Reactivity of Excited Triplet Alkyl Ketones in Solution. I. Quenching and Hydrogen Abstraction of Triplet Acetone

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The photolysis of acetone in various solutions has been investigated by analysis of reaction products as well as absorption spectroscopy. The rate of photolysis of acetone in aqueous solution decreases on addition of methanol or with increasing concentration of acetone, being much higher than that in methanol and heptane solutions. The results suggest that intermolecular hydrogen abstraction plays a significant role in quenching of triplet acetone. This is supported by spectroscopic studies which reveal formation of the enol form of acetone as an intermediate in the decay process of triplet acetone.

The photolysis of acetone in the liquid as well as in the gas phase has been studied by many workers.[1] The quantum yields for the photolysis were found to be much lower in neat acetone than in aqueous solution, the nature of such a difference being discussed. Porter *et al.*[2] investigated the lifetime of the excited triplet state of acetone in various solutions, and suggested that intermolecular hydrogen abstraction plays a significant role in quenching of triplet acetone, *i.e.*, photolysis and triplet self-quenching by intermolecular hydrogen abstraction may be competitive processes.

Although information on the intermolecular hydrogen abstraction of the excited triplet state of alkyl ketones is important for understanding its reactivity in solution, there is relatively little work along this line. Intermolecular and intramolecular hydrogen abstraction of the excited carbonyl compounds appears to be of interest from a theoretical point of view.[3] We have investigated the photolysis of alkyl ketones in various solutions in order to obtain more detailed information on the relationship between the quenching and the intermolecular hydrogen abstraction in the photolysis of alkyl ketones.

Experimental

Materials. All the compounds (Tokyo Kasei Kogyo Co., Ltd., Grade SG) were purified by fractional distillation. Deionized double-distilled water was degassed by alternate freezing and thawing *in vacuo*. Acetone-d_6 of 99.5 mol% and deuterium oxide of 99.9 mol% isotopic purity (E. Merck, Darmstadt) were used without further purification. Particular care was taken to remove water and oxygen completely from the solvents and reactants.

Apparatus and Procedure. Details of the apparatus and procedure were described previously.[4] A conventional vacuum system was used in conjunction with a rectangular quartz cell (4.0×1.0 cm) of path length 0.5 cm, having two outlets. One was sealed off after admission and degassing of the sample solution. Another had a breakable seal which made it possible to attach the cell to a conventional analytical system after irradiation. Photolysis was carried out at 25±2 °C with light of 270±2.5 nm using a monochromator equipped with a 500 W xenon lamp. The intensity of incident light was determined by means of potassium ferrioxalate actinometry. Intensity in the range 6.4—6.7×10^{13} quanta/s was used. The analytical system consists of three traps and a modified Ward still. The gaseous products were separated by fractional distillation and analyzed by gas chromatography. The absorption spectra before and after irradiation were measured with a Hitachi EPS 3T spectrophotometer. Details of the isotopic analysis of the deuterated methane and acetone were described previously.[5] The CD_2HCOCD_3/CD_3COCD_3 ratio was determined by measurement of the parent peaks at $m/e=63$ [$CD_2HCOCD_3^+$] and $m/e=64$ [$CD_3COCD_3^+$].

Results and Discussion

Table 1 shows the effect of solvents upon the quantum yield of methane formation in the photolysis of acetone. The corresponding results with 2-butanone and 2-pentanone are also included. It should be noted that the quantum yield for the photolysis of acetone is much lower than that for other alkyl ketones, especially in heptane and methanol.

Table 1. Quantum yields for disappearance of alkyl ketones in the photolysis in various solvents at 25 °C

	Heptane	Methanol	Water
Acetone[a)]	0.003	0.004	0.061
Acetone-d_6[b)]	—	0.004	0.064
2-Butanone[c)]	0.217	0.297	0.306
2-Pentanone[d)]	0.237	0.319	0.337

The concentration of alkyl ketones was a) 0.085—0.091 mol/l, b) 0.085 mol/l, c) 0.048 mol/l, and d) 0.051 mol/l. a, b) As seen in Table 3, in view of much lower yield of ethane (less than 2% of methane formation) the value can be regarded as the quantum yield for disappearance of acetone. c, d) The values are obtained from the quantum yields of major products (larger than 95% of total products) such as ethane for 2-butanone and propane (type I) as well as ethylene (type II) for 2-pentanone.

Table 2. CD_3H content of the methane formed from the photolysis of acetone-d_6 at 25 °C

	Heptane	Methanol	Water
CD_3H content (%)[a)]	97.9	97.5	8.80
$\frac{CD_2HCOCD_3}{CD_3COCD_3}$ (%)	—	—	7.01

The concentration of acetone-d_6, 0.090 mol/l. Irradiation time, 60 min. a) The methane consists of only CD_4 and CD_3H, other species being negligible.

