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Photochemical Oxidations. III. Acetone

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RECEIVED FEBRUARY 28, 1964

The room-temperature photooxidation of acetone (0.25 to 17 mm.) in oxygen (0.09 to 9.7 mm.) with continuous ultraviolet radiation above 2200 Å. has been studied by the method outlined in part I of this series; observations were made by leaking the reaction mixture directly into the electron beam of the mass spectrometer during photolysis. The principal products of the reaction were H₂CO, H₂O, CH₃OH, and CH₃OOH; minor products were CH₃COOH, HCOOH, CH₃OOCH₃, and higher molecular weight products which were probably CH₃COCHO and CH₃COCH₂OH. Because of the cracking pattern of the reactants, it was impossible to establish the presence or absence of CH₄, CO, CH₃CO, and CO₂. From the identified products at least 14 free radicals are inferred to be intermediates in this system. An exhaustive and impartial examination of all possible radical-radical disproportionation and recombination reactions indicates that the data exclude a large number of possible reactions but that 140 reactions could still be occurring. Formaldehyde, so far as these studies go, could be formed by 39 different reactions. Thus, this experimental method cannot give a complete mechanism, nor can any method that simply analyzes all molecular products.

Introduction

The photooxidation of acetone above 120° has been studied by several investigators.¹⁻⁵ The radicals formed under these conditions abstract readily and undergo unimolecular decompositions with the result that the nature and amounts of products may be quite different from those at room temperature.

Srinivasan and Noyes⁶ and Osborne, Pitts, and Fowler⁷ studied the photooxidation at room temperature with incident radiation at 3130 Å. Under these conditions the principal species that is oxidized is the triplet state of acetone. Kirk and Porter⁸ have also investigated the photooxidation at room temperature with 3130 and 2800 Å. incident radiations. Pearson⁹ has investigated the reaction between 36 and 100° with both 3130 and 2537 Å. radiation.

In the work reported here the room-temperature photooxidation of acetone vapor was studied at low pressure and with incident radiation extending to 2200 Å. Under these conditions CH₃ and CH₃CO radicals were produced and their subsequent oxidations were studied.

Experimental

The apparatus and experimental procedures have been fully described in the preceding articles of this series.¹⁰

Twelve series of runs were made with variation of the oxygen pressure and acetone pressure (and thus the absorbed intensity). The incident intensity was similar in all cases except series 5. The incident radiation passed through a Corning 9-54 glass before entering the reaction cell to remove all radiation below 2200 Å. Replicates of all series were run and agreement was to within 10 or 15% except in a few scattered cases.

Matheson tank oxygen was used and impurities were 0.3% argon and 0.7% nitrogen. Eastman Spectrograde acetone was used. It contained no impurities in amounts greater than 0.1%.

Because of the background cracking peaks, analyses could not be made for CO₂ (44), CH₂O (42), CO (28), and CH₄ (16).

(1) F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, **10**, 236 (1951).

(2) F. B. Marcotte and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **74**, 783 (1952).

(3) D. E. Hoare, *Trans. Faraday Soc.*, **49**, 1292 (1953); J. Caldwell and D. E. Hoare, *J. Am. Chem. Soc.*, **84**, 3990 (1962).

(4) M. I. Christie, *ibid.*, **76**, 1979 (1954).

(5) J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **36**, 42 (1958).

(6) R. Srinivasan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **82**, 5591 (1960).

(7) A. D. Osborne, J. N. Pitts, Jr., and S. L. Fowler, *J. Phys. Chem.*, **65**, 1622 (1961).

(8) A. D. Kirk and G. B. Porter, *ibid.*, **66**, 556 (1962).

(9) G. S. Pearson, *ibid.*, **67**, 1886 (1963).

(10) J. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030, 4394 (1962).

During the course of the experiments the gold foil in the reaction cell was inadvertently damaged, and had to be replaced. The gold foil associated with each series is included with the data, Tables I-III. From the data in Table III, it is apparent that both gold foils have similar sized pinholes as the leak rate is the same for both.

