KINETICS AND EQUILIBRIA IN THE SYSTEM FERROUS ION + FERRIC ION + HYDRO-**QUINONE + QUINONE**

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Received 20th November, 1950

The kinetics of the ferric ion + hydroquinone and ferrous ion + quinone systems have been examined. The dependence of the rates on ferric, ferrous and hydrogen ion concentrations indicate the following reaction mechanism.

 $\begin{array}{c} \mathrm{Fe}^{+++} + \mathrm{QH}^{-} & \overbrace{k_{2}}^{k_{1}} & \mathrm{Fe}^{++} + \mathrm{QH} \\ & & & & \\ \mathrm{QH} & \overbrace{k_{3}}^{k_{3}} & \mathrm{Q}^{-} + \mathrm{H}^{+} \\ \mathrm{Fe}^{+++} + \mathrm{Q}^{-} & \overbrace{k_{4}}^{k_{3}} & \mathrm{Fe}^{++} + \mathrm{Q}. \end{array}$

Values of k_1 , k_4 , k_2/k_3 and their dependence on temperature have been obtained. The equilibrium constants for the overall reaction have been obtained electrometrically and are in good agreement with those calculated from the kinetics.

The first and second acid dissociation constants of hydroquinone and the heats of dissociation bave been measured.

Although the equilibria in reversible redox systems have been studied extensively the reaction kinetics have received relatively little attention. In certain organic systems requiring two electrons for complete reduction of the oxidized form, e.g. quinone \rightarrow hydroquinones, the equilibrium studies have shown the existence of intermediate semiquinones which are the result of a single electron addition to the quinone. These semiquinones are free radicals and although their existence in all such systems cannot be proved from equilibrium measurements, Michaelis has suggested that all two electron reductions or oxidations involve the successive addition or removal of single electrons and thus go through the semiquinone stage. In many systems the semiquinone is so reactive that it is present in minute concentration and hence cannot be observed experimentally. Nevertheless as Michaelis points out such intermediates might be important Thus in certain inorganic reactions the kinetic and other kinetically. evidence indicates the transient existence of radical intermediates 1 and the work of James and Weissberger² on the aerobic oxidation of durohydroquinone has shown the kinetic importance of the durosemiquinone. In the latter case the existence of the semiquinone has been demonstrated by equilibrium studies ³ and it is of interest to examine other systems, e.g. benzohydroquinone + quinone where this has not been possible.

The present study concerns the system ferrous ion + ferric ion + benzohydroquinone + quinone. The kinetics of the ferric + hydroquinone and ferrous + quinone reactions have been previously examined by Porret.⁴ He found that the rates were proportional to [Fe+++]^{3/2}[QH₂][H+]⁻¹ and [Fe++][Q][H+]0.2 respectively, where [Q] and [QH2] are quinone and hydroquinone concentrations. As will be seen below these are at variance with our observations.

¹ Baxendale and Evans, Trans. Faraday Soc., 1946, 42, 195.

 ² James and Weissberger, J. Amer. Chem. Soc., 1939, 60, 98.
 ³ Michaelis, Schubert, Raber, Kuck and Granick, J. Amer. Chem. Soc., 1938, **60,** 1678.

⁴ Porret, Helv. chim. Acta, 1934, 17, 703.

Experimental

Materials .--- All reactions were done in perchloric acid and perchlorates were used throughout.

Perchloric acid was of A.R. quality. Sodium perchlorate was prepared from perchloric acid and caustic soda. Ferrous perchlorate was made either by double decomposition from barium perchlorate and ferrous sulphate (both A.R. materials) or by dissolving spectroscopic iron in perchloric acid under nitrogen. The latter method gave a lower ferric ion content than the former and is to be preterred. Ferric perchlorate was made by oxidizing the ferrous per-chlorate with excess of pure hydrogen peroxide and allowing to stand until the excess had decomposed. Benzoquinone was recrystallized from alcohol and twice sublimed until it gave the correct melting point. Hydroquinone was recrystallized twice from toluene and had a sharp and correct melting point. Both these compounds were stored in the dark. Caustic soda free of carbonate was prepared from sodium amalgam in conditions which excluded carbon dioxide. Methods.—(a) SPECTRA.—The reactions were followed photometrically and

this required a knowledge of the absorption spectra of the various reactants.





