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Product Analysis of Flash Photolysis of Acetone in Gas Phase

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GLC was used to measure the amounts of methane, ethane, ethylene, biacetyl, and methyl ethyl ketone formed in the flash photolysis of acetone in gas phase at 25 °C and at 2 – 20 Torr pressure of acetone and 0 – 270 Torr of nitrogen. The yields in flash photolysis of biacetyl and azomethane were also measured, and the products formed during irradiation with a constant low intensity light source. The results are discussed in terms of hydrogen abstraction reactions between hot radicals and acetone, collisional deactivation processes, dissociation reactions and addition reactions of thermally equilibrated radicals. As the acetone pressure was increased, small changes were observed in the relative yields, while the yield of biacetyl was found to increase rapidly, indicating an increase in the concentration of thermally equilibrated acetyl radicals produced from vibrationally relaxed singlet or triplet acetone. Ethylene was found in the flash photolysis of acetone, biacetyl and azomethane but not when a continuous light source was used. We suggest that ethylene is formed by hydrogen elimination from hot ethane itself, produced from a combination of hot methyl radicals.

Acetone has a broad [1] $(n-\pi)$ absorption from about 240 nm to 360 nm and a molar absorptivity $\varepsilon = 1.24$ m^2 mol^{-1} at the maximum absorption of about 280 nm. The quantum yields [2,3] for fluorescence and phosphorescence are low for acetone, about $\phi_F = 0.002$ and $\phi_P = 0.02$, respectively, with 313 nm excitation at 40 °C and 50 Torr of acetone. The quantum yield of photolytic decomposition is about $\phi = 0.5$ with 315 nm excitation at 25 °C and 10 Torr of acetone pressure. The quantum yield increases with decreasing acetone pressure and with increasing temperature approaching unity at about 120 °C.

O'Neal and Larson [2] proposed the following mechanism for primary processes in acetone photolysis:

$$A + h\nu \rightarrow {}^1A_m \quad (1)$$

$${}^1A_m \rightarrow {}^3A_m \quad (2)$$

$${}^3A_m \rightarrow CH_3^* + CH_3CO^* \quad (3)$$

$${}^3A_m + M \rightarrow {}^3A_0 + M \quad (4)$$

$${}^3A_0 + M \rightarrow {}^3A_n + M \quad (5)$$

$${}^3A_n \rightarrow CH_3 + CH_3 + CH_3CO \quad (6)$$

$${}^3A_0 \rightarrow A_m \quad (7)$$

A denotes acetone; superscrips 1 and 3 the first electronic excited singlet and triplet states, respectively; subscripts 0 the vibrational ground state and m and n the vibrationally excited states, respectively; and superscript * a hot species with an excess of energy. Experimental values for quantum yields of acetone fluorescence, phosphorescence and primary dissociation at different pressures, temperatures and with different concentrations of hydrobromic acid as quencher were explained [2] by the above mechanism.

Various products have been observed previously [1,3–10] in photolysis of acetone, *e.g.* carbon monoxide, hydrogen, methane, ethane, ethylene, acetaldehyde, ketene, biacetyl, methyl ethyl ketone and small amounts of other ketones of higher molecule weight. These products are expected to be formed from the radicals produced in the primary dissociation of acetone by radical combination and hydrogen abstraction reactions. By flash photolysis high con-

centrations of radicals can be produced and therefore the amounts of products of radical combination reactions should increase relative to the amounts of products formed in hydrogen abstraction reactions between a radical and acetone when compared with respective products formed in photolysis of acetone using a low intensity light source. No results on flash photolysis of acetone have previously been published. The present work was done in order to obtain more information about the mechanism of these reactions.

EXPERIMENTAL

A 1000 J discharge light source of about 15 μs half life, filled with about 100 Torr of krypton and about 10 Torr of nitrogen and connected to a 10 μF condenser was charged at about 12 kV as described earlier.[11] About 1 % of acetone reacted after each flash. The discharge tube and photolysis tube were about 2 m long and 2 cm of diameter. The reaction products of photolysis at 25 °C and at different pressures of acetone and nitrogen were analysed by GLC using Porapak Q or Carbowax 4000 columns and flame ionization detector. The relative amounts of products varied slightly with repeated flashing. The amounts of products corresponding to the first flash were obtained from a linear plot of the relative amounts of products against the number of flashes in each experiment. All materials were degassed in a vacuum line. The products were identified by GLC trough comparison with known substances, and partly by mass spectrometry. Calibration curves were prepared by GLC for quantitative analysis.

