Photolysis of 2-Methylcyclopentanone

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The photolysis of 2-methylcyclopentanone has been studied in the gas phase, mainly at 313 nm and at 100 °C. The major photolytic products are ethylene, propene, methylcyclobutane, *cis*- and *trans*-hex-4-enal, 2-methylpent-4-enal, and carbon monoxide. Product quantum yields were determined over a pressure range of 0·69 to 4·62 kN m^{-2} of pure ketone, and also with added nitrogen up to a total nitrogen pressure of 78·1 kN m^{-2}. These results suggested that the hydrocarbon products were formed by a higher energy pathway than the aldehydes and this was confirmed by carrying out photolyses at shorter wavelengths and at higher temperatures. A mechanism involving decomposition through a triplet state is discussed.

Two distinct mechanisms have been suggested to account for the products of the photochemical decomposition of cyclopentanones and cyclohexanones. One of these is a biradical mechanism, first suggested by Benson and Kistiakowsky [1] and also by Blacet and Miller.[2] The other suggestion is for a fully concerted decomposition originally favoured by Srinivasan.[3] Recently the biradical mechanism has received much support from a series of observations on the photolysis of *cis*- and *trans*-2,6-dimethylcyclohexanone [4] and *trans*-2,3-dimethylcyclopentanone [5] as well as 2-methylcyclohexanone.[6] In all cases the lack of stereospecificity in the products and in the first two cases the occurrence of *trans–cis*-isomerization in the reactants are most readily interpreted in terms of a biradical pathway.

The production of hydrocarbons and carbon monoxide by comparison with the alternative isomerization path leading to unsaturated aldehydes (or ketones) has been found to be favoured by low pressure, high temperature, and short wavelength radiation. All these factors suggest that the decomposition is either favoured by, or requires a higher energy species than the isomerization. Lee [7] has produced evidence in the cases of cyclopentanone and 2-^{3}H-cyclopentanone that the isomerization pathway takes place *via* a triplet state, and triplet lifetimes have been estimated for a number of cyclic ketones in solution.[8] It is however not at all clear whether the hydrocarbon products arise entirely, partly or not at all from excited singlet states.

A final problem in the photochemical reactions of cyclopentanones and cyclohexanones concerns the relative rates of different carbon–carbon bond rupture in unsymmetrically substituted derivatives. Thus it has been reported that in the photolysis of 2-methylcyclohexanone bond rupture takes place entirely between the C(1)–C(2) bond (there is no 2-methylhex-5-enal in the products) whereas in the photolysis of *trans*-2,3-dimethylcyclopentanone some C(1)–C(5) cleavage occurs as well as the more important C(1)–C(2) split.

In an attempt to resolve some of these problems we report the results of a study on the photolysis of 2-methylcyclopentanone.

EXPERIMENTAL

The apparatus was essentially as described previously.[5] Photolyses at 313 nm were carried out with a Bausch and Lomb high-intensity grating monochromator fitted with a super-pressure mercury lamp (Wotan HBO 200 W). A band-width of about 10 nm was used. After photolysis the reaction mixture was shared between the reaction vessel and an evacuated sample pipette and the pressure made up to about 13 kN m^{-2} with nitrogen. Mixtures were analysed by gas chromatography with a Perkin-Elmer F 11 instrument fitted with a gas sampling valve, heated glass sampling loop, and a flame ionization detector and used with a 3·4 m × 3·2 mm stainless steel column packed with 20% (w/w) cyanosilicone oil (XF1150) on 60—80 mesh (hexamethyldisilazane treated) Chromosorb W. With this column all important reaction products could be resolved although as usually operated ethylene and propene were not separated. Hydrocarbon products were eluted with the column operated at room temperature and with a carrier gas (N_2) inlet pressure of 69 kN m^{-2}. After the hydrocarbons had been eluted the temperature was rapidly raised to 70 °C and the nitrogen pressure to 137 kN m^{-2}. Calibration factors for hydrocarbons were assumed to be proportional to carbon numbers and this was checked for the particular conditions employed by use of a standard mixture of propane and n-pentane. The C_6 carbonyl compounds were all assumed to have the same calibration factors and these were related to those of the hydrocarbons by determining the relative responses of known mixtures of 2-methylcyclopentanone and cyclohexane.