Results

During irradiation product peaks were observed at $m/e = 17, 18, 30, 31, 46, 48, 60, 62, 72, 73,$ and 74. The first eight peaks are readily identified with H₂O, CH₂O, CH₃OH, HCOOH, CH₃OOH, CH₃COOH, and CH₃OOCH₃. The last three peaks are not so easily recognizable, but in all likelihood they are from CH₃C(O)CHO and CH₃C(O)CH₂OH. The absolute pressures of the products were estimated from calibrations, comparison with the literature, and interpolations among related compounds. However, it is re-emphasized that some of the calibration values may be in error by as much as 30 or 40%.

The experimental results are listed in Tables I-III. For all of the products there are listed the initial rates, R_i ; the steady-state partial pressure, P^{ss} ; the half-time of build-up to the steady-state pressure, τ_L ; and the half-time of decay from the steady-state value after the light was turned off, τ_D .

The results can be summarized in phenomenological terms, using the classification of part I of this series, without reference to mechanism. (1) In decreasing order of abundance the initial measured products are H₂CO, H₂O, CH₃OH, CH₃OOH, CH₃COOH, HCOOH, CH₃COCHO, CH₃COCH₂OH, and CH₃OOCH₃. (2) Relative quantum yields for important products are plotted as solid circles in Fig. 1 and the corresponding quantities found for the photooxidation of methyl iodide¹⁰ are given as open circles. These relative yields are plotted on a log-log scale against the ratio of reactant to oxygen. The relative quantum yield of CH₃OH is about the same in the two systems. The yield of H₂CO is almost twice as great in acetone as in methyl iodide, but CH₃OOCH₃ is much more abundant in methyl iodide than in acetone. The biggest difference between the two systems is in the rate of formation of H₂O, the yield being almost ten times as great in acetone as in methyl iodide. No CH₃CO(OOH) was observed, and both CH₃COOH and HCOOH were very minor products. The relative quantum yields are not sensitive functions of the reactant-oxygen ratio; however, the yield of CH₃OOH and H₂O

TABLE I
 INITIAL RATES OF FORMATION OF PRODUCTS

	Series											
	1	2	3	4	5	6	7	8	9	10	11	12
[O ₂] ^a	9.7	1.0	9.3	2.5	1.0	0.8	9.2	2.6	0.9	0.09	0.9	1.0
[CH ₃ COCH ₃] ^c	0.25	0.23	0.7	0.9	0.9	0.85	3.6	3.5	3.9	3.6	16	17
Gold foil	1	1	2	2	1	2	1	2	1	1	2	1
(R ₀ × 10 ⁶)/[CH ₃ COCH ₃] ^b												
H ₂ O	..	47	27	18.9	241	21.5	15.6	24	16.0	24	18.2	17.6
CH ₂ O	..	34	49	39	260	42	39	43	39	44	41	37
CH ₃ OH	..	16	13	11.7	75	15.4	13.9	12.2	18.5	28	26	12.2
			8								16.7	
HCOOH	4.0
CH ₃ OOH	16.7	12.1	44	11.7	14.5	11.6	7.7	6	8.4	8.8
CH ₃ COOH	1.2	1.5	...	1.2	...	1.1	2
CH ₃ OOCH ₃	3.2	0.83	1
CH ₃ COCHO	0.73	11.3	1.12	0.65	0.83	1.4	1.7	0.95	0.83
CH ₃ COCH ₂ OH	0.5	...	0.56	0.45
(R _i (ΣH) × 10 ⁶)/ 2[CH ₃ COCH ₃] ^b		129	133	109	782	123	116	122	118	144	116	103
(R _i (ΣC) × 10 ⁶)/ [CH ₃ COCH ₃] ^b		59	79	68	425	76	72	74	76	87	70	63
{R _i (CO) + R _i (CO ₂) ^c × 10 ⁶ }/ [CH ₃ COCH ₃] ^b	..	70	54	41	357	47	44	48	42	57	46	40
α × 10 ^{6b}	..	40	39	37	253	40	38	40	38	46	37	33
{α - R _i (CH ₃ COOH)/ [CH ₃ COCH ₃]} × 10 ^{6b}	..	39	38	36	249	39	37	39	37	45	36	32
α = { ¹ / ₆ R _i (ΣH) - R _i (CH ₃ COCHO) - R _i (CH ₃ COCH ₂ OH)}/[CH ₃ COCH ₃]												

^a Millimeters. ^b Sec.⁻¹. ^c Calculated from difference in mass balance of hydrogen and carbon.

tended to decrease and CH₃OH tended to increase with increasing reactant-oxygen ratio. (3) The curves of growth of many of the products fall into case 1 of article I (*i.e.*, the initial product is unaffected as ir-

radiation proceeds). (4) In the dark, CH₃OOH decomposes but all the other products are stable.

