The Exchange Reaction between the Two Oxidation States of Thallium in Solution[1]

By G. Harbottle and R. W. Dodson

The rate of the exchange reaction between the two oxidation states of thallium was studied as a function of thallous and thallic concentrations, acid concentration in perchloric acid–sodium perchlorate mixtures, chloride concentration, and the temperature. It was found that the reaction proceeds at a slow and measurable rate, that it is first order in both thallous and thallic concentrations, that the rate decreases with increasing acidity, and is strongly influenced by the presence of chloride. The results are interpreted in terms of electron transfer reactions between hydrolyzed species and between chloride complexes.

Introduction

Electronic exchange reactions are of interest since they involve the simultaneous oxidation and reduction of atoms of the same element without change in the over-all concentrations of the two oxidation states. Thus, they are equilibrium oxidation–reduction reactions of a very simple type, and in some cases may take place by the direct transfer of electrons. A study of exchange between the oxidation states of thallium was undertaken because, at the time the work was started, no such electron-transfer exchange reaction had been kinetically characterized, and it appeared that rate measurements for this type of reaction were in general difficult because of the great speed of the symmetrical oxidation–reduction process. Exchange between thallous and thallic ions was expected to involve the transfer of two electrons at once, because dipositive thallium is not known. This process might be much less probable than single electron transfer, and thus permit reaction rate measurements. Earlier studies of this type on thallium had been limited to inconclusive experiments[2] which were handicapped by the short half-life of the tracer employed (Thorium C″, half-life 3.1 minutes). Our experiments were facilitated by the availability of radioactive Tl^{204} (half-life 2.7 years) in adequate specific activity. Our preliminary results which showed that reaction rate measurements were feasible in this system have been reported previously.[3]

During this work, similar experiments were independently carried out by Prestwood and Wahl.[4] Where comparable, the data are in agreement. In the interpretation of the data, however, we differ in some respects from Prestwood and Wahl.

Materials

Radioactive thallium was obtained in two forms: thallium metal irradiated with neutrons at the Los Alamos Scientific Laboratory, and thallous nitrate obtained from the U. S. Atomic Energy Commission, Oak Ridge, Tennessee. The latter was used in virtually all experiments described in this paper.

Inactive thallium metal was obtained from the Fairmount Chemical Company, and thallous nitrate from Eimer and Amend Company.

For purification, the radioactive thallium metal was dissolved in nitric acid and the thallous nitrate in water. A trace of ferric ion was then added and the solutions made basic with ammonia; the resulting ferric hydroxide "scavenger" precipitate carries down various radioactive contaminants which might be present in very small concentra-

tions. The ferric hydroxide was filtered off and the cycle repeated. The filtrate was boiled down and thallous nitrate recovered by crystallization. The thallous nitrate was purified by several recrystallizations from distilled water and finally converted to thallous perchlorate by fuming with perchloric acid. The thallous perchlorate was recrystallized from water until free of acid. Inactive thallium was purified in the same way with the omission of the scavenging process.

Thallic hydroxide was precipitated from a solution about 0.01 M in purified thallous nitrate and 0.1 N in sodium hydroxide by oxidation with a 0.1 N solution of potassium ferricyanide. The precipitate was washed by decantation until free of ferro- and ferricyanides and then steeped for a month, with occasional stirring, in 6 f^5 perchloric acid. The clear supernatant liquid was decanted and filtered through a Jena 1-G-4 sintered-glass funnel; the resulting solution was 0.0865 f in thallic perchlorate.

Perchloric acid was obtained from G. Frederick Smith Company; both 60% Reagent (distilled) and 72% lead-free (double-distilled) were used.

Anhydrous sodium perchlorate was also obtained from G. Frederick Smith Co. Some samples appeared to contain chloride, and gave chlorine on acidification; these were not used. All samples of perchloric acid, sodium perchlorate and distilled water which were finally used in reaction mixtures were free from chloride, as tested by silver nitrate.

Hydrochloric acid was distilled from diluted, reagent grade acid through a short column packed with glass beads, in an all-glass apparatus. The middle fraction was retained, and the concentration calculated from the data of Hollingsworth and Foulk.[6]

Rate Measurements

Procedure.—Reaction mixtures were prepared by the addition of appropriate volumes of reagent stock solutions to a volumetric flask, immersed in a constant temperature bath ($\pm0.02°$), the flask serving thereafter as a reaction vessel. Separation of the oxidation states was accomplished by precipitating thallous chromate. At intervals aliquot portions of the reaction mixture were pipetted into a beaker containing about 10 ml. of freshly-prepared precipitant. The composition of the latter was sodium chromate 0.4 f, sodium cyanide 2.0 f, ammonium hydroxide 8.6 f, and ethanol 10% by volume. Before use the precipitant was saturated with thallous chromate, and cooled in an ice-bath.

