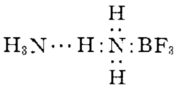
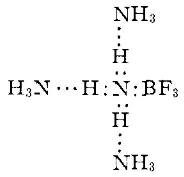
tain verification of the existence of this product. At this temperature the data revealed a sharp increase in pressure at a mole ratio NH_3/BF_3 of 4 to 1, establishing the existence of a total of four ammoniates in this system. Typical data are given in Table II.

It is of interest to consider the probable structures of these higher ammoniates. The powerful electron-withdrawing character of the boron trifluoride group must greatly increase the polar character of the three nitrogen–hydrogen bonds, resulting in a greatly increased ability to form hydrogen bonds with donor molecules. It is suggested that the stable 1:1 addition compound binds the 1, 2 and 3 additional ammonia molecules through a corresponding number of hydrogen bonds.



$\mathrm{H_3N\cdots H:\overset{H}{\underset{H}{N}}:BF_3}$



$\mathrm{H_3N\cdots H:\overset{\overset{NH_3}{\vdots}}{\overset{H}{\underset{\underset{NH_3}{\vdots}}{\underset{H}{N}}}}:BF_3}$

We attempted to test this interpretation by investigating the dimethylamine–boron trifluoride system. Since the 1:1 addition compound here contains but one nitrogen–hydrogen bond, the 1:1 product should be capable of uniting with a maximum of but one additional molecule of dimethylamine. However, the vapor pressure–composition data at 0° and at −64.0° showed no evidence for the existence of compounds other than the stable 1:1 product. It is probable that the accumulation of two methyl groups together with the bulky boron trifluoride group on a single nitrogen atom results in a serious steric barrier to hydrogen bonding involving the relatively bulky base, dimethylamine.

It therefore appears that compounds of higher order are quite possible in systems known to yield stable 1:1 addition compounds and the existence of such compounds of higher order presumably accounts for the difficulties frequently encountered in removing excess base in the presence of the 1:1 products.

Acknowledgment.—This investigation is a portion of a larger study of the chemistry of polyvalent metal halides being carried out with the aid of financial support by the Atomic Energy Commission. This assistance is gratefully acknowledged.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Formation of Formaldehyde in the Photo-oxidation of Acetone[1,2]

BY MARGARET I. CHRISTIE

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The reactions with oxygen of the radicals formed in the photolysis of acetone have been further investigated at low oxygen pressures at 120 and 175°. Quantum yields of formaldehyde formation have been determined colorimetrically. One molecule of formaldehyde, in addition to one molecule of either carbon monoxide or of carbon dioxide, results from the formation of each methyl radical in the acetone–oxygen system. It is suggested that methyl radicals react as follows: $CH_3 + O_2 + CH_3COCH_3 = CH_2O + H_2O + CH_2COCH_3$ (without implying that this reaction necessarily occurs in a single step). The acetonyl radicals would then be responsible for carbon monoxide and for carbon dioxide formation. By use of acetone labeled with carbon-14 in the end carbons it is shown that most if not all of the carbon dioxide comes from these carbon atoms.

Introduction

Acetone decomposes photochemically to methyl and acetyl radicals. When methane is formed, acetonyl radicals must also be formed. Marcotte and Noyes,[3] in an investigation of the photochemical oxidation of acetone at low oxygen pressures, measured the quantum yields of methane, carbon monoxide and carbon dioxide formed and of oxygen consumed. At temperatures of 120° and over and at oxygen pressures up to 2 mm., the quantum yield of oxygen disappearance was approximately constant at 4.0 ± 0.5. The sum of the yields of carbon monoxide and of carbon dioxide was about three irrespective of methane formation under conditions such that the dissociation of acetyl radicals was complete. After correction for carbon monoxide formed by dissociation of acetyl radicals, the CO_2/CO ratio was found to be proportional to the oxygen pressure. A mechanism consistent with the facts was based on the formation of formyl radicals by reaction of both methyl and acetonyl radicals with oxygen. It did not predict large yields of formaldehyde.

