

The Influence of Some Organic π -Electron Systems on the Rate of the Electron Transfer Reaction between Thallium(III) and Iron(II) in Aqueous Perchloric Acid

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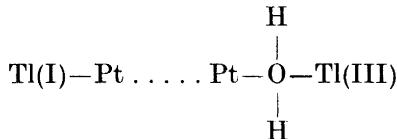
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The influence on the rate of the electron transfer reaction between Tl^{3+} and Fe^{2+} of increasing amounts of a number of organic compounds containing a conjugated double bond system was investigated in $HClO_4$ at an ionic strength of 1.60. Also, the stability constants of complexes of the individual reactants with the compounds, in the same media, were measured where it was possible. For several carboxylic acids and amines, a retardation was observed due to the formation of thermodynamically stable complexes of Tl^{3+} and/or Fe^{2+} . For 2- and 4-aminopyridine however, a strong positive catalysis was observed, even though the interaction with the reactants was very weak. This effect is discussed in terms of an outer sphere electron mediation through the monoprotonated pyridines for the reaction between Tl^{3+} and Fe^{2+} , and it is compared to various similar effects described in the literature.

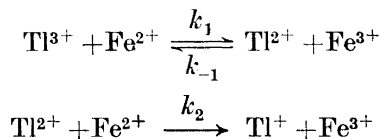
It is often observed that electron transfer reactions in aqueous solution are strongly heterogeneously catalyzed by platinum or other metals.^{1,2} It is believed that the metal acts as an electronic conductor in the electron transfer step,^{3,4} and that the overall reaction in the catalyzed path thus consists of a) transport of the reacting species to the metal surface by convection and diffusion, b) adsorption of the species on active sites of the metal surface, c) electron transfer *via* the metal, and d) transport of the reaction products away from the metal surface, again by convection and diffusion.

Only a few quantitative reports of heterogeneously catalyzed electron transfer reactions in solution have appeared, and apart from reproducible stirring conditions, no particular device was used for transport control. Fronæus and Östman⁵ found that electron exchange between Ce(III) and Ce(IV) in perchloric acid was catalyzed by bright platinum, and the reaction was assumed to be of the outer sphere type. Jonasson and Stranks⁶ investigated in detail the electron exchange between Tl^+ and Tl^{3+} on platinized platinum

surfaces in perchloric acid and also elucidated the independent adsorption behaviour of Tl^+ and Tl^{3+} . The exchange of the catalyzed path was interpreted as an inner sphere mechanism



We report here the results of an attempt to establish whether an outer sphere electron mediation effect could be observed in homogeneous solution by adding to the reaction mixture, organic compounds containing delocalized electron systems in the form of conjugated double bonds. The reaction chosen was the reduction of Tl^{3+} by Fe^{2+} , the mechanism of which in the absence of other species is ⁷



The ratio k_2/k_{-1} has a finite value of about 30, so a deviation from second-order behaviour is observed as the back reaction becomes more and more important during the later parts of the reaction. In the presence of bright platinum, a pure second-order behaviour is observed ⁸ which can be interpreted as a strong increase in k_2/k_{-1} , while k_1 is unchanged.

Various effects on the kinetics were observed when the organic reagents were added, and in most cases also the interaction with the individual reactants was measured and reported in terms of the stability constants. Maleic, fumaric, succinic, and phthalic acid retard the reaction, and this is attributed to the formation of less reactive $Tl(III)$ complexes. 4,4'-Dipyridyl has no effect, while the addition of 1,10-phenanthroline or 2,2'-dipyridyl results in a very strong retardation, considered to be due to the virtual inertness to electron transfer of the complexes formed with both Tl^{3+} and Fe^{2+} . 2- and 4-aminopyridine interact very weakly with the reactants, but nevertheless give rise to a large increase in k_2 , similar to bright platinum. This effect is interpreted as a long-range outer sphere electron mediation, and it is attempted to explain why it is not observed for 3-aminopyridine.

EXPERIMENTAL

Reagents. Stock solutions of ferrous and ferric perchlorate, sodium perchlorate thallium(I) and thallium(III) perchlorate were all made up from pure or p.a. grade reagents and standardized by common procedures.^{7,9} Perchloric acid was diluted from a 70 % p.a. stock solution. Pure sulphuric acid for the Ce(IV) titrations was fumed for half an hour before use and diluted. It contained no oxidizable impurities. The organic reagents were of pure or p.a. grade and used either without further purification or after recrystallization from water (4,4'-dipy) or benzene-hexane (the aminopyridines). All solutions were made up with doubly distilled water.

Determination of stability constants. The interaction between Fe^{2+} and the possible mediators was investigated spectrophotometrically in the wavelength range 326–1200 $m\mu$ in the same perchlorate media as used for the kinetic experiments. A Beckman DU 2400 spectrophotometer and 10 cm quartz cells were used. The Fe^{2+} ion possesses a Jahn-Teller split $d-d$ transition at 960 $m\mu$ and several spin-forbidden transitions in the range 386–505 $m\mu$ ^{10,11} which were all identified. The fact that no change was observed in the spectrum when any of the organic species were added, was taken as evidence against significant complex formation with Fe^{2+} , but does not exclude the possibility of ion pair formation. The complex formation of 2,2'-dipy and 1,10-phen with either Fe^{2+} or Fe^{3+} was not measured for reasons given below.

The possible complex formation of Tl^+ was investigated by measuring the solubility of TlIO_3 in solutions of the proper compositions. A slightly modified form of the method of Bell and George¹² was used. As no change of solubility was observed when the organic species were present, this was again taken as evidence against complex formation of Tl^+ .*

The measurement of the complex formation between the organic species added and Tl^{3+} or Fe^{3+} was based on Leden's method,¹³ no complex formation with Tl^+ and Fe^{2+} being assumed. The thallium or iron half cell initially contained a solution of known concentrations of the metal ion in two oxidation states, perchloric acid and sodium perchlorate. It was connected by a salt bridge to a reference vessel containing a Radiometer K 601 $\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ reference electrode. The bridge and the reference vessel contained perchloric acid and sodium perchlorate in the same concentrations as the measuring cell. The measuring electrode was a piece of platinized platinum foil which had been soaked in the solution for at least one hour before the measurements. After the initial potential had been read, a solution of the same composition but also containing the ligand, was added in portions, after each of which the equilibrium potential was read. Mechanical stirring was maintained throughout the whole experiment. Usually 10–15 min were required before the equilibrium was established, a time somewhat shorter than that found by Ahrland *et al.*¹⁴ in the measurements of formation constants of halide complexes of Tl^{3+} . The potential which was read on a Radiometer pH meter 4 remained constant after having been established, thus showing that no oxidation of the ligands by Tl(III) or Fe(III) was taking place.

Also, using the same potentiometer and a Radiometer glass electrode type G 202 B, the pK values of the aminopyridines and 4,4'-dipy were measured at an ionic strength $\mu=1.60$. Solutions of the proper amine in 1.60 M NaClO_4 were titrated with 0.01 M HClO_4 at the same ionic strength, made up with NaClO_4 .

