The deuterium isotope effect on the rate of the exchange supports the idea that reactions (7) and (8) precede the rate-determining step. Deuterium oxide is less basic than protium oxide[13] hence reactions (7) and (8) should lie farther to the right in D_2O. The relative rates of reduction of bromate ion by halide ions in D_2O and H_2O has been studied.[14] The ratio of k_D/k_H is 3.5 for chloride ion, 2.5 for bromide ion and 2.4 for iodide ion.

A bimolecular nucleophilic displacement was assumed for the bromate–water exchange and for the bromate–halide reactions. An attempt was made to correlate the specific rate constants by the relationship proposed by Edwards[15]

$$\log k/k_0 = \alpha E_n + \beta H \tag{11}$$

The specific rate constants for halide and water substitution are given k and by k_0, E_n and H are nucleophilicity and basicity constants for the donor and α and β are constants of the substrate. Edwards[15] has given values for E_n and H for halide ions and water. When the bromate rate data are fitted into equation 11, a qualitative agreement was obtained between the observed and calculated specific rate constants when the values $\alpha = 0.36$ and $\beta = -0.63$ were used.

The fast exchange between iodate ion and water in alkaline solution indicates that the mechanism for this exchange may be different for this ion than for bromate. This assumes that the rapid exchange observed is not due to separation induced exchange. This seems likely since different methods of separation were used.

Several mechanisms have been proposed that could account for such a rapid exchange. The basic dissociation of HIO_3 has been postulated[16] to account for some oxidations by iodate ion

$$H + IO_3^- = HIO_3 = IO_2^+ + OH^- \tag{12}$$

Taube[3] has considered an increase in the coördination number of iodine as a reasonable possibility

$$H_2O + HIO_3 = H_3IO_4 \tag{13}$$

The corresponding hydration reaction with periodate ion is known to come to equilibrium rapidly.[17]

The relationship[18] between the rate of exchange and the difference in electronegativity between the oxygen and the central atom of the oxy-anion is in agreement with the results of these experiments. Preliminary experiments in this Laboratory[19] show that the chlorate–water exchange is very slow and follows a different rate law than the bromate–water exchange.

(13) The subject of deuterium isotope effects has been reviewed by K. Wiberg, *Chem. Revs.*, **55**, 721 (1955).

(14) E. Abel and F. Fabian, *Monatsh.*, **71**, 153 (1937).

(15) J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954).

(16) E. Abel, *Helv. Chim. Acta*, **33**, 785 (1950); K. J. Morgan, *Quart. Revs.*, **8**, 123 (1954).

(17) C. E. Crouthamel, A. M. Hayes and D. S. Martin, THIS JOURNAL, **73**, 82 (1951).

(18) M. Haissinsky and R. Daudel, *Bull. chim. soc. France*, 557 (1947).

(19) F. Ishimori and T. Hoering, unpublished work.

FAYETTEVILLE, ARK.

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

Photochemical Studies. L. The Ketene–Oxygen System at Higher Temperatures[1]

BY RICHARD A. HOLROYD[2] AND W. ALBERT NOYES, JR.

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Carbon monoxide, carbon dioxide, ethylene, formaldehyde and formic acid have been identified as products in the photochemical ketene–oxygen reaction. At room temperature the yields of all of these products are essentially independent both of intensity and of oxygen concentration except at very low oxygen concentrations. At 160° all quantum yields except that of ethylene are linearly dependent on the inverse of the square root of the light intensity. This fact and the values attained by the number of molecules of oxygen disappearing per quantum absorbed indicate strongly that a chain reaction occurs at 160°. In spite of these facts the quantum yield of ethylene formation is virtually independent of intensity and varies only slowly with change in oxygen concentration. The significance of ethylene formation in the reaction mechanism is open to some doubt, but it is very nearly certain that methylene radicals react rapidly with oxygen. The chain carriers must be radicals which do not form ethylene, and they are almost certainly mono- and not di-radicals. A reasonable mechanism for the chain reaction can be given, but definite proof of it is not now available. Methylene radicals seem to react with oxygen as though they were true radicals.

Introduction

A study of the photochemical ketene–oxygen reaction has recently been presented.[3] At room temperature and at 107° the rates of formation of products were essentially independent of oxygen concentration. A difference in behavior between 2700 and 3700 Å. was noticed both when oxygen was absent and when it was present. A plot of the reciprocal of the carbon monoxide yield against concentration in the absence of oxygen gave straight lines at the temperatures studied at 3700 Å., thus indicating the possibility that active molecules subject to collisional deactivation were present in the system. In the presence of oxygen at 3700 Å. the ratios of products were different from what they were at 2700 Å., thus affording contributory evidence that the active species at the two wave lengths are different.