FIG. 2.—Reaction vessel.



It was found that at the concentrations used ferrous ion was not optically im-The spectra of the other reactants are given in Fig. 1. They were portant. measured on the Beckmann D.U. spectrophotometer in solutions made up to I = 0.650 by sodium perchlorate. This ionic strength was used throughout this work unless otherwise stated.

Spectra of mixtures of equal concentrations of hydroquinone and quinone were also obtained for the concentration range used in the kinetics. No new absorption was present from 2100-5000 Å and the optical densities were exactly the sum of those of the two components. We conclude from this that at these concentrations there is no appreciable amount of quinhydrone present. This is to be expected from the value of the equilibrium constant for quinhydrone formation given by Luther and Leubner.⁴⁶

4a Luther and Leubner, J. prakt. Chem., 1912, 85 (2), 314.

(b) FERRIC ION + HYDROQUINONE REACTION.—This was followed by measuring the change in optical density due to the quinone being formed. Preliminary experiments showed that the reaction was very fast and it was therefore carried out in a cylindrical reaction vessel about 10 cm. long with plane ends (Fig. 2), so that the optical density of the solution could be measured *in situ*. The screw stirrer ensured rapid mixing of the reactants and the jacket through which thermostat water was circulated kept the temperature constant to $\pm 0.1^{\circ}$ C. It was also possible to de-oxygenate the solutions with pure nitrogen but after it had been established that the rates were not affected by this, the procedure was omitted. Optical densities were measured by a photomultiplier. The light source was filtered by an Ilford Violet 601 filter transmitting from about 4000-4500 Å which is convenient for the quinone absorption maximum at 4200 Å. It was established that the light used has no measurable effect on the reaction by conducting experiments in which it was (i) passed through the solution continuously and (ii) only passed through during the time taken for measurement. Reactions were begun by adding a convenient amount of hydroquinone solution to the ferric perchlorate, perchloric acid and sodium perchlorate solutions in the reaction vessel, and readings of the optical density taken at convenient intervals. Optical densities were transformed into concentrations of quinone from a calibration curve.

(c) FERROUS ION + QUINONE REACTION.—This was followed by measuring the optical density of samples of the reaction mixture at 2800 Å (the maximum in the hydroquinone absorption curve). We found that the reaction was accelerated by daylight. The reactants were therefore mixed in blackened vessels immersed in a thermostat and samples were extracted at suitable intervals for measurement in the Beckmann spectrophotometer. Using the known stoichiometry of the reaction and the measured extinction coefficients of the reactants and products, the concentrations of quinone at various times were calculated from the observed optical densities.

(d) EQUILIBRIUM CONSTANTS.—Although the equilibrium constant of the reaction

$$_{2}Fe^{+++} + QH_{2} \xrightarrow{\longrightarrow} Q + _{2}Fe^{++} + _{2}H^{+}$$

can be calculated from the published data on the redox potentials of the ferrous + ferric and hydroquinone + quinone systems, the constant is likely to be dependent on ionic strength and for purposes of comparison with velocity constants it was desirable to obtain values at the ionic strength used in the present kinetic work. An attempt was made to do this photometrically, but the long time required for equilibrium to be set up, together with the decomposition of quinone during long periods in aqueous solution made this impossible. We therefore measured the E.M.F. of the cell

The solutions were made about 10^{-3} M in each of the electromotively active species and the bridge liquid connecting the two half cells contained sodium perchlorate and perchloric acid of the same concentration as that used in the half cells. Each half cell had two bright platinum wire electrodes and the variation in E.M.F. between various combinations of electrodes was never greater than 0.2 mV. These E.M.F.'s were measured over a range of acid concentrations at 20°, 25° and 30° C.

