we use two miscible solvents as a mixing solvent, Θ_{12}/T is smaller than 4. Again, we find the Shultz–Flory model to predict that the Θ temperature of the solvent mixture is more than the simple average of the individual solvents. This is not the case in our coating–sea model, as may be seen from eq 35. We can attribute this unexpected result for Θ in the Shultz–Flory model to an entropy effect. Actually, the volume of the polymer region is rather strongly affected by the change of conformational expansion of the polymer molecule, and the number of solvent molecules trapped in this volume is approximately proportional to this volume, though the change of interaction energy between polymer segments and solvent molecules is probably small. This means a greater expansion of the polymer molecule causes a greater trapping of solvent molecules and a greater decrease of entropy with a slight decrease of the enthalpy. The enthalpy decrease accordingly increases the free energy of mixing and has a tendency to shrink the polymer molecule. This increases Θ and decreases solvent ability. The apparent failure of the Shultz–Flory model is due to the overpowering influence of the entropy factor.

This situation is contrary to the case of a polyelectrolyte molecule in an electrolyte solution. In such a system, the strong gathering of the counterions into the polymer region occurs because of the Coulombic attraction between them, and this effect always results in greater expansion of the polyelectrolyte molecule. This tendency is partly due to the neutralization of the repulsive force between ionic groups of the polymer molecule, but it has been pointed out that the entropy effect plays an important role.[4] That is, owing to the electroneutral condition, the number of gathering counterions is nearly constant and independent of the degree of expansion of the polymer molecule; we can then consider the boundary of the polymer molecule as a semipermeable membrane, and the *osomotic* pressure of the counterions gives rise to the expansion of the polymer region. In our case, however, the number of gathered solvent molecules is not kept constant, and the entropy effect acts in the opposite direction.

On the other hand, in the coating–sea model, the volume of the coating available to the solvent molecules is not as strongly affected by the degree of expansion of the polymer molecule, and the enthalpy effect exceeds the opposite entropy effect and tends to increase the expansion of the molecule. Furthermore, even for cases where Θ_1 and Θ_2 are positive, that is, two solvents which are both poor for the polymer, if these solvents also have a poor compatibility with each other and Θ_{12} is a large (but $\Theta_{12}/T < 4$) positive value, the apparent value may become negative, and the mixed solvent behaves as a good solvent. In such a case, the molecules of the better (but still poor) solvent have a tendency to gather around the polymer molecule, cutting off the less compatible solvent 1–solvent 2 pairs, and this resembles the gathering effect of a good solvent.

Generally speaking, the Shultz–Flory model emphasized the effect of a mean potential in the polymer region, although this is not considered explicitly in the theory. On the other hand, the coating–sea model is based completely on the short-range force acting between nearest-neighbor lattice sites. In an actual system, there may be both of these effects, the results of these effects may cancel out, and the simple average of the solvent power of individual solvents may indeed give a good approximation of the solvent power of a mixed solvent.

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Photochemistry of Ketone Polymers. V. Photochemistry of the Linear 2-Alkanones in Solution

F. J. Golemba and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada.

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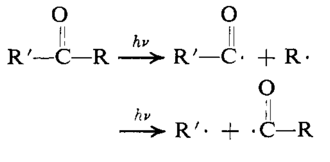
ABSTRACT: Studies have been made of the liquid phase photolysis (at 313 nm) of the linear 2-alkanones ranging from C_6 (2-hexanone) to C_{19} (2-nonadecanone) to determine the effect of chain length on the quantum yields of photolysis products. The major photolytic products are those expected from the Norrish types I and II primary reactions, but for all ketones studied the yields of type I products were less than 10% of the type II products at all temperatures up to 120°. The type II quantum yields are independent of both temperature and solvent viscosity, but the type I yields increase with temperature and decrease with solvent viscosity below 68°. The type I yields decrease with increasing chain length, but type II are only slightly dependent on chain length. Quenching studies indicate that the partition of chemical reaction (type II) between singlet and triplet is independent of chain length. These results confirm that there is a chain-length dependence of total photochemical product yields for linear alkanones in solution.

The photochemistry of aliphatic ketones has been the object of extensive study over the years, and considerable progress has been made in the elucidation of the various photophysical and photochemical pathways by which these compounds dissipate their excitation energy.[1]

The three main photochemical reactions of aliphatic ketones which possess a hydrogen on the carbon γ to the carbonyl are as follows.

