[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Catalytic Polarographic Waves of Hydrogen Peroxide. I. The Kinetic Wave for the Ferric Iron–Hydrogen Peroxide System[1]

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Hydrogen peroxide increases the limiting current observed in the polarographic reduction of ferric iron. The increase is a kinetic current caused by the over-all reaction at the surface of the electrode: $2F_2^{++} + H_2O_2 + 2H^+ \rightarrow 2Fe^{+++} + 2H_2O$. The effects of maximum suppressors, concentration and kind of mineral acid, concentration of ferric iron and of hydrogen peroxide in the presence and absence of organic substances, of temperature and of height of mercury in the reservoir have been investigated. An interpretation is given which qualitatively accounts for the observed facts. Acrylonitrile (AN) decreases the kinetic current to one-half of its original value. The reason is that in the over-all reaction two moles of ferrous iron react with one mole of peroxide, but in the presence of AN the ferrous iron reacts with 1 mol of peroxide with subsequent polymerization of AN.

When a reducible compound is in equilibrium with a non-reducible compound or with a compound which is reduced at the dropping mercury electrode at a more negative potential, and the equilibrium between the two is established very rapidly, a kinetic polarographic wave can be obtained. Pyruvic acid, the undissociated form of which is reduced at a more positive potential than the dissociated form gives a kinetic wave of this type, the characteristics of which were studied and described by Brdicka and co-workers.[2,3,4]

Another type of kinetic wave occurs when an oxidizing agent is reduced at the electrode and the reduction product reacts very rapidly with a second oxidizing agent in the solution, the latter, because of a high overvoltage, not being reduced at the potential where the first one yields a diffusion current. An example which approaches this situation is found in the system ferrihem-hydrogen peroxide.[5] This system is not suitable for an exhaustive study of the characteristics of the kinetic current, because hydrogen peroxide is markedly reduced at the potential of the ferri–ferrohem system and also because hydrogen peroxide is rapidly decomposed by ferrihem. In the present paper are presented and discussed the results of a study of the kinetic wave observed at the dropping electrode with the system hydrogen peroxide–ferric iron. Kinetic waves observed in systems composed of hydrogen peroxide and ions different from ferric iron will be described in future papers.

In the absence of constituents which form complexes with iron, ferric iron gives a wave starting at the potential where mercury dissolves anodically. In the absence of ions which depolarize the mercury anodically and those which form complexes with ferric iron, the fully developed diffusion current of iron can be measured at a potential of +0.20 volt *vs.* the saturated calomel electrode (designated hereafter as S.C.E.).

The reduction of hydrogen peroxide at the dropping electrode is highly irreversible, the half-wave potential being −0.9 volt *vs.* S.C.E.[6] The wave is extremely drawn out and with increasing concentrations of hydrogen peroxide, slight reduction currents are found even at +0.20 volt *vs.* S.C.E. Whenever necessary, the kinetic current was corrected for this hydrogen peroxide reduction current.

The mechanism which determines the kinetic current is briefly as follows: Ferrous iron formed at the electrode surface in the reduction of ferric iron reacts very rapidly with hydrogen peroxide, regenerating ferric iron which is again reduced at the electrode. Thus the limiting current of ferric iron in the presence of hydrogen peroxide is considerably greater than the diffusion current obtained in the absence of hydrogen peroxide, the difference between the two corresponding to the kinetic current (see Fig. 2).

Experimental

Materials.—The chemicals used were all reagent grade and were not further purified. Conductivity water was used for all solutions. A stock hydrogen peroxide solution was prepared by diluting Baker and Adamson reagent grade 30% hydrogen peroxide to approximately 3% (about 1 molar) and adding 0.1% acetanilide as preservative. In a few instances hydrogen peroxide solutions free of organic material were used. They were prepared from a Buffalo Electrochemical Company product containing in excess of 99% hydrogen peroxide. By comparing the results obtained with both samples of peroxide it was shown that the preservative in the concentration used had no effect on the kinetic current. The hydrogen peroxide solutions were standardized iodometrically,[7] and were found to be fairly satble.

Apparatus.—A Heyrovsky Model VIII and a Sargent Model XXI polarograph were used for qualitative observations. Quantitative measurements were made with a manual polarograph.[8]

The electrolysis cells were similar to those described by Hume and Harris.[9] The experiments were carried out in a water thermostat at 30 ±0.1° unless otherwise stated. The capillary used had a drop time of 4.02 seconds at +0.20 volt and an *m* value of 1.680 mg./sec. When oxygen was removed from the solution, tank nitrogen was passed through solutions of acid chromous chloride, sodium hydroxide, mercuric chloride and water and then through the polarographic cell.

