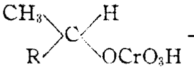
corrected[2] for the fact that only $HCrO_4^-$ is the reactive oxidizing agent.

The acidity of solutions containing perchloric acid was compared to those containing perchloric acid, pyridine and pyridinium ion, using thymol blue as indicator. The method outlined by Brode[18] was used; at a *p*H of 2 the indicator is in its most sensitive range. The acidities of the perchloric acid solutions were identical, within experimental error, with the corresponding solutions containing pyridine; certainly the difference did not exceed 1% of the hydrogen ion concentration.

Conclusions

The objective of the present series of investigations is the elucidation of the mechanisms of chromic acid oxidation in aqueous solution. The ester in benzene is most probably diisopropyl chromate. By contrast, the kinetics of the oxidation in aqueous solution shows that, if the ester mechanism is correct, the intermediate must be monoisopropyl chromate. Since the C–H bond of the alcohol is cleaved in the rate controlling step of the reaction,[4] and since it has here been shown that pyridine catalyzes the reaction in aqueous solution, the mechanism represented by equations (1) and (2) becomes highly probable. Furthermore, a mechanism analogous to that represented by (1) and (2) probably explains the pyridine-catalyzed decomposition of the ester in benzene or toluene solution. (It is possible that the pyridine may also, or in some cases alternatively, complex with the chromium atom of the ester. The mechanism for the reaction in aprotic solvents is not yet completely understood.) The parallel between the decomposition of the ester in benzene and in water is strengthened by the fact that the reaction in aqueous solution[19] as well as that in benzene, can be photochemically accelerated.

The ester mechanism for the chromic acid oxidation of isopropyl alcohol in aqueous solution is consistent with numerous other facts concerning oxidation in polar media. For example, the by-products obtained in the oxidation of methyl-*t*-amylcarbinol[20] may be explained[1,5] by the ester mechanism. The chromic acid ester of this alcohol can decompose by either of two mechanisms; one of these is the normal oxidation to the ketone, analogous to that shown in equations (1) and (2); the other mechanism is represented by equations (6) and (7); where R represents the *t*-amyl group.



$$\mathrm{CH_3(R)C(H)OCrO_3H} \longrightarrow \mathrm{CH_3CHO + HCrO_3^- + R^+} \qquad (6)$$

$$\mathrm{R^+ + H_2O} \xrightarrow{\text{fast}} \mathrm{ROH + H^+} \qquad (7)$$

(The fate of the $HCrO_3^-$, a compound of tetravalent chromium, has been discussed elsewhere.[3,5]) In reaction (6), a solvated *t*-amyl carbonium ion splits from the ester and reacts with water to form *t*-amyl alcohol. This type of by-product will presumably only be formed in those instances where the solvated carbonium ion has reasonable stability, *i. e.*, only where the ion is of the tertiary or benzyl type.[21]

It is pertinent to note that several other oxidizing agents also function by way of esters as intermediates.[22]

Summary

1. A dilute benzene solution of a neutral ester of chromic acid and isopropyl alcohol (presumably diisopropyl chromate) has been prepared.
2. The ester is very unstable; its decomposition is strongly catalyzed by bases such as pyridine.
3. The chromic acid oxidation of isopropyl alcohol in 0.01 molar aqueous acid is also catalyzed by pyridine.
4. These facts, together with those previously known about chromic acid oxidations, indicate that an ester is an essential intermediate in the oxidation of isopropyl alcohol by aqueous chromic acid.

CHICAGO 37, ILLINOIS RECEIVED JUNE 5, 1950

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[18] W. Brode, THIS JOURNAL, **46**, 581 (1924).

[19] E. Bowen and C. Bunn, *J. Chem. Soc.*, 2353 (1927).

[20] W. Mosher and F. Whitmore, THIS JOURNAL, **70**, 2544 (1948).

[21] E. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[22] R. Criegee, L. Kraft and B. Rank, *Ann.*, **507**, 159 (1933); R. Criegee, *Angew. Chem.*, **51**, 519 (1938); **53**, 321 (1940); F. Duke and A. Forist THIS JOURNAL, **71**, 2790 (1949).

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Mechanism of the γ-Ray Induced Oxidation of Formic Acid in Aqueous Solution

BY EDWIN J. HART

Recent work of Allen,[1] Dainton,[2] Krenz,[3] Miller,[4] and Weiss and Stein[5] has given considerable support to the suggestion of Weiss[6] that free hydrogen atoms and hydroxyl radicals are the principal active species liberated in liquid water by ionizing radiation. This present communication reports work on the specific action of the hydroxyl radical in aqueous solutions of formic acid.

