PHOTOCHEMISTRY OF BUTANONE AND METHYL BUTANONE

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SUMMARY

The photochemistry of butanone and methyl butanone at 3130 Å has been reinvestigated. At high pressures, the thermal triplet lifetimes were evaluated as 13×10^{-6} s (butanone) and 0.2×10^{-6} s (methyl butanone). An appreciable change in the lifetime of butanone triplets was observed when the total pressure changed from 12 to 500 Torr. The triplet quantum yields were 1.0 (butanone, gas phase, high pressure) and 0.82 (methyl butanone, n-hexane solution). Decomposition quantum yields were determined under several conditions. At 60°C and high total pressure the values obtained were 0.95 (butanone) and 0.75 (methyl butanone). Contrary to previous results, no evidence of a chain decomposition could be detected in the photolysis of methyl butanone. The main differences between the photochemical behaviour of ketones which can only decompose by a Norrish type I mechanism are discussed in terms of changes in $D(R\text{–}COR')$ with α methyl substitution.

INTRODUCTION

The photochemistry of simple alkyl ketones which can only photodecompose by a Norrish type I mechanism provides one of the simplest systems where correlation of structure with photoreactivity can be established. In spite of this, very few systems of this type have been studied in order to determine the reactivity of the excited states. Gas phase kinetic data have only been reported for acetone[1,2] and 3-pentanone[3,4], and triplet quantum yields have been given only for acetone[1,2], butanone[5] and 3-pentanone[3]. On the other hand, photodecomposition quantum yields (Φ_{Desc}) have been measured for several ketones. Gas phase values of Φ_{Desc} have been reported for acetone[1,2], butanone[5,6], methyl butanone[7], 3-pentanone[3,4], and 2,4-dimethyl pentanone[8]. Data obtained in solution for the t-butyl ketones[9] have to be regarded with caution since cage recombination would be computed as internal conversion[10].

The butanone and methyl butanone triplet lifetimes have not been reported. Furthermore, there are no measurements of the triplet quantum yields in the photolysis of methyl butanone. Biacetyl emission, photosensitized by this ketone, has been measured by Weir[11], and a more complete study of its photochemistry was carried out by Zahara and Noyes[7]. Nevertheless, its behaviour shows several anomalies that deserve further analysis. Some examples include: (a) low values for the sensitized biacetyl emission under conditions of total triplet quenching[7,11]; (b) the presence of two "states" that can be quenched by low oxygen pressures[7]; (c) singlet quenching with a few Torr of biacetyl[11]; and (d) the occurrence of a chain reaction that generates ^{i}Pr radicals without producing carbon monoxide[7].

The present work was carried out in order to gather information about these points and to obtain quantitative data on the photoreactions of butanone and methyl butanone triplets.

EXPERIMENTAL

Experimental conditions were similar to those employed in a previous study[3]. Actinometry was carried out with matched absorbances and employing 3-pentanone as actinometer. Reaction times were kept short enough to avoid formation of significant amounts of products. Photolyses at wavelengths longer than 3200 Å were carried out using a soda-glass filter.

In order to avoid back reactions, cis- to trans-1,3-pentadiene isomerizations were carried out at low conversion. The cis-isomer was employed as internal standard. Analyses were carried out by gas–liquid chromatography (g.l.c.) employing a β, β'-oxidipropionitrile on Chromosorb G column at 0°C.

Liquid phase photolyses were carried out in Pyrex test tubes of 8 mm external diameter. Several samples were photolyzed together in a "merry-go-round" apparatus. The full beam from a medium pressure mercury arc was employed. Acetone/cis-1,3-pentadiene mixtures were employed in the actinometry.

Benzene (Merck), n-butane (Fluka), propane (Matheson, C.P. grade), cis-1,3-pentadiene (Fluka), biacetyl (Eastman), methyl butanone (Eastman or Baker), 3-pentanone (Eastman), butanone (Eastman) and acetone (Merck or Hopkin & Williams) were employed without further purification other than careful degassing and trap-to-trap distillation.

RESULTS

The relative extinction coefficients of the ketones employed were determined at 3130 Å. The values obtained were (methyl butanone taken as unity): 3-pentanone (gas phase), 0.63; butanone (gas phase), 0.55; acetone (gas phase), 0.52; acetone (n-hexane solution), 0.43. These results are in qualitative agreement with previously reported data[12].

Butanone

Values of Φ_{CO} obtained in the photolysis of butanone at 60°C are shown in Fig. 1. The value extrapolated to zero intensity is nearly 0.95.

The quantum yield of biacetyl triplets photosensitized by butanone are shown in Figs. 2 and 3. In Fig. 3 $(\Phi_{3B})_\infty$ measures the quantum yield of biacetyl triplets at "infinite" biacetyl pressure.

Methyl butanone

Φ_{CO} was found to be nearly 0.9 at 120°C (100 Torr total pressure and with an absorbed intensity of 1.5×10^{12} quanta cm^{-3} s^{-1}). This result is similar to the values reported previously[7].

