TEMPERATURE DEPENDENCE OF 4-METHYL-2-PENTANONE PHOTOCHEMISTRY

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Summary

The photochemistry of 4-methyl-2-pentanone in n-hexane solution has been investigated in the temperature range —5 to 74 °C. From the change in triplet quantum yield, triplet lifetime and product distribution with temperature it is concluded that: (a) the intramolecular hydrogen abstraction from the excited singlet state takes place with a pre-exponential factor higher than $10^{11.2}$ s^{-1} and with an activation energy higher than 3.5 kcal/mol; (b) the intramolecular hydrogen abstraction from the triplet state takes place with a rate constant that can be expressed as:

$$\log k = 12.8 - 7.9/\theta$$

(c) the Norrish type I reaction from the triplet state has a higher pre-exponential factor and activation energy than the intramolecular hydrogen abstraction; (d) the behaviour of the singlet biradical is nearly temperature independent but the fraction of triplet biradicals that give type II products increases with an increase in temperature.

Points (a) and (b) seem to indicate that both intramolecular hydrogen transfers take place by similar mechanisms involving the formation of a six-member ring activated complex.

Introduction

The photochemistry of alkyl ketones has been widely investigated and several comprehensive reviews have been published [1 - 4]. The photochemistry of those alkyl ketones that decompose photolytically by a Norrish type I mechanism is well understood, at least in the gas phase, in spite of most of the quantitative work reported having been carried out at a single temperature [5]. The only kinetic study carried out over a significant range of temperature is that of O'Neal and Larson on the photochemistry of acetone [6]. In this study, they obtained kinetic data concerning the triplet state and reported an unusually low pre-exponential factor for its thermal decomposition. The study of the unimolecular photofragmentation of ketones is far more limited in solution since both

cage recombination and photoreaction with the solvent hamper quantitative data being obtained. The photoreaction with the solvent is particularly important for long lived excited states (*i.e.* the acetone triplet) since in this case the lifetime is mainly determined by bimolecular interactions with the solvent [7]. For short lived states (either singlet or triplet) some quantitative data have been reported but there is not a sole interpretation of the results obtained [8, 9].

The photochemistry of alkyl ketones bearing γ hydrogen atoms that photodecompose mainly by a Norrish type II mechanism has been widely investigated. For these compounds there are several reports in the gas phase [10 - 14] and in solution [1 - 3, 13, 14]. The dependence of singlet and triplet states reactivities on structure has been established and the basic features of the reaction are well understood. A serious limitation of the data already reported is that most of them have been obtained at a single temperature.

The situation for those ketones in which both photodecomposition mechanisms are competitive is more confused. In the liquid phase, Guillet and collaborators have studied the effect of temperature on the product distribution for several linear ketones [15, 16], but no study of the change in triplet lifetime or triplet state quantum yield with temperature has been reported. The results obtained by Noyes and coworkers for the photolyses of 2-pentatnone and 2-hexanone indicate that, in the gas phase, the singlet state reaction prevails at high temperature but no quantitative evaluation of the rate parameters was attempted [11, 12]. The effect of temperature on the quantum yield of products was investigated by Nicol and Calvert for a series of n-propyl ketones [17]. Unfortunately, the singlet and triplet excited states reactions were not analyzed separately.

In the present work we have studied the photochemical behaviour of 4-methyl-2-pentanone over an 80 °C range of temperature in order to obtain the kinetic parameters of the photoreactions involved. The only result previously reported for this ketone is that of a single run carried out by Martin and Pitts at 120 °C which seems to indicate that 4-methyl-2-pentanone decomposes mainly by a Norrish type II process and that the quantum yield of the homolytic scission is nearly 0.15 [18]. The data reported do not allow determination of the excited state involved in these photodecompositions to be made.

Experimental

All photolyses were carried out on samples contained in degassed, sealed 0.6 cm o.d. Pyrex tubes. These were held in the turntable of a thermostated "merry-go-round" apparatus at the side of which was a 125 W medium-pressure mercury lamp. The intensity of the light was varied by introducing wire screens in the light path.

Actinometries were carried out with matched absorbances. Extinction coefficients of the ketones employed were determined in the 3030 to

3150 Å region and at different temperatures. These relative values show very little sensitivity to wavelength changes in the region considered.

Triplet quantum yields were obtained from the sensitized *cis—trans* isomerization of 1,3-pentadiene.

After each photolysis, acetone, isobutane and the unresolved 1,3-pentadiene mixture were measured by gas—liquid chromatography (g.l.c.) using 15% Apiezon L on a Chromosorb G column. The quantum yield of *cis—trans* isomerization of 1,3-pentadiene was determined using β,β'-oxidipropionitrile on a Chromosorb G column held at 0 °C.

