

THE PHOTOLYSIS OF 3-PENTANONE

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SUMMARY

The photolysis of 3-pentanone has been re-investigated. It has been found that the decomposition quantum yield at 3130 Å is one over a wide range of experimental conditions (temperature from 30 to 100°C and pressure from 20 to 400 Torr). At 25°C the triplet quantum yield changes with total pressure from 0.31 at 9.2 Torr to 0.92 ± 0.10 at high total pressures. The main reaction of the thermalized triplet is its decomposition by a first order reaction over the whole pressure range studied. The triplet lifetime at 30°C has been estimated as 8×10^{-6} sec.

INTRODUCTION

The mechanism of the gas phase photolysis of aliphatic ketones has been widely studied¹. It is generally agreed that this type of system is one of the more thoroughly understood²; however, two more recent studies on acetone^{3,4} interpret the results obtained with the aid of two basically different mechanisms. Furthermore, the data available for other aliphatic ketones are generally much more limited. The gas phase photolysis of 3-pentanone has been studied by several workers^{5,6} and particularly by Weir⁷. We have re-studied this system in order to answer some of the remaining questions, namely: (a) the dependence of its photodecomposition quantum yield on total pressure and the effect of triplet quenchers upon this yield; (b) the triplet quantum yields, and (c) the triplet lifetime and the relative importance of the different paths for the removal of thermal triplets.

The present work involves a study of the effect of added biacetyl, 2,3-pentanedione, azomethane and propane on the photodecomposition quantum yield. The biacetyl phosphorescence sensitized by 3-pentanone has been also studied. Most of the experimental results were obtained at long wavelengths (3130 Å) and low temperatures (25 to 30°C) in order to minimize reactions from vibrationally hot states.

EXPERIMENTAL

3-Pentanone (Hopkins and Williams, Chem. Service or Eastman Chemicals) was used without purification other than careful degassing and trap-to-trap distillation in which only middle fractions were retained. Head, middle or tail fractions from different batches of reagents gave similar results.

Biacetyl (Eastman Chemicals) was degassed from a -70°C bath and kept in the dark. 2,3-Pentanedione (Eastman Chemicals) was treated in a similar way. Azomethane (Merk, Sharp and Dohme of Canada) was purified by trap-to-trap distillation. The only detected impurity, ethane, was eliminated by this treatment.

Photodecomposition studies

Light from a medium pressure Hg lamp was employed. To isolate the 3130 Å band, a chemical filter similar to that previously described⁸ was used. Metallic screens were employed to decrease the light intensity. The reagents were introduced in the reaction vessel (Pyrex, 310 cm³) from a higher pressure to improve the mixing. The products were examined by gas-liquid chromatography (g.l.c.).

Emission studies

Emission from biacetyl was measured in a standard Hilger and Watts fluorimeter. The reactants were introduced in a Pyrex glass tube, thoroughly degassed and sealed under vacuum. The 3130 Å band was isolated with an Ealing TFP interference filter. Measurements were carried out only after careful mixing of the reactants. A correction was introduced to account for the biacetyl absorption. To avoid the influence of remaining oxygen or impurities introduced with the inert gas, the readings were referred to those obtained when the mixture was irradiated with the 4350 Å line (isolated with a Kodak 547/2 plus a 558/6 and a Chance OB10 glass filters). The corrections introduced were always less than 15%. Furthermore by this method it was shown that the presence of 3-pentanone does not modify the quantum yield of biacetyl phosphorescence.

RESULTS

The absorption coefficient of 3-pentanone, relative to that of acetone, was determined at 3130 Å. It was found that, at room temperature, $\epsilon_{3\text{-pentanone}}/\epsilon_{\text{acetone}}$ was 1.20 ± 0.08 . This result is in disagreement with the value reported by Calvert and Pitts⁹ but is in line with other relative absorption measurements carried out in gas phase and in solution¹⁰. We have then taken that under our conditions $\epsilon_{3\text{-pentanone}}/\epsilon_{\text{acetone}}$ is equal to 1.2.

