tion (Table I) for its half wave potential–*p*H relationship is unlike the others and also in that a second small wave is found (Fig. 1) after the main wave. It is possible that this additional wave corresponds to reduction of the dimer formed as the result of the first one electron reduction. An unidentified dimer from the reduction of quinaldine on mercury has been reported,[11] and apparently a similar dimer was not found in the reduction of quinoline. This might account for the different behavior of 8-hydroxyquinaldine compared to the other substituted 8-quinolinols.

Since aluminum has been found not to form insoluble chelates with 2-substituted 8-quinolinols,[4,5] the effect of adding aluminum ion on the polarographic wave in alkaline solution was investigated as a very sensitive check on this fact. Precipitation of an aluminum chelate as well as a decrease in wave height was obtained with 3- and 4-methyl-8-quinolinols at a *p*H of 12. No significant decrease in wave height and no precipitation was observed with the 2-methyl and 2,3-dimethyl derivatives.

Acknowledgments.—This work was supported in part by a grant from the Research Corporation. The authors are also grateful to Joseph E. Seagram & Sons, Inc., Louisville, Kentucky, in whose laboratories most of this work was done, and also to Edward J. Kimmel of the Seagram research department for technical assistance with the polarograph.

LOUISVILLE 8, KENTUCKY RECEIVED DECEMBER 18, 1951

[11] V. V. Levchenko, *Zhur. Obshchei Khim.*, **18**, 1245 (1948).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

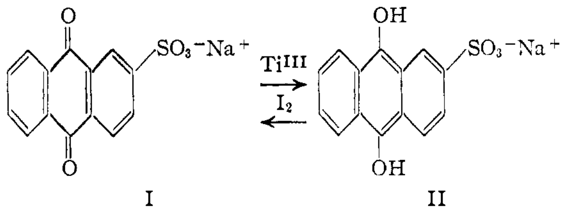
Oxidation–Reduction. III. The Kinetics of the Reduction of Sodium Anthraquinone β-Sulfonate by Titanous Ion and the Oxidation by Iodine

BY CARL E. JOHNSON, JR.,[1] AND S. WINSTEIN

RECEIVED AUGUST 2, 1951

The kinetics of the reduction of sodium anthraquinone β-sulfonate by titanous ion have been investigated spectroscopically. In general, the rate-law for the production of the hydroquinone was found to be of the form: $d(R)/dt = (Ti^{III})[k_1(T)^{1/2}(R)^{1/2} + k_2(T)(R) + k_3(T)^{3/2}(R)^{1/2}]$ where T and R represent the quinone and hydroquinone, respectively. A mechanism has been proposed involving three reaction paths: (1) the reduction of S, the semiquinone, by Ti^{III}; (2) the reduction of S·S, a semiquinone dimer, by Ti^{III}; and (3) the reduction of T·S, a molecular complex composed of one molecule of the quinone and one molecule of the semiquinone, by Ti^{III}, or such alternatives as the reaction between S and a complex ion containing one Ti^{III} ion and one T molecule. The rate of reduction of the quinone molecule itself by titanous ion is insignificant with respect to these three rate-determining reactions. The oxidation of sodium anthrahydroquinone β-sulfonate by iodine proved to be too rapid for accurate kinetic analysis. Under all of our experimental conditions it appears to be much faster than the reduction of the quinone by titanous ion.

The oxidation of hydroquinones by molecular oxygen has been extensively investigated, principally by Weissberger and co-workers[2] and by LuValle and Weissberger[3] who correlated their kinetic data on the basis of semiquinone theory. On the other hand, with the exception of the work of Dimroth[4] on the relation between over-all free energy change and the rate of reduction of a series of quinones, little attention appears to have been paid to the kinetics and mechanism of the reduction of quinones. For this reason, and because of the connection with the already reported[5] catalysis of the titanous chloride–iodine reaction by sodium anthraquinone β-sulfonate (I), we have studied separately the kinetics of reduction of sodium anthraquinone β-sulfonate (I) by titanous ion and the oxidation of the hydroquinone II by iodine. The first portion of this paper presents an analysis of the kinetics of the reduction which was followed spectroscopically. The last portion presents results obtained for the oxidation which proved to be too rapid to lend itself to kinetic analysis by similar methods.