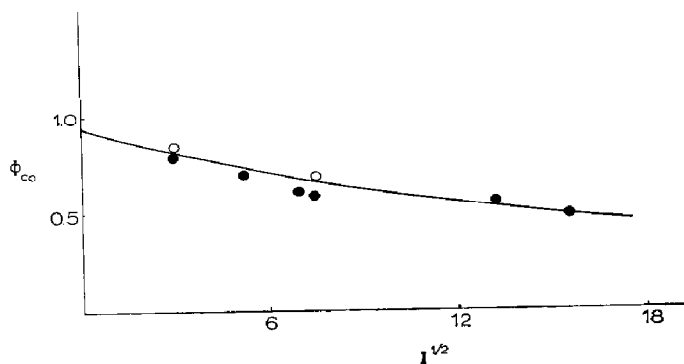Fig. 1. Φ_{CO} for butanone as a function of absorbed intensity. Temperature $= 60°C$; ketone pressure $= 20$ Torr. O, Total pressure 200 Torr; ●, total pressure 20 Torr. Light intensity given in arbitrary units.
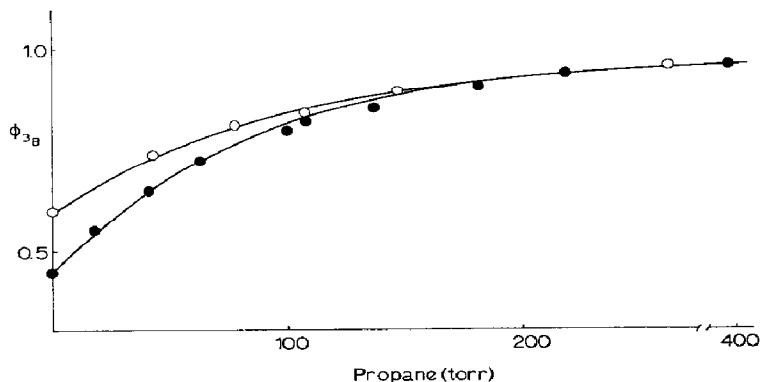

Fig. 2. Effect of added propane on Φ_{3B} in the photolysis of butanone. Temperature $= 25°C$; biacetyl pressure $= 2.3$ Torr. ●, 12 Torr butanone; O, 19.8 Torr butanone.
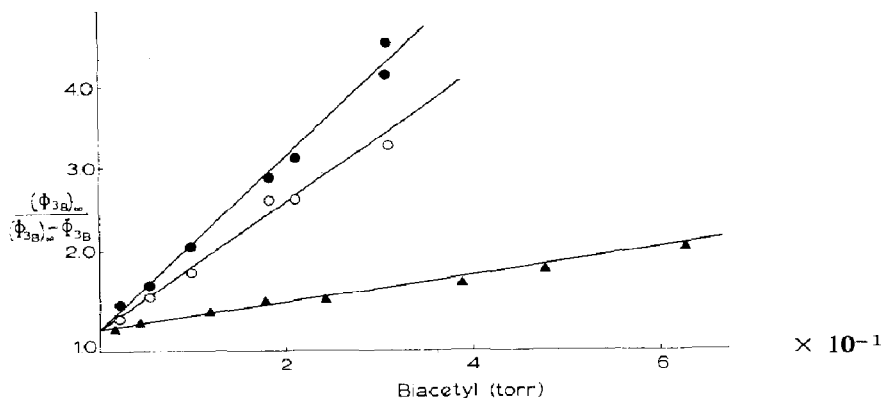
Fig. 3. Stern–Volmer plot for the sensitized biacetyl emission. ●, 12 Torr butanone; ○, 12 Torr butanone plus 220 Torr propane; ▲, 26 Torr methyl butanone plus 483 Torr propane (biacetyl pressures must be multiplied by a factor 10).

An extensive analysis of Φ_{CO} was carried out at $60°C$. The data obtained are shown in Figs. 4 and 5. Furthermore, it was also found that at low intensities Φ_{CO} was nearly independent of total pressure from 50 to 400 Torr. The quantum yields for formation of methyl and isopropyl radicals were also evaluated under different experimental conditions. Some of the results obtained have been included in Fig. 4. These quantum yields were measured using eqns. (1) and (2):

$$\Phi_{Me} = 2\ \Phi_{C_2H_6} + \Phi_{CH_4} + \Phi_{C_4H_{10}} \tag{1}$$

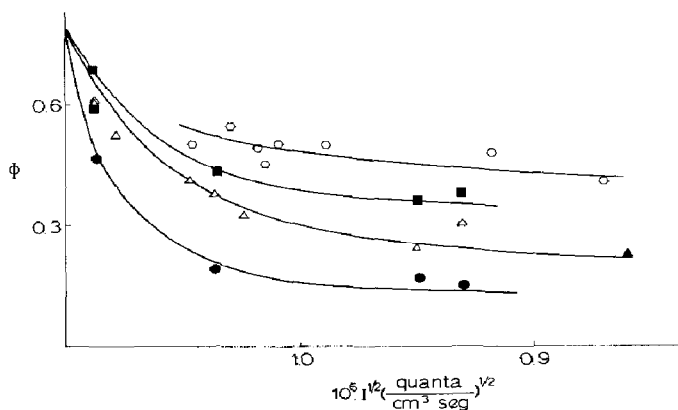$$\Phi_{iPr} = 2\ \Phi_{C_6H_{14}} + \Phi_{C_4H_{10}} + \Phi_{C_3H_6} + \Phi_{C_3H_8} \tag{2}$$

