[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

Salt and Acid Effects on the Thallous–Thallic Exchange Reaction[1]

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In a continuation of previous work, the thallous–thallic exchange reaction in perchloric acid–sodium perchlorate mixtures has been studied at 50°. Measurements were made at values of ionic strength and acid concentration ranging independently from 0.5 to 6.0 *M*. The results are in good quantitative agreement with those of two earlier investigations, which could not be compared formerly because of the different ionic strengths employed. Reasons for doubting that unhydrolyzed thallic ion participates significantly in the reaction are given, but a firm proof of this point is not yet available. At high ionic strengths and constant acid concentration the rate decreases as the ionic strength is increased. This effect is consistent with the behavior of activity coefficients of electrolytes at high concentrations.

Introduction

The kinetics of the thallous–thallic exchange reaction in perchlorate solutions have been studied by Prestwood and Wahl[2] at ionic strength 3.68 *M* and by Harbottle and Dodson[3] at 6.1 *M*. The rates found agreed as to order of magnitude; however, no exact comparison was possible because of the different conditions of the experiments. The two groups differed in their interpretation of the observed decrease in rate with increasing acidity. Prestwood and Wahl proposed that the reaction goes through a path involving unhydrolyzed ions and also through a path involving singly hydrolyzed thallic ion present in small but unknown amount. Harbottle and Dodson concluded that only a single reaction path, one involving singly hydrolyzed thallic ion, is operative. The present work was undertaken in order to bridge the gap in experimental conditions of the two previous studies, and, if possible, to clarify the question of the nature of the reacting species.

Experimental

Materials.—Radioactive thallium^{204} nitrate, obtained from Oak Ridge, was dissolved in dilute nitric acid, and the solution was scavenged by two successive precipitations of ferric hydroxide. Thallic hydroxide was precipitated from the alkaline solution by addition of hydrogen peroxide. The precipitate was washed and dissolved in perchloric acid. This solution was mixed with an amount of inactive thallic perchlorate, prepared in a similar way, sufficient to give the desired specific activity. Thallic hydroxide was reprecipitated from this solution with sodium hydroxide in the presence of ferricyanide. The precipitate was thoroughly washed and redissolved in perchloric acid to give a stock solution of radioactive thallic perchlorate. Test for ferricyanide was negative.

Thallous perchlorate was prepared from Eimer and Amend C.P. thallium metal. The metal was dissolved in nitric acid and thallous nitrate crystallized out by chilling. The crystals were redissolved in water and a large excess of 70% perchloric acid was added. The mixture was evaporated to a slurry, chilled and filtered. The crystal crop was redissolved, reprecipitated in the presence of excess perchloric acid and twice recrystallized from solution in distilled water. It was then dissolved in distilled water to give a stock solution of thallous perchlorate. The solution was neutral and gave a negative test for nitrate with brucine reagent.

Fisher C.P. sodium perchlorate monohydrate was purified by dissolving it in distilled water and reprecipitating by the addition of perchloric acid to the chilled solution. The precipitate was dissolved in distilled water to give a somewhat acid stock solution of sodium perchlorate. Test for chloride, with silver nitrate, was negative.

The perchloric acid was Baker C.P. 70% reagent.

Rate Measurements.—Appropriate weights or volumes of reagent stock solutions and distilled water were added to a 50-ml. volumetric flask immersed in a thermostat at 50.0 ± 0.1° and were thoroughly mixed. Aliquot portions were removed at intervals and thallous chromate precipitated with a solution of sodium chromate, sodium cyanide, ammonium hydroxide and ethanol, as earlier described.[3] The precipitate was filtered on filter paper with the usual glass chimney arrangement, giving a uniform circular deposit. The precipitate was washed with dilute sodium chromate solution, then with acetone, dried and counted with a mica window GM tube in standard geometry. All counts were made to a standard deviation of 1% or less.