It proved impossible to state definitely whether methylene radicals react so rapidly with oxygen that the reaction with ketene may be neglected or whether they react so rapidly with ketene that oxygen reactions are secondary. The present study was undertaken to provide additional evi-

(1) This work was supported in part by contract with the Office of Naval Research, United States Navy. This material may be reproduced or used in any way by the United States Government.

(2) National Science Foundation Predoctoral Fellow, 1953–1954, Eastman Kodak Company Fellow, 1954–1955.

(3) A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954).

dence on this point. At 160° the reaction is markedly different in character from what it is at 107° since it has become a chain reaction. A study of the chain reaction, a study of the effect of added ethylene,[4] and a study of behavior at very low oxygen pressures might provide additional information about the reaction of methylene radicals with oxygen.

Experimental

Ketene was prepared by the thermal decomposition of acetic anhydride following the method of Fisher, MacLean and Schnizer.[5] The carefully degassed acetic anhydride was passed through a quartz cell heated to 500 ± 10°. The effluent passed through two traps at −78° to remove acetic acid and acetic anhydride, and the ketene was condensed in a trap at −183°. Final purification was carried out in a line free from stopcocks by continued pumping during trap-to-trap distillation of the ketene. The ketene was stored at −196° to inhibit thermal reactions. More than 99.99% reacted with acetic acid thus indicating carbon dioxide to be negligible.

Oxygen was prepared by heating potassium permanganate. Cylinder ethylene, purified by repeated degassings at −183°, was used. A J. T. Baker analyzed reagent grade of glacial acetic acid was used. It was degassed at −78° and vacuum distilled, the middle third being retained.

Two different lamps were used: (1) a Hanovia Type S 100 Alpine burner; (2) a General Electric Company AH-6 high pressure mercury arc. The light beam was parallel and essentially filled the reaction vessel. Neutral density filters were used to vary the intensity.[6] Nearly all of the work was carried out at 2700 Å. This spectral region was isolated by the following filter combination: 3 mm. of Corning glass 9863, 3 cm. of $NiSO_4 \cdot 6H_2O$ (500 g./l.), 2 cm. of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene iodide (100 g./l.). This combination transmitted from 2450 to 2950 Å. with a maximum at 2700 Å.[7]

The analytical technique for oxygen, carbon monoxide and ethylene was essentially the same as that already described. The cell was 20 cm. in length, 2.2 cm. in internal diameter, volume = 76 ml. The gases were circulated continuously by a magnetically driven stirrer. When low concentrations of oxygen were used, there was danger of depletion, especially at 160° where a chain reaction occurs. To obviate this difficulty, a one-liter bulb was inserted between the stirrer and the cell. Thus the total circulating volume was 1260 ml., and the partial pressure of oxygen never changed more than a few per cent. during a run.

Condensable products were determined in some runs, but these could not be determined for the same runs as were used for gas analyses. At the end of the run the ketene and the reaction products were dissolved in one milliliter of water and the aqueous sample removed and analyzed. Formaldehyde was determined colorimetrically by the method of Matsukawa.[8] Since formaldehyde may either polymerize rapidly on the walls or may react with ketene to give propiolactone,[9] there is some danger that the values for formaldehyde will be low. Efforts to prove the formation of propiolactone after allowing the products to stand gave negative results, and presumably the error from this source is negligible. It is believed that loss by polymerization was also small.

Formic acid is another of the products. It was suspected that this would react with ketene to give a mixed anhydride, $C_3H_4O_3$. A sample of this mixed anhydride was prepared by the method of Hurd[10] and its mass spectrum determined.[11] Comparison of the mass spectrograms of the condensable products with that of the mixed anhydride indicated beyond question that formic acid is one of the products. On the other hand, its precise determination proved to be impossible because of complications arising from the instability of the mixed anhydride.

The technique for quantum yield measurements was essentially the same as that previously described.[3]

Results

(a) **Pure Ketene.**—Quantum yields of carbon monoxide formation were found to be as follows: 2.4 (26°, 1770 × 10^{-5} mole/l.), 2.04 (28°, 952 × 10^{-5} mole/l.), 2.20 (106°, 540 × 10^{-5} mole/l.), 2.00 (160°, 540 × 10^{-5} mole/l.) all at 2700 Å. These are probably constant within experimental error, and the average is 2.16. Diethyl ketone was used as an internal actinometer. The quantum yield of carbon monoxide from ketene may be taken as 2.0 within experimental error. The ratio $R_{C_2H_4}/R_{CO}$ at 160° is 0.433 ± 0.027 compared to 0.468 ± 0.006 (26°)[3] and 0.453 ± 0.012 (107°).[3]

