[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Kinetics of the Reduction of Thallic Ion by Ferrous Ion

BY CARL E. JOHNSON, JR.

The rate of reduction of thallic ion by ferrous ion between 25 and 45° in aqueous solution, 0.5 to 2.0 *f* in perchloric acid, with ionic strength adjusted to 3.00 *M* with sodium perchlorate has been found to be well represented by the equation: $-\mathrm{d}(\mathrm{Fe}^{\mathrm{II}})/\mathrm{d}t = k_1\left[\frac{K_1}{K_1 + (\mathrm{H}^+)}\right](\mathrm{Tl}^{\mathrm{III}})(\mathrm{Fe}^{\mathrm{II}}) + \frac{k_2K_2}{(\mathrm{H}^+)}\left[\frac{K_1}{K_1 + (\mathrm{H}^+)}\right](\mathrm{Tl}^{\mathrm{III}})(\mathrm{Fe}^{\mathrm{II}})$, where $k_1 = 4.33 \times 10^{11}\, e^{-18,400/RT}$ mole^{-1} liter sec.$^{-1}$, $k_2K_2 = 1.89 \times 10^{14}e^{-22,060/RT}$ sec.$^{-1}$ and K_1, estimated from previously published data, $= 1.43 \times 10^5e^{-5,890/RT}$ mole liter^{-1}. A mechanism has been suggested which consists of two reaction paths corresponding to the two terms of the rate equation. The first of these involves a rate-determining reaction between Fe^{++} and TlOH^{++} and the second a rate-determining reaction between Fe^{++} and TlO^+. The rate of reaction has been found to be accelerated by the presence of sulfate ion. Two anthraquinone sulfonic acids were found to be without catalytic activity.

Of the many attempts to correlate the rates of oxidation–reduction reactions few have emphasized the importance of a knowledge of the nature of the rate-determining steps of the reactions being compared. The relatively small but increasing amount of data available on electron transfer reactions in the inorganic field indicates that in most cases the rate-determining step is preceded by the rapid, reversible formation of complex ions, formed either by partial hydrolysis or by reaction with other ions contained in the reaction medium such as hydrogen ion, halide ion, sulfate ion, nitrate ion, etc. The rates of these reactions depend, therefore, not only upon that of the rate-determining electron transfer but also upon the equilibrium constant for the reversible formation of the reactive ionic species.

In order to compare the rates of electron transfer reactions themselves (1) these equilibrium constants must be known, which is often not the case, or (2) the rate-determining steps being compared must involve the same equilibrium constants in such a way that their effect is nullified upon comparison, or (3) reactions must be utilized which do not involve these unknown equilibrium constants. The possibility that reactions may be found which conform to the first of these requirements is suggested by the recent work of Harbottle and Dodson[1] on the isotopic exchange between thallium(I) and thallium(III). The rate-determining step proposed by these authors may be represented by Equation (1).

$$\mathrm{TlOH}^{++} + \mathrm{Tl}^+ \longrightarrow \mathrm{Tl}^+ + \mathrm{TlOH}^{++} \qquad (1)$$

Both the rate constant for this reaction and the equilibrium constant, K_1, for the hydrolysis of Tl^{+++} according to Equation (2) were calculated.

$$\mathrm{Tl}^{+++} + \mathrm{H_2O} \overset{K_1}{\rightleftarrows} \mathrm{TlOH}^{++} + \mathrm{H}^+ \qquad (2)$$

If thallium(III) were to react similarly with other metallic reducing ions a comparison of reaction rates might be made on the basis of requirement (1).

With this idea in mind the reaction between thallic and ferrous ions, previously reported[2] as exhibiting second order characteristics in aqueous sulfuric acid solution, was chosen for study. The details are presented in this paper.