The intensity of the radiation emerging from the reaction vessel was monitored with a phototube (Rank QVA 39). Signals from the phototube were amplified and displayed on a potentiometric recorder fitted with a ball and disc integrator. In order to minimise errors due to lamp instability photolyses were continued until the integration of the recorder trace showed that a definite number of quanta had entered the reaction vessel. This was maintained constant in all photolyses. The extent of photolysis varied from 0·56 to 0·33% over the pressure range used, and under these conditions any secondary photolysis of the carbonyl products will be quite unimportant. Acetone was used as a chemical actinometer and it was photolysed under exactly the same conditions as used for the 2-methylcyclo-

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[1] S. W. Benson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1942, **64**, 80.

[2] F. E. Blacet and A. Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4327.

[3] R. Srinivasan, *Adv. Photochem.*, 1963, **1**, 83 and references therein.

[4] B. Rickborn, G. O. Pritchard, and R. L. Alumbaugh, *J. Phys. Chem.*, 1965, **69**, 3225.

[5] H. M. Frey and D. H. Lister, *J. Chem. Soc. (A)*, 1970, 627.

[6] C. C. Badcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *J. Amer. Chem. Soc.*, 1969, **91**, 543.

[7] E. K. C. Lee, *J. Phys. Chem.*, 1967, **71**, 2804.

[8] P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, 1969, **91**, 4437.

pentanone.[9] * Methane, ethane, and unchanged acetone were analysed on a 3 m × 3·2 mm column packed with 80—100 mesh Poropak Q. Calibration factors were determined using standard mixtures.

The majority of photolyses were carried out at 313 nm and 100 °C but a few were at higher temperatures and some were at 280 nm. For these experiments the same light source was used. Experiments on the mercury photosensitized decomposition of the ketone used the 253·7 nm emission from a low-pressure mercury lamp. In the experiments with radiation shorter than 313 nm the relative yields of carbonyl compounds were much reduced, and to facilitate analysis photolyses were frequently allowed to proceed to higher conversions than those used in the bulk of the work.

Materials and Identification of Products.—2-Methylcyclopentanone was obtained from K and K Laboratories Inc., and purified by preparative g.l.c. to better than 99·95% pure. Acetone was Fison's ' Analytical reagent ' grade and was used without further purification. *cis*- and *trans*-Hex-4-enal were obtained by the gas-phase pyrolysis of 1-methallyl vinyl ether.

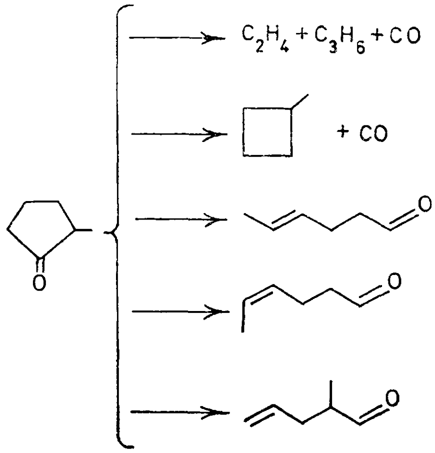
2-Methylpent-4-enal was prepared by the pyrolysis of allyl propenyl ether, which had been obtained by a transvinylation between ethyl propenyl ether and allyl alcohol. (We thank Dr. J. M. Brown of Warwick University for the sample of the ethyl propenyl ether.)

Products were identified by comparison of retention times on two different chromatographic columns with those of authentic samples.

RESULTS

Extinction coefficients were determined for both acetone and 2-methylcyclopentanone at *ca.* 313 nm. The instability of the photolytic source led to appreciable scatter on the Beer–Lambert plots and a least-squares analysis was carried out on a large number of points. The values for ε, the extinction coefficients, so obtained were: 3·57 ± 0·02 (lit.,† 2·86) for acetone and 8·74 ± 0·21 l mol^{-1} cm^{-1} for 2-methylcyclopentanone (both at 313 nm and 100 °C). The difference between the values for acetone is probably mainly due to the relatively wide band-pass used with the monochromator in this work which results in an appreciable fraction of wavelengths shorter than 313 nm entering the reaction vessel. However for our purpose the ' effective ' extinction coefficient with the photolytic apparatus is what is required.