According to present concepts hydrogen and hydroxyl radicals are produced in equal numbers during irradiation of water or aqueous solutions with γ-rays. Unless a complete analysis of all reaction products can be made, it is difficult to differentiate between the chemical effects of these two radicals. This is particularly true in solutions containing organic molecules. However, it is found that the effect of the hydroxyl radical can be

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[1] A. O. Allen, *J. Phys. Colloid Chem.*, **52**, 479 (1948).

[2] F. S. Dainton, *ibid.*, **52**, 490 (1948).

[3] F. H. Krenz, *Can. J. Research*, **B26**, 647 (1948).

[4] N. Miller, *J. Chem. Phys.*, **18**, 79 (1950).

[5] J. Weiss and G. Stein, *Nature*, **161**, 650 (1948).

[6] J. Weiss, *ibid.*, **153**, 748 (1944).

increased by at least fifty-fold by the addition of hydrogen peroxide in very low concentrations to formic acid solutions. This serves as a means of studying the chemical effects of the hydroxyl radical in aqueous solutions under conditions where the relative effect of the hydrogen atom is very small.

Previous studies[7,8] on the effects of X-rays on dilute aqueous solutions of formic acid disclosed that equimolar quantities of carbon dioxide and hydrogen were obtained at *p*H values of 3.0 or lower. The net reaction is

$$HCOOH = H_2 + CO_2 \tag{1a}$$

Upon the addition of hydrogen peroxide to aqueous solutions of formic acid, carbon dioxide–hydrogen ratios considerably higher than one are obtained in the present work. The stoichiometry of this reaction is in agreement with the equation

$$HCOOH + H_2O_2 = 2H_2O + CO_2 \tag{2a}$$

The kinetics of these two reactions were investigated by studying the effect of dose-rate, time of irradiation and concentration of formic acid, hydrogen peroxide and oxygen on the rate of oxidation of formic acid.

Experimental

Irradiations were carried out using radioactive cobalt (Co^{60}) of 25 curies activity as the source of γ-rays. 5.3 year Co^{60} has two γ-rays of 1.1 and 1.3 Mev. energy and so provides a substantially monochromatic source of γ-rays. The radioactive cobalt employed is in the form of a rod 7.6 cm. long and 0.8 cm. in diameter. It is encased in an aluminum capsule 8.9 cm. long and 1.0 cm. in diameter in order to prevent radioactive cobalt oxide from contaminating the irradiation chamber and cells. Dose-rates of 427, 134 and 66 r. per minute[9] were obtained at distances of 3.0, 6.0 and 9.0 cm., respectively, from the source. These dose-rates were measured using air-free 0.001 *M* formic acid in 0.001 *N* sulfuric acid as the actinometer solution. It is assumed that the X-ray value of 3.2×10^{-6} *M* hydrogen and carbon dioxide[7] are produced per liter per 1000 r. Since this yield is independent of dose-rate for X-rays it is further assumed that such an independence holds for γ-rays.

Cylindrical Pyrex cells about 2 cm. in diameter of 10 to 12 ml. capacity provided with a $^5/_{20}$ standard taper capillary tube were used. The irradiations were carried out in a position with the long axis of the cells parallel to the cobalt source at distances of 3, 6 and 9 cm. The cells were mounted on a turntable that was rotated at a rate of one r.p.m. This eliminated variations in dose-rate due to lack of exact centering of the Co^{60} source.

A method of removing air similar to that previously described was used.[8] Air was removed from the aqueous solutions by evacuation through a carbon dioxide trap with a mechanical pump. The solutions were simultaneously warmed with hot water and shaken during evacuation. This operation was continued until the characteristic metallic click of the water against the sides of the evacuation chamber could be heard. The evacuation chamber was then inverted and the air-free solution allowed to flow by gravity into the irradiation cells. At this point the system to the mechanical pump was closed and cold water poured over the cells to reduce the vapor pressure of the water in the cells. With proper evacuation the entire volume of the cells was filled by the solution. On removal from the evacuation chamber, the tips of the cells were sealed with a closed $^5/_{20}$ standard taper ground-glass joint filled with the degassed solution. The oxygen concentration of the formic acid solutions was reduced to less than 10^{-6} *M* by this technique. (See discussion of the effect of oxygen for the details of this method of estimating oxygen concentration in these solutions.)

The evacuation chamber and cells were heated to 500° prior to use before each irradiation. This ensured oxidation of organic impurities on the glassware and was found necessary to prevent the formation of carbon dioxide from these impurities in air-free water during irradiation.