(1) The Norrish type I reaction results in the formation of two free radicals through cleavage of the bond between the carbonyl and the α carbon (eq 1); at elevated temperatures the acyl radical can decarbonylate with the forma-



$$R'\!-\!\overset{O}{\overset{\|}{C}}\!-\!R \xrightarrow{h\nu} R'\!-\!\overset{O}{\overset{\|}{C}}\cdot + R\cdot \qquad (1)$$
$$\xrightarrow{h\nu} R'\cdot + \cdot\overset{O}{\overset{\|}{C}}\!-\!R$$

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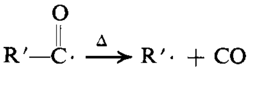
(1) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

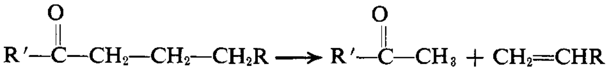
TABLE I
PHOTOLYSIS OF 2-UNDECANONE IN DODECANE

Quantum Yield of Nonane ϕ_{nonane}	Temp, °C
0.00036	24
0.00033	25
0.0019	69
0.0074	99
0.012	117.5
0.012	119
0.012	121

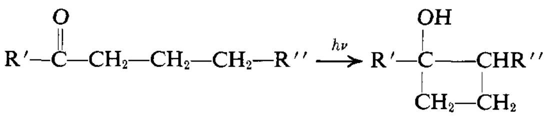
tion of carbon monoxide, for example, eq 2. (2) The Norrish


$$R'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\cdot \xrightarrow{\Delta} R'\cdot + CO \qquad (2)$$

type II reaction, for linear ketones, results in the formation of a methyl ketone and an olefin (eq 3). The existing evi-


$$R'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}CH_2\text{—}CH_2R \longrightarrow R'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3 + CH_2{=}CHR \qquad (3)$$

dence suggests that the hydrogen atom on the γ carbon is transferred to the oxygen of the excited carbonyl through a six-membered-ring intermediate.[2] Elimination then results in the intermediate formation of the enol form of the methyl ketone.[3] The H-atom transfer and elimination may occur in a concerted single step or alternatively in a stepwise process. It has been shown that both excited singlet and triplet states can react by the type II process.[4] (3) A photocyclization reaction results in the formation of a cyclobutanol[5] (eq 4).


$$R'\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}R'' \xrightarrow{h\nu} \begin{array}{ccc} & OH & \\ & | & \\ R'\text{—} & C & \text{—}CHR'' \\ & | & | \\ & CH_2 & \text{—}CH_2 \end{array} \qquad (4)$$

This process has been studied for a few systems and for the methyl ketones, at least, appears to occur primarily from the excited triplet state.[6]

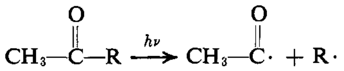
Little attention has been given to the determination of type I quantum yields of linear alkanones in solution or to a study of the effects of chain length on the type I and type II quantum yields. A notable exception is the work of Hartley and Guillet,[7] who studied the types I and II quantum yields of a number of linear symmetric alkyl ketones of varying chain length. They showed that the quantum yields of these reactions could be used to predict qualitatively the photochemistry of poly(ethylene-*co*-carbon monoxide), essentially a polyketone in which the carbonyl groups are separated by long aliphatic chains.[8] Such studies are of interest to the polymer photochemist since they yield information about the effect of polymeric environment on the primary photochemical reactions of ketones, which in turn can lead to information concerning the mechanism of these reactions.

In this work, the type I and type II quantum yields of a number of linear methyl alkyl ketones have been determined with a view to elucidating the effects of chain length, temperature, and solvent viscosity on the types I and II quantum yields of these ketones.

Results and Discussion

The ketones which were studied were all linear aliphatic 2-alkanones whose structures are represented by CH_3COR. These ketones ranged in size from 2-hexanone to 2-nonadecanone. Thus all of the ketones possess a secondary hydrogen on the carbon γ to the carbonyl.