Results

The counting results were analyzed in the usual way (McKay plots) by plotting log $(1 - x/x_\infty)$ against time. In the present instance, x is the activity of the thallous chromate precipitate obtained from the aliquot taken at time t, and x_∞ is the corresponding equilibrium activity. The value of x_∞ was calculated from the concentrations and total activity. Points were taken over at least two half-lives. The plots were linear, with zero time exchange of 5–10%. Since the reaction has been shown[2,3] to be first order in the over-all concentration of each oxidation state, the over-all rate constant is given by $k = 0.693/t_{1/2}(a + b)$, where a and b are the thallous and thallic concentrations, and $t_{1/2}$ is the reaction half-time, as determined from the plot of log $(1 - x/x_\infty)$ *vs.* t. The results are given in Table I. The error, in the sense of a standard deviation, in the values of k is thought to be about ±5%.

TABLE I

OVER-ALL RATE CONSTANTS FOR THALLOUS–THALLIC EXCHANGE IN PERCHLORIC ACID–SODIUM PERCHLORATE MIXTURES AT 50.0°: [Tl(I)] 0.02914 *f*; [Tl(III)] 0.00398 *f*

Ionic strength, mole/l.	Perchloric acid, mole/l.	Sodium perchlorate, mole/l.	k, mole^{-1} l. hr.$^{-1}$
0.5	0.5	0.0	2.68
1.0	0.5	.5	2.68
	1.0	.0	3.14
2.0	0.5	1.5	2.40
	1.0	1.0	2.90
	2.0	0.0	2.90
4.0	0.5	3.5	1.99
	1.0	3.0	1.56
	2.0	2.0	1.46
	4.0	0.0	1.41
6.0	0.5	5.5	0.74
	1.0	5.0	.66
	2.0	4.0	.57
	4.0	2.0	.43
	6.0	0.0	.38

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[1] Research carried out under the auspices of the United States Atomic Energy Commission.

[2] R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949).

[3] W. Harbottle and R. W. Dodson, *ibid.*, **73**, 2442 (1951).

Harbottle and Dodson[3] measured k at ionic strength 6.1 and the same acid concentrations as those employed in the present work, at 25.0, 32.2 and 41.8°. Their values of k give linear $1/T$ plots, which may be extrapolated to 50.0° for comparison with the present results. The values so obtained are given in Table II, along with corresponding data from the present investigation. The agreement is excellent except at the lowest acid concentration, where the compared values deviate from their mean by ±10%. Here, the agreement may be considered acceptable on statistical grounds.

TABLE II

COMPARISON OF VALUES FOR THE OVER-ALL RATE CONSTANT, k, AT 50°

Parentheses indicate interpolated or extrapolated results.

Ionic strength, mole/l.	Perchloric acid, mole/l.	k (Harbottle and Dodson[3]) mole^{-1} l. hr.$^{-1}$	k (Prestwood and Wahl[2]) mole l. hr.$^{-1}$	k (present work) mole^{-1} l. hr.$^{-1}$
6.0	0.5	(0.61)		0.74
	1.0	(.59)		.66
	2.0	(.56)		.57
	4.0	(.44)		.43
	6.0	(.40)		.38
3.68	0.80		1.86	(1.88)
	1.50		1.80	(1.80)
	2.50		1.71	(1.70)
	3.50		1.65	(1.61)

Prestwood and Wahl[2] measured k at 50.1° at ionic strength 3.68 mole/l. and acid concentrations encompassed in the range of the present work. For comparison of results, the present data have been calculated, by interpolation, to the same values of ionic strength and acid concentration. For this purpose, values of k at the acid concentrations of interest were read from linear plots of $1/k$ against (H^+) at various ionic strengths. For each acid concentration, the values of k so obtained were plotted against ionic strength and found to give approximately straight lines, whose ordinate at $\mu = 3.68$ was taken for comparison with the results of Prestwood and Wahl.[2] Since the graphs used were approximately linear, the interpolations are quite precise. These results are also given in Table II and it is seen that there is excellent agreement with the earlier work.