(b) **Ketene–Oxygen Mixtures.**—The magnitude of the carbon dioxide blank seemed to be independent of the size of ketene samples. Non-oxygen runs at 160° gave larger carbon dioxide blanks than room temperature photolyses. Long runs at 160° in the absence of oxygen gave high values for carbon dioxide. Probably a slow, heterogeneous, thermal reaction of ketene produces carbon dioxide. This agrees with Guenther[12] who found a rapid thermal decomposition of ketene to give allene and carbon dioxide at temperatures above 300°. For the runs for which carbon dioxide was determined an appropriate blank was always subtracted. The latter usually gave a correction of less than 20% and the error in the quantum yield of carbon dioxide formation is probably less than 10%. On the other hand, the error is absolute and not relative so that low values of Φ_{CO_2} are unreliable.

Table I shows data both around room temperature and at about 160°. The main variable is the concentration of oxygen, but the lack of effect of intensity at room temperature can also be seen. Table II shows more specifically the effect of intensity at two different oxygen concentrations at 160°.

Table III shows the effect at 160° of ketene pressure when the oxygen concentration and the number of quanta absorbed per milliliter per second are kept constant. Table IV shows analyses of the fractions condensed at −110° from two runs made at 160°.

Formaldehyde was definitely identified as a product. At 27° at an oxygen concentration of 4.65 × 10^{-5} mole/l. the formaldehyde quantum yield was 0.14 whereas at 160° at an oxygen concentration of 4.23 × 10^{-5} mole/l. the yield was 1.66. Thus formaldehyde and formic acid are both important products in the chain oxidation of ketene at 160°.

(c) **Ketene–Ethylene Mixtures.**—The reactions of methylene radicals with ketene have been studied

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[4] W. F. Ross and G. B. Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934).

[5] G. J. Fisher, A. F. MacLean and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

[6] See R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **71**, 3390 (1949).

[7] M. Burton, T. W. Davis, A. Gordon and H. A. Taylor, *ibid.*, **63**, 1956 (1941).

[8] D. Matsukawa, *J. Biochem. (Tokyo)*, **30**, 385 (1939).

[9] H. J. Hagemeyer, Jr., *Ind. Eng. Chem.*, **41**, 765 (1949).

[10] C. D. Hurd and A. S. Roe, THIS JOURNAL, **61**, 3355 (1939).

[11] The authors wish to thank Mr. R. C. Wilkerson of the Celanese Corporation of America, Clarkwood, Texas, for performing the mass spectrographic work.

[12] W. B. Guenther, Ph.D. Thesis, University of Rochester, 1954. This work was performed under the direction of Professor W. D. Walters.

TABLE I

KETENE AND OXYGEN EFFECT OF OXYGEN CONCENTRATION AND INTENSITY (VOLUME OF CELL = 76 ML.)

Cell temp., °C.	Ketene concn., moles/l. × 10^5	Oxygen concn., moles/l. × 10^6	$I_a \times 10^{-11}$ quanta/ml./sec.	Quantum yields CO	C_2H_4	O_2	CO_2
27.0	535	0.019	5.5	2.20	0.76	0.59	..
26.0	535	.023	13.3	2.58	.96	.69	..
27.0	535	.039	12.1	2.48	.92	.68	..
27.0	535	.061	12.7	2.22	.74	.74	..
27.0	540	.065	16.2[a]	2.34	.72	.84	..
27.0	540	.089	11.0	2.36	.75	.95	..
27.0	535	.116	7.9	2.16	.67	.81	..
27.5	540	.164	12.9	2.58	.66	.98	..
27.0	524	.492	3.8[b]	2.22	.64	1.07	..
34.0	519	5.73	29.8	2.36	.68	1.37	0.35
34.5	535	5.93	8.0	2.34	.64	1.62	.41
158	540	0.130	45	2.06	.80	0.25	..
158	540	.143	59	1.80	.70	.13	.13
162	289	.154	38	2.36	.90	.33	..
160	482	.277	57	2.42	.82	.77	.20
160	540	.508	71	2.76	.72	1.40	.34
160	535	.598	33	3.00	.73	2.16	.48
157	289	.618	36	2.92	.82	1.38	..
162	546	1.14	27	3.18	.76	2.84	.74
159	465	1.81	30	3.70	.67	3.64	1.70
162	417	3.45	61	4.08	..	4.92	..
162	508	3.46	32	4.74	..	6.00	..
162	540	4.02	55	4.12	..	5.56	4.4
161	524	4.28	30	4.50	.69	5.98	2.66

[a] Intermittent illumination. [b] $\Phi_{H_2CO} \sim 0.05$.