Discussion

The Primary Process.—The primary process in acetone in the absence of oxygen is complicated. A molecule excited by radiation can either decay into free radicals soon after excitation or it may pass through low vibrational levels of the relatively long-lived triplet state before decomposing.¹¹ This latter process is inhibited if biacetyl is present¹¹ or altered if oxygen is present.¹⁶⁻⁹ However, it has been shown that at low pressures (but still greater than those used here) and with incident radiation of 2800 Å. (and presumably below this) the long-lived triplet state is not important.¹² From the spectral distribution of the lamp, the transmission characteristics of the Corning glass, and the absorption coefficients of acetone,¹³ it was estimated that about 75% of the incident radiation was at wave lengths below 2800 Å. in this work. To confirm this estimate a photooxidation was performed using a Corning 9-53 glass which only passes radiation above 2600 Å. The decomposition in this case was about one-third that obtained when the 9-54 glass (which passes radiation to 2200 Å.) was used. Consequently it is probable that the triplet state oxidation is not dominant, but it may occur to some extent in this work.

The other decomposition might give either methyl and acetyl radicals or carbon monoxide and two methyl radicals. Noyes, Porter, and Jolley¹⁴ have estimated from the data of Herr and Noyes¹⁵ that about 80%

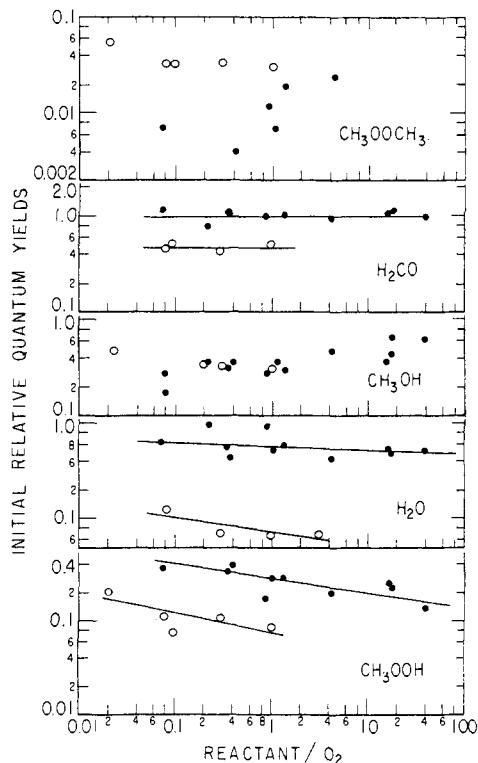


Fig. 1.—Relative quantum yield for products in the photooxidation of acetone, ●, and of methyl iodide, ○ (ref. 10).

radiation proceeds). However, H₂O is an example of case 4 (initial product is also produced from other product) and H₂CO, CH₃OOH, CH₃COCHO, and CH₃COCH₂OH are examples of case 2 (initial product de-

(11) J. Heicklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959).

(12) J. Heicklen, *ibid.*, **81**, 3863 (1959).

(13) C. W. Porter and C. Iddings, *ibid.*, **48**, 10 (1926).

