

The free uncomplexed linear dimethyltin(IV) ion which probably exists rarely, if ever, in chemical systems can be regarded as a very strongly polarizing but virtually nonpolarizable ion. In Pearson's classification of "hard" and "soft" acids,²⁷ it is to be regarded as a very hard acid. It interacts very strongly with hydroxide ion, water, and fluoride ion but much less strongly with more polarizable bases.^{9,10} Under anhydrous conditions complexes can be prepared easily with ligands which are good proton bases. With these hard bases, the coordination number of tin appears generally to be 6, *e.g.*, in the aquo ion,⁷ the hydroxo complex,²⁴ and a variety of β -diketo complexes.¹¹ Aqueous solutions of the dimethyltin(IV) ion appear to be the most extensively hydrolyzed of all of the systems containing divalent ions which have been studied. This reflects the strong polarization of the water molecules in the first coordination sphere of this cation.

Complexation of the dimethyltin(IV) ion with a soft base, as expected, leads to the formation of considerably less polar bonds as indicated by the appearance of intense tin-ligand stretching vibrations in the Raman spectra of the complexes. There is a tendency for the coordination number to decrease to four when soft bases are bound, and this can be rationalized on the basis of Pauling's electroneutrality principle. Thus dimethyltin dichloride involves bonds from tin to the soft methide ion as well as the soft chloride ion, and this should lead to a rather high charge density on the tin atom. Back bonding does not seem to occur to any extent in these complexes, so there is no mechanism to reduce the high charge density at the tin atom. In

(27) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

general, these complexes with soft base ligands are of low thermodynamic stability as has been noted earlier.^{9,10}

The dimethyltin(IV) ion does form a complex, $(\text{CH}_3)_3\text{Sn}^+$, with the very soft base methide ion which is generally regarded as highly stable. In this case the stability is due to the high activation energy for the displacement of the soft methide by a hard base, and the "complex" must be synthesized in the absence of hard bases.

Because of the very high polarizing ability of the dimethyltin(IV) ion, it would be expected that it would give rise to a high electrical field at the near neighbor ligands in complexes with hard bases. It has been observed in compounds containing the lower charged $(\text{CH}_3)_3\text{Sn}^+$ that degenerate vibrations of symmetrical anions like ClO_4^- ,²⁸ BF_4^- ,²⁹ AsF_6^- ,³⁰ and SbF_6^- ³⁰ are often split in crystals. These splittings probably result from the combined effect of the high polarizing power of the cation and low anion site symmetries in the crystals with, perhaps, some degree of covalent character to the tin-ligand bond.

The behavior of the dimethyltin(IV) ion is that of a very small ion of high charge. The two pairs of σ -bonding electrons have little effect in screening the coordinated ligands, *e.g.*, water molecules, from the $4d^{10}$ tin core. Experimentally, it is observed that the tin(II) ion is similar in many respects, and the hard acid nature of Sn(II) was attributed earlier to distortion of the ion from spherical symmetry in the presence of ligands.³¹

(28) R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 13 (1963).

(29) B. J. Hathaway and D. E. Webster, *ibid.*, 14 (1963).

(30) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

(31) See footnote *b* in Table IV.

The Kinetics of the Reaction between Thallium(III) and Vanadium(III)¹

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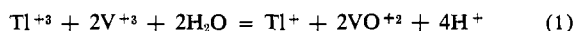
The kinetics of the reaction $\text{Tl(III)} + 2\text{V(III)} = \text{Tl(I)} + 2\text{V(IV)}$ have been studied in acid perchlorate solutions from 0.30 to 1.90 M in HClO_4 over a temperature range from 0.5 to 25.1° at $\mu = 2.0$ M. The reaction is first order with respect to both V(III) and Tl(III). The data do not allow the hydrogen ion dependence to be specified exactly, but the dependence is predominantly inverse first power in H^+ . Values of ΔH^ and ΔS^* for the major path are 13.9 ± 0.8 kcal./mole and 4.1 ± 2.4 e.u. A mechanism involving a two-electron step is not compatible with the data.*

(1) (a) Work done under the auspices of the U. S. Atomic Energy Commission; (b) presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

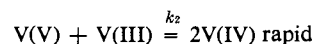
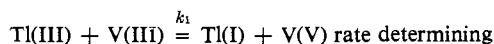
(2) On leave from Colorado State University, Fort Collins, Colo.

Introduction

The reaction between Tl(III) and V(III) is described by eq. 1. Plausible mechanisms involving either one-



electron or two-electron steps can be written for the reaction. A two-electron mechanism is shown below.