TABLE II

KETENE AND OXYGEN EFFECT OF INTENSITY

Cell temp., °C.	Ketene concn., moles/l. × 10^5	Oxygen concn., moles/l. × 10^5	$I_a \times 10^{-11}$, quanta/ml./sec.	Quantum yields CO	C_2H_4	O_2	CO_2
159	546	0.391	59	2.62	0.73	1.50	0.30
160	540	.368	31	2.54	.64	1.52	.30
160	540	.385	6.3	2.92	.63	2.12	.52
164	535	.373	0.63	3.68	.66	3.94	.64
				Av.	.67		
162	540	4.02	55	4.12	..	5.56	4.4
161	524	4.28	30	4.50	.69	5.98	2.66
161	503	4.09	11.6	4.92	.69	7.30	..
160	535	3.99	3.1	6.52	.62	11.32	7.04
				Av.	.67		

TABLE III

KETENE AND OXYGEN

EFFECT OF KETENE CONCENTRATION

Cell temp., °C.	Ketene concn., moles/l. × 10^6	Oxygen concn., moles/l. × 10^5	$I_a \times 10^{-11}$, quanta/ml./sec.	Quantum yield of ethylene	Ratio of rates to rate of ethylene formation R_{CO}/R_E	R_{O_2}/R_E	R_{CO_2}/R_E
160	144	0.572	6.3	0.90	4.13	3.15	1.58
160	225	.594	6.2	.68	4.50	3.31	1.76
159	369	.578	8.0	.66	4.53	3.68	1.24
161	546	.562	5.4	.64	5.32	4.50	1.65
160	963	.546	5.7	.72	5.15	5.05	2.56
			Av.	0.72 ± 0.12			

TABLE IV

KETENE AND OXYGEN

PRODUCTS CONDENSABLE AT −110° BY MASS SPECTROMETRIC ANALYSIS

Cell temp., °C.	162	160
Ketene concn. (moles/l.) × 10^{-5}	535	439
Initial oxygen concn. (mole/l.) × 10^{-5}	4.39	3.80
Products (mole %)		
Diketene	26.4	36.2
Ketene	3.1	1.3
Acetic acid	2.7	2.6
Formic acid	0.2	0.1
Acetic anhydride	57.5	50.5
Acetic-formic anhydride	9.9	7.6
Methanol	0.4	0.3

by Kistiakowsky and his co-workers.[4,13,14] The effect of added ethylene in reducing the carbon monoxide yield should give relative rate constants for reaction of methylene radicals with ketene and with ethylene. The possibility existed also that the competition between oxygen and ethylene for methylene radicals might be studied. Table V shows the data obtained.

TABLE V

KETENE AND ETHYLENE

Cell temp., °C.	Ketene concn., moles/l. × 10^5	Ethylene concn., moles/l. × 10^5	Oxygen concn., moles/l. × 10^5	Quantum yields CO	O_2	Ratio of rate constants ethylene reaction to ketene reaction k_{20}/k_8
28	203	198	4.61	1.78	2.96	..
28	56	1038	5.41	1.32	2.40	..
27	187	198	0	1.47	..	1.07
28	209	658	0	1.23	..	1.06
27	75	776	0	1.09	..	0.99
					Av.	1.04 ± 0.04
55	214	209	0	1.66	..	0.52
55	102	482	0	1.35	..	.40
55	96	690	0	1.35	..	.26
					Av.	0.40 ± 0.13
80	219	219	0	1.74	..	0.35
81	72	621	0	1.29	..	.29
					Av.	0.32 ± 0.04
161	143	102	0	2.18	..	..

Discussion

The great reactivity of ketene complicates analytical procedures because many of the initially formed products will react with ketene before they can be determined. The formation of the mixed acetic–formic anhydride is a case in point, and some doubt exists as to the reliability of the formaldehyde determinations. Acetic anhydride will be formed by reaction of ketene either with acetic acid or with water. Water is undoubtedly one of the reaction products, and Table IV shows acetic anhydride to be present, but its mode and place of formation cannot be determined. Very probably it is formed on the walls or in traps during separation and analysis of the products and has little to do with the mechanism.

The discussion of mechanism must be based on analyses for carbon monoxide, carbon dioxide and ethylene as well as on the amount of oxygen which disappears.

The work was all carried out at 2700 Å. This apparently obviates the difficulty of excited mole-

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(13) G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, **72**, 321 (1950).

