

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

## The Effect of Chloride Ion on the Exchange Reaction between Thallium(I) and Thallium(III) in Sulfuric Acid Solutions<sup>1</sup>

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The effect of chloride ion on the exchange between Tl(I) and Tl(III) has been studied in 2.19 *M* sulfuric acid. As chloride is first added the rate falls until a minimum value of rate  $[Tl(I)]/[Tl(III)]$  is observed at  $[Cl^-]/[Tl(III)] \cong 2.5$ . Then the rate increases as further chloride is added. It is shown that the initial decrease is due to the failure of  $TlCl^{++}$  and  $TlCl_2^+$  to exchange appreciably with Tl(I). The increase at higher  $[Cl^-]/[Tl(III)]$  ratios is believed to be due to rapid exchange between  $TlCl_4^-$  and thallium(I) chloride complexes.

In an earlier paper,<sup>2</sup> we have discussed the exchange between thallium(I) and thallium(III) in aqueous sulfuric acid. We found that exchange in this medium was much more rapid than in nitric or perchloric acid solutions and several empirical rate equations were offered. We felt that one of these was superior to the others for a number of reasons and possible mechanisms, which led to that equation, were presented.

Dodson and co-workers<sup>3</sup> have studied the effect of chloride on the thallium(I)-(III) exchange in perchloric acid solutions. They found that as chloride is substituted for perchlorate, the exchange rate drops markedly and after the ratio  $[Cl^-]/[Tl(III)]$  exceeds a value of 1.5, the exchange rate climbs to rather high values. Eimer and Dodson proposed that  $TlCl^{++}$  and  $TlCl_2^+$  exchange only slowly with the thallium(I) ion, much slower than does the uncomplexed thallium(III). Duke and Bornong<sup>4</sup> have suggested that the exchange involves thallium(II) and that the rate should begin to increase after appreciable  $TlCl_2^+$  appears.

We undertook a study of the effect of chloride on the exchange in sulfuric acid to determine whether similar phenomena would occur and in the hope that we might shed some light on the role of chloro complexes in the exchange.

### Experimental

The experimental techniques are the same we reported in our previous work.<sup>2</sup> Chloride ion in varying amounts was introduced as hydrochloric acid (obtained from E. I. du Pont de Nemours). In our case we did not replace sulfuric acid with hydrochloric, but rather added small amounts of the latter to our solutions which were generally 2.19 *M* in sulfuric acid. The deviation of acidity from 2.90 *M* and the variation of ionic strength from 3.68 was always less than 1%. Had we chosen to maintain the ionic strength and hydrogen ion concentration exactly, by substitution of hydrochloric acid for sulfuric acid, the sulfate ion concentrations would have changed.

In order to obtain solutions with high  $[Cl^-]/[Tl(III)]$  ratios, it was necessary to use 0.005 *M* thallium(I) and (III). In those cases 10-ml. (instead of 5 ml.) aliquots were taken.

### Results

We have investigated the effect of chloride ion on the exchange in 2.19 *M* sulfuric acid and have obtained results which resemble those of Dodson and co-workers. At low  $[Cl^-]/[Tl(III)]$  ratios we

notice (Table I and Fig. 1) that the rate of exchange decreases as chloride is added. In perchloric acid solutions the minimum rate was observed at  $[Cl^-]/[Tl(III)] \cong 1.5$ , but we find the minimum in sulfuric acid is not reached until the ratio is be-

TABLE I  
THE VARIATION OF EXCHANGE RATE BETWEEN Tl(I) AND Tl(III) IN 2.19 *M* H<sub>2</sub>SO<sub>4</sub> AS A FUNCTION OF CONCENTRATION OF ADDED CHLORIDE ION (24.9°)

