

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

Oxidation-Reduction. I. The Kinetics of the Reduction of Iodine by Titanous IonBY CARL E. JOHNSON, JR.,¹ AND S. WINSTEIN

We have chosen to use the titanous chloride-iodine reaction in an investigation of the mechanism of catalysis of oxidation-reduction reactions by quinones, phenazines and similar materials. This paper presents a study of the uncatalyzed reaction. The rate law $-d(I_3^-)/dt = k_1''(Ti^{11})(I_3^-)/(H^+)(I^-) + k_2''(Ti^{11})(I_3^-)/(H^+) + k'(Ti^{11})(H^+)$ has been developed, the major part of the reaction being represented by the first and second terms on the right. These terms indicate rate-determining reactions between $TiOH^{+2}$ and both I_2 and I_3^- .

Although much has been done toward elucidating the mechanisms of individual oxidation-reduction reactions, the necessary electron and atom transfers and the factors affecting the rates of reaction are still not well understood. In this general field we have been interested in the problem of catalysis of oxidation-reduction reactions by quinones and similar materials, qualitative reports of which have appeared a number of times.

For example, Bela Gaspar² has reported that the reductive cleavage by colloidal silver of azo-dyes in hydrochloric acid solution is effectively catalyzed by as little as one part in 100,000 of 2,3-diaminophenazine, 2-hydroxy-3-aminophenazine, quinoxaline, 2,3-diphenylquinoxaline and many other substances including some with the anthraquinone and methylene blue type of structure. Similarly,³ the reductive cleavage of methyl orange by titanous chloride in hydrochloric acid solution is catalyzed by 2-hydroxy-3-aminophenazine. Further, P. A. Shaffer⁴ has reported the reduction of iodine by titanous chloride in hydrochloric acid solution to be catalyzed by indigo sulfonates, pyocyanine, phenazines, rosindulin, flavins, indophenols and the anthraquinone and naphthoquinone sulfonates.

Much of the previous thinking with regard to this kind of catalysis has centered around the fact that almost all of these compounds have been shown by Michaelis,⁵ Preisler⁶ and others⁷ to be capable of reversible two-step oxidation-reduction by way of semiquinones. Catalysis is supposedly due to the incursion of reaction steps, faster than the uncatalyzed one, involving various of the catalyst species and the reducing or oxidizing agent. Proponents of the "principle of compulsory univalent oxidation," which owes its name to Michaelis⁸ and was first suggested by Haber and Weiss,⁹

would make these steps necessarily one-electron changes. P. A. Shaffer, on the other hand, with his "principle of equivalence change"^{4,10} supposes that the role of the catalyst in such reactions is to provide a system which, by virtue of its three oxidation states, can react rapidly with both two-electron and one-electron reagents. For the iodine-titanous ion case, iodine and titanous ion were presumed to be two-electron and one-electron reagents, respectively.

Because the titanous chloride-iodine reaction has a convenient rate, and is catalyzed by a wide variety of substances, many of which have themselves been investigated extensively, and because the reaction is easily subjected to kinetic study by the methods developed by Yost and Zabaro,¹¹ we chose it for use in the study of the role of quinones and similar substances in the catalysis of oxidation-reduction reactions.

Since we were interested in making use of this reaction over a more extensive range of reagent concentrations than was investigated by Yost and Zabaro,¹¹ we found it necessary to repeat and extend some of their work. This paper will present this kinetic study of the titanous chloride-iodine reaction. A survey of a number of compounds for catalytic activity toward this reaction is reported in the following paper, and subsequent papers will deal in detail with specific compounds found to be effective catalysts.

Experimental

Materials.—The water used throughout this investigation was distilled water, redistilled from potassium permanganate in an all Pyrex apparatus. The distillate was washed with dry nitrogen for several hours and stored under nitrogen. Constant boiling hydrochloric acid was prepared by distillation of C.P. hydrochloric acid, properly diluted, through an all-glass apparatus containing a Vigreux column. Stock solutions of Baker reagent grade potassium iodide and potassium chloride were prepared by dissolving weighed amounts of the dry salts in redistilled, oxygen-free water and stored under nitrogen. Triiodide stock solutions were made up by dissolving either Baker and Adamson or Meford resublimed iodine in redistilled water containing a weighed amount of dry potassium iodide.

