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The Direct and Sensitized Photolyses of 2-Pentanone[1]

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Abstract: The direct and sensitized photolyses of 2-pentanone have been studied in the gas phase. Data from the study of benzene sensitization lead to a benzene triplet-state yield at 2537 Å of 0.73 ± 0.07. Since this is in reasonable agreement with values obtained by earlier workers, support is given to the contention that the Norrish type-II reaction may occur through a triplet state. The direct photolyses with added diolefins indicate that both the excited singlet and the triplet states are precursors of the type-II reaction, and that the importance of each state is dependent on exciting wavelength. Rate constants for the type-II dissociation from each state are calculated by use of a general kinetic mechanism. The data indicate that at 2654-Å vibrational deactivation of the excited singlet state is not complete before dissociation, even with 100–200 torr of added gas.

It has been shown that at room temperature at 3130 Å the excited state of 2-pentanone which excites biacetyl to emission upon collision also is responsible for dissociation by the Norrish type-II reaction[3] (hereafter referred to as the type-II reaction). Owing to the relatively high pressure of biacetyl required for maximum sensitized emission, it was concluded that a singlet state was probably involved. Ausloos and Rebbert[4] studied the same system and monitored the 2-pentanone fluorescence to show, however, that a triplet state is almost certainly the one in question.

Recently Wagner and Hammond[5] have presented evidence that the type-II reaction for 2-pentanone occurs from both states at 3130 Å in hexane solution.

The benzene-sensitized type-II dissociation of 2-pentanone in the gas phase has been investigated. It was hoped not only to obtain information about this process but possibly also about the crossover from the $^1B_{2u}$ state to the $^3B_{1u}$ state of benzene.

The effect of added diolefins on the direct photolysis of 2-pentanone has been examined in the long- and in the short-wavelength regions of the first ultraviolet absorption band. In agreement with Wagner and Hammond both the singlet and the triplet states of 2-pentanone may dissociate by a type-II reaction. Furthermore it appears that both states may also give the type-I dissociation. The relative involvements of the two states in the two processes depend on conditions, particularly on wavelength.

Experimental Section

1. Materials. (a) Benzene (Matheson Coleman and Bell Chromatoquality) was distilled bulb-to-bulb with the middle third retained. It showed no measurable impurities.

(b) 2-Pentanone (Matheson Coleman and Bell, bp 100.5–101.5°) was distilled slowly on a Bantamware Vigreux column over a molecular sieve Type 4a and then distilled bulb-to-bulb with the middle third retained. Analysis by vapor phase chromatography equipped with flame ionization detection showed one impurity (0.3%) which eluted after 2-pentanone on a 1.85-m Carbowax 600 column. For some of the photolyses, 2-pentanone purified by preparatory chromatography (9.40-m column of Carbowax 20M, 0.64-cm diameter) was used. These samples contained less than 0.003% of the above-mentioned impurity. No differences in

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[2] Member Academic Year Institute supported by the National Science Foundation 1964–1965; University of Texas Fellow 1966–1967.

[3] J. L. Michael and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **85**, 1027 (1963).

[4] P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964).

[5] P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); **88**, 1245 (1966).

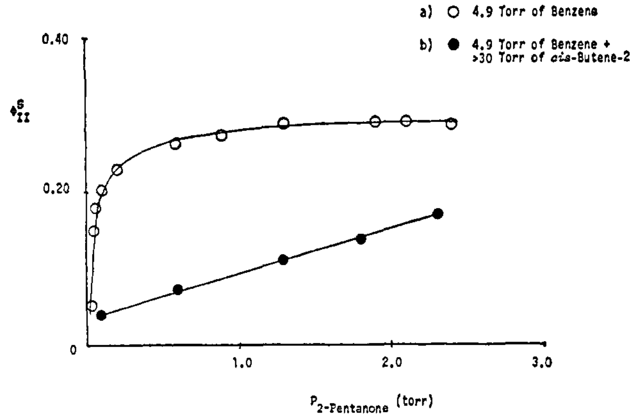

Figure 1. The benzene-sensitized yield of Norrish type-II reaction *vs.* pressure of 2-pentanone at 2537 Å and 25°.

