

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

## Oxidation of the Radicals Produced in Acetone Photolysis

BY ROBERT R. HENTZ<sup>1,2</sup>

RECEIVED APRIL 13, 1953

Photooxidation of acetone proceeds through acetyl and methyl radical oxidation at temperatures from 50–200°. Above 200° acetonyl radical oxidation in a short chain reaction becomes significant. Intensity, acetone concentration and surface affect rate and quantum yield at 250° without altering the extended ratio (rate of oxygen consumption)/(rate of carbon monoxide formation)/(rate of carbon dioxide formation). This result is attributed to similarity in oxidation sequence *via* either acetonyl radical or methyl and acetyl radicals, with acetyl giving rise to carbon dioxide, acetic acid, peracetic acid, and diacetyl peroxide and methyl oxidizing to carbon monoxide, methanol and formaldehyde. Induction periods and slight inhibition by added methane are observed.

## 1. Introduction

Knowledge of the mechanism of oxidation of the RCO radical is fundamental to an understanding of oxidative degradation of hydrocarbons higher than methane.<sup>3,4</sup> Knowledge of the oxidation mechanism of the methyl radical should contribute to an understanding of anomalies in methane oxidation.<sup>3–6</sup> Both acetyl and methyl radicals are primarily produced in photolysis of acetone. Consequently, the photooxidation of acetone was selected to yield information on these points.

The oxidation of methyl radicals has been studied by Bates and Spence<sup>7</sup> and Vaughan and co-workers.<sup>8</sup> Information on oxidation of the acetyl radical has been obtained by McDowell and Thomas<sup>9</sup> from study of acetaldehyde oxidation and may be deduced also from studies on thermal and photochemical oxidations of that compound by numerous other workers.<sup>10</sup> Steacie<sup>11</sup> has studied oxidation of acetone, and Fugassi,<sup>12</sup> Rice and Schildknecht,<sup>13</sup> and Marcotte and Noyes<sup>14</sup> its photochemical oxidation.

## 2. Experimental

**2.1. Chemicals.**—Methane employed was Matheson Co., C.P. specified purity greater than 99% and impurities consisting of ethane, nitrogen and carbon dioxide. Oxygen was Matheson Co., greater than 99.6% purity, theoretically dry, with argon and nitrogen as impurities. These gases were not purified further.

One liter of reagent grade acetone was distilled in the large column of a Todd fractionation still (50 theoretical plates). A middle fraction of 300 ml. was collected with a take-off ratio of 1:30 over a 30-hour period. Head temperature was constant at 56.5°. The purified acetone was stored over a mixture of magnesium sulfate and anhydrous copper sulfate.

(1) Sinclair Research Fellow 1950–1952.

(2) Department of Chemistry, North Carolina State College, Raleigh, N. C.

(3) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951.

(4) W. Jost, "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1946.

(5) W. A. Bone, *J. Chem. Soc.*, 1599 (1933).(6) D. M. Newitt, *Chem. Revs.*, **21**, 299 (1937).(7) J. R. Bates and R. Spence, *THIS JOURNAL*, **53**, 1689 (1931).(8) J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, *ibid.*, **73**, 15 (1951).(9) C. A. McDowell and J. H. Thomas, *J. Chem. Soc.*, 2208, 2217 (1949).(10) E. J. Bowen and E. L. Tietz, *ibid.*, 234 (1930); J. E. Caruthers and R. G. W. Norrish, *ibid.*, 1036 (1936); R. N. Pease, *THIS JOURNAL*, **55**, 2753 (1933).(11) E. W. R. Steacie, *Can. J. Research*, **6**, 265 (1932).(12) P. Fugassi, *THIS JOURNAL*, **59**, 2092 (1937).(13) F. O. Rice and C. E. Schildknecht, *ibid.*, **60**, 3044 (1938).(14) F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, **10**, 236 (1951).