It is generally accepted that, at temperatures higher than 100°C , the carbon monoxide quantum yield can be taken as 1.0 at all wavelengths^{5,6}. Φ_{CO} at lower temperatures can then be obtained by employing 3-pentanone at 100°C as actino-

meter. From comparison with values reported for other ketones¹¹ it was assumed that the absorption coefficient increases by nearly 14% when the temperature changes from room temperature to 100°C.

Figure 1 shows the dependence of Φ_{CO} on light intensity at 30°C. All the results were obtained at a total pressure of 100 Torr. At low intensities, Φ_{CO} was equal to one. The same result was obtained at other pressures (20 to 400 Torr) over the temperature range studied.

The Φ_{CO} values obtained in the presence of azomethane and 2,3-pentanedione are shown in Fig. 2. The results are similar to those obtained by Weir⁷ employing biacetyl as quencher. Most of the quenchers employed show a plateau in the carbon

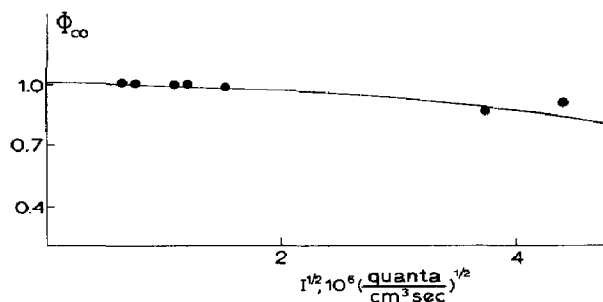


Fig. 1. Dependence of Φ_{CO} on light intensity at 30°C. 3-Pentanone pressure: 20 Torr; propane pressure: 80 Torr.

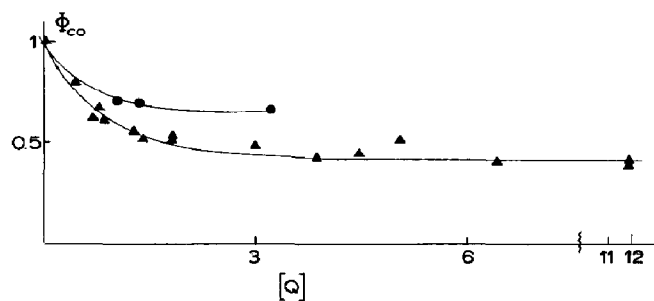


Fig. 2. Φ_{CO} as a function of added quencher at 30°C. ▲, Q = azomethane (concentration given in 10^{-8} mole/cm³), 3-pentanone pressure: 20 Torr, total pressure: 200 Torr (propane added as inert gas). ●, Q = 2,3-pentanedione (concentration given in 10^{-7} mole/cm³), total pressure: 20 Torr.

monoxide quantum yield. The Φ_{CO} in the plateau is a function of total pressure but is independent of the quencher employed. These results are shown in Fig. 3. The results obtained with biacetyl as quencher have been corrected by the small amount of carbon monoxide produced when this compound was photolyzed alone under similar conditions.

The photosensitized biacetyl phosphorescence is shown in Figs. 4 and 5. Figure 4 gives the phosphorescence intensity as a function of biacetyl pressure at