Procedure.—Mercury in the polarographic cell reacts with ferric iron. At small iron concentrations but at relatively high hydrogen peroxide concentrations as used in the present work, the iron was found to catalyze the oxidation of mercury by hydrogen peroxide. The reason is that the ferrous iron formed in the reaction between ferric iron and mercury is rapidly reoxidized by hydrogen peroxide. Under our experimental conditions, the oxidation of mercury was slow when the solution was not stirred. If the polarogram (or current reading) was obtained within 5 minutes after the electrode was inserted, the oxidation was found not to

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(1) From a Ph.D. thesis submitted by E. P. Parry to the Graduate School of the University of Minnesota, 1950.

(2) R. Brdicka and K. Wiesner, *Collection Czechlov. Chem. Comm.*, **12**, 138 (1947).

(3) R. Brdicka and K. Wiesner, *ibid.*, **12**, 212 (1947).

(4) K. Wiesner, *ibid.*, **12**, 64 (1947).

(5) R. Brdicka and K. Wiesner, *ibid.*, **12**, 39 (1947).

(6) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 1013 (1941).

(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., Inc., New York, N. Y., 1943, p. 630.

(8) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1938).

(9) D. E. Hume and W. L. Harris, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 465 (1943).

affect the value of the kinetic current. Stirring the solution (*e.g.* by bubbling with nitrogen) increases considerably the rate of the reaction and should be avoided if mercury is present in the polarographic cell. The interaction could be eliminated for longer periods of time by collecting the dropping mercury under carbon tetrachloride or chloroform. The S.C.E. was always used as the reference electrode. For the reason mentioned above, a mercury pool anode could not be used.

Results

Polarographic Reduction of Iron(III) in Sulfuric Acid

The wave of uncomplexed ferric iron exhibits a rather rounded maximum. Figure 1(a) gives the tracing of a polarogram of a 10^{-4} *M* ferric iron solution in 0.25 *M* sulfuric acid. Figure 1(b) shows that 0.005% gelatin in the solution eliminates the maximum. Peptone and gum arabic were also found to be effective. Table I summarizes the data obtained with various maximum suppressors. The values of the current reported have been corrected for residual current. The data show that the concentration of a maximum eliminator can be varied relatively much without affecting the diffusion current. As was to be expected, the apparent diffusion current at +0.20 v. in the absence of a maximum eliminator is not found proportional to the concentration, but it is in the presence of a maximum eliminator. For example, in the absence of a maximum suppressor, the apparent diffusion current found for 10^{-4} *M* ferric iron in 0.25 *M* sulfuric acid at +0.20 volt was 1.04 μa., and 14.1 μa. in 10^{-3} *M* solution. In the presence of 0.005% gelatin these values were 0.64 and 6.30 μa., respectively, and they remained the same in 0.01% gelatin or 0.015% peptone.

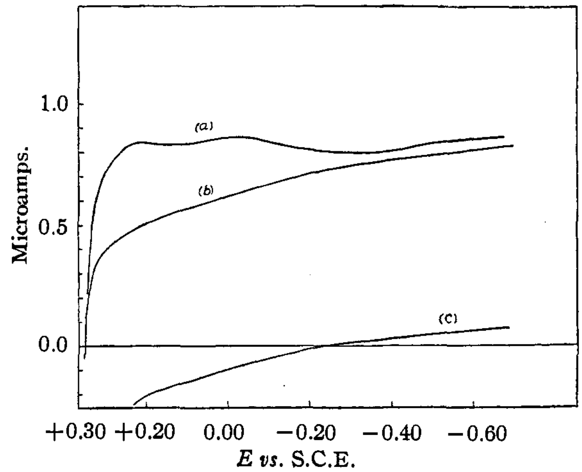

Fig. 1.—10^{-4} *M* ferric iron in 0.25 *M* air-free sulfuric acid; (a) no maximum suppressor, (b) 0.005% gelatin, (c) residual current; temp. 25°.

