CHAPTER - I

THE VANADIUM(V) OXIDATION OF THALLIUM(I) IN HYDROCHLORIC ACID

A considerable decrease in the redox potential of the couple thallic/thallous[1] in hydrochloric acid from 1.25 V to about 0.682 V facilitates reactions which would otherwise not occur[2]. In this medium and in presence of ethanoic acid, while studying the oxidation of thallium(I) by chromium(VI)[3] it was observed that added vanadium(V) increases the reaction rate presumably due to formation of a complex between vanadium(V) and thallium(I). A further study on this system revealed that vanadium(V) itself oxidises thallium(I) in aqueous hydrochloric acid medium, the exact reverse of the well studied thallium(III) - vanadium(IV) reaction[4]. Such a change is mainly due to the reactant species in the medium chosen, namely thallium(III) sulphate complexes[4] and thallium(I) chloride complexes[2]. This chapter gives details of the mechanism of such a reversed reaction.

Experimental :

Reagent grade chemicals (BDH) and doubly distilled H_2O were used unless specified otherwise. Stock solutions of the oxidant, vanadium(V) were prepared by dissolving NH_4VO_3 in 0.5 mol dm^{-3} HCl and the concentrations were ascertained by titrating against standard ferrous ammonium sulphate using Ph_2NH as indicator[5]. Dissolution of TlCl and standardization by $KBrO_3$ gave Tl(I) solution. $HClO_4$ (Merck 70%) and NaCl were the source of H^+ and Cl^- ions utilised to vary acid and chloride ion concentrations respectively. The ionic strength was maintained by $NaClO_4$ obtained by dissolving requisite amounts of Na_2CO_3 and $HClO_4$. $TlCl_3$ solution was prepared by dissolving Tl_2O_3 in HCl (0.25 mol dm^{-3}). The vanadium(IV) solution was obtained by dissolving $VOSO_4$ in H_2O standardized against $KMnO_4$ and precipitating the sulphate by $BaCl_2$.

Kinetic studies :

The thermally equilibrated solutions of vanadium(V) and thallium(I) also containing required quantities of HCl and $NaClO_4$ were mixed and transferred to one of matched cells which was placed in thermostated cell compartment of shimadzu UV-160A instrument and the absorbance of vanadium(V) at 360 nm was followed. The application of Beer's law under the reaction conditions had earlier been verified in the 5.6×10^{-4} - 3.0×10^{-3} mol dm^{-3} concentration range of vanadium(V) ($\epsilon = 82.35$) (Table I(i))(Figure I(i)). The second order rate constants (k_{expt}) were obtained from the plots of log $[b(a-x)/a(b-x/2)]$ versus time, where a and b representing the oxidant and reductant concentrations respectively. The values of k_{expt} could be reproduced to within ± 6%. (one example run is given in Table I(ii) and the corresponding second order plot is shown in Figure I(ii)).

Table I(i) : Beers law varification for V(V) at 360 mm in 4.0 M. Hydrochloric acid at an ionic strength of 4.1 mol dm^{-3}

V(V)x10^4 mol dm^{-3}	O.D. at 360 nm.	V(V)x10^4 mol dm^{-3}	O.D. at 360 nm.
5.64	0.051	18.8	0.157
7.54	0.063	20.68	0.171
9.40	0.079	22.56	0.184
11.28	0.093	24.44	0.201
13.16	0.108	28.20	0.230
15.0	0.125	30.08	0.238
16.92	0.140		

Figure I(1). Beer's law varification for V(V) [—⊙—] and V(IV) [-△-] at 360 nm and 766 nm respectively in solutions containing 4.0 mol dm^{-3} hydrochloric acid.