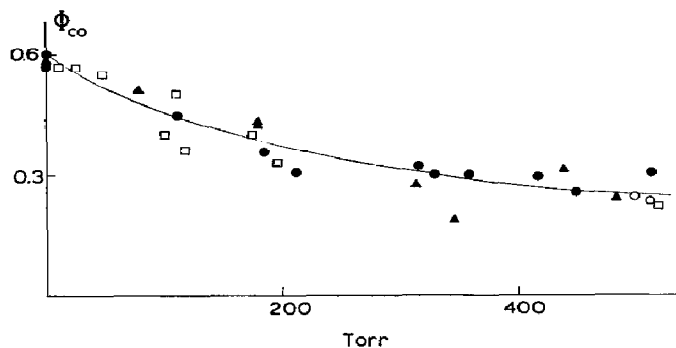


Fig. 3. Φ_{CO} at total triplet quenching as a function of added propane. Temperature: 30°C. \blacktriangle , Q = azomethane (2 Torr), 3-pentanone pressure: 20 Torr; \bullet , Q = 2,3 pentanedione (2.5 Torr), 3-pentanone pressure: 19.5 Torr, blank points have been displaced 100 Torr towards lower pressures; \square , Q = biacetyl (5 Torr), 3-pentanone pressure: 17 Torr.

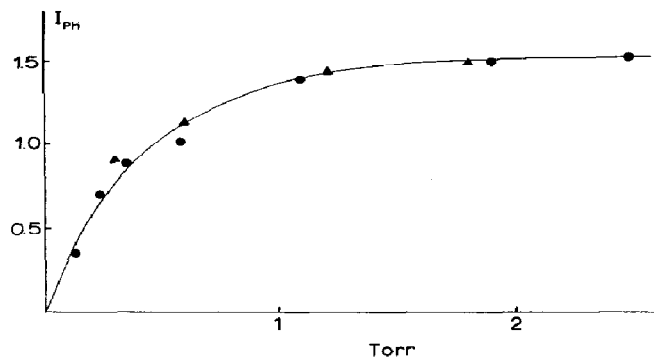


Fig. 4. Photosensitized biacetyl emission as a function of biacetyl. I_{ph} given in arbitrary units. Temperature: 25°C. \bullet , 3-Pentanone pressure: 19 Torr, total pressure: 330 Torr (propane added). \blacktriangle , Data from ref. 7, total pressure: 25 Torr.

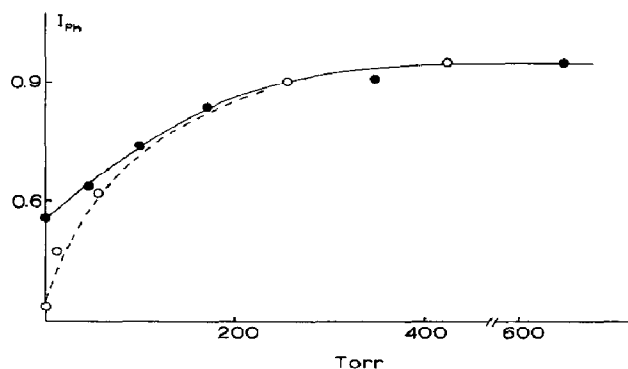
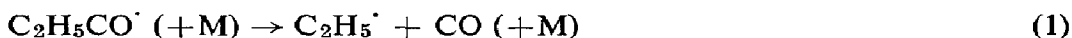


Fig. 5. Photosensitized biacetyl emission as a function of added propane. \bullet , 3-Pentanone pressure: 19 Torr, biacetyl pressure: 2 Torr. \circ , 3-Pentanone pressure: 9.2 Torr, biacetyl pressure: 2 Torr.

constant total pressure. The data previously reported by Weir have been also included⁷. Figure 5 shows the increase in biacetyl emission arising from an increase in total pressure.

DISCUSSION

The photodecomposition quantum yields can be evaluated either from a complete analysis of the reaction products or by working in conditions such that reaction (1)



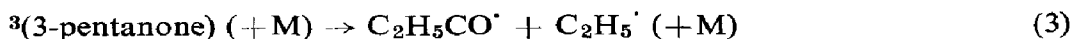
can be considered as the only reaction of the propionyl radicals. At low temperatures this condition will only be fulfilled at low intensities and high pressures. Under these conditions we have that:

$$\Phi_{\text{Desc.}} = \Phi_{\text{CO}} \quad (2)$$

The data shown in Fig. 1 show that at low intensities the value of Φ_{CO} and hence $\Phi_{\text{Desc.}}$, is practically one. The mass balance obtained under these conditions also indicates a quantitative decomposition of the propionyl radicals. Values of $\Phi_{\text{Desc.}} = 1.0$ even at room temperature have been reported in previous works where low intensities were employed⁵. On the other hand, this value is slightly higher than that estimated by Weir at 25°C from a complete analysis of the reaction products⁷. This method involves the estimation of 3-pentanone and 3,4-hexanedione produced and can be affected by large experimental errors. This fact is stressed by the different efficiency of biacetyl in increasing the photosensitized emission relative to that found in decreasing the estimated decomposition quantum yield (see Table 1 and Figure 1 of ref. 7). We can then conclude that at all the temperatures studied $\Phi_{\text{Desc.}}$ is nearly one. Its behaviour is then different from that shown by acetone³, methyl isopropyl ketone¹² and 2-butanone¹³. The photodecomposition of 3-pentanone can arise from the hot singlet, the thermal singlet, the hot triplet and the thermal triplet.

Reactions of thermal triplets

$\Phi_{\text{Desc.}}$ has been found to be nearly one over the whole pressure range studied (20 to 300 Torr). If it is considered that in this pressure range there is a considerable increase in the quantum yield of thermalized triplets (see Fig. 5 and following discussion) it can be concluded that reaction (3) must be the only significant reaction of the thermal triplet.



This result contrasts with that reported for acetone triplets^{3,4}.

The plateau obtained by Weir⁷ as well as those obtained by us (see Fig. 2) show that the decomposition must arise from at least two states. The most easily quenched state can be identified with the thermal triplet since (i) the pressures of quencher employed are not enough to quench appreciably the thermal singlet state, and (ii) its importance increases with an increase in total pressure (see Figs. 3 and 5), but the pressure of biacetyl needed to quench half of the excited molecules is independent of total pressure (see Fig. 4).

The last point indicates that the lifetime of the triplet is independent of total pressure. The same conclusion can be reached from the increase in biacetyl emission obtained when 300 Torr of propane were added to a mixture of 3-pentanone (20 Torr) and different amounts of biacetyl (from 0.05 to 1.5 Torr). The relative increase obtained is independent of biacetyl pressure, showing that the lifetime of the triplet is not pressure dependent. Since reaction (3) is the main reaction of the thermal triplet, this indicates that reaction (3) must be in its first order region even at 20 Torr. This finding is in contrast with that reported for acetone³. The fact that 3-pentanone, in spite of a shorter lifetime (see following discussion), is in the first order region at pressures much lower than that needed for acetone must be related to the greater complexity of 3-pentanone.

Azomethane is one of the most efficient quenchers of acetone triplets¹⁵. If we assume that the rate of reaction (4):



is similar to that of reaction (5):

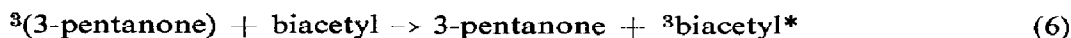


the data shown in Fig. 2, together with those reported by Rebbert and Ausloos¹⁵, allow an estimation of the lifetime of 3-pentanone triplets. From this analysis it can be concluded that $\tau_{(3\text{-pentanone})} = 8 \times 10^{-6}$ sec at 30°C. A similar treatment of the data obtained by Heicklen and Noyes¹⁶ (recalculated at 25°C with data of ref. 3) and those shown in Fig. 4 gives $\tau_{(3\text{-pentanone})} \approx 5 \times 10^{-6}$ sec at 25°C. Owing to the high uncertainty of the biacetyl-acetone data the agreement can be considered within experimental errors. From the preceding discussion it can be concluded that at 30°C, $k_3 \approx 0.13 \times 10^6$ sec⁻¹ showing that reaction (3) is nearly 10² times faster than the corresponding reaction of acetone at the same temperature³. Accordingly, the value of E_3 that can be estimated from Weir's data⁷ (5.5 kcal) is substantially lower than that obtained for acetone³. These facts can be the consequence of a weaker C-CO bond in 3-pentanone (This bond can be estimated as being nearly 3 kcal weaker than that of acetone¹⁷.)

