formulas in Herzberg's book[6] for H_2O and H_3O^+ together with the familiar formulae for diatomic molecules for HO^-. The bond length and angle of H_2O were as above. The bond length and angle of H_3O^+ were taken to be 0.98 Å.[7] and 107°.[8] The bond length of HO^- was of course not needed. The librational frequency shifts were calculated from the inverse square roots of the average moments of inertia,[2] calculated according to Herzberg's formula.[5] The calculated frequencies for O^{18} species and resulting partition function ratios are in Table II.

TABLE II

FREQUENCIES OF H_2O, H_3O^+ AND HO^- AND ISOTOPIC PARTITION FUNCTION RATIOS AT 25°

Molecule	Frequencies, cm.$^{-1}$ O^{16a}	O^{18}	Degeneracy	Q'/Q
H_2O	3440	3431.11	1	
	1645	1638.95	1	
	3440	3425.90	1	
	667	665.12	3	1.2752
H_3O^+	3235	3230.22	1	
	1150	1141.46	1	
	2590	2578.27	2	
	1700	1695.80	2	
	643	642.18	3	1.3047
HO^-	3615	3603.05	1	
	477	475.42	2	1.2279

[a] Ref. 2.

From these partition function ratios two especially interesting equilibrium constants can be calculated.

$$H_3O^{18\,+} + H_2O^{16} \underset{}{\overset{K_2}{\rightleftharpoons}} H_3O^{16\,+} + H_2O^{18}$$

$$HO^{18\,-} + H_2O^{16} \overset{K_3}{\rightleftharpoons} HO^{16\,-} + H_2O^{18}$$

It is found that $K_2 = 1.2752/1.3047 = 0.9774$ and $K_3 = 1.2752/1.2279 = 1.0385$.

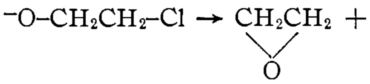
Discussion

The temperature dependence of these equilibrium isotope effects could be calculated, but since isotope effects are usually not very temperature dependent, this has not been done.

The effects of the halide ions, although fairly small, should be considered when studying reactions involving the production or destruction of these ions. Fluoride has $K_1 < 1$ because it increases the structure of water, while all the other ions break down the structure of water.

The isotope effects for the hydronium and hydroxide ions show that $H_3O^{16\,+}$ is a stronger acid than $H_3O^{18\,+}$, and that $HO^{18\,-}$ is a stronger base than $HO^{16\,-}$. In many reactions involving H_2O, H_3O^+ and HO^- (or the analogs $HO\text{-}C\!\lessdot$ and $H_2O^+\text{-}C\!\lessdot$) a bond to oxygen is being made or broken in the transition state, and a primary isotope effect due to that bond will appear along with the solvent isotope effect. However, in reactions involving a prior equilibrium, *e.g.*

$$HO^- + HO\text{-}CH_2CH_2\text{-}Cl \rightleftharpoons HOH + {}^-O\text{-}CH_2CH_2\text{-}Cl$$



$$^-O\text{-}CH_2CH_2\text{-}Cl \rightarrow CH_2CH_2(O) + Cl^-$$

the solvent isotope effect alone will determine the relative rates in H_2O^{16} and H_2O^{18}.

The isotope effect K_2 for changing $O<$(neutral) to ${}^+O\lessdot$(positively charged) means that positive charge formation is more favorable on the heavy than on the light oxygen atom. A reaction such as enolization by water as the base, in which positive charge is developed on the oxygen atom in the transition state, might therefore have an *inverse* kinetic isotope effect. This tendency for the heavy water to react faster would be lessened by the primary isotope effect and might be overbalanced by a large primary effect to give a "normal" kinetic isotope effect. It is possible, however, that some significant results could be obtained by considering these two opposing effects.

Reactions similar to K_3, *i.e.*, in which a bond is formed to a hydroxide ion, may in some cases also have an inverse kinetic isotope effect, since the heavy hydroxide ion is a stronger base than the light hydroxide ion. Again, the primary isotope effect would tend to cancel this effect, *i.e.*, to make the light ion react faster.

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(6) Ref. 4, pp. 187, 188, respectively.

(7) C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

(8) Taken as a compromise between 105° for water[4] and 109° (tetrahedral), this angle is also the observed one in NH_3 (ref. 4, p. 439).