Titanous chloride solutions A, B and C were prepared from titanous chloride obtained from three different sources. Titanous chloride A was obtained from Eimer and Amend 20% solution in hydrochloric acid after four recrystallizations by the method of Kolthoff and Furman.¹² The purified crystals, still wet, were dissolved in dilute hydrochloric acid to give a ca. 0.1 M stock solution which was stored under nitrogen. Titanous chloride B was made up by diluting La Motte 20% titanous chloride solution to yield a dilute hydrochloric acid solution approximately 0.1 M in titanous

(1) Department of Chemistry, University of Illinois, Urbana, Illinois.

(2) Bela Gaspar, U. S. Patent 2,270,118 (1932).

(3) Private communication from Drs. Gaspar and Dreyfus of Gasparcolor, Inc., Los Angeles, California.

(4) P. A. Shaffer, *Cold Springs Harbor Symposium on Quantitative Biology*, **VII**, 50 (1939).

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(6) P. W. Preisler and L. H. Hempelmann, *THIS JOURNAL*, **59**, 141 (1937).

(7) (a) B. Elema, *Rec. trav. chim.*, **52**, 569 (1933); (b) N. H. Furman and K. G. Stone, *THIS JOURNAL*, **70**, 3055 (1949).

(8) L. Michaelis, *Cold Springs Harbor Symposium on Quantitative Biology*, **VII**, 33 (1939).

(9) (a) Haber and Weiss, *Naturwissenschaften*, **20**, 948 (1932); (b) *Proc. Roy. Soc. (London)*, **A143**, 332 (1934); (c) *Weiss, Nature*, **133**, 648 (1934); (d) *Naturwissenschaften*, **23**, 64 (1935); (e) *J. Chem. Soc.*, 309 (1944).

(10) (a) P. A. Shaffer, *THIS JOURNAL*, **55**, 2169 (1933); (b) *J. Phys. Chem.*, **40**, 1021 (1936).

(11) D. M. Yost and S. Zabaro, *THIS JOURNAL*, **48**, 1181 (1926).

(12) I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, N. Y., 1926, p. 355.

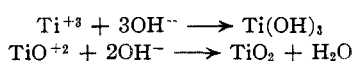
chloride. Titanous chloride C was prepared electrolytically from purified titanous chloride. One pound of MacKay titanous chloride was refluxed for 36 hours with *ca.* 10 g. of metallic sodium. During this treatment the sodium became encrusted with a black scale and the liquid changed from bright orange to yellow-green in color. The titanous chloride was then distilled at atmospheric pressure through a 4-foot vacuum jacketed column. Fractions at 56° and 133.0–134.5° were discarded. Clear colorless titanous chloride was collected in *ca.* 60% yield at 134.5–135.0° (reported¹³ 136°). This fraction was redistilled with no change in boiling range, small head and tail fractions being discarded. This purified product (0.5 mole) was dissolved in 150 cc. of constant boiling hydrochloric acid and electrolytically reduced in an all-glass apparatus, the carbon rod anode and the platinum screen cathode compartments being connected by means of a hydrochloric acid bridge.

Iron was an obvious impurity in both the A and B titanous chloride. Both solutions contained an estimated 10^{-5} to 10^{-6} *M* concentration of ferrous iron, the unpurified Bimer and Amend solution being heavily contaminated. Titanous chloride C contained no detectable amount of iron.

Analytical Procedures.—Triiodide stock solutions were standardized by the usual methods against thiosulfate, using reagent grade potassium iodate and potassium dichromate as primary standards.

The titanous chloride solutions were, at first, standardized for Ti^{III} by titration under nitrogen with a ferric ammonium sulfate solution which had been standardized against thiosulfate. For the greater part of the investigation, it was found more convenient to standardize the Ti^{III} against the already standardized triiodide solution. This was made possible by the use of 2-hydroxy-3-aminophenazine or 2,3-diaminophenazine as a catalyst. Less than two equivalents of one of these compounds per 1000 equivalents of titanous chloride was found sufficient to cause complete reaction between 10 cc. of 0.1 *M* titanous chloride and 12 to 15 cc. of standard triiodide solution of about the same concentration in less than five minutes, the excess triiodide then being titrated back with standard thiosulfate.