Standard analytical techniques were employed for the analysis of products formed during exposure to γ-rays. Gas analyses for oxygen, carbon dioxide and hydrogen were carried out using the Van Slyke apparatus. The regular procedure worked satisfactorily for hydrogen peroxide concentrations of 0.001 *M* or less. However for hydrogen peroxide concentrations above this value serious decomposition of the hydrogen peroxide remaining in the irradiated formic acid solution took place upon the addition of potassium hydroxide. Consequently the analysis for carbon dioxide could not be made in the presence of the formic acid–hydrogen peroxide solution. It was found necessary to collect the gas obtained after the initial equilibration, eject the solution and reintroduce the gas into the Van Slyke chamber. This was done after the chamber was cleaned and re-evacuated. Hydrogen peroxide was determined in the presence of formic acid by potentiometric and colorimetric analysis. In the former case, an excess of ceric sulfate was added to the solution to react with the hydrogen peroxide. The excess was back titrated with ferrous sulfate. For concentrations less than 0.0001 *M*, hydrogen peroxide was determined by the following colorimetric method developed by J. A. Ghormley.[10] Two solutions were made consisting of (a) 10 ml. of 1% ammonium molybdate, 1 g. of sodium hydroxide and 33 g. of potassium iodide; and (b) 10 g. of potassium acid phthalate each diluted to 500 ml. with water. Equal volumes of these solutions were mixed just prior to use. Five ml. of this mixture and one ml. of the sample were then diluted to 10 ml. with water and the optical density measured at 3500 Å. The concentration of hydrogen peroxide is then given by the equation

$$C = 40dD$$

where

C = concentration in units of 10^{-6} *M*
d = dilution factor = 10 for case discussed above
D = optical density.

Reagents.—Water from a Barnstead still was redistilled from an alkaline potassium permanganate solution, passed through a silica tube heated to 800° and condensed. A third distillation from a sulfuric acid–chromic acid solution was next carried out and the water passed through a second silica tube heated to 800°. The water was then condensed and collected in a silica reservoir. This water showed of the order of 10^{-6} mole per liter of carbon dioxide after exhaustive irradiation. Reagent grade 30% fuming sulfuric acid (Baker and Adamson) and Eastman Kodak Co. 98–100% formic acid were used without purification. Merck reagent grade 30% hydrogen peroxide was steam distilled using triple distilled water. The middle fraction usually of about 0.5 *M* was used.

Results and Discussion

Effect of Time and Dose-rate of Irradiation.—The oxidation of dilute aqueous solutions of formic acid by γ-rays follows the same course as for X-rays.[7,8] Equimolar amounts of hydrogen and carbon dioxide are produced at formic acid concentrations of 0.001 and 0.01 *M*. Figure 1 shows that the amount of product depends linearly on dosage.

The addition of hydrogen peroxide to the formic acid system results in a marked acceleration of rate of oxidation by γ-rays. The effect of 1.4×10^{-4} *M* hydrogen peroxide is shown in Fig. 2. No perceptible dark reaction is observed during the time necessary for irradiation and analysis of samples. In the presence of hydrogen peroxide, the main reaction follows equation (2a).

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(7) H. Fricke and E. J. Hart, *J. Chem. Phys.*, **2**, 824 (1934).

(8) H. Fricke, E. J. Hart and H. P. Smith, *ibid.*, **6**, 229 (1938).

(9) r., the roentgen, is defined as "the quantity of X- or γ-radiation such that the associated corpuscular emission per 0.001293 g. of air produces, in air, ions carrying one electrostatic unit of quantity of electricity of either sign."

(10) A. O. Allen, T. W. Davis, G. V. Elmore, J. A. Ghormley, B. M. Haines and C. J. Hochanadel, ORNL-130 (October 11, 1949).

