standards. Actual dimer yields were measured by glpc analysis. Total conversion was never allowed to exceed 5%. At large conversions the dimers undergo secondary photoreactions. Actinometry was performed by parallel irradiation of samples containing 0.1 *M* acetophenone and 0.15 *M* *cis*-1,3-pentadiene. The quantum yield for the sensitized *cis*-to-*trans* isomerization is 0.555.[12] Dimerization quantum yields are listed in Table I for both ketones.

Table I. Dimer Quantum Yields at Various Concentrations of Cyclopentenone and Cyclohexenone in Acetonitrile

Concn, *M*	ϕ_{CP-CP}[a]	ϕ_{CH-CH}[a]
1.00	0.342	0.204
0.50	0.324	0.115
0.38	0.308	0.091
0.25	0.292	0.064

[a] Total quantum yields for HH and HT dimers; relative values precise to ±0.003.

Quenching Studies. Degassed acetonitrile solutions containing a given concentration of enone, internal standard, and various concentrations of 1,3-pentadiene or 1,3-cyclohexadiene were irradiated in parallel at 3130 Å. Relative quantum yields of dimer formation were determined by glpc analysis. Stern–Volmer plots were invariably linear out to Φ_0/Φ values greater than 10, and HH/HT dimer ratios remained constant no matter how much of the reaction was quenched. Table II lists the Stern–Volmer slopes at various ketone concentrations as $k_q\tau$ values, where k_q is the bimolecular rate constant for quenching and τ is the triplet lifetime of the ketone.

Table II. Stern–Volmer Slopes for Quenching of Dimerization

Ketone	Diene	[Ketone], *M*	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 sec^{-1} [a]
CP	1,3-Pentadiene[b]	1.52	9.1	11.0
		1.00	12.5	8.0
		0.75	16.5	6.1
		0.50	26.5	3.8
CH	1,3-Pentadiene[c]	1.00	13.7	4.2
		0.50	17.5	3.5
		0.48	17.5	3.5
		0.25	18.5	3.3
CH	1,3-Cyclohexadiene[b]	0.75	27.0	3.7
		0.50	28.1	3.5

[a] k_q values were corrected for changes in viscosity at different enone concentrations. [b] $k_q = 1.0 \times 10^{10}$ M^{-1} sec^{-1} in CH_3CN. [c] k_q assumed equal to 6×10^9 M^{-1} sec^{-1} in pure CH_3CN.

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \quad (1)$$

Schuster and coworkers have reported that cyclopentenone is quenched with equal efficiency by cyclohexadiene and by pentadiene,[13] whereas cyclohexenones are frequently quenched more efficiently by cyclohexadiene.[13,14] We find that cyclohexadiene is approximately 1.5 times better than pentadiene at quenching cyclohexenone itself. This difference makes it difficult to estimate values for k_q from which to calculate τ values. Since with cyclopentenone k_q is the same for both dienes, we arbitrarily assign it a value of 1.0×10^{10} M^{-1} sec^{-1}, the same as our earlier studies indicated for exothermic energy transfer from triplet valerophenone to dienes in solvents of the viscosity of acetonitrile.[15] We also assume this value for cyclohexenone–cyclohexadiene, with the realization that it may lie only within a factor of 2 of the true value.

Intersystem Crossing Yields. Since the maximum dimerization quantum yields for both ketones are appreciably below unity, it was necessary to ascertain intersystem crossing yields. These were obtained by measuring the efficiency with which the two ketones (0.50 *M*) sensitize the *cis*-to-*trans* isomerization of various concentrations of 1,3-pentadiene. Figure 1 displays the results plotted according to eq 2, where ϕ_{ISC} is the intersystem crossing quantum yield for the sensitizer, τ is its triplet lifetime as before, k_t is the rate constant for energy transfer to the diene, and [Q] is the diene concentration.

$$\frac{0.56}{\Phi_{c\rightarrow t}} = \frac{1}{\phi_{ISC}}\left(1 + \frac{1}{k_t\tau[Q]}\right) \quad (2)$$

---

(11) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(12) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(13) D. I. Schuster, *et. al.*, *J. Am. Chem. Soc.*, **90**, 5027 (1968).

(14) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968).

(15) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

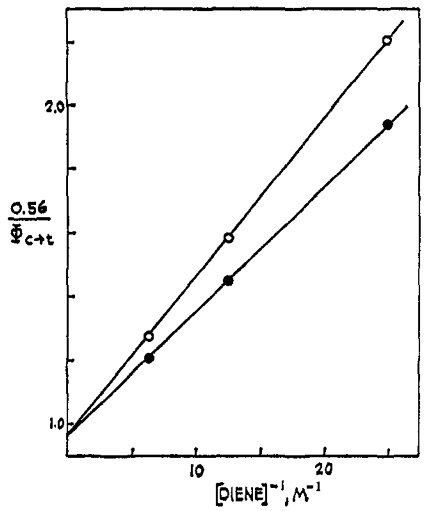


Figure 1. Variation in quantum yields of sensitized *cis* → *trans* isomerization of 1,3-pentadiene as a function of pentadiene concentration. Sensitizer: 0.5 *M* cyclopentenone, ●; 0.5 *M* cyclohexenone, ○.