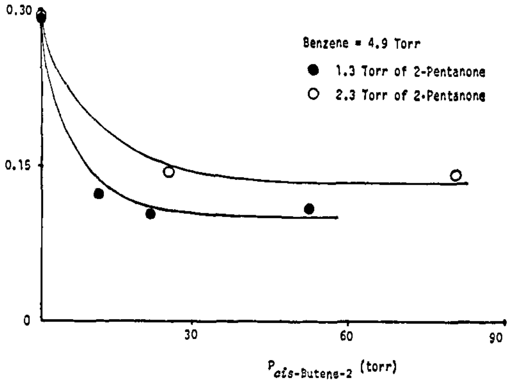

Figure 2. The benzene-sensitized yield of Norrish type-II reaction *vs.* pressure of added *cis*-butene-2 at 2537 Å and 25°.

yields of dissociation were observed in the two samples. Care was taken to ensure that no 3-pentanone was present.[6] A Zyonyl E-7 column (Varian Aerograph) served to separate 2- and 3-pentanone, and the sample was found to be free of the latter isomer.

(c) 1,3-Butadiene (Phillips Research Grade, 99.89 mole %) was distilled bulb-to-bulb. The major impurity was butene-1.

(d) *trans*-1,3-Pentadiene (Aldrich Chemical Co., n^{20}D 1.4300) contained about 0.3% of the *cis* isomer and about 0.3% of an impurity which eluted slightly before *trans*-1,3-pentadiene (6.1-m column of 10% dimethyl sulfolane on 60–80 Firebrick). No attempt was made to purify the sample further except for bulb-to-bulb distillation.

(e) *cis*-Butene-2 (Phillips Research Grade, 99.91 mole %) contained 0.07% *trans*-butene-2. The sample was distilled bulb-to-bulb.

(f) Acetone (Matheson Coleman and Bell Spectroquality) showed no impurities by vapor phase chromatography and was used without further purification after bulb-to-bulb distillation.

The ketones were stored on the vacuum line in black bulbs over Drierite or a molecular sieve Type 13x at −196°. No differences were observed in samples stored over the two desiccants.

2. Apparatus. A conventional grease-free, mercury cutoff, vacuum line was employed. The T-shaped quartz cell was 12.0 cm long and 3.8 cm in diameter with a total volume including access tubing of 194 cm³. The cell was attached to the vacuum line through a small mercury float valve and was encased in a brass housing which could serve as a furnace.

The analysis section consisted of a Toepler pump-McLeod gauge, capillary tubes which could be sealed and removed for analysis by vapor phase chromatography, and a mass spectrograph sample bulb.

3. Light Source. A Hanovia S-100 medium-pressure mercury arc was used for both the sensitization and the direct photolysis experiments.

For the benzene sensitization experiments a filter[7] served to isolate the 2537–2654-Å region. Intensities of transmitted light were measured with an RCA 935 phototube. Benzene emission was measured with an RCA 1P28 photomultiplier tube placed at the side window.

For the direct photolyses a Bausch and Lomb monochromator, Model 33-86-40 (dispersion 16 Å mm^{-1}), replaced the filter system.

4. Procedure. Each sample was thoroughly degassed at −160° and allowed to stand for several hours to ensure complete mixing prior to photolysis. Light absorption was used as a measure of mixing.

Actinometry was performed by photolysis of acetone at 130°. The yield of carbon monoxide was taken as unity and was determined by mass spectrographic analysis of the fraction noncondensable at −215°.

Products from the photolyses were measured with a McLeod gauge by removing the noncondensable gases at −215° (CO and CH_4) and at −160° (C_2H_4, C_2H_6, and most of the C_3H_6 and C_3H_8). Compositions were determined either by the mass spectrograph (−215° fraction) or by vapor phase chromatography (−160° fraction). One aliquot from each run was taken of all products except CO and CH_4 so that higher hydrocarbons could be determined relative to C_2H_4 by vapor phase chromatography.

