
CHAPTER - III

**RESULT AND DISCUSSION:
TETRACHLOROAUROATE (III)
OXIDATION OF THALLIUM (I)**

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The oxidation of thallium(I) by chromium(VI)⁴⁵ hexacyanoferrate(III)⁴⁷ and vanadium(V)⁴⁹ takes place in hydrochloric acid medium. These reactions rendered possible due to decrease in the redox potential of the thallic/thallic couple from 1.25 v in sulphuric and perchloric acid to 0.682 v in hydrochloric acid. This decrease can be attributed to the difference in the stabilities of thallium(III) and thallium(I) chlorocomplexes. A slight higher redox potential of 0.93 v of the $\text{AuCl}_4^-/\text{AuCl}_2^-$ couple favours a complementary reaction between thallium(I) and tetrachloroaurate in hydrochloric acid. A literature survey also revealed that only few inorganic reactions have been investigated^{54,55} kinetically with tetrachloroaurate as an oxidant as compared with isoelectronic tetrachloroplatinum(IV) ion. Therefore we have investigated thallium(I) tetrachloroaurate reaction kinetically. In addition, we have also carried out the pyridinium chloro chromate oxidation of thallium(I), in order to know the change in the course of the reaction, if any, by modifying the nature of oxidant either by complexation or by taking it in the form of an adduct. The details are given in the following chapters III and IV.

RESULTS

The order's in oxidant and reductant were determined from log (Initial rate) against log (concentration) plots. The order with respect to oxidant and reductant were found to be 0.9 each in the concentration range of 2.0×10^{-4} to 4.0×10^{-4} M and 1.95 to 5.85×10^{-4} M for the oxidant and reductant respectively. The data are given in Table 3.1 and 3.2 and the plots are shown in Figure 3.1 to 3.2 respectively. The values of second order rate constants are given in Table 3.3. The data of two example runs are given in Table 3.4 and 3.5 with respective second order plots in Figure 3.3 and 3.4.

The effect of hydrogen and chloride ions on the reaction was studied between the concentration range of 1.0 to 3.0 M and 0.5 to 3.0 M respectively keeping the concentrations of reactants constant at 3.1×10^{-4} M each. The effect of hydrogen and chloride ions on the second order rate constant, k_s is given in Table 3.6 and 3.7 respectively. The order in hydrogen and chloride ions were found to be 0.3 and 1.9 respectively as found from log k_s against log (concentration) plots (Figure 3.5 & 3.6). The data for two example runs are given in Table 3.8 and 3.9 and the second order plots are shown in Figure 3.7 and 3.8 respectively.

Table 3.1 : Order in $[\text{AuCl}_4^-]$

$[\text{Tl(I)}] = 3.12 \times 10^{-4} \text{ M}$, $[\text{HCl}] = 3.0 \text{ M}$,

$I = 3.1 \text{ M}$,

Temp = 25° C

$[\text{AuCl}_4^-] \times 10^4$ M	Inl. Rate $\times 10^7 \text{ s}^{-1}$	$-\log [\text{AuCl}_4^-]$	$-\log (\text{Inl. Rate})$
2.0	1.81	3.6989	6.7407
2.5	2.16	3.6020	6.6642
3.0	2.31	3.5228	6.6351
3.5	2.91	3.4559	6.5351
4.0	3.36	3.3979	6.4728

Figure 3.1: Order in tetrachloroaurate(III) (conditions as in Table 3.1)