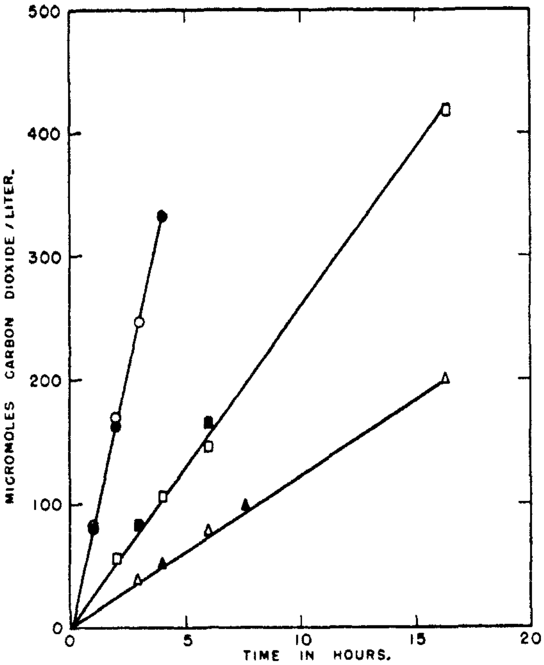

Fig. 1.—Effect of time of irradiation, dose-rate and concentration of formic acid on the oxidation of formic acid in 0.001 *N* sulfuric acid: solid points, 0.01 *M* HCOOH; open points, 0.001 *M* HCOOH ○●, 3 cm.; □■, 6 cm.; △▲, 9 cm; from Co^{60} source.

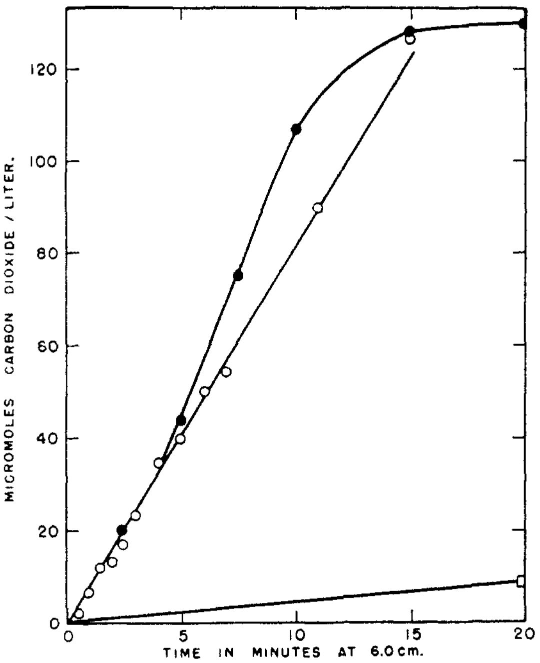

Fig. 2.—Effect of hydrogen peroxide on the oxidation of 0.01 *M* formic acid in 0.001 *N* sulfuric acid: □, NO H_2O_2; ○, 0.140 × 10^{-3} *M* H_2O_2; ●, 0.130 × 10^{-3} *M* H_2O_2.

Actually the reactions represented by equations (1a) and (2a) are occurring simultaneously but, as discussed below, reaction (2a) predominates by a factor of at least 10 for hydrogen peroxide concentrations in the range from 0.000030 to 0.01 *M*.

Table I shows that the oxidation of formic acid in the presence of hydrogen peroxide is nearly independent of dose-rate whereas the decomposition of hydrogen peroxide is dependent on the square root of dose-rate. Here it is assumed that the γ-ray yield for the production of hydrogen and carbon dioxide is independent of dose-rate and equal to 3.2×10^{-6} mole/liter/1000 r., the X-ray yield. As explained in the experimental section, air-free formic acid is used as the actinometer solution for measuring γ-ray dose-rates. Employing this method of dosimetry, a dependence on $I^{0.5}$ which is identical with the X-ray result of Fricke[11] is found for the decomposition of hydrogen peroxide. In view of this agreement, it is concluded that the oxidation of formic acid in the absence of hydrogen peroxide is independent of γ-ray dose-rate.

In contrast to the linear dosage curves for the formic acid reaction, the dosage curves for the hydrogen peroxide–formic acid solutions are by no means linear nor reproducible. S-Shaped curves characteristic of chain reactions were often obtained. This was especially true at hydrogen peroxide concentrations below 0.001 *M* where the accelerating effect of the hydrogen peroxide was very pronounced. This behavior is probably due to the presence of traces of oxygen or of other inhibitors. (The effect of oxygen was investigated and is reported below.) Characteristic curves appear in Fig. 2.

TABLE I

EFFECT OF DOSE-RATE ON THE OXIDATION OF 0.01 *M* FORMIC ACID

Distance from Co^{60} source, cm.	3.0	6.0	9.0
Dose-rate, r./sec.	7.12	2.24	1.095
Oxidation of 0.001 *M* HCOOH[a]	3.2	3.2	3.2
Oxidation of 0.01 *M* HCOOH + 0.005 *M* H_2O_2[a]	53.5	48.4	41.4
Decomposition of 0.0039 *M* H_2O_2[a]	5.5	9.8	12.9

[a] Yields are expressed in units of 10^{-6} mole/l./1000 r. All solutions are 0.001 *N* in sulfuric acid.