TABLE I

EFFECT OF MAXIMUM SUPPRESSORS ON THE WAVE OF 10^{-4} *M* FERRIC IRON IN 0.25 *M* SULFURIC ACID

Temp. 25°; oxygen removed; residual current = −0.20 μa. at + 0.20 volt and + 0.07 μA. at −0.50 volt

Suppressor	"i_d" (μa.) at +0.20 volt	at −0.50 volt	Remarks, stirring
None	0.99	0.70	Considerable
0.005% camphor	1.02	.63	Considerable
.005% caffeine	0.97	.64	Considerable
.005% thymol	1.02	.63	Considerable
.005% methyl red	0.71	.63	Some
.005% gelatin	.64	.66	No
.01% gelatin	.63	.64	No
.005% peptone	.64	.66	No
.01% peptone	.66	.65	No
.015% peptone	.64	.65	No
.005% gum arabic	.72	.65	Slight
.01% gum arabic	.66	.63	Very slight
.015% gum arabic	.63	.63	No
.02% gum arabic	.65	.63	No
None[a]	2.02	1.51	Considerable
.005% gelatin[a]	1.25	1.27	No
.01% gelatin[a]	1.24	1.27	No

[a] 2 × 10^{-4} *M* Fe^{+++}.

The Kinetic Wave in the Absence of Organic Compounds

Figure 2 presents some polarograms in 0.25 *M* sulfuric acid as supporting electrolyte. The increase due to the presence of hydrogen peroxide (denoted by i_k) is the kinetic current.

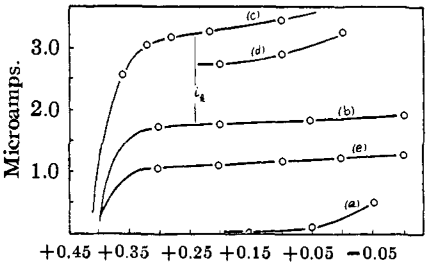

Fig. 2.—The kinetic wave in 0.25 *M* air-free sulfuric acid; temperature 30°: (a) 0.147 *M* H_2O_2, (b) 2 × 10^{-4} *M* Fe^{+++}, (c) mixture 0.0147 *M* H_2O_2 and 2 × 10^{-4} *M* Fe^{+++}; (d) and (e) same as (a) and (b), but in presence of 0.005% gelatin.

The presence of oxygen was found to have no effect on the value of the kinetic current when measurements were made at a potential more positive than that at which oxygen is reduced. In the following experiments all measurements of the kinetic current were made at a potential of +0.20 volt *vs.* S.C.E. unless stated otherwise.

Curves (d) and (e) in Fig. 2 refer to the same solutions as used for curves (b) and (c) except that they contained 0.005% gelatin. It appears that both the limiting current and the diffusion current of iron

TABLE II

EFFECT OF MAXIMUM SUPPRESSORS ON THE KINETIC CURRENT; SUPPORTING ELECTROLYTE 0.25 *M* SULFURIC ACID; TEMP. 30°

Suppressor	Ferric iron concn. (*M*) × 10^{-4}	Hydrogen peroxide concn. (*M*)	i_d (Fe^{+++})	$i_{H_2O_2}$	i_{total}	i_k
None	2.0	0.0147	1.97	0.02	3.50	1.51
0.005% gelatin	2.0	.0147	1.33	.02	2.95	1.60
None	2.4	.0368	2.55	.10	6.29	3.64
.005% gelatin	2.4	.0368	1.56	.10	5.26	3.60
.005% gelatin	2.0	.0374	1.35	.10	4.36	2.99
.005% peptone	2.0	.0374	1.34	.10	4.31	3.05

are decreased to the same extent so that the kinetic current is unaffected by the maximum suppressor. This is further illustrated by the data in Table II.

Effect of Kind of Acid and of Concentrations of Acid, Iron and Hydrogen Peroxide.—In 0.25 *M* sulfuric acid a linear relation was found between the kinetic current and the ferric iron concentration for variations between 7 × 10^{-5} and 2.5 × 10^{-4} *M* at a peroxide concentration of 0.04 *M* (see Fig. 3). The kinetic current remained the same when the acid concentration was varied between 0.1 and 0.33 *M*. With nitric and perchloric acids instead of sulfuric, kinetic currents of the same order of magnitude were observed.

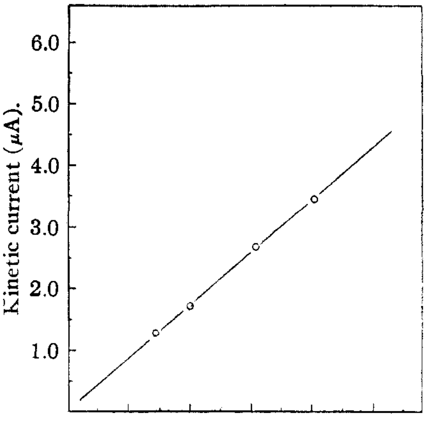

Fig. 3.—The kinetic current in 0.25 *M* sulfuric acid as a function of ferric iron concentration: 0.04 *M* hydrogen peroxide, 0.005% gelatin.