The following products were identified by GLC after the flash photolysis of acetone in gas phase; methane, ethane, ethylene, acetaldehyde, methyl ethyl ketone and biacetyl, Table 1. Small amounts of propane were also observed but it is expected to be a secondary product of photolysis of methyl ethyl ketone because by extrapolation to correspond to the first flash the relative amount of propane approached zero. In addition, two unidentified products, amounting to less than 1 % of the main product, ethane, were found. Because a flame ionization detector was used on GLC analysis, carbon monoxide and hydrogen could not be detected. Small amounts of hydrogen have been observed [4,5] in acetone photolysis with ultraviolet light below 200 nm.

The material balance of the products observed in flash photolysis of acetone, Table 1, is not satisfactory, indicating that a product is missing which contains relatively less hydrogen than acetone and hence is formed by a reaction involving hydrogen abstraction. The missing product could be ketene, though we could not detect it among the products. Ketene is difficult to detect in small amounts by GLC method. Ketene has been observed [6,7] in acetone photolysis at temperatures above 100 °C.

RESULTS AND DISCUSSION

The amounts of products observed in flash photolysis of acetone are shown in Table 1 and Fig. 1. The main product, ethane, is formed by combination of two methyl radicals.[11]

Methane is formed by hydrogen abstraction reaction (8) by methyl radical with acetone.

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 \qquad (8)$$

Table 1. Products of acetone photolysis formed during one flash at 25°C. Carbowax 4000 and Porapak Q columns were used in the GLC analysis of the first seven and the last four mixtures, respectively. Each column was capable of resolving only a part of the reaction products.

Reaction mixture P/Torr		Products 10^4 P/Torr					
CH_3COCH_3	N_2	CH_4	C_2H_4	C_2H_6	CH_3CHO	$(CH_3CO)_2$	$C_2H_5COCH_3$
2.09	276			136	1.02	2.23	2.36
4.29	16			219	2.70	6.76	2.57
4.23	103			217	3.25	5.78	2.71
9.10	0			314	4.72	24.5	3.66
9.32	35			355	4.08	27.3	4.90
9.08	223			328	4.92	17.9	5.31
19.77	251			471	7.42	54.8	8.25
2.02	283	10.6	2.71	105	1.39		
4.28	290	19.6	3.53	191	3.37		
9.38	274	22.0	3.95	279	5.69		
19.91	271	32.7	5.76	438	6.92		

Owing to the relatively large activation energy [8] $E = 40.1$ kJ mol^{-1}, the hydrogen transfer reaction (8) between thermally equilibrated methyl radicals and acetone molecules at 25 °C and at high concentrations of methyl radical is slow compared with the rate of combination [9,11] of methyl radicals to ethane. Since a primary decomposition of the excited acetone to methane is unlikely, methane is probably produced [9] in collisions between hot methyl radicals and acetone molecules, reaction (9).

$$CH_3^* + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 \quad (9)$$

$$CH_3^* + CH_3COCH_3 \rightarrow CH_3 + CH_3COCH_3^* \quad (10)$$

$$CH_3 + CH_3 + M \rightarrow CH_3CH_3 + M \quad (11)$$

Energy-rich methyl radicals are formed by dissociation of vibrationally excited triplet acetone molecules, reaction (3). The enthalpy of dissociation of acetone [10] is $\Delta H = 334$ kJ mol^{-1}, corresponding to light with $\lambda = 358$ nm. When acetone is excited at about the maximum absorption with 280 nm light, molecules with energy of about 427 kJ mol^{-1} are formed, which is more than is needed to break the C – C bond of acetone. Because we used unfiltered light, excited acetone molecules with even higher excess energy were formed. The zero point level of acetone triplet [2,3] is estimated to be about 314 kJ mol^{-1} and that of acetone singlet about 330 kJ mol^{-1}. The dissociation of acetone from zero point level of the triplet state [3] has an activation energy of $E = 40 \pm 4$ kJ mol^{-1}.

At high acetone pressures of about 20 Torr the relative amounts of methane produced in flash photolysis of acetone approach a constant value (Fig. 1). As the amount of methane is only about 8 % of that of ethane, the energy transfer process (10) is more effective than the hydrogen transfer reaction (9) in collisions between acetone and energy-rich methyl radicals. At low acetone pressures there is a slight increase in the relative amounts of methane. This could be due to the two competing processes (3) and (4), the latter becoming more important at higher pressures, resulting in a decrease in the amounts of energy-rich methyl radicals.