I II

The Reduction by Titanous Ion.—Since the anthrahydroquinone II exhibits a sharp maximum in its light absorption at 382 mμ, while the anthraquinone I absorbs very much less and the titanous chloride and other reagents are transparent in this region, the course of the reduction could be followed spectrophotometrically at 382 mμ. Figure 1 shows optical density plotted *vs.* wave length for various combinations of sodium anthrahydroquinone β-sulfonate II and titanous chloride in acid solution. It is seen that titanous ion, even at concentrations higher than those employed in the rate determinations, and titanic ion have no specific effect on the absorption of the hydroquinone II, for an identical absorption is obtained for the hydroquinone II whether produced by reduction of I with excess titanous ion or with zinc dust. Absorption due to sodium anthraquinone β-sulfonate (I) at the beginning of typical reductions amounted to *ca.* 3–

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[1] Department of Chemistry, University of Illinois, Urbana, Illinois.

[2] (a) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937); (b) T. H. James, J. M. Snell and A. Weissberger, *ibid.*, **60**, 2084 (1938); (c) A. Weissberger and G. Kornfeld, *ibid.*, **61**, 361 (1939); (d) A. Weissberger, J. E. LuValle and D. S. Thomas, Jr., *ibid.*, **65**, 1934 (1943); (e) A. Weissberger and J. E. LuValle, *ibid.*, **69**, 1576 (1947).

[3] J. E. LuValle and A. Weissberger, *ibid.*, **69**. 1567 (1947).

[4] O. Dimroth, *Z. angew. Chem.*, **46** 571 (1933).

[5] (a) C. E. Johnson, Jr. and S. Winstein, THIS JOURNAL, **73**, 2601 (1951); (b) *ibid.*, **74**, 755 (1952).

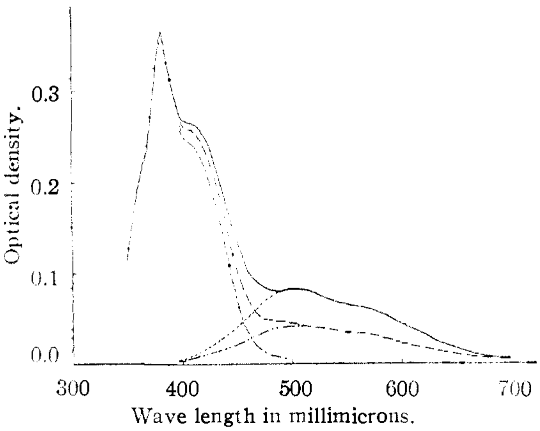

Fig. 1.—Optical density *vs.* wave length for sodium anthrahydroquinone β-sulfonate: ———, sodium anthrahydroquinone β-sulfonate 5.00 × 10^{-5} *M* plus $TiCl_3$ 0.0217 *M*; — — —, sodium anthrahydroquinone β-sulfonate 5.00 × 10^{-5} *M* plus $TiCl_3$ 0.0108 *M*; — - — -, sodium anthrahydroquinone β-sulfonate 5.00 × 10^{-5} *M* by reduction of the quinone with zinc dust; - - - - - -, $TiCl_3$ 0.0217 *M*; — - - — - -, $TiCl_3$ 0.0108 *M*. HCl was 0.325 *M* in all cases. Light path was 1.00 cm.

5% of the final absorption at 382 mμ of the hydroquinone II after reduction was complete.

If Beer's law is obeyed by both the quinone starting material I and the hydroquinone product II, then Δ*D*, the change in optical density upon reduction, should be proportional to the hydroquinone concentration. Table I summarizes the results of several experiments which show that this relationship is obeyed. In each case, sodium anthraquinone β-sulfonate (I) was reduced by titanous chloride and the reaction allowed to go to completion. Δ*D* was obtained by subtracting the initial optical density from the final optical density at 382 mμ.