The variation of kinetic current with hydrogen peroxide concentration is shown in Fig. 4. Measurements were made in the absence of a maximum suppressor [curves (a) and (b)] and in the presence of 0.005% gelatin [curve (c)]. Curve (d) was obtained in the complete absence of organic impurities. In this experiment the hydrogen peroxide solution was prepared from the 99% product. For preparation of iron and supporting electrolyte solutions and for dilution of the hydrogen peroxide and the sample, conductivity water redistilled from potassium permanganate was used. From the results obtained, it is evident that organic impurities (as inhibitors) generally present in hydrogen peroxide have no influence on the kinetic wave. As a matter of fact, some acetanilide was added to the solution after curve (d) was obtained and identical results were observed.

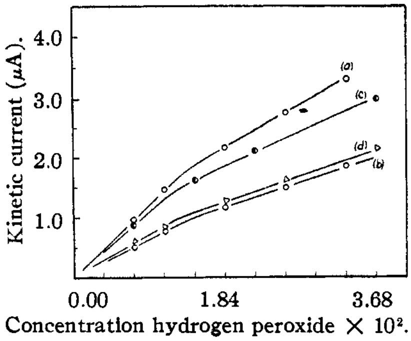

Fig. 4.—The kinetic current in 0.25 *M* sulfuric acid as a function of hydrogen peroxide concentration: (a) 2.4 × 10^{-4} *M* Fe^{+++} no maximum suppressor, (b) 1.2 × 10^{-4} *M* Fe^{+++}, no maximum suppressor, (c) 2.0 × 10^{-4} *M* Fe^{+++}, 0.005% gelatin, (d) 1.3 × 10^{-4} *M* Fe^{+++}, no maximum suppressor, pure reagents used (see text).

In Fig. 5 a comparison is made of hydrogen peroxide concentration *vs.* the kinetic current at +0.20 and −0.05 volt, respectively. The values read at −0.05 volt are larger than those at +0.20 and are more difficult to reproduce.

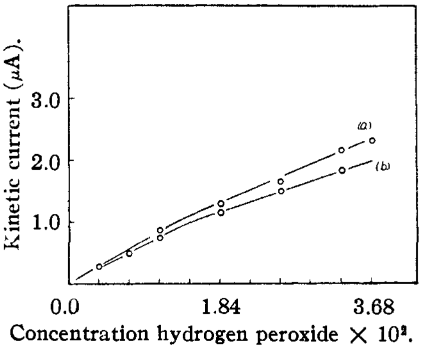

Fig. 5.—The kinetic current as a function of hydrogen peroxide concentration in 0.25 *M* sulfuric acid at 30° and in the absence of air and maximum suppressor, 1.2 × 10^{-4} *M* Fe^{+++}: (a) measurements at −0.05 volt, (b) at +0.20 volt.

Effect of Temperature.—The values of kinetic current at 25° in 0.25 *M* sulfuric acid and 0.04 *M* hydrogen peroxide were 2.71 μa. for a 2.0 × 10^{-4} *M* ferric iron solution and 4.30 μa. for a 3.2 × 10^{-4} *M* solution. At 30° these values were 3.39 and 5.22 μa., respectively. Hence the kinetic current at 30° is 1.24 times as large as at 25° and the temperature coefficient is equal to (1.24 − 1.00)/(5.0) × 100 = 4.6% per degree in this temperature interval.

Effect of Mercury Height.—The effect of height of mercury in the reservoir on the kinetic current is given in Table III.

TABLE III

EFFECT OF HEIGHT OF MERCURY ON THE KINETIC WAVE AT +0.20 VOLT; 10^{-4} *M* Fe^{+++} AND 2.9 × 10^{-2} *M* H_2O_2 IN 0.25 *M* SULFURIC ACID; 0.005% GELATIN; TEMP. 30°

h_{Hg}(cm.)	i_{total} (μa.)	i_d(Fe)	i_k
91.1	1.84	0.46	1.38
76.6	1.82	.43	1.39
59.1	1.84	.38	1.46
41.2	1.83	.33	1.50

The diffusion current of the ferric iron changes according to the square root of the height of the mercury in the reservoir as predicted by the Ilkovic equation. The kinetic current increases slightly when the mercury height is decreased. A true kinetic current should be independent of mercury height.[5]

The Kinetic Current in the Presence of Organic Compounds

The effect of methanol on the kinetic current is illustrated clearly by Fig. 6. The experiments were