The activation energy is $E = 91 \pm 7.5$ kJ mol^{-1} for the dissociation reaction of thermally equilibrated acetyl radicals.[12] The rate of dissociation at 25 °C and at high concentrations of

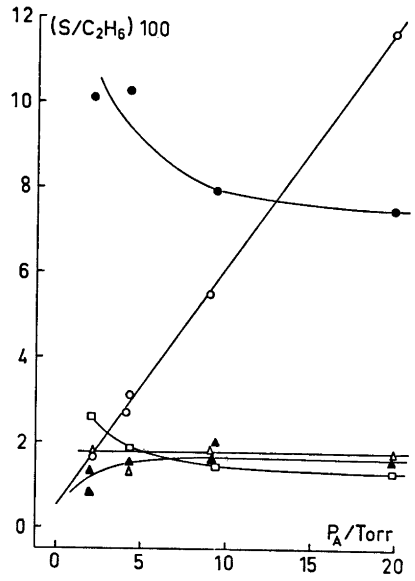

Fig. 1. Relative amounts of different products (S) formed in the flash photolysis of acetone in gas phase at 25 °C and different acetone (A) pressures and about 270 Torr of nitrogen. Symbols for different products (S): ●, CH_4; ○, $(CH_3CO)_2$; ▲, CH_3CHO; △, $CH_3COC_2H_5$; and □, C_2H_4.

acetyl radicals is slow compared with the rates of combination of acetyl radicals with methyl or acetyl radicals. The following reactions of acetyl radicals are expected to be important:

$$CH_3CO^* \rightarrow CH_3 + CO \quad (12)$$

$$CH_3CO^* + CH_3COCH_3 \rightarrow CH_3 + CO + CH_3COCH_3 \quad (13)$$

$$CH_3CO^* + CH_3COCH_3 \rightarrow CH_3CHO + CH_2COCH_3 \quad (14)$$

$$CH_3CO + CH_3COCH_3^* \quad (15)$$

$$CH_3CO + CH_3CO \rightarrow CH_3COCOCH_3 \quad (16)$$

$$CH_3CO + CH_3 \rightarrow CH_3COCH_3 \quad (17)$$

When the acetone pressure is increased the amount of biacetyl formed in flash photolysis of acetone increases rapidly (Fig. 1). As the amount of biacetyl formed is much less than the amount of ethane, the dissociation reactions (12) and (13) of hot acetyl radicals are faster than the reactions (14) and (15) in the pressure

range of 2 to 20 Torr of acetone. This also implies that the dissociation of vibrationally excited acetone triplets, reaction (3), is faster than the energy transfer process (4) which produces acetyl radicals of low energy. The increase in the amount of biacetyl produced when the pressure of acetone is increased is due to the increase in rates of energy transfer processes (4) and (15) relative to the unimolecular rates of dissociation reactions (3) and (12).

Acetaldehyde is probably formed in a hydrogen abstraction reaction (14) between an energy-rich acetyl radical and an acetone molecule. The amounts of acetaldehyde produced are approximately constant at different acetone pressures (Fig. 1) except for a small decrease at low pressures. At low pressures the unimolecular dissociation of hot acetyl radicals, reaction (12), should become more important relative to the bimolecular reaction (14) producing acetaldehyde, resulting in a decrease in the amounts of acetaldehyde produced. As only small amounts of acetaldehyde are produced, the dissociation of hot acetyl radicals (13) is faster than the hydrogen abstraction reaction (15). Equal amounts of methyl and acetyl radicals are produced in dissociation reaction (3), but the amount of methane is about four times larger than the amount of acetaldehyde produced in the photolysis, which indicates that the competing dissociation reaction (13) of hot acetyl radicals is faster than the energy transfer reaction of methyl radicals relative to the hydrogen abstraction reactions of the respective radicals.