The intercepts indicate that $\phi_{ISC} = 1$ for both ketones. This conclusion agrees with that already published for cyclopentenone[5,9] and corrects the suggestion that cyclohexenone forms triplets inefficiently.[6] Interestingly, the slopes yield the *same* $k_t\tau$ values for *both* ketones as the $k_q\tau$ values derived from the quenching studies. These results confirm that the quenching involves only triplet energy transfer and suggest that the *same* ketone triplet is responsible for dimerization and for sensitization.

The decay ratio of 56% *trans* in acetonitrile was determined by measuring the photostationary state with benzophenone as sensitizer. It is the same as in benzene.[12] However, as other workers have noted,[5,6] the photostationary state (pss) with the enones as sensitizers contains somewhat more *trans* isomer. If the difference is due to mixed sensitization by two triplets of different energies, we would expect the pss to vary with diene concentration, since different proportions of the sensitization would then occur from the two different triplets. With 0.20 *M* cyclopentenone as sensitizer, the same pss of 58.5% *trans* was observed at both 0.01 and 0.30 *M* pentadiene. Under these conditions 20 and 90% of the dimerizing ketone triplets are quenched, and 25 and 3% of the reactive triplets decay to a lower state. If that state were long-lived enough to transfer energy to the diene, the relative amounts of sensitization from T_2 and T_1 would be 4:5 for 0.01 *M* diene and 30:1 for 0.30 *M* diene. The constant pss demands a single energy triplet sensitizer; the pss value might suggest a sensitizer E_T near 62 kcal.[5,6] The conflict between this interpretation and that necessitated by sensitization studies[5,8] is discussed further below.

Discussion

Mechanism. The following mechanistic scheme is necessitated by our results, where E_0, ${}^1E^*$, and ${}^3E^*$ represent enone in its ground, excited singlet, and reactive excited triplet states, E′ is the product of radiationless decay of the reactive triplet state, and *E–E* is a metastable intermediate.

$$E_0 \xrightarrow{h\nu} {}^1E^* \xrightarrow{100\%} {}^3E^* \tag{3}$$

$${}^3E^* \xrightarrow{k_i} E' \tag{4}$$

$${}^3E^* + E_0 \xrightarrow{k_a} {}^*E\text{–}E^* \tag{5}$$

$${}^*E\text{–}E^* \xrightarrow{k_{-a}} 2E_0 \tag{6}$$

$${}^*E\text{–}E^* \xrightarrow{k_c} \text{dimer} \tag{7}$$

Normal kinetic analysis yields expressions 8–11.

$$\tau^{-1} = k_i + k_a[E] \tag{8}$$

$$\Phi_{DIM} = \phi_{ISC}\phi_P k_a[E]\tau \tag{9}$$

$$\Phi_{DIM}^{-1} = \phi_{ISC}^{-1}\phi_P^{-1}(1 + k_i/k_a[E]) \tag{10}$$

$$\phi_P = \frac{k_c}{k_c + k_{-a}} \tag{11}$$

Figure 2 displays the data in Table I plotted according to eq 10. Unlike the results previously obtained in benzene,[6] these plots in acetonitrile are linear. This linearity is consistent with the constant HH/HT dimer ratios and indicates that k_a is a constant independent of enone concentration. Such behavior is possible only when the solvent is as polar as the enone. Similar behavior has been noted for isophorone in acetic acid.[7] If cycloaddition were a concerted or irreversible process, there would be no ϕ_P in eq 10 and the intercepts in Figure 2 would equal ϕ_{ISC}^{-1}, which for these two ketones is unity. The fact that the intercepts in Figure 2 are greater than unity is direct evidence that a major source of inefficiency in the photodimerization of these ketones does not involve the triplet state and in fact must arise after the triplet has reacted. Consequently, the primary reaction product of triplet enone with ground-state enone cannot be a stable dimer. A metastable dimeric species must intervene and it must be capable of decaying to two ground-state ketone molecules as well as proceeding on to stable ground-state dimer, as indicated by reactions 5–7. Similar conclusions have been reached for the cycloadditions of cyclopentenone to olefins[16] and of benzophenone to furan[17] as well as for the dimerization of pyrimidines.[18] The factor ϕ_P describes the percentage of these metastable adducts which do proceed on to stable products. The intercepts of Figure 2 yield ϕ_P values of 36% for cyclopentenone and 74% for cyclohexenone. The slopes yield k_i/k_a values of 0.06 and 2.7, respectively.

For isophorone in acetic acid, the intercept of a plot such as in Figure 2 is 3.[7] Although it has been suggested that $\phi_{ISC} = 0.33$,[7] it is more likely that $\phi_P = 0.33$ and $\phi_{ISC} = 1$. The slope yields a k_i/k_a value of 6, similar to that for cyclohexenone.

Rate Constants. Actual values for the primary triplet-state rate constants are determined by plotting the data in Table II according to eq 8, as in Figure 3. The slopes yield k_a values; k_i values are then calculated from the measured k_i/k_a values. This procedure for evaluating k_i should furnish more exact values than those of the intercepts in Figure 3. The actual values of the intercepts are within 50% of the calculated k_i

---

(16) P. de Mayo, A. A. Nicholson, and M. Tchir, *Can. J. Chem.*, **47**, 711 (1969).