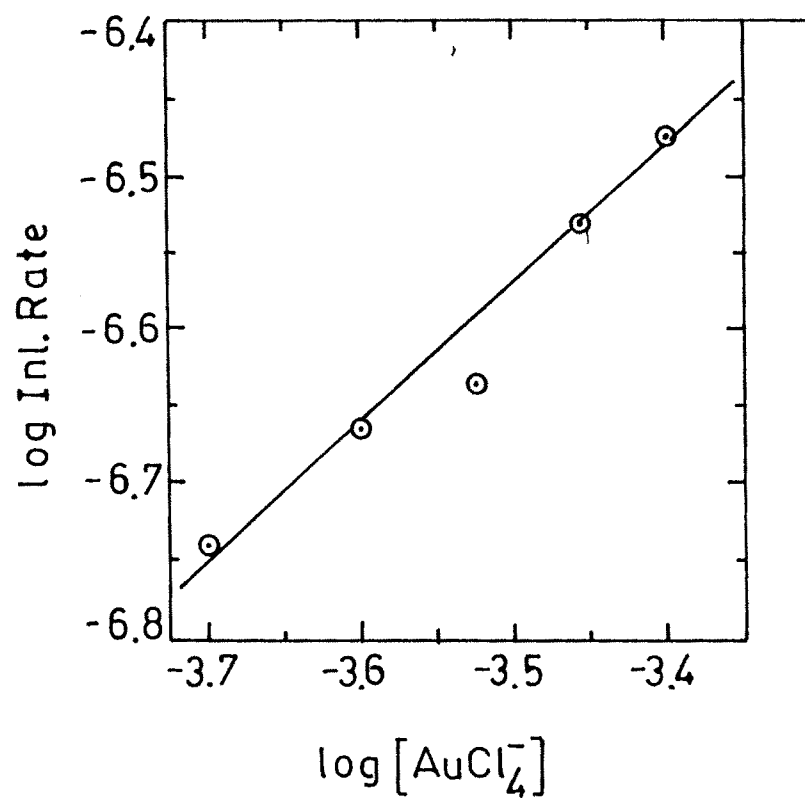
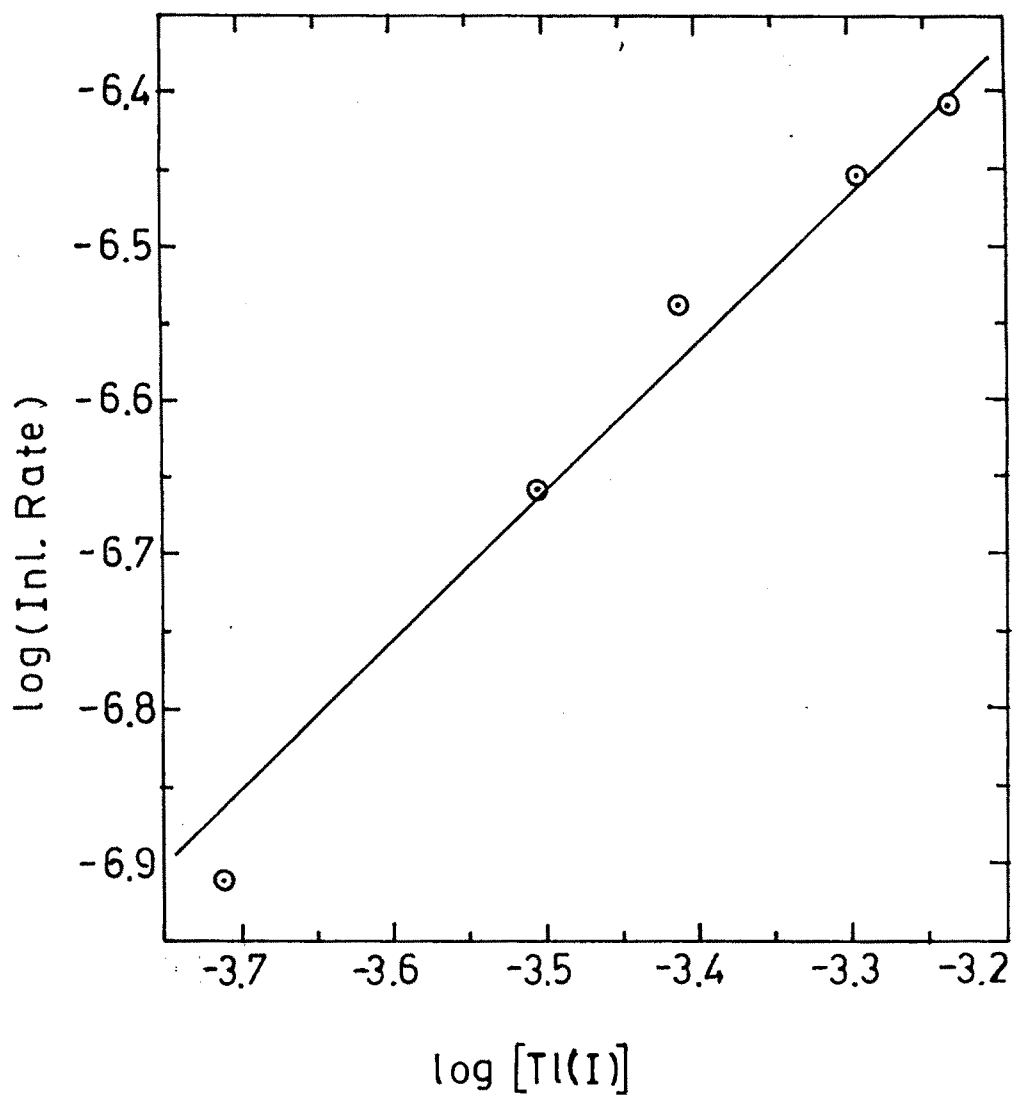


Table 3.2 : Order in Tl(I)
[AuCl₄⁻] = 3.0x10⁻⁴ M, [HCl] = 3.0 M,
I = 3.1 M, Temp = 25° C

[Tl(I)]x10 ⁴ M	Inl.Ratex10 ⁷ s ⁻¹	-log [Tl(I)]	-log (Inl.Rate)
1.95	1.23	3.7099	6.9089
3.12	2.20	3.5058	6.6575
3.90	2.90	3.4089	6.5376
5.07	3.53	3.2949	6.4518
5.85	3.91	3.2328	6.4070

Figure 3.2: Order in thallium(I) (conditions as in Table 3.2)



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Table 3.3 : Effect of reactants on second order rate constant k_s , at 25° C.

[HCl] = 3.0 M, I = 3.1 M

[Au(III)] x 10 ⁴ M	[Tl(I)] x 10 ⁴ M	K M ⁻¹ s ⁻¹
2.0	3.12	3.0
2.5	3.12	3.0
3.0	3.12	2.9
3.5	3.12	3.0
4.0	3.12	3.0
3.0	1.95	3.1
3.0	2.73	3.1
3.0	3.12	3.0
3.0	3.90	3.1
3.0	5.07	3.0
3.0	5.85	3.1

Table 3.4 : Example run AuCl_4^- oxidation of thallium(I)
 $[\text{AuCl}_4^-] = 2.5 \times 10^{-4} \text{M}$, $[\text{Tl(I)}] = 3.12 \times 10^{-4} \text{M}$
 $[\text{HCl}] = 3.0 \text{ M}$, $\text{I} = 3.1 \text{ M}$, $\text{Temp} = 25^\circ \text{C}$

Time in minutes	O.D.	$[\text{AuCl}_4^-] \times 10^4 \text{ M}$	$\text{Tl(I)} \times 10^4 \text{M}$	$\log \frac{b(a-x)}{a(b-x)}$
0	0.117	2.52	3.12	0.0000
1	0.110	2.37	2.97	0.0052
2	0.105	2.26	2.86	0.0095
3	0.100	2.15	2.75	0.0141
4	0.096	2.07	2.67	0.0178
5	0.092	1.98	2.58	0.0222
6	0.088	1.89	2.49	0.0269
7	0.085	1.83	2.43	0.0304
8	0.080	1.72	2.32	0.0372
9	0.077	1.66	2.26	0.0412
10	0.074	1.59	2.19	0.0462
15	0.062	1.33	1.93	0.0689
20	0.049	1.05	1.65	0.1035

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Figure 3.3: Example run: tetrachloroaurate(III) oxidation of thallium(I) (conditions as in Table 3.4)