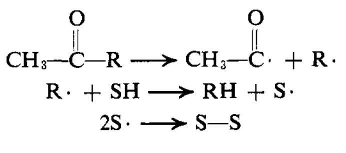
The Norrish Type I Reaction. Absorption of ultraviolet light by the methyl ketones leads primarily to the formation of acetyl and alkyl radicals


$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R \xrightarrow{h\nu} CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\cdot + R\cdot$$

Evidence for this has been presented by other authors on two systems. (1) In the gas-phase irradiation of methyl ethyl ketone with light of wavelength 313 nm, the primary cleavage to form ethyl radicals outweighs the formation of methyl radicals by 40:1.[9] (2) In the irradiation of pure 2-pentanone at 0° with light of wavelength 313 nm, propane and biacetyl account for over 90% of the products attributable to the type I reaction.[4e]

(1) The Dependence of the Type I Quantum Yield on Temperature. The effect of temperature on the quantum yield of alkane was investigated for 2-undecanone. Nonane is the alkane formed from the type I break followed by hydrogen abstraction. Table I shows the quantum yield of nonane for the photolysis of 2-undecanone in dodecane. It can be seen that this yield is strongly temperature dependent. If an apparent activation energy, E, for nonane formation is defined by: $\phi = \phi_0 e^{-E/RT}$, where T is in degrees absolute, then a plot of log ϕ *vs.* reciprocal temperature yields a value of E equal to 8.5 kcal/mol.

In a separate experiment, the quantum yields of methane and carbon monoxide were measured for the photolysis of 2-undecanone in dodecane at 120°. The apparatus and method of analysis have previously been described by Hartley and Guillet,[7] and the quantum yields were $\phi_{CO} = \phi_{CH_4} = 0.014$. The agreement among the yields for CO, CH_4, and nonane was good and suggested that the nonyl radical primarily reacted to abstract hydrogen from the solvent or ketone rather than terminate by addition to nonyl, methyl, or solvent radicals, *e.g.*


$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R \longrightarrow CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\cdot + R\cdot$$
$$R\cdot + SH \longrightarrow RH + S\cdot$$
$$2S\cdot \longrightarrow S\text{—}S$$

where SH represents solvent (dodecane). Thus for the methyl ketones in solution it appears that ϕ_{alkane} is representative of the number of effective bond breaks.

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(2) (a) W. Davis, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **69**, 2153 (1947); (b) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

(3) (a) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **86**, 3602 (1964); (b) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(4) (a) V. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim. Fr.*, 121 (1958); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 2475 (1962); (c) J. L. Michael and W. A. Noyes, Jr., *ibid.*, **84**, 2475 (1962); (d) R. Borokowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961); (e) P. Ausloos and R. E. Rebbert, *J. Amer. Chem. Soc.*, **83**, 4897 (1961); (f) R. E. Rebbert and P. Ausloos, *ibid.*, **86**, 4803 (1961); (g) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); (h) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966); (i) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

(5) N. C. Yang and D. D. H. Yang, *ibid.*, **80**, 2913 (1958).

(6) (a) D. R. Coulson, and N. C. Yang, *ibid.*, **88**, 4511 (1966); (b) J. A. Baltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

(7) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 413 (1968).

(8) G. H. Hartley and J. E. Guillet, *ibid.*, **1**, 165 (1968).

(9) J. N. Pitts, Jr., and F. E. Blacet, *J. Amer. Chem. Soc.*, **72**, 2810 (1950).

TABLE II
PHOTOLYSIS OF 2-UNDECANONE IN SOLVENTS OF DIFFERENT VISCOSITY

Solvent	Temp, °C	Viscosity, cP	ϕ_{nonane}
Hexane	25	0.29	0.0006
Dodecane	25	1.35	0.00035
Hexane	57	0.22	0.0023
Dodecane	57	0.76	0.0014
Dodecane	121	0.40	0.012
Decalin	121	0.62	0.013
Mineral oil	123	2.1	0.011

(2) The Dependence of the Type I Quantum Yield on Viscosity. The yields of nonane formed in the photolysis of 2-undecanone in solvents of varying viscosity and at different temperatures are shown in Table II. At the lower temperatures the quantum yield decreased with increasing solvent viscosity. This decrease would be expected if a "cage" mechanism was involved in solution. At 120° solvent viscosity had no effect on the quantum yield.

Conceivably, at 120°, rapid evolution of carbon monoxide could hamper cage recombination. This idea is supported by the fact that, for the irradiation of 2-undecanone at 120°, the methyl and nonyl radicals formed reacted mainly by abstracting hydrogens from the surrounding medium rather than by combining to form decane.

(3) The Dependence of the Type I Quantum Yield on Chain Length. The quantum yield of alkane was determined for a number of methyl ketones at various temperatures. The yields are shown in Table III. The photolysis of 2-heptanone and 2-nonanone were carried out in decane solution, while the others were photolyzed in dodecane. The results are probably accurate to ±10% based on reproducibility of measurement and confidence in the actinometry (2-nonadecanone ±20%).