Since k_2 is known from previous work,³ a kinetic study

(3) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).

of the Tl(III)-V(III) system may allow a choice to be made between alternative mechanisms.

Higginson⁴ has reported that the reaction of Tl(III) and V(III) is complete within 45 sec. in 6.0 *M* HClO₄ at ca. 5° using 9×10^{-3} *M* reactant concentrations. Although the reaction is quite rapid, the rate can easily be measured using an extension of the techniques described previously.⁵

Experimental Section

Reagents. Thallous formate was converted to the nitrate by reaction with cold, concentrated HNO₃. The TlNO₃ was recrystallized twice from water and was converted to TlClO₄ by fuming it with HClO₄. The TlClO₄ was recrystallized twice from 4.0 *M* HClO₄ and then was electrolytically oxidized to Tl(ClO₄)₃ by the method described by Biedermann.⁶

The Tl(III) content of the solution was determined by reaction of an aliquot of the solution with excess V(III) followed by the addition of excess Ce(IV) and titration of the excess Ce(IV) with Fe(II) to the ferroin end point. The Tl(III) content was also checked by the reaction of an aliquot of the Tl(III) with excess Fe(II) followed by the addition of excess Ce(IV) and titration of the excess Ce(IV) with Fe(II). The two methods gave results which were in excellent agreement. Total Tl content was determined by titration with standard KIO₃ to the ICl end point using CCl₄ as an indicator after reduction of the Tl(III) with Na₂SO₃ and HCl. Essentially all of the Tl in the Tl(ClO₄)₃ was present as Tl(III). The acid content of the Tl(ClO₄)₃ stock solution was determined by titration with NaOH in the presence of KBr to the phenolphthalein end point.

A Tl(ClO₄)₃ stock solution was also prepared from Tl(ClO₄)₃ obtained by dissolving Tl₂O₃ in fuming HClO₄. Rate runs made using this solution gave rate constants which averaged about 8% higher than those obtained using the electrolytic Tl(ClO₄)₃ solution. The electrolytic preparation was used to obtain the data presented in this paper.

The preparation of V(III) from V(II) and V(IV) has been described elsewhere.³ A solution of V(ClO₄)₃ was prepared by electrolytic reduction of V(IV) for comparison with V(III) prepared by the usual method. There was no difference in the rate constants obtained using V(III) prepared electrolytically from those obtained using V(III) prepared in the usual manner.

Procedure. In order to have the reaction occur at a measurable rate, low reactant concentrations (*i.e.*, about 10^{-4} *M*) were employed which resulted in absorbance changes of only about 0.030 to 0.090 during the course of the reaction. It was necessary to use the expanded-scale slidewire available for the Cary Model 14 spectrophotometer to record these small absorbance changes. Slight, but significant, base-line drift required that the absorbance at infinite time be calculated from data obtained in runs using the regular slidewire. To further minimize the effect of base-line drift, the

reaction was followed for only 25–30 sec. (70–90% completion in most runs). The rest of the apparatus, the procedure, and the least-squares method of calculation were essentially the same as used in previous work.⁵ The course of the reaction was followed by observing the change in absorbance at 7600 Å., the absorption maximum for V(IV), as a function of time. The reproducibility of the rate constants obtained was slightly better than 5%.

Induction Experiments. Attempts to induce the slow reaction between Fe(II) and Tl(III) by the addition of V(III) were carried out by a difference in order of mixing technique. In one case, 0.04 mequiv. of V(III) was pipetted into a stirred solution containing 0.38 mequiv. (1.26×10^{-2} *M*) of Tl(III) followed by the addition of 0.08 mequiv. of Fe(II). The reaction was then quenched by the addition of 0.15 mequiv. of Ce(IV). In the other case, the order of addition of the V(III) and Fe(II) was reversed. The reaction medium was 0.26 *M* HClO₄ maintained at 0.5°. The amount of Fe(II) consumed was measured by titration of the excess Ce(IV) with FeSO₄.

Results

Stoichiometry. The stoichiometry of the reaction is given by eq. 1. No oxidation of V(IV) to V(V) could be detected spectrophotometrically at 3200 Å. where the molar extinction coefficient of V(V) exceeds 350 l. mole⁻¹ cm.⁻¹. Moreover, the change in absorbance during the course of the reaction is constant when either excess V(III) or excess Tl(III) is used.