The beaker containing the precipitate was swirled in the ice-bath for about a minute after the precipitation in order to dissipate the heat of neutralization of the perchloric acid. The precipitate was then filtered off into a sintered-glass funnel; the filtrate contained the trivalent thallium, whose activity was determined by the procedure described below. When it was desired also to determine the activity in the precipitate, the latter was dissolved in a dilute, acid solution of sodium bisulfite.

Experiments showed that when 0.02 f thallous ion was precipitated as thallous chromate by the use of the reagent described above, less than 1% remained in solution. Under these conditions trivalent thallium does not precipitate. The cyanide complex formed by trivalent thallium must be quite stable, as thallic hydroxide will dissolve in 2 f sodium cyanide, even though the solubility product $(Tl^{+++})(OH^-)^3$ has been reported as approximately 10^{-44}.[7]

(1) Research supported in part by the Atomic Energy Commission.

(2) (a) J. Zirkler, Z. Physik, **99**, 669 (1936), et al.; (b) V. Majer, Z. physik. Chem., **A179**, 51 (1937).

(3) G. Harbottle and R. W. Dodson, THIS JOURNAL, **70**, 880 (1948).

(4) R. J. Prestwood and A. C. Wahl, ibid., **70**, 880 (1948), and ibid., **71**, 3137 (1949).

(5) In this paper "*f*" is used to designate concentration in formula weights per liter of solution ("volume-formal" concentration).

(6) M. Hollingsworth and C. W. Foulk, THIS JOURNAL, **45**, 1220 (1923).

(7) M. S. Sherrill and A. J. Haas, Jr., ibid., **58**, 953 (1936).

TABLE I

DETERMINATION OF ORDER OF THE EXCHANGE REACTION

Per-chloric acid, f	Hydro-chloric acid, f	Temp., °C.	(a) Thallic f	(b) Thallous f	R, f-hr.$^{-1a}$ × 10^5	$k = \frac{R}{ab} f^{-1}$-hr.$^{-1}$	α (order in a)	β (order in b)
6.0	0	41.8	0.00847	0.0251	3.89	0.182		
			.01692	.0201	5.94	.174		
			.00677	.0201	2.38	.175	1.00	0.94
			.00677	.01005	1.24	.182		
5.4	0.6	31.8	.000677	.000100	3.24	479		
			.000135	.000100	0.69	511	0.96	1.04
			.000677	.00100	35.7	527		

^{a} The abbreviation f-hr.$^{-1}$ represents moles per liter of solution per hour.

It was necessary to modify the above procedure for reaction mixtures very dilute in thallous ion, as the slow formation of the precipitate precluded quantitative recovery. In such cases about 20 mg. of carrier, inactive thallous ion was added to the precipitant after addition of the aliquot portion of the reaction mixture. The procedure described above was then followed.

The radioactivity of the various thallium fractions was determined with thin-walled glass Geiger–Müller tubes which could be immersed with reproducible geometry in the solutions. Under such conditions the counting rate is proportional to the volume concentration of the radioactive substance. When it was desired to compare the radioactivity of solutions of differing density, it was necessary to apply a correction for the effect of density on the counting rate. The correction never exceeded 4%. In addition to the density correction, a further correction was made for coincidence loss in counting. This correction, determined empirically, was usually small, and only reached 3% at a counting rate of 7,000 counts per minute, corresponding to a resolving time of approximately 3.4 × 10^{-4} second. The counter tubes were operated with a scale-of-32 counting circuit (Instrument Development Laboratories, Model 161).

All counting was made in comparison to a standard, which was a dilute solution of radioactive thallous perchlorate, kept, when not in use, in a tightly-sealed container. The standard was counted before and after each set of determinations; if the values obtained differed by more than 5% the entire set was recounted. The background was determined daily and subtracted from all observed counting rates.

Order of the Reaction.—The rate data are interpreted in terms of the first order law which applies to exchange reactions occurring at equilibrium[8]

$$\ln (1 - x/x_\infty) = - \frac{R}{ab} (a + b)t \qquad (1)$$

where x and x_∞ are the specific activities of the initially-inactive reactant measured at time t and at infinite time, and a and b are the over-all concentrations of the two reactants. R is the constant rate at which exchange processes are occurring in the reaction mixture. Sample plots of the data in terms of equation (1) are given in Fig. 1. The curves indicate a zero time exchange of about 5%. This effect is believed to be caused by the separation method, and in our measurements ranged from 5–10%. It has been shown[4] that if the effect is reproducible in any given run it does not introduce error in the slope, from which the rate is calculated.