Gas cylinders were connected through needle valves and tygon tubing to the high vacuum line. Acetone was poured from the storage bottle into a tube which fit into the vacuum line at a ground glass joint. It was pumped on directly, until occurrence of bumping, for removal of most residual air and traces of moisture contained therein. It was then frozen with liquid nitrogen, pumped to a vacuum of less than 10<sup>-6</sup> mm. and warmed, and a portion was then transferred to a permanent storage tube on the line. Thereafter, it was thoroughly degassed by repeated freezing, pumping and warming.

**2.2. Reaction System.**—The reaction cell was a quartz tube with a plane fused-quartz window at one end. At the other end it was connected *via* a 3-mm. quartz tube, graded seal and stopcock to the vacuum line. It had an inner diameter of 2.4 cm., a length of 12.4 cm., and a calibrated volume of 61.8 ml. The reaction cell was mounted vertically in an aluminum block furnace fitted at the top with two quartz windows separated by an insulating space. The whole furnace was protected from air drafts by an outer brass cylinder with an aluminum top equipped with a shutter.

Temperature was controlled to  $\pm 1^\circ$  by a Brown pyrometer. The temperature gradient over the length of the cell was less than 3° at 250°. The volume of dead space containing reaction mixture at room temperature was less than 2% of the total volume. Temperatures were measured with iron-constantan thermocouples and a Leeds and Northrup potentiometer.

**2.3. Light Source.**—A Hanovia "L" burner was employed. It operates at 135 v., 2.8 amp., 400°, and a mercury vapor pressure close to atmospheric. A high-intensity band spectrum with reversal of the resonance lines is obtained. The spectrum employed was limited approximately to the range of 3200–2000 Å. by the absorption limit of acetone and quartz windows in the system. Most of the output of the lamp in this range is in the 2537–3120 Å. range. The lamp was mounted in a brass housing with chimneys for air circulation and the light escaped through a brass cylinder of 5 cm. length and 3.5 cm. inner diameter, aligned over the shutter and windows of the reaction system. This arrangement tended to collimate the light entering the cell.

**2.4. Procedures.**—Acetone in the storage tube on the line was thoroughly degassed prior to each use. It was admitted at the desired pressure to the 532-ml. volume of a Saunders-Taylor<sup>15</sup> type gas analysis apparatus. It was then forced into an approximately 500-ml. storage vessel. The gases, oxygen and methane, were individually admitted at the desired pressure to this volume after pumping the needle-valve, tygon-tubing inlet system to a good vacuum and passing the gases through the system and out a mercury bubbler to ensure removal of residual traces of air. The gas mixture was then pumped repeatedly into and out of the storage vessel to ensure a homogeneous mixture. Composition of the mixture was checked at intervals during its use by the same procedure employed in the various runs. The gas mixture was admitted to the reaction cell by expansion from the storage vessel into the large volume of the gas analysis apparatus. Adjustment of the mercury level permitted establishment of pressure in the cell at room temperature at any desired value. The cell cock was turned, remaining gas mixture was transferred to the storage vessel, and the furnace and cell were brought to the reaction tem-

(15) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

perature. At 250° this procedure required 30 minutes. There was no dark reaction in this interval. The lamp was turned on 15 minutes prior to an exposure whereupon the shutter was opened for the desired length of time. The mixture was thereafter opened to a liquid-nitrogen trap and non-condensable gases were transferred into the gas-analysis apparatus and their pressure measured in a 78.2-ml. volume calibrated relative to the reaction cell volume. A small portion was analyzed. Another fraction was removed at -120° and measured, and a portion was analyzed. Oxygen consumption was taken as the difference between oxygen values in the blank run and after reaction.

Acetone photolysis was used for internal actinometry and for check on constancy of lamp intensity at frequent intervals. For such purposes it was measured into the reaction cell directly, photolyzed, and the liquid-nitrogen non-condensable gas was measured in a 3.11-ml. volume (on the gas analysis apparatus calibrated relative to the reaction cell) and analyzed for carbon monoxide. Lamp intensity did not vary over  $\pm 5\%$  in all of the runs reported.

At the maximum pressure employed in any run, 10 cm., acetone was found to behave as a perfect gas within the limits of accuracy required in this work.