The major products of photolysis of 2-methylcyclopentanone at 100 °C and 313 nm were found to be ethylene, propene, methylcyclobutane, 2-methylpent-4-enal, and *cis*- and *trans*-hex-4-enal. Carbon monoxide was also formed but not analysed: on the basis of carbon balance it was assumed to be formed in amounts equivalent to [½(ethylene + propene) + methylcyclobutane] (Scheme 1). Ethylene and propene were not normally resolved under the conditions employed, but periodic checks confirmed that they were always produced in almost exactly equimolar amounts. The ratio of total aldehyde to total hydrocarbon products, represented by RCHO/CO, showed a linear variation with the pressure of 2-methylcyclopentanone. A plot of RCHO/CO against the pressure of 2-methylcyclopentanone for 18 different ketone pressures in the range 0·69—4·62 kN m^{-2} yielded a good straight line of slope 0·1222 ± 0·0050 (kN m^{-2})$^{-1}$ and intercept 0·218 ± 0·016. (All errors quoted in this paper are standard deviations obtained by the normal least-squares analysis of the experimental results.) Values of RCHO/CO were also determined for photolyses carried out in the presence of added nitrogen. It was found that if a collision efficiency for nitrogen relative to methylcyclopentanone of 0·261 was assumed then the data obtained with added nitrogen fitted the ' ketone only ' line. This enabled results to be obtained at relatively high ' effective ' pressures of ketone. The results are plotted in Figure 1.



SCHEME 1

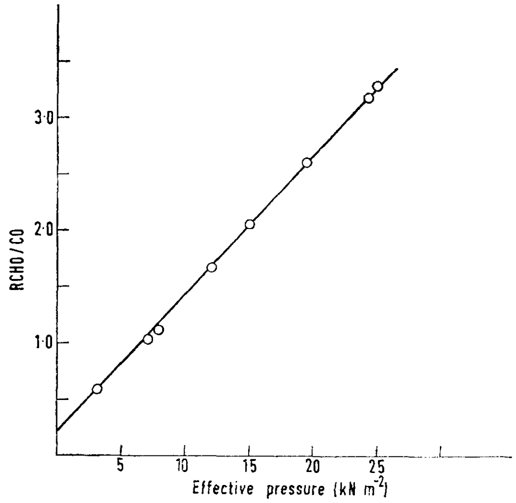


FIGURE 1 The ' ketone only ' line of the variation of RCHO/CO with pressure (points not shown). The points plotted are for ketone + added nitrogen, a collisional efficiency of 0·261 for nitrogen being assumed

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* The value for acetone at 100 °C and 313 nm of $\Phi(CO) = \Phi(CH_4)/2 + \Phi(C_2H_6) = 0{\cdot}716$ was taken, as the mean of results taken from ref. 9(*a*), and interpolated from the graph shown in ref. 9(*b*). Quantum yields in ref. 5 should be multiplied by a factor of 0·731, since Φ(CO) for acetone was originally taken to be 0·98 from ref. 9(*c*).

† The value of ε = 2·86 l mol^{-1} cm^{-1} for acetone at 25 °C and 313 nm is quoted in ref. 10(*a*); interpolation from the data in ref. 10(*b*) yields a value of ε = 3·15 l mol^{-1} cm^{-1} at 313 nm.

[9] (*a*) G. S. Pearson, *J. Phys. Chem.*, 1963, **67**, 1686; (*b*) R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.*, 1966, *A*, **290**, 563; (*c*) D. S. Herr and W. A. Noyes, *J. Amer. Chem. Soc.*, 1940, **62**, 2052.

[10] (*a*) P. Ausloos and E. Murad, *J. Phys. Chem.*, 1961, **65**, 1519; (*b*) C. W. Porter and C. Iddings, *J. Amer. Chem. Soc.*, 1926, **48**, 40.

Owing to the scatter in the results obtained for the amount of decomposition of acetone, the absolute values for the quantum yields are probably only accurate to ±10%. The relative values for the various products however are generally appreciably better than this as can be seen from Figure 2 where the quantum yields of total products, of aldehydes and of hydrocarbons are plotted as a function of methylcyclopentanone pressure. A plot of the reciprocal of the yield of total hydrocarbons ($1/\Phi_{CO}$) against pressure yielded a reasonably good straight line (see Figure 3) of slope 0·527 (kN m^{-2})$^{-1}$ and intercept 3·01.