The commercial samples of 2-pentanone (B.D.H.), acetone (Hopkin & Williams), 2-heptanone (Hopkin & Williams), 2-octanone (Hopkin & Williams), 1,3-pentadiene (Fluka), n-hexane (Merck), diethylamine (Fluka) and iso-octane (Merck) were used without purification but the 4-methyl-2-pentanone (Hopkin & Williams) was carefully distilled. The purity of the compounds employed was higher than 99% (determined by g.l.c.) on an Apiezon L column.

Results

Triplet state lifetime

The triplet state lifetime of 4-methyl-2-pentanone in n-hexane was determined by selective quenching of its triplet state with 1,3-pentadiene. The extent of the triplet state quenching was evaluated from the change in the quantum yield of acetone. When 1,3-pentadiene is added to 4-methyl-2-pentanone (K), the yield of acetone decreases until it reaches a constant value (*i.e.* at 25 °C the acetone quantum yield remains nearly constant when the 1,3-pentadiene concentration changes from 0.05 to 1 M). This behaviour, which is similar to that shown by other aliphatic ketones [1, 4, 19], indicates that all triplet states have been selectively quenched [20].

A modified Stern—Volmer plot was used to evaluate the triplet state lifetime. These plots are shown in Fig. 1 where $(\Phi_A^0 - \Phi_A^\infty)/(\Phi_A - \Phi_A^\infty)$ is given as a function of the quencher concentration (Φ_A^0 is the quantum yield of acetone obtained without added quencher and Φ_A^∞ is the one obtained at total triplet quenching). Similar results were obtained at the other temperatures investigated. All data were obtained at low conversion (less than 3%) and low 4-methyl-2-pentanone concentration (less than 0.1 M) in order to avoid significant quencher consumption [13]. In all runs the 1,3-pentadiene concentration was determined after the photolysis. In those cases where the value obtained after the photolysis was different to the initial concentration, an average value was used. All runs in which the quencher consumption was over 30% were not considered.

The slope of the plots shown in Fig. 1 are equal to $(k_Q \tau_T)$. The values obtained are shown in Table 1.

Triplet quantum yield

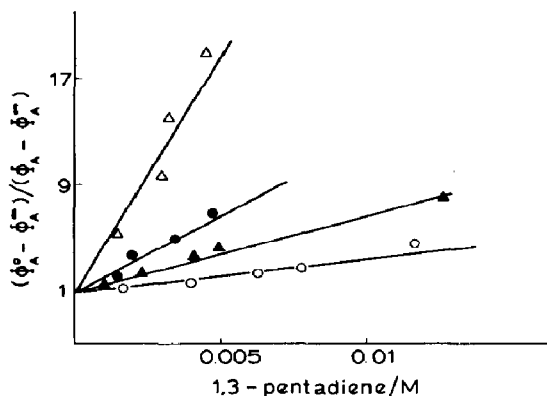The triplet quantum yield (Φ_T) was obtained from the sensitized *cis* to

Fig. 1. Plot of $(\Phi_A^0 - \Phi_A^\infty)$ against 1,3-pentadiene concentration: △, 268 K; ●, 293 K; ▲, 314 K; ○, 344 K.

TABLE 1

Experimental data

Temperature/K	$k_Q\tau_T/M^{-1}$ $\times 10^{-3}$	Φ_T [a]	Φ_A^S [b]	Φ_A^T [c]	$\Phi_{isobutane}$ [d]
268	3.44	0.88 ± 0.05	0.025	0.19	—
291	1.46				
293	1.26	0.78 ± 0.03	0.031	0.18	0.0085
314	0.57	0.70 ± 0.03	0.047	0.16	0.014
333	0.26	0.61 ± 0.03	0.058	0.15	0.028
344	0.19	0.55 ± 0.03	0.065	0.15	0.032
349	—	0.52[e]	0.073	0.14	0.034

[a] From the *cis—trans* isomerization of 1,3-pentadiene ($\Phi_T = 1.0$ for acetone is taken as a reference).
[b] The yields are accurate to ± 15%.
[c] The yields are accurate to ± 7%.
[d] The yields are accurate to ± 10%.
    The errors given are based on the precision of the measurements and their reproducibility. The error introduced by the actinometry is not included.
[e] Assumed value.

trans isomerization of 1,3-pentadiene. Acetone was employed as actino-meter and for this compound the triplet quantum yield was assumed to be 1 over all the range of temperatures investigated [2, 6, 21]. The values obtained are included in Table 1. A similar decrease in the triplet quantum yield with increasing temperature has been recently reported for 2-hexanone [22].