Experimental

Reagents.—All reaction mixtures were made up from the following solutions:

0.050 *f* thallium(III) perchlorate (A) in 2.00 *f* perchloric acid
0.050 *f* thallium(III) perchlorate (B) in 2.00 *f* perchloric acid
0.100 *f* iron(II) perchlorate in 0.50 *f* perchloric acid
0.025 *f* thallium(I) perchlorate in 1.00 *f* perchloric acid
0.050 *f* iron(III) perchlorate in 1.00 *f* perchloric acid
5.00 *f* perchloric acid
1.00 *f* sulfuric acid
1.00 × 10^{-3} *f* sodium anthraquinone 2-sulfonate
1.00 × 10^{-3} *f* sodium anthraquinone 1,5-disulfonate

Thallium(III) perchlorate (A) was prepared by dissolving Fischer pure thallium(III) oxide in 8 *f* perchloric acid followed by dilution. Thallium(III) perchlorate (B) was prepared by dissolving Fischer pure thallium(I) sulfate in water and precipitating thallium(I) chloride by the addition of hydrochloric acid. These crystals were filtered and oxidized with aqua regia. After evaporation and dilution, thallium(III) chloride was extracted with ether. Thallium(III) oxide was precipitated from the extract by addition of water and concentrated ammonium hydroxide. The precipitate was redissolved in 72% perchloric acid and reprecipitated by dilution and addition of concentrated ammonium hydroxide. This precipitate was filtered and washed with water until the washing gave no test for chloride ion when treated with silver nitrate solution. The thallium(III) oxide was dissolved while still moist in 72% perchloric acid and properly diluted with water. Iron(II) perchlorate, chloride-free, was prepared by dissolving Merck and Co., Inc., reagent grade (99.8%) iron wire in 2.00 *f* perchloric acid followed by dilution in a volumetric flask. Thallium(I) perchlorate was prepared by refluxing thallium(III) perchlorate solution with a small excess of 30% hydrogen peroxide solution until tests with titanium(IV) sulfate showed that the last traces of excess peroxide had been decomposed. Iron(III) perchlorate was prepared from iron(II) perchlorate in the same manner. Acid solutions were prepared from either G. F. Smith C.P. 72% perchloric acid or Baker C.P. concentrated sulfuric acid. Sodium perchlorate solution was obtained by neutralizing Merck reagent grade sodium hydroxide dissolved in water with a standard perchloric acid solution. The Eastman Kodak Co. white label sodium anthraquinone 2-sulfonate used was recrystallized twice from hot water and dried in a vacuum desiccator over calcium chloride.

Anal. Calcd. for $\mathrm{C_{14}H_7O_5SNa}$: C, 54.20; H, 2.26. Found: C, 53.95; H, 2.29.

Sodium anthraquinone-1,5-disulfonate was obtained in crude form through the courtesy of E. I. du Pont de Nemours and Co. and was used without purification. The water used throughout the investigation was distilled water redistilled through a block tin still containing potassium permanganate. All stock solutions when not freshly prepared were stored under nitrogen.

Analysis of Reagents.—Iron(II) was determined by titration against either cerium(IV) perchlorate which had previously been standardized against Mallinckrodt analytical reagent grade arsenic(III) oxide, or against Merck reagent grade potassium dichromate. Thallium(III) was determined by addition of excess iron(II) in 6 *f* sulfuric acid and back-titration by one of the methods described above after reaction was complete. Thallium(I) in the thallium(III) solutions was determined by titration against Baker reagent grade potassium bromate. Iron(III) in the iron(II)

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[1] G. Harbottle and R. W. Dodson, THIS JOURNAL, **73**, 2442 (1951).

[2] A. J. Berry, *J. Chem. Soc.*, **121**, 394 (1922).

TABLE I

SUMMARY OF KINETIC RATE RUNS[f]