Intensity reduction was effected by a fine-mesh, blackened copper screen.

For establishment of any dark reaction effects blank runs were made according to the same procedure employed in photolyses. In these blank runs the results appeared to be affected by steady change in the character of the cell wall with prolonged usage (*cf.* section 3.1). Initially (*e.g.*, when samples were exposed at various temperatures for mass spectrometric analysis, *cf.* section 2.5) no dark reaction occurred in a three-hour period at 250°. Later (at the time of studies of effect of acetone concentration and intensity, 3.4) all rates had increased, and, for the case of low-intensity exposure of a 10 cm. acetone-20 cm. oxygen mixture for 90 minutes at 250°, a dark reaction correction became necessary. The dark reaction exhibited a very marked induction period so that the correction was insignificant in 60 minutes and no reaction was measurable in 30 minutes.

Non-photolytic reaction became very rapid at 300°. The extended ratio (oxygen consumption)/(carbon monoxide formation)/(carbon dioxide formation) was identical with that in the photolyses indicating that the reaction very probably follows a parallel course.

The light reaction rate, as will be discussed later, is either a square root or more complex function of intensity and acetone concentration. Therefore, the total reaction rate was taken as being the square root of the sum of the squares of the light and dark rates.<sup>16</sup> Further justification for this assumption is found in consistency of the values obtained with those of three shorter runs not requiring a correction.

**2.5. Analyses.**—Analyses were performed in the gas analysis apparatus. A small portion of product gas was measured in a 3.11-ml. volume. The liquid-nitrogen fraction was exposed to white phosphorus for oxygen determination. It was then admitted to a tube containing anhydrous backed by copper oxide at 300°. This treatment was followed with exposure to a tube containing anhydrous backed by ascarite. This procedure removed carbon monoxide and reduced the pressure to zero except in those experiments in which methane had been added initially. The residue in such case was considered to be methane. Complete absorption in ascarite-anhydrous tube showed the -120° fraction to be pure carbon dioxide in all runs.

Mass spectrometric analyses of condensable fractions in long runs at 50, 150 and 250° were performed by the Consolidated Engineering Corp. Samples were prepared by removal of all gases non-condensable at -120°, and liquid nitrogen transfer of the condensable residue into tubes equipped with break-off seals.

**2.6. Quantum Yields.**—Accurate measurement of quantum yields was complicated by the fact that under the conditions of these experiments the rate of production of carbon monoxide from pure acetone at constant concentration and incident light intensity increased steadily with temperature (*cf.* Table I) by a factor of 1.6 in the range 100-250°. Noyes and Luckey<sup>17</sup> measured extinction coefficients for ace-

tone over the temperature range 25-300° using the 3130 Å. region of a quartz burner with characteristics similar to those of the light source described in section 2.3. An increase in absorption by a factor of 1.3 over the range 100-250° is obtained by application of the extinction coefficients they report to the conditions of this work. This suggests a possible contribution of increase in absorption to the factor of 1.6 observed, although the magnitude would be difficult to estimate since the whole 2000-3300 Å. range was used.

TABLE I

RATE OF CARBON MONOXIDE PRODUCTION AS A FUNCTION OF TEMPERATURE IN PHOTOLYSIS OF ACETONE<sup>a</sup>

<i>t</i> , °C.	103	107	152	202	250	300
<i>p</i> <sup>b</sup>	0.92	0.99	1.20	1.50	1.54	1.85

<sup>a</sup> At constant light intensity and acetone concentration (10 cm. in 61.8 ml. at 25°). <sup>b</sup> Rate of carbon monoxide formation in cm. per hr. measured in 61.8 ml. at 25°.

The factor of 1.6 observed is not exclusively attributable to increase in absorption. At the high intensities used in this work the quantum yield is probably not unity at 100° and some of the increase in rate of carbon monoxide production at 250° may result from the chain formation and decomposition of ketene.<sup>18</sup> Therefore, the quantum yields in the tables were calculated by dividing the rates of consumption of reactants and formation of products, respectively, by the rate of carbon monoxide formation from pure acetone at 105° and the concentration occurring in the mixtures. The quantum yield for carbon monoxide production from pure acetone at this temperature is assumed to be unity.<sup>19</sup> The tabulated quantum yields are then maxima. The minimum value is thus a factor of 1.6 smaller than the tabulated value (*cf.* Table I). This fact will be taken into account in the interpretation of these results (*cf.* section 3.3).

