

Table I

Cyclopentanone concn, <i>M</i> Solvent ^a	Neat	6.2				1.2				0.12			
		A	B	C	D	A	B	C	D	A	B	C	D
Dimer II/dimer I	1.1	2.0	1.6	1.4	1.9	4.3	2.2	1.7	1.9	6.4	2.1	4.3	1.9

^a A = cyclohexane, B = propanol, C = ethanol, D = methanol.

The quantum yield for photodecomposition of cyclopentenone is very small.^{2,3}

We shall now address our attention to the nature and multiplicity of the excited state. Turro⁶ suggests the possibility that *two* excited states, singlet and triplet, participate in the reaction. Thus the ratio of I to II might be expected to prove a function of the cyclopentenone concentration as singlet dimerization would become less competitive with triplet dimerization as the concentration decreased.

We have studied the ratio dimer II/dimer I as a function of concentration in cyclohexane, 2-propanol, ethanol, and methanol as solvents. The samples were irradiated for 3 hr at 3130 Å by a 450-w Hanovia mercury arc lamp. The reaction mixtures were analyzed by vpc, using a Carbowax 20M column (Table I).

That one of the dimers should be favored strongly suggests (but does not prove) a nonconcerted mechanism of some sort, though apparently not the one shown above.³ Furthermore, the concentration dependence of this effect in cyclohexane provides support to Turro's suggestion that both triplet and singlet states may be involved in the reaction. The apparent inertness of cyclohexane makes the results in that solvent the most relevant to this question. In the alcohols, dimer yield was markedly reduced as compared with cyclohexane solutions, and side reactions (including, perhaps, the triplet photoreduction of the enone) were decidedly enhanced.

Next, reactions identical with those in cyclohexane were carried out, except the solutions were made 0.1 *M* in the triplet quencher *cis*-piperylene (Table II). Absorption of 3130-Å light by the quencher was negligible.

Table II

Cyclopentenone concn, <i>M</i>	Neat	6.2	1.2	0.12
Factor of dimer yield suppressed	1.34	1.45	3.34	7.9

This provides excellent evidence that some and possibly all the dimerization is accounted for by a triplet-state intermediate.

Energy-transfer attempts were carried out using a variety of sensitizers. Cyclohexane solutions, 0.12 *M* in cyclopentenone and 0.1 *M* in sensitizer, were irradiated for 3 hr at 3130 Å. The dimer yield was then compared to that obtained without sensitizer (Table III). It would appear that the table establishes a minimum value on the triplet state of the enone.

Our efforts to establish the triplet sensitization of the photodimerization of cyclopentenone leave us less than fully satisfied that the reaction proceeds *via* a triplet-state mechanism, although Eaton's very recent demonstration of the piperylene quenching of the reaction with high concentrations of piperylene⁷

(6) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 203-204.

(7) P. E. Eaton, private communication.

Table III

Sensitizer	E_t , kcal/mole	% adsorption due to sensitizer	Effect on dimer yield
Acetophenone	73.6	52	None ^a
Benzophenone	69	80	Uncertain ^b
Naphthalene	61	<30	85% reduction
Nitrobenzene	60	>95	>95% reduction
2-Acetonaphthone	59	100	>90% reduction

^a That the quantum yield for dimerization is considerably less than unity was demonstrated by the fact that acetophenone drastically increased the yield of an unidentified by-product without affecting the yield of dimer. ^b Benzophenone appeared on the vpc at the same point as dimer II; however, dimer I was reduced by about 65%.

is most impressive. Our failure to demonstrate actual increase in dimer yield by sensitization (even though all "sensitization" experiments are somewhat ambiguous) is difficult to reconcile with a wholly triplet mechanism, provided the quantum yield for dimerization is substantially less than unity, as it almost certainly is.