TABLE I

RELATION BETWEEN INCREASE IN OPTICAL DENSITY UPON REDUCTION AND THE CONCENTRATION OF SODIUM ANTHRAHYDROQUINONE β-SULFONATE PRODUCED[a]

No.	Initial (T) 10^5 *M*	(Ti^{III}) 10^4 *M*	(H^+) *M*	(R) 10^5 *M*	(T) 10^5 *M*	Δ*D*[b]	10^{-4}Δ*D*/(R)
1	20.00	Excess[c]	0.608	20.00	0.00	1.387	6.94
2	5.00	Excess	.809	5.00	.00	0.345	6.90
3	2.50	Excess	.809	2.50	.00	.165	6.60
4	2.50	Excess	.809	2.50	.00	.173	6.92
5	2.50	Excess	.809	2.50	.00	.181	7.24
6	2.50	Excess	.809	2.50	.00	.178	7.12
7	2.50	Excess	.405	2.50	.00	.172	6.88
8	2.50	Excess	.201	2.50	.00	.174	6.96
9	2.50	Excess	.201	2.50	.00	.185	7.40
10	2.50	Excess	.101	2.50	.00	.171	6.84
11	2.50	Excess	.101	2.50	.00	.175	7.00
12[d]	2.50	Excess	.101	2.50	.00	.174	6.96
13[e]	40.00	2.58	.608	12.9	27.1	.895	6.94
14[e]	20.00	2.64	.304	13.2	6.8	.915	6.93
15[e]	20.00	2.64	.608	13.2	6.8	.910	6.89
16[e]	20.00	2.58	.101	12.9	7.1	.895	6.94
17[f]	20.00	2.42	.101	12.1	7.9	.840	6.94
18[e]	20.00	2.74	.201	13.7	6.3	.950	6.93

[a] Ionic strength of 1.00 ± 0.01 *M* maintained by addition of KCl in all experiments. [b] *D* measured at 382 mμ over a light path of 1.00 cm. Δ*D* is the change in optical density when the reduction is allowed to go to completion. [c] "Excess" means more than enough to reduce all the quinone present. [d] (KI) is 0.900 *M*. [e] (KI) is 0.164 *M*. [f] (KI) is 0.491 *M*.

In reactions 1–12, excess titanous chloride was used so that the hydroquinone II produced at infinite time was equal in concentration to the amount of quinone starting material. In reactions 13–18, excess sodium anthraquinone β-sulfonate (I) was used so that the concentration of the hydroquinone at infinite time was limited by the amount of reducing agent added. The proportionality between Δ*D* and the hydroquinone concentration, (R), is shown by the constant value for Δ*D*/(R) which is recorded in the last column of the table. The possibility that the absorption measured at 382 mμ is due in part to semiquinone or a similar intermediate species seems to be ruled out by the fact that Δ*D*/(R), as is shown in Table I, is not affected by the presence or absence of excess quinone. Semiquinone concentration, (S), would be related to quinone concentration, (T), and hydroquinone concentration, (R), by equation 1, (S) having a maximum value when (T) equals (R).

$$(S) = K_s^{1/2}(T)^{1/2}(R)^{1/2} \qquad (1)$$

In measuring the progress of the reduction $(R)_t$, the concentration of anthrahydroquinone II at any time, *t*, was obtained from the relationship in equation 2

$$(R)_t = (\Delta D_t/\Delta D_\infty)(T)_0 \qquad (2)$$

where $(T)_0$ represents the initial concentration of sodium anthraquinone β-sulfonate (I). Since titanous chloride was always present in excess, the amount of R produced was always limited by the initial concentration of T. ΔD_∞ was measured separately for each individual rate determination.