Total titanium in the titanous chloride solutions was determined by first converting all the titanium to Ti^{III} by shaking with 1% zinc amalgam and then determining the Ti^{III} by one of the methods already described. The triiodide catalytic method was regarded as the most convenient because it greatly reduced the possibility of oxygen errors during titration with the ferric solution. Hydrogen ion concentration in the titanous chloride solutions was determined by precipitation of the titanium with excess standard sodium hydroxide, filtration, washing and back-titration of the filtrate with standard hydrochloric acid. Correction was made for the reactions



Iron impurity in the titanous chloride solutions was estimated roughly by oxidizing the Ti^{III} in a 5-cc. aliquot with a drop or two of 6 *M* nitric acid, boiling to remove oxides of nitrogen, and adding potassium thiocyanate. The faintly pink color obtained was compared with the color given by solutions of known ferric chloride content.

Kinetic Measurements.—The reaction vessel was a one-liter Pyrex flask, the bottom creased inward so as to form two compartments each of about 150-cc. capacity. The stopper contained a delivery tube for introducing a slow stream of nitrogen and a gas outlet which also served as an opening for withdrawing samples.

Measured volumes of the stock solutions were placed in the two compartments of the reaction flask, the iodine and titanous chloride occupying different compartments. Enough potassium chloride was added to maintain the ionic strength at 1.025 ± 0.007 *M* and the flask was swept free of air by a continuous stream of dry nitrogen. The reaction flask and contents were allowed to stand in the thermostat at $25.00 \pm 0.02^\circ$ until thermal equilibrium was reached. Then the reaction was started by tilting the flask and quickly pouring the solution back and forth from one compartment to the other. It was then replaced in a tilted position.

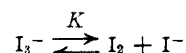
The initial volume of the reaction mixture was always 200 ml., 26-cc. aliquots being removed and analyzed for total iodine content at intervals during the reaction. The total

number of analyses was thus limited to 7 per run. Time was counted from five seconds after initiation of the mixing procedure to the half-way point in the delivery of the aliquot to the quenching solution. The total reaction time for individual runs varied between 30 minutes and several hours.

The reaction progress was followed by determination of total iodine in the reacting mixture by the method of Yost and Zabaro. The analytical method was as follows: 25 cc. of the reacting mixture was pipetted into 65 cc. of a solution containing 1 g. of potassium iodide, 6.5 cc. of 6 *M* hydrochloric acid, and 1 cc. of a 1% soluble starch solution. A small excess of 0.025 *N* thiosulfate solution was run into the mixture from a buret and the excess titrated back with 0.02 *N* triiodide solution. The total time required for this procedure was less than one minute.

The Rate Law

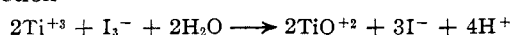
Under the conditions employed in this work, the equilibrium



is displaced far enough to the left so that the concentration of triiodide ion is nearly equal to total iodine. Washburn and Strachan¹⁴ report a value for *K* of 0.0013 in 0.15 *M* hydroiodic acid. Brønsted and Pedersen¹⁵ report a value of 0.0061 in 1.65 *M* potassium chloride solution and a linear interpolation yields 0.0041 for the ionic strength employed in this work. Thus even at the lowest iodide ion concentration encountered, 0.098 *M*, when total iodine is 0.00250 *M* the amount of iodine present as triiodide accounts for 96% of the total. The triiodide concentration is thus approximated as equal to the total iodine concentration in the present work.

It is also assumed that the major part of the Ti^{III} and Ti^{IV} is present as Ti^{+3} and TiO^{+2} , respectively, and that these species are not extensively hydrolyzed in hydrochloric acid solution, 0.1 *M* or higher.

Due to the fact that hydrogen and iodide ion concentrations were relatively large in our experiments, minimum average values being 0.101 *M* and 0.098 *M*, these quantities were regarded as constant in any single run. The maximum deviation from the mean values which we used due to the reaction



in any one run was ± 5.0 and $\pm 4.0\%$, respectively, and much less in most cases.

A summary of the various rate runs carried out in this study is presented in Table I. Concentrations of reagents are initial values unless otherwise designated and the ionic strength was maintained at 1.025 ± 0.007 *M* with potassium chloride unless otherwise noted.

The rate data were analyzed graphically starting with concentration-time plots, a typical plot being illustrated in Fig. 1 for Run 9, Table I. With the aid of a flexible spline the best smooth curve was drawn through the six to eight points available including the initial calculated point. Except in one or two cases in which a small amount of mixing may have occurred prematurely, the initial calculated iodine concentration fell nicely on the smooth curve drawn through the other

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(15) J. N. Brønsted and K. Pedersen, *Z. physik. Chem.*, **109**, 307 (1922).