(17) S. Toki and H. Sakurai, *Bull. Chem. Soc. Japan*, **40**, 2885 (1967).

(18) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **90**, 6530 (1968).

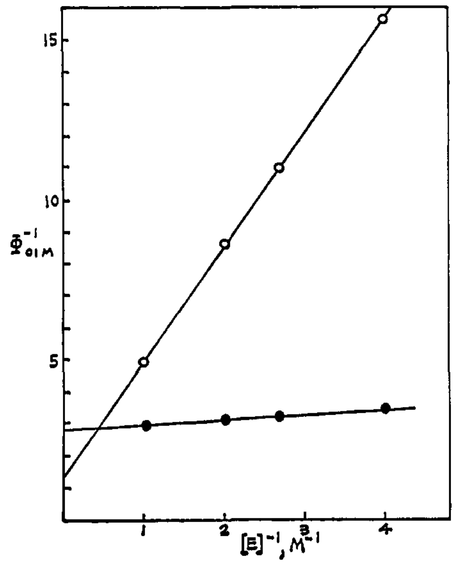


Figure 2. Variation in quantum yields for dimer formation in acetonitrile as a function of cycloalkenone concentration: cyclopentenone, ●; cyclohexenone, ○.

values. All the excited-state rate parameters are tabulated in Table III.

Table III. Kinetic Parameters for Photodimerizations in Acetonitrile

Quantity	Cyclopentenone	Cyclohexenone
k_i/k_a, M	0.06	2.7
k_a, M^{-1} sec^{-1}	6.6×10^8	1.1×10^8
k_i, sec^{-1}	0.4×10^8	3.0×10^8
ϕ_{ISC}	1.0	1.0
ϕ_P	0.36	0.74

A comparison of the triplet-state rate constants for the two ketones is revealing. The k_i/k_a ratio for cyclohexenone is 45 times larger than that of cyclopentenone. If a similar increase occurs upon proceeding up to cycloheptenone, it is not surprising that no dimerization takes place from the triplet,[11] since the rate constant for radiationless decay would be at least 100 times greater than that for addition.

The order of magnitude increase in k_i upon going from cyclopentenone to cyclohexenone plus the knowledge that the only significant triplet-state reaction of larger cyclic enones is decay to *trans* ground states[11] suggest very strongly that E′ is a species with considerable twisting about the double bond. The rate constant for formation of such a twisted species would be expected to increase with ring size, as k_i is observed to do.

In this regard, it is interesting to compare these k_i values to those reported for other enones. We have measured values near 2×10^5 sec^{-1} for the fairly rigid pyrimidine bases thymine and uracil.[18] Zimmerman and Lewin have just reported a k_i value near 10^9 sec^{-1} for 4,4-diaryl-2-cyclohexenones.[19] The fact that we find such a similar value for cyclohexenone itself verifies their conclusion that irreversible rearrangement barely competes with radiationless decay of the triplet. However, the maximum value of k_i for the hydrophenanthrone below is 4×10^7 sec^{-1}, since quenching studies reveal that value for $1/\tau$.[20] It might be expected that the fusion of the cyclohexenone to another ring would decrease its ability to twist. The even lower k_i value of 6×10^6 sec^{-1} reported for isophorone[7] is not so easy to rationalize.

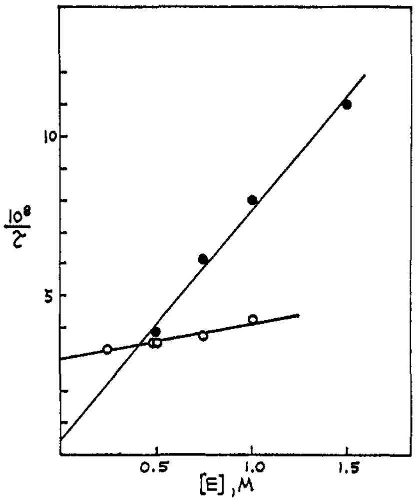
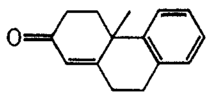
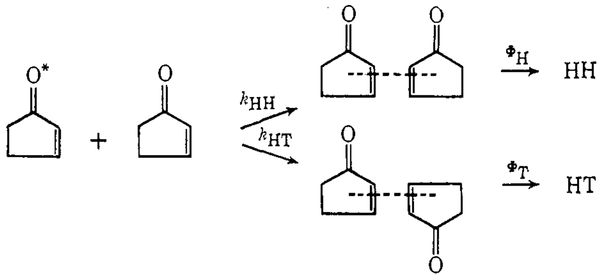


Figure 3. Variation in triplet lifetimes of enones in acetonitrile as a function of enone concentration: cyclopentenone, ●; cyclohexenone, ○.



Photodimerization is a special case of photoaddition to olefins, so that the k_a value for any ketone triplet must depend on the nature of the substrate olefin. The k_a value for cyclopentenone triplet adding to ground-state cyclopentene is larger[16] than that for its addition to cyclopentenone. The enone double bond is somewhat electron poor and consequently reacts less rapidly with the electrophilic[21] ketone triplet. The lower k_a value for triplet cyclohexenone reflects changes both in its reactivity and in that of the ground state. Knowledge of the relative reactivities of the two ketone triplets themselves awaits study of their cycloaddition to a common olefin.[9]

The intermediacy of metastable dimeric species prevents quantitative evaluation of solvent effects on the rate constants. The measured k_a equals the sum of two rate constants: one leading to head-to-head dimer and one leading to head-to-tail dimer. The problem is exemplified for cyclopentenone.