Kinetic experiments. The procedure in Ref. 7 was used, and also blank experiments were carried out on solutions containing no Tl(III) , to see whether Ce(IV) oxidised the organic species during the quenching process. Such an interference took place in the case of 3-aminopyridine only, where a slightly different procedure was applied. Assuming from qualitative experiments that Ce(IV) was reduced much faster by Fe(II) than by the amine, a slight excess of Ce(IV) was added to the sample, followed by further titration with Ce(IV) to the ferroin end point. Due to the slow reaction between Tl(III) and Fe(II) , only a negligible uncertainty arises in the concentration determination.

All equilibrium and kinetic experiments were carried out at $\mu=1.60$ and at $25 \pm 0.1^\circ\text{C}$. Glass vessels were used throughout.

RESULTS

Stability constants. The redox potential of the Fe(III)/Fe(II) couple showed practically no change when the ligands were added, and it was then assumed that only a negligible complex formation took place with Fe^{3+} . The redox potential of the $\text{Tl}^{3+}/\text{Tl}^+$ couple in the absence of mediators is given by the Nernst equation which at constant activity coefficients at 25°C is

* From the variation of the solubility with $[\text{H}^+]$, the dissociation constant of HIO_3 was found to be 0.67 M.

$$E = E_0 + 0.0296 \log \frac{[\text{Tl}^{3+}]}{[\text{Tl}^+]} = E_0 + 0.0296 \log \frac{[\text{Tl(III)}]}{[\text{Tl(I)}]} \quad (1)$$

where $[\text{Tl(III)}]$ is the total concentration of Tl(III) . The constancy of E_0 for different values of $[\text{Tl}^{3+}]/[\text{Tl}^+]$ was taken as evidence for the validity of this equation within the concentration range used. Adding ligands which form complexes with Tl^{3+} , but not with Tl^+ gives

$$[\text{Tl(III)}] = [\text{Tl}^{3+}] + K_1[\text{Tl}^{3+}][\text{A}] + K_1K_2[\text{Tl}^{3+}][\text{A}]^2 + \dots \quad (2)$$

where A is the concentration of free ligand and the K 's are the successive formation constants. The potential change measured is then

$$\frac{\Delta E}{0.0296} = \log [1 + K_1 [\text{A}] + K_1K_2 [\text{A}]^2 + \dots] \quad (3)$$

The ligands present in the metal complexes are presumably the mono- or deprotonated anions. However, at the value of $[\text{H}^+]$ used (1.00 M) the principal carboxylic acid species present in the bulk of solution are the fully protonated acids,¹⁵ and it is therefore preferable to express eqn. (3) in terms of the concentrations of these species. If A refers to the fully protonated acid, eqn. (3) takes the same form, provided that K_1 and K_2 are expressed in terms of the true stability constants K_1^t and K_2^t and the first and second dissociation constants of the acids K_{s1} and K_{s2} as

$$K_1 = K_1^t \frac{[\text{H}^+]^2}{K_{s1} K_{s2}}; \quad K_2 = K_2^t \frac{[\text{H}^+]^2}{K_{s1} K_{s2}}$$

$$K_1 = \frac{K_1^t[\text{H}^+]}{K_{s2}}; \quad K_2 = K_2^t \frac{[\text{H}^+]}{K_{s2}}$$

when the de- and monoprotated species are ligands.

As the kinetic results had yielded relatively low values of K_1 for all the complexes but those of 2,2'-dipy and 1,10-phen (see below), it was assumed that at highest two consecutive complexes would be formed. Eqn. (3) was therefore plotted in the usual way¹³ and K_1 and K_2 calculated by successive approximation.

Tables 1 and 2 a, b, and c show typical examples of corresponding values of E , the total concentration of A, C_A and $[\text{A}]$ when the proper ligands are added to solutions of Tl^{3+} and Tl^+ , and Fig. 1 shows plots of $\left(\frac{[\text{Tl(III)}]}{[\text{Tl}^{3+}]} - 1\right)/[\text{A}]$ against $[\text{A}]$ for maleic, fumaric, succinic, and phthalic acid. In these cases $[\text{H}^+] = 1.00$ M. For the aminopyridines, $[\text{Tl(III)}]/[\text{Tl}^{3+}]$ was plotted against $[\text{A}]$, as shown in Fig. 2, since here $\left(\frac{[\text{Tl(III)}]}{[\text{Tl}^{3+}]} - 1\right)/[\text{A}]$ was constant within the experimental accuracy, *i.e.* only complexes containing one ligand molecule per central atom were formed. Also here, the formation constants are so small that there is only a negligible difference between C_A and $[\text{A}]$. From the slopes and intercepts of the lines, values of K_1 and K_2 were calculated and collected in Table 3 together with the $\text{p}K$ values of the aminopyridines and 4,4'-dipy

Table 1. Corresponding values of E , C_A and $[A]$. $[Tl(III)] = 6.74 \times 10^{-4}$ M, $[Tl^+] = 4.24 \times 10^{-4}$ M for fumaric acid, 8.48×10^{-4} M for the others.

Maleic acid			Fumaric acid		
E mV	C_A mM	$[A]$ mM	E mV	C_A mM	$[A]$ mM
585.4	0	0	574.0	0	0
582.1	2.00	1.84	572.3	0.62	0.57
578.8	3.97	3.69	571.9	1.24	1.14
576.1	5.89	5.53	570.0	2.43	2.25
574.2	7.77	7.35	568.4	3.68	3.34
572.3	9.63	9.17	566.8	4.69	4.39
569.4	13.24	12.70	565.4	5.73	5.43
566.0	18.38	17.77	563.2	8.22	7.87
561.1	26.40	25.70	559.0	12.60	12.08
558.2	40.40	39.50	556.5	14.60	14.02
553.2	46.70	45.90	554.0	18.00	17.38
Succinic acid			Phthalic acid		
579.2	0	0	580.8	0	0
578.1	0.62	0.57	574.8	3.49	3.23
575.2	2.42	2.25	572.7	5.13	4.78
573.7	3.56	3.32	570.8	6.71	6.31
571.0	5.73	5.40	569.0	8.24	7.79
564.0	12.60	12.10	565.4	11.81	11.28
559.9	18.00	17.42	561.0	18.13	17.49
558.0	21.00	20.40	559.3	20.90	20.20
556.7	23.60	23.00			

Table 2a. Corresponding values of E and C_A . 4-Aminopyridine, $[Tl(III)] = 6.74 \times 10^{-4}$ M, $[Tl^+] = 8.48 \times 10^{-4}$ M.