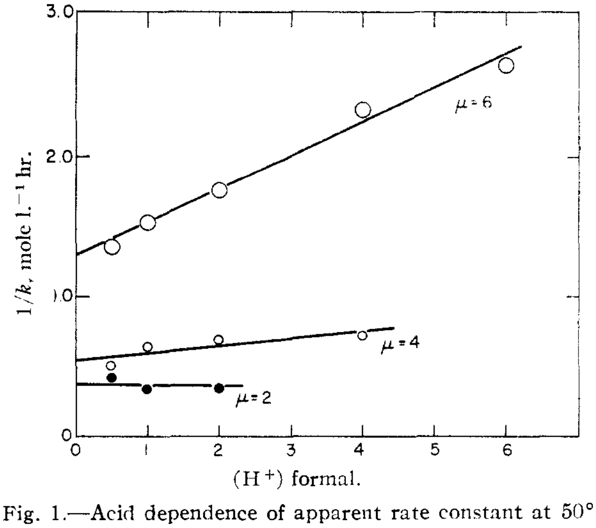

Fig. 1.—Acid dependence of apparent rate constant at 50° and various ionic strengths.

The exchange rate is given by

$$R = k[\mathrm{Tl(I)}][\mathrm{Tl(III)}] \qquad (1)$$

where [Tl(I)] and [Tl(III)] represent the over-all or formal concentrations of the two oxidation states. On the assumption that the only thallic species which is exchanging is $TlOH^{++}$ and that the only thallous species is Tl^+

$$R = k_2[\mathrm{Tl}^+][\mathrm{TlOH}^{++}] \qquad (2)$$

and the following relation prevails between the apparent rate constant k and the true rate constant k_2

$$1/k = 1/k_2 + (H^+)/k_2K \qquad (3)$$

where K is the hydrolysis constant of thallic thallium. Figure 1 shows graphs of $1/k$ against acid concentration at various ionic strengths. The graphs are reasonably linear, in conformity with (3). At ionic strength 6, the value of k_2 found from the intercept is 0.78 mole^{-1}/l./hr.$^{-1}$, and from this value and the slope the hydrolysis constant is 5.5. The value found by extrapolating previous[3] values of k_2 on a $1/T$ plot with a slope corresponding to an activation energy of 14.7 kcal./mole, calculated from these data, is 0.63 f^{-1} hr.$^{-1}$. Taking the present result into account, a better value for the activation energy is 16.0 kcal./mole. The errors in the estimate of hydrolysis constant are considerably greater; the value expected from the previous data is 10 or twice that found.

Discussion

As has been brought out in the preceding section, the data obtained in the present work are gratifyingly consistent with earlier measurements.[2,3] It is thus clear that the somewhat differing interpretations[2,3] of the effect of acid do not rest on systematic experimental errors in one or the other of these studies. At each ionic strength, the dependence of rate on acid concentration in the present measurements is in accord with the assumption[3] that only hydrolyzed thallic thallium contributes appreciably to the observed rate. The acid dependence is in less satisfactory agreement with the assumption[2] that unhydrolyzed Tl^{+++} also contributes appreciably. The fact that the present results show only slight dependence of k on (H^+) at ionic strengths 4 and 2 suggests that the hydrolysis is almost complete and that it is the hydrolyzed species which is participating in the exchange reaction. The apparent slight reversal of trend with (H^+) at ionic strengths 2 and 1 may, on this view, result from the effect of a second hydrolysis step, but would seem quite inexplicable in terms of Wahl and Prestwood's assumption.

It should be noted that in the present, as in the previous,[2,3] discussions, it is assumed that the activity coefficients of the reactants are unaltered by the substitution of (Na^+) for (H^+) in the solution. The degree to which this assumption may be valid is at present unknown. It has, however, proved to be a useful assumption in other similar investigations.[4] Throughout this paper the difference between formal and molal activity coefficients and the effect of temperature on activity coefficients are ignored, since these are not quantitatively significant in the discussion.