From the results in Table III, it can be seen that the type I quantum yield decreases with increasing chain length. These results suggest that radiationless deactivation processes become more efficient as the chain length increases or that cage recombination of radicals formed in the primary cleavage is facilitated as the chain length of the alkyl radical increases. However, for reasons discussed earlier, we believe that at the higher temperatures cage recombination would not be frequent enough to cause the observed decrease.

Thus, the effects of temperature, viscosity, and increasing chain length on the type I quantum yields appear to be similar to those of the linear symmetrical aliphatic ketones determined by Hartley and Guillet.[7]

The Norrish Type II Reaction. The methyl ketones studied undergo the Norrish type II reaction to produce acetone and an olefin.

TABLE III
PHOTOLYSIS OF THE METHYL KETONES

Ketone	ϕ_{alkane} 25°	70°	100°	120°
2-Heptanone		0.0060	0.015	
2-Octanone				0.018
2-Nonanone		0.0046	0.011	
2-Undecanone	0.00033	0.0019	0.0074	0.012
2-Nonadecanone		~0.002		

TABLE IV
TYPE II QUANTUM YIELDS

Ketone chain length	Concn, M	Temp, °C	ϕ_{II}	Solvent	Conversion, %
6	0.2	35	0.250	Dodecane	2
8	0.2	35	0.191	Dodecane	2
8	0.1	36	0.203	Dodecane	3.5
8	0.2	120	0.195	Dodecane	2
9	0.2	120	0.218	Dodecane	3
11	0.2	35	0.197	Dodecane	2
11	0.2	35	0.196	Dodecane	2
11	0.2	121	0.189	Decalin	3
19	0.5	43	0.154	Dodecane	2

TABLE V
TYPE II QUANTUM YIELDS

Ketone chain length[a]	Temp, °C	ϕ_{II}	Solvent	Conversion, %
7	26	0.19	Decane	3
7	69	0.20	Decane	4
7	99	0.20	Decane	4
9	26	0.19	Decane	6
9	27.5	0.20	Decane	6
9	70	0.19	Decane	5
9	100	0.23	Decane	8
9	100	0.19	Decane	4
11	26	0.21	Hexane	3
11	40	0.18	Hexane	2.5
11	57	0.20	Hexane	2.5
19	69	0.15	Dodecane	2

[a] Concentration 0.1 to 0.2 M.

The type II quantum yields for the ketones are shown in Tables IV and V. In earlier experiments the quantum yields of acetone and olefin were shown to be equal. Except in the case of 2-hexanone, values of ϕ_{II} shown were calculated from the quantum yield of olefin since the quantum yield of acetone was less precise, especially for photolyses carried out at higher temperatures.

(1) Dependence of the Type II Quantum Yield on Temperature and Viscosity. The quantum yield of the type II reaction of the methyl ketones of chain length (number of carbon atoms) 7, 8, 9, and 11 appears to be independent of temperature. This insensitivity of the quantum yield to temperature is typical of a number of aliphatic ketones which possess only one type of γ hydrogen.[10] For the symmetrical ketones, it has been shown that there is a small temperature dependence ($E \simeq$ 1 kcal/mol) of ϕ_{II}.

The type II quantum yield of 2-undecanone showed no viscosity dependence at any temperature. This result would be expected for this reaction. The constancy of ϕ_{II} of 2-undecanone in a number of solvents suggests that quenching impurities were absent in these solvents.[7]

The results in Table IV were determined using uranyl oxalate actinometry. The precision is ±3% based on gas chromatographic measurements and the accuracy is ±5%. The results in Table V were calculated using the photolysis of 2-undecanone in dodecane as actinometer with a value of $\phi_{\text{II}} = 0.20$. The yields are accurate to ±10%.

(2) Dependence of the Type II Quantum Yield on Chain Length. The type II quantum yields for various methyl ke-

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(10) C. H. Nicol and J. G. Calvert, *J. Amer. Chem. Soc.*, **89**, 1790 (1967).