It is doubtful if formyl radicals are oxidized to carbon dioxide since this is not a major product in the photochemical oxidation of formaldehyde.[4,5] Other authors[6,7] favor the reaction $HCO + O_2 = CO + HO_2$. The photo-oxidation of dimethylmercury and of methyl iodide give CO_2/CO ratios almost independent of oxygen pressure.[8]

Formaldehyde has recently been identified[9] as a product in the acetone–oxygen system.

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[1] This work was supported in part by contract between the Office of Naval Research, United States Navy, and the Department of Chemistry, University of Rochester.

[2] The author wishes to express her gratitude to the Celanese Corporation of America for a postdoctoral fellowship for the year 1952–1953. Present address: Newnham College, University of Cambridge, England.

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[4] J. E. Carruthers and R. G. W. Norrish, *J. Chem. Soc.*, 1036 (1936).

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[6] K. Faltings, W. Groth and P. Harteck, *Z. physik. Chem.*, **41B**, 15 (1938).

[7] G. von Elbe and B. Lewis, *J. Chem. Phys.*, **7**, 717 (1939).

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[9] D. E. Hoare, *Trans. Faraday Soc.*, **49**, 1292 (1953).

In this paper quantum yields of formaldehyde formation are reported. Some results are also given with isotopically labeled acetone, $C^{14}H_3COC^{14}H_3$, to indicate the source of the carbon dioxide.

Experimental

Redistilled Baker C.P. acetone was introduced into the apparatus through anhydrous calcium chloride. The acetone was redistilled at low pressures and the middle third retained. The labeled acetone (purchased from the Nuclear Instrument and Chemical Corporation) with one millicurie of activity was diluted 100 to 1 with acetone purified as above. Oxygen was obtained by heating potassium permanganate and dried by passage through a trap immersed in liquid nitrogen.

The light source was an Alpine burner (Type S100). The beam, collimated by a quartz lens and a series of stops, was 1.5 cm. in diameter as it passed through the quartz reaction vessel 20 cm. in length and of 2.2 cm. internal diameter. A Pyrex filter was used so that the effective wave lengths were 3130 and 3020 Å.

Oxygen could be dosed into the system from a small volume between two capillary stopcocks. A magnetically driven stirrer prevented local depletion of the oxygen.

Methods of analysis for CO, CO_2, CH_4 and O_2 have been described.[3] Acetone was used as an internal actinometer since the quantum yield of carbon monoxide formation at 3130 Å. at the temperatures used is unity.[1] Approximately 10^{12} quanta/cc./sec. were absorbed.

The colorimetric methods for determination of formaldehyde and of acetaldehyde have been described.[11] Acetone in thousand-fold excess did not interfere with these methods. Samples for the colorimetric determinations were obtained by condensing the products into a trap containing water cooled to the temperature of liquid nitrogen. Formaldehyde could not be successfully separated from the other products by a Ward still fractionation.

TABLE I

QUANTUM YIELDS IN THE PHOTOCHEMICAL ACETONE–OXYGEN REACTION

Acetone pressure 130 mm.

Oxygen pressure, mm. × 10^3	Quantum yields CH_2O Phenylhydrazine method	CH_2O *p*-Hydroxydiphenyl method	CH_3CHO *p*-Hydroxydiphenyl method	$CH_3 + O_2$ calcd. for reaction 4
		120°		
17	1.6	...	...	1.4
56	1.9	...	...	1.8
73	1.8	...	...	1.8
262	2.3	2.2	0.1	1.7 (2.0)[a]
380	2.0	...	...	1.6 (1.9)[a]
494	1.5	...	...	1.5
650	1.7	1.8	0	1.4
1400	1.3	1.0	0	1.0
2240	1.2	1.0	0	1.0
		175°		
20	1.0	0.8	0.3	1.1
62	2.0	1.8	0.1	1.7
100	...	2.0	0.1	1.9
400	2.5	2.4	0	2.0
710	2.1	1.9	0	1.9
1750	...	2.2	0	1.8
2330	...	2.0	0	1.7
5000	...	1.6	0	...

