[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Radiation Chemistry of the Aqueous Formic Acid–Ferric Sulfate System

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A study of the γ-ray induced reaction between formic acid and ferric sulfate is reported in the pH range from 0.3 to 2.5. Radiation yields, G_{CO_2}, G_{H_2} and $G_{Fe^{++}}$ are given as a function of formic acid and ferric sulfate concentrations. The reactions are dependent on the relative formic acid/ferric ion ratios. At low ratios of these reactants, the stoichiometry is expressed by: $2Fe^{+++} + HCOOH = 2Fe^{++} + 2H^+ + CO_2$. At high ratios, the reaction is: $2Fe^{+++} + 2HCOOH = 2Fe^{++} + 2CO_2 + H_2 + 2H^+$. The mechanism is discussed in terms of free radical reactions involving hydrogen, hydrogen molecule ion, hydroxyl and formate free radicals.

An efficient reduction of ferric ion occurs upon γ-ray irradiation of aqueous formic acid solutions. This reduction reaction was demonstrated in a previous study of the γ-ray induced oxidation of ferrous sulfate–formic acid–oxygen solutions.[1]

Normally the hydroxyl radical, produced in aqueous solutions by ionizing radiations, is an oxidizing species and does not reduce ferric ions. However, with formic acid added, the hydroxyl radical is converted into a formate radical capable of reducing ferric ions. At low formic acid concentrations relative to ferric ion concentrations, the following reaction expresses the stoichiometry observed

$$2Fe^{+++} + HCOOH = 2Fe^{++} + 2H^+ + CO_2$$

At relatively high concentrations of formic acid, hydrogen is an additional product of the irradiation and the net reaction is

$$2Fe^{+++} + 2HCOOH = 2Fe^{++} + 2CO_2 + H_2 + 2H^+$$

The behavior of this ferric sulfate–formic acid system is a complex function of the hydrogen ion, ferric ion and formic acid concentrations. Studies on the effect of formic acid and ferric sulfate concentrations in the pH range from 0.3 to 2.5 were carried out and data regarding the relative reactivity of hydrogen free radicals with formic acid and ferric ion is provided.

Experimental

The experimental techniques of water purification, preparation of evacuated solutions and irradiation by Co^{60} γ-rays were similar to those previously described.[1] Dosage rates were measured by means of the ferrous sulfate dosimeter using the Hochanade–Ghormley value of $G = 15.5$ ferric ions/100 e.v. of energy.[2] Formic acid was purified by distilling Matheson 98–100% acid at 20 cm. pressure through a 30-plate column at 59°. A product having a $n^{20}D$ of 1.3715 was obtained. Reagent grades of sulfuric acid and ferric sulfate were used without further purification. The ferric ion concentration was determined by measuring the optical density at 3020 Å. with a Beckman quartz spectrophotometer. The equation, $C = 449D$, was used to calculate the amount of ferric ion present in 0.8 N sulfuric acid solutions when one-centimeter cells were used. In this equation C is the concentration in microequivalents per liter and D is the optical density. Ferrous ion was measured by direct titration with ceric sulfate. Carbon dioxide and hydrogen were determined by analysis in the Van Slyke microgas analysis apparatus.

Experimental Results

In general, the rate of formation of products is constant for a particular set of initial conditions and the yield of products can be calculated from the rate of energy input. However, at low concentrations of reactants, the products interfere with the primary reaction. Under these conditions, product *vs.* energy absorption curves are concave downward. In these cases the initial yields of products are reported. The experimental results appear in Table I. The yields of products are given in units of G, molecules or ions formed per 100 e.v. of energy absorbed in the solution. At high concentrations of solute, a small correction to the energy absorbed in the system is necessary. This correction has been applied to the present results by a method previously described.[3]

Effect of pH.—The pH was varied in the range from 0.38 to 2.49 using sulfuric acid. (See exp. 1–5 in Table I and Fig. 1.) Carbon dioxide and hydrogen were found to decrease with increasing pH. A slight drop occurs in G_{CO_2} but a marked decrease takes place in G_{H_2}. Under these conditions the hydrogen yield at pH 2.49 corresponds to the molecular product yield.[4,5]

Effect of Ferric Ion Concentration.—The effect of this variable was studied in 0.01 M formic acid using 0.01 and 1.00 N sulfuric acid. Figure 2 demonstrates the effect of ferric sulfate concentration in the range from 0.000024 to 0.108 M. $G_{Fe^{+++}}$ is constant at a value of 6.4. G_{CO_2} and G_{H_2} decrease as the concentration of ferric ion increases. Noteworthy also is the fact that the difference between the carbon dioxide and hydrogen yields ($G_{CO_2} - G_{H_2}$), is 3.07. At ferric ion concentrations above 0.030 M, G_{CO_2} is constant at 3.4 and G_{H_2} is constant at 0.45, the accepted molecular hydrogen yield.