TABLE VI
TYPE II QUANTUM YIELD FOR THE METHYL KETONES

Total chain length	6	7	8	9	11	19
ϕ_{II}	0.25	0.20	0.20	0.20	0.20	0.15

TABLE VII
ϕ_{II} AS A FUNCTION OF CHAIN LENGTH FOR KETONES

R (carbon atoms)	CH_3COR	$RCOR^a$	$C_6H_5COR^b$
4	0.25	0.11	0.31
5	0.20		0.31
6	0.20	0.092	0.25
7	0.20	0.080	0.30
8			0.29
9	0.20		
11		0.072	R = 8–13
17	0.15		0.31 ± 0.02
21		0.059	

[a] References 7 and 11; 70° in paraffin oil solution. [b] Reference 12; ambient temperature in benzene or hexane solution.

TABLE VIII
QUENCHING BY COD

Ketone	Concn, M	[COD], M	Temp, °C	ϕ_{II}
2-Hexanone	0.9		24	0.238
	0.9	2.5	24	0.084
2-Octanone	1.0		23	0.181
	0.8	2.5	24	0.070
	Neat		25	0.181
	Neat	2.6	24	0.064
2-Nonadecanone	0.5		43	0.154
	0.4	2.5	40	0.056
	0.5	4.6	40	0.055

TABLE IX
SINGLET AND TRIPLET TYPE II QUANTUM YIELDS

Ketone	Concn, M	ϕ_{II}	ϕ_{II}^S	ϕ_{II}^T	ϕ_{II}^T/ϕ_{II}
2-Hexanone	0.9	0.238	0.084	0.154	0.65
2-Octanone	0.8	0.181	0.070	0.111	0.61
2-Octanone	Neat	0.181	0.064	0.117	0.65
2-Nonadecanone	0.4	0.154	0.056	0.098	0.64

tones are shown in Table VI. The values are composites from Tables IV and V and are accurate to within ±10%.

Increasing chain length has a small but noticeable effect on the type II quantum yield of these ketones. This trend can be compared with data obtained by other workers for the symmetrical ketones[7,11] and the phenyl alkyl ketones.[12] As chain length increases, ϕ_{II} decreases smoothly for the symmetrical ketones, while ϕ_{II} of the phenyl ketones remains relatively constant (Table VII).

The type II reaction has been shown to occur from both the excited singlet and triplet states of 2-hexanone and 2-octanone. We have investigated the participation of the singlet and triplet excited states of 2-hexanone, 2-octanone, and 2-undecanone to determine if increasing chain length favors the participation of either state in the reaction. Table VIII shows the results of the study using *cis*-1,3-cyclooctadiene (COD) as quencher.

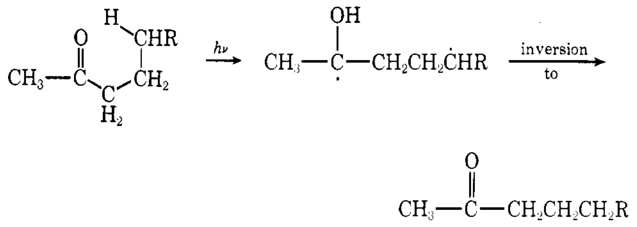
That 2.5 M COD was sufficient to quench virtually all of the triplet reaction can be seen from the results for 2-nonadecanone, when ϕ_{II} was not changed when the concentration of COD was increased from 2.5 to 4.6 M. The values of ϕ_{II} obtained in the presence of 2.5 M COD represent the type II quantum yield from the singlet state (ϕ_{II}^S) and ϕ_{II}^T was taken to be $\phi_{II} - \phi_{II}^S$. The results are shown in Table IX.

As the chain length increases from 2-hexanone to 2-nonadecanone the decrease in the type II quantum yield occurs at the expense of both the singlet and triplet states, so that the ratio of singlet to triplet reaction remains constant for the ketones listed in Table IX.

When one combines the above facts with the fact that the quantum yield of cyclobutanol formation[13] appears to decrease with increasing chain length of the methyl ketones, it becomes apparent that the total photochemical quantum yield of the methyl ketones decreases with increasing chain length. This would confirm that radiationless deactivation processes are increasing in importance as the chain length increases.

The decrease in quantum yield of cyclobutanol formation has been estimated by combining results obtained by other workers.[4i,5,6]

To date, the experimental evidence suggests that the inefficiency of the methyl as well as certain other ketones toward chemical reaction is due to the reversal of a biradical intermediate[14] with the resultant formation of ground-state ketone, *e.g.*



Although these results do not provide evidence for or against the intermediacy of a biradical species, they do suggest that any mechanism which includes the biradical must also explain the decrease in efficiency of such an intermediate for elimination as the chain length of the ketone increases.