Quantum yields of thermal triplets

The Φ_T can be obtained from the quantum yield of sensitized emission or from the carbon monoxide diminution when all the triplets are quenched. When biacetyl is employed as quencher, both methods are valid if there is no decomposition of the excited biacetyl. A significant induced decomposition of the biacetyl

has been reported when 2-hexanone is employed as sensitizer¹⁸, although the sensitization is assumed to occur from the singlet state. Under our conditions, the sequence of reactions



and



or



is not contributing significantly since (i) the diminution of Φ_{CO} observed when biacetyl is added is equal to half the diminution in the quantum yield of ethyl radicals; (ii) there is no production of methyl radicals; and (iii) the carbon monoxide remaining at total triplet quenching (at a given total pressure) is similar when biacetyl, 2,3-pentanedione or azomethane are employed as quenchers.

We can then employ the data obtained from the photosensitized biacetyl emission to evaluate Φ_T .

Φ_T at high pressures

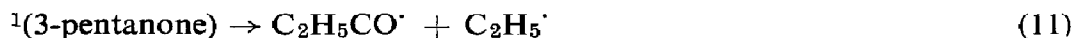
The Φ_T can be obtained from the emission data if we relate the I_{ph} obtained with 3-pentanone to that obtained when acetone is employed as sensitizer under conditions of equal absorption. At high pressures (added propane) the acetone triplet quantum yield can be taken as 1.0^{3,4}. We then have that:

$$\Phi_T = (I_{\text{ph}})_{3\text{-pentanone}} / (I_{\text{ph}})_{\text{acetone}} \quad (9)$$

At high pressures the value obtained for 3-pentanone is 0.92 ± 0.10 at 25°C. From extrapolation at infinite pressure of the data shown in Fig. 2, a value of 0.9 ± 0.1 can be obtained at 30°C (see Fig. 7). Since fluorescence is a minor process, Φ_T at high pressures can be equated to

$$\Phi_T = k_{13} / (k_{11} + k_{12} + k_{13}) \quad (10)$$

where



Our data show that k_{13} is the main reaction path and that less than 5% of the singlet molecules react by reaction (12). Furthermore, from both the emission data and from the remaining carbon monoxide at total triplet quenching, it can be concluded that

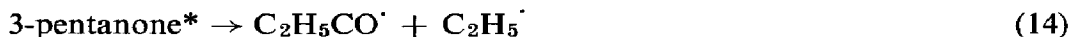
$$k_{11}/k_{13} \approx 0.1$$

which shows that for 3-pentanone, decomposition of the thermal singlet is a minor process. The high yield of triplets found in the present work is similar to that

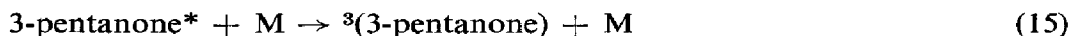
obtained with acetone but different to that found for most aliphatic ketones where it is found that even in solution Φ_T is considerably lower than one¹⁹.

Dependence of Φ_T on total pressure

The simplest way of explaining the results shown in Figs. 2 and 4 must include a competition between a hot decomposition:



and a thermalization:



where reaction (15) can include more than a step. It is difficult to decide where reactions (14) and (15) involve singlet or triplet molecules. Nevertheless, the fact that with methyl isopropyl ketone (a ketone with the same number of atoms and with equal or shorter lifetime²⁰), 20 Torr of total pressure seems to be enough to thermalize the singlet¹² would indicate that our observed pressure effect is a consequence of deactivation in the triplet manifold^{4,13}. The same conclusion can be reached from an analysis of 2-pentanone fluorescence data²¹. This oversimplified mechanism predicts that

$$1/\Phi_T = \left[1 + \left(\frac{k_{14}}{k_{15}} \right) \frac{1}{M} \right] \frac{k_{11} + k_{13}}{k_{13}} \quad (16)$$

where M is a "corrected" total concentration. All our data fit this simple equation if we take:

$$M = (\text{3-pentanone}) + (\text{quencher}) + 0.2 (\text{propane}) \quad (17)$$