If an independent estimate of the hydrolysis constant of thallic thallium in the media employed were available, a firmer choice between the two assumed rate laws might be made, since one of them permits calculation of this equilibrium constant from the rate data. Benoit[5] has given a rough estimate of $K_h = 0.6$ for infinitely dilute solution at 18°. The value calculated from the kinetic data is 2.8 in terms of concentrations at this temperature and at ionic strength 6. Since not all of the relevant activity coefficients are known, comparison of these values is at best speculative. However, it may be concluded that if both estimates of K_h are to be accepted, the ratio (mean ionic activity coefficient of $TlOH^{++}$ perchlorate)^3/(mean ionic activity coefficient of Tl^{+++} perchlorate)^4 at ionic strength 6 must be about 0.5×10^{-3}, which does not seem likely. (This comparison employs a value 13 for the mean ionic activity coefficient of perchloric acid and 0.45 for the activity coefficient of water.[6]) This difficulty can probably not be resolved without measurements of the hydrolysis equilibrium in concentrated salt solutions.

Since the mechanism is thought to involve an encounter between two positive ions, it would be expected that in dilute solutions an increase of ionic strength would lead to an increase in the specific rate constant. Over most of the range of the present experiments, just the opposite occurs. This might be expected as a consequence of the way in which the activity coefficients increase with ionic strength in concentrated salt solutions. Although again no quantitative treatment is possible because of the lack of experimental data, it is of some interest that the trend can be rationalized by assuming that the unknown activity coefficients change in the same way with ionic strength (established with $HClO_4$ and $NaClO_4$) as do those of some salts of the same charge type in their own aqueous solutions. For this comparison rubidium nitrate was chosen as an analog of thallous perchlorate (these salts have almost identical activity coefficients up to 0.5 molal; above 4.5 molal, the data for rubidium nitrate were extrapolated), strontium chloride for $TlOH^{++}$ perchlorate, and lanthanum chloride for the transition complex. These data, for solutions at 25°, were obtained from standard tabulations.[7]

The rate constant is expected to vary proportionally with the ratio $r = \gamma^2_{1\pm}\gamma^3_{2\pm}/\gamma^4_{3\pm}$, where the γ's are the mean ionic activity coefficients. Table III lists the values assumed for the activity coefficients and compares the expected and observed trends.

TABLE III

ASSUMED ACTIVITY COEFFICIENTS, AND TREND OF RATE CONSTANT WITH IONIC STRENGTH

Ionic strength, mole/l.	$\gamma_1\pm$	$\gamma_2\pm$	$\gamma_3\pm$	$\frac{r(\mu)}{r(\mu = 1)}$	$\frac{k(\mu)}{k(\mu = 1)}$ obsd.
0.5	0.52	0.47	0.34	1.1	0.9
1.0	.42	.44	.30	(1.0)	(1.0)
2.0	.30	.44	.28	0.7	0.9
4.0	.20	.58	.32	.4	.6
6.0 (8.3 molal)	.18	1.00	.50	.3	.3

It is seen that the observed trend is reasonably well accounted for. It should perhaps be emphasized that the comparison is not presented as proof of the assumptions involved, but rather to show that a set of assumptions which suggest the observed trend and which at the same time are not completely *ad hoc* can be found.

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[4] *E.g.*, in the case of the Ce(III)–Ce(IV) exchange reaction, J. W. Gryder and R. W. Dodson, THIS JOURNAL, **73**, 2890 (1951), and the Fe(II)–Fe(III) exchange reaction, J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

[5] R. Benoit, *Bull. soc. chim. France*, **5-6**, 518 (1949).

[6] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. 5. Auflage, 3. Ergänzungsband, 3. Teil, p. 2144.

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950 pp. 563, 573 and 602.