The quenching results for 2-octanone presented in Tables VIII and IX indicate that the type II quantum yield and the relative participation of the singlet and triplet excited states in the type II reaction were the same for the neat and dilute ketone.

It has been stated[15] that in the pure ketone the triplet quantum yield would be enhanced by a polar effect similar to that caused by alcohols. This enhancement would increase the total type II quantum yield of the ketone.

Tables X and XI show the results obtained for the photolyses of 2-undecanone and 2-octanone at various concentrations. The results may also be compared with a value of ϕ_{II} of

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(11) G. H. Hartley, Ph.D. Thesis, University of Toronto, 1968.

(12) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Amer. Chem. Soc.*, **90**, 5900 (1968).

(13) J. E. Guillet, J. Dhanraj, F. J. Golemba, and G. H. Hartley, *Advan. Chem. Ser.*, No. **85**, 272 (1968).

(14) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

(15) See P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 98 (1968).

0.20 ± 0.01 determined for degassed solutions 0.2 *M* in 2-undecanone photolyzed in hexane, dodecane, mineral oil, and decalin at temperatures over the range 20–120°.

The results in Tables X and XI show that the type II quantum yields of these two ketones are not dependent on ketone concentration over the concentration range studied. Also, for both ketones, neat or in solution, the presence of air did not affect the quantum yield, presumably due to the low concentration of oxygen in solution and the short lifetimes of the ketone excited states.

Only one value was obtained for the quantum yield of a cyclic product. In the photolyses of 2-nonanone, the quantum yield of formation of a product which was identified as the cyclobutanol from its retention volume was 0.02. By comparison with the value reported for 2-hexanone of 0.075,[6a] it can be surmised that ϕ_{cyclic} decreases with chain length.

These results would predict a decrease in overall photochemical quantum yields for chromophores located in high polymers; this has indeed been shown for copolymers of ethylene and carbon monoxide[8] and poly(methyl vinyl ketone).[16] The apparent insensitivity of ϕ_{II} for phenyl alkyl ketones to chain length suggests that high polymers containing C_6H_5CO as chromophores would have high quantum yields for scissioning. This is indeed true, and copolymers of phenyl vinyl ketone and stryene exhibit a chain-scissioning quantum yield of $\sim$0.2.[17]

Wagner has suggested a mechanism for the radiationless deactivation of excited states of ketones involving the formation of a biradical intermediate which may revert to starting ketone or give products.[14] Recently Yang and Elliot have provided quite convincing experimental evidence for the biradical.[18] We suggest that, for the methyl and symmetrical ketones, as the chain length increases biradical reversal becomes increasingly more efficient than elimination. The explanation may lie in the case of rotation near the carbonyl chromophore. The probability of biradical reversal can be thought to depend on the maintenance of the six-membered ring in existence after γ-hydrogen abstraction. As the chain length increases, ease of rotation near the chromophore will decrease. This decrease should be more pronounced in the case of symmetrical ketones than for the methyl or phenyl ketones and suggests a reason for the more pronounced decrease in ϕ_{II} with chain length for these symmetrical ketones.

The experimental results presented in this paper are summarized below. (1) The type I quantum yield of the methyl ketones increases with increasing temperature and decreases with increasing chain length of the methyl ketone. (2) For the ketones studied at temperatures up to 120°, the type I quantum yields were less than 10% of the respective type II quantum yields. (3) At temperatures below 60°, the type I quantum yield is reduced in solvents of high viscosity; this is consistent with a mechanism involving "cage recombination" of radical fragments. (4) The type II quantum yield is independent of both temperature and solvent viscosity. (5) Quenching studies indicate that the participation of singlet and triplet states in the type II reaction is independent of chain length and both $\phi_{II}{}^{S}$ and $\phi_{II}{}^{T}$ decrease slightly with chain length. (6) The type II quantum yields of 2-octanone and 2-undecanone are independent of ketone concentration and are not affected by the presence of air. (7) By combining these quantum yields with estimates of the quantum yields of cyclobutanol formation found in the literature,[4i,5,6] it is observed that the total photochemical quantum yield of methyl ketones possessing secondary γ hydrogens decreases as the chain length of the methyl ketone increases; however, the effect is less pronounced than in the case of the dialkyl ketones R_2CO.