Run no.	T, °C.	$10^5(\text{Fe}^{\text{II}})$	$10^5(\text{Tl}^{\text{III}})$	$10^5(\text{Fe}^{\text{III}})$	$10^5(\text{Tl}^{\text{I}})$	(H^+)	10^2k, mole^{-1} liter sec.$^{-1}$ Obsd.	Calcd.
1	25.00 ± 0.02	530	265	4	22	2.063	1.531	1.528
2		530	451[e]	4	38	2.063	1.484	1.528
3		527	496	7	16	2.063	1.498	1.528
4		527	496	7	16	1.000	2.26	2.28
5		1054	248	14	264	1.000	2.41	2.28
6		527	496	7	16	1.000	2.26	2.28
7		527	496	7	16	0.668	2.95	2.95
8		527	496	7	16	0.668	2.91	2.95
9		527	496	274	16	0.668	2.99	2.95
10		527	496	7	16	0.500	3.69	3.60
11		527	496	7	16	0.500	3.65	3.60
12		527	496	7	16	0.500	3.53	3.60
13		1054	248	14	8	0.500	3.55	3.60
14	35.00 ± 0.02	513	496	20	16	2.000	5.04	5.06
15		513	496	20	16	1.000	7.53	7.55
16		513	496	20	16	0.667	10.01	9.87
17		513	496	20	16	0.500	12.05	12.14
18	45.00 ± 0.03	513	496	20	16	2.000	14.03	14.13
19		513	496	20	16	1.000	21.2	21.1
20		513	496	20	16	0.667	27.8	27.7
21		513	496	20	16	0.500	34.1	34.2
22[a]	25.00 ± 0.02	527	496	7	16	0.500	3.71	3.60
23[b]		527	496	7	16	0.500	3.69	3.60
24[c]		513	496	20	16	2.063[d]	6.14	1.528

[a] Contains $0.92 \times 10^{-4} f$ sodium anthraquinone 2-sulfonate. [b] Contains $1.04 \times 10^{-4} f$ sodium anthraquinone 1,5-disulfonate. [c] Contains $0.0975 f$ sulfuric acid. [d] $(\text{H}^+) = 2.063 \pm 0.049$ and $\mu = 3.00 \pm 0.10$ depending on the extent to which HSO_4^- is ionized. [e] Thallium perchlorate A used. All other runs made with thallium perchlorate B. [f] All concentrations listed are initial values.

solutions was calculated from the iron(II) content and the weight of iron wire dissolved in making up the solution. Acid in the thallium(III) solutions was determined by direct titration with standard base to the methyl orange endpoint in the presence of 1 f potassium bromide. Acid in the iron(II) solution was determined by precipitation of the hydroxide with excess standard base, filtration, and back titration of the excess base in the filtrate with standard acid.

Kinetic Measurements.—The reaction vessel was a one-liter Pyrex flask, the bottom creased inward so as to form two compartments of about 150-ml. capacity. The stopper contained a delivery tube for the introduction of a slow stream of nitrogen and a gas outlet which also served as an opening for the removal of samples. Measured volumes of the stock solutions were placed in the two compartments of the reaction flask, the thallium(III) and iron(II) occupying different compartments. Enough sodium perchlorate was added to maintain the ionic strength at 3.00 ± 0.005 M and the flask was swept free of air by a slow stream of dry nitrogen. During periods of several minutes between the withdrawal of aliquots from the flask the gas outlet was closed and the nitrogen stream cut off to prevent unnecessary evaporation of water from the reaction mixture. The reaction flask and contents were allowed to stand in a thermostat until thermal equilibrium was reached. The reaction was then started by tilting the flask, quickly pouring the solution back and forth from one compartment to the other, and replacing it in a tilted position. The initial volume of the reaction mixture was always 200 ml., 25-ml. aliquots being removed and analyzed for iron(II) at intervals during the reaction. 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. Total reaction times varied between a few minutes at 45° to several hours at 25°.

The progress of the reaction was followed by determination of iron(II) in the reaction mixture. Two different methods were employed. In several of the runs at 25° the iron(II) determination was made by pipeting a 25-ml. aliquot of the reaction mixture into a flask containing a slight excess of 0.025 f cerium(IV) perchlorate, about 2 ml. of 72% perchloric acid and about 0.5 ml. of a saturated ferrous phenanthroline perchlorate indicator solution. This procedure was followed by immediate back titration of the excess cerium(IV) with 0.02 N iron(II) perchlorate solution. The whole operation required about 1.5 minutes to complete. In the majority of the runs carried out iron(II) was determined by a second method, a modification of that used in earlier work on the reaction in sulfuric acid.[2] A 25-ml. aliquot of the reaction mixture was pipeted into a flask containing a small excess of 0.025 N potassium dichromate solution, 2 ml. of 72% perchloric acid and 0.5 ml. of saturated ferrous phenanthroline perchlorate indicator solution. This mixture was back titrated immediately with 0.02 N iron(II) perchlorate solution when convenient, but could be allowed to stand for several minutes when the interval between the withdrawal of aliquots was too short to permit careful back titration. Both of these methods were shown experimentally to be capable of accuracy to within 0.25%.