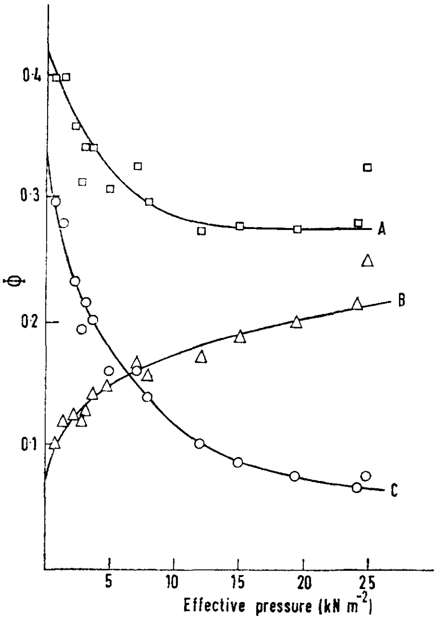

FIGURE 2 Variation with pressure of quantum yields of total products, Φ_{TOT} (A); of aldehydes, Φ_{RCHO} (B); and of hydrocarbons, Φ_{CO} (C)

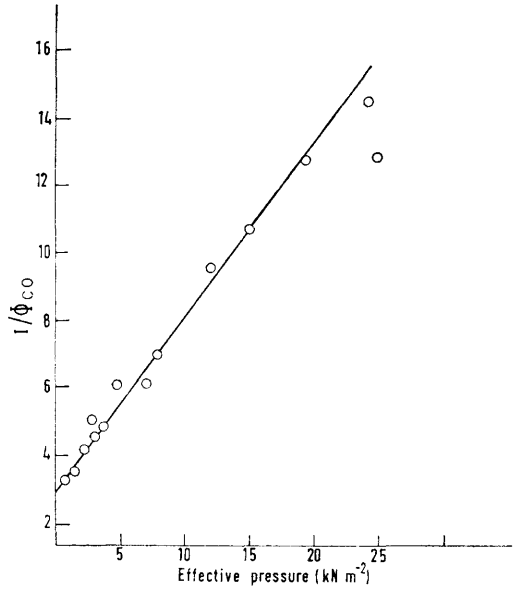

FIGURE 3 Variation of $1/\Phi_{CO}$ with pressure

Various product ratios, which correspond to ratios of different modes of decomposition, are given in Table 1. These are mean values obtained from results at 14 different pressures. While the ratios do show experimental scatter, they do not show any systematic trend with pressure. The effects of changing the temperature at which photolyses were carried out and also the wavelength of the photolytic radiation are shown in Table 2.

With photolysis at 253·7 nm the addition of a sevenfold excess of nitrous oxide resulted in a reduction in total yield of products from the decomposition of the methylcyclopentanone by a factor of 5 as compared with the estimated yield in its absence. Since nitrous oxide only competes for the 6^3P_1 Hg atoms and does not absorb at 253·7 nm then we conclude that more than 80% of the decomposition products formed under our experimental conditions at 253·7 nm result from mercury-photosensitized decomposition.

TABLE 1

Product ratios

(1)	(Ethylene + propene) : 2 × methylcyclobutane	1·855 ± 0·028
(2)	*trans*-Hex-4-enal : *cis*-hex-4-enal	1·221 ± 0·029
(3)	Total hex-4-enal : 2-methylpent-4-enal	14·8 ± 1·5

TABLE 2

RCHO/CO

T/°C	λ/nm	RCHO/CO at 2·07 kN m^{-2}	RCHO/CO at 8·48 kN m^{-2} *	Ratio (1) †	Ratio (3) †
100	313	0·420	1·255	1·855	14·8
146·5	313	0·249	0·482	1·871	16·3
100	280	0·142	0·223	1·885	10·8
100	253·7	0·0176	0·0223	1·813	11·5

* Effective pressure at 313 nm and 100 °C. † For definition see Table 1.

DISCUSSION

Our results are qualitatively similar to those obtained for the photolysis of *trans*-2,3-dimethylcyclopentanone.[5] The qualitative features of the photochemical decomposition of cyclopentanones can be explained on the basis of Scheme 2 for 2-methylcyclopentanone.