(14) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

(15) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

TABLE II
 STEADY-STATE PRESSURE OF PRODUCTS

	Series											
	1	2	3	4	5	6	7	8	9	10	11	12
[O ₂] ^a	9.7	1.0	9.3	2.5	1.0	0.8	9.2	2.6	0.9	0.009	0.9	1.0
[CH ₃ COCH ₃] ^a	0.25	0.23	0.7	0.9	0.9	0.85	3.6	3.5	3.9	3.6	16	17
Gold foil	1	1	2	2	1	2	1	2	1	1	2	1
(P ^{ss} × 10 ³)/[CH ₃ COCH ₃]												
H ₂ O	10.0	16.7	15.1	8.6	59	8.5	3.5	8.7	7.4	9.4	5.7	2.9
						17.7	5.2					
CH ₂ O	..	11.0	10.9	9.5	38	11.3	8.2	8.2	7.3	5.8	5.0	6.1
CH ₃ OH	1.4	4.1	2.7	3.3	34	4.8	4.2	4.8	7.1	11.4	8.0	3.6
HCOOH	0.09	0.89	0.11	0.22
CH ₃ OOH	0.5	<1	2.2	1.58	3.0	1.40	1.6	1.95	0.88	0.36	0.75	0.89
												0.68
CH ₃ COOH	0.29	0.34	1.25	0.4	<0.2	0.31	0.29	0.2	0.082	..
(CH ₃ O) ₂	<0.1	..	0.88	0.088	0.06	0.20	0.2	0.2
CH ₃ C(O)CHO	<0.18	0.17	0.79	0.26	0.10	0.14	0.26	0.26	0.17	0.17
CH ₃ C(O)CH ₂ OH	<0.20	0.05	<0.3	<0.07	~0.03	0.04	0.07	0.07	0.042	0.064

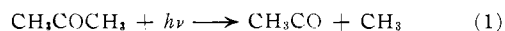
^a Millimeters.
 TABLE III
 HALF-LIVES OF PRODUCTS

	Series											
	1	2	3	4	5	6	7	8	9	10	11	12
[O ₂] ^a	9.7	1.0	9.3	2.5	1.0	0.8	9.2	2.6	0.9	0.009	0.9	1.0
[CH ₃ COCH ₃] ^a	0.25	0.23	0.7	0.9	0.9	0.85	3.6	3.5	3.9	3.6	16	17
Gold foil	1	1	2	2	1	2	1	2	1	1	2	1
τ _D ^b												
H ₂ O	260 ± 40	240 ± 40	290 ± 30	290 ± 20	290 ± 20	>300	240 ± 20	280 ± 20	300 ± 30	270 ± 20	230 ± 30	..
CH ₂ O	..	205 ± 20	170 ± 30	200 ± 10	220 ± 10	230 ± 30	200 ± 20	175 ± 10	195 ± 20	..	160 ± 20	..
CH ₃ OH	..	260 ± 40	160 ± 20	~200	240 ± 20	170 ± 20	195 ± 20	210 ± 20	..	230 ± 20	190 ± 20	190
HCOOH	240 ± 30	260 ± 60	160
CH ₃ OOH	90 ± 40	..	85 ± 15	110 ± 10	60 ± 10	80 ± 10	100 ± 10	135 ± 10	120 ± 20	80 ± 10	130 ± 15	110
CH ₃ COOH	180 ± 80	..	300 ± 50	200 ± 40	..	200 ± 60	250 ± 50
CH ₃ OOCH ₃	230 ± 40	200 ± 40	200 ± 40
CH ₃ C(O)CHO	190 ± 20	225 ± 20	200 ± 30	170 ± 30	170 ± 40	185 ± 15	225 ± 20	165 ± 20	..
CH ₃ C(O)CH ₂ OH	220 ± 80	220 ± 60	220 ± 50	200 ± 40	190
τ _I ^b												
H ₂ O	1000 ± 200	550 ± 100	750 ± 150	800 ± 50	400 ± 20	750 ± 70	500 ± 50	700 ± 70	580 ± 60	650 ± 50	270 ± 20	250
CH ₂ O	..	230 ± 20	140 ± 20	165 ± 10	100 ± 5	150 ± 5	155 ± 10	135 ± 10	132 ± 10	90 ± 10	87 ± 5	98
						(210 ± 10)						
CH ₃ OH	..	260 ± 60	180 ± 30	270 ± 20	250 ± 15	280 ± 40	220 ± 20	230 ± 20	250 ± 20	270 ± 30	240 ± 30	165
HCOOH	250 ± 40	205
CH ₃ OOH	90 ± 15	90 ± 10	57 ± 10	80 ± 15	75 ± 20	95 ± 10	85 ± 15	45 ± 15	63 ± 10	58
								140 ± 10				
CH ₃ COOH	220 ± 40	..	235 ± 50	250 ± 100
CH ₃ OOCH ₃	215 ± 20	165 ± 30	190 ± 30
CH ₃ C(O)CHO	160 ± 20	82 ± 10	160 ± 20	120 ± 20	115 ± 15	135 ± 10	125 ± 10	120 ± 10	145
CH ₃ C(O)CH ₂ OH	120 ± 25	100