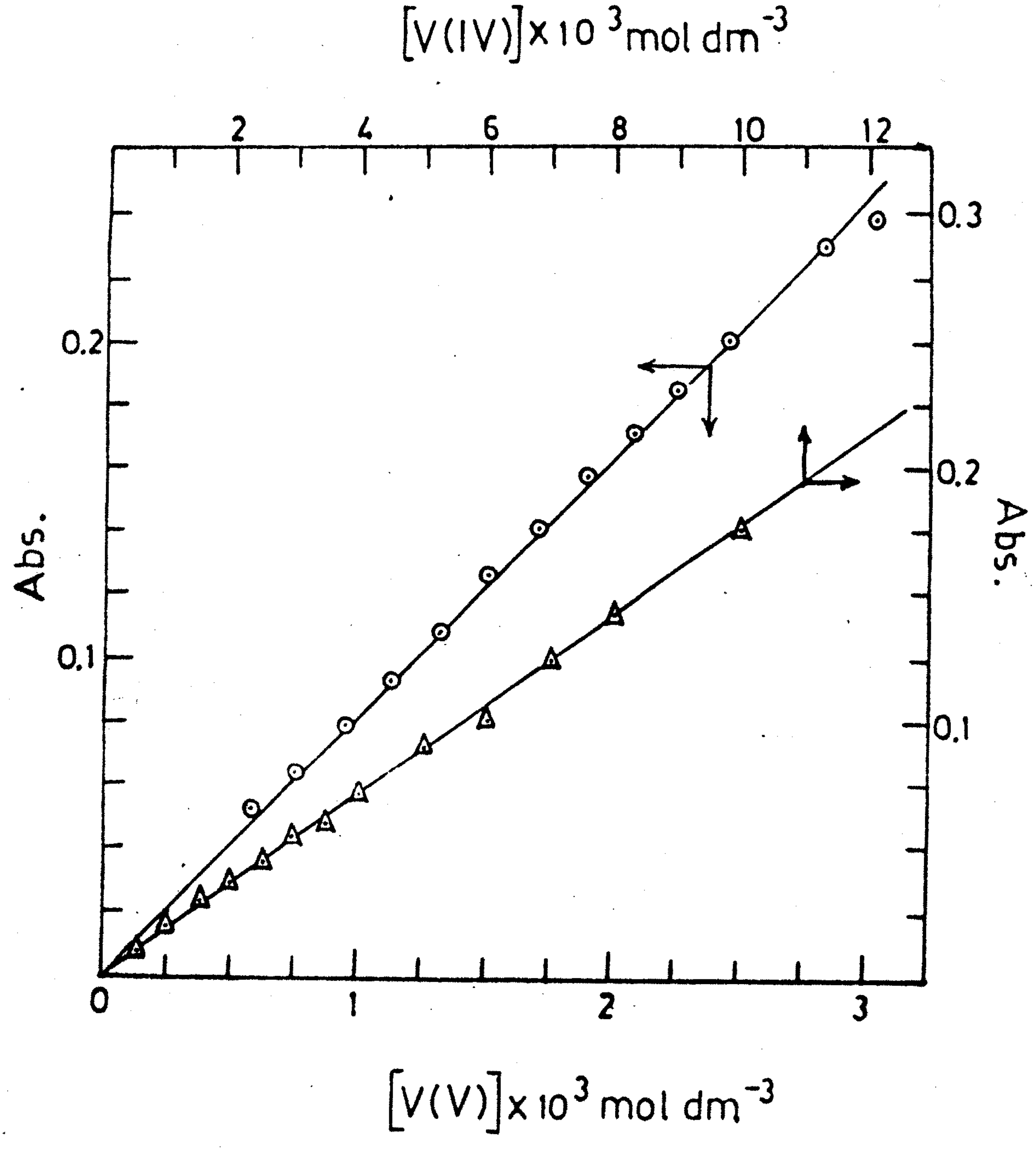


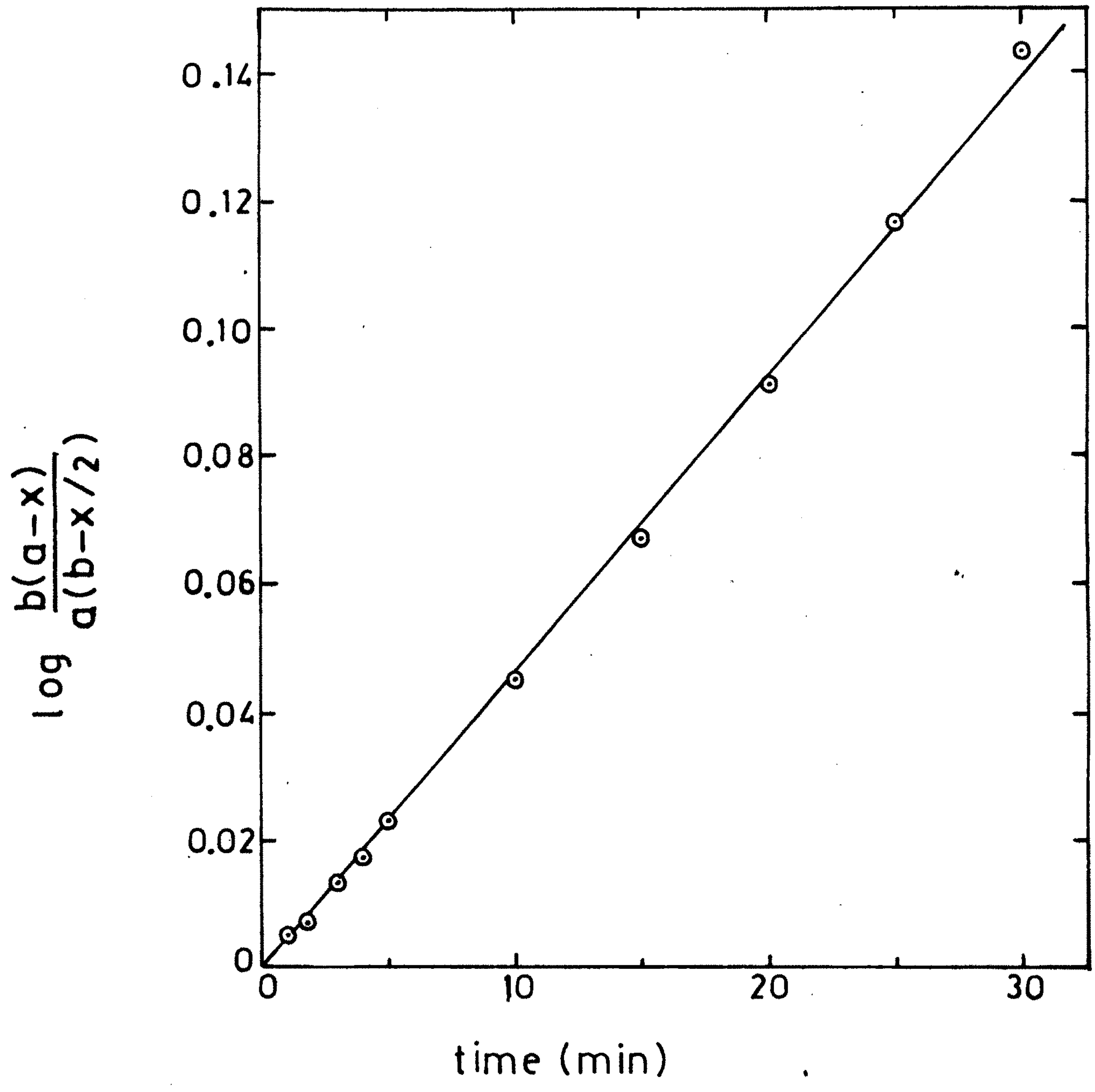
Table I(ii) : Oxidation of thallium (I) by vanadium (V)
Example run.

