A Kinetic Study of the Isotopic Exchange of Thallium(III) between the Thallium(III) Ion and the Thallium *N*-2-Hydroxyethylethylenediamine-*N*, *N'*, *N'*-triacetate Complex in Water

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The kinetic study of isotopic exchange involving co-ordinated compounds with a d^{10} structure, will in this paper be extended to thallium(III), with ^{204}Tl as tracer. The exchange of thallium in its *N*-2-hydroxyethylethylenediamine-*N,N',N'*-triacetate (henceforth written as EDTA-OH with the formula H_3Z) is very fast in strongly basic and acid solutions. The rate is measurable in the pH regions from 4 to 6 and from 7 to 10 under appropriate experimental conditions. This paper will give the results of kinetic studies of the thallium EDTA-OH complex $[TlZ\cdot OH_2]\cdot H_2O$ with thallium(III), in basic, neutral and acid media separately, and the mechanisms will be discussed.

Unlike the cases involving corresponding gallium and indium complexes, tervalent thallium is very unstable and is readily reduced to thallium(I) or precipitated as thallium(III) oxide. Hence, the exchange kinetics can be studied only in the presence of triethanolamine and chloride; their contribution to the reaction kinetics was precisely examined, as will be seen below. The thallium(III) ion will be present in a rather complicated form in the given solutions, but the state does not appear important in discussing the reaction mechanism. The rate constant is independent of the concentration of uncomplexed thallium, although it is proportional to that of the complex throughout these regions. Hence, it is written in the chemical equations in rather arbitrary forms, such as $[Tl(TEA)_x]^n$ or $[Tl(TEA)_xCl_y]^n$.

Experimental

The Preparation of the Complex.—The processed radioisotope ^{204}Tl (half life 3.56$_y$, Radio Chemical Centre, Amersham) with a specific activity about 0.15 mc./mg. was diluted to produce radioactive thallium with a specific activity of 0.4 μc./mg. Commercial univalent thallium nitrate in water (extra pure grade) was oxidized by bromine in an acid solution and precipitated with an aqueous ammonia solution as thallium(III) oxide. The precipitate was then filtered off, dried for about 2 hr. at 120°C, weighed, and dissolved in 6 N nitric acid to give a thallium(III) nitrate solution. The absence of thallium(I) was confirmed with a potassium chromate solution.

The thallium EDTA-OH complex was formed instantaneously on mixing a thallium(III) nitrate solution in nitric acid with an equivalent amount of EDTA-OH in water. The labeled complex was prepared immediately before use from a radioactive thallium(III) nitrate solution with a suitable specific activity and an equivalent amount of EDTA-OH in water. When titrated with a sodium hydroxide solution, an aqueous solution of this complex gave the titration curve shown in Fig. 1. From analogy to the corresponding gallium and indium homologue[2,3] and thallium(III) EDTA complex,[5] it is very probable that the [TlZ] complex contains one mole of co-ordinated water. The first rise in the curve will correspond to the neutralization of the H^+ liberated from H_3Z, and the second, to that of the H^+ liberated from the co-ordinated water.

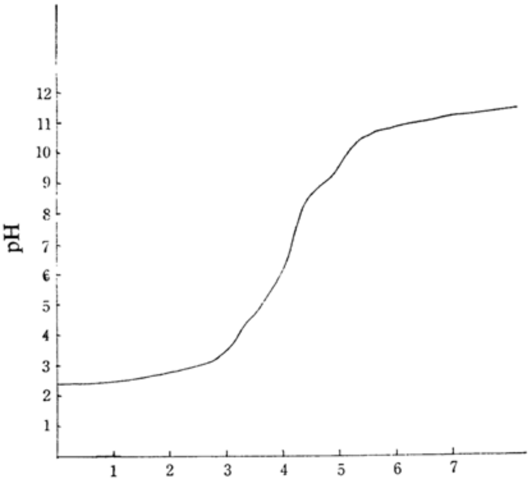

Fig. 1. Titration of $[Tl\cdot EDTA\text{-}OH\cdot OH_2]\cdot H_2O$ with sodium hydroxide.
$[TlZ\cdot OH_2]\cdot H_2O$, 1.2×10^{-4} M; $\mu=0.20$ (KNO_3); 25°C

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1) H. A. C. Mckay, *Nature*, **142**, 997 (1938).

2) K. Saito and M. Tsuchimoto, *J. Inorg. Nucl. Chem.*, **23**, 71 (1961).

3) K. Saito and M. Tsuchimoto, This Bulletin, **36**, 1073 (1963).

4) K. Saito and M. Tsuchimoto, *J. Inorg. Nucl. Chem.*, **25**, 1245 (1963).