(13) G. P. Baxter and G. J. Fertig, *THIS JOURNAL*, **45**, 1228 (1923).

TABLE I
 SUMMARY OF KINETIC RATE RUNS WITH CALCULATED AND OBSERVED VALUES OF k AND κ

Run no.	$10^4 (I_3^-)$	$10^4 (Ti^{III})^a$	Av. (I^-)	Av. (H^+)	$10^4 (Ti^{IV})$	k , liter mole $^{-1}$ min. $^{-1}$		$10^4 \kappa$, min. $^{-1}$	
						Obsd.	Calcd. from Eq. 4	Obsd.	Calcd. from Eq. 5
1 ^b	242.0	1004	0.098	0.101	152	5.78 ± 0.056	6.14	131 ± 7.0	91.6
2	251.5	1066	.098	.101	90	$6.63 \pm .091$	6.14	109 ± 11.5	91.6
3 ^c	236.0	967	.098	.103	49	$6.27 \pm .080$	6.07	105 ± 10.1	89.9
4	256.5	1084	.098	.178	72	$3.24 \pm .048$	3.49	76 ± 6.0	53.3
5	254.5	1084	.098	.178	72	$3.43 \pm .107$	3.49	42 ± 13.6	53.3
6	251.5	1072	.098	.329	71	$1.69 \pm .015$	1.89	25 ± 1.9	30.2
7	251.5	2134	.098	.349	152	$1.62 \pm .008$	1.77	26 ± 1.0	28.7
8	256.5	1084	.098	.633	72	$0.95 \pm .011$	0.98	6 ± 1.4	17.1
9	251.5	1066	.179	.101	90	$3.80 \pm .041$	3.64	59 ± 5.2	91.6
10	251.5	1072	.179	.177	71	$2.28 \pm .049$	2.08	60 ± 6.2	53.6
11	251.5	1072	.179	.177	71	$2.06 \pm .079$	2.08	54 ± 9.9	53.6
12	251.5	2144	.179	.196	142	$1.92 \pm .031$	1.88	67 ± 3.9	48.6
13 ^d	251.5	955	.179	.200	47	$1.93 \pm .061$	1.84	64 ± 7.7	47.7
14	251.5	1072	.179	.329	71	$0.98 \pm .021$	1.13	31 ± 2.7	30.2
15	251.5	1058	.179	.329	85	$1.33 \pm .017$	1.13	39 ± 2.1	30.2
16	251.5	2144	.179	.349	142	$1.04 \pm .014$	1.05	43 ± 1.8	28.7
17	254.5	1040	.342	.101	103	$2.24 \pm .022$	2.21	54 ± 2.8	91.6
18	256.5	1084	.342	.173	72	$1.37 \pm .025$	1.29	46 ± 3.2	54.7
19	251.5	533	.342	.319	58	$0.59 \pm .005$	0.70	38 ± 0.7	31.1
20	251.5	1067	.342	.329	76	$0.71 \pm .009$	0.68	15 ± 1.1	30.2
21	251.5	1063	.424	.329	93	$0.57 \pm .005$	0.58	35 ± 0.6	30.2
22	251.5	1062	.506	.101	94	$1.52 \pm .022$	1.70	81 ± 2.8	91.6
23	256.5	1084	.506	.177	72	$1.05 \pm .010$	0.97	35 ± 1.3	53.6
24	251.0	1062	.506	.329	94	$0.45 \pm .006$	0.52	19 ± 0.8	30.2
25	244.0	1506	.179	.329	1566	$1.15 \pm .007$	1.13	26 ± 0.8	30.2

^a Titanous chloride B used unless otherwise noted. ^b Potassium bromide concentration, 0.755 *M*. ^c Titanous chloride C used. ^d Titanous chloride A used with ionic strength at 1.040 *M*.

points. The tangent to this curve was measured at eight equally spaced triiodide concentrations with a Bausch and Lomb tangent meter. The tangent at each point was expressed in terms of moles of triiodide disappearing per minute. When these values were divided by the corresponding titanous ion concentration and plotted as ordinate against triiodide concentration as abscissa, a linear relationship was observed, the lines having positive slope and positive intercept. Figure 2 gives a typical plot obtained by this method from the triiodide concentration-time curve shown in Fig. 1. This and all other straight lines developed in this paper were obtained by the method of least squares. A careful examination of the data for 25 of these straight lines indicated no significant trend