Effect of Variable Hydrogen Peroxide and Formic Acid Concentration.—The effect of the hydroxyl radical on the oxidation of formic acid was studied with the aid of hydrogen peroxide. At a constant formic acid concentration of 0.01 *M*, the hydrogen peroxide concentration was varied from 1.5×10^{-5} to 0.01 *M*. All experiments were carried out in the presence of 0.001 *N* sulfuric acid at a distance of 6 cm. from the Co^{60} source.

The initial rate of the oxidation reaction, or in cases where an induction period occurred the maximum rate of the reaction, was measured. These data on rates of oxidation *versus* hydrogen peroxide concentration appear in Fig. 3. The rate of carbon dioxide development which is used as a measure of formic acid oxidation increases at first with increasing hydrogen peroxide concentration. A maximum increase in rate of 55-fold was found experimentally at 0.00074 *M* hydrogen peroxide in 0.01 *M* formic acid solutions. Thereafter in the range up to 0.01 *M* hydrogen peroxide the rate of oxidation decreases with increasing hydrogen peroxide concentration.

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(11) H. Fricke, *J. Chem. Phys.*, **3**, 364 (1935).

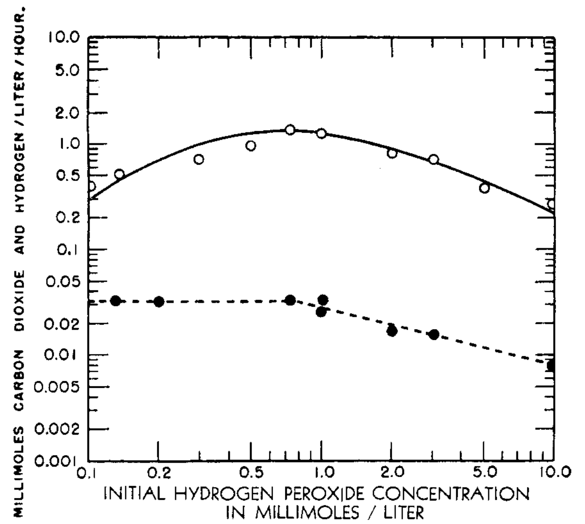

Fig. 3.—Effect of hydrogen peroxide concentration on the rate of oxidation of 0.01 *M* formic acid in 0.001 *N* sulfuric acid: —, theoretical curve; ○, CO_2; ●, H_2.

The increased yield of carbon dioxide, the autocatalytic character of dosage curves and the sensitivity to inhibitors in the hydrogen peroxide–formic acid oxidation are indicative of a chain reaction. Since one molecule of formic acid is oxidized per hydrogen peroxide molecule, the propagation steps are postulated

$$OH + HCOOH = H_2O + HCOO$$
$$HCOO + H_2O_2 = H_2O + CO_2 + OH$$

Under the experimental conditions employed oxygen was not found. If formed, it is present in amounts of less than 1 to 2 × 10^{-6} mole per liter. This indicates that hydrogen peroxide is not decomposed into oxygen, its normal product, but to a radical that is effective in oxidizing formic acid.

From the above propagation steps, it is seen that the hydroxyl and formate free radicals alternate in the hydrogen peroxide sensitized reaction. The existence of the maximum in the curve of Fig. 3 provides important clues as to the chain terminating steps. At hydrogen peroxide concentrations lower than 0.00074 *M* the main chain terminating step involves incidental ions or impurities associated with the water, sulfuric acid or formic acid. This reaction may be

$$HCOO + X = CO_2 + HX$$

The introduction of this step into the mechanism is necessary in order to obtain the correct form for the equation used to represent the experimental data. Induction periods frequently found at low concentrations may be caused by an impurity such as oxygen that gradually disappears during irradiation.

At hydrogen peroxide concentrations above 0.00074 *M*, the rate of formic acid oxidation gradually drops. This indicates that the chain terminating step involves the hydroxyl radical and hydrogen peroxide or an impurity associated with the hydrogen peroxide. In the absence of more specific information, this step will be represented simply as

$$OH + H_2O_2 = \text{termination}$$

In contrast to the marked acceleration in rate of carbon dioxide development as hydrogen peroxide is added to formic acid, hydrogen production remains substantially constant until after the maximum rate of carbon dioxide production has been reached. Thereafter a gradual decrease in hydrogen production occurs (see Fig. 3). This drop in hydrogen yield is believed to be caused by a competition between formic acid and hydrogen peroxide for the hydrogen free radicals. Since hydrogen is not found in the hydrogen peroxide decomposition by X-rays, the primary reaction is probably

$$H + H_2O_2 = H_2O + OH$$

Figure 4 shows the effect of variable formic acid concentration in 0.001 *M* hydrogen peroxide. The rate of carbon dioxide formation increases with formic acid concentration in the range from 0.0002 to 0.01 *M*. In the absence of hydrogen peroxide the rate of oxidation of formic acid is nearly independent of formic acid concentration.[7,8]