[CONTRIBUTION FROM THE IBM RESEARCH CENTER, YORKTOWN HEIGHTS, NEW YORK]

Photochemistry of Methoxyacetone

BY R. SRINIVASAN

RECEIVED DECEMBER 28, 1961

Photolysis of methoxy acetone at 3130 Å. led to acetone and formaldehyde as the important products. A small amount (about 1/20th of the acetone) of carbon monoxide was the only other significant product. Although estimates of the yield of formaldehyde led to lower values than for acetone, it is likely that methoxy acetone decomposes mainly to one molecule each of acetone and formaldehyde. The quantum yield of acetone was 0.32. This value was unaffected by changes in pressure and was only slightly affected by an increase in temperature. Addition of biacetyl or nitric oxide had no observable effect. Oxygen had no effect at 105° but at room temperature a decrease in the yield of acetone was noted. It is believed that acetone (and formaldehyde) are formed by the Norrish type II intramolecular process. The effect of oxygen at room temperature may be due to changes in the surface of the walls of the reaction cell.

Introduction

The photochemistry of the simple aliphatic ketones has been extensively studied and is fairly well understood. It seemed logical to extend this knowledge to aliphatic ketones with more than one functional group. Methoxyacetone which is isoelectronic with 2-pentanone contains an ether function in addition to the carbonyl group. The interaction between the two groups should be small as the ultraviolet spectrum above 2000 Å. is very little different from that of 2-pentanone.[1]

Experimental

Materials.—Methoxyacetone was prepared by the oxidation of 1-methoxy-2-propanol with chromic acid as described by Mariella and Leech.[2] The product that was obtained was distilled on a spinning-band column of 23 theoretical plates. Even under the best conditions for distillation, the sample of methoxyacetone (b.p. 114°[3]) that was collected contained a little of 1-methoxy-2-propanol (b.p. 118–120°[2]). Final separation of the pure ketone was carried out in a gas chromatograph on a polyethylene glycol column (2 meters) at 70°. The sample that was collected was rerun at a lower temperature and found to be free from any impurity in detectable amount.

Oxygen and carbon dioxide were Matheson reagent grade samples that were used as obtained. Nitric oxide from the Matheson Co. was distilled from −157 to −195° before use. The biacetyl used was an Eastman Kodak (white label) sample. It was dried and degassed before use.

Apparatus.—A conventional vacuum line in which the methoxy acetone did not come in contact with stop-cock grease was used. Photolyses were conducted in a cylindrical quartz cell 4.4 × 4.2 cm. It was set in an aluminum furnace that could be heated electrically. The light source was a Hanovia S-100 medium pressure mercury arc filtered by 2 mm. of Pyrex glass. The useful radiation was the group of lines at 3130 Å. The extinction coefficient of methoxyacetone at 3130 Å. at room temperature was determined to be 6.49. The fraction of the incident radiation that was absorbed (which was never more than 6%) was calculated assuming Beer's law. The intensity of the light source was calibrated by the use of diethyl ketone at 100° as the actinometer. Absorbed intensities were of the order of 10^{15} quanta/sec. in the volume of the cell. In experiments in which a gas or vapor was added, the reactants were mixed by repeated expansion into a large volume.

Light emission studies were attempted in a cylindrical quartz cell 4.0 × 3.4 cm. with a window 1.5 cm. dia. on one side. The incident light (3130 Å.) was admitted through a monochromator and the emitted radiation was monitored through another monochromator. Either the human eye or a photomultiplier tube was used to detect the radiation. In the latter case, an electronic recorder traced the emission spectrum.

It was observed that the photomultiplier along with the amplifier circuit was capable of detecting $^1/_{100}$th of the light intensity of phosphorescence of pure biacetyl ($p = 2$ mm.) when excited by 3660 Å. radiation of intensity equal to the 3130 Å. source used.

Results

Photolysis of methoxyacetone led to the formation of a small amount of gas volatile at −195°. No other gaseous product was detected. Gas chromatographic analysis of the higher boiling fraction showed only one major peak which was identified as due to acetone by comparison with the retention time of a pure sample. The infrared spectrum of this product was also in agreement with the published spectrum[4] of acetone. No polymer was observed. Since none of the products other than acetone that were observed in the gas chromatogram amounted to more than 4% of the acetone fraction, a consideration of mass balance suggested that formaldehyde may also be a product.