In general, R will be some function of the over-all concentrations of the reactants, and considering the over-all reaction we assume that

$$R = ka^\alpha b^\beta \qquad (2)$$

where α is the dependence on the concentration a

(8) (a) H. A. C. MacKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

and β the dependence on b. The quantity k is a specific rate constant. The order of the reaction is then $\alpha + \beta$. If these are each unity, equations (1) and (2) may be combined to give a useful expression

$$k = \frac{0.693}{t_{1/2}(a + b)} \qquad (3)$$

where $t_{1/2}$ is the half-time for the isotope exchange reaction whose first order law is given by equation (1), in analogy with the radioactive decay law.

We have determined the dependence of R on the concentrations a and b in two media: 6.0 f perchloric acid, and a mixture containing 5.4 f perchloric and 0.6 f hydrochloric acids. The results, given in Table I, indicate that the reaction is first order in the over-all concentration of each oxidation state. Preliminary measurements of lower accuracy, made at $\mu = 0.41$ (HClO$_4$ 0.41 f), led to values 0.82 and 1.03 for α and β, respectively. The departure from unity is within the estimated error of these measurements.
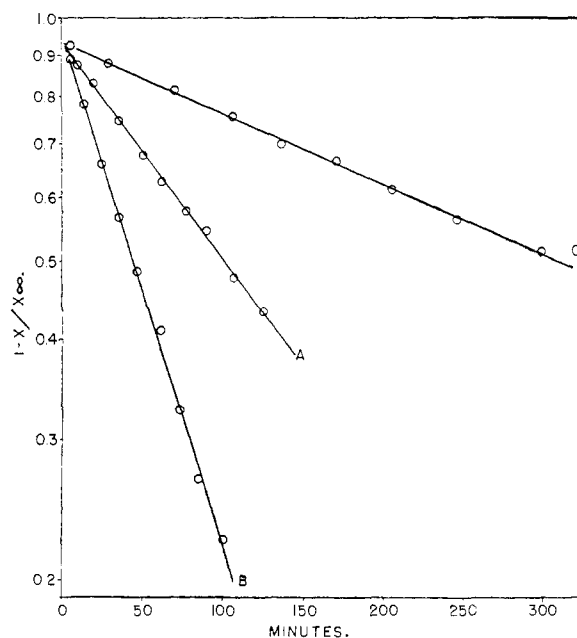

Fig. 1.—Typical rate data. Solutions 5.4 f in HClO$_4$, 0.6 f in HCl: Curve A, thallous 6.8 × 10^{-4}, thallic 1 × 10^{-4} f; Curve B, thallous 6.8 × 10^{-4}, thallic 1 × 10^{-3}; Curve C, thallous 1.35 × 10^{-4}, thallic 1 × 10^{-4}.

Rates in Perchloric Acid–Sodium Perchlorate Mixtures.—Since it seemed probable that thallic

ion is extensively hydrolyzed in solution, the effect of variation of acid concentration on the rate was determined. To this end, the reaction was studied in mixtures of sodium perchlorate and perchloric acid in which the ionic strength was maintained constant at 6.0 formal. The concentration of perchloric acid assumed the values 6, 5, 4, 3, 2, 1, 0.5 and 0.3 formal. The reactants were present in small concentrations, and their contributions to the ionic strength were not con-

sidered. Half-times and other data for the exchange reactions are presented in Table II.

Rates in Solutions Containing Chloride.—The reaction was also studied in solutions containing mixed hydrochloric and perchloric acids, with constant ionic strength 6.0 formal. Data relating to rate determinations in these solutions are presented in Table III.

The rate data are exhibited in Fig. 2, which shows a plot of rate constant k versus chloride added.

It is seen that chloride has a powerful effect on the rate. A surprising feature is that the rate in the presence of low concentrations of chloride is considerably depressed below its value in the absence of chloride, while it is strongly accelerated above this value at higher chloride concentrations. In several runs at 0.01 f chloride, no homogeneous exchange whatever was observed over a period of two months, whereas in the absence of chloride exchange would have been 75% complete.

Thallium Complexes

Because of their relevance to the effect of chloride on the rate, we summarize here the results of some observations we have made on the chloride complexes of thallium.