While it is possible to envisage a mechanism in which the olefins arise by the decomposition of vibrationally hot methylcyclobutane molecules, the experimental evidence in the present study, and even more strongly from other work, rules this out.[5,11] However the relative invariance of the ratio of olefins to methylcyclobutane with pressure and wavelength do indicate a common precursor. If this precursor is the substituted tetramethylene biradical, then two simple possibilities may be considered. If it is always formed with the same energy content then a constant ratio is to be expected. It does however appear unreasonable that the biradical should have an energy content which is independent of the experimental variables. The second possibility is that the cyclization of the biradical and its fission have the same (or very closely similar) energies of activation. Evidence on this may be obtained by a

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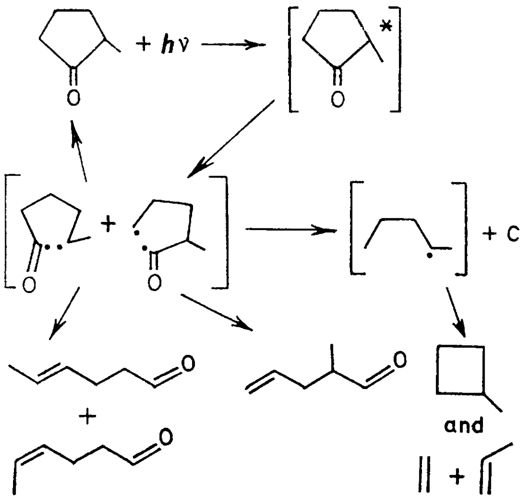
[11] R. Srinivasan, *J. Amer. Chem. Soc.*, 1959, **81**, 1546.

consideration of the rates of *cis–trans* isomerization compared with decomposition to olefins of 1,2-dimethylcyclobutane. These kinetic data have been analysed[12] on the basis of a biradical mechanism and it is concluded that cyclization and decomposition (to propene) have the same energy of activation. In the present situation, even if there is a small difference between these energies, this is likely to be masked by the excess of energy that the biradical will possess.



SCHEME 2

The hydrocarbon products are certainly produced by a higher energy pathway than the aldehydes: their production is favoured by a decrease in total pressure, or wavelength, or by an increase in temperature. The linear dependence of RCHO/CO on pressure up to at least 25 kN m^{-2} suggests that collisional deactivation occurs and this is supported by the plot of $1/\Phi_{CO}$ against pressure (Figure 3).

The formation of aldehydes in the photolysis of cyclic ketones has been related to a triplet precursor. Thus in the liquid-phase photolysis of cyclopentanones, aldehydes are the only products, and their formation is completely suppressed by triplet quenchers such as piperylene.[13] Further supporting evidence comes from studies on the benzene-photosensitised decomposition of cyclopentanone in the gas phase. This evidence for a triplet precursor for the aldehydes is convincing; a more difficult problem concerns the spin state of the hydrocarbon precursor. The simplest interpretation of the results obtained by mercury-photosensitized decomposition is that a triplet precursor may also yield hydrocarbon products. While there is evidence that some excited singlet species may be formed in systems of this kind[14] there is little reason to believe that such processes will predominate. Thus we believe there is very strong evidence that hydrocarbons can arise from a high energy triplet precursor; what is uncertain is whether any of the hydrocarbons arise directly from a singlet precursor. For simplicity we assume that all the products arise *via* triplet methylcyclopentanone but should further results indicate that some hydrocarbons in fact arise from a singlet ketone then the mechanism of Scheme 3 can readily be modified to encompass such a finding. Equations are labelled by their rate constants. S_1 and T_1 are respectively the first excited singlet and triplet species. Vibrational excitation is indicated by an asterisk and although several levels are certainly involved, only two are considered for simplicity.

2-Methylcyclopentanone (S_0) + $h\nu$

$$\begin{array}{rcl}
 & \longrightarrow & S_1{}^{*}\ I_{\text{abs}} \\
S_1{}^{*} & \longrightarrow & T_1{}^{*}\ (k_1) \\
[\text{M}] + S_1{}^{*} & \longrightarrow & S_1 + [\text{M}]\ (k_2) \\
S_1 & \longrightarrow & T_1\ (k_3) \\
S_1 & \longrightarrow & S_0 + h\nu'\ (k_f) \\
T_1{}^{*} & \longrightarrow & \text{hydrocarbons} + \text{CO}\ (k_4) \\
T_1{}^{*} & \longrightarrow & \text{RCHO (aldehydes)}\ (k_5) \\
T_1{}^{*} & \longrightarrow & S_0\ (\textit{via}\ \text{recyclization})\ (k_6) \\
[\text{M}] + T_1{}^{*} & \longrightarrow & T_1 + [\text{M}]\ (k_7) \\
T_1 & \longrightarrow & \text{RCHO}\ (k_8) \\
T_1 & \longrightarrow & S_0\ (\textit{via}\ \text{recyclization})\ (k_9)
\end{array}$$