(14) G. B. Kistiakowsky and W. L. Marshall, *ibid.*, **74**, 88 (1952).

cule formation which is known to occur at 3700 Å. and may occur to some extent at 3130 Å.[3] Fluorescence has not been observed, and little is known about upper electronic states. One may assume a direct dissociation with a primary quantum yield of unity in the absence of oxygen. There are no indications that oxygen changes either the nature or the extent of the primary process at 2700 Å. We will assume the primary quantum yield ϕ to be unity at 2700 Å.[15] A further study of this matter would be advisable although at present the proper way to approach the problem of the primary quantum yield in the presence of oxygen is not apparent.

Previous data[3] and the data in Table I show that at 2700 Å. and 30° (approx.) the yields of carbon monoxide and of ethylene are independent of intensity and virtually independent of oxygen concentration except when the latter is very low. The same is almost true as regards the number of molecules of oxygen which disappear per quantum absorbed Φ_{O_2}, but there is probably a slight increase with oxygen concentration. If this effect is real, there must be some increase in yields of condensable products (formaldehyde and formic acid) at high oxygen concentrations. These must be the main products of the chain reaction.

The situation at 107°[3] is similar to that at 30°, and there may be some trend in Φ_{O_2}, but it scarcely exceeds experimental error.

At 160° and 2700 Å. (Tables I, II and III) the situation is very different. Over the range studied all yields (except those of ethylene) increase with oxygen concentration with no indication of maxima. The yields (except ethylene) decrease at high intensities and follow equations of the form $\Phi = a + b/I_a^{1/2}$ where the constants a and b depend on the oxygen and (to a lesser extent) on the ketene concentrations.

The constant a is the quantum yield at infinite intensity and may be obtained by extrapolation of a plot of Φ *vs.* $1/I_a^{1/2}$. At 160° the data in Table II give the results shown in Table VI. Clearly both a and b increase with oxygen concentration for all yields except ethylene.

TABLE VI

VALUES OF a AND b

Cell temperature = 160°

Oxygen concn.	CO_2	CO	O_2	C_2H_4
0.38×10^{-6}, mole/l.				
a[a]	0.3	2.5	1.2	0.7
b[b]	0.76×10^5	2.9×10^5	6.8×10^5	0
4.10×10^{-5}, mole/l.				
a[a]	0.7	3.4	3.6	0.7
b[b]	36×10^5	17×10^5	43×10^5	0

[a] a has the same units as Φ. [b] b has the units molecules, quantum$^{-1/2}$ ml.$^{-1/2}$ sec.$^{-1/2}$.

There are two general types of products: (1) those apparently not formed in the chain reaction (*e.g.*, ethylene) since yields do not vary with the quantum yield of oxygen disappearance; (2) those formed in the chain and whose yields increase with the number of molecules of oxygen consumed per quantum absorbed and decrease as the intensity increases. These products are carbon monoxide, formic acid, probably carbon dioxide and possibly formaldehyde.

The system under investigation has peculiarities not ordinarily found in chain reactions. The primary process at 2700 Å. may be represented as

$$CH_2CO + h\nu = CH_2 + CO;\ R_1 = \phi I_a \qquad (1)$$

where CO is a stable molecule and the fragment CH_2 is either a diradical or has some of the properties of a diradical. ϕ = primary quantum yield. (Note: I_a should be expressed in units such that the rate R_1 will be in the desired units, usually moles per liter per second.) If CH_2 produces ethylene by reaction with ketene,[16] then CH_2 is not one of the chain carriers. On the other hand, there is some (but not conclusive) evidence that the chain carriers are monovalent radicals and not diradicals. None of the products (other than ethylene) need necessarily be formed by a diradical reaction. We must conclude, therefore, that each CH_2 radical which succeeds in starting chains may start two and not one.

It is not possible to specify all of the steps in the mechanism. Let us make the following assumptions: (a) Each radical produced by (1) forms α_i molecules of product (1) and introduces directly or indirectly β radicals into the system. The α_i molecules are not formed in the chain reaction. (b) The chains are assumed to be propagated by reactions of the type

$$X_1 + M = P_1 + X_2;\ R_2 = k_2(X_1)(M) \qquad (2)$$

$$\vdots$$

$$X_n + M' = P_n + X_1;\ R_3 = k_3(X_n)(M') \qquad (3)$$

where the R's stand for reaction rates (moles per liter per second), the k's are rate constants, $X_1 \ldots X_n$ are radicals, and M and M′ are reactant gases. M and M′ may or may not be identical. $P_1 \ldots P_n$ represent products which are not necessarily all different. (c) Chains are ended by a radical–radical reaction

$$X_1 + X_1\,(+M) = P(+M);\ R_4 = k_4(X_1)^2 \qquad (4)$$

Only one radical-radical reaction is considered, but others could occur without changing the general form of the equation. Let γ_i be the number of molecules of a given substance (i) formed or used up in each link of the chain. Quantum yields are now found to be

$$\Phi_i = \phi\alpha_i + k_2\gamma_i(M)(\phi\,\beta/2I_a k_4)^{1/2} \qquad (5)$$

where Φ_i is the over-all quantum yield of the product P_i.