Results

Benzene-Sensitized Dissociation of 2-Pentanone. Figure 1 shows (a) quantum yields of the benzene-sensitized type-II process, Φ_{II}^{s}, at 25° as measured by the quantum yield of ethylene, *vs.* pressure of 2-pentanone at a constant benzene pressure of 4.9 torr, and (b) the same quantum yields in the presence of ≥30 torr of *cis*-butene-2. The fraction of light absorbed by pure benzene (2537 Å) was 0.25 and the fraction absorbed by pure 2-pentanone was 0.015(K), where (K) is the pressure of the ketone in torr. Curve a indicates a constant Φ_{II}^{s} is reached at about 1 torr of 2-pentanone. At this pressure significant quenching of benzene fluorescence occurs. The effective quenching cross section, σ^2, was determined to be 2.6×10^{-16} cm² from a plot of $1/Q_f$ *vs.* 2-pentanone pressure. Since the mean lifetime of 5.9×10^{-7} sec[8] and the radiative lifetime calculated from absorption coefficients[9,10] agree, the radiative life of benzene in the $^1B_{2u}$ state was taken to be 5.9×10^{-7} sec for the purpose of this calculation. Curve b shows that Φ_{II}^{s} decreases in the presence of *cis*-butene-2, a known acceptor of benzene triplet energy.[11,12] The decrease was essentially complete at about 30 torr of *cis*-butene-2 (see Figure 2).

Direct Photolysis of 2-Pentanone. In addition to the sensitization experiments, the direct photolysis of 2-pentanone has been studied with and without various added gases. The presence of 40 torr of *cis*-butene-2 at 3130 Å and 60 torr of *cis*-butene-2 at 2537 Å results in no measurable change in the type-II quantum yield. Cundall and Davies[13] recently reported that 250 torr of *cis*-butene-2 reduces the type-II reaction by 25%. However, for the pressures used in the present study it appears safe to attribute the reduction of Φ_{II}^{s} in the presence of *cis*-butene-2 to energy transfer to *cis*-butene-2 from benzene rather than from 2-pentanone. In agreement with this observation, Rebbert

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(7) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(8) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961).

(9) G. W. Robinson and R. P. Frosch., *ibid.*, **38**, 1187 (1963).

(10) S. Lipsky, *ibid.*, **38**, 2786 (1963).

(11) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 1151 (1966).

(12) W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

(13) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 2444 (1966).

Table I. Photolysis of 2-Pentanone and 2-Pentanone–Diolefin Mixtures

λ, Å	Temp, °C	K, torr	D,[a] torr	I_a[b]	$t \times 10^{-4}$, sec	Quantum yields: CO + CH_4	CO	CH_4	C_3H_8	C_3H_6	C_2H_4
3130	25	9	...	0.41	3.96	...					0.300
		10	...	0.41	4.32	0.065					0.308
		10	9	0.41	4.87	0.019					0.180
		9	25	0.41	4.39	0.020					0.140
		13	128p	0.47	5.96	0.024					0.100
		9	168p	0.41	6.12	0.023					0.110
		9	200	0.41	4.70	0.017					0.115
		9	107	0.41	3.60	0.01					0.107
		10	3.5	0.41	4.32	...					0.213
		9	51	0.41	4.32	...					0.109
2654	25	9	0	1.30	3.75	0.044					0.283
		10	0	1.74	3.06	0.042					0.284
		10	50	1.74	3.24	0.013					0.234
		10	102	1.25	3.24	0.027					0.228
		10	205	1.01	3.24	...					0.230
		13	169p	1.58	5.73	0.01					0.220
	47	9[c]	111	0.80	7.50	0.09					0.254
	48	11[c]	...	1.05	4.56	0.24					0.310
2540	25	9	0	0.53	6.48	0.059					0.292
		9	104	0.53	4.14	0.01					0.245
		9	50	0.53	3.71	0.05					0.257
2804	128	24.5		1.16	7.56	0.39	0.20	0.19	0.18	0.018	0.430
		25	160p	1.04	7.56	0.095	0.095	Very small	0.003	0.0013	0.390

[a] 1,3-Butadiene unless followed by p in which case D = 1,3-pentadiene. [b] $\times 10^{-11}$ quanta second^{-1} centimeter^{-3}. [c] 80 torr of C_6H_{12} added.