The Rate Law

Table I presents a summary of 24 individual rate runs carried out.

Figure 1 shows a typical plot of the quantity log $(a - 2x)/(b - x)$ *versus* time where a and b are the initial concentrations of iron(II) and thallium(III), respectively, and x is the amount by which the concentration of thallium(III) has been reduced at the time, t. The data employed correspond to those of run 16, Table I. The points shown cover the first 60% of reaction[3] and are seen to fall nicely along the straight line obtained by the least squares method. Since the initial acid concentration is large enough to be considered constant throughout each run, it follows that

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[3] A consistent trend toward small positive deviations from linearity was noted in all runs carried out during the last 30% of reaction. These are probably due to a small constant positive error in the analysis for iron(II) which becomes noticeable at low concentrations. In order to eliminate the effect of these deviations on k values only the first 60 to 70% of reaction has been plotted in each case.

$$dx/dt = k(a - 2x)(b - x) \qquad (3)$$

If s is the slope of the line shown in Fig. 1, then

$$k = 2.303s/(a - 2b) \qquad (4)$$

Values of k obtained in this manner are shown in column 7 of Table I. Comparison of the rate constants for runs 12 and 13 shows that k has the same value whether thallium(III) or iron(II) is in excess. Runs 5 and 6 indicate that a sixteen-fold increase in initial thallium(I) concentration does not affect the rate appreciably. Comparison of runs 8 and 9 shows that nearly a forty-fold increase in initial iron(III) concentration does not alter the rate significantly. Runs 2 and 3 show that the thallium(III) perchlorate solutions prepared by two different methods described in the experimental section give identical results and may be considered pure for the purposes of these experiments.

A glance at Table I will show that k increases markedly with decreasing acid concentration. This strongly suggests that hydrolysis products of the predominant ionic species are important in the rate-determinating step, or steps. The identification of particular hydrolyzed species as reactive depends upon some knowledge of the equilibrium constants involved. Bray and Hershey[4] report a value of 18×10^{-4} for the equilibrium constant for the first hydrolysis of ferric ion at an ionic strength of 1 M, so that in 0.5 f perchloric acid iron(III) must exist principally as Fe^{+++}. On the basis of this evidence it seems safe to assume that iron(II) in the same solutions exists as Fe^{++}. Harbottle and Dodson[1] report convincing evidence for values from 3.2 to 6.9 for the equilibrium constant, K_1, for the first hydrolysis of thallic ion (Equation 2) at temperatures ranging from 25.0 to 41.8° at an ionic strength of 6 M. These values indicate that most of the thallium(III) in perchloric acid solutions less concentrated than 3 M exists as $TlOH^{++}$. In order to obtain an estimate of K_1 at an ionic strength nearer to 3.00 M, the data of Prestwood and Wahl[5] for the thallium(I)–thallium(III) exchange at an ionic strength of 3.68 M were replotted according to the scheme of Harbottle and Dodson[1] to yield values of K_1 at 9.9, 24.9, 37.3 and 50.1°. The log of K_1 was then plotted *versus* $1/T$ yielding a straight line from which K_1 could be estimated at the temperatures employed in this work. All of the linear relations involved in this procedure were treated by the method of least squares. The estimates of K_1 obtained in this manner at 25, 35 and 45° are shown in Table II. As might be expected these values are somewhat larger than those measured at the higher ionic strength and indicate that in perchloric acid, 0.5 to 2.0f, $TlOH^{++}$ may be expected to be the principal thallium(III) species. It should be pointed out that the treatment of Harbottle and Dodson[1] and the work of Prestwood and Wahl,[5] as well as the kinetic analysis which follows, are based upon the assumption that activity coefficients of the reactants remain constant when hydrogen ion is substituted for sodium ion at constant (high) ionic strength. Should this assumption later prove to be invalid the estimates of K_1 and the following interpretation of the data would correspondingly be subject to revision.