(e) ACID DISSOCIATION CONSTANTS OF HYDROQUINONE.—These were determined by potentiometric titration of hydroquinone with caustic soda. This was done in the presence of a hydrogen electrode connected by an agar-saturated potassium chloride bridge to a saturated calomel electrode. The apparatus used enabled the caustic soda and hydroquinone solutions to be de-oxygenated by a stream of purified hydrogen before titrating, and during titration the hydrogen was bubbled through the solution. The presence of a little colloidal palladium assisted in the removal of oxygen and ensured reduction of any quinone which might be present. Potentials were measured a few minutes after each addition of caustic soda to allow mixing of the solution by the hydrogen stream.

Results

(a) Ferric Ion + Hydroquinone Reaction.—Reaction rates were obtained with hydroquinone concentrations about 7×10^{-4} M and ferric ion concentrations $8 \cdot 20 \times 10^{-3}$ M. A typical run with ferric ion in large excess over hydroquinone is given in curve (a) of Fig. 3. Here the results are plotted to test for first-order reaction in hydroquinone. It can be seen that the reaction

deviates slightly from first order as it progresses. This is not due to the change in ferric ion concentration since we find that plotting the results as for a secondorder reaction does not remove the deviation. It was also established that the



FIG. 3.—Effect of ferrous ion on the rate of oxidation or bydroquinone with ferric ion.

Temp. 20·1° C. $[H^+] = 0.473$. $[Fe^{+++}] = 19\cdot7 \times 10^{-3}$. \odot $[Fe^{++}] = 0$. \Box $[Fe^{++}] = 3.94 \times 10^{-3}$. \triangle $[Fe^{++}] = 9.85 \times 10^{-3}$ M.

Temp. °C	[H +]	[Fe+++] 10 ³	[Fe ⁺⁺] 10 ³	k _{obs} min1 mole l1
ſ		19.7 {	0·0 3·94 9·85	44 [.] 9 18·2 8·51
20.1	0'473	7.88 {	0·0 1·97 3·94	46·8 14·8 7·96
	0•350	15.8 {	0·0 3·94 9·85	62·5 24·6 12·7
	0.200	7.88 {	0·0 3·94 7·88	100·0 38·5 24·0
25.0	^{0•} 473	15.8 {	0·0 3·94 9·85	87·1 32·2 15·9
15.3	0.423	19.7 {	0∙0 3∙94 9∙85	21·4 7·35 3·71

TABLE I.—FERRIC ION + HYDROQUINONE RATE CONSTANTS AT DIFFERENT FERROUS, FERRIC AND HYDROGEN ION CONCENTRATIONS AND TEMPERATURES

quinone produced in the reaction had no effect on the rate since experiments begun with quinone present initially followed exactly the same course as those with no quinone. However, we found that ferrous ion, the other reaction product, when present initially caused an appreciable decrease in the reaction rate. Examples of this effect are shown in curves (b) and (c) of Fig. 3. It is to be noted that the concentrations of ferrous ion required to produce this effect were not large enough to prevent the reaction going to completion, and therefore the retardation produced is not due to the reverse reaction between ferrous ions and quinone becoming appreciable.

We have studied the effect of a range of ferrous ion concentrations on the second-order constant k_{obs} which is given by

$- d[QH_2]/dt = k_{obs} [QH_2][Fe^{+++}].$

Because of the changing concentration of ferrous ion during the reaction the second-order plots invariably have some curvature so that values of k_{obs} were obtained from the slopes of curves similar to those in Fig. 3. It was also found that k_{obs} is decreased by increase in acid concentration. The results at various ferrous, ferric and hydrogen ion concentrations and at three temperatures are given in Table I. These are discussed below.

given in Table I. These are discussed below.
(b) Ferrous Ion + Quinone Reaction.—These experiments were carried out with quinone concentrations of the order of 10⁻⁴ M and ferrous ion in large



FIG. 4.—Reduction of quinone at various ferrous ion concentrations (temp. 35.7° C).

