[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Photochemical Oxidation of Acetone*

BY F. O. RICE AND C. E. SCHILDKNECHT

(1) Introduction

In studying the photochemical decomposition of acetone, Damon and Daniels[1] observed that traces of oxygen produced an initial reaction much more rapid than the decomposition that occurred after all the oxygen was used up; this oxidation reaction was accompanied by a blue fluorescence and proceeded with a decrease in pressure. Damon and Daniels suggested that a chain reaction might be occurring but did not examine the products or investigate the oxidation reaction further. However, Fugassi,[1b] working in Daniels' laboratory, measured the quantum yield of the oxidation and concluded that if one molecule of oxygen reacts with one molecule of acetone, the quantum yield for the oxidation of acetone is the same as that for its decomposition. In contrast with our work, the experiments of Damon and Daniels and of Fugassi were performed with oxygen at partial pressures of less than 1% of that of the acetone.

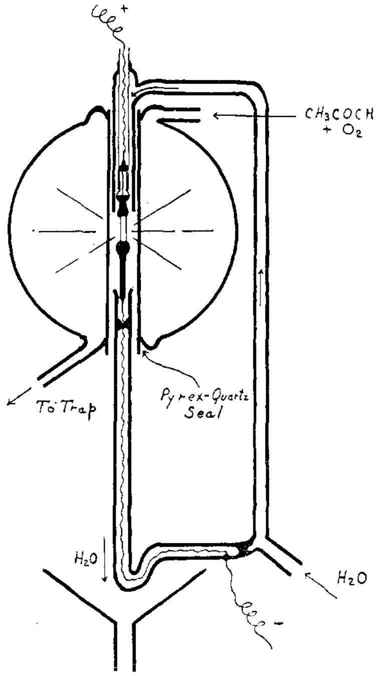

Fig. 1.

We have found that the oxidation occurs through a short chain and that the principal over-all reaction may be expressed by the stoichiometric equation

$$CH_3COCH_3 + O_2 \longrightarrow CH_3COOH + HCHO$$

This is followed by a photochemical chain oxidation of the aldehyde according to the equation

$$HCHO + O_2 \longrightarrow H_2O + CO_2$$

These products are accompanied by various peroxides in smaller amount formed in secondary reactions.

The photochemical oxidations of formaldehyde and acetaldehyde have been studied by Carruthers and Norrish[2] and have been found to be short chains also. This is in marked contrast to the ordinary photodecomposition of these compounds, since the aldehyde decompositions are chains,[3] but the acetone decomposition is not a chain,[4] at least not at temperatures up to about 400°.

(2) Experimental

Various types of flowing systems were used in the work and one of them which was particularly satisfactory is shown in Fig. 1. Dry oxygen was bubbled through acetone at about 150 cc. per minute in a bubbler at 22° and gave a mixture containing about 25% of acetone. This was passed directly into the reaction vessel, a 1-liter Pyrex bulb containing a high pressure capillary quartz mercury arc of the type described by Daniels and Heidt.[5] The lamp was mounted in a quartz test-tube through which water was circulated; the temperature of the cooling water was kept at about 40° to prevent condensation of products on the walls of the tube. The lamps which we used had an output of from 0.05 to 0.2 einstein per hour between 2536 and 4350 Å. as measured by the uranyl sulfate-oxalic acid actinometer solution.[6] In the apparatus shown, a large part of the active light is absorbed and the photolysis presents a striking appearance by the condensation of droplets of products upon the walls of the jacket.

All experiments, including especially distillations, were performed behind shatter-proof glass because of the explosive nature of the peroxides formed. We had several explosions during the course of distillations but illumination of the pure acetone-oxygen mixture never resulted in an explosion. In one experiment we mixed hexane vapor with the acetone-oxygen mixture and observed that a

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(1) (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Fugassi, *ibid.*, **59**, 2092 (1937).

(2) Carruthers and Norrish, *J. Chem. Soc.*, 1036 (1936).

(3) Akeroid and Norrish, *ibid.*, 890 (1936); Leermakers, THIS JOURNAL, **56**, 1537 (1934).

(4) Leermakers, *ibid.*, **56**, 1899 (1934).

(5) Daniels and Heidt, *ibid.*, **54**, 2381 (1932). In some runs we used other types of lamps, especially the mercury argon type. This of course necessitated suitable modifications of the apparatus.

