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PHOTOLYSIS OF ACETONE AT 100 - 170 K: AN ELECTRON SPIN RESONANCE STUDY OF RADICAL FORMATION AND DECAY IN THE SOLID STATE

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Summary

Solid acetone was photolysed in an electron spin resonance (ESR) spectrometer at 100 - 170 K at wavelengths above 250 nm. The nature of the trapped radicals depended on the photolysis temperature. From 100 to 110 K, methyl and acetyl radicals were formed, with acetyl radicals predominating. Above 110 K, the spectrum consisted of a seven-line signal, attributed to the isopropanol radical $CH_3\dot{C}(OH)CH_3$, resulting from hydrogen atom addition to the carbonyl group. The singlet spectrum of the acetyl radical was also observed, but no methyl radicals. This difference between photolysis below and above 110 K may reflect a solid state transformation. In the range 100 - 110 K, the concentration of acetyl radicals increased linearly with the photolysis time, but the concentration of methyl radicals showed distinct curvature, which could be analysed quantitatively in terms of zero-order formation and first-order disappearance kinetics. The variation in concentration of the $CH_3\dot{C}(OH)CH_3$ radical with the photolysis time at 100 - 170 K was analysed similarly. Acetonyl radicals $\dot{C}H_2COCH_3$ were photolabile and hence were observed only as a minor component of the ESR spectra at 100 - 170 K.

1. Introduction

Acetone is a convenient solvent for the photolysis of a variety of solutes on account of its good optical transmission and solubility characteristics, low volatility and toxicity and low melting temperature.

A large number of investigations of the photolytic degradation of acetone in the gaseous phase have been made. The primary process in the degradation is

$$CH_3COCH_3 \xrightarrow{h\nu} \dot{C}H_3 + CH_3\dot{C}O \qquad (1)$$
$$\phantom{CH_3COCH_3 \xrightarrow{h\nu} } \text{I} \qquad \text{II}$$

Methyl (I) and acetyl (II) radicals have been identified by electron spin resonance (ESR) spectroscopy [1], mass spectroscopy [2] and by the detection of acetyl and methyl iodides after photolysis in the presence of iodine [3].

Methyl radicals react either by hydrogen atom abstraction from an acetone molecule or by dimerization, the ratio of methane to ethane increasing with increasing temperature [4]. Acetyl radicals predominately undergo decomposition via the reaction

$$CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO \qquad (2)$$

or dimerize to form diacetyl in a wall-catalysed reaction [5].

The volatile products from photolysed liquid acetone have been reported by Berthelot and Gaudechon [6] as being approximately equal amounts of carbon monoxide and ethane, with a trace of methane. Radical formation during the photolysis of liquid acetone has been studied by ESR by Zeldes and Livingston [7, 8] using a flow system. They examined liquid acetone, solutions of hydrogen donors in acetone [7] and aqueous solutions of acetone at 27 °C [8]. Paul and Fischer [9, 10] have used ESR to study the photolysis of solutions of acetone in alcohol [9], methylcyclopentane [10] and trichlorofluoromethane [10].

The UV photolysis and the post γ irradiation photolysis of acetone in the solid state at 77 K have been reported by Pukhal'skaya *et al.* [11]. They studied the stability of acetyl and methyl radicals at 77 K and on warming. Barton *et al.* [12] have also investigated the ESR spectrum of UV-photolysed acetone at 77 K, although their spectra were poorly resolved and no kinetic information was given. The ESR spectra of radicals produced by γ irradiation of pure acetone and in solutions have been reported for the solid state [11, 13 - 15] and in the liquid [15] phase.

The purpose of the present study was to identify the radicals produced in pure acetone by photolysis in the solid state at different temperatures (when radical species should be stabilized). The relative stabilities of the different radicals in an acetone matrix were determined from kinetics studies of their rates of formation and disappearance. This work provides a better understanding of the intermediate radical species in the photolysis of acetone and is of importance to studies of the photolysis of solutes in acetone in the liquid and solid phases. Of special interest is the effect of acetone radicals on photopolymerization and photodegradation of polymers in acetone solutions.

2. Experimental details

Acetone (AnalaR) was fractionally distilled and bubbled with nitrogen gas for 2 h to remove oxygen. It was freeze–thaw degassed on a high vacuum line, decanted into Spectrasil high purity quartz ESR tubes (4 mm diameter) and sealed under vacuum.