[a] Bracketed figures are CO_2 yields which, from the mechanism, should be a minimum for $CH_3 + O_2$ when no CH_4 is formed. There is some divergence from the simple mechanism here since $\Phi_{CO_2} > 1 + \Phi_{CO}$, which should represent a maximum value for $\Phi_{(CH_3 + O_2)}$.

For the radioactive counts carbon dioxide was absorbed in potassium hydroxide solution. The activity per millimole of acetone was determined by converting methane and ethane from photolysis of acetone in the absence of oxygen to carbon dioxide and absorption in potassium hydroxide. An estimate of acid, assumed to be acetic, was made by condensing products not volatile at −100° into barium hydroxide solution. Acetone was removed by evaporation to dryness and ignition at 450°.[12]

Tests for peroxides were negative.[13]

Results

Preliminary runs, in which analyses were made for carbon monoxide, carbon dioxide, methane and oxygen, were in general agreement with previous work.[3,9] Experiments with the carbon-14 labeled acetone showed that most, if not all, of the carbon dioxide came from the radioactive carbon in the methyl groups. The quantum yield of acetic acid formation was at least unity assuming that no other acid is formed and that the acetic acid molecule contains one radioactive carbon atom. A degree of uncertainty is attached to these results since, owing to some unidentified impurity in the labeled acetone, quantum yields of carbon dioxide were higher than for pure acetone.

The main results are given in Table I.

Discussion

The following mechanism is in general agreement with the experimental facts

$$CH_3COCH_3 + h\nu = CH_3 + COCH_3 \quad \phi \qquad (1)$$

$$CH_3CO = CH_3 + CO \quad \alpha\phi \qquad (2)$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \quad \beta(1 + \alpha)\phi \qquad (3)$$

$$CH_3 + O_2 + CH_3COCH_3 = CH_2O + H_2O + CH_2COCH_3 \quad (1 - \beta)(1 + \alpha)\phi \qquad (4)$$

$$CH_3COCH_2 + O_2 = X \quad (1 + \alpha)\phi \qquad (5)$$

$$X = HCO + CH_3COOH \quad \gamma(1 + \alpha)\phi \qquad (6)$$

$$HCO + O_2 = CO + HO_2 \quad \gamma(1 + \alpha)\phi \qquad (7)$$

$$HO_2 = {}^1/_2H_2O + {}^3/_4O_2 \quad \gamma(1 + \alpha)\phi \qquad (8)$$

$$X + O_2 = CO_2 + OH + CH_3COOH \quad (1 - \gamma)(1 + \alpha)\phi \qquad (9)$$

$$OH = {}^1/_2H_2O + {}^1/_4O_2 \quad (1 - \gamma)(1 + \alpha)\phi \qquad (10)$$

$$O_2 + CH_3CO = Y \quad (1 - \alpha)\phi \qquad (11)$$

ϕ = the quantum yield of the primary process, probably unity at these temperatures.[14]

The quantum yield of oxygen disappearance may be calculated by substituting values of α, β and γ derived from experimental results[3,9] as follows:

Oxygen press., mm. × 10^3	20	100	500	1000
120°	3.8	4.5	4.3	3.8
175°	3.9	4.8	4.9	4.7

The ultimate fate of the OH and HO_2 radicals is uncertain. The fact that no peroxides were detected

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(10) D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

(11) R. Gomer and W. A. Noyes, Jr., *ibid.*, **72**, 101 (1950). The author wishes to thank Dr. W. D. Walters of this Laboratory for additional information about these methods.

(12) The radioactive analyses were performed in the Atomic Energy Commission Project at the University of Rochester under the supervision of Dr. L. Miller.

(13) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 880.