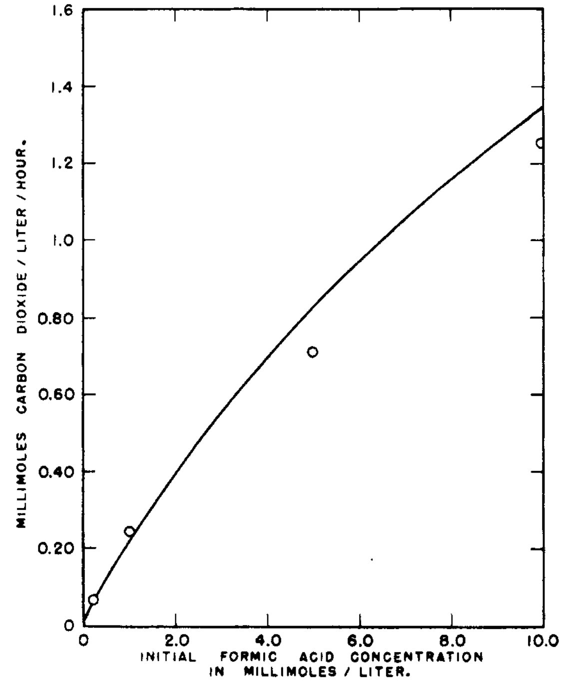

Fig. 4.—Effect of formic acid concentration in 0.001 *M* hydrogen peroxide and 0.001 *N* sulfuric acid: —, theoretical curve; ○, experimental points.

Effect of Oxygen.—Oxygen is found to play an important role as inhibitor for the formic acid–hydrogen peroxide reaction. Induction periods and many of the erratic points obtained on dosage curves are attributed to this effect.

In the absence of oxygen, hydrogen peroxide at concentrations of 0.00003 *M* rapidly disappears from 0.01 *M* formic acid solutions when irradiated with γ-rays. Furthermore the rate of hydrogen peroxide disappearance is not changed in the presence of prepurified nitrogen. Oxygen was blended with nitrogen and added to the above-mentioned formic acid–hydrogen peroxide solution at oxygen concentrations of 0.48 and 1.01 × 10^{-5} *M*. Figure 5 shows that oxygen present is converted to hydrogen peroxide. This is evident by an increase in hydrogen peroxide concentration corresponding to one hydrogen peroxide molecule per molecule of oxygen present. After consumption of the oxygen, the characteristic rapid reaction of hydrogen peroxide with formic acid takes place. In this low range of oxygen concentrations, the time required for decrease of hydrogen peroxide concentration to its initial value is a linear function of the oxygen concentration.

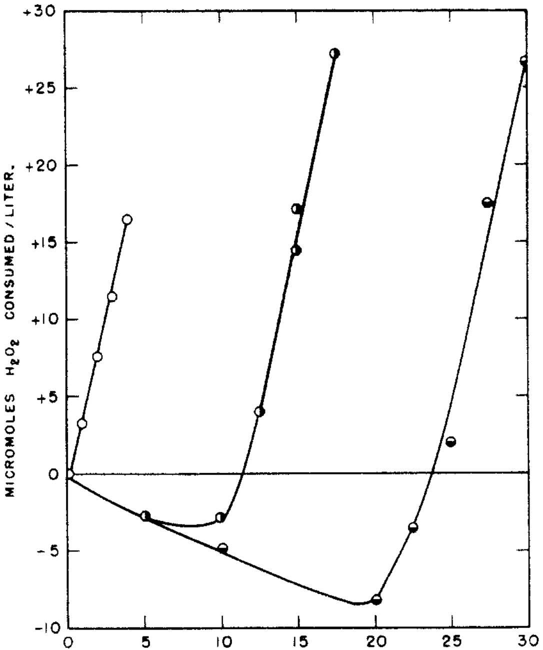

Fig. 5.—Effect of oxygen on the X-ray induced decomposition of hydrogen peroxide in aqueous solution containing 0.01 *M* formic acid, 0.00003 *M* hydrogen peroxide and 0.001 *N* sulfuric acid: ○, oxygen-free; ◑, 4.8×10^{-6} *M* O_2; ◒, 10.1×10^{-6} *M* O_2.