---

(19) H. E. Zimmerman and N. Lewin, *J. Am. Chem. Soc.*, **91**, 879 (1969).

(20) H. E. Zimmerman, *et al.*, *ibid.*, **88**, 1965 (1966).

(21) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

$$k_a = k_{HH} + k_{HT} \quad (12)$$

$$HH/HT = \frac{\phi_H k_{HH}}{\phi_T k_{HT}} \quad (13)$$

$$\phi_P k_a = \phi_H k_{HH} + \phi_T k_{HT} \quad (14)$$

$$\Phi_{DIM} = \Phi_{HH} + \Phi_{HT} = \phi_{ISC}(k_{HH}\phi_H + k_{HT}\phi_T)\tau[E] \quad (15)$$

We cannot assume that the intermediates leading to the two stable dimers do so with the same probability. The factor ϕ_P is only a weighted average as expressed by eq 14. Unfortunately, we are faced with the mathematically vexing problem of having four unknowns but only three independently measurable quantities.

Some general features can be discussed. A short extrapolation of our results to 3 M cyclopentenone indicates a $k_q\tau$ value of 5, the same as obtained in benzene by other workers.[4b,13] Likewise, $k_q\tau$ for piperylene quenching of 1 M cyclohexenone is 14 in acetonitrile and 13 in benzene.[6] For each ketone we would estimate that $1/\tau$ is twice as large in acetonitrile as in benzene, because k_q is estimated to be that much greater in acetonitrile.[15] That there is a polar solvent enhancement of k_a and that most of this enhancement involves k_{HH} are suggested by the following facts. The k_i value for cyclopentenone is the same in hexane[16] as in acetonitrile if the same value is assigned to k_q in the two solvents, which have identical viscosities at room temperature. The k_i/k_a value for dilute cyclohexenone in benzene is approximately 6,[6] twice as large as in acetonitrile. The difference indicates an increase in k_a in the more polar solvent, provided that k_i remains constant. The same twofold increase in k_a for both ketones is attended by unequal increases in the HH/HT dimer ratios. The HH/HT dimer ratio in very dilute benzene solutions is approximately 0.19 for both ketones and rises to 0.44 for 1 M cyclohexenone and 3 M cyclopentenone.[4b,6] Acetonitrile as solvent increases the ratio to 0.80 for cyclopentenone and to 2.0 for cyclohexenone. Unfortunately, it cannot be determined how much of the HH/HT increase involves k_{HH} and how much ϕ_H. Both parameters measure formation of the strong permanent dipole in the HH dimer; other workers have already pointed out that such a process should be aided by polar solvents.[6]

Since formation of the HT dimer does not involve much change in dipole moment, it is probably safe to assume that the corresponding kinetic parameters k_{HT} and ϕ_T are relatively immune to polar solvent effects. On the basis of that assumption, some limiting values can be determined. For cyclohexenone, $\phi_T k_{HT}$ equals 0.27 M^{-1} sec^{-1}; for cyclopentenone, $\phi_T k_{HT} = 1.25\ M^{-1}$ sec^{-1}. Table IV contains values of the various parameters under the two extreme conditions that $\phi_T = 1$ and that $\phi_H = 1$. The last row of entries for both ketones is included on the assumption that the minimum ϕ_T value in acetonitrile cannot be lower than the minimum value in benzene.

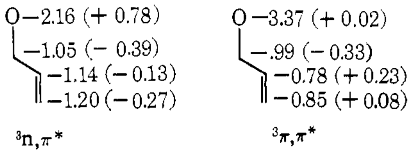
The Nature of $^3E^*$ and E'. Recent spectroscopic studies suggest that α,β-unsaturated ketones have very close-lying n,π^* and π,π^* triplet levels.[22-24] These findings verify the theoretical calculations of Zimmerman and coworkers.[25] The 0–0 phosphorescence bands occur near 74 kcal for a planar cyclopentenone[22] and a few kilocalories lower for several cyclohexenone systems of varying flexibility.[20,24] The long phosphorescence lifetimes of the steroidal enones indicate a π,π^* configuration for the lowest triplets.[24] It is to be expected that the nature of substituents[22,24] as well as the polarity of the solvent will determine the relative positions of the two triplets in much the same manner as for phenyl alkyl ketones.[26] Twisting about the double bond can presumably stabilize both triplets, although the 69-kcal emission from 4,4-diphenyl-2-cyclohexenone[25] suggests that the extent of twisting is not large.