0	$[Fe^{++}] = 1.43 \times 10^{-2} M.$	Δ	$[Fe^{++}] =$	2.86 X	10-2 M.
	$[Fe^{++}] = 4.29 \times 10^{-2} M.$	+	$[Fe^{++}] =$	7.15 X	10-2 M.
V	$[Fe^{++}] = 10.0 \times 10^{-2} M.$			-	

excess from 0.01 to 0.1 M. Typical plots showing that the reaction is first order in quinone at various ferrous ion concentrations are given in Fig. 4. In Fig. 5 the first-order constant is shown to be proportional to ferrous ion concentration. Hence the reaction is also first order in ferrous ion concentration. A change of acid concentration from 0.35 to 0.15 N does not affect the reaction rate.

It would appear therefore that the rate is given by

$$- \mathrm{d}[\mathrm{Q}]/\mathrm{d}t = k_4[\mathrm{Fe}^{++}][\mathrm{Q}].$$

Values of k_4 at different temperatures are given in Table II. These lead to

$$k_4 = 4.2 \times 10^4 \exp(-7,900/RT).$$

(c) Equilibrium Constants.—Values of the equilibrium K_{obs} given by



FIG. 5.—Variation with ferrous ion concentration of the first-order rate constant for quinone reduction at 35.7° C.

TABLE II.—Ferrous Ion + Quinone Rate Constants at different Temperatures

Temp. °C	$k_4 \times 10^2$ min1 mole l1		
25·0	7 ^{.2}		
30·3	9 ^{.3}		
35·7	11 ^{.4}		

were obtained potentiometrically at several acid concentrations at $20 \cdot 1^{\circ}$ C. It can be seen from Fig. 6 that K_{obs} - $\frac{1}{2}$ is linear with [H+] as is expected from the overall equilibrium

$$2Fe^{+++} + QH_2 \xrightarrow{\Lambda} 2Fe^{++} + Q + 2H^+,$$

i.e. $K_{obs} = K/[H^+]^2.$

The results of measurements at $[H^+] = 0.211$ at three temperatures are given in Table III. From these the overall heat of reaction is calculated to be 22.4 kcal.

TABLE III.—Equilibrium Constant K_{obs} at different Temperatures

Temp. °C	K _{obs}		
20•1	400		
25•1	790		
29•8	I,400		

(d) Acid Dissociation Constants of Hydroquinone.—As was described above, hydroquinone was titrated with caustic soda at a hydrogen electrode which was connected by a salt bridge to a calomel electrode. As is usual in such a cell there are some uncertainties connected with the interpretation of the results.

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Thus the liquid junction potentials are indefinite and might well change with the electrolyte concentration which varies throughout the titration. Moreover this change in electrolyte concentration will affect the activities of the species concerned in the acid dissociation equilibrium. We have tried to minimize uncertainties in the liquid junction potentials by the following procedure. A solution (25 ml.) 0.05 M in hydroquinone and 10-3 N in perchloric acid (to prevent aerobic oxidation before the solutions are de-oxygenated) was titrated with 0.1295 N caustic soda and potentials taken throughout the titration. The titration was then repeated omitting the hydroquinone. The potentials given in the latter titration were used to obtain combined values for the potentials of the calomel and any liquid junctions. This was done by calculating hydrogen ion concentrations and hence the potentials of the hydrogen electrode at points along the titration from the amount of alkali added and values of K_{w} . Hydrogen ion concentrations for the titration of hydroquinone were then calculated using these effective calomel E.M.F.'s in conjunction with the potentials measured during the titration. The classical equilibrium constants for the dissociations

$$\begin{array}{c} \mathrm{QH}_2 \xrightarrow{K_1} & \mathrm{QH}^- + \mathrm{H}^+ \\ \mathrm{QH}^- \xrightarrow{K_2} & \mathrm{Q}^- + \mathrm{H}^+ \end{array}$$

were then calculated from these hydrogen ion concentrations. The published values of K_1 and K_2 , although not agreeing among themselves, show that K_1 and K_2 are sufficiently different for the equilibria not to overlap thus simplifying the calculation. A typical set of results is given in Table IV. Values of K_1



FIG. 6.—Variation of equilibrium constant K_{obs} with [H+] at temp. 20.1° C.