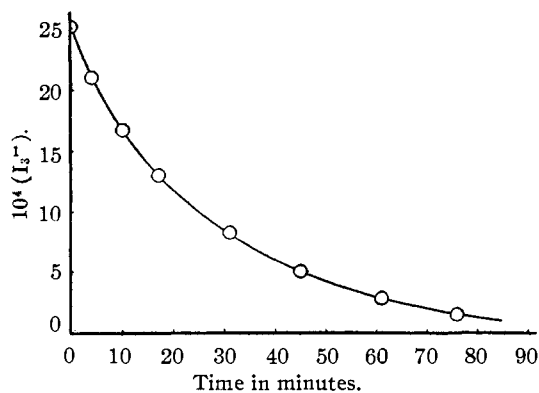


Fig. 1.—Triiodide concentration-time curve for the titanous chloride-iodine reaction, Run 9, Table I.

away from linearity. The fact that straight lines are obtained when the data are plotted in the above manner indicates that the rate equation has the form of equation 1.

$$-d(I_3^-)/dt = k(Ti^{III})(I_3^-) + \kappa(Ti^{III}) \quad (1)$$

The slopes k , and the intercepts κ , of the straight lines are summarized in columns seven and nine of Table I. Comparison of k and κ for Runs 12 and 13 demonstrates that there is no significant difference in the rate when titanous chloride A is substituted for B. Comparison of Runs 1 and 2 with 3 shows that no difference is noticeable on substitution of titanous chloride C for B. The fact

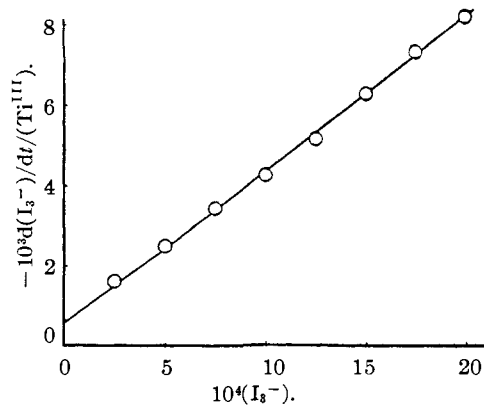


Fig. 2.—Rate of disappearance of triiodide divided by titanous concentration plotted against triiodide concentration for the titanous chloride-iodine reaction. The data were obtained from Fig. 1.

that the three titanous chloride solutions obtained from widely varying sources give rise to the same rate constants appears to be good evidence that no part of Equation (1) is a function of impurities in the titanous solutions. Comparison of k and κ for Run 1 with those of 2 and 3 indicates that substitution of most of the chloride ion by bromide ion in the reaction mixture leads to no significant change in the rate constants. This suggests that specific anion effects are not important in determining the constants of Equation (1).

Equation (1) represents contributions from two reaction modes, one first order in both titanous and triiodide ions, the other first order in titanous ion but independent of triiodide. It was possible to deal quite satisfactorily with the effects of variations in hydrogen and iodide ion concentrations on the first term of Equation (1). Thus k plotted as ordinate against $1/(H^+)$ as abscissa gave a series of straight lines, one for each iodide ion concentration. Figure 3 presents such plots of k vs. $1/(H^+)$ at four different iodide ion concentrations.

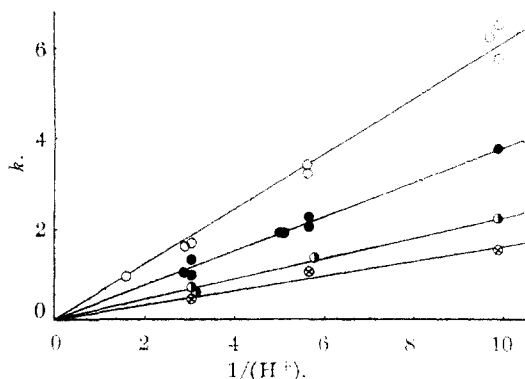


Fig. 3.— k for the titanous chloride-iodine reaction vs. $1/(H^+)$ at various iodide ion concentrations: \circ , $(I^-) = 0.098 M$; \bullet , $(I^-) = 0.179 M$; \odot , $(I^-) = 0.342 M$; \otimes , $(I^-) = 0.506 M$.