Equation 5 has the right form to fit the facts. In the case of ethylene $\alpha_E \sim 0.7$ and depends very little on oxygen pressure. Also $\gamma_E = \beta_E = 0$ as regards any radicals which may lead to ethylene formation through a chain sequence of steps. The data demand that both α and $k_2\gamma(M)(\beta/2\,k_4)^{1/2}$ be dependent on oxygen concentration for all products except ethylene (Table VI).

The fraction α must in some way be dependent on oxygen concentration as though the radical responsible for starting and for propagating chains could suffer some other fate independent of oxygen

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[15] See W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956).

[16] Much of the earlier work on ketene was done in the laboratories of Professor R. G. W. Norrish and of Professor G. B. Kistiakowsky. Reference 3 gives most of the references.

concentration. Thus one could write (M) = $(O_2)/(1 + k(O_2))$, where k is a ratio of rate constants, and quantum yields would attain limiting values at a given intensity. The values of Φ_{CO} and of Φ_{O_2} for runs at 160° show this dependence. In fact the quantum yields given in Tables I and II are found to fit almost exactly the following general equations

$$\Phi_{O_2} = \frac{x(O_2)}{1 + y(O_2)} + \frac{z(O_2)}{1 + y(O_2)} \times \frac{1}{I_a{}^{1/2}} \qquad (6)$$

$$\Phi_{CO} = 2 + \frac{0.41x(O_2)}{1 + y(O_2)} + \frac{0.41z(O_2)}{1 + y(O_2)} \times \frac{1}{I_a{}^{1/2}} \qquad (7)$$

x, y and z are constants at any one temperature.

Thus a general mechanism of the type presented in reactions 1–4 is found to have the right form to fit the experimental results.

The Formation of Ethylene in the Presence of Oxygen.—In earlier work it was impossible to decide definitely whether CH_2's react quantitatively with ketene or whether they react quantitatively with oxygen. In the present instance a chain reaction is started, but ethylene is not formed in the chain. Hence it must be formed in one of the following ways:

(a) As a side reaction so that

$$CH_2 + CH_2CO = C_2H_4 + CO \qquad (8)$$

with a yield of about 0.7 and all of the chains are started by those radicals which react with ketene in such a way as not to give ethylene. Thus for each quantum absorbed 0.3 methylene radical would remain to account for all other products. Even if the radical–radical chain stopping step is very slow compared to $CH_3 + CH_3 = C_2H_6$[17] and that the rate of the chain propagating step is exceptionally fast, it is still impossible to account for all of the yields by assumption (a).

(b) In the radical–radical chain ending step. If this is true, the yield should not exceed 0.5 unless CH_2's are produced in chain branching steps so that more than one enters the system per quantum absorbed.

(c) By some step which also initiates chains, *i.e.*, CH_2 would react rapidly with oxygen, and the resultant intermediate would yield ethylene part of the time and simultaneously start chains. This is the probable mechanism.

Let us assume that the following reaction is rapid

$$CH_2 + O_2 = CH_2O_2 \qquad (9)$$

except at low oxygen concentrations where 8 and 9 may be expected to compete with each other. The radical CH_2O_2 may not be allowed to rearrange directly to formic acid, since this would not start chains. It must rather react with ketene. At low oxygen concentrations the yield of products formed or consumed in the chain will depend on the fraction of CH_2O_2's formed per quantum absorbed. The yield of CH_2O_2's can be derived from equations 1, 8 and 9 and is

$$\Phi_{CH_2O_2} = \frac{k_9(O_2)}{k_8(K) + k_9(O)_2} \qquad (10)$$

where (K) is the ketene concentration. This has the desired type of oxygen dependence for the intercepts in equations 6 and 7. The lack of dependence of the yields on oxygen at large oxygen concentrations is therefore interpreted to mean that all CH_2's are reacting with oxygen and that reaction 8 has become relatively unimportant.