Table IV. Possible Combinations of Kinetic Parameters for Dimerization

Ketone	Solvent	ϕ_T	ϕ_H	k_{HH}, 10^8 M^{-1} sec^{-1}	k_{HT}, 10^8 M^{-1} sec^{-1}
CH	Benzene	1	0.41	0.28	0.27[a]
	Benzene	0.63	1	0.12	0.43
	CH_3CN	1	0.65	0.83	0.27
	CH_3CN	0.50	1	0.55	0.55
	CH_3CN	0.63	0.83	0.66	0.44
CP	Benzene	1	0.27	2.05	1.25[a]
	Benzene	0.45	1	0.55	2.75
	CH_3CN	1	0.19	5.35	1.25
	CH_3CN	0.22	1	1.0	5.6
	CH_3CN	0.45	0.28	3.8	2.8

[a] Values in benzene calculated on assumption that $\phi_T k_{HT}$ is solvent independent; [CH] = 1 M, [CP] = 3 M.

Zimmerman's calculations of the π electron densities of triplet excited enones[25] are very revealing. These and the changes in electron density relative to that in the ground state for ^{3}n,π^* and $^3\pi,\pi^*$ states are depicted below. The carbon–carbon double bond of the n,π^* triplet is more electron rich *at both positions* than in the ground state. In contrast, the double bond of the π,π^* triplet, especially at the α position, is significantly electron deficient. Inasmuch as the cyclic enones are electrophilic in photocycloadditions,[9,21] it would appear that the $^3\pi,\pi^*$ states are responsible for addition reactions involving the double bond. This conclusion is consistent with the fact that the π,π^* triplets of the pyrimidine bases thymine and uracil[27] add to ground-state molecules very rapildy ($k_a \sim 10^9\ M^{-1}$ sec^{-1})[18] to yield cyclodimers. Moreover, the rate constants for interaction of known n,π^* ketone triplets with cycloalkenes to yield oxetanes are some two orders of magnitude lower than the k_a values for the enones.[28]



As noted in the Results section, for both ketones which we studied quenching plots are linear and HH/

---

[22] W. Herz and M. G. Nair, *J. Am. Chem. Soc.*, 89, 5475 (1967).

[23] D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, 49, 3316 (1968).

[24] G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, 51, 1890 (1968).

[25] H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Am. Chem. Soc.*, 89, 6589 (1967).

[26] (a) N. C. Yang and S. L. Murov, *J. Chem. Phys.*, 45, 4358 (1966); (b) A. A. Lamola, *ibid.*, 47, 4810 (1967); (c) D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, 88, 5087 (1966); (d) R. D. Rauh and P. A. Leermakers, *ibid.*, 90, 2246 (1968).

[27] A. A. Lamola, *Photochem. Photobiol.*, 7, 619 (1968).

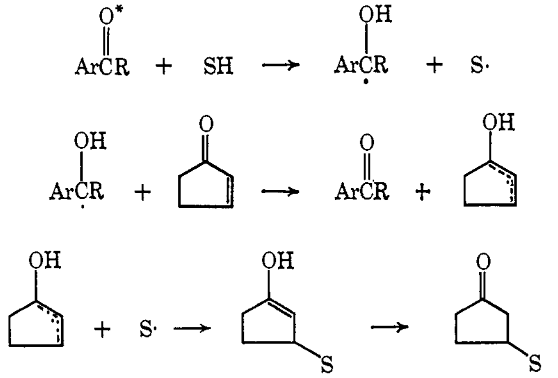
[28] I. Kochevar, unpublished results.

HT ratios are independent of the extent of quenching. Therefore for each ketone only one excited state is reactive in dimerization. If two states were involved, they would have to possess identical lifetimes and yield the same ratio of dimers. Such a coincidence for two separate ketones would be remarkable. It is conceivable that the excited state unreactive in dimerizations might react with a substrate more reactive than ground-state enone. For example, several cyclohexenones undergo photoaddition to 1,1-dimethoxyethylene to yield oxetanes as well as bicyclo[4.2.0]octanones, apparently from different triplets.[10] From the reported solvent effects,[10] namely that oxetane formation is favored by nonpolar solvents, it would appear that oxetane arises from an $^3n,\pi^*$ state while the *cis*-fused bicyclooctanones (analogous to the enone photodimers) arise from a $^3\pi,\pi^*$ state.

Our sensitization results indicate that the lifetimes of the triplet which dimerizes and of that which transfers energy to pentadiene are the same. This observation suggests that only one triplet is involved. If there is a triplet below the reactive triplet, it must have either the same lifetime as the upper triplet or such a short ($<10^{10}$ sec) lifetime that it cannot transfer energy to the diene. The first possibility would demand a remarkable coincidence for not just one but two ketones and thus seems very unlikely. There are only two reasons for invoking a low-energy triplet. First, the observation that benzophenone sensitizes photoreduction but not photodimerization of cyclopentenone[8] is consistent with there being a low-energy, nondimerizing, *long-lived* triplet—the presence of which, however, is inconsistent with our sensitization results. Second, the photostationary state of 58.5% *trans*-pentadiene indicates that energy is transferred to the *cis* isomer some 5% faster than to the *trans*-diene, as would be expected of a triplet with an E_T of 61–62 kcal. However, our inability to detect any dependence of the pss on diene concentration indicates that there is but one sensitizing triplet, which must also be the dimerizing triplet, which has an $E_T \geq 70$ kcal. The fact that the observed pss is measurably greater than the natural decay ratio of triplet pentadiene is probably another manifestation of the uncomfortable fact that exothermic triplet energy transfer, especially that involving the probably twisted triplets of enones,[13] is inefficient enough to be somewhat slower than diffusion controlled.[15]

All the evidence taken together suggests that the lowest triplet of the enones lies approximately 70 kcal above the ground state, is π,π^*, and is responsible for dimerization. It is probably twisted about the double bond, and the more readily it twists the faster it decays to a ground-state molecule. There must be an n,π^* triplet a few kilocalories higher in energy. In polar solvents, the energy separation between the two triplets is large enough that no reactions attributable to an n,π^* triplet occur. In hydrocarbon solvents, the energy separation is diminished and various reactions such as photoreduction[5,7] and oxetane formation[10] can compete with cycloadditions involving the C–C double bond.