The same general behavior is observed at pH 0.33 ± 0.05. However, for a given ferric ion concentration, hydrogen evolution is greater at pH 0.33 than at pH 2.0. (See exp. 13–16.)

Effect of Formic Acid Concentration.—At low formic acid concentrations (10^{-5} to 10^{-3} M) using 0.01 M ferric sulfate and 0.01 N sulfuric acid, G_{H_2} is constant at about 0.3. G_{CO_2} rises continuously throughout the concentration range from 10^{-5} to 1.0 M formic acid. Above 0.001 M formic acid, the hydrogen yield parallels the carbon dioxide yield (exp. 18–23). The general nature of these results is shown in Fig. 3.

Mechanism of Reaction

Under conditions where secondary reactions are

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[1] E. J. Hart, THIS JOURNAL, **74**, 4174 (1952).

[2] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

[3] E. J. Hart, *Radiation Research*, **2**, 33 (1955).

[4] A. O. Allen, *ibid.*, **1**, 85 (1954).

[5] E. J. Hart, *ibid.*, **1**, 53 (1954).

TABLE I

γ-RAY INDUCED REACTION BETWEEN FORMIC ACID AND FERRIC ION IN AQUEOUS SOLUTION

Irrad. no.	(HCOOH), *M*	(Fe^{+++}), *N*	H_2SO_4, *N*	*p*H	G_{CO_2}	G_{H_2}	$G_{Fe^{++}}$	$G_{CO_2} - G_{H_2}$
1	0.01	0.01	0.001	2.49	3.59	0.49	..	3.10
2	.01	.01	.001	2.32	3.57	0.47	..	3.10
3	.01	.00924	.01	2.01	3.76	0.56	..	3.20
4	.01	.01	.10	1.22	3.88	1.17	..	2.71
5	.01	.01	1.00	0.38	4.26	2.36	..	1.90
6	.01	.000024	0.01	..	5.61	3.26	6.43	2.35
7	.01	.000097	.01	..	6.05	2.99	5.81	3.06
8	.01	.000293	.001	2.75	5.51	2.35	6.73	3.16
9	.01	.00092	.01	2.02	4.87	1.71	6.43	3.16
10	.01	.00277	.01	2.02	4.08	1.13	6.4	2.95
3	.01	.00924	.01	2.01	3.76	0.56	..	3.20
11	.01	.0277	.03	1.68	3.49	0.49	6.53	3.00
12	.01	.108	.01	..	3.34	0.36	6.08	2.98
13	.01	.0001	1.00	0.33	5.40	4.2	4.0	1.8
14	.01	.0010	1.00	0.32	5.20	3.60	6.0	1.60
5	.01	.010	1.00	0.38	4.26	2.36	..	1.90
15	.01	.100	1.00	0.29	2.88	0.68	3.92	2.20
16	.01	.475	1.00	0.28	2.31	0.28	3.44	2.03
17	.00001	.010	0.01	2.08	0.63	0.35	..	0.28
18	.00010	.010	.01	2.02	2.18	0.27	..	1.91
19	.0010	.0924	.01	2.00	3.13	0.37	..	2.76
3	.010	.00924	.01	2.01	3.76	0.56	..	3.20
20	.100	.01	.001	2.17	4.55	1.39	6.82–7.55	3.16
21	1.00	.01	.001	1.76	5.74	2.30	7.3 - 7.7	3.44

unimportant, the principal features of the above results are explained by the following mechanism

	Rate or equil. const.	
$H_2O + \gamma\text{-rays} = H + OH$	k_1	(1)
$H_2O + \gamma\text{-rays} = {}^1/_2H_2 + {}^1/_2H_2O_2$	k_2	(2)
$H_2O\ \gamma\text{-rays} = H + {}^1/_2H_2O_2$	k_3	(3)
$OH + HCOOH = H_2O + HCOO$	k_4	(4)
$HCOO + Fe^{+++} = Fe^{++} + H^+ + CO_2$	k_5	(5)
$H + HCOOH = H_2 + HCOO$	k_6	(6)
$H_2^+ = H + H^+$	K_7	(7)
$H_2^+ + HCOOH = H_2 + H^+ + HCOO$	k_8	(8)
$H + Fe^{+++} = Fe^{++} + H^+$	k_9	(9)
$Fe^{++} + H_2O_2 = Fe^{+++} + OH + OH^-$	k_{10}	(10)