Fig. 4. Effect of absorbed intensity on the photolysis of methyl butanone at $60°C$. Total pressure = 10 Torr: ●, Φ_{Me}; ■, Φ_{iPr}; △, Φ_{CO}; ▲, Φ_{CO} from ref. 7. Total pressure = 200 Torr: ○, Φ_{CO}.
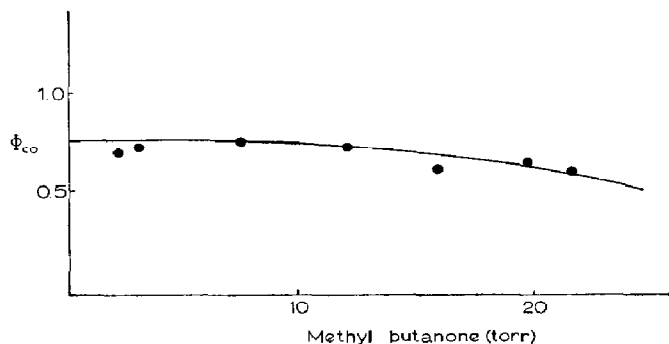
Fig. 5. Φ_{CO} as a function of methyl butanone pressure. Temperature $=$ 60°C; total pressure $=$ 400 Torr.

No attempt was made to measure other reaction products (*i.e.* biacetyl, acetone, acetaldehyde).

The effect of added azomethane upon Φ_{CO} is shown in Fig. 6. The effect of 1,3-butadiene upon Φ_{CO} has been reported elsewhere[13].

The quantum yield of *cis* to *trans* isomerization of 1,3-pentadiene was also employed to obtain the triplet quantum yield. Since the decay ratio of the ketones can be assumed to be similar[14], we find that under conditions of equal absorption:

$$\Phi_{3p} = \Phi_{3\,\text{acetone}} \frac{(R_{trans}) \text{ methyl butanone}}{(R_{trans}) \text{ acetone}} \tag{3}$$

where

Φ_{3p} measures the quantum yield of pentadiene triplets obtained in the photolysis of methyl butanone/*cis*-pentadiene mixtures;

R_{trans} is the rate of *trans*-isomer production. (The value for acetone is that obtained at "infinite" *cis*-pentadiene.)

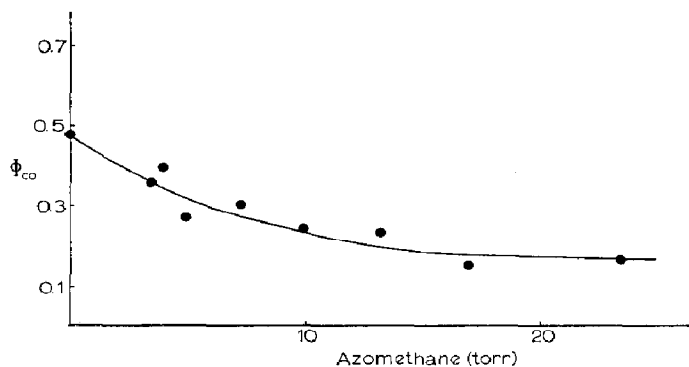$\Phi_{3\,\text{acetone}}$ is the quantum yield of acetone triplets.

Fig. 6. Effect of added azomethane on photolysis of methyl butanone at 60°C. Total pressure $=$ 100 Torr; absorbed intensity $=$ 0.2 $\times$ 10^{12} quanta cm^{-3} s^{-1}.

Values of Φ_{3P} obtained in the gas phase are shown in Fig. 7. The total pressure was kept constant (70 Torr) by adding benzene. Values of Φ_{3P} were also obtained in n-hexane solutions with 1,3-pentadiene concentrations ranging from 10^{-2} to 10^{-1} M. The quenching of the singlet state can be disregarded at these concentrations[16]. The value of Φ_{3P} obtained at "infinite" diolefin concentration was 0.82 ± 0.05. This value can be equated to the quantum yield of methyl butanone triplets. The lack of monochromacity of the light employed introduces only a small error since shorter wavelengths were completely absorbed and longer wavelengths present contribute insignificantly to the total absorbed intensity. Furthermore, the relative extinction coefficients change only moderately with wavelength.
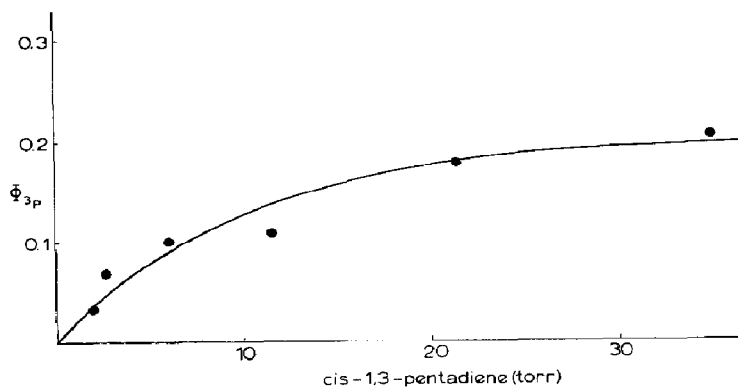
Fig. 7. Photolysis of methyl butanone: quantum yield of 1,3-pentadiene triplets. Temperature = 30°C; total pressure = 70 Torr (benzene added).