Since the distance from the origin was within the probable error for all but one of the intercepts, the lines of Fig. 3 were obtained by the method of least squares modified to require them to pass through the origin. Thus k is related to $1/(H^+)$ by Equation (2). Now plotting k' against $1/(I^-)$

$$k = k'/(H^+) \quad (2)$$

produces a straight line with positive slope and positive intercept as shown in Fig. 4. Therefore, the relation between k' and (I^-) is as shown in Equation (3)

$$k' = k_1''/(I^-) + k_2'' \quad (3)$$

and k may be expressed in terms of (H^+) and (I^-) by Equation (4).

$$k = k_1''/(H^+)(I^-) + k_2''/(H^+) \quad (4)$$

The least squares value of k_1'' is (0.0545 ± 0.0012) mole liter $^{-1}$ min. $^{-1}$ and for k_2'' is (0.0640 ± 0.0073) min. $^{-1}$.

An impression of the fit of the data attained with the above values of k_1'' and k_2'' is gained from substitution of these in Equation (4) and then comparing the values of k obtained in this way with the values derived from plots of the type illustrated

in Fig. 2. This comparison is summarized in columns seven and eight of Table I and it is clear that the values of k are fitted with a mean deviation of 6.8%.

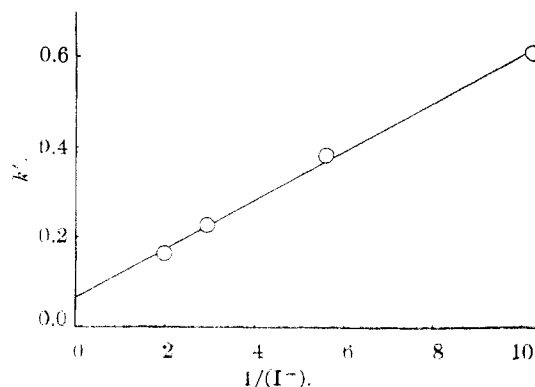


Fig. 4.— k' for the titanous chloride-iodine reaction vs. $1/(I^-)$.

The situation with regard to the triiodide-independent term of Equation (1) is less satisfactory. When κ is plotted against $1/(H^+)$ as it is in Fig. 5, it appears that κ tends to be proportional to $1/(H^+)$ and independent of iodide ion. The least squares

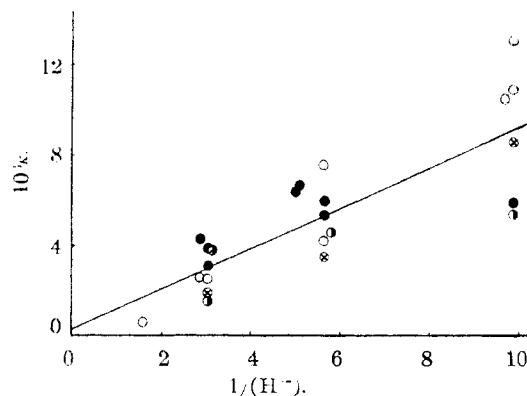


Fig. 5.— κ for the titanous chloride-iodine reaction vs. $1/(H^+)$: \circ , $(I^-) = 0.098 M$; \bullet , $(I^-) = 0.179 M$; \odot , $(I^-) = 0.342 M$; \otimes , $(I^-) = 0.506 M$.

line through 23 points has an intercept of $(3.0 \pm 5.8)10^{-5}$ which is probably without significance, and a slope κ , defined by Equation (5)

$$\kappa = \kappa'/(H^+) \quad (5)$$

of $(8.95 \pm 0.93)10^{-3}$ mole liter $^{-1}$ min. $^{-1}$. Comparison of κ obtained experimentally with κ calculated from Equation (5) is shown in columns nine and ten of Table I. This comparison shows that Equation (5) fits the data with an average deviation of 27%. An important contributing factor to the poor precision of the κ values is undoubtedly the fact that they are obtained from the intercepts of lines like that of Fig. 2. These intercepts are very small and slight errors of judgment in drawing the initial concentration-time curve may lead to large errors in the intercept values.