5) M. Tsuchimoto and K. Saito, ibid., in press.

$$H_3Z+Tl^{3+}\ aq. \rightleftharpoons [TlZ\cdot OH_2]+3H_2O$$

$$[TlZ\cdot OH_2] \rightleftharpoons H^+ + [TlZ\cdot OH]^-$$

Buffers.—Since thallium(III) is readily reduced to the thallium(I) state, only a few varieties of buffers are useful. The tartrate and citrate used in the studies with gallium and indium are not useful. In basic media *p*-hydroxybenzoate, glycine, ammonia, and barbiturate were used, whereas in the neutral region only barbiturate was useful. In the weakly acid region acetate was used. Their participation in the kinetics was carefully examined, as will be seen in the next section.

The Procedure for Kinetic Runs.—An aqueous thallium(III) nitrate solution (not radioactive) was mixed with potassium nitrate (or potassium chloride and nitric acid in the acid region), triethanolamine and the buffer in order to give it an appropriate pH value and ionic strength. A radioactive thallium(III) nitrate solution was mixed with an equivalent amount of EDTA-OH, potassium hydroxide (or nitric acid), and potassium chloride, and the pH value was made approximately the same as that of the thallium(III) solution with which the isotopic exchange is studied. Both solutions were mixed in a thermostat. An aliquot was taken at selected intervals, and a part of the initially-inactive thallium(III) precipitated with 8-quinolinol in ethanol, less than the equivalent of that of the initially-inactive thallium(III), the pH being adjusted to 5—7 with diluted nitric acid (or an aqueous ammonia solution). The precipitate was swiftly filtered through a filter paper of fine texture, washed with water, and dried under an infrared lamp. The composition of the thallium(III) 8-quinolinol complex remained unchanged in the presence of an excess of thallium(III) and the thallium(III) EDTA-OH complex. The pH value of the reaction mixture was measured carefully with a glass electrode pH meter from time to time during the kinetic runs in order to confirm the maintenance of the chemical equilibrium.

The Measurement of Radioactivity.—The Geiger-Müller counting method was adopted. ^{204}Tl gives β rays of a maximum energy, 0.764 MeV. Dried thallium(III) oxinate on the filter paper was placed about 27.5 mm. below a Geiger-Müller tube, and the counting rate was measured. It was proportional to the amount of radioactive thallium on the filter.

The Measurement of the Thallium.—After the measurement of the radioactivity, the precipitate on the filter paper was placed in a flask containing a few drops of 6 N hydrochloric acid and treated with 50 ml. of hot water and a known excess of a disodium EDTA solution. After the pH had been adjusted to 4—5 with an ammonium acetate solution, excessive EDTA was back-titrated with an indium nitrate solution, using xylenol orange as an indicator. The specific activity was calculated from the titrated amount of thallium(III). The direct titration of thallium(III) with disodium EDTA was not successful because of the precipitation of thallium(III) oxide and the 8-quinolinol complex.

The fractional exchange, *F*, is expressed by:

$$F=(x_i-x_0)/(x_\infty-x_0)$$

where x_∞, x_i and x_0 are the specific activities at infinite time, time *i* and time zero respectively, the last being about 5—30 min. after the solution is mixed.

The reaction was very slow in a neutral solution at 25°C, and so the kinetics was mainly studied at 40°C.

Results and Discussion

The rate of exchange, *R*, is expressed by McKay's[1] formula:

$$R=-2.303\cdot\frac{a\cdot b}{a+b}\cdot\frac{\log(1-F)}{t}$$

where *a* and *b* are the molar concentrations of the uncomplexed thallium (initially inactive) and of the thallium EDTA-OH respectively; *t* is the lapse of time in seconds, and *F*, the fractional exchange.

The *R* values are independent of the concentration of uncomplexed thallium ions (*a*)

TABLE I. RELATIONSHIP BETWEEN THE EXCHANGE RATE AND THE CONCENTRATION OF UNCOMPLEXED THALLIUM AND THALLIUM EDTA-OH COMPLEX