TABLE X
TYPE II QUANTUM YIELD OF 2-UNDECANONE

Concn, *M*	ϕ_{octene}	Temp, °C	Conversion, %	Atmosphere
Neat	0.201	22	0.3	Vacuum
Neat	0.204	22.5	0.4	Vacuum
Neat	0.194	22	0.4	Air
Neat	0.198	22.5	0.4	Air
0.6 (dodecane)	0.195	22.5	2	Vacuum
0.6 (dodecane)	0.196	22.5	2	Vacuum
0.6 (dodecane)	0.189	22	2	Air
0.2 (dodecane)	0.197	35	2	N_2
0.2 (dodecane)	0.196	35	2	N_2

TABLE XI
TYPE II QUANTUM YIELD FOR 2-OCTANONE

Concn, *M*	$\phi_{pentene}$	Temp, °C	Solvent	Conversion, %	Atmosphere
0.2	0.191	35	Dodecane	2	N_2
0.4	0.184	25	Nonane	1	Air
1.0	0.181	23	Dodecane	1	Air
Neat	0.183	25		0.3	N_2
Neat	0.179	25		0.2	Air

The last result is perhaps the most significant, for it has been tacitly if not openly assumed in the literature that, for a specific ketone series possessing a specific type of γ hydrogen, the quantum yield would remain unchanged as the chain length increased. This is indeed borne out by the results obtained for the phenyl alkyl ketones. However, the results for the methyl alkyl ketones and those which have been obtained by Hartley and Guillet for the symmetrical alkyl ketones point out that the assumption is not generally true. This may possibly be attributed to the fact that reaction occurs from both singlet and triplet states for the alkanones but from the triplet only in alkyl aryl ketones. This might imply that only the singlet reaction shows a chain-length dependence, but this seems unlikely, since for the methyl alkyl ketones the ratio $\phi_{II}{}^{T}/\phi_{II}{}^{S}$ remains constant while ϕ_{II} decreases with increasing chain length, as shown in Table IX.

Experimental Section

Apparatus. Light of wavelength 313 nm was used to irradiate the ketones. The source of light was a 250 W, type ME/D medium-pressure mercury arc obtained from Associated Electrical Industries. The lamp was powered by a direct current power supply. The desired wavelength was isolated by one of two filter systems: (1) a sheet of Pyrex plate glass and 2 cm of filter solution made from 115 g of $NiSO_4 \cdot 6H_2O$ + 35 g of $CoSO_4 \cdot 7H_2O$ in 250 ml of water; (2) a Jena Glaswerk precision interference line filter, UV-PIL (λ_{max} 315 nm, T_{max} 22%, half-width 7.5 nm), mounted in an air-

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[17] F. J. Golemba and J. E. Guillet, *SPE* (*Soc. Plast. Eng.*) *J.*, **26**, 88 (1970).

[18] N. C. Yang and S. P. Elliot, *J. Amer. Chem. Soc.*, **91**, 7550 (1969).

cooled brass holder and the above-mentioned filter solution. Analysis of the light filtered by the first system showed smaller peaks at 304 and 336 nm as well as the main peak at 313 nm. The second system showed virtually only the peak at 313 nm. The analyses were carried out using a Jarrel–Ash 82-410 grating monochromator with 25-μ slits, a 1P28 photomultiplier tube, and a Hewlett–Packard 425-A vacuum-tube voltmeter. Measurements of the quantum yield of the type II reaction of 2-undecanone resulted in the same values independent of the filter system. The light intensity from the lamp was monitored by a 1P28 photomultiplier tube, powered by a Lambda Model 25 regulated power supply The tube signal was measured by a Hewlett–Packard 425-A voltmeter. Uranyl oxalate actinometry was used to measure the light intensity and calibrate the signal from the photomultiplier tube. The linearity of the response of the tube to the intensity of the light was proven by using blackened copper screens to reduce the light intensity. The light falling on the photomultiplier tube was further reduced by a neutral density filter prepared by vacuum coating a quartz disk with gold. This filter ($\sim$1% *T*) was used to protect the photomultiplier tube.

The light from the lamp was collected and rendered parallel by a quartz lens (4-cm diameter, 8.4-cm focal length) purchased from Bausch and Lomb. The light passed through a reaction cell and into the photomultiplier tube. The reaction cells were made of quartz and had path lengths of 0.1 and 2.0 cm with volumes of 0.5 and 20 cm^3, respectively. Temperature was controlled by a hot air blower ($\pm$1°) or a Lambda K-2 circulating bath ($\pm$0.2°). The cell holder was a polyurethane foam insulated bath with quartz windows in the former case and an insulated aluminum block in the latter case.