Values of the quantum yields of biacetyl triplets sensitized by methyl butanone under different experimental conditions are shown in Figs. 8 and 9.
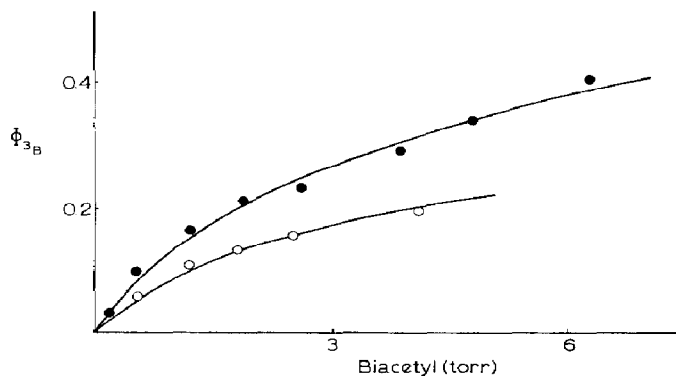
Fig. 8. Photolysis of methyl butanone: Φ_{3B} change with biacetyl pressure. Temperature = 25°C. O, 26.6 Torr methyl butanone; ●, 26.6 Torr methyl butanone plus 480 Torr propane.

Fig. 9. Photolysis of methyl butanone: Φ_{3B} change with propane pressure. Biacetyl pressure = 2 Torr; methyl butanone pressure = 27 Torr; temperature = 25°C.

DISCUSSION

Our experimental results can be rationalized by a mechanism similar to that proposed for acetone[2] and 3-pentanone[3]. This mechanism comprises reactions (4) to (17):

$$
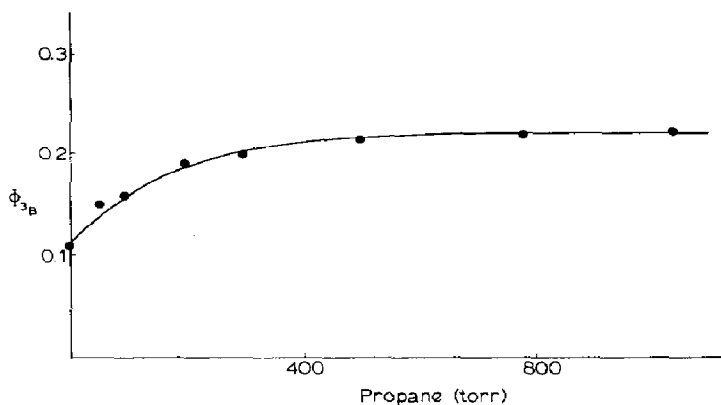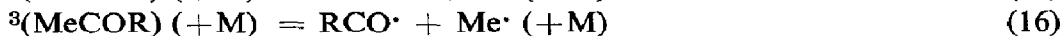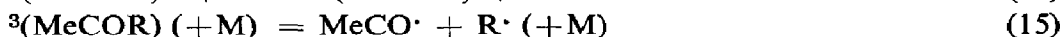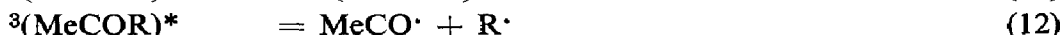\begin{array}{llr}
\text{MeCOR} + h\nu & = {}^1(\text{MeCOR})^* & (4) \\
{}^1(\text{MeCOR})^* & = \text{MeCO}^{\cdot} + \text{R}^{\cdot} & (5) \\
{}^1(\text{MeCOR})^* & = \text{RCO}^{\cdot} + \text{Me}^{\cdot} & (6) \\
{}^1(\text{MeCOR})^* + \text{M} & = {}^1(\text{MeCOR}) + \text{M} & (7) \\
{}^1(\text{MeCOR}) & = \text{MeCO}^{\cdot} + \text{R}^{\cdot} & (8) \\
{}^1(\text{MeCOR}) & = \text{RCO}^{\cdot} + \text{Me}^{\cdot} & (9) \\
{}^1(\text{MeCOR}) & = \text{MeCOR} & (10) \\
{}^1(\text{MeCOR}) & = {}^3(\text{MeCOR})^* & (11) \\
{}^3(\text{MeCOR})^* & = \text{MeCO}^{\cdot} + \text{R}^{\cdot} & (12) \\
{}^3(\text{MeCOR})^* & = \text{RCO}^{\cdot} + \text{Me}^{\cdot} & (13) \\
{}^3(\text{MeCOR})^* + \text{M} & = {}^3(\text{MeCOR}) + \text{M} & (14) \\
{}^3(\text{MeCOR}) \, (+\text{M}) & = \text{MeCO}^{\cdot} + \text{R}^{\cdot} \, (+\text{M}) & (15) \\
{}^3(\text{MeCOR}) \, (+\text{M}) & = \text{RCO}^{\cdot} + \text{Me}^{\cdot} \, (+\text{M}) & (16) \\
{}^3(\text{MeCOR}) & = \text{MeCOR} & (17)
\end{array}
$$

where several minor reactions have been neglected. We prefer this mechanism to that proposed by O'Neal and Larson[1] since the latter disagrees with some of the reported data (see following discussion regarding the effect of total pressure on triplet decomposition) and with the change in fluorescence quantum yield associated with a change in total pressure reported for 2-pentanone[15].

Methyl butanone

Data obtained in the photolysis of methyl butanone in the presence of 1,3-butadiene indicate that, at 60°C and at pressures higher than 50 Torr, Φ_{CO} < 0.05[13]. Such a low value shows that the production of "hot" acetyl radicals can be neglected and also that:

$$\Phi_6 + \Phi_9 + \Phi_{13} + \Phi_{16} < 0.05 \tag{18}$$

This result is in agreement with the data reported for other unsymmetric ketones[17,18]. The high selectivity can be related to the fact that $D(^iPr–COMe)$ is nearly 5 kcal lower than $D(Me–CO^iPr)$[19].