Our conclusions require a modified explanation of the reported sensitization experiments with cyclopentenone.[5,8] Recent studies indicate that benzophenone sensitizes the photoreduction of camphorquinone both by triplet energy transfer and by hydrogen atom transfer.[29] Such a process could explain why the photoreduction of cyclopentenone is markedly more efficient upon sensitization than upon direct irradiation.[5,8] The queuching of benzophenone photoreduction[8] could also occur by this process. Even at 77°K, a 2-kcal *endothermic* energy transfer would be fast enough to quench benzophenone phosphorescence.


(16)
(17)
(18)

Nature of *E–E*. There are two distinct structural possibilities for the metastable intermediate: an excited-state charge-transfer complex and a biradical. The presence of a 1,4-biradical intermediate is consistent with most of the known behavior of systems undergoing photocycloaddition. In fact, the photoaddition of cyclohexenone to isobutylene,[21] the photorearrangement of citral,[30,31] and the photodimerization of 3-ethyl-2-cyclohexenone[3] all yield products with structures that could arise cleanly only from the intramolecular disproportionation of biradicals. The lack of stereospecificity in cycloadditions to olefins[9,21] is highly suggestive of a biradical intermediate. Finally, the kinetic fact that a good percentage of these intermediates dissociate back to two ground-state molecules would be an expected feature of a 1,4 biradical.

If the intermediacy of biradicals is reasonably clear, it is not so clear whether they are the primary photoproducts. Two kinds of evidence suggest the presence of some sort of charge-transfer complex. First, the k_a values for dimerization are some two orders of magnitude larger than those for oxetane formation by n,π^* ketone triplets[28] and those for cyclodimerization by olefin[28] and diene[32] π,π^* triplets. Second, the orientation of enone addition to olefins varies from being highly specific to almost nonspecific.[11] The major adduct usually corresponds to the more stable of the two biradicals which might arise from addition of the α position of the cycloalkenone to the olefin.[21] However, addition of the β position should yield an even more stable biradical in which one radical site is α to a carbonyl. This puzzling stereoselectivity led Corey to postulate that a charge-transfer π complex precedes the biradical and determines the orientation of addition.[21]

If formation of a charge-transfer complex is the primary reaction of excited enone with olefin, as is thought to be the case for most electrophilic additions to olefins, eq 9 and 13 would have to be revised with ϕ_H' and ϕ_T'

---

[29] B. M. Monroe and S. A. Weiner, *J. Am. Chem. Soc.*, **91**, 450 (1969).

[30] R. C. Cookson, J. Hudac, S. A. Knight, and B. Whitear, *Tetrahedron Letters*, 79 (1962).

[31] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 119 (1968).

[32] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

representing the probabilities that HH and HT would be formed from different biradicals, χ_H and χ_T equalling the probabilities that the charge-transfer complex would proceed on to different biradicals, and k_a referring to π-complex formation. The terms $\chi_H k_a$ and $\chi_T k_a$ would be kinetically equivalent to k_{HH} and k_{HT}. The factor χ, which represents the total probability that the complex

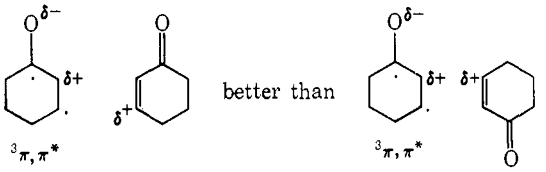
$$\Phi_{\mathrm{DIM}} = \phi_{\mathrm{ISC}}\chi\phi_{\mathrm{P}}'k_a\tau[\mathrm{E}] \qquad (19)$$

$$\mathrm{HH/HT} = \frac{\chi_H\phi_H'}{\chi_T\phi_T'} \qquad (20)$$

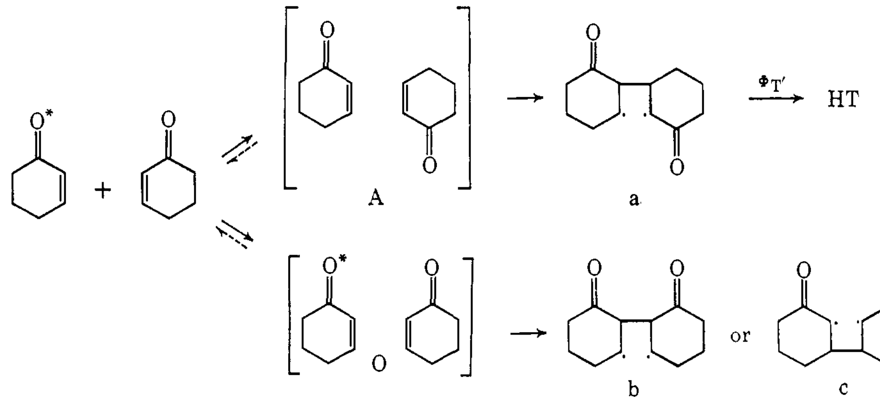
will collapse to biradicals, cannot be much smaller than unity, since the total ϕ_P for cyclohexenone is high.