[V(V)] = 14.8×10^{-4} mol dm^{-3} [Tl(I)] = 6.0×10^{-4} mol dm^{-3}

[HCl] = 4.0 mol dm^{-3} I = 4.1 m. Temp. 25°C

Time (min)	O.D. at 360 nm.	[V(V)]x10^{-4} mol dm^{-3}	[Tl(I)]x10^{-4} mol dm^{-3}	$\log \frac{b(a-x)}{a(b-x/2)}$
0	0.114	13.84	5.52	-
1	0.109	13.23	5.22	0.0047
2	0.107	12.99	5.10	0.0068
3	0.102	12.38	4.79	0.0132
4	0.099	12.02	4.61	0.0170
5	0.095	11.54	4.37	0.0225
10	0.082	9.95	3.58	0.0447
15	0.073	8.85	3.03	0.0668
20	0.065	7.89	2.55	0.0913
25	0.059	7.16	2.18	0.1172
30	0.054	6.56	1.88	0.1435

Figure I(ii) : Second order plot for vanadium(V) oxidation of thallium(I) : Conditions as in Table I(ii)



Stoichiometry :

Different concentrations of reactants were mixed at constant HCl (4.0 mol dm^{-3}) and ionic strength (4.1 mol dm^{-3}). The oxidant was analysed by measuring its absorbance at 360 nm. Thallium(I) was analysed by titrating with $KBrO_3$ in 6 mol dm^{-3} HCl with methyl orange indicator. The product thallium(III) was analysed iodometrically and vanadium(IV) concentration was determined by measuring its absorbance at 766 nm. The Beer's law for vanadium(IV) under reaction conditions was also verified in the 5.0×10^{-4} to 3.5×10^{-3} mol dm^{-3} range at 766 nm (ϵ=17.77). (Table I(iii) (Figure I(i)). The stoichiometry was found to be two moles of oxidant to one mole of reductant. The results are shown in Table I(iv). Therefore stoichiometry can be represented as

$$2\ V(V) + Tl(I) = 2\ V(IV) + Tl(III) \qquad \ldots (1)$$

Results :

Rate law :

The order in oxidant and reductant was determined by plotting log. Inl. rate against log concentration at 4.0 mol dm^{-3}. The order with respect to thallium(I) between 1.0×10^{-4} to 7.0×10^{-4} mol dm^{-3} at constant vanadium(V) concentration of 14.8×10^{-4} mol dm^{-3} was found to be 0.78 (Table I(v) Figure I(iii)) and order with respect to oxidant between 7.40×10^{-4} to 22.2×10^{-4} mol dm^{-3} keeping thallium(I) concentration constant

Table I(iii) : Beer's law varification for V(IV) at 766 nm in 4.0 M. Hydrochloric acid at an ionic strength of 4.1 mol dm^{-3}

[V(IV)] x 10^3 mol dm^{-3}	O.D. at 766 nm
0.497	0.010
9.94	0.019
1.49	0.028
1.99	0.035
2.48	0.043
2.98	0.053
3.48	0.060

Table I(iv) : Stoichiometry for the V(V)-Tl(I) reaction in 4.0 mol dm^{-3} hydrochloric acid at an ionic strength of 4.1 mol dm^{-3}

[Tl(I)] Taken mol dm^{-3}	[V(V)] Taken mol dm^{-3}	[V(V)] Remaining mol dm^{-3}	[V(IV)] Found mol dm^{-3}	[Tl(III)] Found mol dm^{-3}
2.0×10^{-4}	11.29×10^{-4}	7.3×10^{-4}	-	-
3.0×10^{-4}	11.29×10^{-4}	5.22×10^{-4}	-	-
2.5×10^{-3}	2.45×10^{-2}	1.94×10^{-2}	4.95×10^{-3}	-
4.0×10^{-3}	2.45×10^{-2}	1.65×10^{-2}	7.93×10^{-3}	-
2.0×10^{-3}	2.0×10^{-3}	-	2.09×10^{-3}	1.05×10^{-3}
2.0×10^{-3}	3.0×10^{-3}	-	2.95×10^{-3}	1.48×10^{-3}

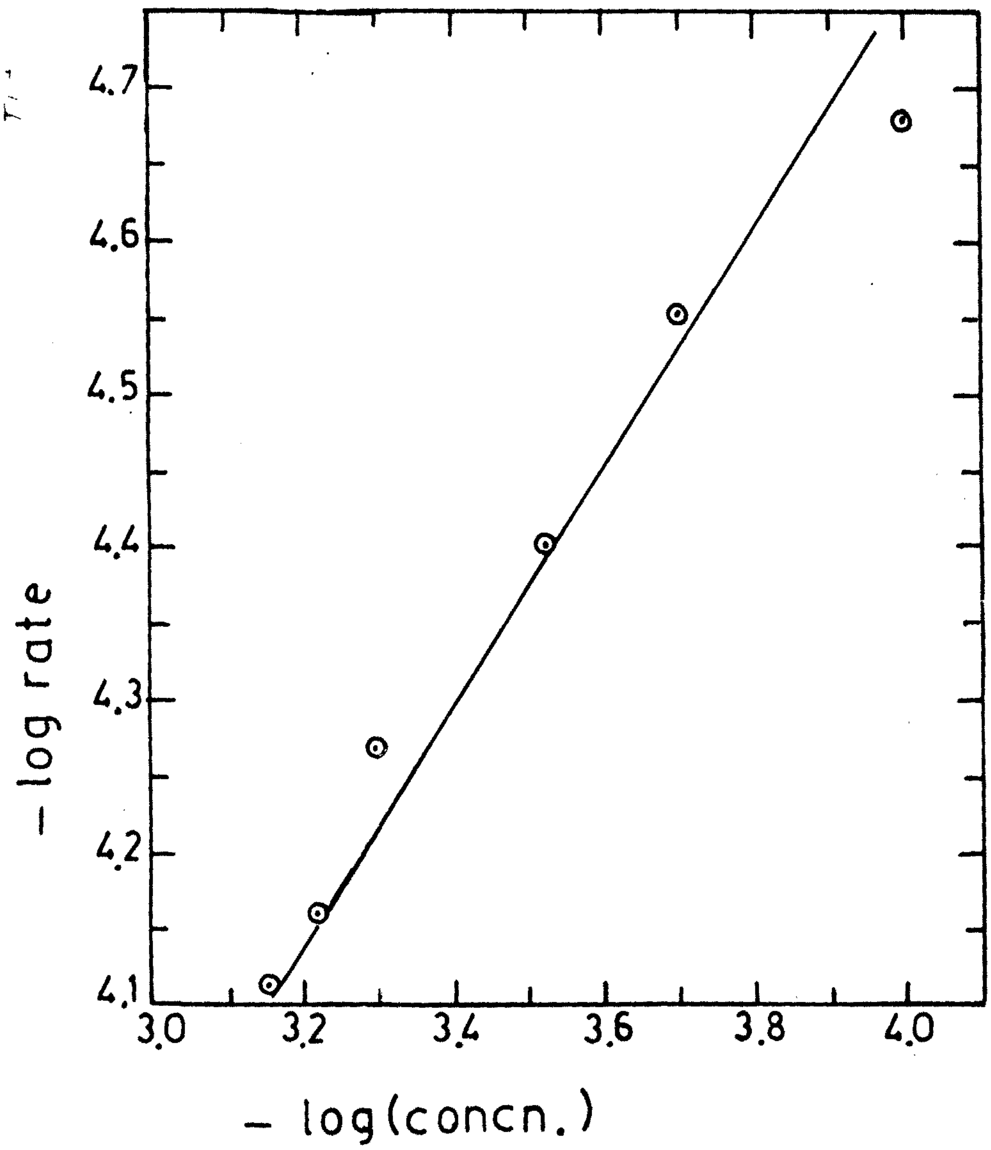
Table I(v) : Order w.r.t. thallium (I)