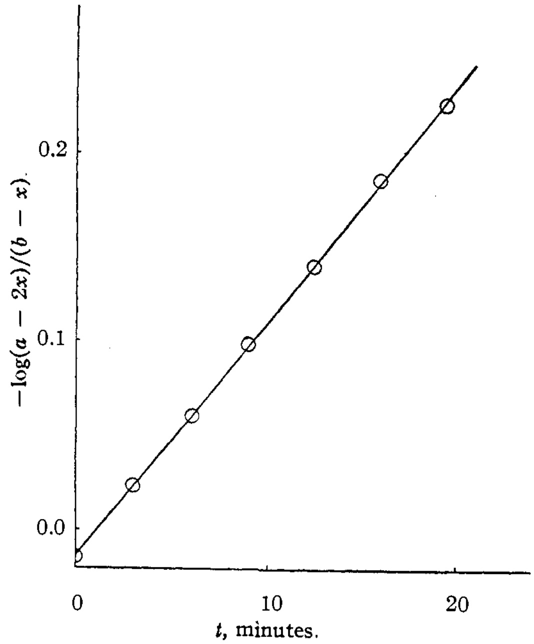

Fig. 1.—The quantity $-\log (a - 2x)/(b - x)$ plotted *vs.* time for the reduction of thallium(III) by iron(II) in perchloric acid. The data is from run 16, Table I.

Making use of K_1, the concentration of $TlOH^{++}$ may be accurately expressed by Equation (5) where (Tl^{III}) represents total thallium(III) concentration. Further hydrolysis of a small part of

$$(TlOH^{++}) = \left[\frac{K_1}{K_1 + (H^+)}\right](Tl^{III}) \qquad (5)$$

the $TlOH^{++}$ according to Equation (6)

$$TlOH^{++} \rightleftarrows TlO^+ + H^+ \qquad (6)$$

would give rise to TlO^+, the concentration of which may be expressed approximately as shown in Equation (7). It is reasonable to suppose that K_2 will be much smaller than K_1 and that (H^+) will be large in comparison with K_2 in the denominator of Equation (7). Equation (7) may therefore be reduced to Equation (8).

$$(TlO^+) = \left[\frac{K_1}{K_1 + (H^+)}\right]\left[\frac{K_2}{K_2 + (H^+)}\right](Tl^{III}) \qquad (7)$$

$$(TlO^+) = \left[\frac{K_1}{K_1 + (H^+)}\right]\frac{K_2}{(H^+)}(Tl^{III}) \qquad (8)$$

Upon the assumption that $TlOH^{++}$ and TlO^+ are the reactive thallium(III) species the rate of reaction may be expressed as in Equation (9) and

$$-d(Fe^{II})/dt = k_1\left[\frac{K_1}{K_1 + (H^+)}\right](Tl^{III})(Fe^{II}) + \frac{k_2K_2}{(H^+)}\left[\frac{K_1}{K_1 + (H^+)}\right](Tl^{III})(Fe^{II}) \qquad (9)$$

k of Equation (3) may be written as shown in Equation (10). The estimates of K_1 described

$$k = k_1\left[\frac{K_1}{K_1 + (H^+)}\right] + \frac{k_1K_2}{(H^+)}\left[\frac{K_1}{K_1 + (H^+)}\right] \qquad (10)$$

above make it possible to plot the quantity

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[4] W. C. Bray and A. V. Hershey, THIS JOURNAL, **56**, 1889 (1934).

[5] R. J. Prestwood and A. C. Wahl, *ibid.*, **71**, 3137 (1949).

$k\left(\frac{K_1 + (\mathrm{H}^+)}{K_1}\right)$ *versus* $1/(\mathrm{H}^+)$ which, if Equation (9) fits the data, should lead to a straight line, the intercept giving the value of k_1 and the slope the value of k_2K_2. Figure 2 shows the data plotted in this manner at three different temperatures. The linear relationship appears satisfactory at all three temperatures and the values for k_1 and k_2K_2 obtained from this plot are listed in Table II opposite the estimates of K_1 upon which they depend.