In addition, *the very sensitive stereospecific dependence upon concentration (see Table I) suggests that more than one intermediate is involved in the dimerization; i.e., that the singlet state may be important at high concentrations of cyclopentenone.*

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The Lifetime of Triplet Acetone in Solution¹

Sir:

In 1958 Yang reported that irradiation of acetone in cyclohexane yields 50% isopropyl alcohol plus other reduction products.² Walling and Gibian have since shown that ketones are photoreduced in a variety of hydrocarbon as well as alcoholic solvents.³ Very recently Borkman and Kearns described the acetone-photosensitized isomerization of the 2-pentenes in solution.⁴ In interpreting their data, these authors concluded that triplet acetone has an unusually short intrinsic lifetime in solution, and that in neat acetone as solvent, triplet energy transfer may be faster than dif-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Research Corporation and NSF grants are also gratefully acknowledged.

(2) N. C. Yang and D.-H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(3) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(4) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

fusion controlled. These conclusions, if true, would be of considerable importance in our attempts to understand the behavior of excited states. However, they were apparently based on the assumption that photoreduction of acetone proceeds with negligible quantum efficiency. The data to be described do not support this assumption, and permit reasonable alternatives to Borkman and Kearns' conclusions.

Degassed hexane solutions containing 1.0 *M* acetone, 0.02 *M* benzene as internal standard, and various concentrations (0 to 0.0015 *M*) of 2,5-dimethyl-2,4-hexadiene were irradiated at room temperature at 3130 Å to less than 2% conversion. Relative quantum yields of 2-propanol formation were determined by glpc analysis. A Stern-Volmer plot of ϕ_0/ϕ values was linear with a slope, representing $k_q\tau_T$, of 9400 M^{-1} . With $1 \times 10^{10} M^{-1} \text{sec}^{-1}$ as the rate constant, k_q , for diffusion-controlled quenching in hexane,⁵ the lifetime of triplet acetone, τ_T , calculated from these experiments, is 0.94×10^{-6} sec, in excellent agreement with the values 1×10^{-6} sec determined by Borkman and Kearns⁴ and 0.8×10^{-6} sec measured by Wilkinson and Dubois⁶ in studies of the acetone-sensitized phosphorescence of biacetyl.

The lifetime of an excited state is, of course, the reciprocal of the sum of the rates of all processes, both physical and chemical, which destroy it, in this case hydrogen abstraction from solvent and radiationless decay

$$\tau_T = 1/(k_H[\text{SH}] + k_d)$$

The sensitization studies in the literature provide no means for apportioning the relative importance of the two processes. In order to actually measure the quantum yield of photoreduction, degassed hexane solutions 0.24 *M* in acetone and 0.08 *M* in fluorobenzene were irradiated at 3130 Å in parallel with degassed hexane solutions 0.20 *M* in 2-hexanone and 0.20 *M* in chlorobenzene. Relative quantum yields of disappearance of the two ketones and of appearance of 2-propanol were again determined by glpc analysis. Assuming a quantum yield of 0.50 for photolysis of 2-hexanone in solution,^{7,8} the quantum yields for acetone disappearance and 2-propanol appearance were found to be 0.80 and 0.42, respectively. Several long retention time peaks on the glpc traces of the acetone-hexane system revealed the expected² formation of pinacol and various hexyldimethylcarbinols and bihexyls.

The important point of the present experiments is that 80% of the decay of triplet acetone in hexane occurs by hydrogen abstraction from the solvent, yielding estimates of 8×10^5 and $2 \times 10^6 \text{sec}^{-1}$ for $k_H[\text{SH}]$ and k_d , respectively.

Borkman and Kearns⁴ found that $k_q\tau_T$ for the acetone-2-pentene system is approximately 10 M^{-1} in hexane, heptane, 3-methylpentane, and methanol, but five times larger in concentrated acetone. Moreover, they found no difference for acetone-*d*₆. We

thus have to explain the constancy of τ_T ⁹ for the first four solvents and the increase in $k_q\tau_T$ in acetone.