(6) Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

cloud formed during the course of the oxidation. After running for a few minutes, the mixture exploded, completely shattering the apparatus. The most difficult part of the work was the separation, identification and estimation of the products formed in the photoöxidation. The results of a typical run are shown in Table I.

TABLE I

PHOTOCHEMICAL OXIDATION OF ACETONE

Temp. 80–100°. Total pressure, 760 mm. Acetone, 200 mm.; O_2, 560 mm. Acetone passed, 2.73 moles; time, 16 hours. High pressure Hg arc.

Fraction	Boiling range °C.	Volume, Mm.	Cc.	Composition
1	15–20	760	0.1	Dimethyl peroxide
2	20–40	760	.1	Acetone[a]
3–10	40–53	760	165	Acetone
11–14	24–45	75	3.0	Acetone[b]
15–18	45–49	75	5.0	Acetone[b]
19–20	49–50	75	3.0	Acetic acid[c]
21–22	50–54	75	3.0	Acetic acid[c]
23	30–35	13	0.5	Peroxide
24	35	13	.5	Peroxide[d]

[a] Contained some peroxide. [b] Contained some acetic acid. [c] Contained all the formaldehyde largely as paraformaldehyde. [d] Explosive white solid, m. p. ~30°.

The twenty-four fractions were obtained by distillation in a 30-cm. column with a rotating receiver and constant pressure control. Each fraction was weighed and a weighed portion of each was dissolved in water and used for quantitative estimations. The remainder was used for qualitative tests and preparation of derivatives.

Fractions (1) and (2) consisted of a gas with a sweetish, ethereal smell reminiscent of nitrous fumes but producing a stinging sensation in the nose when inhaled. The gas was soluble in water, did not give an aldehyde test and slowly liberated iodine from a potassium iodide solution acidified with acetic acid; it was very explosive. These properties and its boiling point indicate that it is dimethyl peroxide CH_3–O–O–CH_3.

Unreacted acetone was estimated by the iodoform method making a correction for the formaldehyde. Methanol was absent and acetaldehyde was present only in traces. Formaldehyde and its polymer were present in all the acetic acid fractions; the formaldehyde was identified as the 2,4-dinitrophenylhydrazone and was estimated volumetrically by reduction of copper.

Water was formed in the oxidation but was not estimated; free hydrogen was absent from the gases leaving the reaction vessel. There was a considerable amount of carbon dioxide formed which was estimated by absorption by Ascarite.

The last fractions, before distillation was completed, consisted of an oily residue; as this was heated to about 120° it turned reddish-brown and exploded with a bright flash of light demolishing the apparatus. Distillation at low pressure gave a white waxy solid, melting just above room temperature, which detonated violently if dropped on a hot-plate. It was sparingly soluble in water and reacted with acidified potassium iodide. This material was probably largely diacetyl peroxide which has already been reported by Carruthers and Norrish as a product of the photochemical oxidation of acetaldehyde. In Table II we summarize the analytical results for a typical run.

TABLE II

PHOTOCHEMICAL OXIDATION OF ACETONE

Conditions same as in Table I

	Moles	Moles
Acetone passed	0.582	..
Acetone recovered	.555	..
Acetone oxidized	.027	1.0
Acetic acid	.023	0.85
Carbon dioxide	.020	.74
Formaldehyde	.003	.11
Peroxide	.002	.07
Carbon monoxide	.002	.07
Water (not determined)	...	..

The quantum yield of the oxidation process had an average value of 0.3 as compared with the value 0.03 for the photochemical decomposition of acetone carried in a stream of carbon dioxide in the same flowing system. In one of these experiments a mercury–argon glow lamp was used as light source and the output of the lamp was determined in position in the reaction chamber just before and after each oxidation run by filling the jacket with actinometer solution. We assumed that the glow lamp emitted only light of wave length 2536 Å. (actually the figure is 86%) and from the extinction coefficient for acetone[7] and the dimensions of the irradiation jacket we calculated the quantum yields. In other experiments we used a capillary arc following the same method and made a graphical estimate of the distribution of energy in the spectrum of the lamp. The amount of acetone decomposed was found by titrating for acetic acid in the oxidation experiments and by estimating the carbon monoxide produced in the photodecomposition of pure acetone. The results obtained are shown in Table III.

The refractive index of the recovered acetone in the experiments in absence of oxygen was increased only very slightly (1.358 to 1.360) and no yellow color appeared on evaporation; a test for acetonylacetone was negative.