Acetone quantum yield
    The acetone quantum yield was obtained from:

$$\Phi_A = [(A)_K/(A)_{K'}] \, (\Phi_A)_{K'} \tag{1}$$

where $(A)_K$ and $(A)_{K'}$ are the concentrations of acetone obtained when K and K' (2-heptanone or 2-octanone) were photolyzed under identical conditions. $(\Phi_A)_{K'}$ was taken as equal to 0.20 and assumed to be independent of temperature for both 2-heptanone and 2-octanone [16]. Both sets of results (employing 2-heptanone or 2-octanone as actinometer) gave similar results. The values obtained (which are the average of three determinations at each temperature) are given in Table 2. From these data it can be assumed that: Φ_A = 0.21 ± 0.02 over all the temperature range investigated. The same experimental method, applied to the photolysis of 2-pentanone, gave $(\Phi_A)_{2\text{-pentanone}}$ = 0.23 ± 0.02 over all the range of temperatures investigated (−5 to 69 °C). The result obtained at room temperature is then in agreement with the data previously reported [1, 23, 24].

The quantum yield of the type II reaction of 2-pentanone and 4-methyl-2-pentanone appears to be independent of temperature. This insensitivity of the quantum yield to temperature is typical of a number of aliphatic ketones [16, 17, 25].

The values of Φ_A obtained in the presence of a high 1,3-pentadiene concentration represent the type II quantum yield from the singlet state (Φ_A^S) and (Φ_A^T) was taken to be ($\Phi_A - \Phi_A^S$). The results are shown in Table 1. This Table clearly shows that the contribution of the singlet state increases with temperature.

TABLE 2

Acetone quantum yield

Temperature/°C	Φ_A
−5	0.19 ± 0.02
20	0.21 ± 0.01
40	0.23 ± 0.02
69	0.20 ± 0.01

The Norrish type I reaction

Isobutane is the alkane formed from the type I break followed by hydrogen abstraction. At the lower temperatures the isobutane quantum yield decreased with increasing light intensity. This intensity dependence was attributed to a loss of isobutyl radicals in secondary reactions other than hydrogen abstraction (*i.e.* combination or disproportionation). In order to evaluate Φ_I from the value of $\Phi_{\text{isobutane}}$ we used two methods: (i) $\Phi_{\text{isobutane}}$ was extrapolated to "zero" light intensity; and (ii) iso-octane (a source of "weak" tertiary carbon–hydrogen bonds) was added to the reaction mixture. The iso-octane (0.5 to 1.0 M) was not able to quench the excited ketone since Φ_A remained unchanged.

Low light intensities and high iso-octane concentrations increased $\Phi_{\text{isobutane}}$ to a constant value (the values obtained by the two methods were similar). The values of $\Phi_{\text{isobutane}}$ so obtained have been included in Table 1.
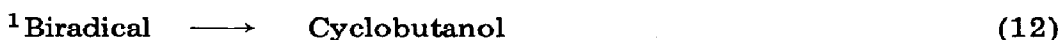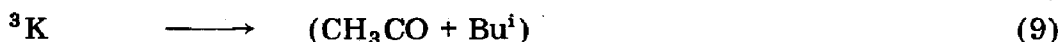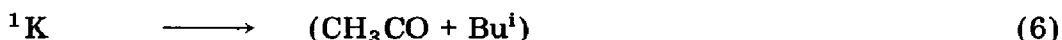
1,3-Pentadiene cannot be used to determine the excited state from which the type I reaction products originate since the isobutyl radicals readily add to the diolefin. We then used diethylamine as a selective quencher of the excited triplet state (when the isobutyl radicals react with the amine, isobutane will be produced and $\Phi_{isobutane}$ can still be used to estimate Φ_I). At concentrations lower than 0.1 M diethylamine is a selective quencher of 2-pentanone triplets [26]. The change in Φ_A with diethylamine concentration obtained using 4-methyl-2-pentanone indicates that the same applies for the triplet state of this ketone. Unfortunately, there is a significant quenching of the excited singlet state before all triplet states can be considered quenched [27]. When diethylamine is added to 4-methyl-2-pentanone, both $\Phi_{isobutane}$ and Φ_A decrease markedly and the relationship $\Phi_A/\Phi_{isobutane}$ remains constant or increases slowly. This result indicates that, at all temperatures:

$$(\Phi^T_{isobutane})/(\Phi^S_{isobutane}) \geqslant (\Phi^T_A)/(\Phi^S_A) \tag{2}$$

At 20 °C (the lowest temperature at which the isobutane could be measured) eqn. (2) indicates that less than 12% of the isobutane arises from the singlet state. Then, we have that, at this temperature, $\Phi^S_{isobutane} \leqslant 10^{-3}$. At 70 °C, the quantum yield of isobutane arising from the singlet can be estimated as less than 0.01.