Making use of Equations (4) and (5) to substitute for k and κ in Equation (1) the complete rate law for the reaction may be expressed by Equation (6).

$$-d(I_3^-)/dt = k_1''(Ti^{III})(I_3^-)/(H^+)(I^-) + k_2''(Ti^{III})(I_3^-)/(H^+) + \kappa'(Ti^{III})/(H^+) \quad (6)$$

The first term on the right of Equation (6) accounts for the greater part of the reaction except at very low triiodide concentrations, and itself constitutes the rate law as derived by Yost and Zabaro.¹¹

The Mechanism

If Equation (6) is simplified by use of the mass action expression (7) and previous assumptions

$$(TiOH^{+2}) = K_b(Ti^{+3})/(H^+) \quad (7)$$

it is converted to Equation (8).

$$-d(I_3^-)/dt = (k_1''/K_b)(TiOH^{+2})(I_3^-)/(I^-) + (k_2''/K_b)(TiOH^{+2})(I_3^-) + (\kappa'/K_b)(TiOH^{+2}) \quad (8)$$

If the first term on the right of Equation (8) is further simplified by use of expression (9)

$$(I_3^-)/(I^-) = (I_2)/K \quad (9)$$

Equation (8) becomes

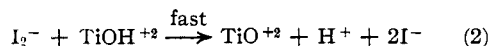
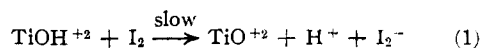
$$-d(I_3^-)/dt = (k_1''/K_bK)(TiOH^{+2})(I_2) + (k_2''/K_b)(TiOH^{+2})(I_3^-) + (\kappa'/K_b)(TiOH^{+2}) \quad (10)$$

This suggests that the rate-determining steps, exclusive of that represented by the last term, consist of the reaction of $TiOH^{+2}$ with I_2 and with I_3^- , respectively. On the other hand, Jakowkin¹⁶ has reported the constant $(I_2Cl^-)/(I_2)(Cl^-)$ as *ca.* 2 in solutions 1 *M* in sodium chloride at 25°. Thus under our experimental conditions a small concentration of I_2Cl^- , equal to or slightly greater than the I_2 concentration, will exist in equilibrium with other iodine species. In such a circumstance there is the possibility that the k_1'' term represents reaction between I_2Cl^- and $TiOH^{+2}$, or at least contains a contribution of this sort. The kinetic data are not sufficient to differentiate between these two paths. The single experiment (Run 1, Table I) in which most of the chloride ion was replaced by bromide ion may be compared with that of Run 2, Table I. The concentration of I_2Cl^- in Run 1 is only about 12% of that in Run 2, while the concentration of I_2 in Run 1 is about 80% of that in Run 2. The fact that k values (Table I), which reflect principally the k_1'' contribution in this case, are nearly the same for these two reactions may be explained on the assumption that the I_2Cl^- reaction path is not very important.

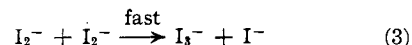
(16) Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

Such is not proven however since the constant $(I_2Br^-)/(I_2)(Br^-)$, reported by Jakowkin¹⁶ to be *ca.* 12 in 0.5 *M* sodium bromide solution, indicates that a relatively large amount of I_2Br^- would be present in Run 1. This species, if it possessed the proper reactivity toward $TiOH^{+2}$, could serve to hold k at nearly the same value as was found in Run 2, even though the concentration of the reactive species I_2Cl^- had been greatly decreased. In view of these considerations it seems reasonable to suppose that the k_1'' term of the rate equation may contain contributions from reaction paths involving I_2Cl^- and I_2Br^- when it is present, but probably not to the exclusion of the I_2 reaction path.

A plausible, but not the only possible, mechanism for the reaction of I_2 with $TiOH^{+2}$ is represented by the sequence of steps



or



A similar sequence can be proposed for the reaction of $TiOH^{+2}$ with I_2Cl^- , I_2Br^- and I_3^- . The proposal that molecular iodine may act as a one-electron oxidizing agent yielding the product I_2^- is not unusual.^{17,18}

The possibility that the last term of Equation (10) arises as the result of a surface reaction has been considered, but the poor precision with which κ is obtained prohibits drawing a definite conclusion concerning this at the present time.

It is to be emphasized again that the mechanism presented here is one of several which fit the data and does not exclude other mechanisms involving intermediate Ti^V , although there is no independent evidence for the existence of a plus five oxidation state of titanium.

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