Table II. Effect of Wavelength on the Photolysis of 2-Pentanone

λ, Å	K, torr	I_a[a]	Temp, °C	$t \times 10^{-4}$, sec	Quantum yields: C_2H_4	CO	C_3H_8	C_3H_6	C_4H_{10}	C_6H_{14}	CH_4
2540	19.5	1.33	25	7.70	0.280	0.046	...	...	...	...	...
2804	17.5	1.35	25	7.20	0.266	0.058	0.029	0.0064	0.022	0.052	0.019
2965	17.0	1.37	25	7.20	0.244	0.056	0.032	0.011	0.021	0.066	0.021
2540	24.0	1.12	25	6.84	0.300	0.052	0.024	0.004	0.015	0.012	0.017
2804	17.0	1.28	25	6.84	0.290	0.072	0.022	0.009	0.034	0.043	0.016
2965	20.0	1.50	25	6.84	0.236	0.077	0.023	0.008	0.014	0.017	0.018
3130	25.0	0.74	25	6.84	0.274	0.056	0.022	0.004	0.017	0.026	0.022
2540	32.0	1.35	128	7.20	0.342	0.113	0.10	0.011	0.003	...	0.15
2654	24.5	1.15	130	7.57	0.349	0.156	0.084	0.010	0.003	...	0.18
2804	29.5	1.36	129	7.20	0.297	0.186	0.14	0.014	0.006	0.009	0.22
2965	25.0	1.16	129	7.56	0.300	0.356	0.19	0.024	0.025	0.012	0.26
3130	55.0	1.16	129	7.56	0.268	0.386	0.24	0.013	0.008	0.007	0.32

[a] $\times 10^{-11}$ quanta second^{-1} centimeter^{-3}.

and Ausloos[14] have shown that butene is a very inefficient quencher of acetone phosphorescence.

Figure 3 shows the effect of added 1,3-butadiene and 1,3-pentadiene on the type-II yield from 2-pentanone at 3130, 2654, and 2540 Å. The ratio of the quantum yield of C_2H_4 with added diolefin to that without added diolefin, Φ_{II}/Φ_{II}^0, is plotted against pressure of diolefin (2-pentanone = 10.0 ± 1.0 torr). Results of the photolysis of 2-pentanone and 2-pentanone–diolefin mixtures for a variety of conditions are shown in Tables I and II.

Recently Haller and Srinivasan[15] have reported the production of ethylene in the Hg(6 $^3P_1$) + 1,3-butadiene reaction. To account for this possibility acetone–butadiene mixtures were photolyzed for periods up to twofold the exposure times and at intensities up to fourfold the intensities used in the 2-pentanone–butadiene system. The amount of ethylene produced by sensitization of the diolefin by acetone is not more than 2–3% of the ethylene produced in the 2-pentanone–butadiene system.

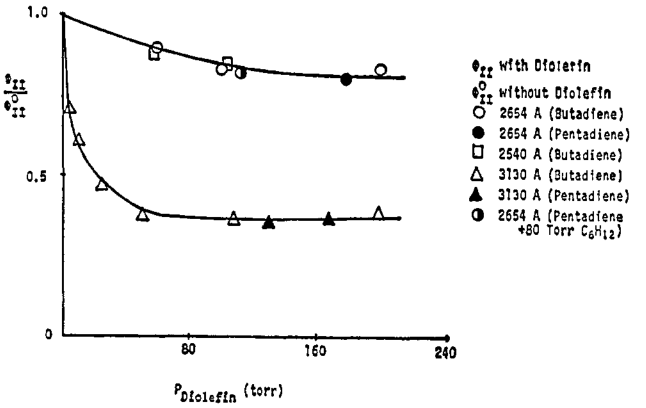

Figure 3. The ratio of the type-II yield with added diolefin to the yield without added diolefin *vs.* pressure of diolefin at 25°. 2-Pentanone pressure = 10.0 ± 1.0 torr.