The results of transference experiments showed that while trivalent thallium moved toward the cathode, as expected, in 5 f perchloric acid, it moved toward the anode in a mixture 4.5 f in perchloric and 1.5 f in hydrochloric acid. With a solution 0.0067 f in thallic, 0.01 f in hydrochloric acid and 6 f in perchloric acid, the thallium moved toward the cathode carrying chloride with it. No chloride migrated toward the anode. Potentiometric titrations of trivalent thallium with hydrochloric acid were carried out. The titration curves showed breaks corresponding to two and four chlorides added per trivalent thallium. The empirical formula of the trivalent thallium com-

Table II

EXCHANGE IN MIXED SODIUM PERCHLORATE–PERCHLORIC ACID SOLUTIONS OF CONSTANT IONIC STRENGTH 6.0 FORMAL

Temp., °C.	Perchloric acid, f	(a) Thallic f	(b) Thallous f	$t_{1/2}$ hr.	Rate constant k (equation 3) f^{-1} hr.$^{-1a}$
25.0	6	0.00677	0.02008	823	0.0313
	4	.00677	.02008	600	.0430
	3	.00677	.02008	507	.0508
	2	.00677	.02008	391	.0660
	1	.00677	.02008	370	.0697
	0.5	.00339	.02008	381	.0774
	0.3	.00339	.02008	387	.0762
32.2	6	.00847	.02452	302	.0695
	5	.00847	.02462	256	.0818
	4	.00847	.02510	214.5	.0962
	3	.00847	.02510	197.5	.105
	2	.00847	.02510	177	.117
	1	.00847	.02510	157	.131
	0.5	.00339	.02510	171	.142
	0.3	.00339	.02510	175	.139
41.8	6	.00847	.02510	113.2	.182
	5	.00847	.02510	102	.202
	4	.00847	.02510	96	.215
	3	.00847	.02510	82.5	.250
	2	.00847	.02510	73.5	.281
	1	.00847	.02510	68	.304
	0.5	.00339	.02510	76	.320
	0.3	.00339	.02510	77.2	.315

[a] The abbreviation f^{-1}hr.$^{-1}$ represents reciprocal moles per liter of solution per hour.

Table III

EXCHANGE IN MIXED PERCHLORIC ACID–HYDROCHLORIC ACID SOLUTIONS OF CONSTANT IONIC STRENGTH AND CONSTANT ACID CONCENTRATION 6.0 FORMAL

Temp., °C.	Chloride added, f	(a) Thallic f	(b) Thallous f	$t_{1/2}$ min.	Rate constant k (equation 3) f^{-1} min.$^{-1}$
31.8	1.50	1.354×10^{-4}	1.00×10^{-4}	84.8	34.7
	1.00	1.354	2.006	90	22.9
	0.60	6.772	1.003	112	8.0
	.60	6.772	1.00×10^{-3}	47.3	8.75
	.60	1.354	1.00×10^{-4}	348	8.5
	.40	6.772×10^{-3}	1.00×10^{-3}	32.5	2.75
	.20	6.772	1.003	254	.351
	.12	6.772	1.003	834	.107
	.09	6.772	1.003	2770	.032
	.06	6.772	2.51	7470	.010
	.035	6.772	2.51	90000	.001
	.02	6.772	2.01×10^{-2}	$ca.\ 4.3 \times 10^{5}$	6×10^{-5}
	.01	6.772	2.01	v. long	$<5 \times 10^{-4}$
	.01	6.772	2.01	v.v. long	$<1.7 \times 10^{-6}$
	0				1.0×10^{-3a}
41.8	1.50	1.354×10^{-4}	1.00×10^{-4}	26.9	114 ± 9
	.40	6.772	1.00×10^{-3}	31.7	13 ± 0.6