(3) Discussion of Quantum Fields

Our average value of 0.36 for the quantum yield of the oxidation process is near to Fugassi's[1b] value of 0.24, which is the number of molecules of oxygen reacting per quantum absorbed when the acetone is in very great excess. However, Damon and Daniels[1a] report a yield of 0.17 molecule per quantum for the decomposition in absence of oxy-

[7] Porter and Iddings, THIS JOURNAL, **48**, 40 (1926).

TABLE III

QUANTUM YIELD DETERMINATIONS FOR PURE ACETONE AND FOR ACETONE + OXYGEN

Temp. 80–100°. The light source was a mercury argon lamp in Expt. (1) and a high pressure capillary arc in all the others.

Expt.	Gas present	Length of run, hrs.	Output of lamp, einsteins/hr.	Light absorbed in run, einsteins	Moles product	Quantum yield
1	O_2	4.64	0.0011	0.00088	0.00034 CH_3COOH	0.39
8	O_2	2.75	.071	.025	.009 CH_3COOH	.36
9	O_2	2.16	.071	.0152	.0061 CH_8COOH	.40
11	O_2	1.50	.050	.0104	.003 CH_3COOH	.33
12	O_2	1.90	.050	.0123	.004 CH_3COOH	.33
1P	CO_2	1.00	.070	.0091	.0003 CO	.03

gen, in contrast with our value of 0.03; they found that the quantum efficiency was diminished by increasing the light intensity and by lowering the pressure of acetone. Since we used much higher light intensities and also a lower pressure of acetone, the difference may be due to different experimental conditions. Norrish, Crone and Saltmarsh[8] also obtained results substantially in agreement with Damon and Daniels, and reported values for the quantum yield of the decomposition process in the range 0.2 to 0.4.

There is a possibility of error in our results for the quantum yield of the decomposition process because we estimated the extent of decomposition by analyzing for carbon monoxide and Barak and Style[9] have shown that acetone partly decomposes photochemically into diacetyl below 60°. Unfortunately, while we tested for acetonylacetone, and examined the refractive index of the residual acetone, we did not make a direct test for diacetyl; however, it seems highly unlikely that 80–90% of the acetone decomposed would form diacetyl under our conditions, and this amount would be necessary to bring our result up to previous values.

(4) Mechanism of the Oxidation of Acetone.—The following scheme gives a satisfactory representation of the course of the reaction from the point of view of products formed as well as from the standpoint of certain rules concerning the course of elementary reactions.[10]

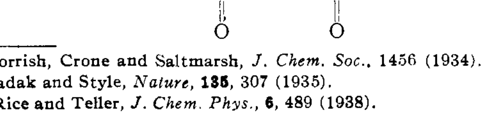
$$CH_3COCH_3 + h\nu \longrightarrow CO + 2CH_3 \qquad (1)$$

$$CH_3 + O_2 \longrightarrow CH_3{-}O{-}O \qquad (2)$$

$$CH_3O_2 \longrightarrow HCHO + OH \qquad (3)$$

$$OH + CH_3COCH_3 \longrightarrow H_2O + CH_3COCH_2 \qquad (4)$$

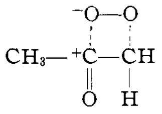
$$\left.\begin{array}{l} CH_3COCH_2 + O_2 \longrightarrow CH_3COCH_2{-}O{-}O \\ CH_3COCH_2O_2 \longrightarrow HCHO + CH_3COO \\ CH_3COO + CH_3COCH_3 \longrightarrow \\ \qquad CH_3COOH + CH_3COCH_2 \end{array}\right\}\text{Chain} \quad \begin{array}{l} (5) \\ (6) \\ \\ (7) \end{array}$$



$$2CH_3COO \longrightarrow CH_3\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}\,CH \qquad (8)$$

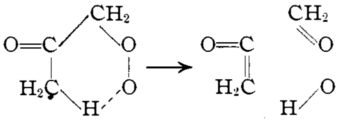
Since the oxidation occurs in the range 80–100° we have represented the primary step as a direct decomposition into carbon monoxide and methyl radicals since probably the acetyl radical is very unstable in this temperature range.[11] The reaction of methyl with oxygen (2) and the decomposition into formaldehyde and hydroxyl (3) as well as the reaction of hydroxyl with acetone (4) seem quite reasonable from the standpoint of the principle of least motion. Since the heavy fractions did not seem to contain any CH_3COOH, we have represented the radical CH_3–O–O as decomposing, instead of attacking the acetone.