and K_2 determined for two concentrations of hydroquinone at three temperatures are summarized in Table V. In view of the uncertainties in the procedure and the variation in ionic strength over the titration the results are reasonably consistent. The heats of the two dissociations ΔH_1 , ΔH_2 are found to be 5.3 \pm 0.8 kcal. and 5.9 \pm 0.4 kcal. respectively. Hence to this accuracy

$$K_1 = 7.6 \times 10^{-7} \exp(-5,300/RT)$$

 $K_2 = 2.8 \times 10^{-8} \exp(-5,900/RT).$

These values of K_1 agree fairly well with those obtained by Abichandani and Jatkar⁵ by a similar method. Other literature values⁶ vary over a factor of 5 among themselves. Our values of K_2 are about twice those of Abichandani and Jatkar and differ much more from those of Sheppard, 60 and Ball and Chen. 6d

⁵ Abichandani and Jatkar, Quart. J. Indian Inst. Sci., 1938, **21**A, 417. ⁶ (a) Euler and Bolin, Z. physik. Chem., 1909, **66**, 71; (b) Cameron, J. Physic. Chem., 1938, **42**, 1217; (c) Sheppard, Trans. Amer. Electrochem. Soc., 1921, **39**, 429; (d) Ball and Chen, J. Biol. Chem., 1933, 102, 691.

and

Previous values of ΔH_1 6.2 kcal. and 6.0 kcal. have been obtained by Berthelot,⁷ and by Euler and Bolin,^{6a} and the former has also given 6.0 kcal. for ΔH_2 .

TABLE IV.—25 ML. 0.05 M Hydroquinone Titrated with 0.1295 N Alkali at 28.2° C

NaOH Added ml.	Added [NaOH] × 10 ²	[H+] × 10 ¹²	Total Hydroquinone × 10 ²	[QH-] × 10 ²	K
2.00	0.812	520.0	4·31	0.809	$\begin{array}{c} 1 \cdot 20 \\ 1 \cdot 18 \\ 1 \cdot 18 \\ 1 \cdot 18 \\ 1 \cdot 26 \\ 1 \cdot 45 \end{array} \\ K^{1} \\ K^{1} \\ K^{1} \\ K^{1} \\ K^{1} \\ K^{2} \\$
3.00	1.22	288.0	4·17	1.21	
4.00	1.60	178.0	4·04	1.59	
5.00	1.95	115.0	3·90	1.94	
6.00	2.29	78.9	3·79	2.27	
7.00	2.60	54.3	3·68	2.57	
8.00	2.90	37.2	3·58	2.85	
12.00	3·94	7.00	3.20	2·72	$ \begin{array}{c} 1 \cdot 23 \\ 1 \cdot 41 \\ 1 \cdot 55 \\ 1 \cdot 56 \\ 1 \cdot 63 \\ 1 \cdot 71 \end{array} \right) \mathcal{K}_{1013}$
14.00	4·38	3.72	3.05	2·21	
16.00	4·78	2.51	2.91	1·80	
18.00	5·15	1.78	2.78	1·48	
20.00	5·48	1.38	2.68	1·22	
22.00	5·80	1.12	2.55	1·01	

TABLE V.—Values of K_1 and K_2 at different Temperatures

T 8C	Initial [QH ₂] = $2 \cdot 50 \times 10^{-2}$ M		Initial [QH ₂] = 5.00×10^{-2} M		
Temp. *C	$K_1 \times 10^{10}$	$K_{2} \times 10^{12}$	$K_1 imes 10^{10}$	$K_2 imes 10^{12}$	
19.4	0.91	1.2	0.79	0.83	
28·2 34·8	1·1 1·4	1.6 1.8	1·20 1·3	1.0 2.1	