Secondary reactions must include all the reactions of the radicals produced. Φ_{Desc} can then be equated to Φ_{CO} if:

$$MeCO^{\cdot} (+M) = Me^{\cdot} + CO (+M) \tag{19}$$

is the only reaction of the acetyl radicals and there is no secondary production of carbon monoxide. Previous results in this system[7,20], as well as the value of Φ_{CO} obtained in the present work at higher temperatures, would indicate that there is no secondary carbon monoxide production under the present experimental conditions. The fact that, at 60°C and under all the conditions employed, Φ_{CO} is smaller than one, indicates either that Φ_{Desc} is lower than one or that there are other acetyl radical reactions (*i.e.* with other radicals, with the reaction products or with the parent compound or its impurities). The data shown in Fig. 5 would then provide a good estimate of Φ_{Desc} since extrapolation to zero ketone pressure also involves an extrapolation to zero absorbed intensity and to zero reaction products (the time of photolysis and the incident light intensity were kept constant). The value obtained in this extrapolation is 0.75 (400 Torr total pressure). From Fig. 4 it can be concluded that similar values can be obtained at lower pressures (down to 20 Torr). Furthermore, Fig. 4 also shows that at low intensities:

$$\Phi_{CO} \approx \Phi_{Me} \approx \Phi^{iPr} \tag{20}$$

suggesting complete acetyl radical dissociation and lack of secondary methyl butanone decomposition. The occurrence of an induced secondary decomposition has been postulated in order to take into account several unexpected results[7]. To test this point, we have carried out the photolysis of biacetyl (a source of acetyl radicals) and azomethane (a source of methyl radicals) in the presence of methyl butanone. Propylene could not be detected among the reaction products. In agreement with this, in the photolysis of methyl butanone we found that under all conditions:

$$\Phi_{C_3H_6} < \Phi_{C_2H_6} \tag{21}$$

We can conclude, then, that our results are similar to those obtained at shorter wavelengths[20], and that they can be interpreted with only "conventional" free radical reactions.

Values of Φ_{CO} obtained at higher intensities are similar to those reported by Zahra and Noyes[7]. On the other hand, these authors did not find an effect of intensity on Φ_{CO} although the effect could be masked by the simultaneous change in total pressure. The data given in Fig. 4 show a strong dependence of Φ_{CO} on absorbed intensity when all the other parameters are kept constant. This effect is larger at lower pressures due to the pressure dependence of reaction (19)[21].

As $\Phi_{Desc} \approx 0.75$, we can conclude that at 60°C and pressures higher than 20 Torr,

$$\Phi_{10} + \Phi_{17} \approx 0.25 \tag{22}$$

Furthermore, since increasing the population of thermal triplets (by increasing the total pressure) does not decrease the decomposition quantum yield,

$$k_{17}/(k_{15} + k_{17}) \approx 0 \tag{23}$$

and hence

$$k_{10}/(k_8 + k_{10} + k_{11}) \approx 0.25 \tag{24}$$

The sensitized biacetyl emission has been measured previously by Weir[11] and by Zahra and Noyes[7]. The intensity of this emission can be related to the quantum yield of:

$$^3(MeCO^iPr) + B = MeCO^iPr + {}^3B \tag{25}$$
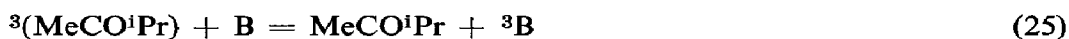
provided that there is neither singlet quenching nor photosensitized biacetyl decomposition. This last possibility seems unlikely since this effect was not observed in similar systems[3]. Furthermore, the pressure of biacetyl employed in the present work seems too low to significantly quench the singlet state[22]. Previously reported data[7,11], as well as the data reported in Fig. 8, indicate, then, that the quantum yield of reaction (25) is substantially lower than one even with 4 Torr of biacetyl. This result can indicate that either: (a) Φ_T (the quantum yield of thermalized triplets) is small and then Φ_{25} is low even at complete triplet quenching; or (b) higher biacetyl pressures are necessary to completely quench the thermal triplets.

Weir has interpreted his data in terms of possibility (a)[11]. He concluded that all the triplets were quenched with less than 1 Torr of biacetyl and that any further increase in emission was due to singlet quenching. Two states quenched at different rates were also indicated by the data of Zahra and Noyes, who employed oxygen as quencher[7]. If we assume that the state most easily quenched is the thermal triplet, both sets of data allow an estimation of the triplet lifetime (assuming that the rate constant for triplet quenching of methyl butanone is similar to that reported for acetone)[23]. The values obtained are 2.5×10^{-4} s (from ref. 7) and 5×10^{-6} s (from ref. 11). These values, besides being different by nearly two orders of magnitude, seem to be too long for this ketone (see following

discussion). On the other hand, the data given in Figs. 6, 7 and 8 can be interpreted in terms of only one quenchable state. The same conclusion can be obtained from the data shown in Fig. 5 of ref. 7. Furthermore, the pressures employed by Weir[11] do not seem high enough to quench the singlet state[22]. In agreement with this, the relative slopes of both curves of Fig. 8 at high biacetyl pressures are not compatible with singlet quenching under these conditions. We shall therefore treat our data assuming that only one state is being quenched under our experimental conditions. The data of Fig. 9 can be employed to find the change in Φ_T with total pressure. The proposed mechanism leads to:

$$\Phi_{3B} = \Phi_T \cdot k_{25} (B)/[k_{15} + k_{25} (B)] \tag{26}$$

The data of Fig. 9 allow an estimation of $P_{1/2}$ (the pressure needed to obtain $\Phi_T = 1/2 \, (\Phi_T)_\infty$). The value obtained was:

$$P_{1/2} \geqslant 29 \text{ Torr} \tag{27}$$

where the inequality takes into account the fact that reaction (15) can be pressure dependent.