The Rate Law.—When a reduction reaction is initiated, the optical density remains relatively constant for a short time and then begins to increase. The rate of change reaches a maximum a little short of the half-way point in the reaction and then the optical density gradually approaches a maxi-

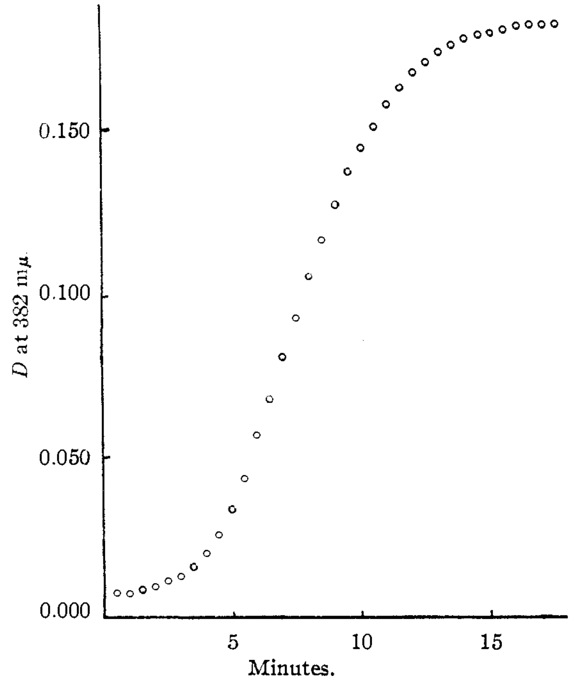

Fig. 2.—Optical density *vs.* time curve for Run 7, Table II.

mum value representing complete reduction to the hydroquinone. Optical density plotted against time has the general form shown in Fig. 2 which is a reproduction of the data for Run 7 of Table II which contains the details for all of the rate determinations carried out in this investigation. The speed of reaction was found to increase with increasing Ti^{III} concentration and with increasing initial anthraquinone concentration.

TABLE II

RATE CONSTANTS AND CORRESPONDING CONCENTRATIONS FOR THE REDUCTION OF SODIUM ANTHRAQUINONE β-SULFONATE BY TITANOUS CHLORIDE

Run No.	(H^+) M	(Ti^{III}) 10^4 M	(T) 10^5 M	k_1 l. mole^{-1} min.$^{-1}$	$10^{-5}k_2$ l.^{2} mole^{-2} min.$^{-1}$	$10^{-5}k_3$ l.^{2} mole^{-2} min.$^{-1}$
1	0.101	2.83	2.50	641	470	396
2	.101	2.77	2.50	494	572	528
3[a]	.101	2.70	2.50	522	545	409
4	.201	2.83	2.50	214.4	406	149
5	.201	2.77	2.50	205.3	292	251
6	.405	5.54	2.50	68.1	181	82.5
7	.809	20.10	2.50	20.7	85.6	11.2
8	.809	2.83	2.50	54.6	28.9	25.7
9	.809	10.19	5.00	13.2	20.1	14.1
10	.809	20.38	2.50	21.9	56.0	28.7
11	.809	10.19	2.50	10.8	64.5	31.8

[a] (KI) is 0.900 M.

The D *vs.* time curves were analyzed by drawing a smooth curve through the experimental points with the aid of a flexible spline and measuring $d(D)/dt$ at 5, 50 and 95% reaction with a tangent-meter. Values of $d(R)dt$ were obtained with the aid of equation 2, and then values of $d(R)/dt/(Ti^{III})$ were calculated for each of the points. The rate law shown in equation 3 was found to fit the data well.

$$d(R)/dt = (Ti^{III})[k_1(T)^{1/2}(R)^{1/2} + k_2(T)(R) + k_3(T)^{3/2}(R)^{1/2}] \quad (3)$$

Since (T) and (R) are known at any point on the D *vs.* time curve, values for $d(R)/dt$, (Ti^{III}), (T), and (R) may be substituted in equation 3 at 5, 50 and 95% reaction yielding three equations which may be solved for k_1, k_2 and k_3. The values of the constants are summarized in Table II. By calculating $d(R)/dt$ at other points with the aid of these constants and comparing with observed values of $d(R)/dt$, it is seen that the constants reproduce the data well. Table III shows this comparison for a typical case (Run 4, Table II). The calculated value of $d(R)dt$ is tabulated beside the measured value for a number of points on the curve, the average deviation from the calculated values being 4.1%. A similar treatment of the data from Run 7, Table II, results in an average deviation of 5.5%. The constants k_1, k_2 and k_3 were not tested for fit in every case. Presumably slightly better results could be obtained by a more laborious least squares treatment, but this was not carried out.