$[H^+] = 0.250$ M		$[H^+] = 0.516$ M		$[H^+] = 0.746$ M		$[H^+] = 1.00$ M	
E mV	C_A mM	E mV	C_A mM	E mV	C_A mM	E mV	C_A mM
591.0	0	584.6	0	581.3	0	576.4	0
590.3	6.50	584.0	5.04	580.6	4.90	576.0	3.89
590.1	7.99	583.8	8.09	580.0	7.88	575.1	9.19
589.9	11.40	583.7	9.57	579.8	9.28	574.3	13.20
589.7	14.60	583.2	13.60	579.2	13.20	574.0	15.42
589.5	17.60	583.1	14.80	578.7	17.26	573.8	16.86
589.3	20.30	582.9	17.80	578.2	20.00	573.2	20.20
589.1	22.90	582.7	20.60	577.9	22.50	572.8	23.40
588.8	27.30	582.4	23.10	577.4	24.70	572.2	26.20
588.7	29.30	582.3	25.50	577.2	26.90	571.9	28.90
588.7	31.10	582.3	29.70	577.0	28.90	571.8	31.40

Table 2b. Corresponding values of E and C_A . 2-Aminopyridine, $Tl(III) = 6.74 \times 10^{-4}$ M, $Tl^+ = 8.48 \times 10^{-4}$ M.

$[H^+] = 0.378$ M		$[H^+] = 0.516$ M		$[H^+] = 0.746$ M		$[H^+] = 1.00$ M	
E mV	C_A mM	E mV	C_A mM	E mV	C_A mM	E mV	C_A mM
589.2	0	587.2	0	582.0	0	577.0	0
588.5	4.54	586.8	3.21	581.3	5.77	576.0	6.20
588.0	7.27	586.2	7.60	580.9	8.36	575.8	8.98
587.4	10.42	585.9	10.86	580.5	11.90	575.6	10.92
587.0	13.30	585.5	13.90	580.1	15.60	575.3	12.80
586.2	18.60	585.2	16.70	579.9	18.00	575.1	13.96
585.6	22.90	585.0	19.30	579.6	20.20	575.0	16.80
585.2	24.80	584.8	21.70	579.3	22.30	574.8	19.40
581.1	26.70	584.7	23.90	579.1	24.20	574.6	21.80
581.1	28.40	584.5	26.00	579.0	26.00	574.4	24.00

Table 2c. Corresponding values of E and C_A . 3-Aminopyridine, $Tl(III) = 6.74 \times 10^{-4}$ M, $Tl^+ = 8.48 \times 10^{-4}$ M.

$[H^+] = 0.378$ M		$[H^+] = 0.516$ M		$[H^+] = 0.746$ M		$[H^+] = 1.00$ M	
E mV	C_A mM	E mV	C_A mM	E mV	C_A mM	E mV	C_A mM
589.8	0	585.2	0	580.5	0	577.0	0
588.1	3.10	583.4	3.10	579.0	3.06	575.2	3.06
587.6	4.56	583.0	4.56	578.5	4.51	574.8	4.51
587.0	5.98	582.4	5.98	578.0	5.89	574.3	5.89
586.1	8.62	582.0	7.34	577.6	7.25	574.0	7.25
585.5	10.60	580.3	12.30	577.1	9.39	573.6	9.39
584.6	13.40	578.0	18.60	576.5	10.40	573.0	10.40
583.7	16.10	577.2	20.90	576.0	12.20	572.1	13.20
582.9	18.60	576.6	23.00	575.8	13.20	570.6	18.40
582.0	20.90	576.0	25.00	574.9	15.90	570.0	20.60
581.3	23.00	575.4	26.90	574.2	18.40	568.8	24.60
580.8	25.00	575.0	28.60	573.4	22.80	568.0	28.20

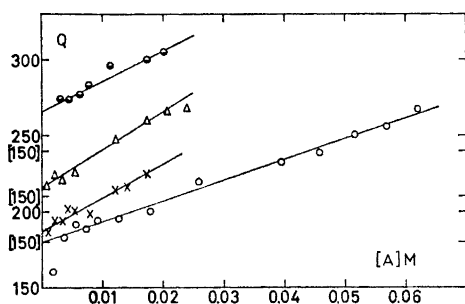


Fig. 1. Plots of $Q = \left(\frac{[Tl(III)]}{[Tl^{3+}]} - 1 \right) / [A]$ against $[A]$ for A = maleic (O), fumaric (x), succinic (Δ) and phthalic acid (\bullet). Plots have their origins separated by 30 ordinate units.

obtained from the glass electrode measurements. All tabulated K -values are the averages of results from several different concentration ratios of the metal ions.

4,4'-Dipy did not interact with the thallium couple. For the complexes of 2,2'-dipy and 1,10'-phen the successive approximation method did not work as the observed potential changes were too big. The stability constants of the complexes of these ligands with Fe^{2+} , Fe^{3+} , and Tl^{3+} are, however,

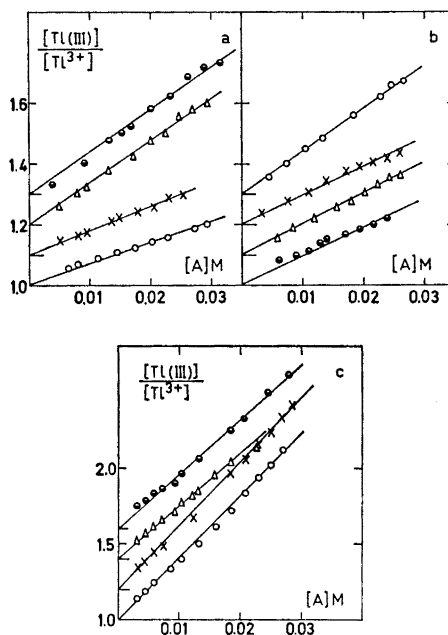


Fig. 2. Plots of $[\text{Tl(III)}]/[\text{Tl}^{3+}]$ against $[\text{A}]$ for A=2-aminopyridine (Fig. 2 a), 4-aminopyridine (Fig. 2 b) and 3-aminopyridine (Fig. 2 c). \circ $[\text{H}^+]=0.250$ M, \times $[\text{H}^+]=0.516$ M, \triangle $[\text{H}^+]=0.746$ M, \square $[\text{H}^+]=1.00$ M. Plots have their origins separated by 0.1 (2- and 4-aminopyridine) or 0.2 (3-aminopyridine) ordinate units.

Table 3. Stability constants and pK-values for mediators.

a)				b)			
Ligand	K_1 M ⁻¹	K_2 M ⁻¹	pK	Ligand	$[\text{H}^+]$ M	K_1 M	pK
Mal. acid	169	9.4	—	2-AP	0.378	13.4	6.60
Fum. acid	166	10.0	—	—	0.516	9.5	
Succ. acid	158	5.0	—	—	0.746	9.8	
Phth. acid	169	12	—	—	1.00	9.4	
4,4'-dipy	0	0	$\text{p}K_1=4.82$ $\text{p}K_2=3.27$	4-AP	0.250	7.1	9.42
				—	0.516	8.4	
				—	0.746	13.3	
				—	1.00	14.8	
				3-AP	0.378	36.0	6.15
				—	0.516	40.0	
				—	0.746	34.9	
				—	1.00	36.1	

known from the literature,¹⁵⁻¹⁷ and no further attempts were made to measure them in the present work.