[HCl] = 4.0 mol dm^{-3} [V(V)] = [4.8 x 10^{-4} mol dm^{-3}

I = 4.1 mol dm^{-3} at 25°C

[Tl(I)]x10^{4} mol dm^{-3}	rate x 10^{5} min^{-1}	- log [Tl(I)]	- log rate
1.0	2.1	4.0000	4.6778
2.0	2.8	3.6989	4.5528
3.0	3.9	3.5228	4.4089
4.0	4.8	3.3979	4.3187
5.0	5.4	3.3010	4.2676
6.0	6.9	3.2218	4.1611
7.0	7.7	3.1549	4.1135

Figure I (iii) Order w.r.t. Tl (I)
(Conditions as in Table I (V))



at 7.0×10^{-4} mol dm^{-3} was 0.93 (Table I(vi), Figure I(iv)). The effect of changing concentrations of reactants is shown in Table I(vii) all other concentrations being constant.

While the second order rate constant, k_{expt}, is not altered significantly as concentration of vanadium(V) increases at constant thallium(I) there is decrease in k_{expt} with increase in thallium(I) concentration at constant vanadium(V) concentration.

Effect of added products :

The added products either the thallium(III) or vanadium(IV) did not have any significant effect on the reaction as k_{expt} for added thallium(III) between 1.0×10^{-4} to 7.0×10^{-4} mol dm^{-3} and for added vanadium(IV) between 3.0×10^{-4} to 12.6×10^{-4} mol dm^{-3} did not change. The data are given in Table I(viii).

Effect of added hydrogen ion concentration :

Increasing acid concentration, at constant chloride concentration, accelerates the reaction and the order in hydrogen ion concentration as determined by plots of log. Inl. Rate against log concentration was found to be 2.08 in the 2.0 to 4.0 mol dm^{-3} range of hydrogen ion concentration (Table I(ix) (Figure I(v)). The effect of added hydrogen ions on the k_{expt} is shown in Table I(x).

Table I(vi) : Order w.r.t. vanadium (V)

[HCl] = 4.0 mol dm^{-3} [Tl(I)] = 7.0 x 10^{-4} mol dm^{-3}

I = 4.1 mol dm^{-3} at 25°C

[Tl(I)]x10^4 mol dm^{-3}	rate x 10^5 min^{-1}	- log [V(V)]	- log rate
7.40	3.40	3.1308	4.4685
9.87	4.30	3.0057	4.3665
12.34	5.80	2.9087	4.2366
14.80	7.60	2.8297	4.1192
19.74	8.60	2.7046	4.0655
22.20	9.50	2.6536	4.0223

Figure I (iv) Order w.r.t. V (v)

(Conditions as in Table I (vi))