Reference to Run 3, Table II, indicates that substitution of potassium iodide for most of the potassium chloride does not change the rate constants significantly. With regard to the effect of hydrogen ion concentration on the rate constants, k_1, k_2 and k_3, all appear to be roughly proportional to $1/(H^+)$, but the relationship is not precise. This dependence on $1/(H^+)$ parallels the analogous dependence on $1/(H^+)$ of the rates of reaction between titanous ion and iodine.[5]

TABLE III

CALCULATED RATE OF PRODUCTION OF R COMPARED WITH THE EXPERIMENTAL VALUE AT 19 DIFFERENT STAGES OF REACTION. MEASUREMENTS TAKEN FROM RUN 4 OF TABLE II

No.	(Ti^{III}) 10^4 M	(T) 10^5 M	(R) 10^5 M	$10^6d(R)/dt$ calcd.	$10^6d(R)/dt$[a] exptl.
1	2.82	2.47	0.0270	0.50	0.51
2	2.82	2.45	.0541	.75	.79
3	2.81	2.42	.0811	.94	.99
4	2.81	2.39	.1082	1.11	1.15
5	2.80	2.34	.162	1.40	1.48
6	2.78	2.23	.270	1.86	2.01
7	2.73	1.96	.541	2.60	2.54
8	2.67	1.69	.811	2.95	2.89
9	2.62	1.42	1.082	3.02	2.99
10	2.56	1.15	1.35	2.85	2.86
11	2.55	1.082	1.42	2.78	2.77
12	2.49	0.811	1.69	2.36	2.32
13	2.43	.541	1.96	1.78	1.66
14	2.38	.270	2.23	1.05	0.96
15	2.36	.162	2.34	0.71	.68
16	2.35	.1082	2.39	.52	.51
17	2.35	.0811	2.42	.42	.41
18	2.34	.0541	2.45	.32	.30
19	2.34	.0270	2.47	.20	.18

[a] Units are moles liter^{-1} minutes^{-1}.

Mechanism.—The work of Michaelis[6] and others[7] has shown that the following equilibria are commonly encountered in quinone–hydroquinone mixtures.

$$T + R \overset{K_s}{\rightleftarrows} 2S$$

$$S + S \overset{K_d}{\rightleftarrows} S{\cdot}S$$

$$T + S \overset{K_{t{\cdot}s}}{\rightleftarrows} T{\cdot}S$$

Here K_s is the semiquinone formation constant, K_d is the semiquinone dimer formation constant, and $K_{t\,s}$ is the equilibrium constant for the formation of a T·S molecular complex from one quinone and one semiquinone molecule. Equations 1, 4 and 5 follow from these equilibria.

$$(S{\cdot}S) = k_d(S)^2 = K_dK_s(T)(R) \quad (4)$$

$$(T{\cdot}S) = k_{t{\cdot}s}(T)(S) = K_{t{\cdot}s}K_s^{1/2}(T)^{3/2}(R)^{1/2} \quad (5)$$

Referring now to the rate law, equation 3 and equations 1, 4 and 5 above, it will be noted that: $k_1(T)^{1/2}(R)^{1/2}$ is proportional to (S) and k_1 includes $K_s^{1/2}$; $k_2(T)(R)$ is proportional to (S·S) and k_2 includes K_dK_s; $k_3(T)^{3/2}(R)^{1/2}$ is proportional to (T·S) and k_3 includes $K_{t\,s}$ and $K_s^{1/2}$.

On the above basis the three contributing paths to the reduction reaction indicated by the rate law in equation 3 may be identified. The rate determining step corresponding to k_1 may be regarded

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(6) (a) L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); (b) *Ann. Rev. Biochem.*, **7**, 1 (1938); (c) *Cold Springs Harbor Symposium on Quantitative Biology*, **VII**, 33 (1939).