A sample of methoxyacetone after exposure to light was condensed at −195° in a cold finger in the vacuum line. After a short time, the volatile material was distilled off at room temperature. The material left in the cold finger was sealed off and detached from the line. The contents were dissolved in dil. H_2SO_4 and tested with chromatropic acid.[5] A violet color indicated the presence of formaldehyde. Attempts were made to apply the test quantitatively to estimate formaldehyde by a procedure similar to that described by Strong and Kutschke.[6] The presence of acetone and methoxy acetone along with formaldehyde necessitated a preliminary separation which complicated the procedure. The estimate of formaldehyde was erratic and even at best was only 10% of the acetone. It is believed that part of the formaldehyde polymerized on the walls of the vacuum line. In the absence of other products it was considered safe to assume that methoxyacetone decomposed mainly by the over-all process

$$CH_3COCH_2OCH_3 \xrightarrow[3130]{h\nu} CH_3COCH_3 + HCHO \qquad (1)$$

In quantitative studies only the fraction non-volatile at −195°, which will be referred to as carbon monoxide, and acetone was determined.

Quantum yields for the formation of acetone under various conditions are given in Table I. The experiments in the presence of oxygen are divided into three groups. The first group of seven experiments at room temperature was carried out in

TABLE I

QUANTUM YIELDS OF ACETONE IN THE PHOTOLYSES OF METHOXYACETONE AT 3130 Å.

Ketone, mm.	Added gas	Pressure, mm.	Temp., °C.	Φ Acetone
17.4			25.0	0.32[a]
7.6			25.0	.32
3.1			25.0	.33
15.4	CO_2	39.7	25.0	.31
16.2	CO_2	248.0	25.0	.33
18.5			52.0	.33
17.6			74.1	.37
18.8			106.0	.38[b]
15.9	Biacetyl	1.0	25.0	.33
15.2	Biacetyl	2.1[c]	25.0	.37
16.0	Nitric oxide	11.8	25.0	.29
17.0	Oxygen	4.9	25.0	.28
16.2	Oxygen	0.8	25.0	.24
15.9	Oxygen	1.6	25.0	.25
16.0	Oxygen	2.3	25.0	.23
15.6	Oxygen	27.3	25.0	.22
16.6	Oxygen	28.8	25.0	.23
17.1	Oxygen	94.1	25.0	.20
15.6	Oxygen	44.6	25.0	.30
16.2	Oxygen	44.1	25.0	.31
17.7	Oxygen	8.2	103.0	.39
17.1	Oxygen	17.6	106.0	.38

[a] $\Phi_{CO} = 0.018$. [b] $\Phi_{CO} = 0.055$. [c] Appreciable absorption of 3660 Å. radiation by biacetyl occurred.

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(1) S. F. Marsocci and S. Mackenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

(2) R. P. Mariella and J. L. Leech, *ibid.*, **71**, 3558 (1949).

(3) "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1953, p. 280.

(4) American Petroleum Institute Research Project 44, Spectrum No. 1222.

(5) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem. Anal. Ed.*, **17**, 400 (1945).

(6) R. L. Strong and K. O. Kutschke, *Can. J. Chem.*, **37**, 1456 (1959).

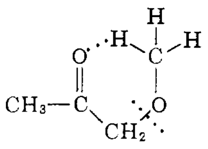
a cell that had previously been used in several runs on the pure ketone and one in the presence of oxygen. The first run listed was chronologically the second experiment in the presence of oxygen. The quantum yield for acetone that was obtained in this run does not fit in with the trend indicated by the remaining six runs. The second group of two runs at room temperature in the presence of oxygen were conducted in a cell that had previously been heated to 110° for several hours in the presence of oxygen. The two runs were made under nearly identical conditions. Although they agree with each other, they do not fit in with the trend indicated by the majority of runs in the first group. The two runs conducted in the presence of oxygen at about 105° were made at different times. They show very little effect due to oxygen at this temperature.

Some emission studies were also attempted on methoxyacetone. No emission was observed from the vapor (p = 18.9 mm.) either visually or with a photomultiplier, when excited by 3130 Å. radiation. A mixture of 17.4 mm. of methoxyacetone and 3.0 mm. of biacetyl did not give rise to any detectable emission when excited by the same radiation.