Kinetics. No ligands added. As in Ref. 7 the kinetic results were treated on the basis of the rate expression.

$$\frac{k_{-1}(a+c)}{k_2-k_{-1}\left(1+\frac{a+c}{b-a}\right)} \times \frac{1}{[\text{Fe(II)}]_t} - \ln \frac{[\text{Fe(II)}]_t}{[\text{Tl(III)}]_t} = \frac{k_2(b-a)}{k_2-k_{-1}\left(1+\frac{a+c}{b-a}\right)} k_1 t + M \quad (4)$$

In agreement with Ref. 7 it was found that the most accurate values of k_1 were obtained when $-\ln\{[\text{Fe(II)}]_t/[\text{Tl(III)}]_t\}$ was plotted against t and the value of k_2/k_{-1} chosen which resulted in the best linear plot of eqn. (4).

Table 4.

- a) Values of k_1 at various reactant concentrations. $[\text{H}^+] = 1.00 \text{ M}$, $k_2/k_{-1} = 27.0$.
 b) k_1 and k_2/k_{-1} at various $[\text{H}^+]$
 $[\text{Tl(III)}]_0 = 6.65 \times 10^{-3} \text{ M}$,
 $[\text{Fe(II)}]_0 = 4.98 \times 10^{-3} \text{ M}$.

$[\text{Tl(III)}]_0 \text{ M}$ $\times 10^3$	$[\text{Fe(II)}]_0 \text{ M}$ $\times 10^3$	$k_1 \text{ M}^{-1} \text{ min}^{-1}$	$[\text{H}^+] \text{ M}$	$k_1 \text{ M}^{-1} \text{ min}^{-1}$	$\frac{k_2}{k_{-1}}$
7.99	2.41	0.91	0.250	2.64	7.6
7.99	5.09	1.00	0.344	2.19	10.6
7.99	5.82	1.04	0.516	1.62	15.1
7.99	6.99	1.01	0.746	1.26	18.6
7.99	9.31	0.99	1.000	0.99	27.0
4.04	5.88	0.96			
6.65	4.98	1.00			
15.68	5.71	1.04			
23.07	5.60	1.02			

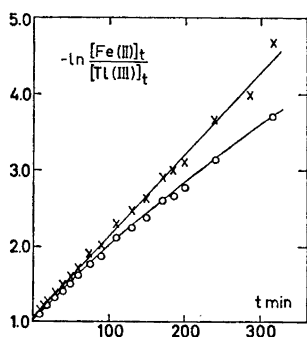


Fig. 3. Second-order plot (O) and plot of eqn. (5) (x). $[\text{H}^+] = 1.00 \text{ M}$, $[\text{Tl(III)}]_0 = 7.99 \times 10^{-3} \text{ M}$, $[\text{Fe(II)}]_0 = 5.82 \times 10^{-3} \text{ M}$.

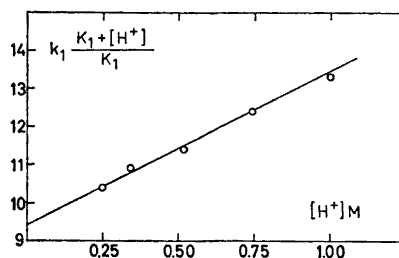


Fig. 4. Plot of left hand side of eqn. (6) against $[\text{H}^+]$. $[\text{Tl(III)}]_0 = 7.99 \times 10^{-3} \text{ M}$, $[\text{Fe(II)}]_0 = 5.09 \times 10^{-3} \text{ M}$.

Fe^{3+} was not added initially. Fig. 3 shows a typical plot of $-\ln\{[\text{Fe(II)}]_t/[\text{Tl(III)}]_t\}$ against t and the linear plot obtained when correction for the back reaction was made. Table 4 a gives values of k_1 for various reactant concentration at $[\text{H}^+] = 1.00 \text{ M}$, using $k_2/k_{-1} = 27.0$,⁷ while Table 4 b gives values of k_1 and k_2/k_{-1} at various $[\text{H}^+]$. Good agreement with the results of Ref. 7 is obtained where the two sets of data are comparable.

From the known hydrolysis constants^{18,19} it is calculated that the principal Tl(III) species are Tl^{3+} and TlOH^{2+} and that at highest 3 % of the total Tl(III) is present as Tl(OH)_2^+ . As neither Fe^{2+} nor Fe^{3+} are hydrolyzed to any appreciable extent under the present experimental conditions,¹⁵ the expression for the observed k_1 can be written

$$k_1 \frac{[K_1 + \text{H}^+]}{K_1} = \frac{k_1'}{K_1} [\text{H}^+] + k_1'' + k_1''' K_2 \frac{1}{[\text{H}^+]} \quad (5)$$

where the K 's are the hydrolysis constants of Tl^{3+} and k_1' , k_1'' , and k_1''' the rate constants of Tl^{3+} , TlOH^{2+} , and Tl(OH)_2^+ . Since a plot of the left hand side of eqn. (5) against $[\text{H}^+]$ is linear, as shown in Fig. 4, the contribution of the reaction of Tl(OH)_2^+ to the overall kinetics must be very small. From the plot and from a K_1 -value of 0.086¹⁹ it is found that $k_1' = 0.33 \text{ M}^{-1}$ and $k_1'' = 9.4 \text{ M}^{-1} \text{ min}^{-1}$. The kinetics of the first step of the reaction is thus interpreted in terms of reactions of Tl^{3+} and TlOH^{2+} rather than Tl(OH)_2^+ , as opposed to Refs. 7 and 20, where different values of K_1 were applied.

Kinetics. Carboxylic acids added. Also here, the treatment of Ref. 7 was used. Figs. 5 and 6 show the second-order plots, uncorrected for the backreaction of Fe^{3+} , in the presence of increasing amounts of maleic, fumaric, succinic,

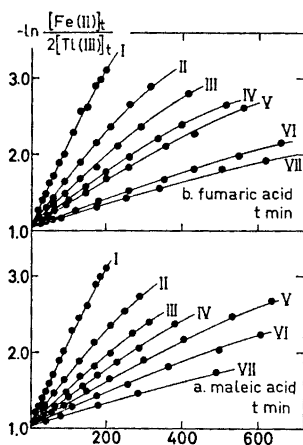


Fig. 5. Second-order plots for increasing concentrations of maleic (a) and fumaric (b) acid. $[\text{Tl(III)}]_0 = 7.99 \times 10^{-3} \text{ M}$, $[\text{Fe(II)}]_0 = 5.82 \times 10^{-3} \text{ M}$. Increasing roman numerals denote the increasing carboxylic acid concentrations of Table 7.