[a] This value of k, included for purposes of comparison, refers to the exchange reaction in 6.0 f perchloric acid, and was calculated from data reported in Table II.
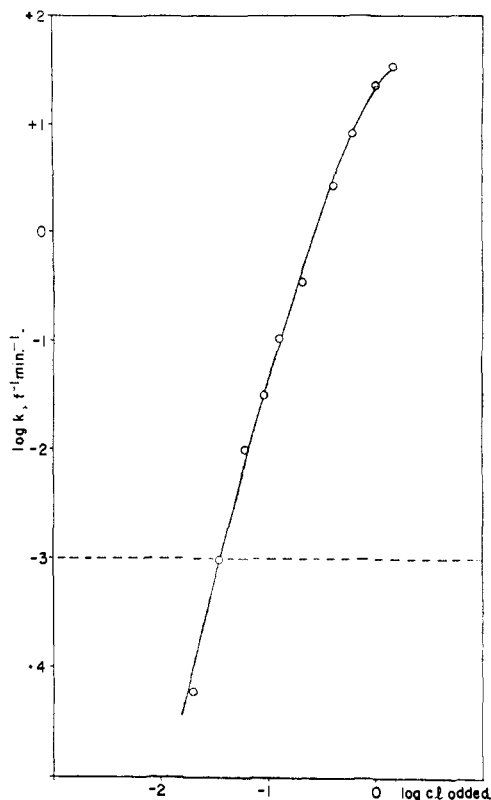
Fig. 2.—Rate constant vs. chloride concentration in per-chloric–hydrochloric acid mixtures, total concentration 6.0 f. Dotted line indicates value of rate constant in absence of chloride.
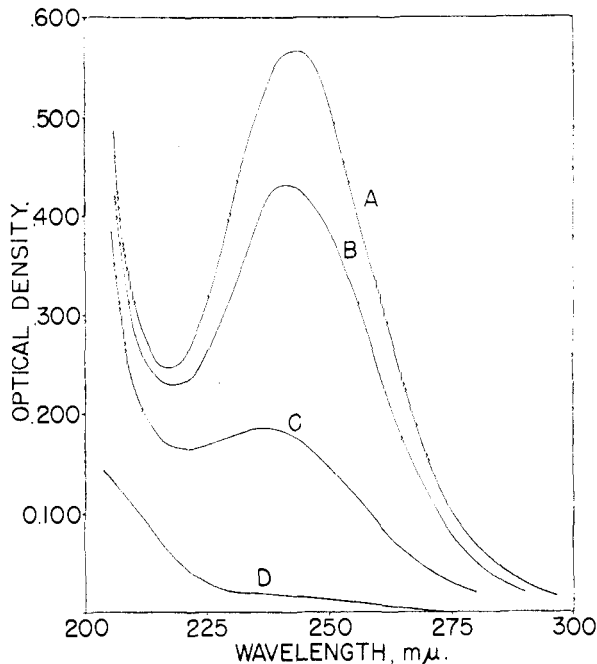

Fig. 3.—Absorption spectra of thallic perchlorate in 6.0 f perchloric–hydrochloric acid mixtures. Thallic perchlorate 3.4 × 10^{-4} f; hydrochloric acid, Curve A, 0.96–0.02 f (ten solutions). Curve B, 0.0005 f. Curve C, 0.0001 f. Curve D, no chloride.

pound extracted[9] into diethyl ether from 1 f hydrochloric acid was found by analysis of the ether phase to be $H_{1.0}TlCl_{4.0}$, with uncertainties of about ± 0.05 in the subscripts. It is evident that quite stable chloride–thallic complexes exist; our work gives definite evidence for the species $TlCl_2^+$ and $TlCl_4^-$. These observations are compatible with the study of Benoit,[10] reported after the present work was done. He estimates dissociation constants from $10^{-8.1}$ to $10^{-2.2}$ for the successive complexes from $TlCl^{++}$ to $TlCl_4^-$.

Figure 3 shows absorption spectra (obtained with a Beckman DU spectrophotometer) of perchloric acid solutions containing trivalent thallium and varying amounts of chloride. The spectra exhibit a peak at 245 mμ, undoubtedly due to complex formation, at chloride as low as 0.0001 f. The absorption increases markedly as chloride is increased above this concentration; but the effect is saturated at chloride 0.02 f, no increase occurring between 0.02 f and 0.96 f.

Solutions of thallous chloride are reported[11] to contain undissociated TlCl, the dissociation constant of which has been estimated as about 0.25. When excess chloride is added, an absorption peak appears at 229–245 mμ. Its intensity continues to rise as chloride concentration is increased

(9) A. A. Noyes, W. C. Bray and E. B. Spear, THIS JOURNAL, 30, 515, 559 (1908).

(10) R. Benoit, Soc. chim. France, 5–6, 518 (1949).

(11) See, e.g., (a) W. C. Bray and W. J. Winninghoff, THIS JOURNAL, 33, 1663 (1911); (b) E. Hogge and A. B. Garrett, ibid., 63, 1089 (1941); (c) O. D. Black and A. B. Garrett, ibid., 65, 862 (1943).

to 6 f. This peak was attributed by Fromherz and Lih[12] to chloride–thallous complexes such as $TlCl_3^-$ or $TlCl_4^-$. It is clear from their spectrophotometric data and ours that these higher chloride complexes of univalent thallium are only weakly associated.