From Walling and Gibian's data,⁸ it is possible to state that triplet acetone would abstract hydrogen from the three hydrocarbons at virtually indistinguishable rates. The exact reactivity of methanol has not been ascertained, but, by analogy with the behavior of alkoxy radicals, its reactivity is probably on the same order as that of the three alkanes. However, because of its electron-withdrawing carbonyl group, acetone is a very poor hydrogen donor toward electrophilic species such as ketone triplets.⁸ Therefore, probably the entire increase in $k_q\tau_T$ in pure acetone can be attributed to the greater triplet lifetime in this unreactive solvent and not to an enhanced value of k_q such as Borkman and Kearns⁴ suggested.

The value of $2 \times 10^6 \text{sec}^{-1}$ for the rate of radiationless decay of triplet acetone in solution is very similar to the values found for triplet benzophenone in benzene¹⁰ and triplet acetophenone in isopropyl alcohol.¹¹ Borkman and Kearns⁴ presented a very good discussion as to why this value is probably intrinsic and not due to impurity quenching. Their conclusion that acetone-*d*₆ has the same triplet lifetime is readily understood, since most of its decay occurs by chemical reaction. Any change in the rate of the minor radiationless decay process could have been lost in experimental error. More likely, the rapid rate of radiationless decay of excited triplet species at room temperature in solution involves vibrational coupling with solvent C-H bonds and not with those of the excited species.

(9) The viscosities of these solvents are all similar; hence k_q would be expected to have an almost identical value in each.

(10) J. A. Bell and J. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(11) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

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Concerning the Isomerization of Δ^1 - to $\Delta^{1(6)}$ -Tetrahydrocannabinol¹

Sir:

The acid-catalyzed isomerization of Δ^1 -3,4-*trans*-tetrahydrocannabinol (Δ^1 -3,4-*trans*-THC) (Ia),² the major psychotomimetic principle in hashish, to $\Delta^{1(6)}$ -3,4-*trans*-THC (IIa)³ is well documented.^{3c,e} In a recent communication Taylor, *et al.*,^{3d} have reported the synthesis of *dl*- Δ^1 -3,4-*cis*-THC (IIIa) and have claimed that this compound is similarly isomerized to *dl*- $\Delta^{1(6)}$ -3,4-*cis*-THC (IVa). We wish to point out that the compound described as IVa possesses in fact structure V, for which we suggest the name $\Delta^{4(8)}$ -iso-THC.⁴

(1) Hashish. IX. For part VIII see Y. Gaoni and R. Mechoulam, *Chem. Commun.*, 20 (1966).

(2) (a) Y. Gaoni and R. Mechoulam, *J. Am. Chem. Soc.*, **86**, 1646 (1964); (b) R. Mechoulam and Y. Gaoni, *ibid.*, **87**, 3273 (1965); (c) K. E. Fahrenholtz, M. Lurie, and R. W. Kierstead, *ibid.*, **88**, 2079 (1966).

(3) (a) R. Adams, C. K. Cain, W. D. McPhee, and R. B. Wearn, *ibid.*, **63**, 2209 (1941); (b) H. Budzikiewicz, R. T. Alpin, D. A. Lightner, C. Djerassi, R. Mechoulam, and Y. Gaoni, *Tetrahedron*, **21**, 1881 (1965); (c) Y. Gaoni and R. Mechoulam, *ibid.*, **22**, 1481 (1966); (d) E. C. Taylor, K. Lenard, and Y. Shvo, *J. Am. Chem. Soc.*, **88**, 367 (1966); (e) R. Hively, W. A. Mosher, and F. Hoffmann, *ibid.*, **88**, 1832 (1966).

(4) Taylor, *et al.*,^{3d} report that IVa (now shown to be V) has been prepared also by Hively, Hoffmann, and Mosher *via* an as yet unpublished

(5) A manuscript describing the effect of solvents on quenching rates is in preparation.

(6) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 398.

(8) 2-Hexanone was employed as an actinometer rather than more conventional systems because its absorption spectrum is so similar to that of acetone.