No. of runs	[Cl <sup>-</sup> ]	[Tl(III)] moles/liter	[Tl(I)]	[Cl <sup>-</sup> ]/ [Tl(III)]	R/ab, l. moles <sup>-1</sup> min. <sup>-1</sup>	
					Obsd.	Calcd.
6	0	0.0108	0.0100		0.78 <sup>a</sup>	
2	0	.0105	.0100		.80	
3	0.001	.0108	.0100	0.0925	.71	0.72
2	.002	.0108	.0100	.185	.68	.66
1	.003	.0108	.0100	.278	.62	.58
2	.005	.0108	.0100	.463	.41	.43
2	.008	.0108	.0100	.740	.22	.20
1	.0091	.0105	.0100	.866	.17	.15
4	.0100	.0108	.0100	.927	.13	.12
1	.0120	.0115	.0100	1.06	.090	.083
1	.0140	.0115	.0100	1.23	.049	.040
1	.0150	.0108	.0100	1.39	.018	.019
1	.0170	.0115	.0100	1.49	.014	.012
2	.0200	.0108	.0100	1.85	.0023	.00064
1	.0230	.0115	.0100	2.00	.0026	
1	.0250	.0115	.0100	2.17	.0021	
1	.0270	.0115	.0100	2.35	.0019	
2	.0300	.0108	.0100	2.78	.0019	
1	.035	.0114	.0100	3.07	.0025	
2	.040	.0108	.0100	3.70	.0040	
1	.025	.0065	.0050	3.85	.0041	
2	.045	.0108	.0100	4.17	.0059	
1	.030	.0065	.0050	4.61	.0064	
1	.035	.0064	.0050	5.47	.0093	
1	.061	.0065	.0050	9.53	.034	

<sup>a</sup> We have included in this value two additional values, obtained since the first paper appeared.

tween two and three. At higher  $[Cl^-]/[Tl(III)]$  ratios we also observe that the exchange rate rises and when the ratio reaches 10:1, we find Dodson's value and ours become nearly equal; although, at all lower ratios, the exchange rate in sulfuric acid is distinctly higher than was observed in perchloric or nitric acids.

We also have examined the variation of exchange rate at  $\mu = 3.68$  and  $[Cl^-]/[Tl(III)] = 0.93$  in mixtures of sulfuric acid and lithium sulfate. These observations, summarized in Table II, reflect variation in both sulfate and hydrogen ion concentrations and should be compared with the results in Table III of our first paper.<sup>2</sup>

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) C. H. Brubaker, Jr., and J. P. Mickel, *J. Inorg. Nuclear Chem.*, **4**, 55 (1957).

(3) (a) G. Harbottle and R. W. Dodson, *THIS JOURNAL*, **73**, 2442 (1951); (b) L. Eimer and R. W. Dodson, Brookhaven National Laboratory Quarterly Progress Report, 93 (S-8), 67-69 (March 1951).

(4) F. R. Duke and B. Bornong *J. Phys. Chem.*, **60**, 1015 (1956).

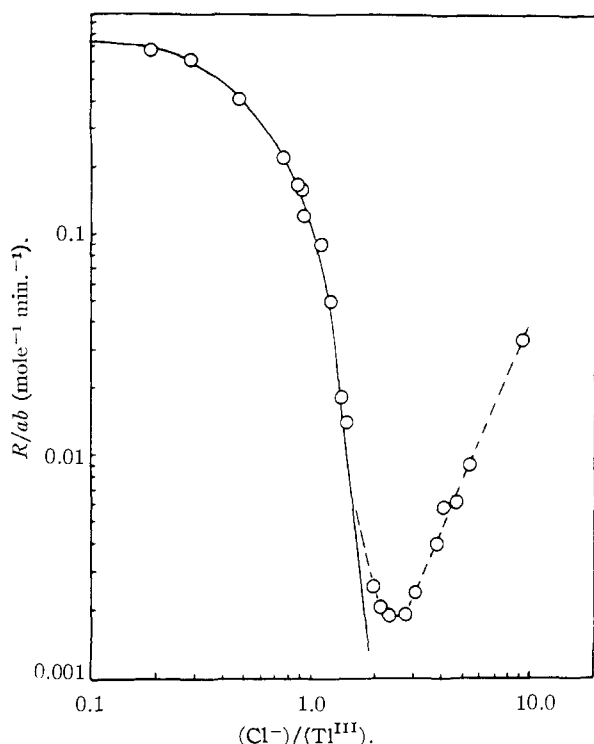


Fig. 1.—The variation of exchange rate with chloride ion concentration: solid line, calculated curve; broken line, experimental curve.