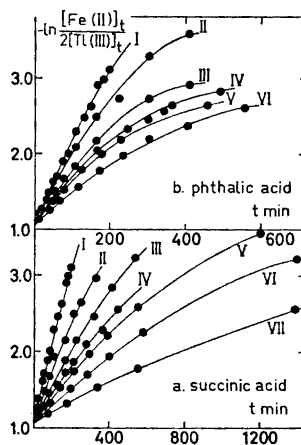


Fig. 6. Second-order plots for increasing concentrations of succinic (a) and phthalic (b) acid. $[\text{Tl(III)}]_0 = 7.99 \times 10^{-3} \text{ M}$, $[\text{Fe(II)}]_0 = 5.82 \times 10^{-3} \text{ M}$. Increasing roman numerals denote the increasing carboxylic acid concentrations of Table 7.

Table 5. k_1 and k_2/k_{-1} for increasing concentrations of carboxylic acids.

Fumaric acid				Maleic acid			
C_A M	[A] M	k_1 M ⁻¹ min ⁻¹	$\frac{k_2}{k_{-1}}$	C_A M	[A] M	k_1 M ⁻¹ min ⁻¹	$\frac{k_2}{k_{-1}}$
0.0049	0.0028	0.687	16.5	0.0051	0.0027	0.690	15.6
0.0098	0.0064	0.508	14.6	0.0102	0.0067	0.495	15.6
0.0147	0.0101	0.372	13.0	0.0153	0.0110	0.397	13.6
0.0196	0.0142	0.330	10.5	0.0204	0.0156	0.327	10.0
0.0294	0.0230	0.194	9.0	0.0305	0.0252	0.240	7.5
0.0502	0.0426	0.145	6.5	0.0500	0.0442	0.175	3.5
Phthalic acid				Succinic acid			
0.0050	0.0028	0.848	11.5	0.0050	0.0030	0.732	14.5
0.0100	0.0063	0.635	7.5	0.0099	0.0066	0.518	14.5
0.0151	0.0104	0.524	6.5	0.0149	0.0109	0.399	12.0
0.0201	0.0146	0.502	5.0	0.0199	0.0150	0.326	11.5
0.0301	0.0235	0.373	3.5	0.0298	0.0240	0.234	7.0
				0.0515	0.0447	0.159	4.5

and phthalic acid, and Table 5 reports the values of k_1 and k_2/k_{-1} giving the best linear plots of eqn. (4). The measurements were carried out at $[\text{H}^+] = 1.00$ M only. Assuming from the potential measurements that three Tl(III) species are present and can react, the rate of the first step can be written

$$-\frac{d[\text{Tl(III)}]}{dt} = k_{10}[\text{Tl}^{3+}][\text{Fe}^{2+}] + k_{11}[\text{TlA}][\text{Fe}^{2+}] + k_{12}[\text{TlA}_2][\text{Fe}^{2+}] \quad (6)$$

where the k 's are the rate constants of the reduction of the proper Tl(II)-species. The overall rate constant k_{obs} becomes

$$\frac{k_{\text{obs}} (1 + K_1[\text{A}] + K_1K_2[\text{A}]^2) - k_{10}}{K_1[\text{A}]} = k_{11} + K_{12}K_2[\text{A}] \quad (7)$$

where k_{10} is known from the kinetic measurements in the absence of ligands. From the potentiometrically determined values of K_1 and K_2 and the known total concentration of ligand C_A , values of the left hand side of eqn. (7) were calculated and plotted against $[\text{A}]$. However, in all of the four cases, within the experimental accuracy, $k_{12}K_2[\text{A}] \approx 0$ showing that the reaction of TlA_2 gives a negligible contribution to the overall kinetics. Instead, the equation

$$k_{\text{obs}} (1 + K_1[\text{A}] + K_1K_2[\text{A}]^2) = k_{10} + k_{11}K_1[\text{A}] \quad (8)$$

was plotted as shown in Fig. 7, and the values of k_{11} included in Table 6.

Attempts were made initially to determine k_{11} and K_1 from the kinetic data, plotting the equation²¹

$$\frac{1}{k_{10} - k_{\text{obs}}} = \frac{1}{k_{10} - k_{11}} + \frac{1}{k_{10} - k_{11}} \frac{1}{K_1} \frac{1}{[\text{A}]} \quad (9)$$

Table 6. Rate constants obtained for carboxylic acid complexes.

Ligand	Maleic acid	Fumaric acid	Succinic acid	Phthalic acid
$k_{11} \text{ M}^{-1} \text{ min}^{-1}$	0.116	0.089	0.078	0.42
$\frac{k_{21}}{k_{-11}}$	0.8	2.6	1.0	2.6
$\frac{k_{-11}}{k_{-10}} K_1'$	100	400	150	1600
$\frac{k_{-11}}{k_{-10}} K_1'$	120	155	145	625

This should be valid for the lower values of $[A]$, where only one complex is formed. Good linear relationships were found, and K_1 -values of 171, 173, 155, and 110 calculated for the complexes of maleic, fumaric, succinic, and phthalic acid. These values are in fairly good agreement with the equilibrium measure-

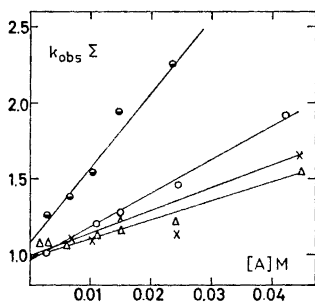


Fig. 7. Plots of eqn. (9) for maleic (O), fumaric (x), succinic (Δ), and phthalic acid (\bullet). $[\text{Tl(III)}]_0 = 7.99 \times 10^{-3} \text{ M}$, $[\text{Fe(II)}]_0 = 5.82 \times 10^{-3} \text{ M}$.

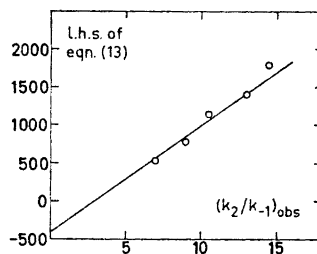


Fig. 8. Plot of eqn. (13) for fumaric acid.

ments, but as the accuracy of k_{11} becomes very low, the other treatment was preferred.