Discussion

Noteworthy facts revealed by the data are as follows. (1) The Norrish type-II quantum yield in pure 2-pentanone vapor is virtually independent of wavelength from 2537 to 3130 Å; (2) the benzene-sensitized type-II reac-

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(14) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

(15) I. Haller and R. Srinivasan, *ibid.*, **88**, 3694 (1966).

tion has about the same quantum yield as that of the unsensitized reaction; (3) the type-I yield (dissociation into radicals) is much lower than the type-II yield but tends to increase with decrease in incident wavelength and with increase in temperature; (4) addition of substances presumed to destroy triplet-state molecules effectively (*e.g.*, diolefins) indicates that the type-II reaction may originate either from the singlet or from the triplet state of 2-pentanone; (5) the proportion of the reaction arising from the singlet state increases with decrease in wavelength; (6) addition of substances effective in destroying the $^3B_{1u}$ state of benzene (*e.g.*, *cis*-2-butene) indicates that as the pressure of 2-pentanone is increased the fraction of the sensitized reaction which arises by energy transfer from the $^1B_{2u}$ molecules of benzene increases; (7) the fluorescent efficiency of 2-pentanone is very low but is enhanced by the addition of unreactive gas (*e.g.*, butane); (8) as the incident wavelength decreases, the pressure of inert gas required to produce maximum emission increases, and at 2654 Å maximum efficiency has not been fully reached even at 600 torr of added butane; (9) the sum of all quantum yields (fluorescence, types I and II) is well below unity (less than 0.4) under all experimental conditions studied at room temperature. (Data bearing on points 7 and 8 will be published separately by F. S. W.)

A complete and unambiguous interpretation of all of these facts is not possible in the light of present theory. It is apparent that certain processes must be very rapid compared to vibrational relaxation. The independence of the type-II yield of wavelength would indicate that the vibrational level of the initially formed excited singlet state is not critical but that some other factor is very important. This other factor could be the geometrical form of the absorbing molecule.

With a complex molecule such as 2-pentanone and in view of the fact that the incident radiation is never truly monochromatic, many different vibrational levels must always be formed in the upper singlet state in each experiment. The ratios of rate constants may vary from one level to another and vibrational relaxation is always a competing process. In consequence a detailed description of the behavior of excited molecules would be difficult and would lead to rate expressions of such complexity that they would be of little use. The following treatment is recognized to be a greatly simplified version of the true situation. Nevertheless, a few conclusions are possible. For simplicity the formation of a single vibrational level with each monochromator setting will be assumed and the steps may be visualized as shown in eq 1–11, where P_I and P_{II} are type-I and type-II products, respectively, K is a ground-state ketone molecule, ^1K and ^3K are excited singlet and triplet state molecules, respectively, with vibrational levels indicated by subscripts, and ν_f and ν_p are the frequencies of fluorescence and of phosphorescence, respectively. All products other than type II are included under type I.[16]

$$K + h\nu = {}^1K_{l-v} \qquad (v = 0, 1, 2, \ldots, l) \qquad (1)$$

$${}^1K_{l-v} = P_I \qquad (2)$$

$$= P_{II} \qquad (3$$

$$= {}^3K_{\lambda-v} \qquad (v = 0, 1, 2, \ldots, \lambda) \qquad (4)$$

$$= K + h\nu_f \qquad (5)$$

$${}^1K_{l-v} + M = {}^1K_{l-(v+l)} + M \qquad (6)$$

$${}^3K_{m-v} = P_I \qquad (7)$$

$$= P_{II} \qquad (8)$$

$$= K + h\nu_p \qquad (9)$$

$$= K \qquad (10)$$

$${}^3K_{m-v} + M = {}^3K_{\lambda-(v+1)} + M \qquad (11)$$

The total type-II yield will be given by a summation of rates of (3) for all vibrational levels of importance plus a similar summation of rates of (8) for the triplet levels divided by the number of photons absorbed per second per unit volume

$$\Phi_{II} = [\sum k_3({}^1K_{l-v}) + \sum k_8({}^3K_{\lambda-\nu})]/I_a \qquad (12)$$