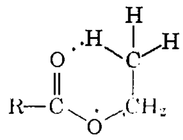
Discussion

The formation of acetone and formaldehyde appears to be the only important process in the photolysis of methoxyacetone at 3130 Å. and up to 105°. This probably occurs by the Norrish type II process[7,8] which has been observed in the photochemistry of all the aliphatic ketones with at least one proton on the carbon atom in the γ-position to the carbonyl group. The insensitivity of the production of acetone to changes in pressure or the addition of nitric oxide may be interpreted to favor this idea. The small increase in the quantum yield of acetone with an increase in temperature may be wholly due to an increase in the absorption coefficient with temperature. Since the quantum yield was calculated from the absorption coefficient at room temperature, the increase may not be real.

The mechanism of the type II process is fairly well understood[9,10] and in this instance would go through an intermediate such as



which would then give the enol form of acetone and formaldehyde. It is noteworthy that the introduction of a second oxygen atom in the six-membered ring of the intermediate has no appreciable effect on the efficiency of the process. This may be expected as esters derived from C_2 and higher alcohols also undergo an analogous process[11,12] (although with radiation of shorter wave length) and may go through the intermediate



which also involves two oxygen atoms in the six-membered ring.

In 2-pentanone, the net reaction

$$CH_3COCH_2CH_2CH_3 \longrightarrow CH_3COCH_3 + C_2H_4 \quad (2)$$

is endothermic by 20–30 kcal./mole for ground state molecules. The quantum yield for the type II process at 3130 Å. has been reported to be 0.22.[13] In methoxyacetone, the corresponding process (reaction 1) must be exothermic by at least 20 kcal./mole. The activation energy for the latter process in the ground state should be smaller as a result. The shift in the quantum yield for the type II process in methoxyacetone as compared to 2-pentanone appears to be in the right direction.

The small yield of carbon monoxide indicates that a free radical split such as

$$CH_3COCH_2OCH_3 + h\nu \longrightarrow CH_3CO + CH_2OCH_3 \quad (3)$$

followed by

$$CH_3CO \longrightarrow CH_3 + CO \quad (4)$$

is relatively unimportant. In support of this view it can be pointed out that the yields of ethane, biacetyl and $CH_3OCH_2CH_2OCH_3$ were virtually zero. Perhaps the methyl radicals abstract hydrogen atoms from the ketone even at room temperature. The formation of acetone by the process

$$CH_3CO + CH_3 \longrightarrow CH_3COCH_3 \quad (5)$$

is probably not competitive with the type II process under the conditions used here.

The effect of oxygen in this system is interesting, although the uncertainty in the data is relatively large. Brunet and Noyes[9] found that the type II process in 2-hexanone at 3130 Å, was unaffected by even 560 mm. of oxygen. Ausloos and Rebbert[13] on the other hand, found a progressive decrease in the quantum yield for the type II process in 2-pentanone with the addition of increasing amount of oxygen.

The formation of acetone from methoxyacetone appears to be unaffected by oxygen at 105°. This result was exactly reproducible over a period of time. At room temperature, oxygen affected the process adversely, but its effectiveness in terms of the decrease in the quantum yield for acetone for a given pressure of oxygen was not reproducible over a period of time. The effect was a minimum in a freshly cleaned cell which suggests that the walls of the cell may be involved. Since the rearrangement of the enol form of acetone that is produced in the type II process to the stable keto form probably involves a wall reaction,[14] the reaction

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[7] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

[8] For a review see J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

[9] V. Brunet and W. A. Noyes, Jr., *Bull. Soc. Chim.* (France), 121 (1958).

[10] R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 5061 (1959).

[11] P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

[12] R. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1053 (1961).

[13] P. Ausloos and R. E. Rebbert, *ibid.*, **83**, 4897 (1961); J. N. Pitts and A. D. Osborne ("International Symposium on Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishing Corp., New York, N. Y., 1961) have reported a value of 0.27.

[14] This has been demonstrated in the case of 2-hexanone (see ref. 10).

may be sensitive to the surface layer on the wall. It is possible that oxygen affects the surface layer and indirectly influences the formation of acetone in its keto structure. A probable mechanism is the oxidation of formaldehyde, which is one of the products, on the wall to give a surface layer which can prevent or slow down the enol to keto reaction. Oxygen can thus influence this photochemical reaction in a way which does not involve the usual routes, *i.e.*, by the trapping of free radicals or by the quenching of triplet states.[15]

If this explanation is correct, it cannot be applicable to the case of 2-pentanone in which *both* acetone and ethylene formation decreased on the addition of oxygen.[13] It should be interesting to see if oxygen is effective as a quencher in that system even at an elevated temperature.