The sample tubes were mounted in a variable-temperature photolysis cavity in a Bruker ER200D spectrometer and maintained at the required temperature in the range 100 - 170 K by a flow of cold nitrogen gas. A 1000 W Hg–Xe lamp was used for photolysis in conjunction with a water filter to remove heat and a 250 nm quartz cut-off filter.

ESR spectra were obtained with 200 s scans over a 20 mT field range at 1.99 μW (20 dB) microwave power level, which afforded maximum sensitivity without significant power saturation.

The first-derivative spectra were stored and manipulated on a PDP 11/34 computer. Double integration of a spectrum using Simpson's rule yielded the area under the absorption peak, which is proportional to the total radical concentration. The component radicals which give rise to the spectra were identified by their spectral parameters, which were obtained from the literature. The proportions of the free-radical components present were determined by simulation of the spectrum.

For the kinetics studies, it was found that a measure of the changing concentration of a particular radical species could be obtained from one spectral line which was free from overlapping lines of other radical species. The changes in the radical concentration were monitored by measuring the peak heights and multiplying these by the square of the linewidth [16].

The best-fit parameters for the kinetic equations expressing the formation and decay of radicals were obtained by fitting the experimentally determined radical concentrations, expressed as peak areas, using Chandler's non-linear minimization procedure [17]. The error in these kinetics parameters, including an estimate of the errors in the radical concentrations, was ±10%.

Gaseous products were analysed using an AEI MS10 mass spectrometer. After photolysis at 77 K, the sample was warmed to 25 °C and then cooled to below the freezing point of acetone. The volatile products were then introduced into the inlet system of the spectrometer.

3. Results and discussion

3.1. Electron spin resonance
3.1.1. 100 - 110 K

The ESR spectrum of pure acetone after photolysis in vacuum at 100 K is shown in Fig. 1(a). It can be analysed into a quartet with a binomial intensity ratio and a hyperfine splitting of 2.24 mT, and an anisotropic singlet centred at a slightly higher field than the quartet. These two components of the spectrum have been assigned to methyl radicals I and acetyl radicals II respectively. These assignments are in agreement with those of Pukhal'skaya *et al.* [11] and Barton *et al.* [12]. These radicals have also been reported from the photolysis of gaseous acetone at 77 K and the photolysis of liquid acetone at 27 °C [7]. The spectrum in Fig. 1 also shows two additional peaks at ±2.0 mT from centre field, and there is evidence
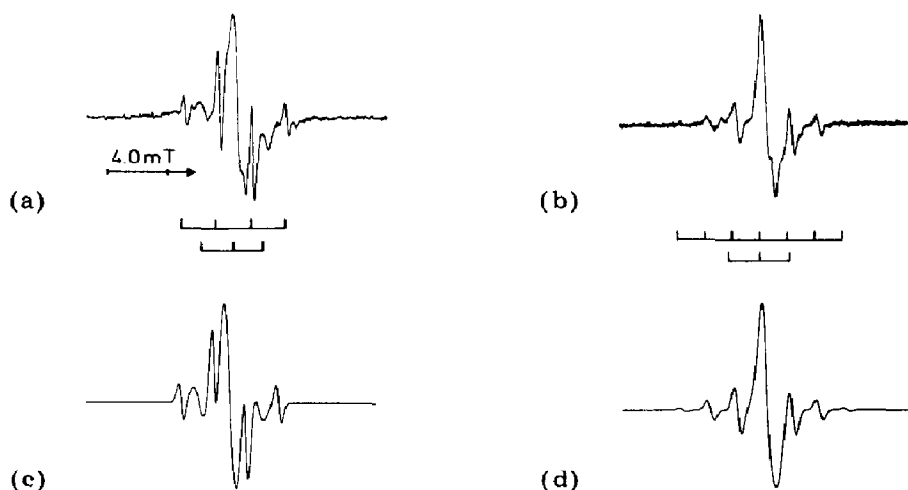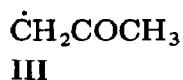
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Fig. 1. ESR spectra recorded during photolysis of acetone: (a) experimental spectrum at 100 K; (b) experimental spectrum at 130 K; (c) simulation of (a); (d) simulation of (b).

of a third peak near the centre of the spectrum. These features have been assigned to a triplet arising from the acetonyl radical III as a minor component:

$\dot{C}H_2COCH_3$

III

Zeldes and Livingston [7] have observed radical III as the major photolysis product of liquid acetone containing 1% H_2O_2 at 53 °C and of pure acetone at 27 °C. The acetonyl radical has also been reported in the γ radiolysis of acetone at 77 K; it is believed to be formed by hydrogen atom abstraction from acetone by an acetone cation. The photobleachable singlet of this cation and the triplet of the acetonyl radical have been reported by Nitta et al. [14] and Akhtar et al. [15].