Discussion

It appears from the data presented above that the exchange reaction remains essentially bimolecular over large ranges of hydrogen-ion activity, and even with the addition of hydrochloric acid (0.6 f) which results in an 8000-fold increase in the specific rate constant. We therefore conclude that all significant exchange reactions are first order in each of the thallous and thallic species which participate.

The variation of rate constant k (Equation 3) with concentration of perchloric acid in sodium perchlorate–perchloric acid mixtures shows that the rate of exchange decreases with increasing hydrogen ion concentration. This suggests that hydrolysis of thallic ion occurs and that the more-hydrolyzed species exchanges more rapidly. It is assumed that thallic, rather than thallous ion hydrolyzes, since thallous hydroxide is known to be a strong base. For this discussion, a rapid hydrolytic equilibrium of the following type is assumed

$$Tl^{+++} + H_2O \rightleftharpoons TlOH^{++} + H^+ \qquad (4)$$
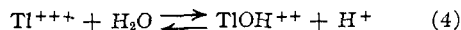
with a hydrolysis "equilibrium constant" given by

$$K = (TlOH^{++})(H^+)/(Tl^{+++}) \qquad (5)$$

where the parentheses indicate concentrations, and the approximation that activity coefficients

(12) H. Fromherz and K. H. Lih, Z. physik. Chem., A153, 335 (1931).

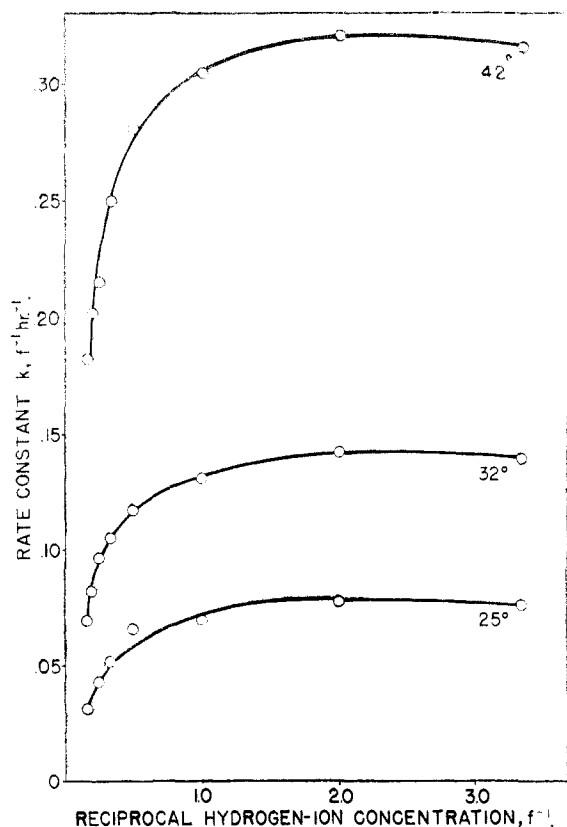are constant at constant ionic strength is implied. Then if only the two species of trivalent thallium,

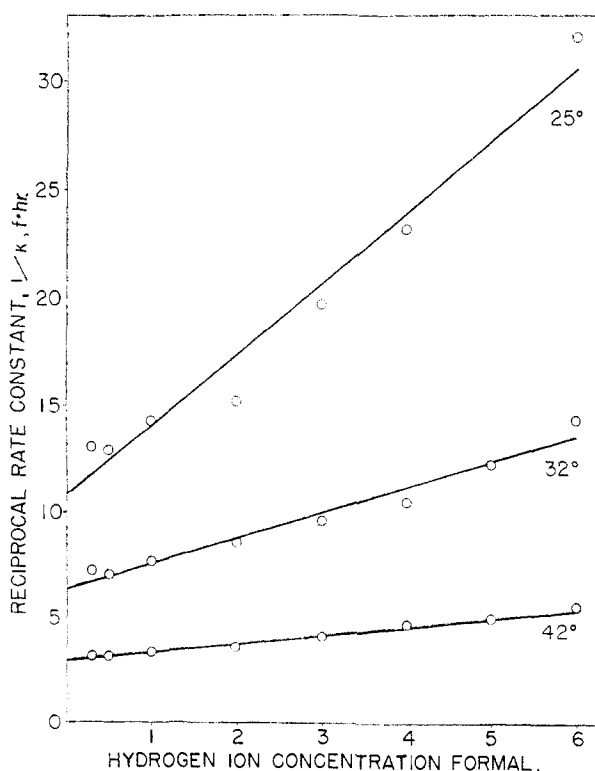Fig. 4.—Rate constant k vs. $1/(H^+)$ for exchange in perchloric acid–sodium perchlorate.