Values of Φ_T can also be obtained from the data of Fig. 7 and also from the results obtained in the *cis* to *trans* isomerization of 1,3-pentadiene in n-hexane solution. These values have been included in Table 1.

The data shown in Figs. 6, 7 and 8 allow estimations of the thermal triplet lifetime. In order to evaluate Φ_T from the data given in Fig. 6, Φ_{CO} was extrapolated to infinite azomethane pressure. From the azomethane pressure needed to quench half of the "quenchable" carbon monoxide, and assuming that the rate constant of:

$$^3(MeCO^iPr) + \text{Azomethane} = \,^3(\text{Azomethane}) + MeCO^iPr \tag{28}$$

is similar to that reported for the quenching of acetone triplets[24], the value of τ_T given in Table 1 was obtained. This value has to be considered only as qualitative since the data were not obtained at "zero" absorbed intensity and some singlet quenching cannot be completely disregarded at high azomethane pressures.

Regarding the sensitized emission data, the proposed mechanism leads to:

$$\Phi_T/(\Phi_T - \Phi_{3B}) = 1 + k_{25} \, \tau_T \, (B) \tag{29}$$

The data obtained at 480 Torr plotted according to equation (29) have been included in Fig. 3 (Φ_T was taken as 0.80 since the data of Fig. 9 show that at this pressure most of the triplets are thermalized). The value of τ_T obtained was 2.5×10^{-7} s (k_{25} was taken as equal to the rate constant for the quenching of acetone triplets for biacetyl[3]). From Fig. 5 of ref. 7, a value of $\tau_T \approx 6 \times 10^{-7}$ s can also be obtained. The total pressure has not been reported but was probably in the 20 to 30 Torr range.

Similarly, if reaction (30) stands for:

$$^3(MeCO^iPr) + cisP = \,^3P + MeCO^iPr \tag{30}$$

TABLE 1

Ketone	Φ_{Desc}	$k_8\tau_S$	$k_{10}\tau_S$	Φ_T	$P_{1/2}$ (Torr) Hot	$P_{1/2}$ (Torr) Thermal	$\tau_T \times 10^{-6}$ (S)	$k_{17}\tau_T$	$k_{16}\tau_T$ obs.	$k_{16}\tau_T$ calc.[a]	k_{15} s^{-1} (30°C)	ΔE_{15}[b] (kcal/mol)	ΔD[c] (kcal/mol)	k_{15}/k_{16} Exp.	k_{15}/k_{16} Calc.[d]
Acetone	0.28[e]	0[f]	0[f]	1.0[f]	3.5[g]	55[g]	200[h]	0.18[h]	0.82[h]	—	1.4×10^3[r]	—	—	—	—
Butanone	0.95[i]	0[j]	0[j]	1.0[j]	16.3[j]	<12	13[k]	0.95[j]	0.05[j]	0.04	6.9×10^4[l]	2.7	3	40[m], 21[n]	40, 20
Methyl butanone	0.75[o]	≤0.18, ≈0[o']	≤0.18, ≤0.25[o']	0.82[p], 0.30[p']	>29		0.12[q], 0.16[r], 0.23[s], 0.3[t], 0.6[v]	1.0	0	0.005	6×10^6	5.2	5	>20	10^8
Dimethyl butanone	0.51[w]	0.22	<0.49[w]	>0.33[w], <0.78[w]			10^{-4}	>0.42	<0.58	<10^{-1}	$\geq5\times10^9$	9.2	8.3		
3-Pentanone[x]	1.0	0.08	0	1.0	16.2	≪10	8	1.0	≈0	0.02	1.2×10^5	2.7	3		
2, 2, 4, 4-Tetramethyl pentanone[w]	0.71	0.31	<0.29	>0.4, <0.69			1.1×10^{-4}	>0.6	<0.4	<10^{-4}	$\geq6\times10^9$	9.0	8.3		
2,4-Dimethyl pentanone	1.0[z'], ~1.0[z']	≈0[z']									2.5×10^7[t]	5.2	5		

a Calculated assuming similar k_{17} for all ketones.
b Calculated assuming similar A_{15} for all ketones (for each R considered).
c $D(R–COR') – D$ (Me–COMe).
d Assuming $A_{15} = A_{16}$ and $E_{15}–E_{16}$ as obtained in (b).
e Ref. 1, 44° C, 65 Torr.
f Ref. 1, high pressure, 25° C.
g Ref. 1, 25° C.
h Ref. 1, 75 Torr, 25° C.

i This work, Fig. 1.
j This work, Fig. 10.
k This work, high pressure (Fig. 3).
l Assuming $k_{17}\tau_T = 0.1$ at 30° C.
m 100° C (ref. 18).
n 175° C (ref. 18).
o This work, Fig. 5.
o' Solution, low temperature (ref. 30).
p This work, n-hexane solution.
p' This work, 70 Torr, room temperature.