At an acetone concentration of 10 cm. in 61.8 ml. at room temperature the average rate of carbon monoxide formation at 105° was  $0.9 \pm 0.05$  cm. in 61.8 ml. at room temperature per hour. This value corresponds to absorption of  $5 \times 10^{18}$  quanta per second in 61.8 ml. for an assumed quantum yield of unity.

Howland and Noyes<sup>20</sup> found that 300-500 mm. of carbon dioxide added to 70 mm. of acetone did not change the absorption. Therefore, absorption in the mixtures was taken as equal to that in pure acetone.

### 3. Results and Discussion

**3.1. Effect of Surface.**—The data of Table II show that the reaction rate at 250° increased with number of runs in the reaction cell without affecting the course of reaction, as shown in the constancy of the extended ratio (oxygen consumed)/(carbon monoxide produced)/(carbon dioxide produced). Lamp intensity actually decreased by 5% over this

TABLE II

DEPENDENCE OF REACTION RATE<sup>a</sup> AT 250° ON NUMBER OF RUNS MADE IN REACTION CELL<sup>b</sup>

Run	O <sub>2</sub>		CO		CO <sub>2</sub>	
	- <i>p</i>	- $\phi^c$	<i>p</i>	$\phi$	<i>p</i>	$\phi$
17	5.4	6.0	2.58	2.9	1.78	2.0
28	6.0	6.7	2.98	3.3	2.08	2.3
36	7.6	8.4	4.02	4.5	2.78	3.1
51	7.6	8.4	3.82	4.2	2.58	2.9
62	9.0	10.0	4.38	4.9	3.06	3.4
81	10.0	11.1	4.86	5.4	3.32	3.7
87	10.4	11.6	5.06	5.6	3.42	3.8

<sup>a</sup> Rate, *p*, is expressed in pressure change in cm. per hour in 61.8 ml. at 25°. One cm.  $\approx 3.33 \times 10^{-6}$  mole. <sup>b</sup> A mixture of 10 cm. acetone and 20 cm. oxygen in 61.8 ml. at 25° was used in all runs. <sup>c</sup> Quantum yield.

(16) *cf.* W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, pp. 198-200.

(17) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951).

(18) R. C. Ferris and W. S. Haynes, *THIS JOURNAL*, **72**, 893 (1950).

(19) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

(20) J. J. Howland, Jr., and W. A. Noyes, Jr., *ibid.*, **63**, 3404 (1941).

period as shown by checks on the photolysis of pure acetone. Fresh reagents reproduced the high values in later runs. Therefore, the effect must be attributed to a slow change in the character of the surface with increasing number of runs. This sensitivity to surface is a common phenomenon in gas phase oxidations and suggests a chain reaction. A non-chain reaction at 50° is indicated by absence of such an effect.

Egerton and Harris<sup>21</sup> have found that alkyl hydroperoxides may decompose by either a slow, heterogeneous process or an explosive, homogeneous process probably proceeding *via* radical intermediates formed in fission of the peroxide. The two processes compete. Thus, a poisoning of the surface to the heterogeneous reaction would favor fission and an increase in reaction rate. Decrease in the chain-breaking efficiency of the walls is also a possible explanation. The surface change may be due to accumulation on the walls in successive runs of peroxides and aldehydes or their polymerization products.

In all series of runs for comparison purposes, a check of the rate on a 10 cm. acetone-20 cm. oxygen mixture was made at 250° at the beginning and end of the series. Only those series were reported which show no appreciable change in rate over the series.