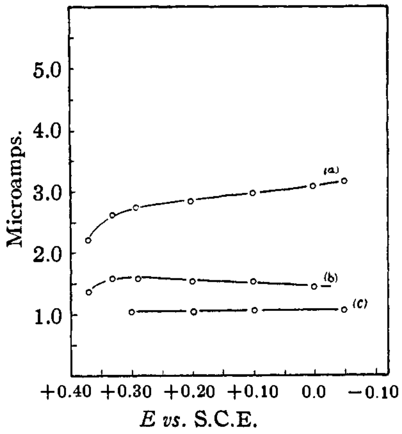

Fig. 6.—The effect of methanol on the kinetic wave in 0.25 *M* sulfuric acid and in the absence of air: 1.2 × 10^{-4} *M* Fe^{+++}, 0.0368 *M* H_2O_2. All currents corrected for current due to hydrogen peroxide: (a) in absence of methanol, (b) 0.1 *M* methanol present, (c) diffusion current of iron.

carried out in the absence of oxygen. It is evident that the kinetic current is decreased to about one-third of its original value when 0.1 *M* methanol is present. This is further illustrated in Fig. 7 where a plot of kinetic current *vs.* methanol concentration is given. Figure 8 compares plots of kinetic current *vs.* concentration of hydrogen peroxide in the absence and presence of 0.04 *M* methanol. The solutions were air free. It is seen that in the presence of methanol the kinetic current increases linearly with hydrogen peroxide concentration.

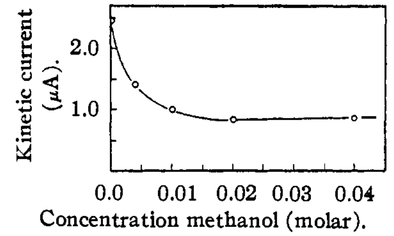

Fig. 7.—The effect of methanol on the kinetic current in 0.25 *M* sulfuric acid and in the absence of air, 2 × 10^{-4} *M* Fe^{+++}, 0.0368 *M* H_2O_2.

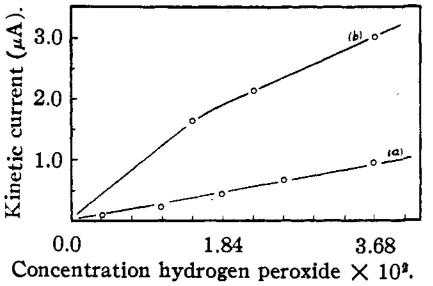

Fig. 8.—The effect of methanol on the kinetic current *vs.* hydrogen peroxide concentration plot in 0.25 *M* sulfuric acid and in the absence of air, 2 × 10^{-4} *M* Fe^{+++}: (a) 0.04 *M* methanol present, (b) methanol absent.

Ethanol was found to have the same effect as methanol on the kinetic current while the effect of acetone or acetic acid was similar but much smaller than that of alcohol (see Table IV). Some experiments were repeated in air-saturated solutions. Under such conditions the presence of the organic compounds decreased the kinetic current but not as much as when oxygen was absent. In Table IV some typical results are given.

TABLE IV

EFFECT OF ORGANIC COMPOUNDS ON THE KINETIC CURRENT AT +0.20 VOLT; 2 × 10^{-4} *M* Fe^{+++}, 0.0368 *M* H_2O_2 IN 0.25 *M* SULFURIC ACID; SOLUTIONS CONTAINED 0.02 *M* ORGANIC COMPOUND; TEMP. 30°

Organic compound	i_k (μa.)
None	2.4
Methanol	0.8
Ethanol	0.7
Acetic acid	1.9
Acetone	2.0
Methanol (air-satd., 0.1 *M* MeOH)	1.7
Acetic acid (air-satd.)	2.2

From Fig. 9 it appears that acrylonitrile (AN) in a concentration of 0.01 *M* or greater decreases the kinetic current by approximately one-half. Electrolysis of a solution containing 0.012 *M* hydrogen peroxide, 1 × 10^{-4} *M* ferric iron and 0.06 *M* AN in 0.25 *M* sulfuric acid for about 30 minutes at the dropping electrode produced a considerable amount of polyacrylonitrile which could be observed suspended in the solution. Figure 10 compares the kinetic current *vs.* peroxide concentration plots in the absence and presence of 0.06 *M* AN. In the presence of AN the kinetic current is a linear function of peroxide concentrations and is equal to one-half the value observed in the absence of AN at hy-

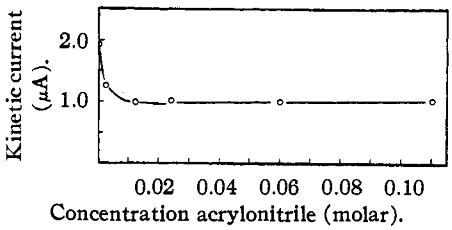

Fig. 9.—The effect of acrylonitrile on the kinetic current in 0.25 *M* sulfuric acid and in the absence of air: 2 × 10^{-4} *M* Fe^{+++}, 0.0149 *M* H_2O_2, 0.005% gelatin.