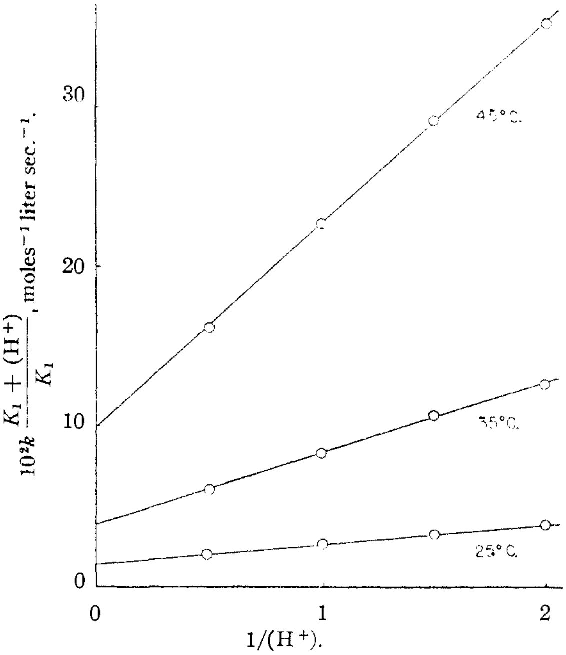

Fig. 2.—The quantity $10^2k\ [K_1 + (\mathrm{H}^+)]/K_1$ plotted *vs.* $1/(\mathrm{H}^+)$ for the reduction of thallium(III) by iron(II) in perchloric acid at three temperatures. The points at 25° represent average values.

TABLE II

SUMMARY OF RATE AND EQUILIBRIUM CONSTANTS

Temp., °C.	K_1, moles liter^{-1}	10^2k_1, moles^{-1} liter sec.$^{-1}$	$10^2k_2K_2$, sec.$^{-1}$
25.00 ± 0.02	6.4	1.406 ± 0.032	1.238 ± 0.022
35.00 ± .02	9.4	3.91 ± .11	4.44 ± .08
45.00 ± .03	12.7	9.96 ± .16	12.80 ± .11

An idea of how well Equation (9) fits the data may be obtained by using K_1, k_1 and k_2K_2 to calculate k according to Equation (10). For purposes of comparison k, calculated in this way, is listed beside the observed values in Table I. The average deviation of observed from calculated values is only 1.3%.

The Mechanism

The rate law of Equation (9), which has been shown to fit the data presented, was derived upon the assumption that two different hydrolyzed thallium(III) species are reactive toward ferrous ion, and that the reaction proceeds *via* two independent paths.

Path (1).—One or two electrons are transferred directly from Fe^{++} to TlOH^{++}. The OH may or may not be exchanged simultaneously with the electron(s). One of several sequences of steps which may describe Path (1) is shown below.

$$\mathrm{Tl}^{+++} + \mathrm{H_2O} \rightleftharpoons \mathrm{TlOH}^{++} + \mathrm{H}^+ \quad K_1 \text{ (rapid, reversible)} \qquad (11)$$

$$\mathrm{Fe}^{++} + \mathrm{TlOH}^{++} \longrightarrow \mathrm{Fe}^{+++} + \mathrm{Tl}^{\mathrm{II}} \text{ (rate-determining)} \qquad (12)$$

followed by

$$\mathrm{Fe}^{++} + \mathrm{Tl}^{\mathrm{II}} \longrightarrow \mathrm{Fe}^{+++} + \mathrm{Tl}^+ \text{ (rapid)} \qquad (13)$$

or

$$\mathrm{Tl}^{\mathrm{II}} + \mathrm{Tl}^{\mathrm{II}} \longrightarrow \mathrm{Tl}^{+++} + \mathrm{Tl}^+ \text{ (rapid)} \qquad [14)$$

If two electrons are transferred in the rate-determining step, the unstable intermediate $\mathrm{Fe}^{\mathrm{IV}}$ will be formed.