Discussion

Reaction Mechanism.—We saw above that the ferric ion + hydroquinone reaction is not a simple second-order reaction, but that its rate is reduced appreciably by the presence of ferrous ion at concentrations insufficient for this retardation to be attributed to the reverse reaction between ferrous ions and quinone. This suggests that the retardation arises from the reaction of ferrous ion with an intermediate. It is to be expected that semiquinones are intermediates in this type of reaction, and the following scheme involving semiquinone (QH) accounts for the observations :

$$\begin{array}{l} \operatorname{Fe}^{+++} + \operatorname{QH}_{2} \xrightarrow[k_{2}]{k_{1}} \\ \hline \\ & \overbrace{k_{2}}^{k_{2}} \end{array} \end{array} \operatorname{Fe}^{++} + \operatorname{QH} + \operatorname{H}^{+} \\ \operatorname{Fe}^{+++} + \operatorname{QH} \xrightarrow[k_{4}]{k_{3}} \operatorname{Q} + \operatorname{Fe}^{++} + \operatorname{H}^{+}. \end{array}$$

Thus consider the ferric ion + hydroquinone reaction under such conditions that the ferrous ion + quinone reaction is not effective, i.e. when the reaction goes to completion. Assuming steady concentrations of the semiquinone we obtain

$$-\frac{d[QH_2]}{dt} = \frac{k_1k_3[Fe^{+++}]^2[QH_2]}{k_2[Fe^{++}] + k_3[Fe^{+++}]}.$$

⁷ Berthelot, Ann. Chim. Phys., 1886, 7, 103; 1890, 21, 327.

The experimental results have been obtained in terms of the second-order constant k_{obs} , hence

$$k_{\text{obs}} = \frac{k_1 k_3 [\text{Fe}^{+++}]}{k_2 [\text{Fe}^{+++}] + k_3 [\text{Fe}^{++++}]}.$$

It can be seen that this accounts qualitatively for the effect of ferrous ion and Fig. 7, where examples of plots of r/k_{obs} against [Fe⁺⁺] are shown



FIG. 7.—Variation of second-order rate constant for hydroquinone oxidation with ferrous ion concentration. Temp. 20.1° C.

 $[H^+] = 0.473$ \bigcirc $[Fe^{+++}] = 7.88 \times 10^{-3}$. \Box $[Fe^{+++}] = 19.7 \times 10^{-3}$.



FIG. 8.—Variation of k_1 and k_3/k_2 with [H+] at 20.1° C.

at constant [Fe⁺⁺⁺], indicates that this expression will also fit the observations quantitatively. From plots similar to those in Fig. 7 we have obtained values of k_1 and k_3/k_2 for a number of acid concentrations at 20·1° C. These are given in Table VI. From Fig. 8 it can be seen that k_1 and k_3/k_2 vary inversely as hydrogen ion concentration. Values of

 k_1 and k_3/k_2 at different temperatures for $[H^+] = 0.473$ are also given in Table VI. These give activation energies of 25.6 and 4.7 kcal. respectively for k_1 and k_3/k_2 . Hence

$$k_1 = 1.9 \times 10^{20} \exp(-25,600/RT)$$

and

We saw above that the ferrous + quinone reaction was first order in both ferrous ion and quinone concentrations and was independent of acid concentration. On the above reaction scheme for conditions such that the reaction goes to completion the rate should be given by

 $k_{3}/k_{2} = 1.7 \times 10^{2} \exp(-4.700/RT)$ at unit [H+].

$$-\frac{d[Q]}{dt} = \frac{k_4 k_2 [Fe^{++}]^2 [Q]}{k_2 [Fe^{++}] + k_3 [Fe^{+++}]}$$

and should therefore show a retardation by ferric ion analogous to that observed by ferrous ion in the ferric ion + hydroquinone reaction. However, from the data given above, k_3/k_2 is found to be about 0.1 to 0.3. Since ferrous ion concentrations of the order 100 times those of quinone were used, and no ferric ion was present other than that produced in the reaction,

TABLE VI.—Values of k_1 and k_3/k_2 at different Acid Concentrations and Temperatures

Temp. °C	[H+]	[Fe ⁺⁺⁺] × 10 ³	k ₁ , mole l1 min1	$\frac{k_2}{k_1k_3[\text{Fe}^{+++}]}$	k ₃ /k ₂
20·1 { 25·0 15·3	0·473 { 0·350 0·200 0·473 0·473	19·7 7·88 15·8 7·88 15·8 19·7	44·9 46·8 62·5 100·0 89·3 21·4	9·76 27·0 6·36 4·02 5·34 20·2	0.110 0.119 0.159 0.313 0.137 0.106

it is clear that $k_2[\text{Fe}^{++}] \gg k_3[\text{Fe}^{+++}]$ and hence the above expression, reduces to the simple second-order equation which is observed experimentally. We have not confirmed the predicted effect of ferric ion by adding it initially, because the concentrations required to produce a measurable effect are so high that the ferric ion + hydroquinone reaction becomes appreciable and complicates the kinetics.