Since Φ_{II} is independent of incident wavelength and essentially independent of pressure, the vibrational level in the upper state does not appear to be critical although quite probably this statement would not be true for very low vibrational levels since it is now generally accepted that the type-II reaction occurs through an intermediate six-membered ring formed by a hydrogen bond between the γ-carbon atom and the carbonyl oxygen.[17] Even at 3130 Å the initially excited singlet-state molecules acquire about 0.4 eV of vibrational energy over and above that normally present in molecules of this complexity.

If one assumes that the effect of diolefins is to destroy triplet-state molecules and thus prevent reactions such as (8), one can conclude that at 3130 Å about 62% of the type-II reaction arises from the triplet state and only about 18% at 2654 Å. Interpretations such as this must be regarded as speculative. The behavior of 2-hexanone is different in that there is no fluorescence, the type-II yield is higher, and oxygen does not inhibit the type-II reaction.[18]

The vital question is whether or not vibrational relaxation is or is not complete and whether or not it is important. If vibrational relaxation is complete, Φ_{II} will be independent of wavelength provided

$$k_3^0/(k_2^0 + k_3^0 + k_4^0 + k_5^0) = k_8^0/(k_7^0 + k_8^0 + k_9^0 + k_{10}^0) \qquad (13)$$

and if $k_4^0 = 0$. The superscript 0 refers to vibrationally relaxed molecules. If (13) is obeyed and vibrational relaxation at all levels except the lowest predominates over all other processes, the fraction of type II which comes from the triplet state will make no difference.

If vibrational relaxation is not complete, the expression for Φ_{II} is a ratio of polynomials in (M) with that in the denominator being one degree higher than that in the numerator. Ratios of rate constants would have to be independent of the vibrational level formed in the absorption act. k_5 and k_9 are not independent of vibrational level,[16] but emission is a relatively unimportant method of losing energy in this system.

Type II yields are essentially the same in the gas as in the liquid phase.[19,20] Thus the assumption of com-

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(16) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).

(17) Reference 6, p 382.

(18) V. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim. France*, 121 (1958).

(19) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1521, 1531, 1566 (1938).

(20) D. R. Coulson and N. C. Yang, *J. Am. Chem. Soc.*, **88**, 4511 (1966).

plete relaxation receives some support in spite of the data on fluorescence.

If complete relaxation is assumed and if k_5 and k_9 may be neglected, some rate constants can be calculated. The reaction

$$^3K_0 + D = K + {}^3D \qquad (14)$$

where D is a molecule of diolefin leads to destruction of the triplet ketone molecule. Let $k_{14} = 1.3 \times 10^{11}$ l. mole^{-1} sec^{-1} (collision diameter of 4 Å). From the plot of Φ_{II}^0/Φ_{II} *vs.* (D) $(k_7^0 + k_8^0 + k_{10}^0) = 6.4 \times 10^7$ sec^{-1} at 3130 Å.

Fluorescence is enhanced by increase in pressure, but at 3130 Å and 100 torr the emission efficiency is about 3.4×10^{-3}.[21] The radiative lifetime calculated by the method of Strickler and Berg[22] is 8.5×10^{-6} sec. Such a calculation is not accurate but should be correct as to magnitude. Hence $k_5^0 = 1.2 \times 10^5$ sec^{-1}. From the fluorescent efficiency $k_3^0 = 3.4 \times 10^6$ sec^{-1}, $k_2^0 + k_4^0 = 3.2 \times 10^7$ sec^{-1}. Since $k_2^0 \sim 0.2k_3^0$, $k_4^0 = 3.1 \times 10^7$ sec^{-1}.