Fig. 5.—Reciprocal rate constant $(1/k)$ vs. (H^+) for exchange in perchloric acid–sodium perchlorate mixtures.

Tl^{+++} and $TlOH^{++}$ are present, the observed rate R (Equation 2) will be a sum of contributions from the reactions of thallous ion with these species

$$R = k_1(Tl^{+++})(Tl^+) + k_2(TlOH^{++})(Tl^+) \quad (6)$$

where k_1 and k_2 are specific rate constants for bimolecular exchange between the pairs as indicated. This leads to the relation

$$\frac{R}{ab} = k = \frac{k_1(H^+) + k_2K}{(H^+) + K} \quad (7)$$

where a is the total thallic, b the total thallous concentration.

The data give no indication that additional hydrolytic steps affect the rate. We have considered two sets of assumptions which lead to simpler rate laws: (1) Both Tl^{+++} and $TlOH^{++}$ contribute to the observed exchange, but Tl^{+++} is only slightly hydrolyzed: this is equivalent to $k_2 \gg k_1$ and $K \ll (H^+)$, and corresponds to the conclusion reached by Prestwood and Wahl.[4] (2) Both Tl^{+++} and $TlOH^{++}$ are present in significant concentrations, but only $TlOH^{++}$ exchanges with thallous ion.

Assumptions (1) lead to a rate law

$$k = k_1 + k_2K/(H^+) \quad (8)$$

which predicts that a plot of k versus $1/(H^+)$ should give a straight line.

Assumptions (2) lead to

$$1/k = ((H^+)/k_2K) + 1/k_2 \quad (9)$$

which predicts that a plot of $1/k$ versus (H^+) should give a straight line.

Plots of our data according to equations (8) and (9) are given in Figs. 4 and 5, respectively. The lines drawn in Fig. 5 were constructed by means of a least-squares treatment. It is clear that assumptions (1) are not consistent with our results. The more limited range of acid concentration employed in the experiments of Prestwood and Wahl[4] did not suffice to reveal the great curvature of plots based on equation (8), as displayed in Fig. 4. Assumptions (2) are supported by the accord between the data and the functional dependence of rate constant on acid concentration predicted by equation (9), as shown in Fig. 5.

Changes of activity coefficients due to the replacement of hydrogen ion by sodium ion at constant ionic strength have been ignored in the foregoing discussion, since available data do not permit an evaluation of such effects in the systems studied. If these effects are subsequently found to be large, the hydrolysis interpretation would correspondingly be subject to revision.

We have also attempted to fit our data with expressions which contain the Hammett acidity function[18] but were unsuccessful.

TABLE IV

TEMPERATURE EFFECTS ON THE EXCHANGE REACTION IN SODIUM PERCHLORATE–PERCHLORIC ACID

Temp., °C.	Rate constant k_2, f^{-1} hr.$^{-1}$	Hydrolysis constant, K
25.0	0.0935	3.2
32.2	.157	5.3
41.8	.346	6.9

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940.

If the rate law derivable from assumptions (2) (Equation 9) is adopted as correct, the intercepts of the three lines give the values of k_2 at different temperatures listed in Table IV, which also gives values of the concentration hydrolysis constant K computed from the data.[14]

A plot of ln k_2 versus $1/T$ is given in Fig. 6. The value obtained for the energy of activation is 14,700 cal./mole.

From the Eyring absolute rate equation for a bimolecular reaction in solution[15] the standard entropy of activation may be calculated. The value obtained is -32 cal./deg. mole, which may be compared with the result -18.8 cal./deg. mole found for the electron transfer exchange reaction between the ethylenediamine complexes of cobaltous and cobaltic cobalt,[16] and values ranging from -20 cal./deg. mole to -32 cal./deg. mole listed by Glasstone, Laidler and Eyring[17] for a number of reactions between ions of like sign.