We have yet to propose a specific ethylene forming step. At infinite intensity oxygen is consumed to an extent dependent on oxygen concentration and simultaneously carbon monoxide, ethylene, formic acid, and possibly carbon dioxide are formed. At high oxygen concentrations the system behaves as though CH_2O_2 radicals reacted about two-thirds of the time to give ethylene, carbon monoxide and OH + HCO radicals, the latter combining most of the time to give formic acid. The other one-third essentially gives OH and HCO (or formic acid) without leading to ethylene. Formally these facts may be written in the equations

$$CH_2CO + h\nu = CH_2 + CO \qquad (1)$$

$$CH_2 + O_2 = CH_2O_2 \qquad (9)$$

$$CH_2O_2 + CH_2CO(+CH_2CO) = C_2H_4 + 2CO + HCO + OH \qquad (11)$$

$$CH_2O_2 + CH_2CO = OH + HCO + CH_2CO \qquad (12)$$

Since at large oxygen concentrations $\Phi_{C_2H_4} = 0.67$, we require that $k_{11}/(k_{11} + k_{12}) \cong 0.67$. In order for this to be true (12) must involve a collision with a ketene molecule. At high intensities and low temperatures formic acid and other products would be formed by radical–radical reactions. At low intensities formyl and hydroxyl could start chains.

The Chain Reaction.—An entirely satisfactory description of the chain reaction is not possible since the yields of all products are not known over a wide range of conditions. The following set of reactions is consistent with the experimental results and is presented as a possible example of the general reactions 2, 3 and 4.

Chain initiation:

$$HCO + O_2 = HO_2 + CO \qquad (13)$$

$$OH + CH_2CO = CH_2OH + CO \qquad (14)$$

Chain propagation:

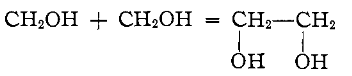
$$HO_2 + CH_2CO = CO_2 + CH_2OH \qquad (15)$$

$$CH_2OH + O_2 = HCOOH + OH \qquad (16)$$

$$CH_2OH + O_2 = HO_2 + CH_2O \qquad (17)$$

Chain termination:

$$CH_2OH + CH_2OH = CH_2O + CH_3OH \qquad (18)$$



$$CH_2OH + CH_2OH = \underset{OH}{\underset{|}{CH_2}}\text{—}\underset{OH}{\underset{|}{CH_2}} \qquad (19)$$

Ethylene Scavenger Results.—Before attempting to estimate the rate constant for (9) we may consider the reaction with added ethylene. It should be noted that the CO/C_2H_4 ratio in the products from pure ketene increases slowly as the temperature increases (2.2 at 30°, 2.3 at 160°) thus indicating that the polymer forming step apparently has a slightly higher activation energy than the ethylene forming step (1.8 ± 1.0 kcal.). The addition of ethylene as a scavenger in the absence of oxygen decreases the quantum yield of carbon monoxide formation (Table V).

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[17] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

If reaction (1) is followed by the two steps

$$CH_2 + CH_2CO = CO + (C_2H_4 \text{ or polymer}) \qquad (8)$$

$$CH_2 + C_2H_4 = C_3H_6 \qquad (20)$$

then

$$\Phi_{CO} = 1 + \frac{k_8(K)}{k_8(K) + k_{20}(E)} \qquad (21)$$

where (E) is the ethylene concentration. At 27° k_{20}/k_8 is approximately unity[13] as shown in Table V since $\Phi_{CO} \sim 1.5$ when (K) = (E). k_{20}/k_8 decreases as the temperature increases and $E_8 - E_{20}$ is approximately 4.8 kcal.

In mixtures of ketene, ethylene and oxygen one may assume first that CH_2 does not react with oxygen. If this is true, it will react equally with ketene and with ethylene at 27° if the concentrations of these two gases are equal. In the second run, Table V, the ethylene to ketene ratio is 18.5 so that virtually no CH_2's would react with ketene. Thus, unless CH_2 reacts with ethylene to give an intermediate which reacts with oxygen, there should be no oxygen uptake. This is contrary to the facts. The evidence that a diradical, such as $CH_2CH_2CH_2$, would rearrange to propylene before it would react with oxygen is fairly good but not absolutely exclusive.[18]

If reference is again made to Table V, one finds that the carbon monoxide yields in the first two runs are below two. Since (1) and (11) together would give at least $\Phi_{CO} = 2$, one must assume that the radical CH_2O_2 reacts with ethylene without giving carbon monoxide.

It is difficult to estimate the activation energy difference $E_8 - E_9$ since it must be based on the effect of low oxygen pressures in decreasing the ethylene yield. Very roughly $E_8 - E_9$ is 3 kcal., but the uncertainty is at least 2 kcal. From the data in Table I, k_9/k_8 is about 0.3×10^5 at 27°. If the rate of (8) at 27° is 10^{-16} ml. molecules^{-1} sec.$^{-1}$ [13] then (9) has a rate of about 3×10^{-12} in the same units. If the activation energy is zero, the steric factor P_9 is about 10^{-2} which is somewhat higher than $CH_3 + O_2$[19,20] and possibly higher than $C_2H_5 + O_2$.[21] On the other hand, 9 may have an activation energy as great as 2 kcal., and therefore the steric factor for (9) could be close to unity.