SCHEME 3

The processes (k_6) and (k_9) permit a return to the ground-state ketone (though presumably initially highly vibrationally excited) by ring closure of the biradical. This process is well supported by analogy with the observation of *cis–trans*-isomerization in the 2,3-dimethylcyclopentanone photolysis and the close relationship between the quantum yield for *cis–trans* isomerization and for aldehyde formation in that system. Failure to observe phosphorescence from cyclopentanones in the vapour phase coupled with the known short lifetime of triplet cyclopentanones in solution allow us to neglect an appreciable deactivation by emission from the T_1 state. Fluorescence (k_f) is regarded as occurring only from S_1. A steady-state treatment of the mechanism yields the following relationships shown in Scheme 4.

$$\frac{[\text{RCHO}]}{[\text{CO}]} = \frac{k_5}{k_4} + \frac{k_8}{k_8 + k_9}\left\{\frac{k_2k_3(k_4 + k_5 + k_6)}{k_1k_4(k_3 + k_f)} + \frac{k_7}{k_4}\right\}[\text{M}] + \frac{k_8}{k_8 + k_9}\left\{\frac{k_2k_3k_7}{k_1k_4(k_3 + k_f)}\right\}[\text{M}]^2$$

$$\frac{1}{\Phi_{CO}} = 1 + \frac{k_5 + k_6}{k_4} + \left\{\frac{k_2(k_4 + k_5 + k_6)}{k_1k_4} + \frac{k_7}{k_4}\right\}[\text{M}] + \frac{k_2k_7}{k_1k_4}[\text{M}]^2$$

SCHEME 4

If $k_1k_4 \gg k_2k_7[\text{M}]^2$ over the pressure range studied, then plots of RCHO/CO and $1/\Phi_{CO}$ against pressure of ketone will be linear. At 313 nm and 100 °C this agrees quite well with the experimental results as shown in Figures 1 and 3. The extrapolations of these graphs to $[\text{M}] = 0$ yield the values $k_5/k_4 = 0{\cdot}22$ and $1 + (k_5 + k_6)/k_4 = 3{\cdot}01$ from which $k_4 : k_5 : k_6 = 4{\cdot}5 : 1{\cdot}0 : 8{\cdot}1$ [the

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[12] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866.

[13] P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, 1965, **87**, 4211.

[14] (*a*) D. C. Montague and F. S. Rowland, *J. Amer. Chem. Soc.*, 1969, **91**, 7230; (*b*) H. M. Frey and R. Walsh, *Chem. Comm.*, 1969, 158.

relative rates for the reaction of T_1^* to give hydrocarbons or aldehydes or to recyclise to (S_0) ketone]. The inequality $k_1k_4 \gg k_2k_7[M]^2$ may arise if either $k_4 \gg k_7[M]$ or $k_1 \gg k_2[M]$ or some combination of the two. We will consider the two extreme cases.