Mechanism of Oxidation of Formic Acid Solutions by γ-Rays

The rate of oxidation of formic acid in dilute aqueous hydrogen peroxide solutions is substantially independent of dose-rate from 7.1 to 1.1 r./sec. At these dose-rates, hydrogen peroxide decomposition is dependent on $I^{0.5}$. In the absence of hydrogen peroxide, formic acid oxidation is independent of dose-rate and also of concentration of formic acid in the range from 0.001 to 0.01 *M* covered in the present work. Under these conditions, hydrogen and carbon dioxide are produced in equimolar quantities. In the presence of hydrogen peroxide the main reaction followed yields carbon dioxide but no hydrogen. The rate of carbon dioxide development increases at first with increasing hydrogen peroxide concentration, passes through a maximum at 0.00074 *M* and then decreases with increasing concentration. Finally the mechanism must account for an oxygen inhibition effect.

The above facts can be accounted for by the series of reactions

	Rate constant	
$H_2O + \gamma\text{-rays} = H + OH$	I_0	(1)
$H + HCOOH = H_2 + HCOO$	k_2	(2)
$OH + HCOOH = H_2O + HCOO$	k_3	(3)
$OH + HCOO = H_2O + CO_2$	k_4	(4)
$HCOO + H_2O_2 = H_2O + CO_2 + OH$	k_5	(5)
$HCOO + X = CO_2 + HX$	k_6	(6)
$OH + H_2O_2 =$ termination products	k_7	(7)

Equation (8) is derived from the above mechanism by assuming that a steady state of free radical concentration is rapidly established and that chain terminating reaction (4) can be neglected. The resulting equation is

$$\frac{d(CO_2)}{dt} = I_0 + \frac{I_0k_3(HCOOH)[2k_5(H_2O_2) + k_6(X)]}{k_7(H_2O_2)[k_5(H_2O_2) + k_6(X)] + k_3k_6(HCOOH)(X)} \qquad (8)$$

If it is further assumed that chain terminating step (6) can be neglected in comparison with chain propagating step (5), equation (8) reduces to

$$\left[\frac{d(CO_2)}{dt}\right] = I_0 + \frac{2I_0}{\frac{k_6}{k_5}\frac{(X)}{(H_2O_2)} + \frac{k_7}{k_3}\frac{(H_2O_2)}{(HCOOH)}} \qquad (9)$$

The constants in this equation are evaluated by taking the derivative with respect to hydrogen peroxide concentration. Then from the point at the maximum in Fig. 3 the two constants $k_6(X)/k_5$ and k_7/k_3 can be obtained by the use of equation (9) and its derivative since I_0, the rate in the absence of hydrogen peroxide, can be separately measured. For 0.01 *M* formic acid containing hydrogen peroxide the resulting equation is

$$\left[\frac{d(CO_2)}{dt}\right]_0 = 0.026 + \frac{20}{\frac{5.38}{(H_2O_2)_0} + 9.84(H_2O_2)_0} \qquad (10)$$

(Concentrations are in millimoles per liter and time is in equivalent hours at 6 cm. from the cobalt source. $(H_2O_2)_0$ is initial hydrogen peroxide concentration.)

A comparison of the experimental and calculated points appears in Figs. 3 and 4. In view of the marked effect that impurities and traces of oxygen have on the chain reaction it is felt that the agreement is within the limits of experimental error.

The primary step in the above mechanism has ample verification through the work of Weiss and others.[1-6] Equation (2), on the other hand, is an uncertain one since hydrogen gas is generally considered to originate in a process involving recombination of hydrogen atoms. Experimental evidence against this recombination process in the oxidation of formic acid is provided by data on hydrogen formation as a function of hydrogen peroxide concentration. In the absence of hydrogen peroxide the rates of carbon dioxide and hydrogen formation are equal to I_0, the rate of production of hydrogen and hydroxyl radicals. According to equation (2) hydrogen production is expected to be independent of hydrogen peroxide concentration. This is actually the case as can be seen from the hydrogen curve of Fig. 3 up to a hydrogen peroxide concentration of 0.001 *M*. Beyond this concentration the hydrogen yield decreases, indicating the onset of a reaction between hydrogen atoms and hydrogen peroxide. The decrease in yield of hydrogen follows the course expected from the following two competing reactions