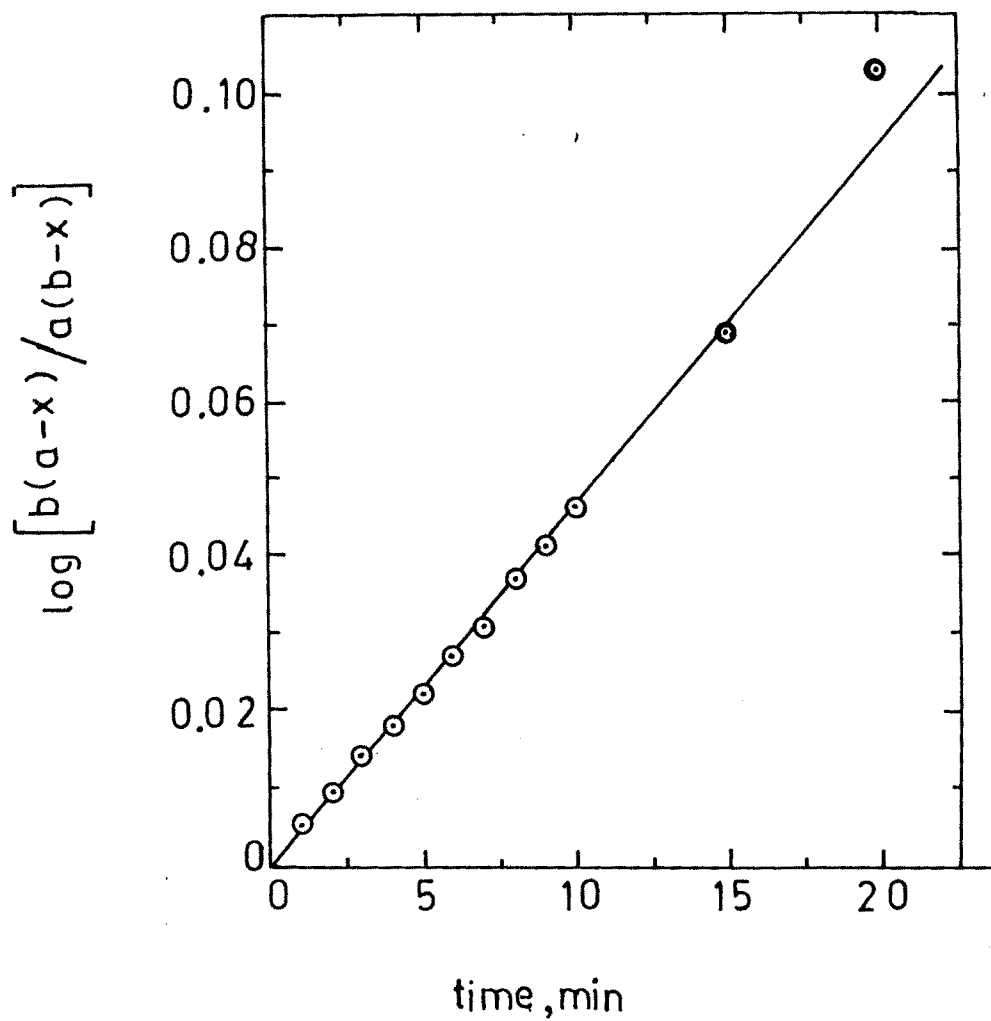


Table 3.5 : Example run AuCl_4^- oxidation of thallium(I)
 $[\text{AuCl}_4^-] = 3.0 \times 10^{-4} \text{M}$, $[\text{Tl(I)}] = 5.85 \times 10^{-4} \text{M}$
 $[\text{HCl}] = 3.0 \text{ M}$, $\text{I} = 3.1 \text{ M}$, $\text{Temp} = 25^\circ \text{C}$

Time in minutes	O.D.	$[\text{AuCl}_4^-] \times 10^4 \text{ M}$	$\text{Tl(I)} \times 10^4 \text{ M}$	$\log \frac{b(a-x)}{a(b-x)}$
0	0.137	2.95	5.80	0.0000
1	0.129	2.78	6.63	0.0128
2	0.116	2.50	5.35	0.0368
3	0.103	2.22	5.07	0.0650
4	0.094	2.02	4.87	0.0886
5	0.085	1.83	4.68	0.1142
6	0.076	1.64	4.49	0.1438
7	0.070	1.51	4.36	0.1669
8	0.062	1.33	4.18	0.2037
9	0.057	1.23	4.08	0.2271
10	0.052	1.12	3.97	0.2559
15	0.037	0.79	3.64	0.3698
20	0.028	0.60	3.45	0.4660

Figure 3.4: Example run: tetrachloroaurate(III) oxidation of thallium(I) (conditions as in Table 3.5)

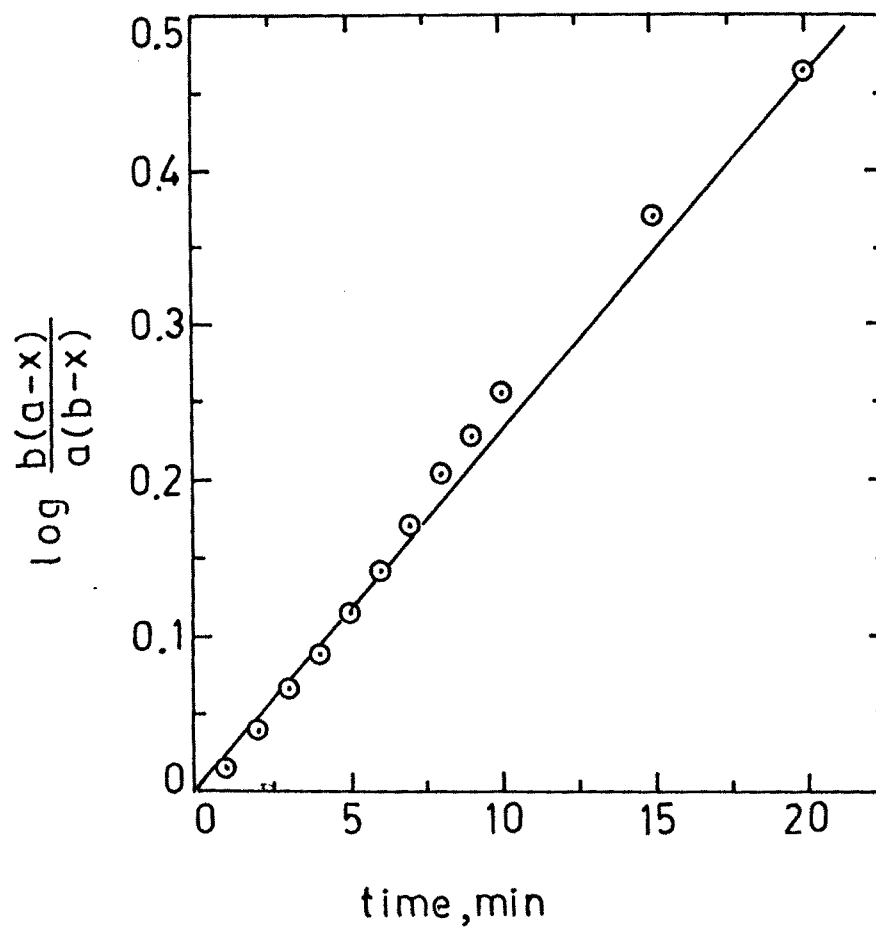


Table 3.6 : Effect of hydrogen ion concentration on second order rate constant k_s .