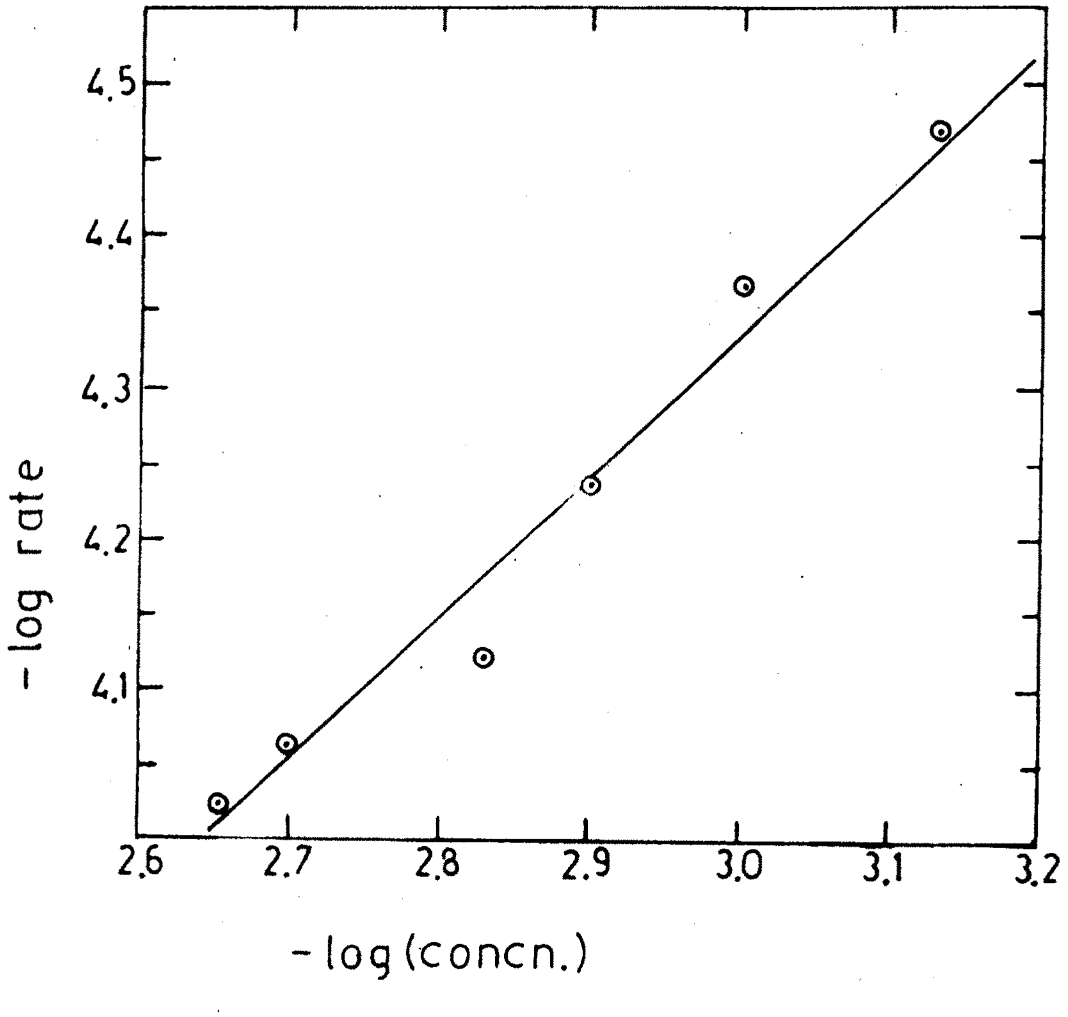


Table II(vii): Effect of reactant concentrations on the second order rate constant, k_{expt}, at 25°C[a]

$10^4[V^V]$ (mol dm^{-3})	$10^4[Tl^I]$ (mol dm^{-3})	k^*_{expt} (mol^{-1}dm^{3}s^{-1})
14.80	1.0	0.94
14.80	2.0	0.94
14.80	3.0	0.94
14.80	4.0	0.94
14.80	5.0	0.64
14.80	6.0	0.64
14.80	7.0	0.64
7.40	7.0	0.55
9.87	7.0	0.65
12.34	7.0	0.67
19.74	7.0	0.71
22.20	7.0	0.67

*[HCl] = 4.0 mol dm^{-3}, I = 4.1 mol dm^{-3}

Table I(viii) : Effect of added thallium (III) and vanadium (IV) on second order rate constant $k_{expt.}$ at 25°C

$[V(V)] = 14.8 \times 10^{-4}$ mol dm^{-3} $[Tl(I)] = 7.0 \times 10^{-4}$ mol dm^{-3}

$[HCl] = 4.0$ mol dm^{-3} $I = 4.1$ mol dm^{-3}

$[Tl(III)] \times 10^4$ mol dm^{-3}	k_{expt} mol^{-1}dm^{3}sec^{-1}	$[V(IV)] \times 10^4$ mol dm^{-3}	k_{expt} mol^{-1}dm^{3}sec^{-1}
0	0.64	0	0.64
1.0	0.63	3.0	0.62
2.0	0.64	3.36	0.64
3.0	0.65	5.60	0.65
5.0	0.63	8.40	0.63
7.0	0.62	12.60	0.64

Table I(ix) : Order w.r.t. hydrogen ion

$[V(V)] = 9.87 \times 10^{-4}$ mol dm^{-3} $[Tl(I)] = 5.0\times10^{-4}$mol dm^{-3}

$[Cl^-] = 4.0$ mol dm^{-3} $I = 4.1$ mol dm^{-3} at 25°C

$[H^+]$ mol dm^{-3}	rate x 10^5 min^{-1}	log $[H^+]$	-log rate
4.0	3.02	0.6020	4.5199
3.5	1.98	0.5440	4.7033
3.0	1.56	0.4771	4.8069
2.5	1.04	0.3979	4.9829
2.0	0.57	0.3010	5.2441

Figure I (v) Order w.r.t. (H+)

(conditions as in Table I (ix))