$$H + HCOOH = H_2 + HCOO$$
$$H + H_2O_2 = H_2O + OH$$

The work of Gieb[12] on the reaction of hydrogen atoms with formic acid in gas phase studies also supports equation (2). Water, carbon monoxide, carbon dioxide and hydrogen were identified among the products. Gieb reported an activation energy of 7–8 kcal. for this reaction. The formation of the carbon monoxide in aqueous solutions is probably prevented since the strongly oxidizing hydroxyl radical is present. Further evidence for the existence of this step is provided in the work of Burton[13] on the photolysis of mixtures of formic and acetic acids. Burton concluded from his work that the hydrogen atoms produced in the acetic acid photolysis rapidly reacted with the formic acid to form molecular hydrogen. This would account for the reduced mirror activity of the photolysis products obtained from the blend of acids compared to the activity found in the photolysis of acetic acid. Equation (2) could also have been written as

$$H + HCOOH = H_2 + COOH \qquad (11)$$

From present work, it is not possible to determine which hydrogen atom in formic acid reacts with the hydrogen free radical. Work is now in progress on deuterated formic acid in order to measure the relative rates of reactions (2) and (11).

The results obtained in this study establish the existence of a reaction between the OH radical and formic acid. There is a negligible "dark" reaction showing that formic acid and hydrogen peroxide molecules do not react. Since the rate of oxidation is 55 times as fast in the presence of hydrogen peroxide as in its absence, it is apparent that a chain reaction must occur. The sequence pictured in equations (3) and (5) is considered likely. According to this mechanism the hydroxyl and formate radicals alternate in propagating the chain. The stoichiometry of the reaction given in equation (2a) is accounted for by equations (3) and (5) since one molecule of hydrogen peroxide disappears per carbon dioxide molecule appearing. This implies that the following thermal reaction is of little importance

$$HCOO = H + CO_2$$

This conclusion is further supported by the fact that the hydrogen yield does not increase in the presence of hydrogen peroxide. If the above reaction occurred, then hydrogen would be produced in view of reaction (2) and larger quantities of this gas would be expected from the radiolysis especially at low hydrogen peroxide concentrations.

The chain terminating reaction (4) is supported by the stoichiometry of the hydrogen peroxide-free formic acid reaction in which equimolar amounts of hydrogen and carbon dioxide are formed. Reactions (1), (2) and (4) provide a mechanism for obtaining this result or the equivalent set (1), (3), with a terminating step

$$H + HCOO = H_2 + CO_2$$

is also conceivable. With present information, it is not possible to distinguish between these two mechanisms.

Chain terminating reactions (6) and (7) are supported by the experimental rate *versus* hydrogen peroxide concentration curve of Fig. 3. At low hydrogen peroxide concentrations, the rate is primarily determined by k_6/k_5. The ratio of rate constants k_7/k_3 is the determining factor at high hydrogen peroxide concentrations.

While the reaction sequence represented by reactions (1) through (7) may not be a unique set capable of explaining the experimental data, the use of hydrogen peroxide has been a definite help in establishing the validity of reactions (3) and (5) leading to the chain reaction. The kinetics are also in accord with chain terminating steps of the type (6) and (7) which were found through the use of hydrogen peroxide. This hydrogen peroxide technique could be successfully employed in chemical and biological systems where it is desired to distinguish between the chemical effects of the hydrogen and hydroxyl radicals. The most serious restrictions placed on its use are that there must be no dark reaction with hydrogen peroxide and that oxygen, a most effective inhibitor for the reaction, must be excluded.

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Summary

The mechanism of formic acid oxidation by γ-rays has been studied in air-free aqueous solutions at *p*H 2.7 to 3.0. Oxidation of the formic acid occurs as a result of its reaction with the H and OH free radicals produced by primary ionization of the water by the γ-rays. The effects of the H and OH radicals are differentiated by increasing the contribution of the hydroxyl radical to the oxidation of formic acid by the addition of hydrogen peroxide. A maximum increase in rate of 55-fold is obtained for 0.01 *M* formic acid at 0.00074 *M* hydrogen peroxide. An oxygen inhibition of the hydrogen peroxide–formic acid reaction is also found. Hydrogen peroxide is formed from the oxygen added and after the oxygen has been consumed, the normal rate of the hydrogen peroxide–formic acid reaction is restored. The mechanism of these reactions is discussed in terms of a chain reaction in which hydroxyl and formate radicals alternate in propagating the chain.

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(12) K. H. Gieb, *Ergeb. exakt. Naturw.*, **15**, 44 (1936).

(13) M. Burton, THIS JOURNAL, **58**, 1655 (1936).