Except for equation 8, the reactions given above have been previously employed or postulated in radiation chemistry. Equilibrium reaction 7 has been used by Rigg, Stein and Weiss[6] to explain the *p*H dependence for the X-ray induced oxidation of oxygen-free ferrous sulfate solutions. Likewise the

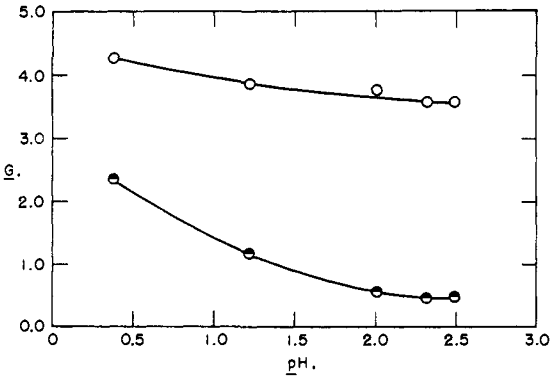

Fig. 1.—Effect of *p*H on the γ-ray induced reaction of 0.01 *M* formic acid–0.01 *N* ferric sulfate solution: ○, G_{CO_2}; ◒, G_{H_2}.

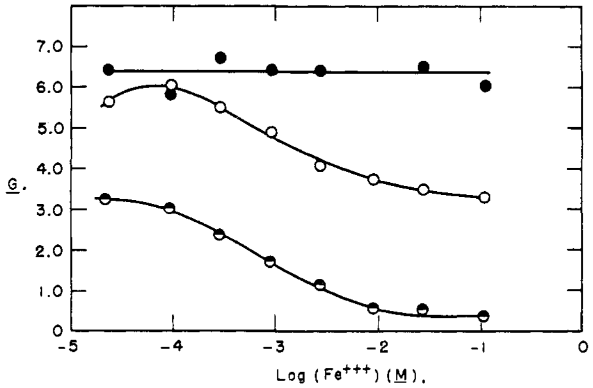

Fig. 2.—Effect of ferric sulfate concentration on the γ-ray induced reaction of 0.01 *M* formic acid–0.01 *N* sulfuric acid solutions: ○, G_{CO_2}; ◒, G_{H_2}; ●, $G_{Fe^{++}}$.

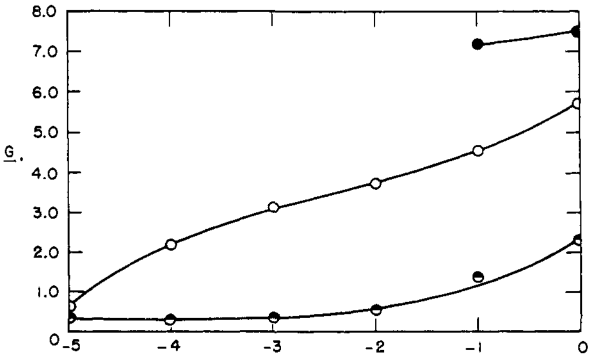

Fig. 3.—Effect of formic acid concentration on the γ-ray induced reaction of 0.01 *N* ferric sulfate–0.01 *N* sulfuric acid solutions: ○, G_{CO_2}; ◒, G_{H_2}; ●, $G_{Fe^{++}}$.

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[6] T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc. (London)*, **A211**, 375 (1952).

postulate of the formation of the hydrogen molecule ion forms the basis for a consistent explanation for the present experimental results.