(7) (a) W. M. Clark, B. Cohen and H. D. Gibbs, U. S. Publ. Health Repts., Suppl. No. 54 (1926); (b) E. Friedheim and L. Michaelis, *J. Biol. Chem.*, **91**, 355 (1931).

as a reaction between titanous ion and semiquinone.

$$Ti^{III} + S \longrightarrow Ti^{IV} + R$$

The reaction corresponding to k_2 may be regarded as a reaction between titanous ion and semiquinone dimer

$$Ti^{III} + S\cdot S \longrightarrow Ti^{IV} + S + R$$

The reaction corresponding to k_3 involves titanous ion, a quinone molecule, and a semiquinone species. Kinetics do not distinguish between such alternatives as reaction between titanous ion and a quinone–semiquinone complex

$$Ti^{III} + T\cdot S \longrightarrow Ti^{IV} + T + R$$

or reaction of a titanous ion–quinone complex with semiquinone as follows

$$Ti^{III} + T \rightleftarrows Ti^{III}\cdot T$$
$$Ti^{III}\cdot T + S \longrightarrow Ti^{IV} + T + R$$

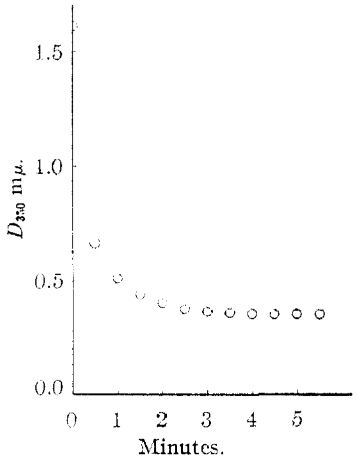

Fig. 3.—Optical density–time curve for the oxidation of sodium anthrahydroquinone β-sulfonate by iodine. Initial concentrations were:

$(I_3^-) = 5.265 \times 10^{-5}\ M$ $(I^-) = 0.490\ M$
$(R) = 9.71 \times 10^{-5}\ M$ $(H^+) = .101\ M$
$(T) = 0.285 \times 10^{-5}\ M$ $(KCl) = .223\ M$

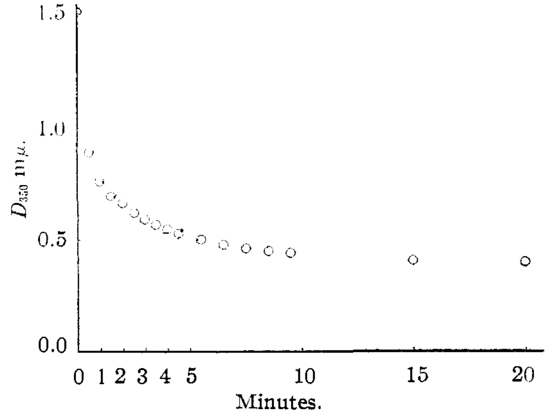

Fig. 4.—Optical density–time curve for the oxidation of sodium anthrahydroquinone β-sulfonate by iodine. Initial concentrations were:

$(I_3^-) = 5.265 \times 10^{-5}\ M$ $(I^-) = 0.490\ M$
$(R) = 5.00 \times 10^{-5}\ M$ $(H^+) = .101\ M$
$(T) = 0.00\ M$ $(KCl) = .223\ M$

A similar need for a rate term involving both T and S has been noted by LuValle and Weissberger[3] in the oxidation of certain hydroquinones.

From the present results and discussion it is clear that quinone I and titanous ion react too slowly to contribute to the reduction reaction. Semiquinone, although present at very low concentrations, is so much more reactive to titanous ion that reaction between these two species is very important. Further mechanistic discussion of the contributing reaction paths in the reduction reaction will be deferred for later reports of further work in this general area.