The values of k_2/k_{-1} were treated in a slightly different way, as the stability constants of Tl^{2+} were not known. It is reasonable to assume that no more than two ligand molecules are associated with Tl^{2+} . Then

$$\left(\frac{k_2}{k_{-1}}\right)_{\text{obs}} = \frac{k_{20} + k_{21}K_1'[A] + k_{22}K_1'K_2'[A]^2}{k_{-10} + k_{-11}K_1'[A] + k_{-12}K_1'K_2'[A]^2} \quad (10)$$

where K_1' and K_2' are the consecutive formation constants of the Tl^{2+} complexes. It is further assumed that $K_2' \ll K_1'$, so provided that k_{22} and k_{-12} are not much bigger than the other rate constants, eqn. (11) takes the form

$$\left(\frac{k_2}{k_{-2}}\right)_{\text{obs}} - \frac{k_{20}}{k_{-10}} = \frac{k_{21}}{k_{-10}} K_1' - \frac{k_{-11}}{k_{-10}} K_1' \left(\frac{k_2}{k_{-1}}\right)_{\text{obs}} \quad (11)$$

Fig. 8 shows a plot of eqn. (13) for fumaric acid. For all the four acids, good straight lines were obtained, and k_{21}/k_{-11} , $k_{21}K_1'/k_{-10}$, and $k_{-11}K_1'/k_{-10}$ were calculated and included in Table 6. k_{21}/k_{-11} is the rate constant ratio for the pure Tl(II) complex. The effect of the ligands on the individual rate constants can be evaluated, provided values of K_1' can be estimated, a matter which has been attempted below.

Kinetics. The dipyridines and 1,10-phen added. When 4,4'-dipy was added in concentrations up to 0.02 M, no effect was observed in the kinetics. This is probably because 4,4'-dipy is present in the diprotonated form only. 2,2'-Dipy and 1,10-phen in concentrations up to 0.015 M cause a very strong retardation of the reaction. As obviously any possible mediation effect is

Table 7. k_1 M⁻¹ min⁻¹ and k_2/k_{-1} for 2- and 4-aminopyridine. In all cases $C_A = [A]$ mM.

4-Aminopyridine														
[H ⁺]=0.250 M			[H ⁺]=0.344 M			[H ⁺]=0.516 M			[H ⁺]=0.746 M			[H ⁺]=1.00 M		
[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$
0	2.64	7.6	0	2.20	10.6	0	1.62	15.0	0	1.27	18.5	0	1.02	27.0
4.88	2.82	9.6	5.19	2.35	12.5	5.03	1.64	19.5	5.19	1.31	26.0	2.01	1.03	30.5
10.33	2.80	14.6	10.38	2.33	14.5	10.1	1.68	21.0	9.29	1.28	29.6	5.00	0.95	29.8
15.52	2.67	18.0	20.76	2.35	18.0	15.2	1.64	32	16.2	1.31	33.5	10.00	0.99	44
20.6	2.77	22.6	51.8	2.50	55	22.8	1.74	38	24.2	1.33	54	19.99	0.99	60
29.8	2.70	31	94.0	2.70	100	30.3	1.71	56	50.9	1.32	75	30.3	1.02	63
51.9	2.70	43				53.5	1.74	90				44.5	1.06	63
98.1	2.70	46				82.3	1.81	95				100.2	0.99	100
						105.6	1.81	110						

2-Aminopyridine											
[H ⁺]=0.250 M			[H ⁺]=0.516 M			[H ⁺]=0.746 M			[H ⁺]=1.00 M		
[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$	[A]	k_1	$\frac{k_2}{k_{-1}}$
0	2.64	7.6	0	1.62	15.1	0	1.26	18.6	0	1.02	27.0
5.08	2.81	21	5.31	1.71	2.16	4.74	1.30	28.6	4.82	1.04	34
10.28	2.81	31	10.57	1.77	29.6	10.41	1.35	31.6	10.38	1.05	41
15.22	2.72	38	15.02	1.71	30.6	16.50	1.35	38	15.06	1.06	47
20.6	2.72	48	20.5	1.74	35.6	21.6	1.35	42	20.6	1.03	55
31.4	2.78	53	31.4	1.74	35.6	34.8	1.37	70	30.4	1.08	70
51.2	2.79	110	51.7	1.75	60	50.3	1.40	66	51.3	1.02	87
99.1	2.79	110	99.7	1.73	75						

obscured by the strong complex formation of the reactants, and as also further complications arose due to the precipitation of complex salts, no attempt was made to treat the results of the amine interactions further.

Kinetics. The aminopyridines added. When 2- or 4-aminopyridine is added, effects arise, which are phenomenologically similar to the catalysis by platinum.⁸ Fig. 9 shows typical second-order plots for increasing concentrations of catalyst. It is seen that the initial slopes are equal to those of the uncatalyzed path, and that the deviation from second-order kinetics gets smaller, the higher the concentration of catalyst added. Similar series of experiments were carried out at a number of different acidities, and Table 7 reports k_1 and k_2/k_{-1} chosen to give the best linear plot for each kinetic run.

As only complexes containing one ligand exist for the aminopyridines, eqn. (11) is valid. When this equation was applied directly, a rather large scatter was observed for the smaller values of $(k_2/k_{-1})_{\text{obs}}$, due to the small difference between $(k_{20}k_{-1})_{\text{obs}}$ and $k_{20}k_{-10}$. As furthermore the larger values of $(k_2/k_{-1})_{\text{obs}}$ indicated that k_{11}/k_{-10} was very close to 1, better values of $(k_2/k_{-1})_{\text{obs}}$ could probably be obtained by rearranging eqn. (11) to

$$\left(\frac{k_2}{k_{-1}}\right)_{\text{obs}} (1 + K_1'[A]) = \frac{k_{20}}{k_{-10}} + \frac{k_{21}}{k_{-10}} K_1'[A] \quad (12)$$

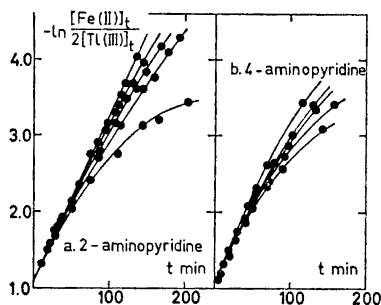


Fig. 9. Second-order plots for 2- (a) and 4-aminopyridine (b). $[Tl(III)]_0 = 6.65 \times 10^{-3}$ M, $[Fe(II)]_0 = 4.98 \times 10^{-3}$ M, $[H^+] = 0.250$ M. For 2-aminopyridine, the curves correspond to I: $[A] = 0$, II: 5.08 mM, III: 15.22 mM, IV: 31.4 mM, V: 99.1 mM. For 4-aminopyridine, I: $[A] = 0$, II: 4.88 mM, III: 10.33 mM, IV: 29.8 mM, V: 98.1 mM.

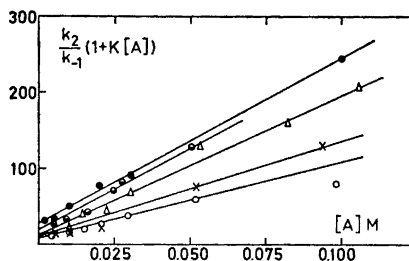


Fig. 10. Plot of eqn. (12) for $[H^+] = 0.250$ M (\circ), 0.344 M (\times), 0.516 M (\triangle), 0.746 M (\square), and 1.00 M (\bullet). A=4-aminopyridine.

assuming that $k_{-10} = k_{-11}$. It is furthermore shown below that it is reasonable to assume that the association constants of the 2- and 4-aminopyridine complexes of Tl^{3+} and Tl^{2+} are equal, or that $K_1 = K_1'$.