$[\text{AuCl}_4^-] = 3.1 \times 10^{-4} \text{M}$, $[\text{Tl(I)}] = 3.1 \times 10^{-4} \text{M}$

$[\text{Cl}^-] = 3.0 \text{ M}$, $I = 3.1 \text{ M}$, Temp. = 25°C

$[\text{H}^+] \text{ M}$	$k_s \text{ M}^{-1} \text{ s}^{-1}$	$\log [\text{H}^+]$	$\log k_s$
1.0	2.4	0.0000	0.3802
1.5	2.6	0.1761	0.4149
2.0	2.9	0.3010	0.4624
2.5	3.0	0.3979	0.4771
3.0	3.1	0.4771	0.4913

Figure 3.5: Order in hydrogen ion concentration (conditions as in Table 3.6)

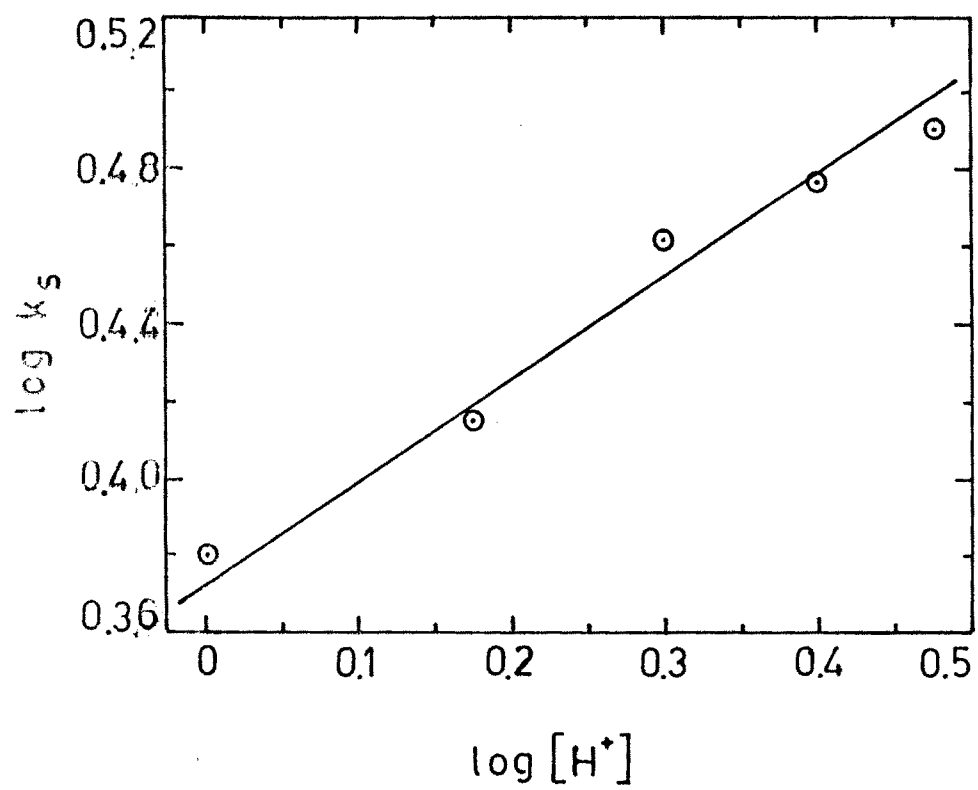


Table 3.7 : Effect of chloride ion concentration on second order rate constant k_s .

$$[\text{AuCl}_4^-] = 3.1 \times 10^{-4} \text{M}, [\text{Tl(I)}] = 3.1 \times 10^{-4} \text{M}$$

$$[\text{H}^+] = 3.0 \text{ M}, \text{I} = 3.1 \text{ M}, \text{Temp.} = 25^\circ \text{C}$$

$[\text{Cl}^-] \text{M}$	$k_s \text{ M}^{-1} \text{ s}^{-1}$	$\log[\text{Cl}^-]$	$\log k_s$
0.5	0.10	-0.3010	-1.0000
1.0	0.38	0.0000	-0.4802
1.5	0.92	0.1761	-0.0362
2.0	1.20	0.3010	0.0792
2.5	1.90	0.3979	0.2787
3.0	3.10	0.4771	0.4913

Figure 3.6: Order in chloride ion concentration (conditions as in Table 3.7)