Vanadium(III) and Thallium(III) Dependences. The course of all of the rate runs was in agreement with the rate law

$$-d[\text{Tl(III)}]/dt = k'[\text{Tl(III)}][\text{V(III)}]$$

where *k'* is the apparent second-order rate constant. Optical densities calculated using a second-order rate law were in good agreement with those observed. Further confirmation that the reaction is first-order with respect to both reactants is given by the data in Table I.

Table I. Apparent Second-Order Rate Constants, *k'*, at Different Reactant Concentrations^a

Initial V(III), <i>M</i> × 10 ⁴	Initial Tl(III), <i>M</i> × 10 ⁴	<i>k'</i> , <i>M</i> ⁻¹ sec. ⁻¹
1.540	1.133	350
3.080	1.133	343
3.080	0.566	367
1.540	0.566	347
1.467	1.360	344
1.467	0.545	346

^a Conditions: 0.5°, 1.0 *M* HClO₄, $\mu = 2.0$ (LiClO₄).

V(IV) and Tl(I) Dependences. The products of the reaction, V(IV) and Tl(I), were found to have no effect on the rate when present in concentrations as high as 0.01 *M*.

(4) W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, 29, 49 (1960).

(5) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, 67, 1090 (1963).

(6) G. Biedermann, *Arkiv Kemi*, 5, 441 (1953).

Hydrogen Ion and Temperature Dependence. Rate runs were made at 0.5, 14.0, and 25.1° in solutions with $\mu = 2.0$ (LiClO_4). The HClO_4 concentration was varied from 0.30 to 1.90 M . The apparent second-order rate constants found in these runs are summarized in Table II.

Table II. Hydrogen Ion and Temperature Dependence^a

HClO_4 , M	0.5°		14.0°		25.1°	
	No. of runs	k'	No. of runs	k'	No. of runs	k'
0.30	4	1.57				
0.40	4	1.06				
0.50			4	2.95		
0.60	6	0.668	5	2.58		
0.70			8	2.02		
0.80	5	0.475	6	1.75		
1.00	11	0.353	15	1.29	3	3.10
1.30	6	0.253	6	0.917	4	2.15
1.60	6	0.196	6	0.736	3	1.75
1.90	6	0.160	6	0.597	4	1.48

^a $\mu = 2.0$ (LiClO_4). Values of k' in $M^{-1} \text{sec.}^{-1} \times 10^{-3}$.

Ionic Strength and Medium Effects. The effect of ionic strength, μ , on the reaction rate was investigated in a series of runs made at 0.5° in 0.30 M HClO_4 . LiClO_4 was used to vary μ from 0.30 to 3.00. The results are summarized in Table III. The effect of substituting NaClO_4 for LiClO_4 was investigated in a series of runs in 0.50 M HClO_4 at 0.5° with $\mu = 2.0$. The apparent second-order rate constants were 9.1% per mole lower in the NaClO_4 solutions.

Table III. Effect of Ionic Strength, μ , on the Apparent Second-Order Rate Constant^a

μ , M	0.30	0.50	1.50	3.00
k' , $M^{-1} \text{sec.}^{-1} \times 10^{-3}$	0.918	0.953	1.48	1.78

^a Conditions: 0.5°, 0.30 M HClO_4 , $2.475 \times 10^{-4} M$ V(III) , $1.359 \times 10^{-4} M$ Tl(III) .

The Effect of Chloride Ion. Some rate runs were made in which part of the HClO_4 was replaced with HCl so that the chloride concentration ranged from 0.1 to 25 times the concentration of the Tl(III) concentration. Under these conditions, the reaction does not exhibit second-order kinetics and the rate is greatly decreased. Even at chloride concentrations as high as 1.0 M , the rate was significantly less than in the absence of chloride.

Induction Experiments. It was found that V(III) induces the slow reaction between Tl(III) and Fe(II) . At 0.5° in 0.26 M HClO_4 the induction factor, equivalents of Fe(III) produced/equivalent of V(III) added, was about 0.6. The concentrations of the reactants were Fe(II) , $3.28 \times 10^{-3} M$; Tl(III) , $1.26 \times 10^{-2} M$; V(III) , $1.78 \times 10^{-3} M$.

Interpretation and Discussion

The Rate Law. In order to specify the reaction paths and formulas of the activated complexes, a rate law which includes the hydrogen ion dependence is needed.