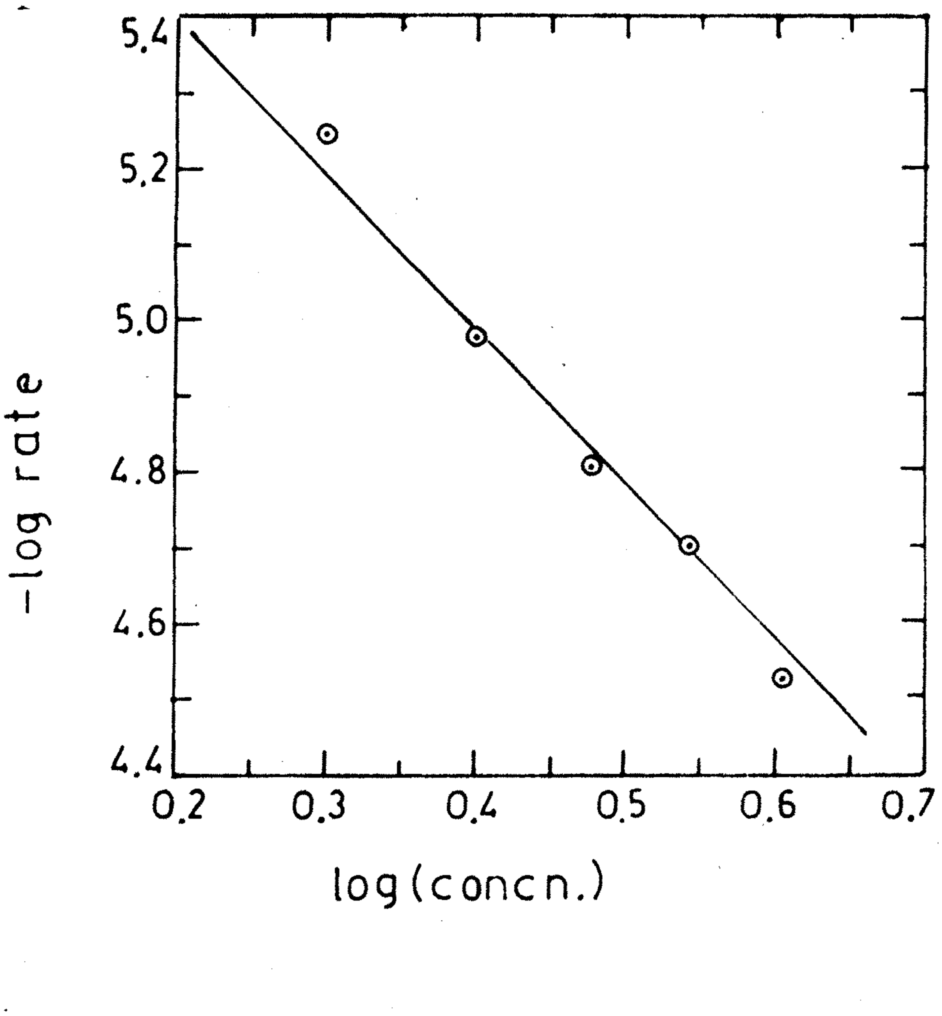


Table I(x) : Effect of hydrogen ion concentration on the second order rate constant, k_{expt}, at 25°C^a

$[H^+]$ (mol dm^{-3})	4.0	3.5	3.0	2.5	2.0
k^*_{expt} ($mol^{-1} dm^3 s^{-1}$)	0.69	0.26	0.18	0.12	0.09

* $[Cl^-]$ = 4.0 mol dm^{-3}, I = 4.1 mol dm^{-3}

10^4 $[Tl^I]$ = 5.0 mol dm^{-3} $10^4[V^V]$ = 10.0 mol dm^{-3}

Effect of added chloride :

The effect of added chloride ions on the reaction in the 2.0 to 4.0 mol dm^{-3} concentration range was studied while keeping all other concentrations constant. The results are shown in Table I(xi). k_{expt} being the second order rate constant. The order in chloride between 2.0 to 4.0 mol dm^{-3} as found from log-log plots of Inl. rate versus concentration was 2.22 Table I(xii), Figure I(vi).

Discussion :

The order with respect to reactants and the stoichiometry suggests the mechanism to be as given in Scheme 1, where the intermediate thallium(II) is forming

$$V(V) + Tl(I) \longrightarrow V(IV) + Tl(II) \quad \ldots \text{ Slow}$$
$$V(V) + Tl(II) \longrightarrow V(IV) + Tl(III) \quad \ldots \text{ Fast}$$

Scheme-1

in the first slow step and consumed in the fast second step. The products vanadium(IV) and thallium(III) do not have any effect on the reaction.

The second order rate constant, k_{expt} is found to decrease as the thallium(I) concentration increases above 4.0×10^{-4} mol dm^{-3}, at constant vanadium(V) concentration (Table I(vii). Thallium can form compounds of the type $TlVX_6$ with vanadium(V)[6]. Therefore, interaction between thallium(I) and vanadium(V) may be expected in that range of conentrations. The difference in the second order rate

Table I(xi) Effect of chloride ion concentration on the concentrations of the different Tl^{I} complexes and on the second order rate constant, k_{expt}, at 25°C[a]

$[Cl^-]$ ($mol\ dm^{-3}$)	k_{expt} ($mol^{-1}dm^{3}s^{-1}$)	$10^6[Tl^{I}]$ ($mol\ dm^{-3}$)	$10^4[TlCl]$ ($mol\ dm^{-3}$)	$10^4[TlCl_2^-]$ ($mol\ dm^{-3}$)	$10^4[TlCl_3^{2-}]$ ($mol\ dm^{-3}$)
4.0	0.69	0.83	1.29	1.81	1.81
3.5	0.45	1.09	1.48	1.82	1.59
3.0	0.32	1.46	1.71	1.79	1.34
2.5	0.22	2.03	1.98	1.73	1.08
2.0	0.13	2.94	2.29	1.61	0.80

[a] $[H^+] = 4.0\ mol\ dm^{-3}$, $I = 4.1\ mol\ dm^{-3}$, $10^4[Tl^{I}] = 5.0\ mol\ dm^{-3}$
$10^4[V^{V}] = 10.0\ mol\ dm^{-3}$

Table I(xii) : Order w.r.t. chloride ion

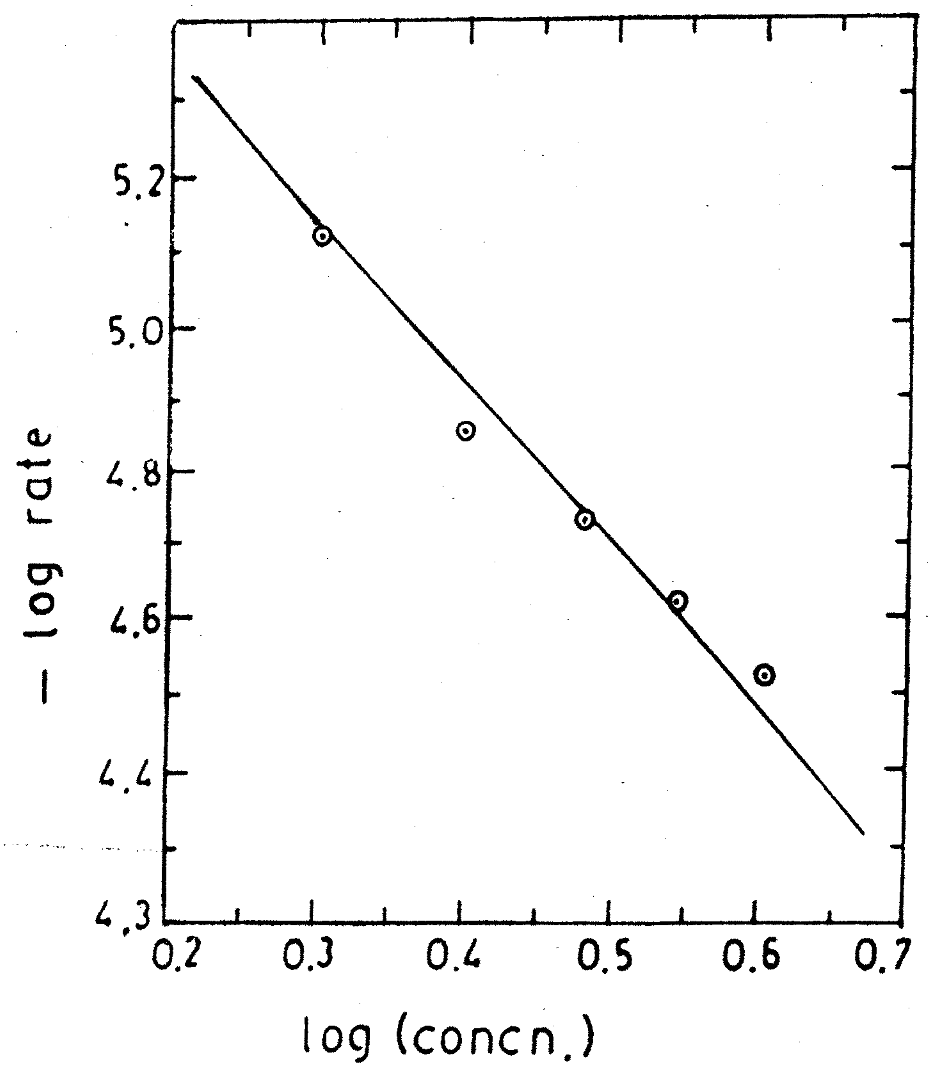
[V(V)] = 9.87×10^{-4} mol dm^{-3} [Tl(I)] = 5.0×10^{-4} mol dm^{-3}