TABLE 1

Characteristics of the free radicals observed during photolysis of acetone at 100 - 170 K

Radical	Structure	Number of lines	Hyperfine splittings (mT)	Reference
I	$\dot{C}H_3$	4	$a_H = 2.24$	[15]
II	$CH_3\dot{C}O$	1	—	[18]
III	$\dot{C}H_2COCH_3$	3	$a_\alpha = 1.95$ $a_\gamma = 0.095$	[15]
IV	$CH_3\dot{C}(OH)CH_3$	7	$a_\beta = 1.95$ $a_{OH} = 0.032$	[7]

A simulated spectrum of Fig. 1(a) is shown in Fig. 1(c) using the peak intensities and hyperfine splittings a_H shown in Table 1. The simulation uses 16% radical I, 78% radical II and 6% radical III.

3.1.2. 110 - 170 K

The ESR spectrum after photolysis above 110 K is shown in Fig. 1(b). It consists mainly of a seven-line component, which is attributed to the isopropanol radical IV formed by hydrogen atom addition to the carbonyl oxygen of the acetone:

$$CH_3\dot{C}(OH)CH_3$$

IV

This radical has also been observed in the photolysis of acetone in the liquid phase [7] and in acetone–water mixtures after irradiation at 77 K and warming to 137 K [15].

Sevilla et al. [19] have also reported the isopropanol radical as the major product after electron attachment to acetone in aqueous solutions at 77 K. There are also contributions in the spectrum from acetyl radicals II and to a lesser extent from acetonyl radicals III.

A simulated spectrum using the parameters given in Table 1 and using 76% radical II, 7% radical III and 17% radical IV is shown in Fig. 1(d). The marked difference in the ESR spectra obtained by photolysis below and above 110 K can be attributed to a change in the matrix properties. The glass transition temperature of acetone, corresponding to the onset of free rotational motion, has been reported to be approximately 100 K [20].

3.2. Kinetics of radical formation

3.2.1. Acetyl radicals

The concentration of acetyl radicals increased linearly with photolysis time from 100 to 170 K, as is shown in Fig. 2, and remained constant after the lamp was switched off. The mechanism for the zero-order formation of acetyl radicals suggested by Pukhal'skaya et al. [11] is the homolytic cleavage of the C—C bond in acetone (reaction (1)). Calculated pseudo-zero-order rate constants R_1 for the formation of acetyl radicals are given in Table 2.

3.2.2. Methyl radicals

The increase in methyl radical concentration with photolysis time at 100, 105 and 110 K showed a marked deviation from linearity as shown in Fig. 3, indicating that methyl radicals were reacting during photolysis. We have fitted the time dependence of the methyl radical concentration by a combination of pseudo-zero-order formation (reaction (1)) and first- or second-order decay kinetics, attributable to
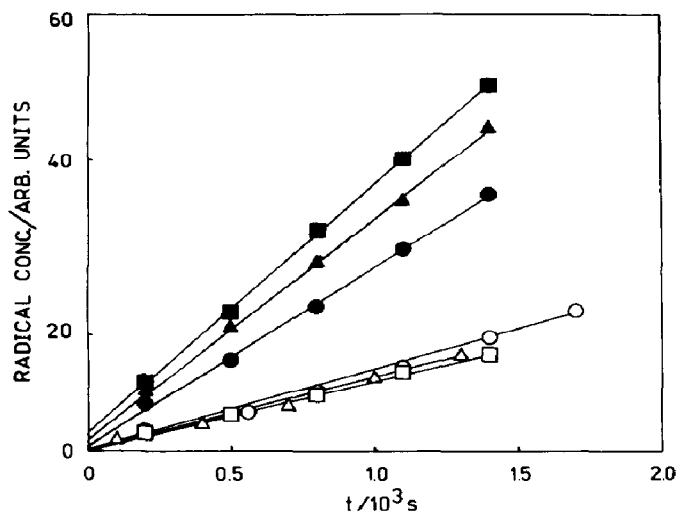
$$\dot{C}H_3 + CH_3COCH_3 \xrightarrow{k_3} CH_4 + \dot{C}H_2COCH_3 \tag{3}$$