(14) See W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

might be taken to indicate that oxygen is eventually regenerated according to (8) and (10). In the table it is seen that the experimental values for the quantum yield of formaldehyde formation agree fairly well with that of $CH_3 + O_2$ (reaction 4) when based on α and β derived from experiment.

The mechanism predicts satisfactorily the variations in the quantum yields of methane, carbon monoxide, carbon dioxide, and the sum of carbon monoxide and carbon dioxide with oxygen pressure and with temperature. If the primary quantum yield is unity, one finds the following: Φ_{CO} (max.) = 3 when $\alpha = 1, \gamma = 1$; Φ_{CO} (min.) = 0 when $\alpha = 0, \gamma = 0$; Φ_{CH_4} (max.) = 2 when $\alpha = 1, \beta = 1$; Φ_{CH_4} (min.) = 0 when $\beta = 0$; Φ_{CO_2} (max.) = 2 when $\alpha = 1, \gamma = 0$; Φ_{CO_2} (min.) = 0 when $\gamma = 1$; $\Phi_{CO + CO_2}$ (max.) = 3 when $\alpha = 1$; $\Phi_{CO + CO_2}$ (min.) = 1 when $\alpha = 0$.

The experimental results of Marcotte and Noyes[3] confirm that these maxima and minima are reached or tend to be reached under those conditions of oxygen pressure and temperature which one would predict if the activation energies of (11), (4) and (9) are small compared to those of (2), (3) and (6), respectively. In addition the relationship $\Phi_{CO_2}/(\Phi_{CO} - \alpha) = k(O_2)$, which may be predicted from the mechanism, was also confirmed experimentally.

Reaction 4 may either occur as a single step or by one of the sequences

$$CH_3 + O_2 = CH_2O + OH \qquad (12)$$

$$OH + CH_3COCH_3 = H_2O + CH_3COCH_2 \qquad (13)$$

or

$$CH_3 + O_2 = CH_3O_2 \qquad (14)$$

$$CH_3O_2 + CH_3COCH_3 = CH_3O_2H + CH_3COCH_2 \qquad (15)$$

$$CH_3O_2H = CH_2O + H_2O \qquad (16)$$

Step 12 has often been postulated.[15-19] While there is no direct evidence that hydroxyl radicals abstract from acetone at these temperatures, the hydroxyl radicals formed in step (12), which is exothermic (*ca.* 50 kcal.[17]), might retain sufficient energy for this purpose.

Methyl hydroperoxide has been isolated[20] at lower temperatures in the mercury photosensitized methane oxidation. It is doubtful if reaction 16 would proceed quantitatively, however.[21,22]

A third possibility would be based on the reactions suggested by Marcotte and Noyes,[3] but the reasons against some of these steps have already been given.

The reaction[23,24]

$$2CH_3O_2 = 2CH_3O + O_2 = CH_2O + CH_3OH + O_2 \qquad (17)$$

would be expected to become important only at high radical concentrations.

It has been suggested[25] that methyl glyoxal may be an intermediate in the oxidation of acetonyl radicals to carbon dioxide in the liquid acetone–oxygen system. If this were the case in the gas phase also, X would be replaced by $CH_3COCHO + OH$. Equations 6 and 7 would follow only if OH radicals have a specific effect on methyl glyoxal and reaction 9 would imply oxidation of methyl glyoxal to acetic acid and carbon dioxide by oxygen at the temperatures used. A reaction of X to give acetaldehyde would seem to be of little or no importance in view of the small amount of this compound formed.

The reaction of acetyl radicals with oxygen has not been elucidated. They must react with oxygen but cannot produce directly or indirectly either carbon monoxide or carbon dioxide except to a very limited extent (see footnote to Table I). The formation of peracetic acid[26] is not possible since presumably this would be accompanied by formation of acetonyl radicals which would in turn lead either to carbon monoxide or to carbon dioxide. Possibly acetyl radicals could form ketene by a hydrogen abstraction reaction.

The author wishes to thank Professor W. A. Noyes, Jr., for his interest and encouragement in this work and for many helpful discussions throughout the year.

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