**3.2. Effect of Concentration of Oxygen and Added Methane.**—In agreement with previous workers<sup>7,8,13,14</sup> no methane or ethane formation is found at the oxygen concentrations employed. In addition, Table III shows that neither rate nor course of reaction is affected by change in oxygen concentration at constant acetone concentrations. This lack of dependence on oxygen concentration is evidence that all radicals capable of an oxygen

reaction react rapidly with oxygen and undergo no other reaction over the range of concentrations employed, even at 250°.

Table III shows a real but small decrease in rate due to added methane at 250°. The effect would fall within the limits of accuracy at 50° and not be apparent. Methane may have a specific effect in acting as third body in recombination of some radical pairs or in deactivation of "hot" intermediates such as peroxy radicals.<sup>22</sup> Methane consumption did not occur in any of these runs.

**3.3. Effect of Temperature.**—Table IV shows the effect of temperature on photooxidation of acetone. At ~50° approximately one molecule of oxygen is consumed per quantum absorbed, the yield of carbon monoxide is very low, and is exceeded by the yield of carbon dioxide. With increase of temperature to 150°, the rates of oxygen consumption and carbon dioxide formation remain constant while that of carbon monoxide increases steadily. At 200° the latter overtakes the carbon dioxide rate. Around 200° the character of the reaction seems to change and all rates increase rapidly.

TABLE IV

EFFECT OF TEMPERATURE ON PHOTOCHEMICAL OXIDATION OF ACETONE<sup>a</sup>

Run	Temp., °C.	Time, min.	$\phi_{O_2}$	$\phi_{CO}$	$\phi_{CO_2}$	$\phi_{CO}$	$\phi_{CO_2}$
51	251	30	7.6	8.4	3.82	4.2	2.58
52	229	30	3.6	4.0	1.26	1.4	1.20
53	200	60	1.7	1.9	0.71	0.8	0.63
54	150	60	1.1	1.2	.50	.6	.57
55	101	60	1.1	1.2	.38	.4	.57
56	48	60	1.1	1.2	.11	.1	.48

<sup>a</sup> Conditions and symbols as in Table II.

TABLE III

PHOTOLYSIS OF ACETONE AT FIXED INITIAL CONCENTRATIONS (10 CM. AT 25°) IN PRESENCE OF OXYGEN AND METHANE AT VARIOUS INITIAL CONCENTRATIONS<sup>a</sup>

Run	Temp., °C.	Time, min.	$\phi(O_2)$ , cm. <sup>b</sup>	$\phi(CH_4)$ , cm. <sup>b</sup>	$\phi_{O_2}$	$\phi_{CO}$	$\phi_{CO_2}$
32	251	30	30	0	7.4	3.90	2.58
33	252	30	30	0	7.6	4.08	2.78
34	252	30	10	0	7.6	3.92	2.78
36	251	30	20	0	7.6	4.02	2.78
41	252	30	20	20	6.8	3.90	2.41
42	251	30	20	0	8.2	4.42	3.04
43	252	30	20	20	6.6	3.98	2.20
44	252	15	10	0	7.6	3.5	2.7
45	250	15	10	20	6.0	3.9	2.0
46	251	15	10	0	6.8	3.2	2.4
48	252	15	10	20	6.4	4.2	2.4
49	251	15	10	0	7.6	3.6	3.0
37	47	61	10	0	1.2	0.17	0.55
38	47	60	30	0	1.1	.12	.49
39	49	60	20	20	1.1	.46	.46
40	48	60	20	0	1.2	.15	.49

<sup>a</sup> Vessel and symbols, as in Table II. <sup>b</sup> Initial pressure at 25°, measured prior to run. <sup>c</sup> In analysis of mixtures containing CH<sub>4</sub> some combustion to CO occurs. Thus, the values of  $\phi(CO)$  in those cases are incorrect and apparently higher than normal.

(21) A. C. Egerton and E. J. Harris, *Proc. Roy. Soc.*, **A168**, 1, (1938); E. J. Harris, *ibid.*, **A173**, 126 (1939).