NOTE ADDED IN PROOF.—Borkowski and Ausloos (*J. Phys. Chem.*, **65**, 2257 (1961), have shown that oxygen is an effective quencher of the type II process at 305°K. as well as at 420°K. in the photolysis of 2-pentanone-4,5,5-d_3 at 3130 Å.

Acknowledgment.—The author wishes to thank Dr. Harold L. Friedman for his advice and encouragement during the course of this work.

(15) It has been pointed out by one of the referees that if the scavenging effect of oxygen on free radicals in this system is not complete, other mechanisms may also be devised to account for the observed products. The formation of acetone may be by the reaction

$$CH_3COCH_2\cdot + CH_3O\cdot \rightarrow CH_3COCH_3 + CH_2O$$

if the primary process is

$$CH_3COCH_2OCH_3 + H\nu \rightarrow CH_3COCH_2\cdot + CH_3O\cdot.$$

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY, STANFORD, CALIFORNIA, AND THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA, AND LOS ANGELES, CALIFORNIA]

Kinetics of the Thermal Decomposition of Nitric Acid Vapor. IV. A Shock Tube Study Between 800–1200°K.

BY HALSTEAD HARRISON,[1] H. S. JOHNSTON AND E. R. HARDWICK

RECEIVED OCTOBER 26, 1961

The decomposition of nitric acid vapor in excess argon was studied in a shock tube between 800 and 1200°K. The reaction was followed in terms of the appearance of nitrogen dioxide and of the appearance and disappearance of the intermediate, NO_3. At total concentrations near 10^{-5} mole/cc. the decomposition is controlled by the unimolecular reaction

$$M + HNO_3 \xrightarrow{a} HO + NO_2 + M$$

near its second order limit, with

$$\log a = (15.2 \pm 1.0) - \frac{30.6 \pm 1.8}{2.303\,R} \cdot \frac{1000}{T}\ (\text{mole/cc.})^{-1}\ \text{sec.}^{-1}$$

The presence in this system of NO_3 and its rate of disappearance are consistent with previous work on the decomposition kinetics of nitric acid and nitrogen pentoxide.

Introduction

The decomposition of nitric acid vapor has previously been studied between 500 and 700°K. in conventional systems and at slow rates.[2] The reaction was found to involve a complex, non-chain mechanism

$$M + HNO_3 \underset{a_{-1}}{\overset{a}{\rightleftharpoons}} HO + NO_2 + M$$

$$HO + HNO_3 \xrightarrow{j} H_2O + NO_3$$

$$NO_3 + NO_2 \xrightarrow{e} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{f} 2NO_2$$

$$NO_3 + NO_3 \xrightarrow{g} 2NO_2 + O_2$$

The unimolecular decomposition was essentially second order at pressures below 10 mm., and rate j was fast compared to a_{-1}. At one atmosphere the reaction was in its complicated intermediate zone between second and first order kinetics, and rates j and a_{-1} were approximately equal. The free radical, NO_3, was not observed, but its presence was inferred from kinetic behavior.

Much is known of NO_3 from work by Schott and Davidson,[3] who studied the decomposition of N_2O_5 in a shock tube between 500 and 1200°K. Their efforts, combined with extensive previous work at lower temperatures, give separately evaluated elementary rate constants for steps e through g. Above 1000°K., Schott and Davidson noted in addition the onset of a unimolecular decomposition of NO_3 with an activation energy of about 50 kcal./mole, presumably

$$M + NO_3 \xrightarrow{k} NO_2 + O + M$$

The rapid reaction of oxygen atoms with NO_2 is known,[4] as is the decomposition of nitrogen dioxide[5]

$$O + NO_2 \xrightarrow{m} NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{l} 2NO_2 + O_2$$

This large body of quantitative data of elementary reactions goes a long way toward predicting

(1) Chemistry Departmenu, University of Michigan, Ann Arbor, Michigan.

(2) H. S. Johnston, L. Foering and J. R. White, *J. Am. Chem. Soc.*, **77**, 4208 (1955), and references cited therein.

(3) G. Schott and N. Davidson, *ibid.*, **80**, 1841 (1958), and references cited therein.

(4) W. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1156 (1957).

(5) R. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **81**, 2311 (1959).