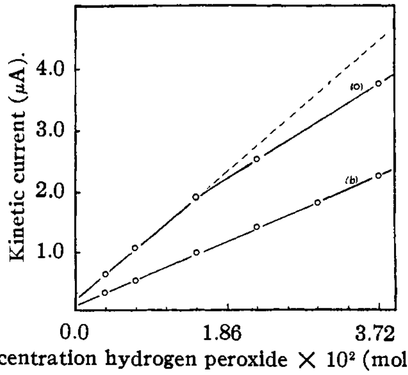

Fig. 10.—The effect of acrylonitrile on the kinetic current *vs.* hydrogen peroxide concentration plot in 0.25 *M* sulfuric acid; 2 × 10^{-4} *M* Fe^{+++}, 0.005% gelatin; AN put in after air removed; temperature 30°, (a) absence of AN, (b) 0.06 *M* AN.

drogen peroxide concentrations smaller than 0.015 *M*. The kinetic current observed in the presence of acrylonitrile was not affected by addition of methanol.

Discussion

The kinetic current is caused by the reduction of the ferric iron which is formed by interaction of ferrous iron at the electrode with hydrogen peroxide. The reaction between ferrous iron and hydrogen peroxide is complex. Adopting the Haber and Weiss[10] mechanism, we can write

$$\mathrm{Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + HO\cdot} \qquad \mathrm{I}$$

$$\mathrm{HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot} \qquad \mathrm{II}$$

$$\mathrm{HO_2\cdot + H_2O_2 \longrightarrow O_2 + H_2O + HO\cdot} \qquad \mathrm{III}$$

$$\mathrm{Fe^{++} + HO\cdot \longrightarrow Fe^{+++} + OH^-} \qquad \mathrm{IV}$$

The kinetic current is determined by the electrode reaction

$$\mathrm{Fe^{+++} + e^- \longrightarrow Fe^{++}} \qquad \mathrm{V}$$

and the kinetic reactions I and IV in which I is rate determining. Brdicka[5] derived an expression which gives the relation between the kinetic current and the factors which determine it. Applying this to our system we find

$$i_{\mathrm{k}}\ (\mu\mathrm{a.}) = \frac{nF\mu k_{\mathrm{I}}q10^3\, a[\mathrm{Fe^{+++}}][\mathrm{H_2O_2}]}{a + nFq\mu k_{\mathrm{I}}10^3[\mathrm{Fe^{+++}}]} \qquad (1)$$

$$\mu k_1 = \frac{i_{\mathrm{k}}a}{nFq\,10^3[\mathrm{Fe^{+++}}](a[\mathrm{H_2O_2}] - i_{\mathrm{k}})} \qquad (2)$$

where n is the number of electrons transferred in the stoichiometric kinetic reaction ($n = 2$) k_{I} is the rate constant of reaction I, F is the Faraday, μ is "the thickness of the reaction layer," 10^3 is a factor to make units agree, q is the average area exposed by the mercury drop, a is the Ilkovic constant and equal to $605nD^{1/2}{}_{\mathrm{H_2O_2}}m^{2/3}t^{1/6}10^3$, $[\mathrm{H_2O_2}]$ and $[\mathrm{Fe^{+++}}]$ denote concentrations of these species in moles per liter, and i_{k} is the maximum kinetic current in microamperes.

It can easily be shown that when the concentration of iron is small (3×10^{-4} *M* or less), the second term in the denominator of equation (1) is negligibly small compared to the first term. For example, with a value of 1.742 mg.$^{2/3}$ sec.$^{-1/2}$ for $m^{2/3}t^{1/6}$ and a diffusion coefficient of hydrogen peroxide of 2.2×10^{-5} cm.^{2}/sec at 30°, we obtain a value of a of 1.0×10^4. The value of $nF\mu k_{\mathrm{I}}q10^3[\mathrm{Fe^{+++}}]$ becomes 1.3×10^2 using a value of q of 1.8×10^{-2} ($q = 3/5 \times 0.0085\ m^{2/3}\ t^{2/3}$), an iron concentration of 3×10^{-4} *M* and an experimental value (from equation 2) of μk_{I} of 0.12. It is evident, therefore, that the second term in the denominator of equation (1) may be neglected with respect to a and the equation then simplifies to

$$i_{\mathrm{k}} = nF\mu k_{\mathrm{I}}q10^3[\mathrm{Fe^{+++}}][\mathrm{H_2O_2}] \qquad (3)$$

Assuming μ to be of the order 10^{-7} cm., as was done by Brdicka and co-workers,[3,5] k_{I} is calculated from equation (3) to be 1.2×10^6 liters per mole second at 30°.