The Oxidation

In the study of the oxidation of the anthrahydroquinone II by triiodide ion solutions, it was convenient to follow the disappearance of iodine rather than hydroquinone since triiodide solutions are rather strongly absorbing. The decrease in optical density of the reaction mixture at 350 mμ was followed. Optical densities of 0.217 and 0.226 at 352 mμ have been reported[8] for 1 cm. of a solution of iodine in water (2.13 micrograms per ml.) containing 5 and 10%, respectively, of potassium iodide. The same study showed Beer's law to be obeyed at this wave length. These figures yield molecular extinction coefficients for iodine of 2.58×10^4 in 0.301 *M* potassium iodide and 2.69×10^4 in 0.602 *M* potassium iodide. A linear interpolation with respect to iodide concentration between these values results in an extinction coefficient of 2.65×10^4 in 0.500 *M* potassium iodide. A check experiment which we carried out at 350 mμ gave an extinction coefficient of 2.66×10^4 for a solution 5.76×10^{-5} *M* in iodine, 0.500 *M* in potassium iodide and 0.500 *M* in potassium chloride indicating that a change to an ionic strength of 1.00 *M* does not materially affect these coefficients. In addition, both the quinone and hydroquinone are only weakly absorbing at 350 mμ. One cm. of a 5.00×10^{-5} *M* solution of sodium anthraquinone β-sulfonate (I) has an optical density of 0.157 while the same concentration of the hydroquinone II has an optical density of 0.112. It is apparent, then, that during a run, as hydroquinone is oxidized to quinone, there will be only a small decrease in density due to the oxidation of the hydroquinone. By far the major portion of any decrease in optical density at this wave length will be due to disappearance of iodine and it has therefore been assumed that the decrease in D is proportional to the decrease in iodine concentration in the reaction mixture.

Optical Density–Time Curves.—Figure 3 shows the optical density–time curve for a reaction of iodine with sodium anthrahydroquinone β-sulfonate (II), the hydroquinone being present in excess. Figure 4 is the optical density–time curve for a similar reaction, the reactants being present in approximately equivalent concentrations. Initial concentrations of all reactants are listed under each figure. The initial optical density in each case has been calculated by adding the measured density due to the initial concentration of the hydroquinone to the calculated density due to the initial concentration of iodine.

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(8) J. J. Custer and S. Natelson, *Anal. Chem.*, **21**, 1005 (1949).

Figure 3 shows that the reduction of iodine was more than three-fourths complete by the time the first density reading was taken one-half minute after mixing. In Fig. 4 it may be seen that the reaction was more than half complete after one-half minute under conditions such that the reactants were present in approximately equivalent concentrations. Since there are not enough data in either of these figures to justify a kinetic analysis, their value lies in emphasizing the rapid rate of the reaction. If the rate law of equation 7 is assumed to

$$-\mathrm{d}(\mathrm{I_3^-})/\mathrm{d}t = k_{\mathrm{ox}}(\mathrm{I_3^-})(\mathrm{R}) \qquad (7)$$

apply to this reaction a rough comparison of the rate of oxidation of sodium anthrahydroquinone β-sulfonate (II) by iodine with the rate of reduction of sodium anthraquinone β-sulfonate (I) by titanous ion may be made. The slope of the straight line between the first two measured points of Fig. 4 is -0.300 density unit per minute. If the molecular extinction coefficient for iodine is 2.65×10^4, the slope is equal to -1.13×10^{-5} mole per liter per minute. This is approximately the rate of disappearance of iodine half-way between the two measured points at which time the reaction is apparently 10.5/12.8 complete, and the concentrations of total iodine and the hydroquinone are 0.955×10^{-5} and 5.405×10^{-5} M, respectively. These figures substituted in equation 7 yield a value for k_{ox} of 2.19×10^4 l. mole^{-1} min.$^{-1}$. The stoichiometry of this reaction requires that $-\mathrm{d}(\mathrm{I_3^-})/\mathrm{d}t = -\mathrm{d}(\mathrm{R})/\mathrm{d}t$. For purposes of comparison with the reduction reaction, $-\mathrm{d}(\mathrm{R})/\mathrm{d}t$ would then be equal to 8.14×10^{-5} mole per liter per minute when the concentrations of total iodine and the hydroquinone are 2.62×10^{-4} and 1.42×10^{-5} M, respectively.