[H^+] = 4.0 mol dm^{-3} I = 4.1 mol dm^{-3} at 25°C

[Cl^-] mol dm^{-3}	rate x 10^5 min^{-1}	log [Cl^-]	- log rate
4.0	3.02	0.6020	4.1599
3.5	2.38	0.5440	4.6234
3.0	1.86	0.4771	4.7305
2.5	1.40	0.3979	4.8539
2.0	0.76	0.3010	5.1192

Figure I (vi) Order w.r.t. Cl^-

(Conditions as in Table II(xii))



constant may be due to this reason. However, above 4.0 x 10^{-4} mol dm^{-3} of thallium(I) concentration there is no change in the values of k_{expt} as thallium(I) concentration increased further.

In strongly acidic medium at a concentration lower than 10^{-3} mol dm^{-3}, vanadium(V) exists mainly at VO_2^+ ion[7,8]. Although, vanadium(V) forms protonated species like HVO_4^{2-}, $H_2VO_4^-$ and H_3VO_4 in acidic medium, a rough calculation of concentrations of these species using reported stability constants[7] showed that either the concentrations are very low or they do not parallel the change in the second order rate constant as hydrogen ion concentration changes. Therefore, under the present conditions, VO_2^+ ion may be taken as the main active species. The dependance of the rate on the hydrogen ion concentration to the order of two can be due to formation of VO_2^+ ion by stepwise protanation of vanadate ion, VO_3^-, in prior equilibria 2 and 3.

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \quad (K_1) \qquad \ldots (2)$$

$$HVO_3 + H^+ \rightleftharpoons VO_2^+ + H_2O(K_2) \qquad \ldots (3)$$

The concentration of VO_2^+ ion can be obtained from equation 4 where $[VO_3^-]_T$ and $[VO_3^-]_f$ are total and free VO_3^- ion concentrations and β_1 and β_2 are respective cumulative stability constants of equilibria 2 and 3.

$$[VO_3^-]_T = [VO_3^-]_f \, (1 + \beta_1[H^+] + \beta_2[H^+]^2) \qquad \ldots (4)$$

The exact claculation of $[VO_2^+]$ becomes difficult due to various other equilibria of VO_3^- ion in aqueous acidic medium[7,8].

At constant hydrogen ion concentration increasing chloride ion concentration accelerates the reaction (Table I(xii)) Thallium(I) is known to form different chloride complexes[9] of the general formula $(TlCl_n)^{n-1}$, n being the number of chlorides complexed and respective equilibria are shown in 5 to 7 :

$$Tl^+ + Cl^- \rightleftharpoons TlCl \quad K_3 \qquad \ldots (5)$$

$$TlCl + Cl^- \rightleftharpoons TlCl_2^- \quad K_4 \qquad \ldots (6)$$

$$TlCl_2^- + Cl^- \rightleftharpoons TlCl_3^{2-} \quad K_5 \qquad \ldots (7)$$

The complexes 5 to 7 have the equilibrium constants K_3, K_4 and K_5 as 3.9,[10] 0.35 and 0.25[2] respectively at 25°C. The concentrations of thallium(I) complexes were calculated using equation 8, where $[Tl(I)]_T$ and $[Tl(I)]_f$ are

$$[Tl(I)]_T = [Tl(I)]_f \; (1 + \beta_3[Cl^-] + \beta_4[Cl^-]^2 + \beta_5[Cl^-]^3) \quad ..(8)$$

total and uncomplexed thallium(I) concentrations respectively and β_3, β_4 and β_5 are the cumulative stability constants of complexes 5,6 and 7 respectively. The concentrations, shown in Table I(xi), indicate that there is a rough parallel between the concentrations of $TlCl_3^{2-}$ and the rate constant k_{expt}. The data of Table I(xi), are also used to obtain Figure I(vii) showing the plots of k_{expt} and $[TlCl_3^{2-}]$ as function of $[Cl^-]$. It would appear from the results of Table I(xi) and Figure I(vii) that $TlCl_3^{2-}$ can reasonably be taken as the main active species under the present conditions.