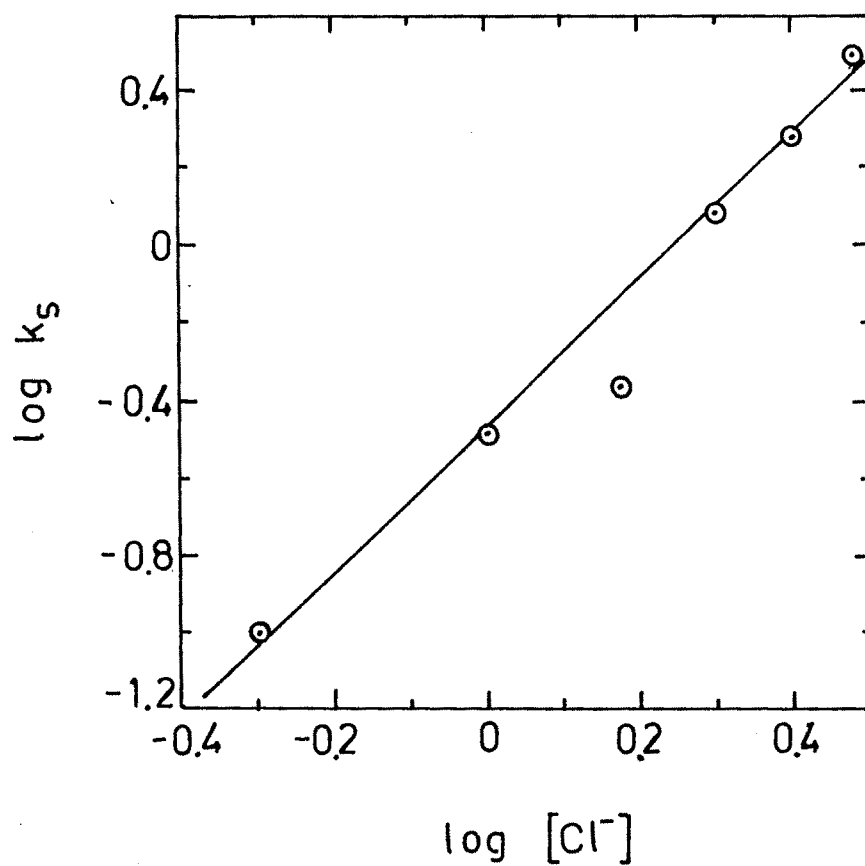


Table 3.8: Example run AuCl_4^- oxidation of thallium(I)
 $[\text{Tl(I)}] = [\text{AuCl}_4^-] = 3.10 \times 10^{-4} \text{M}$
 $[\text{H}^+] = 1.5 \text{ M}, [\text{Cl}^-] = 3.0 \text{ M},$
 $I = 3.1 \text{ M}, \text{Temp.} = 25^\circ\text{C}.$

Time	O.D.	$[\text{AuCl}_4^-] \times 10^4$	$\frac{1}{a-x}$
0	0.145	3.12	3.2×10^3
1	0.140	3.01	3.32
2	0.135	2.91	3.44
3	0.130	2.80	3.57
4	0.125	2.69	3.72
5	0.119	2.56	3.90
6	0.114	2.45	4.08
7	0.109	2.35	4.25
8	0.104	2.24	4.46
9	0.100	2.15	4.65
10	0.097	2.09	4.78
15	0.082	1.77	5.65
20	0.066	1.42	7.04



Figure 3.7: Example run: tetrachloroaurate(III) oxidation of thallium(I) (conditions as in Table 3.8)

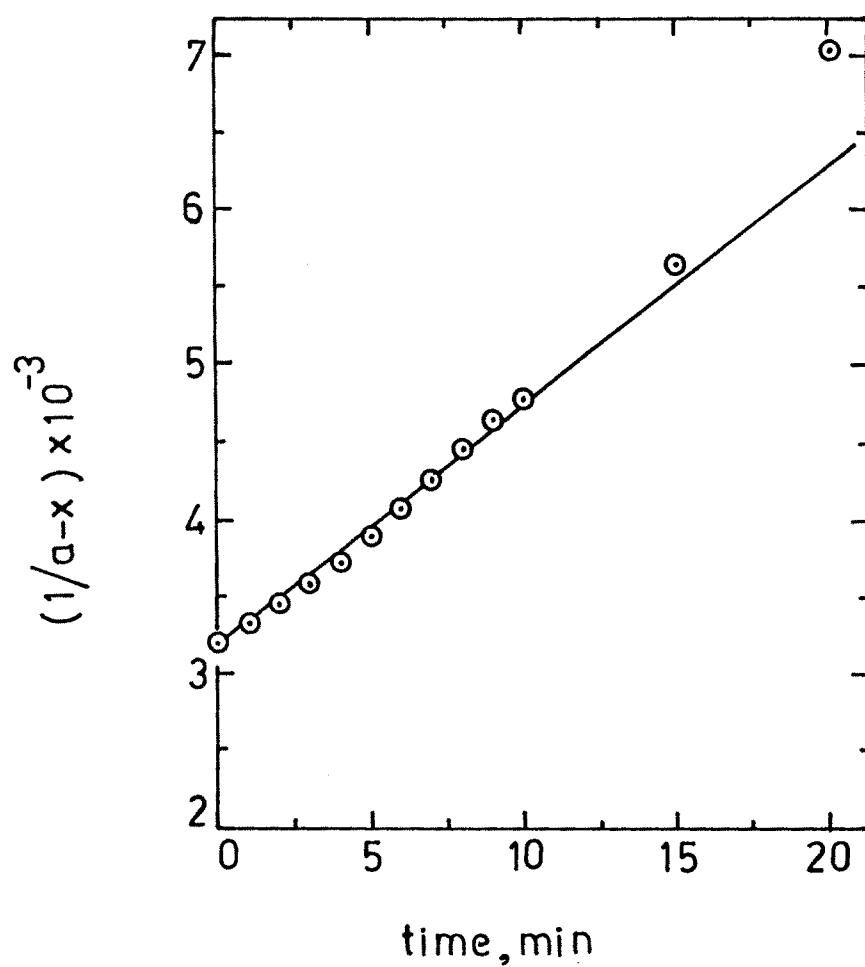


Table 3.9: Example run AuCl_4^- oxidation of thallium(I)