Equations 11, 12 and 13 are derived from the above mechanism. A readily established steady-state concentration of hydrogen atoms, hydroxyl radicals, HCOO radicals, hydrogen molecule ions and hydrogen peroxide molecules is assumed.

$$G_{CO_2} = G_1 + \frac{G_2 + G_3}{2} + \frac{G_1 + G_3}{1 + \dfrac{k_9(\text{Fe}^{+++})}{\left[k_6 + \dfrac{k_8(\text{H}^+)}{K_7}\right][(\text{HCOOH})]}} \qquad (11)$$

$$G_{H_2} = \frac{G_2}{2} + \frac{G_1 + G_3}{1 + \dfrac{k_9(\text{Fe}^{+++})}{\left[k_6 + \dfrac{k_8(\text{H}^+)}{K_7}\right][(\text{HCOOH})]}} \qquad (12)$$

$$G_{Fe^{++}} = 2G_1 + G_3 \qquad (13)$$

Carbon dioxide and hydrogen yields are observed to depend on ferric ion, hydrogen ion, and formic acid concentrations. The ferrous ion yield on the other hand is independent of ferric ion concentration. Since the yields of the primary radiation reactions 1, 2 and 3 are pH dependent, it is expected that the above mechanism is incomplete with regard to a quantitative treatment of this variable.

The constant difference experimentally observed between G_{CO_2} and G_{H_2} is obtained from eq. 11 and 12.

$$G_{CO_2} - G_{H_2} = G_1 + G_3/2 \qquad (14)$$

A comparison of (14) with (13) further shows that

$$G_{Fe^{++}}/2 = G_{CO_2} - G_{H_2} \qquad (15)$$

The validity of eq. 15 is verified experimentally using 0.01 M formic acid in dilute sulfuric acid. Averages of $(G_{CO_2} - G_{H_2})$ and $G_{Fe^{+++}}$ for the series of experiments 6–12 and 3 are 3.07 and 6.33, respectively. (See Table II.) Ferric ion concentration varies from 0.108 to 2.4×10^{-5} M in these experiments. Therefore, participation of reactions 5, 6, 7 and 8, involving competition between formic acid and ferric ions for hydrogen atoms, is supported. Under these conditions hydrogen gas cannot be formed by the reaction

$$\text{H} + \text{HCOO} = \text{H}_2 + \text{CO}_2$$

Ferrous ion formation is equal to the primary yield of free radicals whether they be hydrogen or hydroxyl radicals. Consequently radical–radical reactions of the above type cannot be important in the mechanism.

The complex constant $k_9/\{k_6 + [k_8(\text{H}^+)]/K_7\}$, can be evaluated from eq. 12 by using previously obtained experimental values for G_1, G_2 and G_3.[7] At pH 2.10, $G_1 = 2.56$, $G_2 = 0.70$, and $G_3 = 0.91$. A plot of $(G_1 + G_3)/(G_{H_2} + G_2/2)$ *vs.* ferric ion concentration gives a straight line. From the slope of this line, $k_9/\{k_6 + [k_8(\text{H}^+)]/K_7\} = 16$ at pH 2.0 and 0.8 at pH 0.33. Under these conditions the ratio of constants, k_8/K_7k_6, is found to equal 68. Since K_7 is of the order of 0.02, $k_8 \simeq k_6$. Therefore the reactivity of the hydrogen atom is about the same as the reactivity of the hydrogen molecule ion with formic acid. However, the hydrogen atom is about 30 times as reactive with ferric ions as with formic acid molecules.

With the limited data available, it has not been possible to explain the results of irradiations at very low formic acid concentrations. The reverse reaction

$$\text{Fe}^{++} + \text{OH} = \text{Fe}^{+++} + \text{OH}^-$$

probably plays a role and accounts for the low yield of carbon dioxide. This reaction coupled with reaction 9 would lead to the catalytic recombination of hydrogen and hydroxyl free radicals.

An alternative explanation of the experimental results is afforded by the assumption that secondary electrons produced by the primary ionization are captured by hydrogen ions, ferric ions and formic acid molecules instead of water molecules. However, until experimental evidence for the direct participation of electrons is obtained, the simpler assumption involving hydrogen atoms remains adequate for explaining the mechanism of this reaction.

TABLE II

COMPARISON OF EXPERIMENTAL RESULTS WITH DERIVED RELATIONS

Eq. no.	Equation	Exptl.	Theor.[a]
13	$G_{Fe^{++}} = 2G_1 + G_3$	6.33	6.03
14	$G_{CO_2} - G_{H_2} = G_1 + G_3/2$	3.07	3.02
15	$G_{Fe^{++}}/2 = G_{CO_2} - G_{H_2}$	3.16	3.07

[a] Based on assumption that $G = 2.56$, $G_2 = 0.70$ and $G_3 = 0.91$ at pH 2.10.

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LEMONT, ILLINOIS

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[7] E. J. Hart, THIS JOURNAL, **76**, 4198 (1954).