The contents of CD_3H in methane formed from the photolysis of acetone-d_6 in various solvents are given in Table 2. Very large contents observed with heptane and methanol solutions show that methyl radicals formed from the primary processes abstract hydrogen atoms only from the solvent molecules. Table 2 also suggests that in aqueous solution most part of CD_3H in methane arises from the H-D exchange reaction between acetone-d_6 and water molecules. It is therefore concluded that methyl radicals scarcely abstract hydrogen atoms from water molecules. Although the conclusion has already been suggested by Pieck and Steacie,6) the above results offer an unambiguous evidence for it.

TABLE 3. EFFECT OF ADDED METHANOL UPON THE PHOTOLYSIS OF ACETONE IN AQUEOUS SOLUTION AT 25 °C

Concentration of added methanol mol/l	Yield of methane 10^{-4} ml/h	Yield of ethane 10^{-6} ml/h
0	6.67	8.01
0.901	3.63	3.51
1.61	2.69	1.02
2.49	2.02	0.50
2.90	1.85	0
4.40	1.32	0

The concentration of acetone, 0.102 mol/l.
Irradiation time, 60 min.

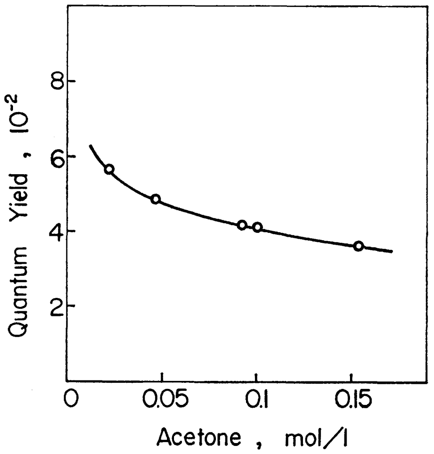


Fig. 1. The effect of the concentration of acetone upon the quantum yields for methane formation from the photolysis of acetone in aqueous solution at 25 °C. Irradiation time, 60 min.

Table 3 shows the effect of added methanol upon the photolysis of acetone in aqueous solution. The rates of methane and ethane formation decrease with increasing concentration of methanol. A similar decrease in the quantum yields for the photolysis of acetone in aqueous solution was obtained when the concentration of acetone increased (Fig. 1). Considering that acetone besides methanol is an efficient hydrogen donor, the results suggest that quenching of the excited acetone molecule is closely associated with hydrogen abstraction reactions. It is well-known that in the condensed phase efficiency of the intersystem crossing from the excited singlet state to the triplet state of acetone is unity.7) In fact, it was found in the present work that the rate of photolysis is reduced to zero on addition of oxygen. Thus, there is no doubt that the photolysis of acetone in solution proceeds *via* the excited triplet state. Porter *et al.*2) found that the lifetime of the triplet acetone molecule is much shorter in neat acetone than in aqueous solution and suggested that self-quenching of triplet acetone molecules occurs by intermolecular hydrogen abstraction and may compete its α-cleavage. Thus, the decrease in the rate of photolysis of acetone in aqueous solution caused by addition of methanol or with increasing concentration of acetone would be explicable on the basis of quenching of triplet acetone due to such intermolecular hydrogen abstraction. Furthermore, markedly higher quantum yields of the photolysis in aqueous solution as compared with those in heptane and methanol solutions could be attributed to an unefficient hydrogen abstraction in aqueous solution.

For quenching by methanol of radical products formation from acetone photolysis in aqueous solution, the following Stern-Volmer quenching equation holds:

$$Q_0/Q = 1 + \tau k_q[\text{Methanol}],$$

where Q_0 and Q are the rates of formation in the absence and presence of methanol, respectively; τ and k_q are the lifetime of excited triplet acetone and the quenching rate constant, respectively. The value of τ under our conditions (0.09 mol/l) can be determined to be 17.5×10^{-6} s by using the τ value at 0.05 mol/l, 20×10^{-6} s reported by Porter *et al.*,8) together with its dependence upon the concentration of acetone (Fig. 2). The value of k_q thus determined is 0.54×10^5 l/mol s, being smaller than the corresponding value for acetonitrile solution, *i.e.*, 1×10^5 l/mol s reported by Porter *et al.*2) Such a difference would be attributed to the fact that hydrogen bond strength is larger between acetone and water than between acetone and acetonitrile.

Information on the mechanism of quenching of excited

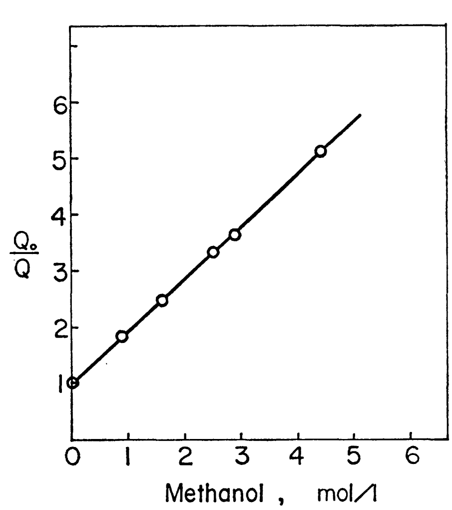


Fig. 2. Stern-Volmer quenching plots for the effect of added methanol upon the yields of methane formed from the photolysis of acetone in aqueous solution at 25 °C. The concentration of acetone, 0.120 mol/l. Irradiation time, 60 min.