Complete oxidation of acetone would give quantum yields for oxygen consumption and carbon dioxide formation of 4 and 3, respectively, in the absence of a chain reaction. At ~250° (*cf.* run 51 of Table IV and particularly run 87 of Table II) the quantum yields of oxygen consumption and the sum of the carbon monoxide and carbon dioxide yields are seen to exceed these values. If minimum values for quantum yields in runs 51 and 87 are calculated using the larger rate of carbon monoxide formation from pure acetone at 250° as a measure of light absorption 5.2, 2.6, 1.8 and 7.2, 3.5, 2.4 are obtained, respectively, and this statement still holds. Predominance of carbon monoxide in the yield and the presence of condensable products (*cf.* Table V) indicate that oxidation is not complete. High quantum yields and incomplete oxidation indicate that chains are involved. In run 87 of Table II about 4 molecules of acetone are decomposed per quantum absorbed. Thus, it follows that in the neighborhood of 200° radical attack on acetone becomes significant.

Accurate measurement of absolute amounts of condensable products in the experimental arrangement employed was not possible. A rough estimate showed condensable product yields to be of the same order as gas product yields. Table V gives relative yields of condensable products as determined

(22) A. D. Walsh, *Discussions Faraday Soc.*, **10**, 320 (1951).

mass spectrometrically. Water, methanol, acetic acid and formaldehyde are seen to be the major products. Formaldehyde may be low due to loss through polymerization and condensation with methanol to give methylal. Methylal or peracetic acid or both could be responsible for the unidentifiable peaks of large mass. It is to be noted that the ratio of water to other condensable products is considerably greater at 250° and the ratio of methanol to formaldehyde is a minimum at 50°.

TABLE V  
RUNS WITH MASS SPECTROMETRIC ANALYSIS<sup>a</sup> OF CONDENSABLE FRACTION<sup>b</sup>

Run	22	23	24
Temp., °C.	252	152	50
Time, min.	180	300	300
$-\dot{p}(\text{O}_2)$	4.5	1.4	1.4
$\dot{p}(\text{CO})$	2.38	0.56	0.19
$\dot{p}(\text{CO}_2)$	1.56	0.50	0.48
Mole percentages			
Acetone	43.0	59.2	63.6
Acetic acid <sup>c</sup>	5.4	5.1	3.6
Formic acid <sup>c</sup>	....	0.7	1.9
Formaldehyde <sup>c</sup>	3.1	4.5	5.7
Methanol	10.1	20.0	11.7
Water	36.3	9.7	11.2
Carbon dioxide	2.0	0.8	2.3
Unidentifiable <sup>d</sup>	1.0	3.2	4.2

<sup>a</sup> Analyses made by Consolidated Engineering Corp. <sup>b</sup> Conditions of exposure and symbols as in Table II. <sup>c</sup> Identity questionable, possible maxima are indicated. <sup>d</sup> Unidentified components contributed to masses 60, 73, 74, 75; estimates by Consolidated.

**3.4. Effect of Intensity and Acetone Concentration.**—In the intensity and acetone concentration studies discovery of an induction period dictated further studies of yield as a function of time. Induction periods ranging from 2–17 minutes were observed in oxygen consumption and carbon monoxide and carbon dioxide formation under the three sets of experimental conditions of Table VI. Induction periods were greatest in the presence of the screen and those for carbon monoxide production were greatest in each case. As a consequence, carbon monoxide yields at the shortest times measured are only slightly larger than carbon dioxide yields, but increase relative to those yields with time.

TABLE VI  
EFFECT OF LIGHT ABSORPTION RATE AND ACETONE CONCENTRATION ON PHOTOOXIDATION RATE AT 250°<sup>a</sup>

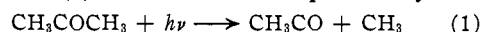
$i^b$	(Acetone), cm. <sup>c</sup>	$\text{O}_2$	Rate, $\dot{p}$ + 60 CO	$\text{CO}_2$
1	10	0.173	0.091	0.057
0.16 <sup>d</sup>	10	.088	.048	.029
0.63	5	.085	.049	.030

<sup>a</sup> Pressure of oxygen at 25°, vessel and symbols as in Table II. <sup>b</sup> Rate of light absorption relative to that of line 1. <sup>c</sup> Initial pressure at 25°. <sup>d</sup> Intensity reduction effected by a screen.