The value of k_{I} has been determined by Baxendale, Evans and Park,[11] using solutions approximately 10^{-5} *M* in both hydrogen peroxide and ferrous iron. They found rate constants of 61 and 110 liters per mole sec. at 25 and 35°, respectively. Thus the velocity constant obtained polarographically is of the order of 10^4 times greater than that reported by Baxendale. A discrepancy of the same order of magnitude has been found by Brdicka,[12] using a different kinetic system. The deviation probably is due to the uncertainty in the value of μ. Calculation of rate constants from kinetic currents, therefore, does not yield reliable results.

By writing equation (3) in logarithmic form, differentiating with respect to temperature, substituting the known temperature coefficients of the capillary characteristics and concentrations,[13] and assuming μ to be independent of temperature, equation (4) is obtained which relates the temperature coefficient of the kinetic current to the rate constant of the kinetic reaction.

$$\frac{\mathrm{d}\ln k_{\mathrm{I}}}{\mathrm{d}t} = \frac{\mathrm{d}\ln i_{\mathrm{k}}}{\mathrm{d}t} - 0.25\% \qquad (4)$$

Using the experimental value of d ln i_{k}/dt of 4.6% per degree, the value of d ln k/dt becomes 0.043. From this the energy of activation may be calculated. This value is 7,750 cal./mole as compared to 10,100 cal./mole reported by Baxendale, *et al.*[11]

The discrepancy can probably be attributed to changes in the value of μ and in the steady state concentration of hydrogen peroxide with temperature. The latter variation would arise if the energies of activation of free radical reactions II and III were not zero or practically so. Undoubtedly the assumption that μ is independent of temperature is the source of greatest error.

According to equation (3), the kinetic current should be directly proportional to the concentration of iron when the hydrogen peroxide concentration is constant and to the concentration of hydrogen peroxide when the iron concentration is held constant. The first proportionality was found (Fig. 3). From Fig. 4 it is obvious that the kinetic current is not strictly proportional to the hydrogen peroxide concentration. This experimental fact can be accounted for qualitatively by considering the decomposition of hydrogen peroxide induced by its reaction with ferrous iron (Reactions II and III).

The active intermediate (HO·) can react with ferrous iron, hydrogen peroxide or other components, if present (*e.g.*, organic compounds). When hydrogen peroxide is in excess over ferrous iron, which is the condition at the electrode in the present work, reactions II and III occur, causing an induced decomposition of hydrogen peroxide.

From the kinetic current (about 1 μa.) obtained in a solution approximately 0.01 *M* in hydrogen peroxide and 1.2×10^{-4} *M* in ferric iron, the amount of hydrogen peroxide which reacts only by steps I and IV can be roughly calculated to be 5×10^{-12} mole/sec. Thus the amount of hydrogen peroxide disappearing by these reactions is negligibly small compared to the bulk concentration. If no other reaction would occur, the concentration of hydrogen peroxide at the electrode surface ($[\mathrm{H_2O_2}]_0$) would be

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[10] F. Haber and J. Weiss, *Naturwiss*, **20**, 948 (1932); *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

[11] J. H. Baxendale, *et al.*, *Trans. Faraday Soc.*, **42**, 155 (1946).

[12] R. Brdicka, private communication.

[13] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 74-75.

essentially the same as that in the body of the solution ($[H_2O_2]$). This assumption was made in equation (3).

Reactions II and III do not contribute to the kinetic current. However, if they do occur to a appreciable extent, the steady state concentration of hydrogen peroxide at the electrode surface may become significantly less than the hydrogen peroxide concentration in the bulk of the solution. It would be expected that at constant iron concentration, the relative decrease in steady state concentration would become larger as the bulk hydrogen peroxide concentration becomes greater. This is found as shown in Fig. 4.

Experimentally it can be shown that at the electrode part of the hydrogen peroxide is decomposed with formation of oxygen (reactions II and III). In Fig. 5, the kinetic current measured at -0.05 volt (a potential at which oxygen is reduced) is greater than that measured at $+0.20$ volt (a potential at which oxygen is not reduced).