Discussion

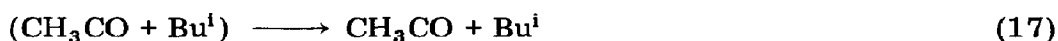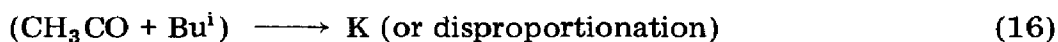The photochemistry of 4-methyl-2-pentanone in n-hexane solution can be represented by eqns. (3) to (15):

$$K + h\nu \longrightarrow {}^1K \tag{3}$$

$$^1K \longrightarrow K \tag{4}$$

$$^1K \longrightarrow {}^1Biradical \tag{5}$$

$$^1K \longrightarrow (CH_3CO + Bu^i) \tag{6}$$

$$^1K \longrightarrow {}^3K \tag{7}$$

$$^3K \longrightarrow {}^3Biradical \tag{8}$$

$$^3K \longrightarrow (CH_3CO + Bu^i) \tag{9}$$

$$^1Biradical \longrightarrow K \tag{10}$$

$$^1Biradical \longrightarrow A + C_3H_6 \tag{11}$$

$$^1Biradical \longrightarrow Cyclobutanol \tag{12}$$

$$^3Biradical \longrightarrow K \tag{13}$$

$$^3Biradical \longrightarrow A + C_3H_6 \tag{14}$$

$$^3Biradical \longrightarrow Cyclobutanol \tag{15}$$

where phosphorescence, fluorescence and α cleavage to methyl and Bu^iCO radicals have been neglected [1, 5, 17]. Furthermore, the possibility of

photoreduction by the solvent can be neglected under most of our experimental conditions since: (i) photoreduction of 2-pentanone triplets by n-hexane is a borderline reaction [13, 24] and 4-methyl-2-pentanone has a shorter triplet lifetime (see following discussion); (ii) photoreduction of acetone triplets by n-hexane has a rate constant of approximately $1.8 \times 10^5 \ M^{-1} \ s^{-1}$ at 23 °C [7]. Since this is a "radical like" reaction, an A factor of 10^8 - 10^9 $M^{-1} \ s^{-1}$ can be assumed [28], leading to an activation energy of nearly 5 kcal. Since the activation energy for the photoreactions of ^3K are considerably higher (see following discussion) the importance of photoreduction by the solvent will decrease at higher temperatures. This conclusion is in agreement with data obtained on the photoreduction of ^3K by cyclohexane [29]. Then we can conclude that only at the lowest temperature studied in the present work (−5 °C) photoreduction could contribute to the triplet state lifetime of 4-methyl-2-pentanone.

Photoreduction by the parent ketone has also been neglected. This assumption is supported by the lack of dependence of the results upon 4-methyl-2-pentanone concentration.

Secondary reactions which are relevant to the following discussion are:

$$(CH_3CO + Bu^i) \longrightarrow K \ (or \ disproportionation) \tag{16}$$

$$(CH_3CO + Bu^i) \longrightarrow CH_3CO + Bu^i \tag{17}$$

At low intensities (or in the presence of a reactive RH) the only reaction of Bu^i radicals to be considered is:

$$Bu^i + RH \longrightarrow isobutane + R \tag{18}$$

where RH can be the solvent, 4-methyl-2-pentanone, iso-octane or diethylamine.

Singlet state reactions

The small amount of isobutane obtained from the singlet state indicates that the Norrish type I reaction is a minor process and, therefore, this reaction can be disregarded in the following discussion. The absence of Norrish type I reaction from the singlet state is in agreement with previous work on aliphatic and cyclic ketones [3, 30]. Then, we shall consider only the singlet reactions leading to ^3K, K, cyclobutanol and acetone plus propylene. The present results can be explained by two alternative mechanisms: (a) there are a "concerted" and a "biradical" reaction that take place in parallel, or (b) all the photophysical and photochemical pathways involve the formation of a singlet biradical that can further react before geometrical equilibration [1, 13]. The present results cannot distinguish between these two possibilities but for simplicity we shall assume that all the reactions go through a biradical disregarding the occurrence of reaction (4). We have then that:

$$\Phi_T = k_7 / (k_5 + k_6 + k_7) \tag{19}$$

and, since $k_6 \ll (k_5 + k_7)$ eqn. (19) can be rearranged to:

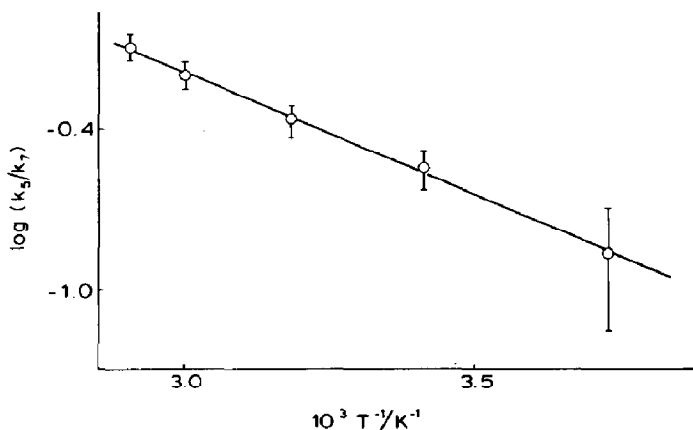$$k_5 / k_7 = (1/\Phi_T) - 1 \tag{20}$$

Fig. 2. Plot of log (k_5/k_7) against the reciprocal of temperature. [Values of (k_5/k_7) from eqn. (20).]

The values of log (k_5/k_7) obtained by introducing the values of Φ_T given in Table 1 in eqn. (2) are plotted against the inverse of temperature in Fig. 2. From this Figure we obtain:

$$\log (k_5/k_7) = 2.5 - 4.2/\theta \tag{21}$$

where $\theta = 0.0046 \, T$. Equation (21) indicates that reaction (5) has an activation energy of $(4.2 + E_7)$ kcal/mol. The pre-exponential factor of reaction (5) can be estimated if we know k_7 at a given temperature. Since the values of the intersystem crossing rate constant for aliphatic ketones are almost independent of methyl substitution other than α [1, 24, 31, 32], we can assume that k_7 will be similar to that reported for the excited singlet state of 2-butanone $(0.52 \times 10^9 \, M^{-1} \, s^{-1})$ [31]. This assumption leads to:

$$\log A_5 = 11.2 + 0.75 \, E_7 \tag{22}$$

Since E_7 is probably small [2, 33], it can be concluded that the pre-exponential A factor for the singlet reaction is similar to the one reported for the intramolecular hydrogen abstraction of aromatic ketones [34, 35], and it is compatible with the one expected for an adiabatic reaction that takes place through a six-member ring activated complex [36].

The value assumed for k_7 leads to: $(k_5)_{20\,°C} = 1.4 \times 10^8 \, M^{-1} \, s^{-1}$.

This value can be compared with that of 2-pentanone. For the triplet quantum yield of 2-pentanone the values previously reported are 0.63 (n-hexane solution [24]) and 0.81 (benzene solution [4]). We have again determined this value under identical conditions to those used with 4-methyl-2-pentanone and we have obtained a value of 0.84 ± 0.03. At present, we cannot explain the difference between these values but it appears that most of the values reported by Yang's group are rather low [4]. If we take for 2-pentanone the 0.84 value and assume that k_7 for this compound is similar to the one reported for 2-butanone, we conclude that: $(k_5)_{2\text{-pentanone}} = 1.0 \times 10^8 \, M^{-1} \, s^{-1}$ at 20 °C. This result is similar to the one obtained by

Dalton and Turro (1.5×10^8 M^{-1} s^{-1}) by a completely different method [37].

For 4-methyl-2-pentanone the singlet lifetime is estimated as 1.3×10^{-9} s. This value is compatible with the small influence of 1,3-pentadiene concentration upon the photoproducts arising from the singlet state found in the present work. If we assume that 1,3-pentadiene quenches ^{1}K at a rate similar to that reported for the quenching of the excited singlet state of acetone [38], we find that, even at the highest 1,3-pentadiene concentration employed, less than 12% of the excited ^{1}K molecules would react with the quencher.

^{1}Biradical reactions

If we define β_S as the fraction of molecules that, reacting from the singlet state, give type II products, we have that:

$$\beta_S = \Phi_A^S /(1 - \cdot\Phi_T) \tag{23}$$

The values of Φ_S obtained are given in Table 3. Since for most aliphatic ketones [1, 39]: $k_{12} \ll (k_{10} + k_{11})$ and β methyl substitution is not expected to increase the cyclobutanol yield [40] the proposed mechanism leads to

$$\beta_S = k_{11} /(k_{10} + k_{11}) \tag{24}$$

The fact that β_S appears to be independent of temperature indicates that the difference in activation energy between reactions (10) and (11) is very small.