Path (2).—A small fraction of one of the reactants, probably TlOH^{++}, is further hydrolyzed and either one or two electrons are passed from Fe^{++} to the hydrolysis product, TlO^+. Again, the oxygen atom may or may not be exchanged simultaneously with the electron(s). One sequence of steps describing this path may be written as

$$\mathrm{TlOH}^{++} \rightleftharpoons \mathrm{TlO}^+ + \mathrm{H}^+\ K_2 \text{ (rapid, reversible)} \qquad (15)$$

$$\mathrm{Fe}^{++} + \mathrm{TlO}^+ \longrightarrow \mathrm{FeO}^+ + \mathrm{Tl}^{\mathrm{II}} \text{ (rate-determining)} \qquad (16)$$

$$\mathrm{FeO}^+ + 2\mathrm{H}^+ \longrightarrow \mathrm{Fe}^{+++} + \mathrm{H_2O} \text{ (rapid)} \qquad (17)$$

followed by either reaction (13) or (14). There is also the possibility that K_2 pertains to the hydrolysis of Fe^{++} and that TlOH^{++} reacts with FeOH^+ in the rate-determining step of Path (2).

Catalysis.—The reaction exhibits second order kinetics also in the presence of added sulfate ion. However, it will be noticed that k for run 24 of Table I is considerably larger than that expected in the absence of the sulfate ion. This large increase in rate indicates a third path for reaction involving sulfate or bisulfate complexes of one of the reactants, probably thallium(III). Runs 22 and 23 exhibit expected k values indicating that neither sodium anthraquinone 2-sulfonate nor sodium anthraquinone 1,5-disulfonate possesses the catalytic ability in this reaction which they have been shown to possess in the titanium(III) chloride–iodine reaction.[6]

Discussion

The experimental energy of activation has been calculated over the range of temperature from 25 to 45° from the rate constants in Table II. The entropy of activation for reaction (12) was calculated from the experimental rate constant and the energy of activation according to absolute rate theory.[7] For purposes of comparison these thermodynamic functions, along with the experimental rate constants at 25°, for both the reduction and the exchange reaction reported by Harbottle and Dodson[1] are listed in Table III. The rate constant and the heat and entropy of activation for reaction (16) cannot be calculated because the unknown equilibrium constant and heat of reaction (15) are included in the measured quantities.

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(6) C. E. Johnson, Jr., and S. Winstein, THIS JOURNAL, **74**, 755 (1952).

(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

TABLE III

COMPARISON OF THE Fe^{II}–Tl^{III} REDUCTION WITH THE Tl^{I}–T^{III} EXCHANGE REACTION

Reaction	Rate constant, m.$^{-1}$l.sec.$^{-1}$	E‡, cal. mole^{-1}	ΔS‡, cal. deg.$^{-1}$ mole^{-1}
(1), exchange	2.60×10^{-5}	14,700	−32
(12), reduction	1.406×10^{-2}	18,400 ± 100	− 7.3
(16), reduction	1.238×10^{-2}	22,060 ± 530	....

Although no reaction path corresponding to reaction (16) has been reported for the exchange reaction, the figures for the exchange reaction (1) and that portion of the reduction which proceeds by way of reaction (12) are subject to comparison. As might have been predicted by those who emphasize the importance of charge interaction,[8] or because of the necessity for the intermediate production of an unstable ionic species in the rate-determining step by those who adhere to the "equivalence change" principle[9] as modified[10] to include the theory of "potential humps,"[11] the experimental activation energy is less for the exchange reaction than for the analogous oxidation-reduction reaction. The entropy of activation for reaction (12) is surprisingly high, in view of the fact that Glasstone, Laidler and Eyring[12] list values from −20 cal. deg.$^{-1}$ mole^{-1} to −32 cal. deg.$^{-1}$ mole^{-1} for a number of reactions between ions of like sign, and is much higher than that reported for the exchange reaction. Although it is not felt that sufficient data are available to permit an adequate explanation of this feature, it is interesting to note that it is this difference in entropy which accounts for the fact that reaction (12) has a velocity which is more than 500 times that of the exchange reaction (1), in spite of the unfavorable difference in activation energies.

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(8) J. Weiss, *J. Chem. Soc.*, 309 (1944).

(9) P. A. Shaffer, *Cold Springs Harbor Symposium Quant. Biol.*, VII, 50 (1939).