Fig. 2. The dependence of the concentration of acetyl radicals on the photolysis time: O, 100 K; △, 105 K; □, 110 K; ●, 130 K; ▲, 150 K; ■, 170 K.
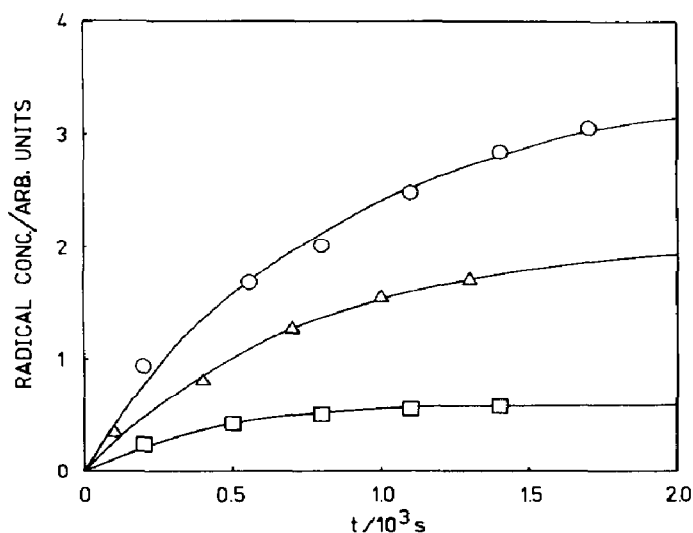

Fig. 3. The dependence of the concentration of methyl radicals on the photolysis time: O, 100 K; △, 105 K; □, 110 K.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6 \qquad (4)$$

respectively, using a non-linear minimization to yield "best-fit" values for the rate constants. First-order decay gave a better fit to the experimental data (Fig. 4), with for example at 100 K the standard error in the fit for the second-order decay process twice that for the first-order decay process. The values of R_1 for the formation of methyl radicals and k_3 for their first-order decay are given in Table 2.

The rate constants for formation of acetyl radicals during photolysis in the range 100 - 110 K are two or three times greater than that for methyl

TABLE 2

Rates R of formation[a] and rate constants k [a] for first-order decay of free radicals during photolysis of acetone at 100 - 170 K

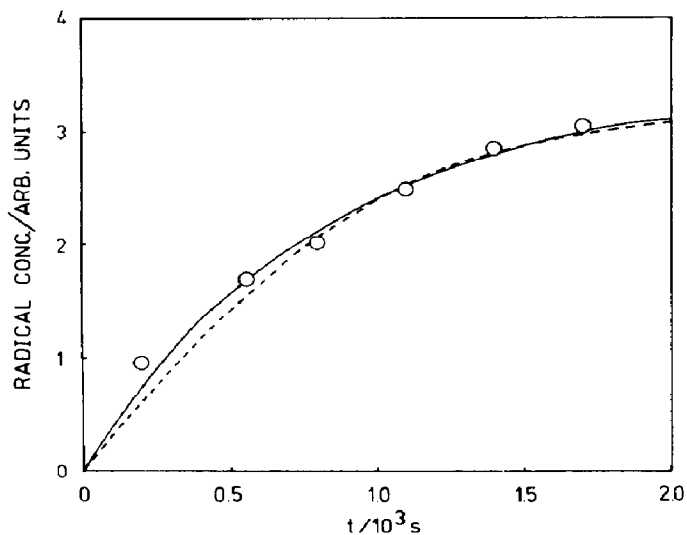| Temperature (K)	Acetyl radical R_1^b (mm^2 s^{-1})	Methyl radical			Isopropanol radical		
		R_1^b (mm^2 s^{-1})	k_3^b (×10^3 s^{-1})	k_3^c (×10^3 s^{-1})	R_2^b (mm^2 s^{-1})	k_6^b (×10^3 s^{-1})	k_6^c (×10^3 s^{-1})
100	1.04	0.57	1.2	5.5	—	—	—
105	0.89	0.38	1.4	6.6	—	—	—
110	0.84	0.21	2.6	7.6	0.78	5	6
130	2.21	—	—	—	2.25	9	2
150	2.72	—	—	—	2.86	4	13
170	3.13	—	—	—	2.88	3	8

[a] ±10%.
[b] Lamp on.
[c] Lamp off.