This means that Tl^{2+} possesses the same ligand and solvent sphere as Tl^{3+} . From a plot of eqn. (12), $(k_2/k_{-1})_{\text{obs}}$ values fitting this linear relationship exactly could then be read for given values of $[A]$. If the assumptions are not strictly correct, a plot of eqn. (12) should yield a smooth curve, on which

Table 8. Corrected values of k_2/k_{-1} , [A] given in mM.

4-Aminopyridine									
[H ⁺]=0.250 M		[H ⁺]=0.344 M		[H ⁺]=0.516 M		[H ⁺]=0.746 M		[H ⁺]=1.00 M	
[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$
0	7.0	0	11.0	0	15.5	0	18.5	0	26.5
4.88	11.6	5.19	12.9	5.03	22	5.19	27	2.01	31
10.33	15.8	10.38	15.5	10.1	30	9.29	31	5.00	34
15.52	19.9	20.76	20.3	15.2	35	16.2	43	10.00	42
20.6	23.6	51.8	73	22.8	45	24.2	52	19.99	55
29.8	30	94.0	128	30.3	54	50.9	75	30.3	65
51.9	43			53.5	76			44.5	77
98.1	62			82.3	95			100.2	100
				105.6	108				

2-Aminopyridine

[H ⁺]=0.250 M		[H ⁺]=0.516 M		[H ⁺]=0.746 M		[H ⁺]=1.00 M	
[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$	[A]	$\frac{k_2}{k_{-1}}$
0	7.6	0	15.1	0	18.6	0	27.0
5.08	21.6	5.31	21.6	4.74	26	4.82	34
10.28	31	10.57	27	10.41	35	10.38	41
15.22	39	15.02	31	16.50	44	15.06	48
20.6	47	20.5	36	21.6	52	20.6	56
31.4	61	31.4	44	34.8	73	30.4	67
51.2	80	51.7	56	50.3	97	51.3	87
99.1	110	99.7	75				

Table 9. k_{21}/k_{-10} , k_{21}/k_{20} , and k_{-11}/k_{-10} for 2- and 4-aminopyridine.

4-Aminopyridine						2-Aminopyridine			
[H ⁺] M	0.250	0.344	0.516	0.746	1.00	0.250	0.516	0.746	1.00
$\frac{k_{21}}{k_{-10}}$	131	168	212	147	147	191	145	155	213
$\frac{k_{21}}{k_{20}}$	18.7	15.2	13.7	8.0	5.5	14.3	9.7	8.4	8.3
$\frac{k_{-11}}{k_{-10}}$	0.89	0.85	0.99	0.90	0.95	1.04	1.09	0.95	1.02

again new values of $(k_2/k_{-1})_{\text{obs}}$ could be read. Fig. 10 shows a plot of eqn. (12) for 4-aminopyridine at five different acidities, giving straight lines within experimental accuracy. This is also the case for 2-aminopyridine, and Table 8 contains all the corrected $(k_2/k_{-1})_{\text{obs}}$ values fitting the straight lines. They have been used in Fig. 11 to plot eqn. (11) for the two aminopyridines (actually divided by K_1) at different acidities. The values of k_{21}/k_{-10} , k_{21}/k_{20} , and k_{-11}/k_{-10} calculated from the slopes and intercepts are collected in Table 9.

When 3-aminopyridine was added, a decrease in $(k_2/k_{-1})_{\text{obs}}$ and possibly in k_1 with increasing $[A]$ was observed. However, the effects were so small, that it was impossible to obtain $[(k_{20}/k_{-1}) - (k_2/k_{-1})_{\text{obs}}]$ with any reasonable accuracy. No quantitative treatment was therefore tried, but a possible mechanism is discussed below.

DISCUSSION

The variation of k_1 with $[H^+]$ in the absence of ligands has already been discussed. The variation of k_2/k_{-1} may be explained on the basis of the principle of microscopic reversibility. As the forward and backward reaction in the first step must pass through the same activated state, k_1 and k_{-1} must show the same dependence on $[H^+]$. This means that k_1/k_{-1} is independent of the acid concentration, and that $(k_2/k_{-1}) \times k_1 = (k_1/k_{-1}) \times k_2$ reflects the acid dependence of k_2 .

From the values

$[H^+]$ M	0.250	0.344	0.516	0.746	1.00
$(k_1/k_{-1}) k_2$	20.0	23.2	24.4	23.5	27.0

it is seen that k_2 is only slightly acid dependent implying that the unhydrolyzed Tl^{2+} is the principal reacting species.

The influence of the dicarboxylic acids and the aminopyridines on the kinetics has been investigated in some detail, and as the observed effects are of two basically different kinds, they are discussed separately below.

a. Dicarboxylic acids. From the experimental data it is possible to deduce the number of carboxylic acid ligands in the Tl(III) complexes, while the number of protons on the coordinating ligands can not be found from measurements at one $[H^+]$ only. It is thus impossible to decide whether maleic, succinic, or phthalic acid form chelate complexes. Steric reasons and the high value of $[H^+]$ would favour the rupture of one coordinating bond and imply that the actual ligand species are the monoprotonated anions.*

As only small differences are observed in the influence of succinic acid and the π -conjugated acids on the kinetics, a remote attack mechanism is unlikely. Furthermore, since the acids coordinate through the same atom as water, drastic changes would be expected neither in the electronic structure of Tl^{3+} nor in the charge distribution of the activated complex when a water molecule in the hydration sphere is replaced by a molecule of one of the acids.

* Maleic and fumaric acid could theoretically coordinate through the olefinic π electrons as has been suggested in Ref. 22. Under such an assumption, diprotonated carboxylic acids may also become possible ligands.

The decrease in rate constant k_1 with increasing ligand concentration therefore reflects the increased thermodynamic stability of the thallium(III) reactants over the thallium(III) aquo ion.

The dependence of k_2/k_{-1} on the concentration of the carboxylic acids is again considered in the light of the principle of microscopic reversibility. If one ligand is coordinated to Tl^{2+} , then

$$\frac{k_2}{k_{-1}} k_2 = \frac{k_1}{k_{-1}} \frac{k_{20} + k_{21} K_1' [A]}{1 + K_1' [A]} \text{ or}$$

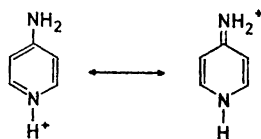
$$\frac{(k_1/k_{-1}) k_2 - (k_1/k_{-1}) k_2}{[A]} = K_1' \frac{k_1}{k_{-1}} k_2 - \frac{k_1}{k_{-1}} k_{21} K_1' \quad (13)$$

Calculating $(k_1/k_{-1}) k_2$ and plotting eqn. (12) yielded straight lines from the slopes of which values of K_1' were obtained. They were next used to find the rate parameters for the four ligand dependent paths, the data of which are summarized below.