a 10^{-3} M	*b* 10^{-3} M	*R* 10^{-8} mol. l$^{-1}\cdot$ sec^{-1}	*k* $10^{-5}\cdot$sec^{-1}
in weakly basic media			
0.80	1.20	3.22	2.68
2.00	1.20	3.53	2.94
1.20	0.72	1.88	2.61
1.20	1.92	5.21	2.54
μ=0.20 (KNO$_3$); 25°C; TEA 0.1205 M; KCl 0.0015 M; pH 9.70; ammonia 0.2 M (0.032 M NH$_4$Cl);			
0.80	1.20	1.84	1.54
2.00	1.20	1.72	1.43
1.20	0.72	1.14	1.58
1.20	1.92	2.75	1.43
μ=0.20 (KNO$_3$); 25°C; TEA 0.1205 M; KCl 0.0015 M; pH 8.50; barbiturate 0.05 M;			
in neutral media, near pH 7			
0.80	1.20	0.560	0.467
2.00	1.20	0.537	0.447
1.20	1.20	0.547	0.456
1.20	2.40	1.13	0.471
μ=0.20(KNO$_3$); 40°C; TEA 0.1205 M; KCl 0.0015 M; barbiturate 0.025 M;			
in acid media, pH 4.40			
0.70	1.20	5.36	4.47
2.00	1.20	5.56	4.63
1.20	0.60	2.35	3.92
1.20	2.40	9.71	4.05
μ=0.20(KCl); 25°C; TEA 0.0268 M; NaAc 0.025 M;			

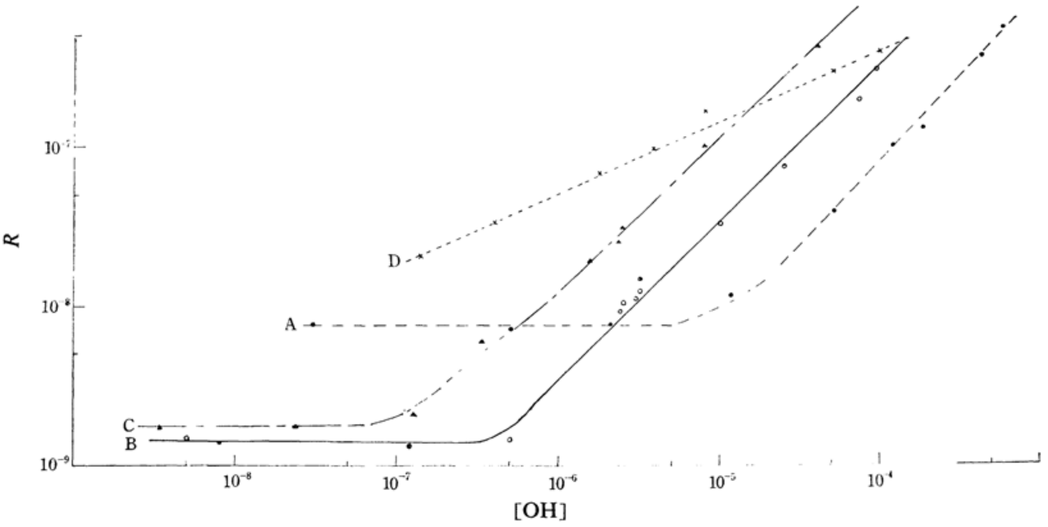


Fig. 2. Relationship between [OH^-] and the exchange constant R.

$\mu=0.2$ (KNO_3) ; 25°C ; (*a*), 1.20×10^{-3} M ; (*b*), 1.20×10^{-3} M ; TEA, 0.1205 M ; KCl 0.0015 M

A: --●-- ammonia 0.2 M (0.032 M NH_4Cl) B: —○— barbiturate 0.05 M

C: —-△— glycine 0.0625 M D: ---×--- *p*-hydroxybenzoate 0.0125 M

and proportional to the concentration of the thallium EDTA-OH complex (*b*), regardless of the pH value in the given range, as is shown in Table I. Hence, the rate constant, *k*, is expressed by R/b and has a dimension of t^{-1} under the experimental conditions.

The kinetics is very different in the acid, the neutral, and the basic regions; these regions will be discussed separately below. Tervalent thallium easily gives a precipitate of thallium(III) oxide over pH 1.5. Triethanolamine and potassium chloride were added to keep the thallium(III) and thallium EDTA-OH complexes respectively in the aqueous phase. Their participation in the exchange kinetics will be discussed in detail below.