Comparison of Equilibria and Kinetics.—At equilibrium the above reaction scheme gives the required relationship at constant $[H^+]$:

$$K_{\rm obs} = \frac{k_1 k_3}{k_2 k_4} = \frac{[{\rm Fe}^{++}]^2[{\rm Q}]}{[{\rm Fe}^{+++}]^2[{\rm QH}_2]}.$$

We saw previously that K_{obs} varied as $1/[H^+]^2$ and this is paralleled by the dependence of k_1 and k_3/k_2 on $1/[H^+]$. At 25° C and unit [H⁺], K_{obs} is calculated to be 35.7 and is in excellent agreement with the kinetic value $\frac{k_1k_3}{k_2k_4}$ of 37.9. The temperature dependence of K_{obs} led to a heat of reaction 22.4 kcal, which agrees very well with 22.2 kcal, obtained kinetically from the temperature dependence of $\frac{k_1k_3}{k_2k_4}$.

Dependence of Rates on [H+].—We saw above that k_1 and k_3/k_3 varied inversely as [H+]. This can be accounted for by the participation of the

ionized forms of hydroquinone and semiquinone in the reactions rather than the undissociated species written above. Thus the scheme:

$$Fe^{+++} + QH^{-} \xleftarrow{k_{1'}}{\underset{k_{2}}{\longleftarrow}} QH + Fe^{++}$$
$$QH \xleftarrow{K_{3}}{\underset{k_{3'}}{\longleftarrow}} Q^{-} + H^{+}$$
$$Fe^{+++} + Q^{-} \xleftarrow{k_{3'}}{\underset{k_{3'}}{\longleftarrow}} Fe^{++} + Q$$

will lead to

and

as observed. However, another alternative is that the inverse $[H^+]$ dependence arises from the reaction of ferric ion in the form FeOH⁺⁺ which exists in equilibrium with Fe⁺⁺⁺ according to

 $\frac{k_3}{k_2} = \frac{K_3 k_3'}{k_2 [\mathrm{H}^+]}$

 $k_1 = \frac{K_1 k_1'}{[\mathrm{H}^+]}$

$$Fe^{+++} + H_2O \xrightarrow{K_F} FeOH^{++} + H^+.$$

At the acid concentrations used here this would lead to similar equations for k_1 and k_3/k_2 with K_1 and K_3 replaced by K_F . Certain combinations of the two alternatives also give the observed dependence on [H⁺]. From the present results it is impossible to decide unequivocably between these possibilities. However, by analogy with other reactions of hydroquinones it would appear that the electron transfer reactions involving QH⁻ and Q⁻ are more probable than the hydrogen transfers required by the participation of FeOH⁺⁺. Thus Weissberger *et al.*² have shown that when oxygen oxidizes hydroquinone the electron transfer reaction

occurs.

 $O_2 + Q^- \rightarrow Q^- + O_2^-$

Assuming this to be the case we calculate from the values of K_1 and k_1 at various temperatures that

$$k_{1'} = 2.5 \times 10^{26} \exp(-20,200/RT).$$

The very high frequency factor associated with k_1 is to be expected from the interaction of the oppositely charged species Fe⁺⁺⁺ and QH⁻ and is paralleled by a value of similar order obtained for the reaction⁸

 $\text{Fe}^{+++} + \text{HO}_2^- \rightarrow \text{Fe}^{++} + \text{HO}_2.$

On the other hand the frequency factor observed for the ferrous + quinone reaction is abnormally low. These and other factors concerning different hydroquinone + quinone systems will be discussed in a further communication.

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⁸ Barb, Baxendale, George and Hargrave, Trans. Faraday Soc., 1951, 47, 462.