(10) A. R. Remick, THIS JOURNAL, **69**, 94 (1947).

(11) Bancroft and Magoffin, *ibid.*, **57**, 2561 (1935); **58**, 2187 (1936).

(12) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 435.

URBANA, ILLINOIS

RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE HALDOR TOPSØE RESEARCH LABORATORY]

Investigation on Surface Properties of Reduced Iron Catalysts for the Synthesis of Ammonia and Correlation with Crystal Sizes and High Pressure Conversion Activities

BY ANDERS NIELSEN AND HANS BOHLBRO

Trvo triply promoted ammonia catalysts have been examined by adsorption measurements, and the adsorption data correlated with X-ray data and high pressure conversion measurements. Crystal sizes determined from line broadening in X-ray patterns and surface areas derived from low temperature A and N_2 adsorption are in satisfactory agreement. The more active catalyst has the smaller surface area and the smaller CO chemisorption at −78°. A first order phase transition of adsorbed nitrogen at liquid nitrogen and liquid oxygen temperatures has furthermore been found and isosteric heats of adsorption have been determined.

Introduction

An investigation on high pressure conversion measurements and on the structure of reduced iron catalysts as determined by X-ray analysis has previously been published by one of the authors.[1]

The present paper reports the results of a series of adsorption measurements that have been made with CO, N_2 and A on two of the commercial iron synthetic ammonia catalysts used in the previous investigations.

Experimental

High Pressure Conversion Measurements.—Catalysts used were commercial triply promoted K_2O–CaO–Al_2O_3–iron catalysts, KM I and KM II, made from fused oxides. Conversions were measured at 330 atm., S.V. = 15000 and $H_2:N_2 = 3:1$. For details see reference 1.

X-Ray Technique.—Samples of reduced and tested catalysts were removed from the converter in an atmosphere of nitrogen and transferred to pentane or benzene. Samples for X-ray exposure were ground in the protecting liquid and specimens were prepared by mixing the wet powder with canada balsam in xylene solution. For details concerning the X-ray technique see reference 1. Cobalt and chromium tubes of Machlett manufacture were used.

Adsorption Measurements.—Samples used were the reduced and tested catalysts stored in pentane or benzene as described above. Samples, still wet, were transferred to the adsorption bulb. Evacuation was started at room temperature. When evacuated at room temperature, the sample was slowly heated and the evacuation always terminated with a 9-hour period at 400°. This temperature was chosen so as to ensure that no further sintering of the samples took place. This was verified by re-reducing a sample *in situ* in the bulb, evacuating and repeating the surface area determination (areas of 4.48 m.^{2}/g. and 4.40 m.^{2}/g. respectively, were found). Areas always refer to grams of reduced catalyst. Effective cross-sectional area of an adsorbed nitrogen molecule is assumed to be 16.2 Å.^{2} at liquid nitrogen temperature. The effectiveness of the shielding against oxygen during storage was verified by comparing CO chemisorption at −78° of one of the samples with CO chemisorption of a re-reduced sample and of a freshly reduced sample reduced at atmospheric pressure with pure hydrogen (chemisorptions of 7, 7 and 12% of a nitrogen monolayer were found).

The apparatus was essentially that of Brunauer, Emmett and Teller.[2] For pressure determinations the apparatus was connected to a McLeod gage (10^{-5}–10^{-1} mm.), to a Pirani gage (10^{-3}–0.75 mm.), and to a U-tube manometer provided with a cathetometer (10^{-2}–1000 mm.). The Pirani gage was especially useful during desorption and further to distinguish between condensable and non-condensable gases when used combined with the McLeod gage. A purification train[3] was used for the purification of H_2, He, A, N_2, CO and CO_2 used for the experiments. The evacua-

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(1) A. Nielsen, "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," Jul. Gjellerups Forlag, Copenhagen, 1950.

(2) *Cf.* P. H. Emmett, "A New Method for Measuring the Surface Areas of Finely Divided Materials and for Determining the Size of Particles," Symposium on New Methods for Particle Size Determination in the Subsieve Range, A.S.T.M. (1941).

(3) L. G. Joyner in W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Company, Pittsburgh, Penna., 1949, p. 272.