Isotopic Exchange in a Weakly Basic Solution.—Figure 2 illustrates the relationship between *k* and the OH^- ion concentration, and Fig. 3, that between *k* and the concentration of triethanolamine in various buffer solutions. In barbiturate, glycine, and ammonia buffers, the rate constant, *k*, is proportional to [OH^-] and to the concentration of triethanolamine (henceforth written as TEA):

$$R=k'\cdot b\cdot[OH^-]\cdot[TEA]$$

where [TEA] denotes the total concentration of TEA. Different ionization states of TEA do not affect the kinetic expression, because this formula is valid at various pH values, where TEA is present in different states. At a given temperature, *k* is little influenced by the concentrations of the buffering agents, ammonia and barbiturate, and it is almost

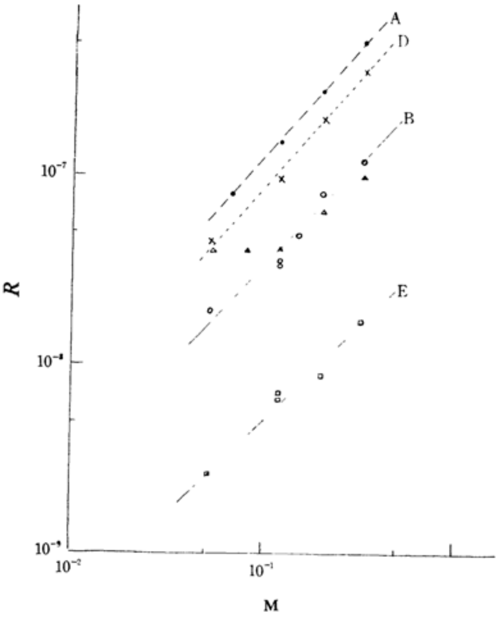


Fig. 3. Relationship between the concentration of triethanolamine and the exchange constant R.

$\mu=0.2$ (KNO_3) ; 25°C ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M ; KCl, 0.0015 M ;

A: --●-- ammonia 0.2 M (0.032 M NH_4Cl) pH 9.70
B: —○— barbiturate 0.05 M
C: —△— glycine 0.0625 M
D: ---×--- *p*-hydroxybenzoate 0.0125 M } pH 8.50
E: —□— barbiturate 0.025 M near pH 7 (40°C)

TABLE II. INFLUENCE OF BUFFER, TRIETHANOLAMINE, POTASSIUM CHLORIDE, AND IONIC STRENGTH (KNO_3) UPON THE EXCHANGE RATE

Concn. of reagents, M		KCl	μ (KNO_3)	k 10^{-5} sec^{-1}
in weakly basic media				
ammonia (NH_4Cl)	pH 9.70			
0.12	(0.019)	0.0015	0.33	3.54
0.60	(0.096)	0.0015	0.33	3.28
0.20	(0.032)	0.0015	0.33	3.22
0.20	(0.032)	0.0015	0.83	3.46
0.20	(0.032)	0.0005	0.33	3.70
0.20	(0.032)	0.0150	0.33	3.51
barbiturate	pH 8.50			
0.025		0.0015	0.33	2.26
0.20		0.0015	0.33	1.04
p-hydroxybenzoate	pH 8.50			
0.025		0.0015	0.33	8.19
0.188		0.0015	0.33	7.50
glycine	pH 8.50			
0.025		0.0015	0.33	2.97
0.0625		0.0015	0.33	4.22
0.1875		0.0015	0.33	14.9
0.25		0.0015	0.33	21.7
25°C ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M ;				
in neutral media				
barbiturate	near pH 7			
0.05		0.0015	0.33	0.306
0.125		0.0015	0.33	0.344
0.025		0.0015	0.33	0.368
0.025		0.0015	0.83	0.356
0.025		0.0010	0.33	0.390
0.025		0.015	0.33	0.350
40°C ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M ;				
in acid media				
sodium acetate	pH 4.40			
	TEA(M)	KCl		
0.025	0.0268	0.20	0	5.21
0.025	0.201	0.20	0	4.97
0.125	0.0268	0.20	0	5.25
0.025	0.0268	0.20	0.50	4.93
25°C ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M ;				

completely independent of the ionic strength and of the concentration of chloride (Table II). The temperature dependence of R is shown in Fig. 4. The Arrhenius activation energy is calculated to be 29 kcal. mol^{-1} in barbiturate and ammonia solutions.

The concentration of triethanolamine contributes to the exchange rate. The thallium(III) EDTA-OH complex is most likely present in the aqueous phase in a mixed complex anion form, containing EDTA-OH and TEA in the ligand.