An estimate may be made of k_8^0 if certain assumptions are made: (1) the data at high (D) permit the ratio of type-II yield from the singlet state to that from the triplet state to be calculated; (2) $k_2^0 \ll k_4^0$ since the type-I yield occurs predominantly from the triplet state and in any case is very small. Assumption 1 appears to be justified on the basis that diolefins do not quench the fluorescent yield of the ketone but must be used with caution since fluorescence may not be competitive with the type-II process. Nevertheless $k_8^0 = 1.2 \times 10^7$ sec^{-1} (see (15) below). Also $k_3^0 \sim k_8^0/3$, a result which agrees with Wagner.[23]

At 2654 Å the data on fluorescence indicate that vibrational relaxation is not complete even at 600 torr of added butane. It must be emphasized, however, that the data in Table II show no significant effect of wavelength on Φ_{II}. The average of all values is 0.29 ± 0.01 except for two values of 0.24 at 2965 Å. Thus the vibrational level of the initially formed excited molecule, the extent of vibrational relaxation, and the apparent fraction of the reaction which comes from the triplet state as revealed by diolefin experiments have no discernible effect on Φ_{II}.

Two experiments were conducted with the following conditions: (a) pentanone (22 torr), butane (232 torr), 1,3-butadiene (207 torr); (b) pentanone (22 torr), butane (488 torr). Φ_{II} for mixture a was 0.76 of the value for b, thus indicating that about 24% of the type-II yield apparently came from the triplet state. At a total pressure of 200 torr, the fraction was 0.82. Thus tentatively one concludes that an increase in pressure favors triplet-state formation.

At 2654 Å one may assume that $k_{14}^0 = k_{14}$ and that Q_f extrapolated to (M) = 0 at 2730 Å may be used to evaluate k_3 and k_4. Table III summarizes calculated rate constants. It must be kept in mind in referring to this table that the incident light was not truly monochromatic and that the extent of vibrational relaxation was indeterminate. Nevertheless trends of the constants with variation in incident wavelength are significant.

Table III. Summary of Calculated Rate Constants

$\lambda_{\text{excitation}} = 2654$ Å
$k_4/k_3 = 3.0$
$k_7 + k_8 + k_{10} = 2.8 \times 10^9$ sec^{-1}
$k_8 = 2.5 \times 10^8$ sec^{-1}
$k_3 = 2.6 \times 10^7$ sec^{-1}
$k_2 + k_4 = 7.8 \times 10^7$ sec^{-1}

$\lambda_{\text{excitation}} = 3130$ Å
$k_4^0/k_3^0 = 9.3$
$k_7^0 + k_8^0 + k_{10}^0 = 6.4 \times 10^7$ sec^{-1}
$k_8^0 = 1.2 \times 10^7$ sec^{-1}
$k_3^0 = 3.4 \times 10^6$ sec^{-1}
$k_2^0 + k_4^0 = 3.2 \times 10^7$ sec^{-1}

Since

$$\frac{^1\Phi_{II}}{^3\Phi_{II}} = \frac{k_3^0(k_7^0 + k_8^0 + k_{10}^0)}{k_4^0k_8^0} \qquad (15)$$

the ratio of type-II yields from singlet and from triplet states, respectively, one can estimate k_8^0. k_2^0 is small compared to k_4^0, and probably the ratio obtained with high (D) will be the same as one would obtain with (D) = 0. Hence $k_8^0 = 1.2 \times 10^7$ sec^{-1}. This value depends on several reasonable but unproven assumptions.

The data for the type-I reaction may not be treated quantitatively, partly because yields are low and partly because not all products arising from it have been determined. Diolefins destroy triplet-state molecules and react with radicals. The rate of dissociation of acetyl radicals may be estimated from the work of Calvert.[24] At 25° (mean lifetime 10^{-5} sec) they might react quantitatively with diolefins while at 128° (10^{-7} sec) they would not. Hot RCO radicals are also a distinct possibility. The data in Table II do not give good material balances, and products must be formed which were not determined.

At 128° in the absence of diolefin, type-I yields increase with increase in wavelength, probably because of increased crossover to the triplet state. Because of longer lifetimes, triplet-state molecules show a greater increase of dissociation with increase in temperature than do singlet-state molecules.