From Table VI it may be seen that increase in light absorption rate (*cf.*  $\dot{I}$ ) by a factor of 6.3 increases all three rates by a factor of approximately 2. Square root dependence would give a factor of

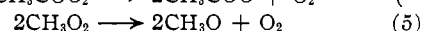
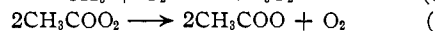
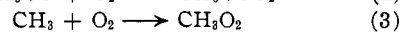
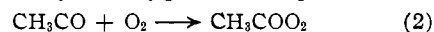
2.5. Increase in  $\dot{I}$  by a factor of 1.6 and acetone concentration by a factor of 2 again increased all three rates by a factor of about 2. It is interesting to note that over the ranges employed both of these variations alter the rate without affecting the course of the reaction (as reflected in the extended ratio). If a square root dependence on rate of light absorption is assumed, a dependence on acetone concentration between square root and first power is obtained. However, the rate is probably a complex function of both.

**3.5. Mechanism.**—The primary process is assumed to be (1) occurrent with a quantum yield of

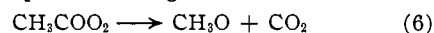


unity in the presence as in the absence of oxygen.<sup>23</sup> Lack of dependence of the rate and course of the photooxidation on oxygen concentration requires a rapid reaction between the radicals produced and oxygen. A scheme is adopted involving peroxy radical formation as the first step in reaction of a radical with oxygen followed by reactions similar to those postulated by Vaughan and co-workers,<sup>8,24</sup> Walsh,<sup>25</sup> and others.

In the low temperature scheme, reaction 1 followed by reactions 2, 3, 4 and 5 would give a quantum yield of unity for oxygen consumption. How-



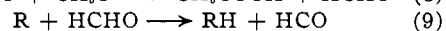
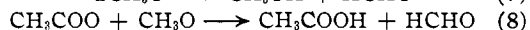
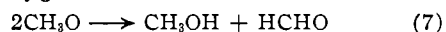
ever, carbon dioxide formation is assumed to occur in the low temperature range *via* reaction 6.



The quantum yield indicates that about one out of two peracetyl radicals are decomposing as in (6) which would give a quantum yield for oxygen consumption of 1.25.

Abstraction and recombination reactions of the acetate radicals formed in (4) would yield acetic acid and diacetyl peroxide, respectively. Thus, acetyl oxidation yields carbon dioxide, diacetyl peroxide and acetic acid, as well as products resultant from methoxy radicals produced in (6) (*cf.* acetaldehyde oxidation studies<sup>9,10</sup> for similarity).

Reactions 7 and 8 would account for methanol and formaldehyde formation, with carbon monoxide resultant from radical attack on formaldehyde as in (9) and (10) where R is any radical not subject to a rapid oxygen reaction.



Thus, methyl radical oxidation yields carbon monoxide, methanol, formaldehyde and perhaps some methylal by condensation of the latter two. Little or no contribution to carbon dioxide yield is attributed to methyl radical oxidation, since under conditions similar to those of this work the yield ratio (carbon dioxide)/(carbon monoxide) has been observed to be

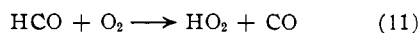
(23) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

(24) F. F. Rust, F. H. Seibold and W. E. Vaughan, *THIS JOURNAL*, **72**, 338 (1948).

(25) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946).