Reference to line 9 of Table III, which shows the data for a reduction of sodium anthraquinone β-sulfonate by titanous ion, indicates that at titanous ion and quinone concentrations of 2.62×10^{-4} M and 1.42×10^{-5} M, respectively, the rate of disappearance of the quinone is 3.02×10^{-6} mole per liter per minute, or approximately $^1/_{27}$th of the rate of oxidation of the hydroquinone by iodine under comparable conditions.

Line 9 was chosen because the rate of reaction at that particular ratio of (R) to (T) was at its maximum value. At other ratios of (R) to (T) this rate becomes smaller, being indistinguishable from zero when pure T is present. Thus the factor twenty-seven is a minimum value and may become much larger for other ratios of (R) to (T). It is possible that the factor twenty-seven may be reduced somewhat by an increase in acid concentration. If the oxidation by iodine were acid-independent, an increase in acid concentration would result in a decrease in the rate of the reduction which has been shown to be roughly proportional to $1/(\mathrm{H^+})$. The data of Table III were obtained at an acid concentration of 0.201 M, and thus an increase to 0.640 M acid, for example, might reduce the factor twenty-seven to something nearer nine. Even under these conditions, the rate of oxidation of the hydroquinone by iodine still appears to be substantially more rapid than the rate of reduction of the quinone by titanous ion.

Experimental

The reagents used and the analytical procedures pertaining to these reagents have been described previously.[5] The titanous chloride was material obtained from the La Motte Co. as a 20% solution in hydrochloric acid.

For the study of the reduction of sodium anthraquinone β-sulfonate (I), the reaction vessel was a glass stoppered Pyrex absorption cell of 1-cm. light path and about 5-ml. capacity. One edge was creased inward near the top to form a small interior shelf upon which a drop or less of titanous chloride solution measured from a micropipet could be placed prior to the initiation of reaction. The other components of the reaction mixture with a total volume of 3 ml. were placed in the main body of the cell which was then flooded with nitrogen and stoppered. Lubriseal stopcock grease was used to obtain an airtight seal. The reaction vessel was then placed in the carriage of a Beckman spectrophotometer which was equipped with a thermostat arrangement, which has been described by McCullough and Barsh.[9] A temperature of 25.0 ± 0.2° was maintained in all experiments. The reaction cell was allowed to remain in the carriage until thermal equilibrium was reached, when it was quickly removed, shaken for 10 seconds and then replaced. Readings of optical density were taken every 30 seconds or at longer intervals for some of the slower runs. Ionic strength was maintained at a value of 1.00 ± 0.01 M in all reactions by the addition of potassium chloride.

For the study of the oxidation of the anthrahydroquinone II, 3.00 ml. of an aqueous solution, containing sodium anthraquinone β-sulfonate, potassium chloride, potassium iodide and hydrochloric acid, was placed in the reaction cell with *ca.* 0.5 ml. of a 1% zinc amalgam. For these experiments the reaction cell was fitted with a stopper consisting of a ground glass joint to which was connected a micro stopcock by means of which the cell could be opened or closed without removing the stopper. The cell was flushed with nitrogen, the delivery tube being inserted through the stopcock. The tube was withdrawn, the stopcock closed and the cell was shaken vigorously for a minute or two in order to ensure complete reduction of the quinone to the hydroquinone. Complete reduction under these conditions was confirmed in several instances by measuring the optical density of the mixture at 382 mμ. After the quinone had been reduced the amalgam was removed by inverting the cell and draining the amalgam out through the stopcock, care being taken not to allow air to enter the cell. The cell was then righted and the upper portions shaken free of adhering solutions. A fraction of a drop of triiodide solution was then placed on the wall of the cell in this area by means of a calibrated micropipet with a long slender outlet which could be inserted through the stopcock for this purpose. The stopcock was then closed, the cell was placed in the carriage of the spectrophotometer, and optical density was measured at intervals.

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[9] J. D. McCullough and M. Barsh, This Journal, **71**, 3096 (1949).