q This work, Fig. 11.
r This work, Fig. 6.
s This work, Fig. 3.
t Tri-n-propyl borane as quencher, extrapolated from low temperature data (ref. 30).
v Ref. 7, Fig. 5.
w Hexane solution, ref. 9.
x Ref. 3.
z Ref. 8, temperatures higher than 50° C.
z' Ref. 32, room temperature.

the proposed mechanism leads to:

$$\Phi_T/(\Phi_T - \Phi_{3_P}) = 1 + k_{30}\, \tau_T \,(cisP) \tag{31}$$

Our data, plotted according to eqn. (31), are shown in Fig. 11. If we take k_{30} equal to the value reported for acetone[25], a value of $\tau_T = 1.2 \times 10^{-7}$ s can be obtained. The similarity between the values obtained for τ_T renders support to the proposed mechanism.

Butanone

At 60°C and 200 Torr total pressure (20 Torr butanone plus propane) the Φ_{Desc} can be estimated as ~ 0.95 (see Fig. 1). On the other hand, this value has been estimated as 1.0 at temperatures higher than 100°C [6], and 0.35 at 48°C [5], although this last value can be affected by an incomplete acetyl radical dissociation. Furthermore, the low value reported by Cundall and Davies can also be partly due to the formation of significant amounts of biacetyl since the reaction times were extremely long. The data obtained in the present work indicate that:

$$k_{17}/(k_{15} + k_{17}) \leqslant 0.05 \tag{32}$$

and also that:

$$k_{10}/(k_8 + k_{10} + k_{11}) \leqslant 0.05 \tag{33}$$

at 60°C.

The data shown in Fig. 3 show that 2 Torr of biacetyl quenches practically all butanone triplets. The data shown in Fig. 2 can then be treated in a similar way to those employed with 3-pentanone[3]. From this treatment, which is shown in Figure 10, Φ_T at infinite pressure can be evaluated as 1.0 ± 0.05. This value is considerably higher than that reported by Cundall and Davies at 48°C, but the data reported by these authors are not enough to establish whether all triplets have been thermalized under the conditions where Φ_T has been evaluated[5]. The value of $(\Phi_T)_\infty$ reported in the present work implies that:

$$k_{10}\, \tau_S \approx k_8\, \tau_S \approx 0 \tag{34}$$

Furthermore, the data of Fig. 2 and 10 show that $P_{1/2}$ is nearly 16 Torr.

The Stern–Volmer plots shown in Fig. 3 allow estimation of the triplet lifetime. The values obtained were:

$$(\tau_T)_{400\ \mathrm{Torr}} = 13 \times 10^{-6}\ \mathrm{s} \tag{35}$$

and

$$(\tau_T)_{14\ \mathrm{Torr}} = 18 \times 10^{-6}\ \mathrm{s} \tag{36}$$

The difference between these values, although small, seems to be beyond our experimental error. The fact that τ_T is pressure dependent can be associated with
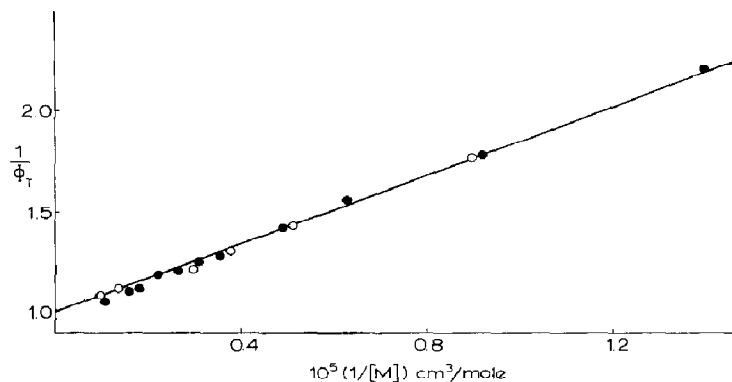
Fig. 10. Photolysis of butanone: Φ_T change with total concentration. Temperature = 25°C. ●, 12 Torr butanone; ○, 20 Torr butanone. Total concentration obtained from: (M) = (butanone) + (biacetyl) + 0.4 (propane).
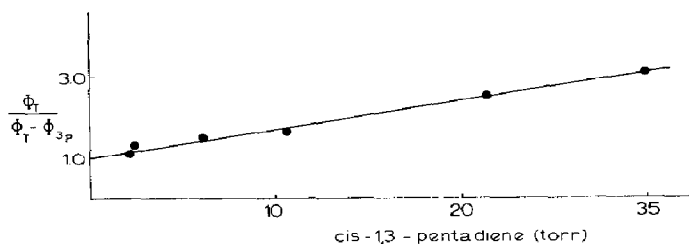

Fig. 11. Data of Fig. 7 plotted according to eqn. (31).

a pressure dependence of reaction (15). A similar result has been reported for acetone[1], but this effect was not observed in 3-pentanone[3]. Nevertheless, there is a striking difference between the present data and those reported by O'Neal and Larson[1], since we found that $P_{1/2}$ is higher than the pressure of medium fall-off for the thermal reaction. The results obtained with 3-pentanone also show that $P_{1/2}$ is considerably higher than the pressure of medium fall-off for the thermal decomposition of the triplet. This type of behaviour is that expected if the "hot" molecule has, on average, a higher energy than the average thermally decomposing molecule. On the other hand, O'Neal and Larson's data can only be explained if (a) there are two states involved; or (b) the "hot" molecule has a lower energy than the average thermally decomposing molecule.