We have differentiated between an excited-state charge-transfer complex and an excimer for two reasons. Triplet excimers seem to be rare.[33] Moreover, compounds such as acenaphthylene[34] and coumarin[35] seem to form exclusively *cis-syn*-fused dimers from singlet excimers. The triplet dimers from both these compounds and from the enones are fused primarily *anti*.

A charge-transfer complex is not a completely satisfying explanation of the stereochemistry of photocycloadditions. For example, Corey's model would predict that HH dimers should predominate in these photodimerizations.



Another factor which must influence the course of cycloaddition is the dipole moment of the collision complex which precedes chemical reaction. A head-to-tail alignment of excited enone and ground-state enone should be greatly favored over a head-to-head approach in nonpolar solvents, less so in polar solvents. Since the twofold increase in k_a in acetonitrile relative to benzene probably consists mostly of an increase in the process leading to HH dimer, that process must include formation of a sizeable dipole. Challand and de Mayo have offered a similar explanation for the large polar solvent effect on the direction of photocycloaddition of a substituted cyclopentenone to an unsymmetrical olefin.[36]



The following scheme incorporates the various intermediates which can lead to dimers. A and O are probably π complexes but may be simply collision complexes. In either case, the specific charge-transfer interactions suggested by Corey would favor O while dipole effects would favor A. In nonpolar solvents, biradicals b and c would probably rotate to conformations with lower dipole moments but which would have their radical sites too far apart for effective coupling. Polar solvents would help maintain the dipole moments in b and c and thus increase ϕ_H'.

Experimental Section

Chemicals. Acetonitrile was purified by a reported procedure[37] which lowers the uv cutoff to 200 nm. Cyclopentenone and cyclohexenone were prepared by Garbisch's prodedure[38] and after distillation were shown to be >99% pure by glpc analysis on several columns. The photodimers from the two ketones were prepared by preparative photolyses of the neat liquids. Addition of ether to the crude cyclopentenone photolysate caused the dimers to precipitate. Sublimation at 90° and 0.1 mm yielded white crystals, mp 115–118°, lit. 125–126°,[39] $\nu_{\mathrm{CO}}(\mathrm{CHCl_3})$ 1730 cm^{-1}, $\lambda_{\max}(\mathrm{CH_3CN})$ 298 nm (ϵ 59). Glpc analysis indicated a 95:5 HT/HH ratio. The cyclohexenone dimers were distilled on a short-path apparatus at 128–132° (0.4 mm). The resulting yellow oil was chromatographed on silica gel. The fractions eluted with methylene chloride were caused to crystallize by the addition of pentane containing a few per cent ethyl acetate at −78°. Recrystallization from hexane and sublimation at 50–60° (0.4 mm) gave a white solid, 85:15 HH/HT by glpc analysis, mp 40–45°, lit. 53–55° (pure HT),[6] $\nu_{\mathrm{CO}}(\mathrm{CHCl_3})$ 1700 cm^{-1}, $\lambda_{\max}(\mathrm{CH_3CN})$ 287 nm (ϵ 52). Eastman isophthalonitrile was used as received as the internal standard for cyclopentenone dimers. Eastmen ethyl stearate, recrystallized from carbon tetrachloride, was used as internal standard for cyclohexenone dimer analysis. *cis*-1,3-Pentadiene and 1,3-cyclohexadiene were obtained from Chemical Samples Co. and were distilled at atmospheric pressure before use. The former contained less than 0.1% *trans* by glpc analysis.

Apparatus. Glpc analysis of dimer formation was performed on a Varian Aerograph Model 1200 Hy-Fi III with a 6 ft × $^1/_8$ in. column packed with 5% QF-1 and 1% Carbowax 20M on 60–80 DMCS-treated Chromosorb G. Column temperature was 170 and 190°, respectively, for CP and CH systems. On-column injection was employed. Analysis of the *cis–trans* isomerization of 1,3-pentadiene was performed on an Aerograph Model 600 Hy-Fi with a 25 ft × $^1/_8$ in. column packed with 25% 1,2,3-tris(β-cyanoethoxy)propane on 60–80 Chromosorb P. Peaks and their areas were recorded on a L and N Model W recorder fitted with a disk integrator.

Irradiations were performed on a rotating turntable assembly contained in a constant-temperature bath held at 25.5°. The emission from a Hanovia 450-W medium-pressure mercury arc, positioned in the center of the turntable, was filtered by a Vycor sleeve

---

[33] A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, 49, 5066 (1968).

[34] D. O. Cowan and R. L. Drisko, *ibid.*, 89, 3068 (1967).

[35] H. Morrison, H. Curtis, and T. McDowell, *ibid.*, 88, 5415 (1966).

[36] B. D. Challand and P. de Mayo, *Chem. Commun.*, 982 (1968).