^a Millimeters. ^b Seconds.

of the time a methyl and an acetyl radical are formed with 2537 Å. incident radiation. At longer wavelengths this percentage should be larger. However, since then it has been found by Roebber, Rollefson, and Pimentel,¹⁶ and recently confirmed by Shilman and Marcus,¹⁷ that in a flash photolysis with 2800 Å. radiation acetone decomposes to two methyl radicals and a carbon monoxide molecule. In order to see what the primary split was in our system, acetone at pressures varying from 1 to 15 mm. was photolyzed in the near absence of oxygen (unfortunately, a small leak prohibited the complete removal of oxygen). Large amounts of biacetyl were produced as could be deduced from the mass spectral product peak at $m/e = 86$. The results indicated that at least 75% of the primary split was to methyl and acetyl radicals. Furthermore, the mass spectral peaks corresponding to $(\text{CH}_3\text{COCH}_2)_2$, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, and $\text{CH}_3\text{COCH}_2\text{CH}_3$ were completely absent, thus eliminating the possibility of a primary process leading to hydrogen atoms and acetonyl radicals.

The previous discussion indicates that the most important primary process in this work was



Initial Oxidation.—In this system CH_4 , CO , CH_2CO , and CO_2 could not be measured. From the literature it is known that small amounts of oxygen completely suppress methane formation in systems with methyl radicals. On the other hand CO and CO_2 are undoubtedly present. Assuming that CH_2CO and CH_4 are absent, the initial rate of production of CO and CO_2 can be estimated from the carbon-hydrogen mass balance. The relationship is

$$R_i(\text{CO}) + R_i(\text{CO}_2) = 0.5R_i(\Sigma\text{H}) - R_i(\Sigma\text{C}) \quad (2)$$

where $R_i(\Sigma\text{H})$ and $R_i(\Sigma\text{C})$ are, respectively, the initial rates of formation of all the hydrogen atoms and carbon atoms in the products. The appropriate quantities are listed in Table I and it is apparent that CO and/or CO_2 are indeed major products.

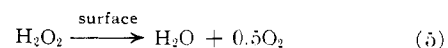
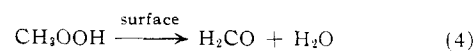
If the assumption is made that all the products except $\text{CH}_3\text{C}(\text{O})\text{CHO}$ and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ result from the primary decomposition, then the rate of acetone decomposition, $\alpha[\text{CH}_3\text{COCH}_3]$, can be estimated from

$$\alpha = [1/6R_i(\text{H}) - R_i(\text{CH}_2\text{COCHO}) - R_i(\text{CH}_2\text{COCH}_2\text{OH})]/[\text{CH}_3\text{COCH}_3] \quad (3)$$

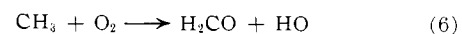
The values of α , which are proportional to the incident intensity, are listed in Table I. Except for series δ , the intensity is similar in all runs; in series δ it is some eight times larger. The rate of CO and CO_2 produced from the carbonyl of the acetone molecule is then given by $\alpha[\text{CH}_3\text{COCH}_3] - R_i(\text{CH}_3\text{COOH})$. These values divided by the acetone pressure are also listed in Table I. At high pressures most, but not all, of the CO and CO_2 comes from the carbonyl carbon. However, at low pressures, a large fraction of the CO and CO_2 comes from the end carbons of the acetone molecule.

The relative quantum yield is the rate of formation of a given product divided by $\alpha[\text{CH}_3\text{COCH}_3]$. The large yield of H_2O in this system indicates that HO and/

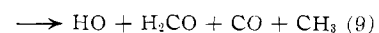
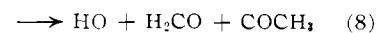
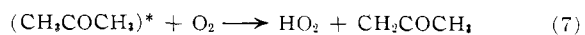
or HO_2 radicals are formed as intermediates, but it is known also that H_2O is rapidly produced by the heterogeneous decomposition of CH_3OOH or H_2O_2 .