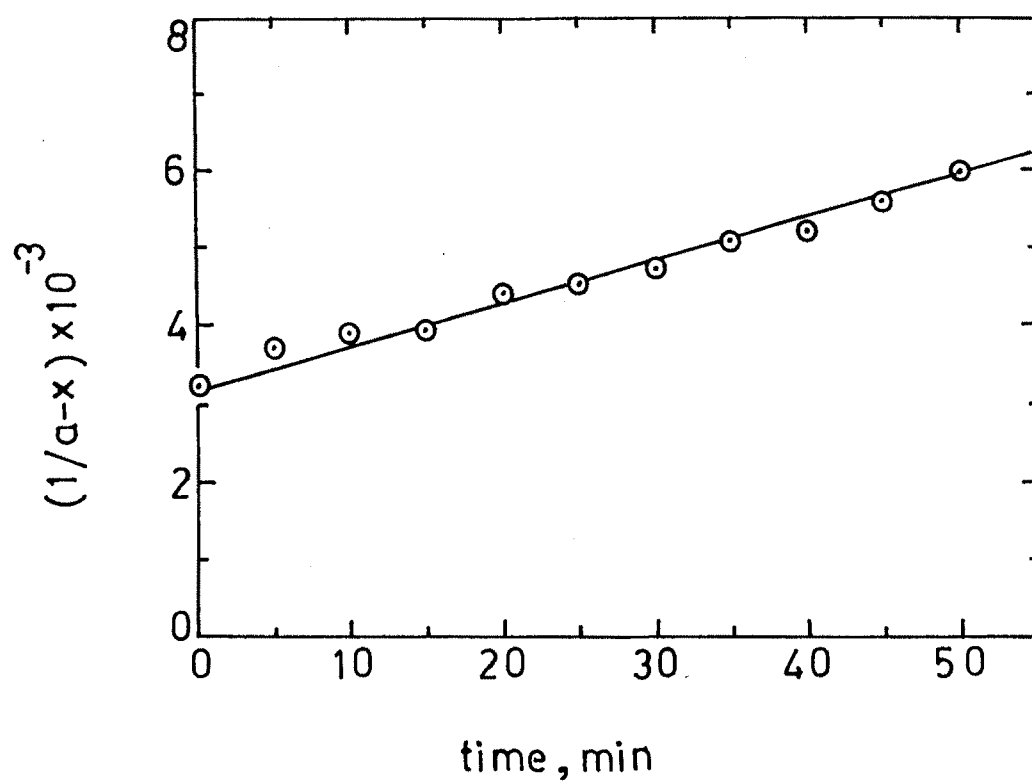
$$[\text{Tl(I)}] = [\text{AuCl}_4^-] = 3.10 \times 10^{-4} \text{M}$$

$$[\text{H}^+] = 3.0 \text{ M}, [\text{Cl}^-] = 1.5 \text{ M},$$

$$I = 3.1 \text{ M}, \text{Temp.} = 25^\circ\text{C}.$$

Time	O.D.	$[\text{AuCl}_4^-] \times 10^4$	$\frac{1}{a-x}$
0	0.145	3.12	3.20×10^3
5	0.125	2.69	3.71
10	0.118	2.54	3.93
15	0.118	2.54	3.93
20	0.105	2.26	4.42
25	0.103	2.22	4.50
30	0.098	2.11	4.74
35	0.092	1.98	5.05
40	0.090	1.94	5.15
45	0.082	1.77	5.65
50	0.078	1.68	5.95

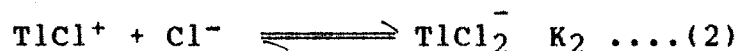
Figure 3.8: Example run: tetrachloroaurate(III) oxidation of thallium(I) (conditions as in Table 3.9)



The added product, thallium(III), between the concentration range of 1.0×10^{-4} to 5.0×10^{-4} M (Table 3.10) and the change in ionic strength from 3.0 to 3.4 (Table 3.11) did not have any effect on the second order rate constant k_s .

DISCUSSION

The experimental results indicate a direct two electron transfer between thallium(I) and AuCl_4^- ion, as observed in case of other two equivalent^{54,55} reductants, with a second order rate law. The oxidant AuCl_4^- , at $\text{pH} < 2$ mainly exists as AuCl_4^- and hydrolysis occurs to a negligible extent⁵³. While in a solution containing chloride ions thallium(I) is known to form chlorocomplexes⁵⁶ of the general formula $(\text{TlCl}_n)^{n-1}$, n being the number of chlorides complexed, the respective equilibria are shown in equation 1 to 2:



Complexes 1-2 have the equilibrium constants K_1 and K_2 as 3.9 and 0.35⁴⁵. The concentrations of thallium(I) complexes were calculated using equation 3, where $[\text{Tl(I)}]_T$ and $[\text{Tl(I)}]_f$ are

$$[\text{Tl(I)}]_T = [\text{Tl(I)}]_f \{1 + K_1[\text{Cl}^-] + K_1K_2[\text{Cl}^-]^2\} \dots\dots(3)$$



Table 3.10 : Effect of added Tl(III) on the second order rate constant k_s

$$[\text{AuCl}_4^-] = [\text{Tl(I)}] = 3.10 \times 10^{-4} \text{ M,}$$

$$[\text{HCl}] = 3.0 \text{ M, I} = 3.1 \text{ M, Temp.} = 25^\circ\text{C}$$

[Tl(III)] x 10 ⁴	K l mol ⁻¹ sec ⁻¹
0.0	3.1
1.0	3.2
3.0	3.2
4.0	3.1
5.0	3.1

Table 3.11 : Effect of ionic strength on the second order rate constant k_g

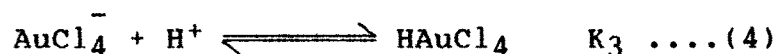
$$[\text{AuCl}_4^-] = [\text{Tl(I)}] = 3.10 \times 10^{-4} \text{ M,}$$

$$[\text{HCl}] = 3.0 \text{ M, Temp.} = 25^\circ\text{C}$$

Ionic Strength	$k \text{ l mol}^{-1} \text{ sec}^{-1}$
3.0	2.90
3.1	3.00
3.2	2.80
3.3	3.10
3.4	2.90

total and uncomplexed thallium(I) concentrations respectively. The concentrations of different thallium(I) species along with second order rate constant as chloride ion concentration is varied are given in Table 3.12. The data of Table 3.12 are used to obtain Figure 3.9 where the fraction of TlCl_2^- to total thallium(I) concentration, α_2 , and $\log k_g$ were plotted against $\log [\text{Cl}^-]$. It would appear from the results of Table 3.12 and Figure 3.9 that TlCl_2^- can be reasonably taken as the main active species under the present conditions.

The order in hydrogen was 0.3 and there was no effect of ionic strength on the reaction. Since one of our reactant TlCl_2^- is charged it seems probable that the protonated form of the oxidant AuCl_4^- may be the active one which is forming in a medium of high hydrogen ion concentration. The formation of HAuCl_4 is represented in equation 4.