Thus the assumption that methylene radicals react with oxygen much more rapidly than they do with ketene fits the facts on the whole much better than the opposite assumption. Moreover, the results which follow from this assumption tend to show that CH_2 behaves as a true radical and not as a relatively unreactive quasi-molecule.

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[CONTRIBUTION NO. 2099 FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Kinetics of the Ferrous Iron–Oxygen Reaction in Sulfuric Acid Solution

BY ROBERT E. HUFFMAN AND NORMAN DAVIDSON[1]

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The reaction $4Fe^{II} + O_2 \rightarrow 4Fe^{III} + 2H_2O$, at 140–180° in 1 *F* H_2SO_4, proceeds by simultaneous bimolecular and termolecular reaction paths: $-d(Fe^{II})/dt = k_b(Fe^{II})P_{O_2} + k_t(Fe^{II})^2P_{O_2}$. At 159°, $k_b = 1.93 \times 10^{-5}$ atm.$^{-1}$ sec.$^{-1}$, $k_t = 1.60 \times 10^{-3}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$; the respective activation energies were measured as 13.4 (±2) and 16.3 (±2) kcal. At 30.5°, only the termolecular path is observed (contrary to the predictions of the high temperature activation energies); $k_t = 2.78 \times 10^{-6}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$ (1 *F* H_2SO_4). The variation of rate with $SO_4^=$ ($\mu \sim 1$, $NaClO_4$) indicates independent reactions, $2Fe^{++} + O_2 \xrightarrow{(1/2)k_u} 2Fe^{III} + H_2O_2$, and $FeSO_4 + Fe^{++} + O_2 \xrightarrow{(1/2)k_s} 2Fe^{III} + H_2O_2$, where $k_u = 1.4 \times 10^{-6}$ $k_s = 3.1 \times 10^{-5}$ M^{-1} atm.$^{-1}$ sec.$^{-1}$, and $K_{FeSO_4} = 1.1$ M^{-1}. The reaction rate increases a small amount with increasing *p*H. Catalysis by Cu^{++} follows the rate law $-d(Fe^{++})/dt = 4k_9(Fe^{II})(Cu^{++})$ and is probably initiated by $Fe^{II} + Cu^{++} \xrightarrow{k_9} Fe^{III} + Cu^{I}$. In 0.23 *F* H_2SO_4, 0.35 *F* Na_2SO_4, $k_9 = 1.9 \times 10^{-3}$ M^{-1} sec.$^{-1}$. The rate-determining step for the bimolecular path is presumably either: (1a) $Fe^{II} + O_2 \rightarrow Fe^{III} + HO_2$, or (1b) $Fe^{II} + O_2 \rightarrow Fe^{IV} + H_2O_2$; for the termolecular path it is $2Fe^{II} + O_2 \rightarrow 2Fe^{III} + H_2O_2$. Possible detailed mechanisms are discussed. There is evidence that the bimolecular path, the termolecular path and the Cu^{++} catalyzed path are all accelerated by complexing anions, X, and to an extent depending on the affinity of X for Fe^{+++}. Furthermore, strong complexers favor the occurrence of the bimolecular path.

The rate of oxidation of ferrous ion by molecular oxygen in acid solution is very dependent upon the nature of the anions present. The rate increases as the complexing affinity of the anion for ferric ion increases. (It is to be expected that the complexing affinity for ferrous ion would be in the same order.) Thus, at a given *p*H, the rate is found to decrease in the series pyrophosphate,[2] phosphate,[3] chloride,[4,5] sulfate[6] and perchlorate.[7] The rate law is $-d(Fe^{II})/dt = 4k(Fe^{II})P_{O_2}$ for the first three media listed above and $-d(Fe^{II})/dt = 4k(Fe^{II})^2 \cdot P_{O_2}$ for the last two. The rate-determining steps are believed to be either (1a) or (1b) for the former case, and (2) for the latter.

$$Fe^{II} + O_2 \longrightarrow Fe^{III} + HO_2 \qquad (1a)$$

$$Fe^{II} + O_2 \longrightarrow Fe^{IV} + H_2O_2 \qquad (1b)$$

$$Fe^{II} + O_2 + Fe^{II} \longrightarrow 2Fe^{III} + H_2O_2 \qquad (2)$$

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