The value of β_S reported previously for 2-pentanone [13] can be recalculated taking 0.84 for the triplet quantum yield and 0.23 for the quantum yield of acetone. Then, applying eqn. (23) we obtain: $(\beta_S)_{2\text{-pentanone}}$ = 0.15. This value is similar to that presently reported for 4-methyl-2-pentanone. Thus, we can conclude that β methyl substitution does not modify the k_{11}/k_{10} ratio.

TABLE 3

Effect of temperature on the biradical behaviour

Temperature/K	β_S	β_T
268	0.22 ± 0.12	0.21 ± 0.02
293	0.14 ± 0.04	0.23 ± 0.02
314	0.14 ± 0.04	0.25 ± 0.03
333	0.15 ± 0.03	0.26 ± 0.04
344	0.14 ± 0.03	0.27 ± 0.04

Triplet reactions
Intramolecular hydrogen abstraction
The triplet lifetime is given by:

$$\tau_T = 1/(k_8 + k_9) \tag{25}$$

The proposed mechanism also leads to:

$$\Phi_I^T = \Phi_T \times k_8 / (k_8 + k_9) \tag{26}$$

and

$$\Phi_I^T = \Phi_{isobutane}^T / (1 - f) \tag{27}$$

where f is defined by:

$$f = k_{16} / (k_{16} + k_{17}) \tag{28}$$

By rearranging these equations we obtain:

$$k_8 = \tau_T^{-1} \left[1 + \frac{\dfrac{\Phi_{isobutane}^T}{1 - f}}{\Phi_T - \dfrac{\Phi_{isobutane}^T}{1 - f}} \right]^{-1} \tag{29}$$

Hence, to be able to obtain k_8 as a function of the temperature, τ_T, f and $\Phi_{isobutane}^T$ must be evaluated. Unfortunately, there is no simple way of evaluating f and its temperature dependence. In the application of eqn. (29), errors in the evaluation of f only introduce a small error in k_8 since, under all our conditions, the Norrish type I reaction is a minor process. Equation (28) indicates that, if k_{16} is assumed to be independent of temperature, f should decrease with temperature due to the increase in k_{17}. The temperature dependence of this rate constant will be similar to that of a diffusionally controlled rate constant and can be evaluated from the change in solvent viscosity with temperature [41]. The value of f at 20 °C can be taken as 0.3 from the data reported for the t-butyl ketones [8, 9]. Lewis and Magyar have reported a value of 0.6 for the cage recombination of the radicals produced in the photolysis of 2-phenyl propiophenone [42]. If we consider that the radicals produced are larger and the solvent used (benzene) is more viscous, this result is in qualitative agreement with our present assumption. The values of f employed in the estimation of k_8 are shown in Table 4. These values are in qualitative agreement with the results of Golemba and Guillet which indicate that at 120 °C cage recombination is negligible [16].
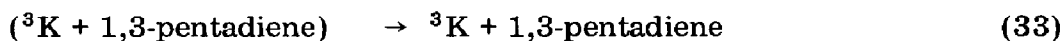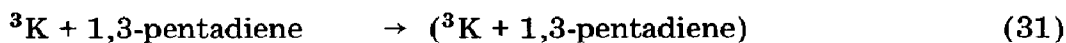
TABLE 4

Estimated values of f and k_Q

Temperature/K	f	$k_Q/M^{-1} s^{-1}$
268	0.38	9.2×10^9
291	0.32	1.07×10^{10}
293	0.31	1.08×10^{10}
314	0.26	1.19×10^{10}
333	0.21	1.29×10^{10}
344	0.20	1.34×10^{10}

In order to obtain τ_T from the data given in Table 1 the values of k_Q are needed. The rate of triplet quenching is given by:

$$k_Q = k_{31} \times k_{32}/(k_{32} + k_{33}) \tag{30}$$

and

$$^3K + 1,3\text{-pentadiene} \quad \rightarrow \quad (^3K + 1,3\text{-pentadiene}) \tag{31}$$

$$(^3K + 1,3\text{-pentadiene}) \quad \rightarrow \quad \text{quenching} \tag{32}$$

$$(^3K + 1,3\text{-pentadiene}) \quad \rightarrow \quad ^3K + 1,3\text{-pentadiene} \tag{33}$$