### Discussion

Benoit<sup>5</sup> has studied the chloride complexes of thallium(III) and gives the following values for the first four chloride complex formation constants

$$\begin{aligned} K_1 &= 1.25 \times 10^8 \\ K_2 &= 3.2 \times 10^6 \\ K_3 &= 1.6 \times 10^2 \\ K_4 &\cong K_3 \end{aligned}$$

However, examination of Dodson's work and our own seems to show that these values cannot be assumed at the relatively high ionic strengths we have employed. It appears<sup>3</sup> that we can assume that  $K_1$  is large, say more than  $10^8$ , and that  $K_1 \gg K_2$ .

TABLE II

THE VARIATION IN EXCHANGE RATE BETWEEN Tl(I) AND Tl(III) WITH SULFATE AND HYDROGEN ION CONCENTRATIONS, AT CONSTANT IONIC STRENGTH (3.68) AND CHLORIDE ION CONCENTRATION (0.01 M). [Tl(I)] = 0.0100 M, [Tl(III)] = 0.0108 M (24.9°)

(H <sub>2</sub> SO <sub>4</sub> )	(Li <sub>2</sub> SO <sub>4</sub> )	(H <sup>+</sup> )	(SO <sub>4</sub> <sup>2-</sup> )	R/ab	R <sup>0</sup> /ab	$\frac{y_0}{R^0/ab} = \frac{R/ab}{R^0/ab}$
2.19	0	2.90	0.70	0.16 <sup>a</sup>	0.78	0.21
1.60	0.386	2.00	.83	.23	0.96	.24
1.28	.574	1.56	.88	.24	1.08	.22
2.852	.805	1.00	.99	.30	1.40	.21
0.652	.947	0.75	1.07	.37	1.75	.21

R<sup>0</sup>/ab is rate at same  $\mu$ , (H<sup>+</sup>), (SO<sub>4</sub><sup>2-</sup>) in absence of chloride<sup>2</sup>

<sup>a</sup> This value is obtained from one run made as a control with this series and is somewhat higher than the average value (Table I).

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

Dodson and co-workers have developed a treatment for the effect of cyanide on the exchange, based on this latter assumption and the additional one that neither of the first two complexes exchanges appreciably with thallium(I). It serves to explain the decrease in exchange rate with increasing cyanide in terms of the removal of exchangeable thallium(III) from the system (*cf.* ref. 6 on the effect of cyanide on the thallium(I)-(III) exchange in perchloric acid).

We have been successful in adapting this treatment to the present system and thus can account for the decrease in exchange rate up to  $[Cl^-]/[Tl(III)] = 1.5$ . In order that we may retain our original definitions<sup>1</sup> of  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$ , we define

$$K_5 = \frac{(TlCl^{++})}{(Tl^{+3})(Cl^-)} \quad (1)$$

$$K_6 = \frac{(TlCl_2^+)}{(TlCl^{++})(Cl^-)} \quad (2)$$

and

$$K'_5 = \frac{(TlCl^{++})}{C_{Tl(III)}(Cl^-)} \quad (3)$$

where

$$C_{Tl(III)} = (TlO^+) + (TlOH^{++}) + (TlSO_4^+) + (Tl^{+3}) \quad (4)$$

Then, following Dodson's notation

$$y_0 = \frac{R/ab}{R^0/ab} = \frac{C_{Tl(III)}}{C_{Tl(III)}}$$

and

$$\alpha = [Cl^-]/[Tl(III)]$$

where [Tl(III)] is total thallium(III) and  $R^0/ab$  is the rate constant in the absence of chloride. Then