So that the rate law may be written in terms of the principal metal ion species in solution, V^{+3} and Tl^{+3} , the apparent second-order rate constant, k' , must be multiplied by a factor $(1/(1 + K_h/[\text{H}^+]))$, where K_h is the hydrolysis constant for Tl^{+3} . Biedermann⁶ reports a $\text{p}K$ value of 1.14 for the first hydrolysis constant of Tl^{+3} measured at 25°. The heat of hydrolysis is not known but was assumed to be 4.85 kcal./mole, the value reported⁷ for In^{+3} . The hydrolysis of V^{+3} is negligible under the conditions used in this investigation.

A plot of $\log k''$ vs. $\log [\text{H}^+]$, where k'' is the apparent second-order rate constant corrected for the hydrolysis of Tl^{+3} , is linear over the entire range of hydrogen ion concentrations studied and has a slope of -1.22 ± 0.01 . The plot of $\log k''$ vs. $\log [\text{H}^+]$ can be used to obtain some information regarding reaction paths. The value of the slope suggests that the rate is predominantly proportional to $[\text{H}^+]^{-1}$ with a smaller contribution from a term proportional to $[\text{H}^+]^{-2}$. Since the plot is linear, the two terms can correspond to reaction mechanisms involving either parallel or consecutive reaction paths.

Mechanisms which involve parallel reactions or consecutive reactions lead to eq. 2 and 3, respectively, where k'' is the apparent second-order rate constant corrected for hydrolysis.

$$k'' = k_{-1}[\text{H}^+]^{-1} + k_{-2}[\text{H}^+]^{-2} \quad (\text{parallel reactions}) \quad (2)$$

$$k'' =$$

$$\frac{1}{\frac{1}{k_{-1}[\text{H}^+]^{-1}} + \frac{1}{k_{-2}[\text{H}^+]^{-2}}} \quad (\text{consecutive reactions}) \quad (3)$$

Both functions were found to reproduce the experimental data equally well with a root-mean-square per cent deviation of about 4%. However, in both cases the pattern of the deviations is not random, indicating that neither function fits the data very well.

Since neither of the two-parameter functions fits the data satisfactorily, several three-parameter functions were tried. A three-parameter, parallel path function fits the data, but requires that one of the rate constants be negative. This model was rejected. Some three-parameter functions which satisfactorily reproduce the data are shown below.

The failure of either two-parameter function to reproduce the data satisfactorily could be due to medium effects. The term $e^{\beta\text{H}^+}$ in eq. 4, where β is an adjustable parameter, is of the form of a Harned term and allows for changes in the medium effect as the acid concentration is varied at constant ionic strength.

$$k'' = (k_{-1}[\text{H}^+]^{-1} + k_{-2}[\text{H}^+]^{-2})e^{\beta\text{H}^+} \quad (4)$$

Equation 5 corresponds to a mixture of consecutive and parallel reactions with various hydrogen ion dependences for the parallel path term, where $N = 0$,

$$k'' = \frac{1}{\frac{1}{k_{-1}[\text{H}^+]^{-1}} + \frac{1}{k_{-2}[\text{H}^+]^{-2}}} + k_N[\text{H}^+]^N \quad (5)$$

(7) K. Schlyter, *Trans. Roy. Inst. Technol. Stockholm*, No. 182, (1961).

1, 2. All four functions reproduce the experimental data equally well with a root-mean-square per cent deviation of about 3%. Changing the heat of hydrolysis of Tl^{+3} to 10 kcal./mole had no significant effect on the fits. In Table IV is shown a comparison of values of k'' calculated from the various functions with observed values of k' at the acidities studied.

Table IV. Comparison of Calculated Values of k'' with Observed k' for Various Hydrogen Ion Dependences at 0.5° and $\mu = 2.0$ ($LiClO_4$)^a

$HClO_4$, M	k' (obsd.)	k'' (calcd.)			
		b	c	d	e
0.30	1.57	1.54	1.51	1.50	1.50
0.40	1.06	1.08	1.09	1.09	1.09
0.60	0.662	0.657	0.669	0.672	0.674
0.80	0.475	0.463	0.467	0.469	0.470
1.00	0.353	0.353	0.351	0.352	0.353
1.30	0.253	0.256	0.252	0.251	0.251
1.60	0.196	0.197	0.196	0.195	0.194
1.90	0.160	0.160	0.160	0.160	0.160
Weighted variance		0.00893	0.0101	0.0106	0.0111

^a k' and k'' values in $M^{-1} \text{ sec.}^{-1} \times 10^{-3}$. ^b Parallel paths with Harned term; best value of β as calculated by least-squares program = -0.1319. ^c Consecutive reactions with zero-order hydrogen ion dependence for parallel term $N = 0$. ^d Consecutive reactions with first-order hydrogen ion dependence for parallel term ($N = 1$). ^e Consecutive reactions with second-order hydrogen ion dependence for parallel term ($N = 2$).