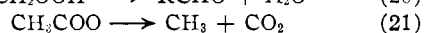
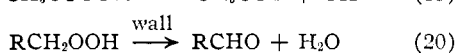
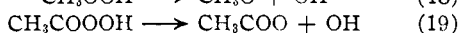
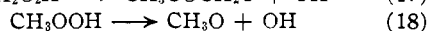
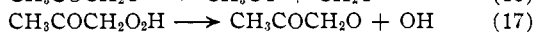
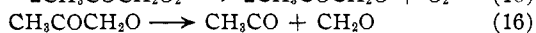
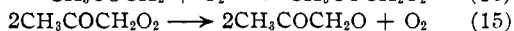
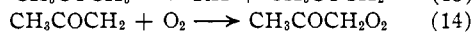
small in methyl radical oxidation,<sup>8</sup> methane oxidation<sup>9</sup> and photochemical and thermal oxidation of formaldehyde.<sup>26</sup>

Reactions 9 and 10 involving peroxy radicals would tend to raise the quantum yield for oxygen consumption to an upper limit of two. The low quantum yield indicates that these are not occurring in the low temperature range. The low quantum yield of carbon monoxide formation at 48° indicates that all reactions 9 and 10 are not significant at this temperature. Reactions 11 and 12 would yield water and regenerate some oxygen so that there is little effect on the oxygen quantum yield.



Invariance of the oxygen and carbon dioxide rates in the temperature range 50–150° requires that reactions 9 and 10 involving peroxy radicals do not become appreciable over this range and that reaction 6 varies slowly with temperature relative to reaction 4. The only change occurring would be an increasing rate of attack of methoxy and acetate radicals on formaldehyde resultant in a steadily increasing yield of carbon monoxide, and increased ratios of methanol to formaldehyde and acetic acid to diacetyl peroxide and formaldehyde as is observed.

At temperatures in the neighborhood of 200° the general rapid rate increase and chain characteristics are explicable in terms of radical attack on acetone with subsequent oxidation of the acetyl radical, and slight peroxide formation with chain branching.

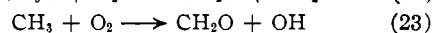
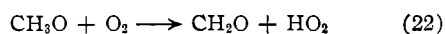


The short chain length observed requires a competition between the chain and non-chain mechanisms at 250°. Insensitivity of the extended ratio (rate of oxygen consumption)/(rate of carbon monoxide formation)/(rate of carbon dioxide formation)

(26) D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **42**, 388 (1946); F. F. Snowdon and D. W. G. Style, *ibid.*, **35**, 426 (1939); R. Spence, *J. Chem. Soc.*, 649 (1936); J. E. Carruthers and R. G. W. Norrish, *ibid.*, 1036 (1936).

to changes in light intensity, acetone concentration and surface condition is observed. This requires a similarity in oxidative degradation of acetone by either the chain or non-chain sequence. This is seen to be the case qualitatively in that the acetyl radical in oxidation breaks into formaldehyde and an acetyl radical.

An essential difference is the direct conversion of the methyl group to formaldehyde without intermediate methoxy formation. This difference may be offset by a change in the mechanism of methyl radical oxidation at high temperature to (22) or (23) which would also account for a decrease in relative yield of methanol with increase in temperature.



Increase in water formation arises from the hydroxyl intermediate. Formaldehyde rapidly converts to carbon monoxide by radical attack at high temperature. Predominance of second-order termination reactions would give dependence on intensity as a complex square root function involving a sum of intensity and acetone concentration terms. This would be observed as a dependence on intensity between zero and one-half power as measured in this work. The acetone dependence would be complicated based on the above mechanism and an attempt at correlation with the result observed is not feasible.

The induction periods observed for carbon monoxide formation are explicable as follows. Formaldehyde is formed in early stages of the reaction. The rate of conversion of formaldehyde to carbon monoxide by hydrogen atom abstraction increases with formaldehyde concentration so that, as formaldehyde builds up, a steady state concentration is reached and the rate of carbon monoxide production becomes constant. This delay is superimposed on a shorter induction period for the reaction as a whole, which may be associated with peroxide build-up as postulated in hydrocarbon oxidation at low temperatures. This induction period for the over-all reaction cannot be related to formaldehyde build-up since formaldehyde acts as an inhibitor in removal of free radicals *via* (9) and (10).

**Acknowledgment.**—The author is greatly indebted to Professor Milton Burton of the University of Notre Dame for suggesting hydrocarbon oxidation and related studies as a field of interest and for the encouragement and assistance which made the work possible.

NOTRE DAME, IND.