Therefore the mechanism of reaction between AuCl_4^- and thallium(I) based on the above results and the stoichiometry of 1;1 can be represented as in equation⁵ in terms of the active species HAuCl_4 for the oxidant and TlCl_2^- for the reductant.



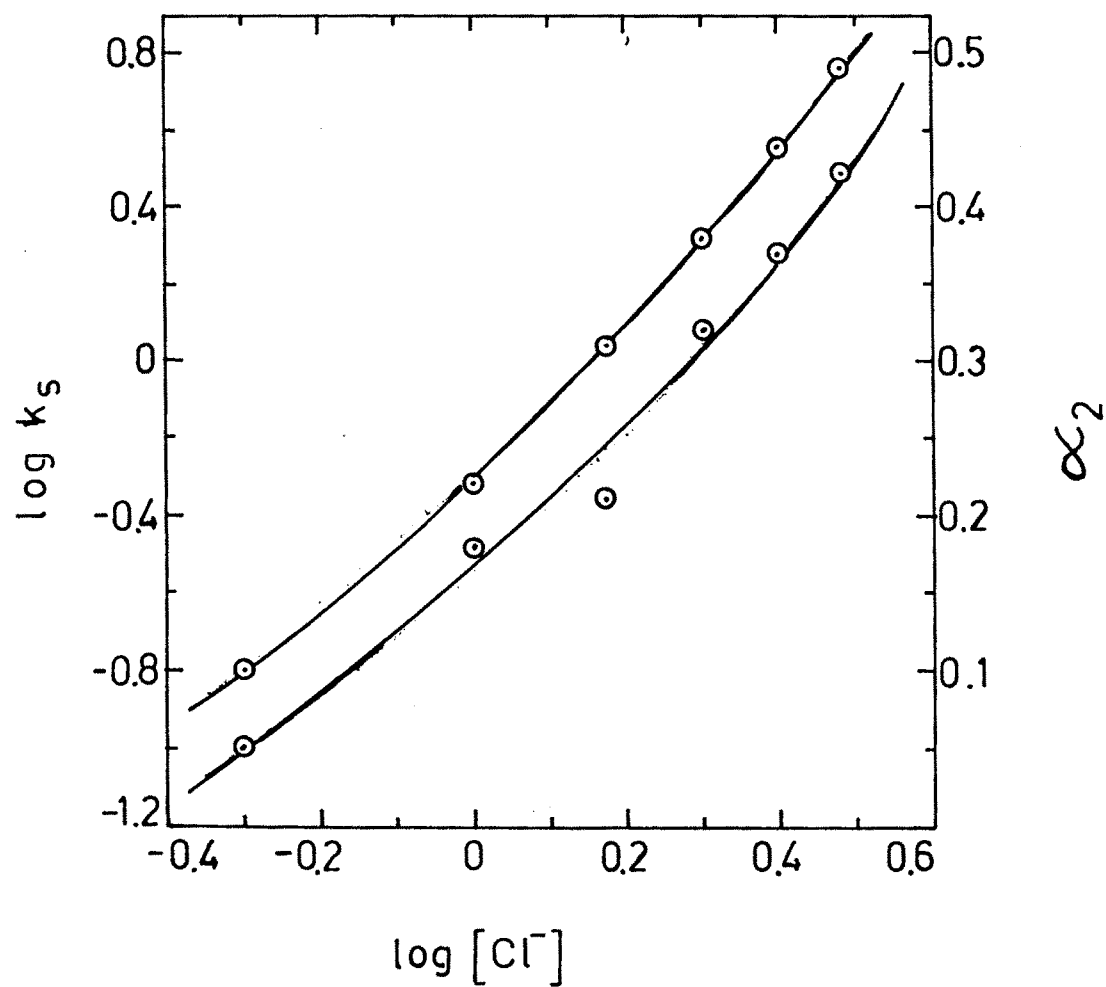
Table 3.12: Effect of chloride ion concentration on different thallium(I) species and on second order rate constant k_s

$$[\text{AuCl}_4^-] = [\text{Tl(I)}] = 3.10 \times 10^{-4} \text{M}$$

$$[\text{H}^+] = 3.0 \text{ M}, \text{ I} = 3.1 \text{ M}, \text{ Temp.} = 25^\circ \text{C}$$

$[\text{Cl}^-] \text{M}$	$k_s \text{ M}^{-1} \text{ s}^{-1}$	$\log[\text{Cl}^-]$	$\log k_s$	$[\text{Tl(I)}]_f \times 10^5 \text{ M}$	$[\text{TlCl}] \times 10^4 \text{ M}$	$[\text{TlCl}_2^-] \times 10^5 \text{ M}$	α_2
0.5	0.10	-0.3010	-1.0000	9.42	1.84	3.21	0.10
1.0	0.38	0.0000	-0.4802	4.94	1.93	6.74	0.22
1.5	0.92	0.1761	-0.0362	3.12	1.84	9.58	0.31
2.0	1.20	0.3010	0.0792	2.17	1.69	11.80	0.38
2.5	1.90	0.3979	0.2787	1.60	1.56	13.60	0.44
3.0	3.10	0.4771	0.4913	1.24	1.45	15.20	0.49

Figure 3.9: Plot of α_2 and $\log k_s$ against $\log [Cl^-]$
(conditions as in Table 3.12)



The corresponding rate law would be as given by equation 6. The concentrations of

$$\frac{d [\text{AuCl}_4^-]}{dt} = k [\text{HAuCl}_4] [\text{TlCl}_2^-] \dots\dots(6)$$

active species TlCl_2^- and HAuCl_4 are obtainable from equation 3 and equilibria 4 as:

$$[\text{TlCl}_2^-] = \frac{K_1 K_2 [\text{Tl(I)}]_T [\text{Cl}^-]^2}{(1 + K_1 [\text{Cl}^-] + K_1 K_2 [\text{Cl}^-]^2)} \dots\dots(7)$$

and

$$[\text{HAuCl}_4] = \frac{K_3 [\text{H}^+] [\text{AuCl}_4^-]_T}{(1 + K_3 [\text{H}^+])} \dots\dots(8)$$