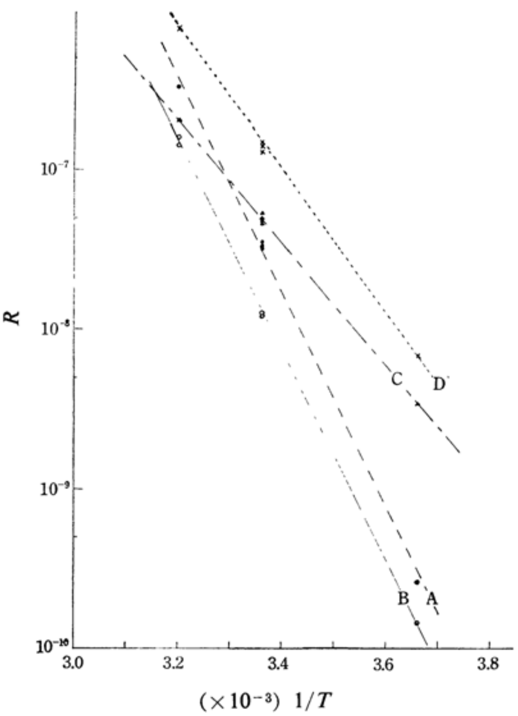


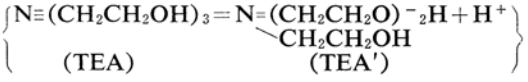
Fig. 4. Temperature dependence of the exchange constant R in weakly basic media.
$\mu=0.2$ (KNO_3) ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M
TEA, 0.1205 M ; KCl 0.0015 M
A: --●-- ammonia 0.2 M (0.032 M NH_4Cl) pH 9.70
B: —○— barbiturate 0.05 M
C: —△— glycine 0.0625 M
D: ---×--- *p*-hydroxybenzoate 0.0125 M
(B, C, D) pH 8.50

$$[{}^*TlZ\cdot OH_2]+N{\equiv}(-CH_2CH_2OH)_3 \rightleftarrows [{}^*TlZ\cdot TEA]+H_2O \qquad (1)$$

Despite their different structures, barbiturate and ammonia give the same kinetics as that mentioned above. Hence, the exchange mechanism would involve the exchange of EDTA-OH, -TEA mixed complexes, as will be shown below. Equilibrium 2 should be shifted towards the right-hand side with a rise in pH, bringing about the de-protonation of triethanolamine:

$$[{}^*TlZ\cdot TEA]+OH^- \rightleftarrows [{}^*TlZ\cdot TEA']+H_2O$$

equilibrium to form a conjugate base (2)



$$\left\{\begin{array}{ccc} N{\equiv}(CH_2CH_2OH)_3 = & N{=}(CH_2CH_2O)^-{}_2H + H^+ \\ & \diagdown CH_2CH_2OH \\ (TEA) & (TEA') \end{array}\right\}$$

$$^*[TlZ\cdot TEA']^- + [Tl(TEA)_x]^n \rightleftarrows [TlZ\cdot TEA']^- + [{}^*Tl(TEA)_x]^n \qquad (3)$$

In the case of corresponding gallium$^{2)}$ and indium[3] complexes, labile conjugate bases are formed by the de-protonation of the co-ordinated water molecule. However, the reaction mechanism does not appear to differ much. Similar values of the Arrhenius activation energies and the insignificant influence of the ionic strength (Table II) seem to support such a view. Other buffers, *p*-hydroxybenzoate and glycine seem to accelerate the exchange reaction.

In the glycine buffer, the reaction becomes more complex, and the rate constant, k, depends on the concentrations of both glycine and triethanolamine. It appears that glycine would replace co-ordinated triethanolamine, at least partly, in the presence of a large amount of glycine, and the exchange reaction proceeds in quite a different manner. Such a complication in the presence of glycine was also observed with indium EDTA[3] and EDTA-OH[4] and thallium EDTA[5] complexes.

In a *p*-hydroxybenzoate buffer solution, the rate of exchange, R, is apparently proportional to $[OH^-]^{1/2}$; therefore, the exchange reaction would involve both [TlZ·TEA] and $[TlZ \cdot TEA']^-$.

As will be shown in the next section, the former complex undergoes a slow exchang with thallium(III) independent of the $[OH^-]$ concentration, and its contribution would be negligible in a high pH region, where the latter complex gives a greater exchange rate. However, in the presence of *p*-hydroxybenzoate, the former exchange would be accelerated so that its contribution would remain significant in a high pH region, thus giving such a complicated kinetic form.

Isotopic Exchange in Neutral Solutions.—In the pH region near 6—7.5, the rate constant little influenced by pH. The exchange rate constant, k, is proportional to the concentration of triethanolamine, and it is independent of the concentrations of barbiturate and potassium chloride and also of the ionic strength (Table II):

$$R = k'' \cdot b' \cdot [\mathrm{TEA}]$$

The temperature dependence of k, which is illustrated in Fig. 5, indicates that the Arrhenius activation energy is 22 kcal./mol. Thus, the exchange seems to proceed as follows:

$$[{}^*\mathrm{TlZ \cdot OH_2}] + \mathrm{N{\equiv}(CH_2CH_2OH)_3} \xrightleftharpoons{\text{equilibrium}} [{}^*\mathrm{TlZ \cdot TEA}] + \mathrm{H_2O} \qquad (4)$$

$$[{}^*\mathrm{TlZ \cdot TEA}] + [\mathrm{Tl(TEA)}_x]^n \overset{\text{slow}}{\rightleftarrows} [\mathrm{TlZ \cdot TEA}] + [{}^*\mathrm{Tl(TEA)}_x]^n \qquad (5)$$

In this pH range, the thallium EDTA-OH complex is present mainly in the aquo complex form, as may be seen in Fig. 1, so the triethanolamine complex [*TlZ·TEA] is formed by the replacement of co-ordinated water.