Relatively few reactions are known to involve consecutive reactions and even fewer have been demonstrated to involve a mixture of consecutive and parallel reactions although at least one example is known.⁸ Therefore, the simplest explanation of the hydrogen ion dependence is to assume that parallel paths are involved in accord with eq. 4. It must be emphasized that a hydrogen ion dependence in accord with eq. 5 cannot be rejected.

Thermodynamic Quantities of Activation. It is of interest to use the temperature dependence of the rates to determine ΔH^* and ΔS^* for the formation of the activated complexes for the various paths. It was assumed that the temperature dependence of each of the k values in eq. 4 and 5 is given by the expression

$$k_i = (k_B/h)T \exp(\Delta S_i^*/R) \exp(\Delta H_i^*/RT)$$

from Eyring's absolute reaction rate theory. The k' values obtained at all of the hydrogen ion concentrations and temperatures were used simultaneously in a least-squares program to find the best values of the heats and entropies of activation.

The precision of the data and the nature of the function made it necessary to fix some of the parameters of the minor terms at reasonable values. The results of the calculations for a model corresponding to parallel paths with a Harned term are summarized in Table V.

The data in Table V clearly show that fixing the value of ΔS^* for the minor path at a variety of reasonable estimates has very little effect on the computed value of ΔS^* and ΔH^* for the major, inverse hydrogen ion

(8) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

Table V. Summary of Heat and Entropy Calculations for the Parallel Path with Harned Term Model^b

-2 term		-1 term		$\beta^{a,b}$	Weighted variance $\times 10^{-3}$
$\Delta S^*{}^a$	ΔH^*	ΔS^* \pm	ΔH^* \pm		
4.0	14.9	5.3	14.2	-0.132	1.80
6.0	15.4	5.1	14.1	-0.132	1.75
8.0	16.0	4.8	14.1	-0.132	1.71
10.0	16.5	4.5	14.0	-0.132	1.69
12.0	17.1	4.1	13.9	-0.132	1.67
14.0	17.7	3.8	13.8	-0.132	1.67
16.0	18.2	3.5	13.7	-0.132	1.68
18.0	18.8	3.1	13.6	-0.132	1.71
20.0	19.3	2.7	13.5	-0.132	1.75
12.0	17.1	5.4	14.2	-0.132 ^d	1.64
12.0	17.1	2.9	13.5	-0.132 ^e	1.77
12.0	17.0	3.9	13.8	-0.112	1.67
12.0	17.1	4.4	13.9	-0.152	1.70
12.0	17.2	4.6	14.0	-0.132	1.64 ^f
12.0	16.7	5.2	14.2	-0.132	1.73 ^g

^a Treated as a fixed parameter. ^b -0.132 is the best value of β obtained by the least-squares program for the data at 0.5°. ^c The uncertainties are standard deviations estimated by the least-squares program. ^d Temperature coefficient of β assumed to be 1.0%/°C. ^e Temperature coefficient of β assumed to be -1.0%/°C. ^f Heat of hydrolysis of $Tl(III)$ assumed to be 10.0 kcal./mole. ^g Value of the hydrolysis constant doubled at 25.0°. ^h Unless otherwise stated, $\Delta S = 11.0$ e.u., $\Delta H = 4.85$ kcal./mole for the hydrolysis constant of $Tl(III)$.

dependent, path. It is also apparent that the heat and entropy values for the major path are rather insensitive to changes in β or to changes in the hydrolysis correction.

Similar calculations were carried out for the mixed, consecutive, and parallel path reaction models. The fits of the data were slightly poorer than in the parallel path with the Harned term case. However, values computed for ΔS^* and ΔH^* for the major path are again fairly insensitive to the estimates chosen for the parameters of the minor terms. The values obtained for the heats and entropies of the major path are also essentially independent of the hydrogen ion dependence of the parallel-path term.

The best values of ΔS^* and ΔH^* for the main path ranged from 7.1 to 8.8 e.u. for ΔS^* and from 14.4 to 14.7 kcal./mole for ΔH^* . The weighted variances of the best fits for the three functions ranged from 1.8×10^{-3} to 1.9×10^{-3} .