[37] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, 37, 1161 (1965).

[38] E. W. Garbisch, Jr., *J. Org. Chem.*, 30, 2109 (1965).

[39] P. E. Eaton, *J. Am. Chem. Soc.*, 84, 2344 (1962).

containing potassium chromate in aqueous potassium carbonate. This filter solution transmits radiation only from 3000–3250 Å and therefore isolates the 3130-Å mercury line.

Procedures. Dimerization quantum yields were determined by parallel irradiation of deaerated samples contained in sealed 13 × 100 Pyrex tubes. Dimer yields at various enone concentrations were determined by glpc analysis. They never exceeded 5% total conversion. The (area ratio)/(mole ratio) response of the FID detectors was calibrated with known mixtures of dimers and internal standards. It was assumed that the HH and HT dimers produce the same response.

Quantum yields for the sensitized isomerization of pentadiene were determined by parallel irradiation of deaerated samples containing 0.5 *M* ketone and various concentrations of *cis*-1,3-pentadiene. With acetophenone as sensitizer, $\Phi_{c \to t}$ equals 0.56;[12] this system was used as an actinometer. Conversions ranged from 3 to 15%. Quantum yields were corrected for back reaction by the following expression, where *F* is the per cent *trans*-diene

$$F_{\text{corr}} = 0.56 \ln\left(\frac{0.56}{0.56 - F_{\text{obsd}}}\right)$$

Quenching studies on the dimerizations were performed by parallel irradiation of deaerated samples containing given concentrations of enone and internal standard and varying concentrations of pentadiene or cyclohexadiene.

Photostationary states for pentadiene were determined by irradiation of two sets of solutions, one initially 60:40 and one 50:50, until no further change in the *trans*/*cis* ratio occurred when approached from either direction.

Acknowledgment. We are grateful for support of this work to the National Science Foundation and to Professor Paul de Mayo for several discussions.

Radiationless Processes in the Photochemistry of Stilbazoles and 1,2-Bispyridylethylenes[1]

David G. Whitten and M. T. McCall[2]

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received November 18, 1968*

Abstract: Reactions of excited states of several stilbazoles and 1,2-bispyridylethylenes have been studied. Quantum efficiencies of fluorescence, intersystem crossing, and internal conversion to the ground state have been determined. Rate constants for these processes were calculated by a comparison of the quantum yields, using the rate constants for fluorescence calculated from absorption spectra. Rate constants for intersystem crossing for several of the azastilbenes (assuming a triplet mechanism for the direct isomerization) are calculated to be quite high even though quantum efficiencies are low. Internal conversion from the excited singlet to the ground state not involving geometric change is shown to be an important process for 2-stilbazole and all of the bispyridylethylenes in contrast to the behavior of excited singlets of stilbene. In this respect the behavior of the azastilbenes resembles that of pyridine, the diazines and other N-heteroaromatics in which radiationless deactivation of the singlet state is the major process. Rates of the various deactivation processes depend on nitrogen location. Possible mechanisms for the enhanced internal conversion processes are discussed.

Phenomena regarding excited states of nitrogen heterocyclic compounds have received much attention. Interest in these compounds has been aroused in part by theoretical studies and in part by the presence of these structures in biologically important systems. The rich array of n–π^* and π–π^* states in these compounds should provide for a variety of interesting physcial and chemical conversion processes. While chemical reactions have been observed in a few nitrogen heterocyclics, a more frequently encountered phenomenon for simpler azines is a high rate and efficiency of radiationless deactivation. Until rather recently, there has been considerable confusion regarding the importance of fluorescence, intersystem crossing, and phosphorescence in several N-heterocyclics. Much of the uncertainty is due to the fact that characterization of excited states of these compounds has been chiefly spectroscopic. Emission spectra are usually weak and reliable quantum efficiencies are difficult to obtain. An interesting example concerns the diazines, which have been the subject of extensive investigation.[3] Based on theoretical considerations, El-Sayed[4] concluded that intersystem crossing between orbitally different states should proceed much more rapidly than transitions between states of the same type. Thus, fluorescence in the diazines, such as pyrazine, was at first believed to be weak due to efficient intersystem crossing.[4,5] Extensive investigations by Cohen and Goodman[6] using piperylene sensitization[7] method for determining intersystem crossing efficiencies indicate that most of the quanta delivered to the various diazines are degraded by radiationless decay of the singlet. Other studies[8] suggest that efficient internal conversion processes may deactivate singlets of other azines although theoretical considerations[9] predict little differences in rates of S_1–S_0 internal conversion for aromatics and N-heteroaromatics.

---

(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-171.

(2) National Aeronautics and Space Administration Predoctoral Fellow, 1966–present.

(3) For a review see K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectry.*, **22**, 125 (1967).

(4) M. A. El-Sayed, *J. Chem. Phys.*, 38, 2834 (1963); S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(5) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1959); L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

(6) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967), and references therein.

(7) A. A. Lamola and G. S. Hammond, *ibid.*, **43**, 2129 (1965).

(8) J. Lemaire, *J. Phys. Chem.*, 71, 612 (1967).

(9) J. P. Byrne, E. F. McCoy, and I. G. Ross, *Australian J. Chem.*, **18**, 1589 (1965).