$$\frac{K_6}{K'_5} = y_0 \frac{(\alpha - 1 + y_0)}{(2 - \alpha - 2y_0)^2}$$

From this treatment, we find  $K_6/K'_5 = 0.032 \pm 0.003$  and hence predict the values of  $R/ab$  shown by the solid line in Fig. 1 and given in Table I. We can correct this ratio to give  $K_6/K_5$ , by employing the values of the hydrolysis and sulfate complexing constants used in our earlier work, in equations 1, 3 and 4. We obtain a ratio of 0.013. This is to be compared with a ratio of  $2.6 \times 10^{-3}$ , calculated from Benoit's constants. However, if we remember that we are working at a fairly high ionic strength, this result is not so disturbing.

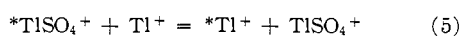
The results of measurements of the exchange rate at  $\mu = 3.68$  and  $[Cl^-]/[Tl(III)] = 0.93$  in lithium sulfate-sulfuric acid mixtures (Table II) seem to give additional support to the theory that the initial result of adding chloride ion is simply the removal of exchangeable thallium. We can compare these results with those in Table III of our earlier work and find that  $(R/ab)/(R^0/ab) = y_0$  appears to be essentially constant as we should demand.

The increase of the exchange rate at higher  $[Cl^-]/[Tl(III)]$  ratios is similar to that observed by Dodson and co-workers and, at present, in view of the uncertainty in the third and fourth thallium(III) chloride and the thallium(I) chloride complexing constants, we can only offer the same qualitative

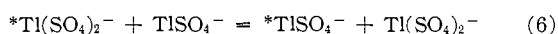
(6) E. Penna-Franca and R. W. Dodson, *Engenharia e quim. (Rio de Janeiro)*, **6**, No. 6, 1 (1954); *THIS JOURNAL*, **77**, 2651 (1955).

explanation. This is, we suggest (with Dodson and co-workers), that the continuing increase in exchange rate at high [Cl<sup>-</sup>]/[Tl(III)] ratios is due to rapid exchange between TlCl<sub>4</sub><sup>-</sup> and one or more of the weakly associated thallium(I) complexes, such as TlCl, TlCl<sub>2</sub><sup>-</sup>, TlCl<sub>3</sub><sup>=</sup> and possibly TlCl<sub>4</sub><sup>=</sup>.<sup>7</sup>

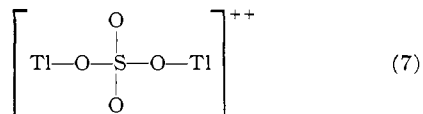
In view of these findings on the effect of chloride on the exchange, we find it extremely difficult to take seriously arguments based solely on coulombic attractions or repulsions, when we come to the consideration of possible mechanisms. In our previous work,<sup>2</sup> such arguments were considered, but now we are inclined to account for the high exchange rate in sulfuric acid as compared to perchloric acid, on the basis that sulfate ion may actually participate in the electron transfer process. We believe that the rapid exchange reactions in sulfuric acid are



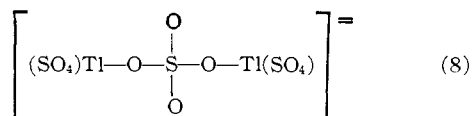
and



We suggest that exchange is accomplished by transfer of electrons through the sulfate bridge in the complexes



and



(This would be formally equivalent to the transfer of a sulfate radical, SO<sub>4</sub><sup>=</sup>, from the thallium(III) to thallium(I).)

We believe this proposal is further supported by the absence of an (SO<sub>4</sub><sup>=</sup>)<sup>2</sup> term in the rate law, since

(7) H. Fromherz and K. H. Lih, *Z. physik. Chem.*, **A153**, 335 (1931); Kuo-Hao Hu and A. B. Scott, *THIS JOURNAL*, **77**, 1380 (1955); *J. Chem. Phys.*, **23**, 1830 (1955).

the symmetrical, bridged complexes (such as 7 and 8) can only occur for odd numbers of sulfates in the complex. The product species are chemically identical with the reactants.