It has been found that the rate of reaction (30) appears to be independent of the ketone employed. Since the rates of reactions (31) and (33) are determined by the solvent, this result implies that the rate of reaction (32) is almost independent of the ketone. This is reasonable since the excitation is of the $n - \pi^*$ type and is localized in the carbonyl group [31, 44]. We can take then that

$$(k_Q)_{20\,°C} = 1.08 \times 10^{10} \ M^{-1} \ s^{-1} \tag{34}$$

and

$$k_{33} \approx 4k_{31} \tag{35}$$

from the work of Wagner and Kochevar on the quenching of the excited triplet state of valerophenone [41]. Furthermore, if we consider that the rate of reaction (32) (an exothermic energy transfer) is independent of temperature, the change in k_Q with temperature will be a consequence of the temperature dependence of k_{31} and k_{33}. This dependence can be evaluated from the change in solvent viscosity with temperature and then we can obtain values of k_Q at any other temperature. The values obtained (that are very little sensitive to the chosen value for k_{33}/k_{31}) are given in Table 4. The data in this Table show that the temperature dependence of k_Q is much smaller than that of k_{31}. A similar result has been experimentally obtained in the quenching of the triplet state of pyrimidine [45].

The values of k_8 obtained by applying eqn. (28) to our data are shown in an Arrhenius plot in Fig. 3. From this plot we obtain:

$$\log k_8 = 12.8 - 7.9/\theta \tag{36}$$

The data obtained for the intramolecular hydrogen abstraction is summarized in Table 5. From this Table it can be concluded that:

(1). $k^S > k^T$ for 2-pentanone and 4-methyl-2-pentanone. A similar result has been previously reported for other aliphatic ketones [1]. The results presented in this work show that this difference is a consequence of the lower activation energy of the excited singlet reaction.

(2). The values obtained for all the pre-exponential factors seem to indicate that the intramolecular hydrogen abstraction takes place through an adiabatic six-member ring activated complex. A common reaction path would predict, owing to their higher exothermicity, a lower activation
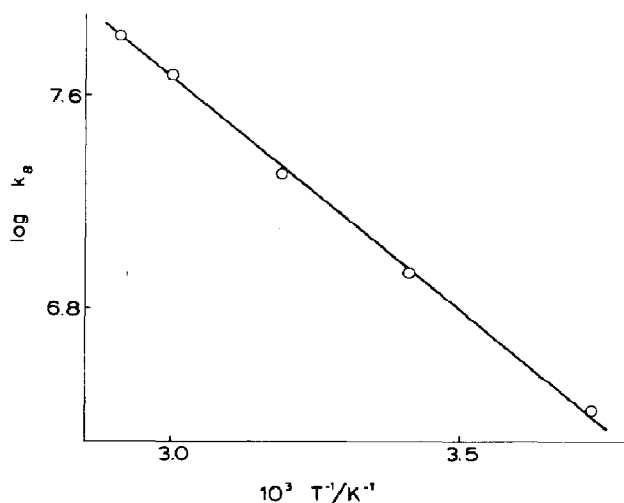
Fig. 3. Plot of log k_8 against the reciprocal of temperature. [Values of k_8 from equation (29).]

TABLE 5

Experimental data for the intramolecular H abstraction

Ketone	$k^S \times 10^{-8}$	$k^T \times 10^{-6}$	log A^S	log A^T	E^S	E^T
2-Pentanone	1.0	4[a]				
4-Methyl-2-pentanone	1.4	8.4	11.2	12.8	3.5	7.9
Butyrophenone[b]		8.5		12.1		6.9
2-Methyl butyrophenone[c]		20				

[a] Ref. 13.   [b] Ref. 34.   [c] Ref. 40.
Values of k and A are given in s^{-1}. Activation energies given in kcal/mol.

energy for the singlet reaction. For the triplet reaction we found that, for each possible reaction path, the A factor is approximately 10^{12} s^{-1}. This value is in fair agreement with that expected for a "radical like" intramolecular hydrogen transfer [46].

(3). Both the singlet and triplet state reactions are faster for 4-methyl-2-pentanone than for 2-pentanone. A similar effect is observed in the aromatic ketones and can be related to the increased reaction path degeneracy introduced by the methyl group. A similar conclusion has been reached from the study of asymmetric alkyl ketones [17].

(4). The aliphatic ketones are less reactive than the related phenyl ketones. This result, which is contrary to previous estimates that relate the rate of the intramolecular hydrogen abstraction to the triplet energy [46], is similar to that obtained for the intermolecular hydrogen abstraction [47]. The data in Table 5 would also indicate that the higher reactivity of butyrophenone is a consequence of its lower activation energy (although it has to be considered that the change in k_Q with temperature has been

estimated differently. The dependence of k_Q with temperature employed in the present work is similar to that proposed as "more probable" by Lewis [35]).