The data in Figure 1 indicate that addition of *cis*-butene-2 reduces the type-II yield in mixtures of benzene and 2-pentanone. *cis*-Butene-2 does not markedly affect benzene fluorescence,[12] although adduct formation is a possibility.[25] It does, however, destroy the triplet state of benzene[11] but not that of 2-pentanone.

The data (Figure 1) show Φ_{II}^s to decrease with addition of *cis*-butene-2 and increase with increase in 2-pentanone pressure. The yield asymptotically approaches the yield of the unsensitized reaction. Quite evidently the higher the 2-pentanone pressure the larger the fraction of the reaction results from energy transfer to 2-pentanone from the singlet state of benzene.

An estimate based on several assumptions may be made of the triplet-state yield in benzene. At 0.2 torr of 2-pentanone the emission efficiency of benzene has been reduced by 14% and Φ_{II}^s is about 0.23. If

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[21] F. S. Wettack, results to be published; see Ph.D. Thesis, University of Texas, 1967.

[22] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37, 814 (1962).

[23] P. J. Wagner, *J. Am. Chem. Soc.*, 89, 2503 (1967).

[24] J. G. Calvert, *J. Phys. Chem.*, 61, 1206 (1957).

[25] See K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 88, 2066 (1966); W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, 46, 678 (1967).

the sensitized has the same yield as the unsensitized reaction (see above), the fraction of excited benzene molecules which have transferred energy to the ketone would be 0.23/0.29 = 0.79. At this ketone pressure Φ_{II}^{s} with added *cis*-butene-2 is 0.046. Hence 0.23 − 0.046 = 0.18 is the type-II yield caused by energy transfer from triplet benzene. Thus 0.18/0.29 = 0.63 would be the triplet-state yield of benzene. However, 14% of the molecules did not transfer energy to 2-pentanone before they could fluoresce and probably before they could cross over to the triplet state. Hence the triplet-state yield in pure benzene might be 0.63/0.86 = 0.73. This calculation is based on several assumptions but is presented as an interesting support of other values.[26]

At pentanone pressures of 2 torr or more, the type-II yield is reduced about 50% by addition of *cis*-butene-2 and the benzene fluorescence is reduced essentially by 50% by this pressure of 2-pentanone. This raises the interesting question as to whether or not benzene fluorescence can be destroyed without preventing intersystem crossover. The two processes may not be competitive.

Ausloos and Rebbert[27] found 60% inhibition of the type-II reaction in 2-pentanone by 56.5 torr of oxygen at 3130 Å. Oxygen does not affect the fluorescence.[4] Oxygen probably preferentially destroys the triplet state, and hence the present data agree with the results of Ausloos and Rebbert. Initial slopes of Φ_{II}^{0}/Φ_{II} *vs.* (O_2) and *vs.* (D) are virtually identical.

Wagner and Hammond[5] propose that 10% of 2-pentanone disappearance at 3130 Å in hexane solution is due to the singlet state, whereas the present work in the gas phase gives 35%. There is no *a priori* reason why figures in the two phases should agree.

The present work sheds no light with regard to the presence or absence of diradicals.[28] This work is in agreement with earlier work that the Norrish type-II process in 2-pentanone may occur either through the singlet or through the triplet state. Although the fraction from each state varies with wavelength, the over-all yield is nevertheless remarkably constant except for two anomalous values at 2965 Å. This raises the question as to whether the reaction which gives the type-II products is in fact competitive with other processes such as fluorescence, phosphorescence, and even vibrational relaxation. Conceivably molecules in a very high vibrational level of the ground state could undergo the reaction as well as molecules in excited electronic states.

Finally it may be suggested that the configuration of the absorbing molecule may be decisive in determining whether or not a type-II reaction can occur. Theory is of little help at the present moment in this connection.

(26) See G. A. Haninger and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967); W. A. Noyes, Jr., and I. Unger, *Advan. Photochem.*, **4**, 49 (1966).

(27) P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).

(28) *Cf.* P. Ausloos and R. E. Rebbert, *ibid.*, **89**, 1573 (1967).