Fig. 4. Kinetic analysis of the net formation of methyl radicals on photolysis time at 100 K assuming first-order decay (——) and second-order decay (— — —), using rate constants obtained by the non-linear least-squares fit method.
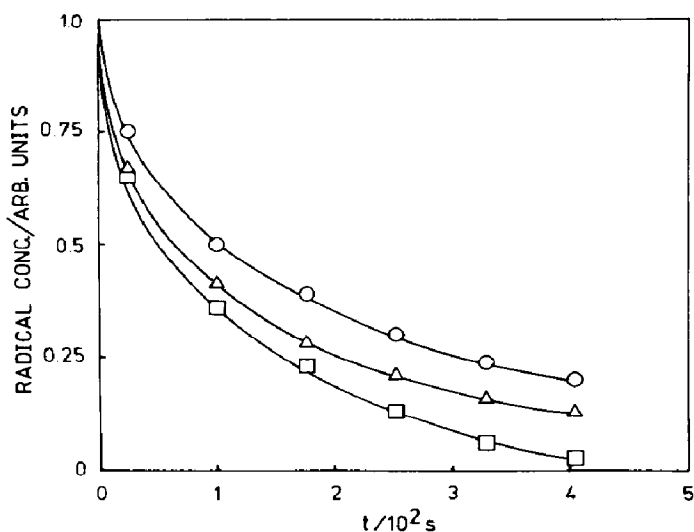

Fig. 5. Decay of methyl radicals with time after cessation of UV illumination: O, 100 K; △, 105 K; □, 110 K.

radicals, whereas reaction (1) predicts that they should be the same. This could indicate that acetyl radicals are also produced during photolysis by another zero-order process. This possibility will be discussed later.

Pukhal'skaya *et al.* [11] reported that at 77 K the rate of methyl radical formation was initially twice that of acetyl radical formation, indicating that acetyl radicals undergo photodecomposition (reaction (2)). However, they appear to contradict this statement elsewhere in their paper by stating that acetyl radicals are stable to UV light at 77 K. Furthermore
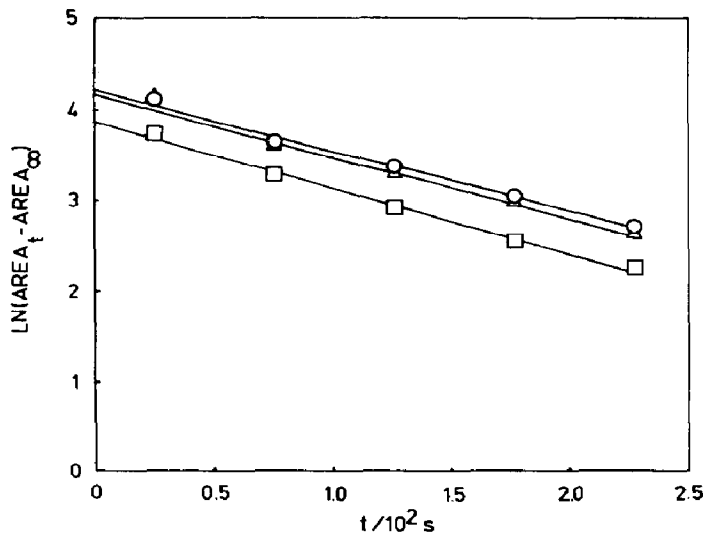
Fig. 6. First-order plots for methyl radical decay: ○, 100 K; △, 105 K; □, 110 K.

their published spectrum shows only a minor methyl radical component compared with the major singlet of the acetyl radical.

The decay of methyl radicals was also followed when the lamp was switched off, and the decay curves are shown in Fig. 5. The decay reaction was not accurately first or second order over 400 s; however, up to 250 s a first-order decay provides excellent agreement with the observed results (Fig. 6). The mechanism of the first-order decay is likely to be a hydrogen atom abstraction reaction (reaction (3)) although this is not unequivocable.