The lamp, lens, filters, and photomultiplier tube were rigidly mounted to an aluminum chassis. Stainless steel "stops" guaranteed reproducibility of placement of the cell holders and thus the cells.

Procedure. All of the irradiations using a 2.0 cm path length cell were carried out under an atmosphere of nitrogen. The light intensity was measured without the cell in place and with the cell containing a measured amount of pure solvent in the beam. Then ketone was added to the desired concentration and the cell and its contents were degassed by alternate applications of vacuum (using a water pump) and a small positive pressure of dry nitrogen. The cell was then closed by a Teflon stopcock and the ketone photolyzed to low conversion. After the irradiation the incident intensity was redetermined. The cell was emptied, cleaned, and filled with pure solvent, and the incident and blank-solvent intensities were determined. Since the incident intensity was higher and proportional to the blank-solvent intensity, this procedure permitted correction for possible fading of the lamp during the time elapsed while degassing and cleaning the cell. All of the type I quantum yields and the type II quantum yields for the 0.2 *M* ketone solutions were determined after photolyses in the 2.0-cm cell. Except where noted, the concentrations used were such that less than 60% of the light was absorbed in passage through the cell. This incident intensity was approximately 10^{-5} einstein/cm^2 hr.

For irradiations which were carried out in the 0.1-cm Teflon-stoppered quartz cells, the procedure was the same except degassing of the solution was carried out in a rubber-septum-stoppered vial and the solution was transferred by syringe to the previously weighed cell in a nitrogen-filled glovebag. During irradiation a stream of dry nitrogen was directed into the cavity of the aluminum block which held the cell. The photolyses of ketones under vacuum were carried out in 0.1-cm quartz cells which were connected to a Pyrex bulb and a 10/30 ground-glass joint by means of a Pyrex–quartz graded seal. The ketone solution was weighed into the 1 cm^3 bulb of the cell. The contents were frozen and the temperature was lowered to that of liquid nitrogen while pumping down to $\sim$10^{-4} Torr. The cell was isolated and the contents allowed to melt. This procedure was repeated four to five times and then the cell was sealed during the final freeze–pump step. All other procedures were the same as those for irradiations carried out in a nitrogen atmosphere except the relationship between the incident and solvent-only intensities was measured separately.

Actinometry was done in the 2.0-cm cells. When this procedure was attempted with the 0.1-cm cells the gases evolved during the irradiation were trapped as bubbles in the beam of light. Quartz cells with 0.5- and 1.0-cm path lengths of otherwise identical dimensions were used to calibrate this system, using actinometer solutions which absorbed all of the light passing through the front face of the cells.

Analysis. The photolyzed ketone solutions were analyzed on a Perkin-Elmer Model 800 gas chromatograph using dual flame ionization detectors and $^1/_8$ in. × 5 ft columns (usually 5% w/w Carbowax on Chromosorb G). The photolysis products were measured by comparing their peak areas to the peak area of a standard added gravimetrically to the irradiated solution. The relative responses of the product and the standard were obtained from standard solutions containing known concentrations of the products. The peak areas were measured by a disk integrating unit attached to the chromatograph recorder.

Ultraviolet absorption spectra of the solvents and ketones were obtained from runs on a Bausch and Lomb Spectronic 505 double-beam spectrophotometer.

Materials. The solvents which were used were transparent over the range of wavelengths of the photolyses, and all trace impurities which could interfere with the analysis of photolysis products were removed by distillation or chromatography.

Except for 2-hexanone and 2-nonadecanone, the ketones were purified by distillation. The minimum purity was 99.9% by gas chromatographic analysis. The 2-hexanone was filtered through silica gel. A sample of 2-nonadecanone was obtained with a purity of 95% by repeated recrystallization from ethanol. The major impurity ($\sim$5%) was presumed to be another methyl ketone. 2-Nonadecanone with a purity greater than 99.9% was obtained using an Aerograph Autoprep 700 gas chromatograph.

Uranyl oxalate was prepared from saturated aqueous solutions of the certified reagents, potassium oxalate and uranyl nitrate. The resultant precipitate was filtered, washed with cold water, dried, and stored in the dark until used.

cis-1,3-Cyclooctadiene (COD) was purchased from Aldrich Chemical Co. and purified by distillation using a spinning band column.

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