	Maleic acid	Fumaric acid	Succinic acid	Phthalic acid
K_1' M	370	450	410	740
$\frac{k_{21}}{k_{20}}$	0.01	0.03	0.01	0.08
$\frac{k_{-11}}{k_{-10}}$	0.33	0.35	0.35	0.85

As k_{-11}/k_{-10} differs very slightly for the three aliphatic acids, it seems reasonable, for these ligands, to ascribe the greatest effect on k_2/k_{-1} to a decrease in the oxidation potential of the Tl(II)/Tl(I) couple. For phthalic acid the possibility of a kinetic effect on the Tl(II)—Fe(III) reaction can not be experimentally ruled out. An attempt was made to settle this point from experiments with *m*-phthalic acid, where no conjugated π -electron system exists in the possible exchange path, but the low solubility of this compound prevented a definite answer.

b. Aminopyridines. 2- and 4-Aminopyridine are stronger bases than pyridine, but take up one proton only, at the ring nitrogen atom.^{23,24} The monoprotonated aminopyridines which are the principal species under the prevailing experimental conditions, are resonance hybrids between the structures

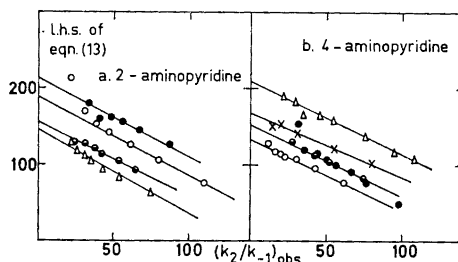


which explains the potential capability of both nitrogen atoms to interact with metal ions, even in strongly acid solution, and thus possibly to mediate an electron transfer.

The interaction of the monoprotonated 2- and 4-aminopyridine with Tl(III) is very weak, however, and may be ascribed to ion-dipole and ion-induced dipole forces strong enough to overcome the electrostatic repulsion between the positive charges of the ligand and metal ion. To find the association constants of Tl^{2+} , the same method was applied as for the carboxylic acid complexes. The values found are within the experimental accuracy the same as for the complexes of Tl^{3+} , and this justifies the treatment of the results given previously. One could also say that, in an equilibrium configuration, Tl^{2+} induces a smaller dipole, but is also less strongly repelled by the positive charge of the ligand. Two counteracting effects are thus met in going from Tl^{3+} to Tl^{2+} , although the net influence on the stability constant can not be deduced from this consideration alone. However, as k_1 is only very slightly dependent on the presence of 2- and 4-aminopyridine, if at all, then also k_{-1} can be very slightly dependent only.²⁵ The observed change in k_2/k_{-1} would consequently have to stem from changes in k_2 which is also what is found from the assumption of equal stability constants of Tl^{3+} and Tl^{2+} (Table 9). It is thus reasonable to assume that there is in fact only a very small difference in the association constants of the Tl^{3+} and Tl^{2+} complexes.

The observed effects (Fig. 11) of the monoprotonated aminopyridines are then ascribed to a pronounced catalysis of the Tl(II)/Fe(II) reaction. As

Fig. 11. Plot of eqn. (13) for 2- (a) and 4-aminopyridine (b). $[\text{H}^+] = 0.250 \text{ M}$ (\circ), 0.344 M (\times), 0.516 M (\triangle), 0.746 M (\ominus), 1.00 M (\bullet).



it is unlikely that an association as loose as the one found should lead to catalytic effects of the order of magnitude observed, if an adjacent attack mechanism were active, it is suggested that the reaction is an example of an outer sphere remote attack mechanism, where Fe^{2+} and Tl^{2+} in the activated state are present at the two nitrogen atoms. Although a proton transfer mechanism cannot be excluded we find it more likely that the electron is transferred through the conjugated electron system of the mediators, in close analogy to the effect observed when platinum is the catalyst. The effect, expressed as k_{21}/k_{20} decreases with increasing acidity, and a rough extrapolation to zero and infinite $[\text{H}^+]$ gives values for the unhydrolyzed Tl(II) of 5 and 4 and of the "monohydrolyzed" Tl(II) of 30 and 35 in the presence of 2- and 4-aminopyridine, respectively. This could be due to less coulombic repulsion between the three positively charged species in the activated complex.

No catalytic effects are observed in the presence of 3-aminopyridine. When protonation of this species takes place, the electron system in the ring loses its aromaticity to some extent. The slight decrease in $(k_2/k_{-1})_{\text{obs}}$

may here be a thermodynamic effect, similar to that of the carboxylic acids, as the formation constants of the Tl(III) complex is somewhat higher than for the other two pyridines.

The presence of homogeneous and heterogeneous electron mediation in the Tl(II)/Fe(II) reaction only, but neither in the Tl(III)/Fe(II) nor in the Tl(II)/Fe(III), reflects the existence of one mechanism common for the forward and back reaction of Tl(III)/Fe(II) and a different one for the Tl(II)/Fe(II) reaction. One could imagine that in the latter, the electron transfer step is rate controlling, facilitated by the mediator, while in the former it is the reorganization of the inner and outer solvent sphere.

The effect observed is phenomenologically similar to the one observed in the presence of bright platinum,⁸ and if the effect is an electron mediation, it might be expected that other reactions which are catalyzed by platinum will also be catalyzed by organic reagents containing large, delocalized electron systems. In homogeneous solution, however, the problem of transport to the catalyst surface is avoided, and also it is easier to distinguish between an inner or outer sphere mechanism from the magnitude of the stability constants than to elucidate the equivalent problem of the degree of adsorption on the catalyst surface. In the previously mentioned catalysis of the Tl^{3+}/Tl^{+} exchange reaction by platinum the oxygen bridge may thus originate from a partly oxidised surface platinum atom, in which case an inner sphere mechanism, accompanied by a partial dehydration of Tl^{3+} , seems plausible; or the hydrated Tl^{3+} may interact directly with platinum in the surface in which case the possibility of an outer sphere mechanism can not be ruled out.

In the literature there are several examples indicating that electron transfer in homogeneous solution can take place over distances of about 10 Å, although they are almost exclusively of the inner sphere type. Thus the bridging ligand²⁶ and the remote attack²⁷ mechanisms are examples of homogeneous long-range inner sphere electron mediations. Also a long-range mediation has been proposed to explain the electron transfer in aqueous solution between Fe^{2+} and Fe^{3+} ²⁸ and between $-SH$ and $-S-S-$ groups in certain proteins.²⁹ Outer sphere electron mediation may be what is observed in the pronounced catalysis of the MnO_4^-/MnO_4^{2-} electron exchange by the alkalic metal ions in the order $Li^+ \lesssim Na^+ < K^+ \ll Cs^+$ ^{30,31} and possibly in the catalysis of the $Fe(CN)_6^{3-}/Fe(CN)_6^{-4}$ by K^+ and other positively charged ions.³²

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