This is shown in Figs. 6 and 7 where the experimental data are plotted according to eqn. (16). The efficiency of propane relative to that of 3-pentanone necessary to

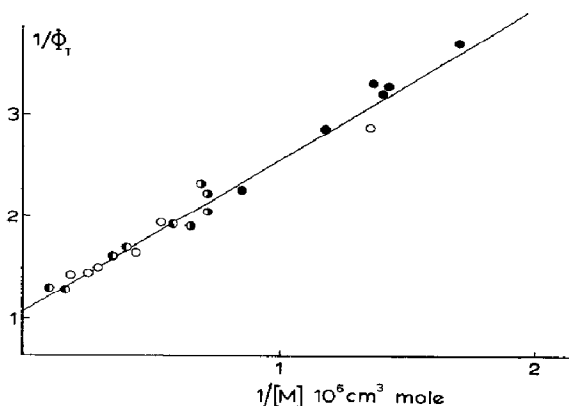


Fig. 6. $(\Phi_T)^{-1}$ as a function of the inverse total concentration. Data obtained from biacetyl phosphorescence at 25°C and 2 Torr biacetyl pressure. ●, No propane added; ◐, 3-pentanone pressure: 19 Torr; ◑, 3-pentanone pressure: 12 Torr; ○, 3-pentanone pressure: 9.2 Torr.

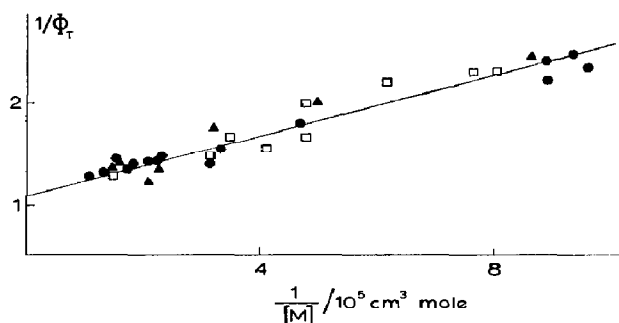


Fig. 7. $(\Phi_T)^{-1}$ as a function of the inverse total concentration. Data obtained at 30°C from the decrease in Φ_{CO} at total triplet quenching. ▲, Q = azomethane; ●, Q = 2,3-pentanedione; □, Q = biacetyl.

fit eqn. (16) is lower than that reported in other systems²². This can be either an artifact of the oversimplification implicit in eqn. (16) or a consequence of the small excess energy present in the excited molecule, which would increase the selectivity²³. A similar conclusion can be obtained from Cundall and Davies results⁴.

From Fig. 6, $k_{14}/k_{15} = 1.2 \times 10^{-6} \text{ cm}^3/\text{mole}$ at 25°C. From Fig. 7, $k_{14}/k_{15} = 1.5 \times 10^{-6} \text{ cm}^3/\text{mole}$ at 30°C. The similarity between both values lends support to the proposed mechanism. Furthermore, it has to be stated that these values are only slightly sensitive to the assumed propane efficiency.

For acetone it has been reported⁴ that this ratio, at 30°C, is equal to $2.5 \times 10^{-4} \text{ cm}^3/\text{mole}$. The fact that acetone, a smaller molecule, decomposes more slowly must be a result of the smaller excess energy over the decomposition barrier present in the acetone molecule. This result is in agreement with the faster decomposition of the thermalized 3-pentanone triplet.

The difference between the photochemical behaviour of acetone and 3-pentanone can then be interpreted in terms of its lower barrier to decomposition and its increased complexity. The data presently available in other alkyl ketones that can only photodecompose by a type I mechanism are not enough to warrant a comparison between their photochemical behaviour and that of acetone and 3-pentanone.

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