Methyl ethyl ketone is most probably produced in an addition reaction between acetonyl and methyl radicals:

$$CH_3 + CH_2COCH_3 \rightarrow CH_3CH_2COCH_3 \quad (18)$$

The acetonyl radical which is formed in hydrogen abstraction reactions between hot methyl and acetyl radicals with acetone, eqns. (9) and (14), may involve an excess energy and dissociate to ketene and methyl radicals:

$$CH_2COCH_3^* \rightarrow CH_2CO + CH_3 \quad (19)$$

As the total amounts of acetonyl radicals formed in reactions (9) and (14) are larger than the amounts of acetonyl radicals disappearing in reaction (18), *i.e.* the yield of methane and acetaldehyde is larger than the yield of methyl ethyl ketone, some additional reaction must occur which consumes acetonyl radicals. One possible reaction is the dissociation of acetonyl radicals to ketene (19).

It has been proposed [11,13] that ethylene is produced in a reaction between two acetonyl radicals in the photolysis of acetone. The amount of ethylene formed does not agree with the amounts of acetonyl radicals produced in our experiments. Ethylene could also be formed *via* a combination of hot methyl radicals, followed by a 1,2-elimination of hydrogen from the energy-rich ethane intermediate:

$$CH_3^* + CH_3 \rightarrow CH_3CH_3^* \rightarrow CH_2CH_2 + H_2 \quad (20)$$

Similar addition elimination reactions were observed by Perona, Bryant and Pritchard [14] in a photolysis of a mixture of 1,1,1-trideuterioacetone and 1,1,3,3-tetrafluoroacetone. With a 250 W medium pressure mercury light source of low intensity, no ethylene was observed in photolysis of acetone (Table 2). At low radical concentrations a bimolecular reaction similar to (20) would be slow compared with reactions

Table 2. Relative amounts of products of photolysis of acetone, biacetyl and azomethane; flash or constant unfiltered light source at 25 °C.

Light source	Reaction mixture P/Torr		Products $10^4\,P$/Torr N_2	CH_4	C_2H_4	C_2H_6	CH_3CHO	CH_3COCH_3	$C_2H_5COCH_3$
Continuous	CH_3COCH_3	1.2	50	5.0		100			14
Continuous	CH_3COCH_3	4.6	18	5.0		100			25
Continuous	CH_3COCH_3	40.0	27	6.2		100			18
Flash	$(CH_3CO)_2$	1.3	216	7.5	2.3	100	6.2	117	
Flash	$(CH_3CO)_2$	3.1	210	9.3	2.5	100	8.8	112	
Flash	$(CH_3)_2N_2$	3.0	30	15.0	0.73	100			
Continuous	$(CH_3)_2N_2$	3.0	23	17.8		100			

(9) and (10). Ethylene was also observed in the flash photolysis of biacetyl and azomethane, the relative amounts being $C_2H_4/C_2H_6 = 0.066$ and $C_2H_4/C_2H_6 = 0.002$, respectively (Table 2). No ethylene was observed in low intensity photolysis of azomethane. At high temperatures of about 400 °C, large amounts of ethylene are produced in photolysis of acetone.[18] Production of ethylene is then favoured by the presence of molecules or radicals of high energy, as is assumed in reaction (20).

REFERENCES

1. Calvert, J. G. and Pitts, J. N., Jr. *Photochemistry*, Wiley, New York 1966, p. 393.
2. O'Neal, H. E. and Larson, C. W. *J. Phys. Chem. 73* (1969) 1011.
3. Cundall, R. B. and Davis, A. S. *Prog. React. Kinet. 4* (1967) 149.
4. Khan, M. A., Norrish, R. G. W. and Porter, G. *Proc. R. Soc. London Ser. A 219* (1953) 312.
5. Wettermark, G. *Ark. Kemi 18* (1961) 1.
6. Ferris, R. C. and Haynes, W. S. *J. Am. Chem. Soc. 72* (1950) 893.
7. Shaw, H. and Toby, J. *J. Phys. Chem. 72* (1968) 2337.
8. Ausloos, P. and Steacie, E. W. R. *Can. J. Chem. 33* (1955) 47.
9. Potzinger, P. and von Bünau, G. *Ber. Bunsenges. Phys. Chem. 72* (1968) 195.
10. Benson, S. W. *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, p. 370.
11. Pohjonen, M.-L., Leinonen, L., Lemmetyinen, H. and Koskikallio, J. *Finn. Chem. Lett. 6* (1974) 207.
12. Watkins, K. W. and Word, W. W. *Int. J. Chem. Kinet. 6* (1974) 855.
13. Mandelcorn, L. and Steacie, E. W. R. *Can. J. Chem. 32* (1954) 79.
14. Perona, M. J., Bryant, J. T. and Pritchard, G. O. *J. Am. Chem. Soc. 90* (1968) 4782.

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