[3]*Biradical reactions*

If β_T is the fraction of the [3]biradicals that gives type II products, the proposed mechanism leads to:

$$\beta_T = k_{14}/(k_{13} + k_{14} + k_{15}) \qquad (37)$$

The values of β_T can be obtained using eqn. (38):

$$\beta_T = \frac{\Phi_A^T}{\Phi_T - \dfrac{\Phi_{isobutane}^T}{1-f}} \qquad (38)$$

The values obtained have been included in Table 3. It can be seen from this Table that $\beta_S < \beta_T$. A similar result has been obtained for 2-pentanone [13] and other aliphatic ketones [1]. The value of β_T reported for 2-pentanone at 20 °C can be recalculated (employing $\Phi_A = 0.23$ and $\Phi_T = 0.84$) as 0.26. This result is similar to that obtained for 4-methyl-2-pentanone. We can conclude that, regarding the production of type II products, the behaviour of [1]biradical and [3]biradical are similar in 2-pentanone and 4-methyl-2-pentanone. This result is in contrast with that found by Lewis and Hillard since these authors found that β methyl substitution decreases the yield of type II products in the photolysis of butyrophenone derivatives [48].

β_T increases with increasing temperature. This dependence of β_T with temperature has not been previously reported but should be present in all those ketones that, having β_S smaller than β_T, have a quantum yield of type II products which is not dependent of temperature [1, 16, 17].

Type I reaction

The values of $\Phi_{isobutane}$ are strongly dependent of temperature (see Table 1). The same result has been obtained by Bamford and Norrish in the photolysis of 4-heptanone in solution [49]. Since this dependence cannot be completely accounted for by a decrease of f with temperature, the present data indicate that Φ_I must increase with temperature. A similar conclusion has been reached previously by Golemba and Guillet for larger ketones [16].

From the values of $\Phi_{isobutane}$ shown in Table 1 and eqn. (2) it is possible to obtain estimates of $\Phi_{isobutane}^T$. A relationship between the intramolecular hydrogen abstraction and the carbon–carbon scission from the triplet state can then be obtained from:

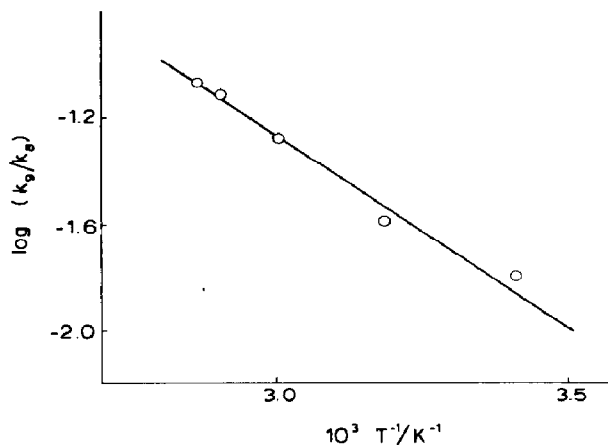$$k_9/k_8 = \frac{\Phi_{isobutane}^T/(1-f)}{\Phi_T - \Phi_{isobutane}^T/(1-f)} \qquad (39)$$

Fig. 4. Plot of log (k_9/k_8) against the reciprocal of temperature. [Values of (k_9/k_8) from eqn. (39).]

The values of k_9/k_8 obtained are plotted in Fig. 4. From this plot it can be seen that:

$$\log (k_9/k_8) = 3.1 - 6.5/\theta \tag{40}$$

Although the errors involved in eqn. (40) are high, we can derive from it several interesting conclusions:

(1). The importance of the Norrish type I reaction from the triplet state increases with temperature. This conclusion is in agreement with previous results in similar systems [16, 17]. On the other hand, it is interesting to note that for cyclic ketones the importance of the α cleavage decreases with increasing temperature [50]. Unfortunately, since the singlet and triplet state reactions were not analyzed separately in Coyle's work, the reason for this difference cannot be established.

(2). From the values of E_8 and A_8 previously determined, it can be concluded that: $E_9 \approx 14.4$ kcal/mol and $A_9 \approx 10^{16}$ s^{-1}.

This pre-exponential factor can be considered as "normal" for a bond-breaking unimolecular reaction but is considerably higher than that reported for the thermal decomposition of acetone triplets in the gas phase [6]. The difference between both values (nearly a 10^6 factor) is beyond our experimental error and would deserve further analysis.

(3). At 20 °C, the value of k_9 is nearly 1.5×10^5 s^{-1}. From previous work in related aliphatic ketones in the gas phase, a value of nearly 0.7×10^5 could be predicted, in reasonable agreement with the presently reported value.

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