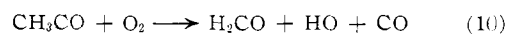
In the photooxidation of methyl iodide in this apparatus the main source of H_2O was thought to be from HO radicals produced directly by oxygen and methyl radicals.



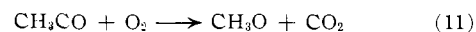
In the photooxidation of acetone the very large increase in H_2O suggests that either oxygen reacts directly with photoexcited acetone



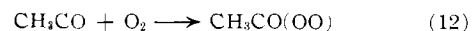
or that oxygen attacks the acetyl radical in a reaction analogous to eq. 6



A reaction which has often been postulated for CH_3CO radicals is



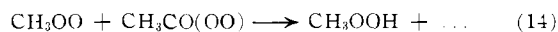
However if this reaction were dominant in our system, the results would be similar to those in CH_3I and it would be difficult to explain the large excess of water and formaldehyde. In other kinetic systems acetyl peroxides and acetyl peroxy nitrites are formed, indicating that acetyl radicals do indeed add oxygen molecules



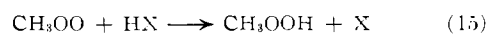
No acetyl hydroperoxide and very little acetic acid were found here. Thus the acetyl peroxy free radical must either be very stable or very vulnerable to attack in this system. If it is highly stable, its fate is probably heterogeneous destruction on the walls of the cell



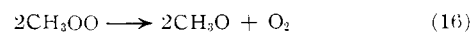
If it is very vulnerable to attack in this system, the large yield of methyl hydroperoxide suggests



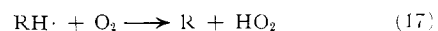
and similar attack by other radicals. The large yield of CH_3OOH and the small yield of CH_3OOCH_3 , relative to methyl iodide oxidation, strongly calls for some very easily abstracted hydrogen atom



to compete strongly with the formation of methoxy radicals from peroxy methyl radicals



At this low temperature the substance HX with an easily abstracted hydrogen must surely be a free radical and eq. 15 must be a radical-radical disproportionation reaction. A very likely candidate for HX would be HO_2 which could be formed from the reaction



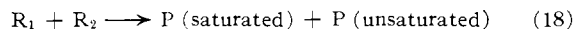
(16) J. L. Roebber, G. K. Rollefson, and G. C. Pimentel, *J. Am. Chem. Soc.*, **80**, 255 (1958).

(17) A. Shilman and R. A. Marcus, *J. Chem. Phys.*, **39**, 996 (1963).

where RH is a free radical. Such a reaction does occur when RH is CH_3CO ,¹⁰ but this is not sufficient to explain the excess CH_3OOH in this system. Reaction 17 is particularly attractive in that it indicates that CH_3OOH and H_2O should rise with the oxygen pressure in conformance with Fig. 1. However, it is not clear what radical besides CH_3O could be involved in (17).

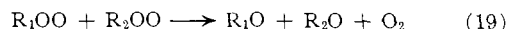
The observed formic acid suggests that formaldehyde is attacked by reactive radicals, probably HO and CH_3O . The observed 72 and 74 mass peaks suggest these radicals also attack the acetone molecule (recall that reaction 7 is a possible alternate).

In general reactions of two monoradicals to give two molecular products can be represented by