This last possibility implies a very unusual situation and is incompatible with O'Neal and Larson's mechanism since Tables I and VIII of their work show that event at 2970 Å the "hot" species require lower pressures to be stabilized. Nevertheless, with this radiation

$$(\bar{E}_{hot})_{2970} \approx \bar{E}_{thermal} + 96 \text{ kcal} \tag{37}$$

and

$$(\overline{E}_{15}) = E_T + E_{15} + \overline{E}_{\text{thermal triplets}} \tag{38}$$

where

$\overline{}_{\text{hot}}$ = average energy of the "hot" molecule,

$\overline{}_{\text{thermal}}$ = average energy of the ground state molecule,

$\overline{E}_{15}$ = average energy of the molecules reacting through reaction (15),

E_{15} = activation energy for reaction (15),

$\overline{E}_{\text{thermal triplets}}$ = average energy of the thermalized triplets,

E_T = energy associated to the O–O absorption to the triplet state.

For acetone and other alkyl ketones E_T has been estimated as 79 kcal[1,26].

Furthermore, for acetone E_{15} has been evaluated as 9.6 kcal[1]. Hence we obtain that:

$$\overline{E}_{15} \approx 89 + \overline{E}_{\text{thermal triplets}} \tag{39}$$

Since $\overline{E}_{\text{thermal}} \approx \overline{E}_{\text{thermal triplets}}$, relations (37) and (39) would predict a higher pressure required to stabilize the "hot" triplets, suggesting that, at least with short wavelengths, the "hot" and the thermal decomposition must arise from different states (presumeably the "hot" singlet and the thermal triplet). The present data, obtained at 3130 Å, are not conclusive regarding the identity of the "hot" species although in previous work the reasons to prefer deactivation in the triplet manifold have been given[3]. This mechanism predicts that:

$$P_{1/2} < (P_{1/2})_{\text{thermal}} \tag{40}$$

if

$$E_S + \overline{E}_{11} < E_T + \overline{E}_{15} \tag{41}$$

and that:

$$P_{1/2} > (P_{1/2})_{\text{thermal}} \tag{42}$$

when

$$E_S + \overline{E}_{11} > E_T + \overline{E}_{15} \tag{43}$$

Since for aliphatic ketones the difference between the singlet and triplet is nearly 5 kcal[27], relation (40) can be expected to hold for acetone if:

$$\overline{E}_{11} < 4.6 + \overline{E}_{\text{thermal triplet}} \tag{44}$$

a relationship compatible with the low activation energies associated with the intersystem crossing. On the other hand, relation (42) can hold in the ethyl ketones due to the lower barrier associated with the thermal decomposition of the triplet (ref. 4 and following discussion).

The fact that the amount by which the energy of the hot molecule exceeds the threshold is small makes the thermal spread in energies more important than in most systems where "hot" species are produced. Furthermore, a unity efficiency in reaction (14) cannot be justified under these conditions[28]. Hence all treatments

which assume monoenergetic species can only be qualitative. Unfortunately, the precision of our experimental data does not justify more sophisticated treatments.

Considerations about Table 1

There is no information about the change in k_{10} with R and k_8 has been evaluated only for the t-butyl ketones[9]. On the other hand, it has been found that k_{11} decreases with an increase in α-methyl substitution[29]. The trend observed in Table 1 for the singlet behaviour can be explained in terms of the change of k_{11} and an increase in k_8 with α-methyl substitution. This increase in k_8 would be similar to the one discussed later for k_{15}.

In Table 1 there is no clear trend in Φ_{Dec} with the structure of the ketone. This can be related to the fact that, even at high pressures, the Norrish type I decomposition can arise from both the singlet and the triplet state. Furthermore, the data reported in solution have to be taken with some caution since the sequence of reactions:

$$^1(RCOR') = (RCO^\bullet + R') \tag{45}$$

and

$$(RCO^\bullet + R'') = RCOR' \tag{46}$$

could be computed as internal conversion[10].

$P_{1/2}$ values for the "hot" molecules

These values can be explained mainly by considering two effects: (a) the height of the barrier, and (b) the number of oscillators in the molecule.

These two effects can explain why $P_{1/2}$ for the "hot" molecules follows the order: acetone $<$ butanone $\approx$ 3-pentanone $<$ methyl butanone.

The similarity between the values for butanone and 3-pentanone must result from a compensation between a lower k and a smaller size in the butanone molecule. Acetone appears to be a very special case since in this molecule the "hot" species is barely over the threshold energy.

Values of k_{15}

The values of k_{15} reported in Table 1 clearly parallel the strengths of the broken bond. We can also see that if we assume similar A factors for all the triplet decompositions (similar A factors have been reported for acetone and 2,4-dimethyl pentanone[1,30]), the change in activation energy can be related to the change in bond dissociation energies. Furthermore, it can also be seen that only this factor is enough to account for the change in $k_{17}\tau_T$ with α-methyl substitution and the high selectivity in bond cleavage shown by the unsymmetric ketones.

From the preceding discussion we can conclude that most differences between the photochemical behaviour of these ketones can be related to the change in rate constant for the triplet cleavage associated to the α-methyl substitution. Qualita-

tively, the same conclusion can be reached from the data of Nicol and Calvert on n-propyl ketones[31], although in this work the different reaction paths could not be analyzed separately.

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