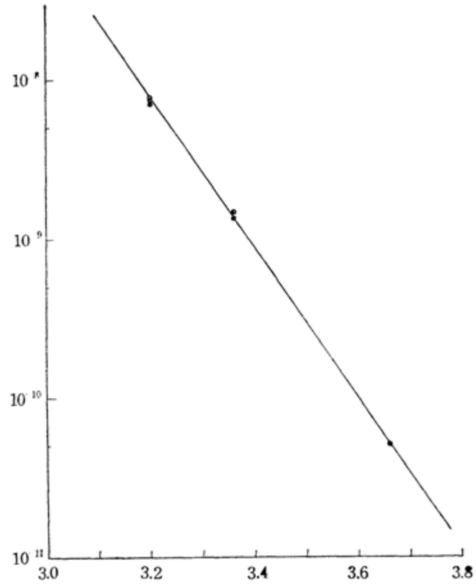


Fig. 5. Temperature dependence of the exchange constant, in neutral media.
$\mu = 0.2$ (KNO_3); (*a*), 1.2×10^{-3} M; (*b*), 1.2×10^{-3} M TEA, 0.1205 M; KCl, 0.0015 M; barbiturate, 0.025 M

Ammonia and *p*-hydroxybenzoate are not useful buffers in neutral media, and glycine reduces thallium(III) to thallium(I). Hence, only barbiturate was used as a buffer.

With a rise in pH, the co-ordinated TEA liberates protons to give a de-protonated ligand, and the isotopic exchange proceeds through the conjugate base, as Eqs. 2 and 3 show. The OH^- concentration that is independent of the exchange in neutral media would also promote the reaction in basic media with a pH of more than 8, but it would be overwhelmed by the faster exchange through the conjugate base, giving an apparent first-order dependence upon the hydroxide ion concentration.

Isotopic Exchange in an Acid Solution.—In the absence of chloride in acid solutions, a white precipitate is formed when thallium(III) nitrate and a disodium EDTA solution are mixed. When the concentration of chloride is of the same order as that of uncomplexed thallium(III), a homogeneous exchange rate is measurable near pH 3.5. However, the relationship between R and a and b is very complicated, and the rate, R, is not expressed in a simple formula. This may be due to the

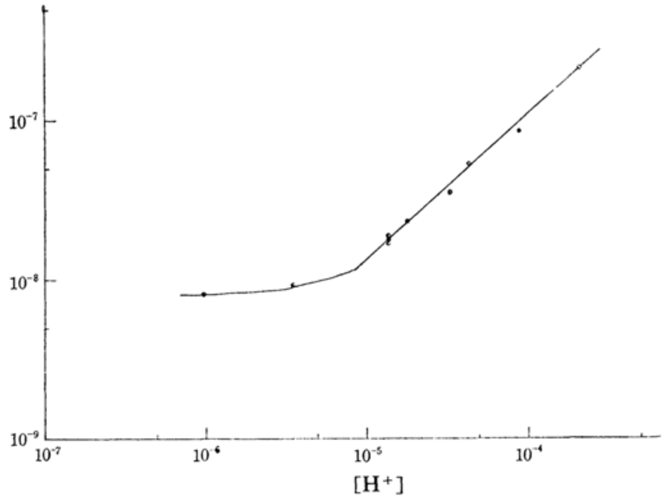


Fig. 6. Relationship between $[H^+]$ and the exchange constant in acid media.
$\mu=0.2$ (KCl) ; 25°C ; TEA, 0.0268 M ; NaOAc, 0.025 M ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M

formation of chloro-complexes, such as $[TlCl_2]^+$ and $[TlCl_4]^-$,⁶⁾ with different labilities. In the presence of a large excess of chloride, the rate, R, is expressed by $R=k\cdot b$, and it is independent of a at pH values from 4 to 6. The following discussion deals with the exchange under such conditions, the ionic strength being adjusted by potassium chloride. Figure 6 shows the relationship between k and the $[H^+]$. The k is proportional to $[H^+]$ and apparently to $[Cl^-]^{1.5}$, as Fig. 7 illustrates, so the rate constant, k, is expressed as $k=k'\cdot[H^+][Cl^-]^{1.5}$. The influence of the concentrations of triethanolamine and sodium acetate (see Experimental section) is not significant. The temperature dependence of R is shown in Fig. 8, from which the Arrhenius activation energy is calculated to be 11 kcal./mol.