That is, one product is saturated and the other unsaturated. From observed products it appears that the following radicals occur as intermediates in the photochemical oxidation of acetone: CH_3 , CH_3OO , CH_3O , CH_3CO , $\text{CH}_3\text{CO}(\text{OO})$, CH_3COO , $\text{HCO}(\text{OO})$, HCOO , CH_3COCH_2 , $\text{CH}_3\text{COCH}_2\text{CO}$, $\text{CH}_3\text{COCH}_2\text{O}$, HO_2 , and HO. All possible disproportionations of these 14 radicals give 196 possible reactions. The matrix of possibilities is given by Table IV. Each row has a common saturated product and each column has a common unsaturated product. These common products are identified on the right-hand and bottom extremes of the table. The symbol O means the product was observed; the symbol X means that the mass number of the product was available and the product was not observed; the symbol ? means that the mass number of the product was obscured by the cracking pattern of other materials in this system. In the body of the table the intersection of two O's gives a possible reaction and is entered as O; the intersection of ? with O or ? gives ? for the reaction; the intersection of X with O, ?, or X gives X for the reaction. Out of 196 mathematical possibilities 88 can be excluded, 35 are in agreement with observed products, and 73 are left ambiguous. Other considerations, such as bond strengths, could be advanced to restrict these possibilities somewhat.

Other possible fast radical-radical reactions are the splitting out of oxygen between peroxy radicals



and the recombination of radicals that are not so highly oxygenated



There are five peroxy radicals in Table V: CH_3OO , $\text{CH}_3\text{CO}(\text{OO})$, $\text{CH}_3\text{COCH}_2\text{OO}$, $\text{HCO}(\text{OO})$, and HOO . Since no radicals were directly observed, all 15 reactions such as eq. 19 are possible so far as these data are concerned. The nine nonperoxy radicals can recombine in the 45 ways shown by Table V. Of these 45 possible reactions, 28 can be excluded since no product was observed at that mass peak, 10 are indeterminate because the mass peak was covered by other products, and 7 are consistent with observed products. These interpretations are given as X, ?, or O in the table.

It thus appears that there could be 140 fast radical-radical reactions in this system, including all O and ? cases. Formaldehyde could be formed by 36 different

TABLE IV
POSSIBLE RADICAL-RADICAL DISPROPORTIONATION REACTIONS^a

R ₁	R ₂														Common saturated product		
	CH_3	CH_3OO	CH_3O	CH_3CO	CH_3COO	CH_3COO	CH_3COO	HCO	HCOO	HCOO	HCOO	$\text{C}_2\text{H}_5\text{COO}$	$\text{C}_2\text{H}_5\text{COO}$	$\text{C}_2\text{H}_5\text{COO}$		HO	
CH_3	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	CH_4
CH_3CO	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	CH_3OOH
CH_3O	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	CH_3OH
CH_3CO	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	CH_3CHO
CH_3CO_2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	$\text{CH}_3\text{CO}_2\text{H}$
CH_3COO	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	CH_3COOH
HCO	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	H_2CO
HCO_2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	HCO_2H
HCO_2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	HCOOH
$\text{C}_2\text{H}_5\text{CO}$	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	$\text{C}_2\text{H}_5\text{CO}$
$\text{C}_2\text{H}_5\text{CO}_2$	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	$\text{C}_2\text{H}_5\text{CO}_2$
$\text{C}_2\text{H}_5\text{COO}$	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	$\text{C}_2\text{H}_5\text{CO}_2$
HO_2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	$\text{CH}_3\text{COCH}_2\text{OH}$
HO	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	H_2O
Common unsaturated product	CH_2	CH_2OO	H_2CO	CH_2CO	CH_2COO	CH_2COO	CH_2COO	CO	CO + O ₂	CO ₂	CO ₂	$\text{C}_2\text{H}_5\text{COCHO}$	$\text{C}_2\text{H}_5\text{COCHO}$	$\text{C}_2\text{H}_5\text{COCHO}$	O	O	
	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	

^a Code: O, product observed; ?, product obscured by cracking pattern of other substances; X, product of this mass number absent from this system.

TABLE V
 POSSIBLE RADICAL-RADICAL RECOMBINATION REACTIONS

R ₁	R ₂								
	CH ₃	CH ₃ O	CH ₃ CO	CH ₃ COO	HCO	HCOO	CH ₃ COCH ₂	CH ₃ COCH ₂ O	HO
CH ₃	X	?	?	?	?	?	?	X	O
CH ₃ O		O	?	X	?	X	X	X	O
CH ₃ CO			X	X	?	X	X	X	O
CH ₃ COO				X	X	X	X	X	X
HCO					X	?	X	X	O
HCOO						X	X	X	O
CH ₃ COCH ₂							X	X	O
CH ₃ COCH ₂ O								X	X
HO									X