If $k_4 \gg k_7[M]$, then almost all collisional deactivation takes place in the singlet state, and under these conditions the slope of the graph of $1/\Phi_{CO}$ against pressure reduces to $k_2(k_4 + k_5 + k_6)/k_1k_4 = 0{\cdot}527$ (kN m^{-2})$^{-1}$ from which $k_1 = 5{\cdot}71\ k_2$ (s^{-1}). If we equate k_2 with the collision number (for our conditions *ca.* $6{\cdot}1 \times 10^7$ kN^{-1} m^2 s^{-1}) then $k_1 = 3{\cdot}5 \times 10^8$ s^{-1}. This value is reasonable, falling between values obtained for aromatic and aliphatic ketones. With such a value, the rate of intersystem crossing of the excited singlet to excited triplet will be nearly six times greater than the collision frequency at 1 kN m^{-2}. Even at the highest ketone pressures used in this work, the rate constants for the reactions of the excited triplet (k_4, k_5, and k_6) must all be larger than for collisional deactivation, which suggests a lower limit to $k_4 + k_5 + k_6$ of *ca.* $1{\cdot}5 \times 10^9$ s^{-1}. A value of this magnitude fits well with the results of Wagner and Spoerke [8] who studied the quenching of triplet cyclopentanones and cyclohexanones by piperylene, in the liquid phase. The rate constant for the decomposition of cyclopentanone was found to be $1{\cdot}1 \times 10^8$ s^{-1}. They also found that α-methyl substitution increased the corresponding rate constant in the case of triplet cyclohexanone by a factor of 14·3. Assuming that this factor can be transferred to the 5-membered-ring ketone, then we expect the value for 2-methylcyclopentanone to be *ca.* $1{\cdot}6 \times 10^9$ s^{-1}. (Note that this value would apply to T_1 in our mechanism, but it appears probable that T_1^* should decompose even more rapidly than T_1.)

The alternative extreme case which would lead to the experimentally observed linear relationships of RCHO/CO and $1/\Phi_{CO}$ with pressure requires $k_1 \gg k_2[M]$ over the pressure range studied. This implies that all effective deactivation occurs in the triplet state of the ketone. Equating k_7 with the collision frequency we then find that $(k_4 + k_5 + k_6) = 3{\cdot}5 \times 10^8$ s^{-1}. This value looks too small if we assume that the liquid-phase results of Wagner and Spoerke are equally applicable to the gas phase. We thus prefer the first mechanism.

Some additional evidence in support of this hypothesis was obtained by studying the effect of various pressures of *cis*-penta-1,3-diene on the photolysis of *trans*-2,3-dimethylcyclopentanone.[15] By measuring not only the effect of the added diene on the photolytic product yields, but also the amount of penta-1,3-diene that underwent *cis–trans* isomerization, it was possible to determine directly the fraction of excited singlets that underwent vibrational deactivation (k_2) compared with the fraction of triplets that were quenched. The penta-1,3-diene was found to be an efficient molecule in the first process, with a relative efficiency on a pressure-to-pressure basis of 0·8 compared with the ketone itself. While some *cis–trans* isomerization did occur the total amount was very small and analytical difficulties made a good quantitative estimation impossible. It was however possible to determine that far more excited ketone molecules underwent vibrational deactivation than quenching as a result of collision with the penta-1,3-diene. If the pentadiene is as efficient a quencher of triplets in the gas phase as in solution then these findings are only consistent with a relatively long-lived excited singlet, which can undergo vibration energy deactivation, and a short-lived triplet species.

The ratio *cis* + *trans*-hex-4-enal : 2-methylpent-4-enal, which was found to be 14·8 ± 1·5 : 1, may be taken to be a crude indication of the relative frequencies of breaking the C(1)–C(2) and the C(1)–C(5) bonds in forming an acyl-alkyl biradical. This assumes that once formed the two biradicals have equal probabilities of forming aldehydes compared with other reaction pathways. While this may not be strictly valid, we do not feel that this assumption is likely to produce a serious error. Further it might be argued that some differences might be expected in both the relative rates of cleavage of the two bonds and possibly also in the subsequent relative yields of aldehydes, depending on whether the biradical had as its precursor T_1^* or T_1. The insensitivity of the ratio to pressure, and also the results from the mercury-photosensitized decomposition and the use of 2800 Å radiation suggest that such an energy effect is relatively slight. While the split of the C(1)–C(2) bond is clearly favoured over that of the C(1)–C(5) bond, the observation of any 2-methylpent-4-enal at all is in marked contrast to the total absence of 2-methylhex-5-enal from the photolysis of 2-methylcyclohexanone.[4] In the case of 2-methylcyclohexanone, Rickborn *et al.*[4] estimate that the prevalence of C(1)–C(2) split over C(1)–C(6) must be greater than 50 : 1. We are unable to suggest a reason for this difference in behaviour, which cannot be simply related to the relative stabilities of the biradicals formed.

Both types of cleavage are postulated to occur in aliphatic ketones and a closely analogous situation occurs in the photolysis of ethyl isopropyl ketone. Unfortunately quantitative data about the relative importance of the reactions are not available for this compound.

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[15] H. M. Frey and I. C. Vinall, unpublished work.