Substituting for the concentrations of active species from equation 7 and 8 in the rate law 6.

$$\frac{d [\text{AuCl}_4^-]}{dt} = \frac{k K_1 K_2 K_3 [\text{Tl(I)}]_T [\text{AuCl}_4^-]_T}{(1 + K_1 [\text{Cl}^-] + K_1 K_2 [\text{Cl}^-]^2) (1 + K_3 [\text{H}^+])} \dots\dots(9)$$

According to equation 9 the plot of $1/k_g$ against $1/[\text{H}^+]$ is expected to be linear. The data for verification of rate law 9 are given in table 3.13 and the plot of $1/k_g$ Vs $1/[\text{H}^+]$ is shown in Figure 3.10 which is linear. The value of K_3 was determined as 2.32 from the slope and intercept of Figure 3.10. Further, using this kinetically determined value of K_3 the concentrations of HAuCl_4 were calculated which are also tabulated in Table 3.13. The concentration of

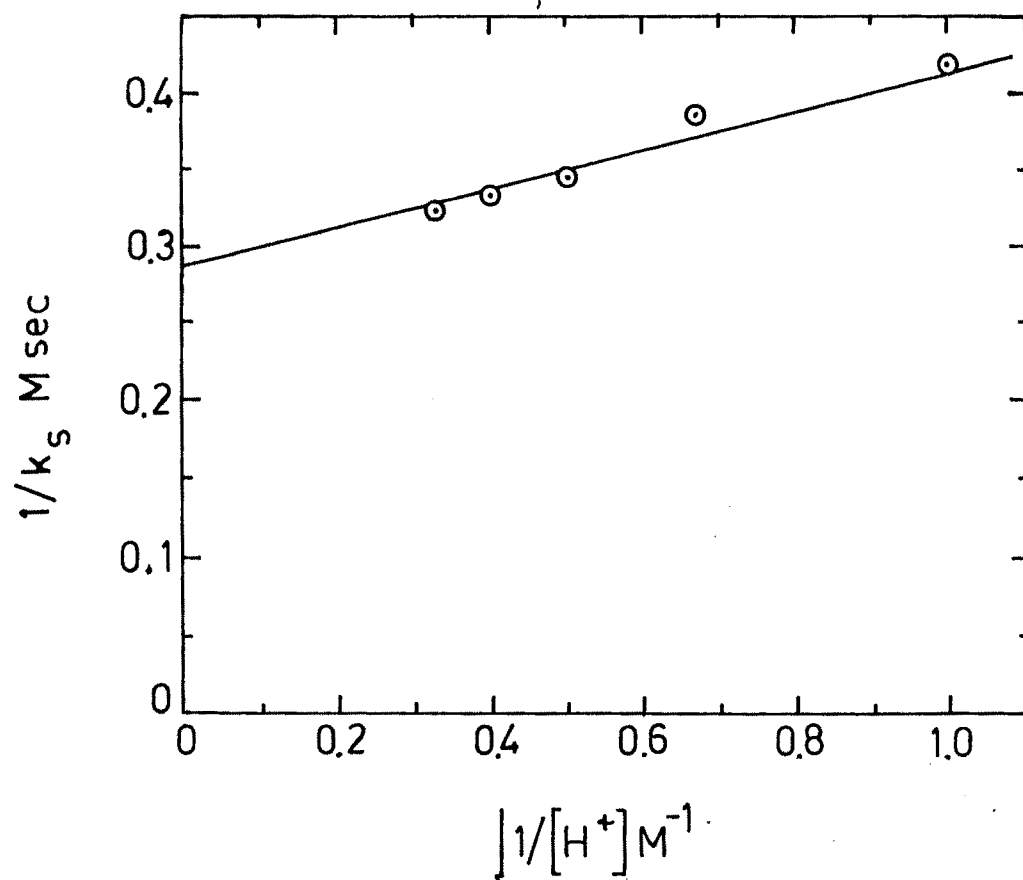
Table 3.13: Effect of hydrogen ion concentration on second order rate constant, $[\text{AuCl}_4^-]$, and $[\text{HAuCl}_4]$

$$[\text{AuCl}_4^-] = [\text{Tl(I)}] = 3.10 \times 10^{-4} \text{ M,}$$

$$[\text{Cl}^-] = 3.0 \text{ M, I} = 3.1 \text{ M, Temp.} = 25^\circ\text{C}$$

$[\text{H}^+]\text{M}$	$1/[\text{H}^+]$	$k_s \text{ M}^{-1}\text{s}^{-1}$	$1/k_s$	$\log[\text{H}^+]$	$\log k_s$	$[\text{AuCl}_4^-]$ $\times 10^5 \text{ M}$	$[\text{HAuCl}_4]$ $\times 10^4$	α_3
1.0	1.00	2.4	0.417	0.0000	0.3802	9.34	2.17	0.70
1.5	0.67	2.6	0.384	0.1761	0.4149	6.92	2.40	0.77
2.0	0.50	2.9	0.345	0.3010	0.4624	5.49	2.54	0.82
2.5	0.40	3.0	0.333	0.3979	0.4771	4.56	2.64	0.85
3.0	0.33	3.1	0.322	0.4771	0.4913	3.89	2.70	0.87

Figure 3.10: Plot of $1/k_g$ against $1/[H^+]$ (conditions as in Table 3.13)



HAuCl_4 were found to parallel the change in the values of k_s as the hydrogen ion concentration is varied which is shown in Figure 3.11 by plotting fraction, α_3 , of HAuCl_4 to the total AuCl_4^- and $\log k$ against $\log [\text{H}^+]$. Precipitation of thallos chloride occurs in solution of hydrogen ion less than 1.0 M due to large quantity of lithium chloride used to keep chloride ion concentration constant. This limits further verification of rate law 9 at low hydrogen ion concentrations. Considerably higher equilibrium constant of 2.32 for the HAuCl_4 formation and no involvement of HAuCl_4 in further equilibria probably transfers the oxidant into HAuCl_4 shifting the equilibrium 4 to the right hand side. This may be the reason for very low order in hydrogen ion of 0.3.



Figure 3.11: Plot of α_3 and $\log k_s$ against $\log [H^+]$ 