The calculated first-order rate constants are given in Table 2. These are a factor of 2 - 5 greater than the k_3 values obtained by analysis of the experimental data obtained with the lamp on. This suggests that during the photolysis methyl radicals are formed by a first-order process, in addition to reaction (1).

3.2.3. Isopropanol radicals

Isopropanol radicals IV were found during photolysis above 110 K. Their concentrations showed a non-linear increase with time, similar to that observed for methyl radicals below 110 K. The mechanism of formation of isopropanol radicals in the liquid phase involves hydrogen atom abstraction by excited state acetone molecules [7]:

$$CH_3COCH_3{}^* + CH_3COCH_3 \xrightarrow{R_2} CH_3\dot{C}(OH)CH_3 + \dot{C}H_2COCH_3 \qquad (5)$$
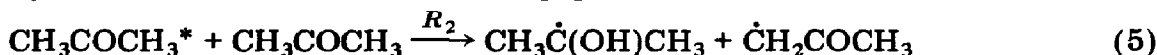
It was found that the experimental radical concentrations followed pseudo-zero-order formation and first-order decay kinetics (Fig. 7). The best-fit values for the rate constants R_2 and k_6 derived from the computer analysis are given in Table 2 (R_2 and k_6 are the zero- and first-order rate constants respectively). The mechanism of the first-order decay reaction cannot be elucidated from the kinetics and ESR data.
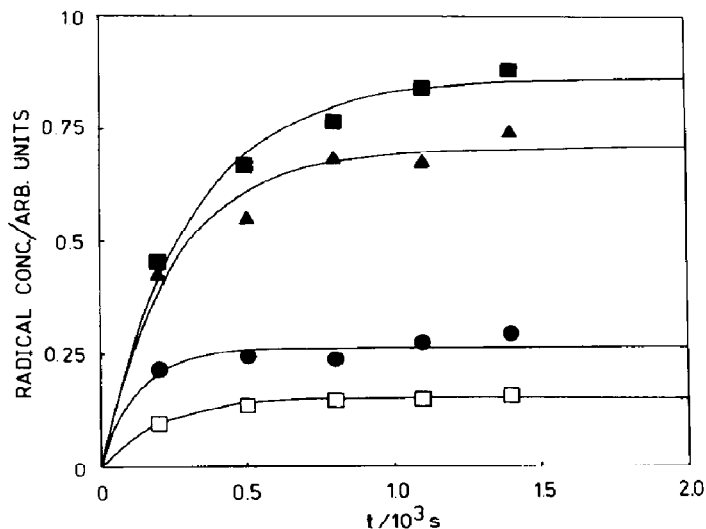
Fig. 7. The dependence of the concentration of isopropanol radicals on the photolysis time: □, 110 K; ●, 130 K; ▲, 150 K; ■, 170 K.

The radical decay was also followed after the lamp was turned off. The decay curves followed first-order kinetics for short time intervals, giving first-order rate constants k_6 of the same order of magnitude as those values in Table 2 obtained from studies made with the lamp switched on.

Isopropanol radicals absorb at wavelengths up to 450 nm and therefore are susceptible to a secondary photolytic reaction. It has been reported that radicals of the straight chain alcohols decay on photolysis by the reaction [21, 22]

$$R\dot{C}H{-}OH \xrightarrow{h\nu} R\dot{C}O + H_2 \qquad (6)$$

An analogous reaction involving isopropanol radicals would yield acetyl radicals and methane. We suggest that this reaction may contribute to the decay of isopropanol radicals during photolysis below 110 K since iso-propanol radicals are not observed at these temperatures. The dispropor-tionately high yields of acetyl radicals compared with methyl radicals and the relatively large methane yields could be satisfactorily accounted for by invoking the participation of this process.

3.2.4. Acetonyl radicals

The concentration of acetonyl radicals III after photolysis from 100 - 170 K increased rapidly to approximately 5% of the total free-radical con-centration, after which it remained relatively constant. The changes in concentration with time could not be followed accurately because the triplet of the acetonyl radical is overlapped by the septet of the isopropanol radical.