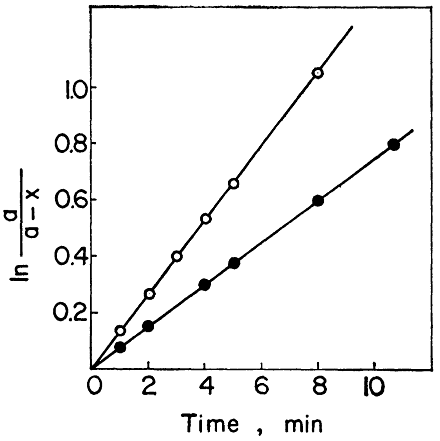
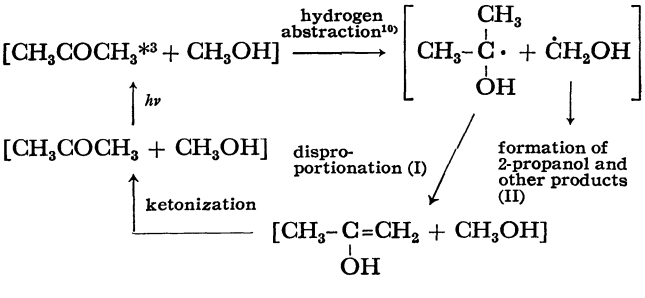


Fig. 3. The recovery of the (n, π^*) band of acetone as a function of time at 25 °C. x represents the recovery of the absorbance at $\lambda_{\max}$ (271 nm). The concentration of acetone, 0.120 mol/l. Irradiation time, 60 min. ○: Acetone, ●: acetone-d_6.

triplet acetone molecules by hydrogen abstraction was obtained from the following results. In methanol and heptane, except in aqueous solution, the UV irradiation led to a much larger decrease in the intensity of the (n, π^*) band of acetone than what would be expected from the extent of its photolysis. As soon as the irradiation ceased, the reduced intensity of the (n, π^*) band began to increase, an almost original intensity being recovered. Such a recovering process was found to obey the first order rate law as shown in Fig. 3. The half-lives obtained from the plots were 5.2 min for acetone and 8.9 min for acetone-d_6. Such a phenomenon was not observed with the photolysis of 2-pentanone or 2-butanone, where the rate of photolysis was unaffected by addition of methanol.

It has been found by ESR and UV studies that ketyl radicals are formed by hydrogen abstraction of excited triplet acetone from 2-propanol.[8,9] Henne and Fischer[9c] found by NMR studies that disproportionation of ketyl radical pairs leads to formation of the enol form of acetone and 2-propanol, and proposed that by ketonization of the former the ground state of acetone is reformed. A similar situation would be expected for the photolysis of acetone in methanol solution. The following mechanism is proposed:



According to the above mechanism, such a recovering process of the reduced intensity of the (n, π^*) band (Fig. 3) would be explicable by the occurrence of ketonization of the enol form of acetone formed by irradiation.

McMillan *et al.*[11] found that in the gas phase photolysis of 2-pentanone enol acetone formed by Norrish type II reaction rearranges to the keto form with a half-life of 4.7±0.3 min, in approximate agreement with that of ketonization determined from Fig. 3. The rate of reactions within the solvent cage such as the disproportionation reaction seems to be greater than that of reaction (II) such as formation of pinacol as well as 2-propanol as has been found by Singh.[12] As regards the disproportionation path, the reaction resulting in formation of enol acetone will be predominant by taking into consideration the fact that $\dot{C}H_2OH$ radicals are more reactive than ketyl radicals toward hydrogen abstraction. Thus, the rate of reaction (II) is expected to be negligibly small as compared with that of reaction (I). In fact, the products of reaction (II) such as 2-propanol and others were found to be negligible.[13]

The absence of such a recovery of the reduced intensity of the (n, π^*) band observed with 2-butanone as well as 2-pentanone would be attributable to a much lower efficiency of hydrogen abstraction of its excited triplet state than that of acetone triplet. In contrast with the case of acetone, a small difference between the rate of photolysis in water and that in heptane or methanol solution was observed for the cases of 2-butanone as well as 2-pentanone. Such behavior would be explained on a similar basis.

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10) $$\dot{R} + CH_3OH \xrightarrow{k_o} CH_3\dot{O} + RH$$
$$\searrow_{k_c}\ \dot{C}H_2OH + RH$$

The k_c/k_o ratio is 0.06 at 30 °C in the gas phase,[14] and 5.0 at the same temperature in the liquid phase.[15]

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13) Even if reaction (II) should occur, its products such as 2-propanol and others will disappear owing to their reactions with excited triplet acetone molecules, since their hydrogen atom-donating ability is higher than that of methanol.[16]

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