The data presented in Table III and Fig. 2 show the marked catalytic effect of chloride on the rate of exchange: as the concentration of chloride is varied from nearly zero to 1.5 formal the specific rate constant changes by several million-fold. It is also striking that at chloride concentrations comparable to those of the trivalent thallium the specific rate constant is several hundred-fold smaller than that observed for perchloric acid solutions containing no chloride whatever. Parallel behavior is shown by the oxidation reaction of stannous tin by ferric iron, studied by Noyes,[18] Robinson and Law,[19] and Gorin.[20] Both Robinson and Law and Gorin found that the rate decreased with increasing concentration of perchloric acid; the latter reported that the rate in perchloric acid was slower by a factor of 10^5–10^6 than that in hydrochloric acid. Robinson and Law also noted that the rate passed through a minimum with the addition of small amounts of chloride. These effects are doubtless due to the formation of chloride complexes.

A reasonable interpretation of the effect of chloride on the exchange rate in the thallous–thallic system is that the chloride complexes which form as chloride is added react with different rates than do the uncomplexed ions. On this view, the complex species first formed are less reactive; these are converted with increasing chloride to higher complexes which are more reactive than the uncomplexed ions.

Conclusive identification of the reacting species

(14) Although no direct check of these values of K with that deduced by Benoit is possible because of the very different ionic strength in his experiments, it is interesting to note that he reports, as a rough value, $10^{-14.00}$ for the constant $([Tl^{+++}][OH^-])/([TlOH^{++}])$ apparently at 18°. This would give 0.6 for $([TlOH^{++}][H^+])/([Tl^{+3}])$ at the same temperature. The brackets represent activities.

(15) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Equation 38, p. 417.

(16) W. B. Lewis, Technical Report No. 19, Laboratory for Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, January, 1949.

(17) S. Glasstone, K. J. Laidler and H. Eyring, ibid., p. 435.

(18) A. A. Noyes, Z. physik. Chem., 16, 546 (1895).

(19) R. A. Robinson and N. H. Law, Trans. Faraday Soc., 31, 899 (1935).

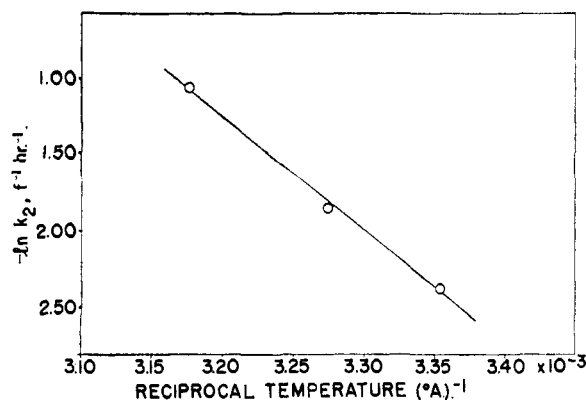(20) M. H. Gorin, THIS JOURNAL, 58, 1787 (1936).

Fig. 6.—Plot to determine energy of activation of exchange in perchloric acid–sodium perchlorate mixtures.

in the chloride system is not possible at present; however, certain inferences can be drawn from the information about thallium complexes given above. It is evident that when the rate is retarded by small amounts of added chloride the univalent thallium is still largely present as Tl^+, while the trivalent thallium exists as $TlCl_2^+$, and possibly as $TlCl^{++}$. We therefore conclude that $TlCl_2^+$ has a much lower specific rate of exchange with Tl^+ than does uncomplexed, or hydrolyzed, thallic ion.

In the region in which the rate is greater than in the absence of chloride the predominant thallic species is probably $TlCl_4^-$. The ultraviolet absorption peak ascribed to the chloride–thallic complexes remains unchanged in height or position as total chloride is varied from 0.02 to 0.96 f, over which range the rate constant increases by about 10^5. This increase cannot be due to increase in the concentration of $TlCl_4^-$; and it seems plausible that it results from the increasing concentration of a weakly associated thallous complex. We are thus led to the hypothesis that the reacting species in the chloride catalyzed reaction are $TlCl_4^-$ and a thallous complex such as the $TlCl_3^-$ or $TlCl_4^-$ proposed by Fromherz and Lih.[12]

The temperature coefficients of rate k for the chloride catalyzed reaction are somewhat larger than for the rate in the absence of chloride. At 0.4 f HCl, 5.6 f HClO$_4$, the activation energy calculated in the usual way is 29.6 $\pm$ 1 kcal./mole. This number of course includes contributions from the ΔH of the reactions in which the reacting species are formed.

With additional data on the chloride complexes of thallium, it should be possible to connect the rate quantitatively with the concentrations of these ions over the complete range from zero added chloride to the region of strongly accelerated rate. It will then be of interest to attempt to relate the variations in the energy and entropy of activation to the structure of the complexes. Further measurements are being carried out with this in mind.

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