The mechanism therefore, may involve VO_2^+ as the oxidant and $TlCl_3^{2-}$ as the reductant. The chloride complex $TlCl_3^{2-}$ of reductant and VO_2^+ ion of oxidant are formed in prior equilibria. In terms of these active species the mechanism can be represented as in Scheme-2.

$$\begin{array}{llcll}
VO_3^- + 2H^+ & \rightleftharpoons & VO_2^+ + H_2O & (\beta_2) & \\
Tl^+ + 3Cl^- & \rightleftharpoons & TlCl_3^{2-} & (\beta_5) & \\
VO_2^+ + TlCl_3^{2-} & \rightleftharpoons & TlCl_3^- + V^{IV} & (k) & \text{slow} \\
VO_2^+ + TlCl_3^- & \longrightarrow & TlCl_3 + V^{IV} & & \text{fast}
\end{array}$$

Scheme-2

According to Scheme-2 the rate law can be derived as follows :

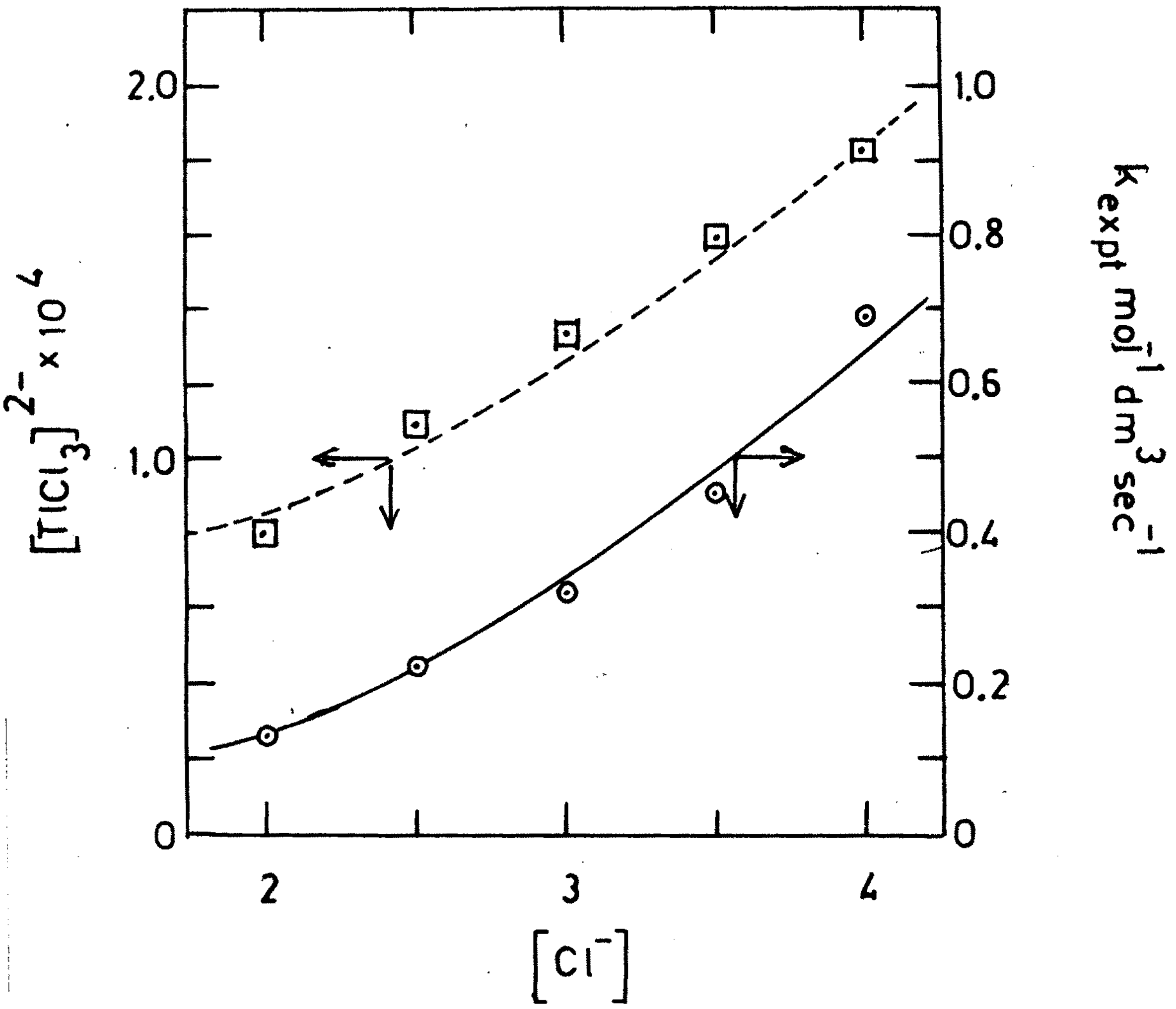
$$\frac{-d[V^V]}{dt} = k\,[VO_2^+][TlCl_3^{2-}] \qquad \ldots (9)$$

But from equation (4) and equilibria 2 & 3 we get

$$[VO_2^+] = \frac{\beta_2\,[V^V][H^+]^2}{1+\beta_1[H^+]+\beta_2[H^+]^2} \qquad \ldots (10)$$

Similarly from equation (8) and equilibria 5,6 & 7

Figure I(vii) Plot of concentrations of $TlCl_3^{2-}$ and k^*_{expt} as a function of Chloride ion concentration.



* conditions as in table I(xi)

$$[\mathrm{TlCl}_3^{2-}] = \frac{\beta_5[\mathrm{Cl}^-]^3[\mathrm{Tl}^{\mathrm{I}}]}{1+\beta_3[\mathrm{Cl}^-]+\beta_4[\mathrm{Cl}^-]^2+\beta_5[\mathrm{Cl}^-]^3} \quad \ldots(11)$$

Thus from equations 9, 10 & 11 the rate law would be

$$-\frac{d[\mathrm{V}^{\mathrm{V}}]}{\mathrm{Cl}} = \frac{k\,\beta_2\beta_5[\mathrm{H}^+]^2[\mathrm{Cl}^-]^3[\mathrm{Tl}^{\mathrm{I}}][\mathrm{V}^{\mathrm{V}}]}{(1+\beta_1[\mathrm{H}^+]+\beta_2[\mathrm{H}^+]^2)(1+\beta_3[\mathrm{Cl}^-]+\beta_4[\mathrm{Cl}^-]^2+\beta_5[\mathrm{Cl}^-]^3)} \quad ..(12)$$

Therefore the reaction between vanadium(V) and thallium(I) is rendered possible due to formation of chloride complexes of thallium(I) such as TlCl_3^{2-} which is main active species in the reaction. Although other chloride complexes of thallium(I) and the protonated vanadium(V) species may be active but to much lesser extents.

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