In the acid solution both aquo- and chloro-mixed EDTA-OH complexes could be present and participate in the exchange reaction.

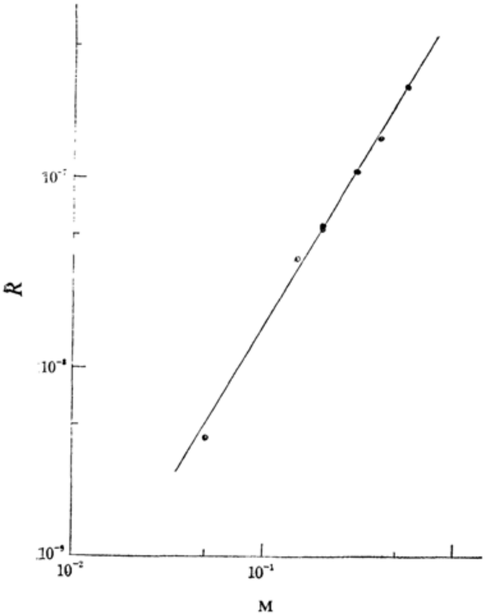


Fig. 7. Relationship between the concentration of potassium chloride and the exchange constant R, in acid media
25°C ; TEA, 0.0268 M ; NaOAc 0.025 M ; pH 4.40 ; (*a*), 1.2×10^{-3} M ; (*b*), 1.2×10^{-3} M

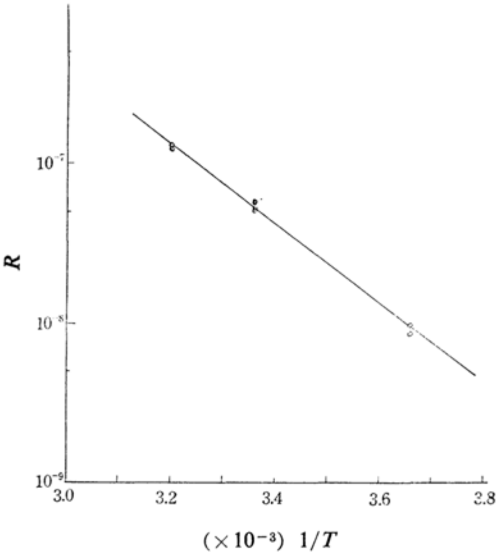


Fig. 8. Temperature dependence of the exchange rate, in acid media.
$\mu=0.2$ (KCl); TEA, 0.0268 M; NaOAc, 0.025 M (*a*) 1.2×10^{-3} M; (*b*), 1.2×10^{-3} M

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6) G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.*, 73, 2442 (1951).

TABLE III. COMPARISON OF KINETIC DATA FOR GALLIUM, INDIUM, THALLIUM COMPLEXES

	Ga·EDTA	Ga·EDTA-OH	In·EDTA	In·EDTA-OH	Tl·EDTA	Tl·EDTA-OH
K_2	1.2×10^{-6}	1.5×10^{-5}	1.6×10^{-9}	1.5×10^{-6}	3.2×10^{-7}	2.5×10^{-9}
in weakly basic media						
k	$k'\cdot[OH^-]$	$k'\cdot[OH^-]$	$k'\cdot[OH^-]^2$	$k'\cdot[OH^-]$	$k'\cdot[OH^-][TEA]$	$k'[OH^-][TEA]$
k'	11.3 (l./mol./sec.)	37 (l./mol./sec.)	52 (l^2/mol^2/sec.)	1.1×10^{-1} (l./mol./sec.)	3.4 (l./mol./sec.)	0.49 (ammonia) 2.7 (barbiturate) (l./mol./sec.)
E_A (kcal.)	25	27	25	25	22	29
in neutral media						
k				k'		$k'\cdot[TEA]$
k'				1.3×10^{-5} (sec^{-1})		9.8×10^{-6} (sec^{-1})
E_A (kcal.)				19		22
in acid media						
k	$k'\cdot[H^+]^{2.4}$	$k'\cdot[H^+]^{2.4}$	$k'\cdot[H^+]^3$	$k'\cdot[H^+]$	$k'\cdot[H^+]^{1.4}\cdot[Cl^-]^{1.5}$	$k'\cdot[H^+][Cl^-]^{1.5}$
k'	4.5×10^{-3} ($l^{2.4}/mol^{2.4}$/sec.)	1.8×10^{-2} ($l^{2.4}/mol^{2.4}$/sec.)	4.3×10 (l^3/mol^3/sec.)	1.0×10^{-2} (l./mol./sec.)	2.7 ($l^{1.4}/mol^{1.4}$/sec.)	12 (l./mol./sec.)
E_A kcal.	15	16	18	11	8.5	11