The best values of the thermodynamic quantities of activation for the inverse hydrogen ion dependent path are listed in Table VI. Activation parameters for the analogous activation processes for the $V(III)$ - $Fe(III)$ and $Ti(III)$ - $Fe(III)$ reactions are also listed for comparison.

Newton and Rabideau⁹ have pointed out the correlation between the charge on the activated complex and the entropy of the complex, S^*_{complex} , which is defined as $\Delta S^* + \sum S^0_{\text{reactants}}$. It is interesting that S^*_{complex} for the $V(III)$ - $Ti(III)$ reaction differs considerably from S^*_{complex} for the similar reactions listed in Table VI. However, the value of S^*_{complex} for the $V(III)$ - $Ti(III)$ reaction is well within the range of values listed by Newton and Rabideau for complexes with charge +5 formed in the reaction of actinide ions.

(9) T. W. Newton and S. W. Rabideau, *ibid.*, **63**, 365 (1959).

Table VI. Thermodynamic Quantities of Activation

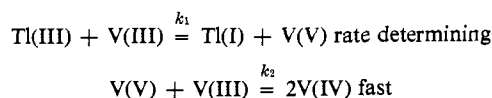
Net activation process	ΔH^* , kcal./mole	ΔS^* , e.u.	S^* _{complex} , e.u.	Ref.
$Tl^{+3} + V^{+3} + H_2O = [TiOHV^{+5}]^* + H^+$	13.9 ± 0.8^a	4.1 ± 2.4	-86	This work
$Fe^{+3} + V^{+3} + H_2O = [FeOHV^{+5}]^* + H^+$	17.6 ± 1.5^b	-10.2 ± 5.3^b	-128	c
$Ti^{+3} + Fe^{+3} + H_2O = [TiOHFe^{+5}]^* + H^+$	13.4 ± 2.6^b	-8.3 ± 0.3^b	-124	d

^a The uncertainty includes the range of values found for ΔH^* independent of the choice of the H^+ dependence function. ^b Higginson's data recalculated by T. W. Newton using a nonlinear, least-squares program. The uncertainties are the standard deviations estimated by the least-squares program. ^c W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962). ^d W. C. E. Higginson, private communication.

The Effect of Chloride. The simplest explanation for the effect of chloride ion on the rate of the reaction is that the chloro complexes of Tl(III) react at a much lower rate than uncomplexed Tl(III).

The possibility of chloride contamination of the reagents, particularly the $HClO_4$, having an effect on the rate measurements was considered. No detectable amount of chloride ion could be found in the reagents using a $AgNO_3$ test. Test solutions containing known amounts of chloride showed that chloride ion concentrations as low as $10^{-5} M$ (about 10% of the lowest Tl(III) concentration used) were easily detectable. Moreover, different sources of $HClO_4$ and $LiClO_4$ used during the investigation had no effect on the value of the rate constants obtained. It is unlikely that the level of chloride contamination would be identical in several sources of materials.

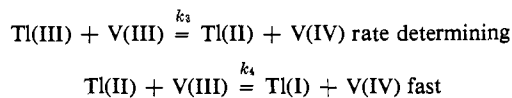
Mechanism of the Reaction. Since the stoichiometry of the net activation process is different from the stoichiometry of the over-all reaction, the reaction cannot occur by a single-step mechanism. A possible intermediate is V(V) produced by a mechanism involving a two-electron step as shown below.



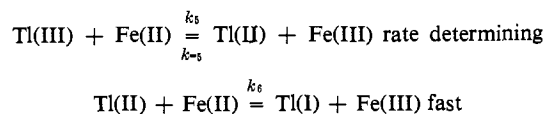
The rate constant, k_2 , for the V(V)-V(III) reaction is known³ and is too small by a factor of ~ 14 for V(IV)

to be produced at the rate observed in the V(III)-Tl(III) reaction.

An alternative mechanism which produces Tl(II) as an intermediate by a one-electron step is shown below.



The mechanism above is similar to the mechanism proposed by Higginson¹⁰ for the reaction between Fe(II) and Tl(III).



The induction experiments show that the V(III)-Tl(III) reaction produces an intermediate which reacts rapidly with Fe(II). Kinetic considerations rule out the possibility that the intermediate is V(V). Hence, a mechanism involving Tl(II) is in accord with the experimental results.

Acknowledgments. The author thanks Dr. T. W. Newton for many helpful discussions, Dr. F. B. Baker for assistance in the experimental part of this work, and Dr. J. F. Lemons under whose general direction this work was done.

(10) K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 3044 (1953).