We also believe that we are now able to offer possible explanations for the seemingly anomalous effects of chloride and sulfate ions in other oxidation or reduction reactions involving either thallium(I) or thallium(III). It has been reported<sup>8</sup> that the Tl(I)-Ce(IV) reaction is fast in aqueous HCl, but is very slow in sulfuric acid and, in fact, sulfate retards the reaction markedly even in the presence of chloride. Further, we are told<sup>9,10</sup> that the reduction of Tl(III) by Fe(II) in HClO<sub>4</sub> is accelerated by sulfate and retarded by chloride.

If we assume, as we have above, that Tl(III) chloride complexes are much stronger than the sulfate complexes and remember that TlSO<sub>4</sub><sup>-</sup> is slightly stronger than TlCl<sup>11,12</sup> and the higher chloride complexes,<sup>7</sup> we believe that it is possible to account, in part, for these effects.

In the oxidation of thallium(I) by cerium(IV) in HCl, the addition of sulfate effectively reduces the concentrations of the various chlorocomplexes, which react readily with the cerium chloro complex, by forming TlSO<sub>4</sub><sup>-</sup>. We are somewhat puzzled by the lack of reaction between Ce(SO<sub>4</sub>)<sub>3</sub><sup>=</sup> and TlSO<sub>4</sub><sup>-</sup> in the absence of chloride.

In the reduction of thallium(III) by iron(II), the chloride ion strongly complexes thallium(III) and removes the reacting species (*i.e.*, TlOH<sup>++</sup> and Tl<sup>+3</sup>) from solution, while sulfate, which forms weak complexes, does not, and any of these complexes that do form, may also react readily with iron(II).

(8) P. A. Shaffer, *J. Phys. Chem.*, **40**, 1021 (1936).

(9) C. E. Johnson, Jr., *THIS JOURNAL*, **74**, 959 (1952).

(10) K. G. Asbust and W. C. S. Higginson, *J. Chem. Soc.*, 343 (1946)

(11) R. B. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(12) V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 318 (1952).

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## Radiation-induced Exchange of Chlorine with Carbon Tetrachloride<sup>1</sup>

BY JOHN W. SCHULTE

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The chemical and virtual changes in CCl<sub>4</sub> containing Cl<sub>2</sub> under the influence of Co<sup>60</sup> γ-rays have been investigated. Two reactions are observed: the exchange of Cl<sub>2</sub> with CCl<sub>4</sub>, and the decomposition of CCl<sub>4</sub> to form C<sub>2</sub>Cl<sub>6</sub> and Cl<sub>2</sub>. The rates of both reactions are independent of the chlorine concentration and directly proportional to the dose rate. The former reaction is interpreted as a measure of the "radical yield" in the system, and it is observed to occur with an efficiency corresponding to 3.5 ± 0.35 molecules of chlorine being brought into exchange with CCl<sub>4</sub> for every 100 e.v. absorbed. The latter reaction is interpreted as a measure of molecular yield and takes place with an efficiency of 0.80 ± 0.06 molecule of C<sub>2</sub>Cl<sub>6</sub> and Cl<sub>2</sub> being formed for every 100 e.v. absorbed. Spontaneous exchange and exchange under the influence of sunlight and ultraviolet light also were noted.

### Introduction

Previous work<sup>2</sup> indicated that in the work on CHCl<sub>3</sub> + O<sub>2</sub>, most of the information obtained re-

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. W. Schulte, J. F. Suttle and R. Wilhelm, *THIS JOURNAL*, **76**, 2222 (1953).

ferred to the chain-carrying processes rather than the primary act. By using a simpler system, CCl<sub>4</sub> + Cl<sub>2</sub>, it was hoped that the reactions observed would be simpler and a direct consequence of the primary act. In such a system *G* values for "radical yields" and "molecular yields" analogous to those determined for water might be measured.