Pukhal'skaya *et al.* [11] suggested that at 77 K acetonyl radicals exhibit limited stability to UV light. The mechanism for decay proposed by them is

$$\dot{C}H_2COCH_3 \xrightarrow{h\nu} CH_2=C=O + \dot{C}H_3 \qquad\qquad (7)$$

on the basis of the relative rates of disappearance of acetonyl radicals and formation of methyl radicals. They claimed that the formation of methyl radicals from acetone photolysis was negligible compared with the yields observed after previous γ radiolysis. However, the appearance of a considerable concentration of acetyl radicals during the post-radiolysis photolysis suggests a major contribution from acetone degradation, possibly photosensitized by the highly absorbing acetonyl species. Reaction (7) was also suggested by Zeldes and Livingston [7] to explain the formation of methyl radicals during the photolysis of liquid acetone at 25 °C.

It was noted previously that methyl radicals appear to be formed during photolysis by a first-order process other than reaction (1). This photolytic decay of acetonyl radicals (reaction (7)) is suggested as the possible source of additional methyl radicals.

Interrupting the UV light source did not result in an appreciable change in the acetonyl radical concentration, although any increase in concentration through hydrogen atom abstraction by methyl radicals (reaction (3)) would be within reasonable error limits for measurement of the acetonyl radical concentration, and therefore it is possible that reaction (3) contributes to the methyl radical decay, as suggested earlier.

3.3. Warming from 100 K

When the lamp was switched off after about 200 s photolysis at 100 K, the methyl radicals I decayed rapidly, but the acetyl radicals II were stable. When the sample was warmed to 110 K, methyl radicals could no longer be detected; they disappeared either by reaction (4) to form ethane or by reaction (3) to form methane and acetonyl radicals III. The acetonyl and acetyl radicals were stable to approximately 140 K, at which point they begin to decay. At 170 K, only a very low concentration of acetyl radicals could be detected. Similar free-radical stabilities have been reported by Pukhal'skaya et al. [11].

3.4. Volatile products

The volatile products of photolysis at 77 K (observed at 160 K) consisted of methane, ethane, carbon monoxide and hydrogen (Table 3). The major product, methane, arises from hydrogen atom abstraction by methyl radicals (reaction (3)) and by the photolysis of isopropanol radicals. The sources of methyl radicals are reactions (1), (2) and (7). The ethane must be formed by the combination of two methyl radicals. These may come from different molecules of acetone and may be produced either by direct photolysis according to reaction (1) or indirectly through reactions (5) and (7), or reactions (3) and (7). Alternatively, the two methyl radicals may come from the same acetone molecule, being formed by reactions (1) and (2). The mechanism of ethane formation was determined by photolysis of a 1:1 mixture of acetone and acetone-d_6 at 77 K. Only C_2H_6 and C_2D_6

TABLE 3

Volatile products observed at 160 K after
photolysis of acetone at 77 K

Product	Amount (mol.%)
C_2H_6	6
CO	30
CH_4	61
H_2	2

were observed in the mass spectrometer. Therefore, the ethane is produced
exclusively by geminate recombination. There is also the possibility that the
methyl radicals are formed by decomposition of adjacent molecules by the
sequence of reactions (5), (6), (2) and (7), and that these radicals combine
within the solvent cage. However, this would give a statistical proportion of
CH_3CD_3, which is not observed.

The ratio of methane to ethane (approximately 10:1) is in marked con-
trast with the results of Berthelot and Gaudechon [6], who observed mainly
ethane and a trace of methane. This difference between photolysis in the
solid and liquid phases reflects the relative mobility of the methyl radicals.

4. Conclusions

The mechanism of photolytic degradation of acetone in the solid state
has been found to be significantly temperature dependent. Between 100 and
110 K the principal photolytic reaction is cleavage of the C—C bond to
produce methyl and acetyl radicals (reaction (1)). Above this temperature
hydrogen atom abstraction by an excited state of acetone is the most impor-
tant reaction. The formation of methyl radicals from 100 to 110 K and of
isopropanol radicals from 110 to 170 K has been described by zero-order
formation and first-order decay kinetics. The differences in the rates of
decay with the UV lamp on or off demonstrate the importance of secondary
radical photolysis reactions.

The major volatile product observed by mass spectroscopy was meth-
ane, indicating that the majority of the methyl radicals decayed by a hydro-
gen atom abstraction reaction. The minor product, ethane, was shown to
be formed by geminate recombination of two methyl radicals formed by
degradation of a single acetone molecule.

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