The effects of certain organic compounds on the kinetic current substantiate the significance of the induced decomposition of hydrogen peroxide. It has been found[14] that in the absence of air, hydroxyl free radicals produced in the ferrous iron–hydrogen peroxide reaction cause the oxidation of ethanol to acetaldehyde by the chain mechanism

$$HO\cdot + CH_3CH_2OH \longrightarrow CH_3\dot{C}HOH + H_2O \quad \text{VI}$$

$$CH_3\dot{C}HOH + H_2O_2 \longrightarrow CH_3CHO + H_2O + HO\cdot \quad \text{VII}$$

A similar chain mechanism applies to methanol. Since reaction VII uses up hydrogen peroxide, these chain reactions, if sufficiently fast, could decrease considerably the steady state concentration of hydrogen peroxide at the electrode surface.

The decomposition of hydrogen peroxide caused by reactions VI and VII is considerable. Haber and Weiss[10] found that in 0.05 *M* sulfuric acid reaction IV is about 80 times as fast as reaction II. At the same acid concentration Merz and Waters[15] found reaction VI to be about 4 times as fast as reaction IV. It follows that in 0.05 *M* sulfuric acid hydroxyl radicals react about 300 times as fast with ethanol as with hydrogen peroxide. This value probably changes somewhat with increasing acid concentration, but even in 0.25 *M* sulfuric acid, reaction VI is undoubtedly much faster than reaction II. Hence in the presence of ethanol, the decomposition of hydrogen peroxide at the electrode surface is greater than in its absence. This results in a decreased kinetic current.

It should be noted that, although a considerable induced decomposition of hydrogen peroxide occurs in the presence of ethanol (or methanol), oxygen is not produced. This follows, *e.g.*, from an inspection of curves (b) and (d) of Fig 6 which show that the kinetic current increases with increasing negative potential in the absence of methanol but remains constant (or decreases slightly) in its presence.

Acetone and acetic acid were found by Kolthoff and Medalia[14] not to affect the stoichiometric reaction when ferrous iron was in excess, but evidence was given that organic free radicals are formed in their presence. Apparently under our experimental conditions (excess hydrogen peroxide) free radicals derived from acetone or acetic acid do react with hydrogen peroxide to a minor extent causing its decomposition, resulting in a small decrease in the kinetic current.

Organic compounds do not decrease the kinetic current as much in the presence as in the absence of oxygen. Kolthoff and Medalia[16] have shown that organic free radicals react with oxygen forming peroxide radicals which can react further with molecules of the organic compound, ferrous iron, hydrogen peroxide, or which may decompose spontaneously. Without considering all the reactions in detail it is apparent that the presence of oxygen limits the extent of reaction VII. Thus the decomposition of hydrogen peroxide would be decreased and the kinetic current in the presence of methanol (or ethanol) and oxygen would be greater than that found in the absence of oxygen.

The effect of acrylonitrile on the kinetic current is particularly striking. Acrylonitrile is known[11] to react with hydroxyl free radicals to produce an organic free radical, which reacts further with acrylonitrile to give polyacrylonitrile. If the reaction between AN and the hydroxyl free radical is sufficiently fast, the monomer could in effect capture all the hydroxyl free radicals produced in reaction I so that reactions II and IV could not occur. From the data of Merz and Waters[15] and Baxendale, *et al.*,[11] it can be shown that the hydroxyl free radical reacts about 400 times as fast with AN as with hydrogen peroxide and 5 times as fast as with ferrous iron. With sufficient AN it would, therefore, be possible to change the stoichiometry of the reaction from $2Fe^{++}$ per H_2O_2 to 1 Fe^{++} per H_2O_2. Under these conditions the *n* of equation (3) would be changed from 2 to 1 and the kinetic current would be decreased by one-half. This decrease is actually observed (Figs. 9 and 10).

In the presence of AN, no induced decomposition of hydrogen peroxide should occur. Indeed, it was found (Fig. 10) that the kinetic current is proportional to the hydrogen peroxide concentration. These observations combined with the visual formation of polyacrylonitrile in the electrolysis cell strongly substantiate the proposed interpretation. It is interesting to note from Fig. 10 that up to about 0.015 *M* hydrogen peroxide, very little catalytic decomposition of hydrogen peroxide occurs in the absence of organic compounds, since curve (b) is just one-half that of (a). At greater hydrogen peroxide concentration the catalytic decomposition becomes significant.

Methanol has no effect on the kinetic current when AN is present. From this it is inferred that the reaction of hydroxyl free radicals with AN is considerably faster than with methanol and that no induced decomposition of hydrogen peroxide occurs under the specified conditions.

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