Presumably we can neglect any decomposition of the acetonyl radical into ketene and methyl because of the high activation energy of this process.[12] However, the decomposition of the acetonyl peroxide presents some difficulties: we may assume that there is an attraction between the positive carbon and negative oxygen as shown



(9)

followed by splitting off of formaldehyde, leaving an acetate radical or we may assume that the radical is chelated



(10)

and decomposes into formaldehyde, ketene and hydroxyl. The process represented by equation (6) is simpler than (10) and probably is to be preferred. Furthermore, if ketene was formed some of it probably would have escaped reaction with water formed in the chain and would have been detected by its characteristic odor. The considerable production of the solid explosive peroxide

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[8] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

[9] Badak and Style, *Nature*, **135**, 307 (1935).

[10] Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938).

[11] Spence and Wild, *J. Chem. Soc.*, 352 (1937).

[12] Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(probably diacetyl peroxide) suggests that the main chain-terminating reaction is the combination of two acetate radicals.

It is of course possible that the attack of the hydroxyl radical on acetone may be represented by the equation

$$OH + CH_3COCH_3 \longrightarrow CH_3COOH + CH_3 \quad (11)$$

instead of (4), followed by equations (2) and (3). This would also represent correctly the chemical course of the decomposition, especially if we assume that reactions (4) to (8) occur to a small extent as side reactions producing diacetyl peroxide; however, we believe that equation (4) is to be preferred to equation (11).

Summary

1. The products of the photochemical oxidation of gaseous acetone at 100° with the full radiation from a mercury vapor lamp are acetic acid and formaldehyde; the formaldehyde is largely oxidized to carbon dioxide and water; there are smaller amounts of organic peroxides formed.

2. The quantum yield of the oxidation process has been found to be about 0.3, approximately ten times the quantum yield of the photochemical decomposition in presence of carbon dioxide in the same system.

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The Oxide-coated Filament. The Relation between Thermionic Emission and the Content of Free Alkaline-earth Metal

BY C. H. PRESCOTT, JR., AND JAMES MORRISON

Introduction

The oxide-coated filament had its beginning in the sealing-wax era of vacuum technique. The obscure accident of its origin is not recorded, but all of our older physicists knew that an enhanced emission of electrons could be obtained by smearing sealing-wax on a platinum ribbon and burning it off in air. The first authentic study is recorded by Wehnelt,[1] who investigated the voltage-drop in a gas discharge tube with cathodes coated with various metallic oxides. Its further evolution and development to the status of a cathode in Western Electric vacuum tubes has been described by H. D. Arnold.[2] A comprehensive treatment of its history, the various modifications in current use, and divergent theories of its preparation and behavior has been given by Saul Dushman[3] in a treatise on "Thermionic Emission." A later review is given by J. H. deBoer.[4]

The present work is devoted to a quantitative determination of the relation between thermionic emission and the content of free alkaline earth metal. To this end we have employed a filament which is a platinum rhodium core coated with barium, strontium, and nickel carbonates. On heating in a reducing atmosphere this coating becomes a grossly homogeneous colloidal mixture of barium oxide, strontium oxide, and free nickel. After a thorough preliminary clean-up of the experimental tube, the requisite amounts of free alkaline-earth metal are generated by reaction with methane. The electrical measurements are summarized by the use of the Richardson equation for thermionic emission. Free alkaline earth metal has been determined by oxidation with carbon dioxide and analysis of the gaseous reaction products.

Acknowledgment is due to Mr. V. L. Ronci and his staff for their care in the assembly of the vacuum tubes used in these studies.

Experimental Procedure

The experimental tube used for these studies, as shown in Fig. 1, contains a filament whose core is a 0.0127-cm. wire of 80% platinum and 20% rhodium. The coating was applied by passing the core through a suspension of barium carbonate, barium nitrate, strontium carbonate, and basic nickelous carbonate in amyl acetate and pyroxylin. Three coats were applied after each of which the filament passed through an oven at 675° in an atmosphere of carbon dioxide. The coating vehicle largely evaporated and the fusion of barium nitrate gave the coating enough adherence to undergo the processes of assembly. The final coating is 0.0025 cm. thick to as close as we can determine.

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(1) A. Wehnelt, *Ann. Physik*, **14**, 424 (1904).

(2) H. D. Arnold, *Phys. Rev.*, **16**, 70 (1920).

(3) Saul Dushman, *Rev. Modern Phys.*, **2**, 381 (1930).

(4) J. H. deBoer, "Electron Emission and Adsorption Phenomena," Cambridge University Press, Cambridge, England, 1935.