$$[{}^*TlZ\cdot H_2O]+Cl^- \rightleftarrows [{}^*TlZ\cdot Cl]^- + H_2O \qquad (6)$$

$$[{}^*TlZ\cdot Cl]^- + Cl^- \rightleftarrows [{}^*TlZ\cdot Cl_2]^{2-} \qquad (7)$$

However, when the chloride ions overwhelm the Tl-EDTA-OH complex, the $[{}^*TlZ\cdot Cl]^-$ complex would predominate to make the relation between R and b simpler. The exchange reaction would proceed through the two chlorinated forms side by side:

$$[{}^*TlZ\cdot Cl]^- + H^+ \rightleftarrows [{}^*TlHZ\cdot Cl] \qquad (8)$$

$$[{}^*TlZ\cdot Cl_2]^{2-} + [H^+] \rightleftarrows [{}^*TlHZ\cdot Cl_2]^- \qquad (9)$$

$$[{}^*TlHZ\cdot Cl] + [Tl\cdot Cl_x(TEA)_y]^n \rightleftarrows [TlHZ\cdot Cl] + [{}^*Tl\cdot Cl_x(TEA)_y]^n \qquad (10)$$

$$[{}^*TlHZ\cdot Cl_2]^- + [Tl\cdot Cl_x(TEA)_y]^n \rightleftarrows [TlHZ\cdot Cl_2]^- + [{}^*Tl\cdot Cl_x\cdot(TEA)_y]^n \qquad (11)$$

At a higher pH than 4.5, the rate is too small to be measured. In the neutral region at pH near 7, the k is independent of $[Cl^-]$ but dependent on [TEA]. Since TEA is present in the ammonium ion form in the pH region <8, its co-ordinating ability would be very small and would increase with a rise in pH. At pH values near 7, TEA in its basic form will replace co-ordinated chloride to give a rather labile mixed complex [TlZ·TEA] (Eq. 4).
Hence, Eq. 4 is more properly written as:

$$[TlZ\cdot Cl]^- + TEA \rightleftarrows [TlZ\cdot TEA] + Cl^- \qquad (4')$$

The chloro-complexes, such as $[TlZ\cdot Cl]^-$ and $[TlZ\cdot Cl_2]^{2-}$, seem to undergo isotopic exchange only through the protonated complex as an intermediate, so the rate is very small in the pH range from 4.5 to 6.

The kinetic data of the EDTA-OH complexes are summarized in Table III. The gallium complex gives kinetics different from that of indium or thallium, but it is rather similar to the EDTA complexes of these three elements. The thallium complex gives kinetic data very similar to those of the indium complex, whereas the thallium-EDTA complex gives kinetics similar to those of the gallium-EDTA complex rather than to the indium complex. Further discussion will be given elsewhere, including the exchange data of the corresponding EDTA complexes.[7]

Summary

1) The kinetics of the isotopic exchange of the thallium(III) EDTA-OH complex with uncomplexed thallium(III) has been studied in acid, neutral and weakly basic solutions, with ^{204}Tl as tracer.

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[7] K. Saito and M. Tsuchimoto, VIII International Conference on Co-ordination Chemistry, Vienna, 1964.

2) The exchange rate is independent of the concentration of uncomplexed thallium and proportional to that of the EDTA-OH complex, giving the relationship $R=k\cdot b$ under appropriate conditions throughout the pH range.

3) In a basic solution buffered by ammonia or barbiturate, the k is proportional to $[OH^-]$ and [TEA] and is little affected by the concentration of buffers. The Arrhenius activation energy is 29 kcal./mol.

4) In a neutral solution, near pH 7, the rate is small but measurable. It is independent of the pH value but proportional to the concentration of TEA, and it is little affected by the concentration of barbiturate. The activation energy is 22 kcal./mol.

5) In an acid solution buffered by acetate, the k is proportional to $[H^+]$, and $[Cl^-]^{1.5}$ and is little influenced by the concentration of acetate. The Arrhenius activation energy is 11 kcal./mol.

6) The features of the isotopic exchange of the thallium EDTA-OH complex are very similar to those of the thallium(III) EDTA complex.[5)]

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