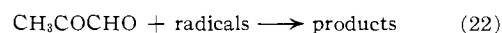
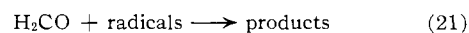
disproportionation reactions, two direct oxygen-radical reactions, and the heterogeneous decomposition of CH₃OOH. Water could be formed by 20 different radical-radical reactions involving HO, plus the heterogeneous decomposition of CH₃OOH, and possibly heterogeneous destruction of HO₂. Methanol could be formed in 13 different radical-radical reactions. Methyl hydroperoxide is possible from 13 such reactions. There appears, however, to be only one source of CH₃OCH₃, and its rate of formation is a qualitative measure of the CH₃O radical concentration.

Undoubtedly these 140 possibilities could be reduced by other arguments, based on energetics, the literature, and aesthetics. However, products were observed at only 12 mass peaks; the initial rates plus curves of growth give at most 24 data. It appears clear that in spite of the great detail in which the products are followed, this investigation is not sufficient to give the first approximation to a definitive mechanism. Furthermore, the analysis of all molecular products is insufficient to establish the mechanism.

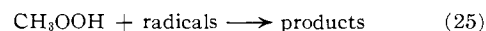
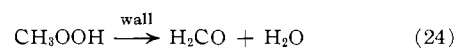
On the other hand, this investigation does give some mechanistic conclusions. The low yield of CH₃OCH₃ and the high yield of CH₃OOH indicates some very easily abstracted hydrogen and an unusually abundant source of free radicals formed either by (i) oxygen molecule attack on excited acetone molecules or (ii) oxygen attack on the acetyl radical.

Subsequent Reactions.—As the reaction proceeds the products enter the reaction. For example, the

half-life data clearly indicate that H₂CO, CH₃COCHO, CH₃COCH₂OH, and CH₃OOH are removed. Since the first three products are stable in the dark, their removal must be due to free radical attack



where the products probably include H₂O, CO, and CO₂. The methyl hydroperoxide decays both in the dark and when illuminated, the decay when illuminated being somewhat greater than in the dark under the same conditions. Thus, the reactions indicated are¹⁰



Apparently, reaction 21 is more important than reaction 24, and the net effect is a diminution of the relative H₂CO pressure with time. The products of reactions 21–23 presumably include H₂O, CO, and CO₂, and thus these products should be examples of case 4 of article I. Analysis of the data does show that all of these products are greater at the steady state than would be predicted solely from the initial reactions.

Acknowledgment.—This work was supported by the Division of Air Pollution, Bureau of State Services, Public Health Service, Grant AP-104.

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Photochemical Oxidations. IV. Acetaldehyde

BY HAROLD S. JOHNSTON AND JULIAN HEICKLEN

RECEIVED FEBRUARY 28, 1964

The room-temperature photooxidation of acetaldehyde (0.4 to 18 mm.) in oxygen (1.0 to 9.2 mm.) with continuous ultraviolet radiation above 2200 Å. has been studied by the method outlined in part I of this series. Observations were made by leaking the reaction mixture directly into the electron beam of the mass spectrometer during photolysis. The principal products of reaction were CH₃OH and presumably CO and CO₂; other products were H₂O, CH₂O, HCOOH, CH₃OOH, CH₃COOH, CH₃OOCH₃, and probably CH₃C(O)OOH. Because of the cracking pattern of the reactants, it was impossible to establish the presence or absence of CH₄, CH₂CO, CO, and CO₂. Oxidation of the primary radicals, CH₂ and HCO, leads to CH₃OO, CH₃O, HO, and HO₂, and probably HCO(OO) and HCOO. There are at least six radicals in this system that can disproportionate in 36 ways and undergo other reactions. Thus this reaction is much too complicated for its mechanism to be revealed merely by analysis of all products.

Introduction

The room-temperature photooxidation of acetaldehyde in the vapor phase, in liquid, and in solution was first studied by Bowen and Tietz.¹ They found the

product(s) of reaction to be a peroxide(s) formed in a chain length of about 1000. Presumably, the peroxide(s) was peracetic acid and/or diacetyl peroxide.

(1) E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).