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## **CHAPTER - IV**

### **RESULT AND DISCUSSION: PYRIDINIUMCHLOROCHROMATE OXIDATION OF THALLIUM (I)**

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## RESULTS

### ORDER OF REACTION

The order of reaction with respect to pyridinium chlorochromate (PCC) and thallium(I) was found by  $\log(\text{Inl. Rate})$  Vs.  $\log(\text{concentration})$  plots in 2.0 M hydrochloric acid at an ionic strength of 2.1 M. The order in PCC in the concentration range of  $2.31 \times 10^{-4}$  to  $6.35 \times 10^{-4}$  M at constant thallium(I) concentration of  $5.85 \times 10^{-4}$  M was one. The data are given in Table 4.1 and plot is shown in Figure 4.1. The order in thallium(I) in the concentration range of  $2.7 \times 10^{-4}$  to  $5.85 \times 10^{-4}$  M (Table 4.2) at a constant PCC concentration of  $4.07 \times 10^{-4}$  M was 0.82 (Figure 4.2). The data for two example runs are given in Table 4.3 and 4.4 with respect second order plots in Figure 4.3 & 4.4. The effect of reactant concentration on the second order rate constant is shown in Table 4.5.

### EFFECT OF HYDROGEN AND CHLORIDE IONS

The effect of hydrogen and chloride ion concentrations on the reaction was studied between the concentration range of 1.0 to 2.0 M in each case by keeping the concentration chloride and hydrogen ion constant at 2.0 M respectively at an ionic strength of 2.1 M. The effect of hydrogen and chloride ion concentration on the second order rate constant,  $k_s$  is given in Table 4.6. Two example runs

Table 4.1: Order in pyridinium chlorochromate (PCC)  
[Tl(I)] =  $5.85 \times 10^{-4}$  M, [HCl] = 2.0 M  
I = 2.1 M, Temp = 25°C

[PCC] $\times 10^4$ M	Ini.Rate $\times 10^4$ s $^{-1}$	-log[PCC]	-log Int.Rate
2.35	1.80	3.6289	3.7447
2.89	2.32	3.5391	3.6345
4.07	3.42	3.3904	3.4664
4.92	4.08	3.3080	3.3889
5.42	4.87	3.2660	3.3125
6.35	5.40	3.1972	3.2676

\* Initial rates were determined from absorbance against time plots

Figure 4.1: Order in pyridinium chlorochromate (conditions as in Table 4.1)

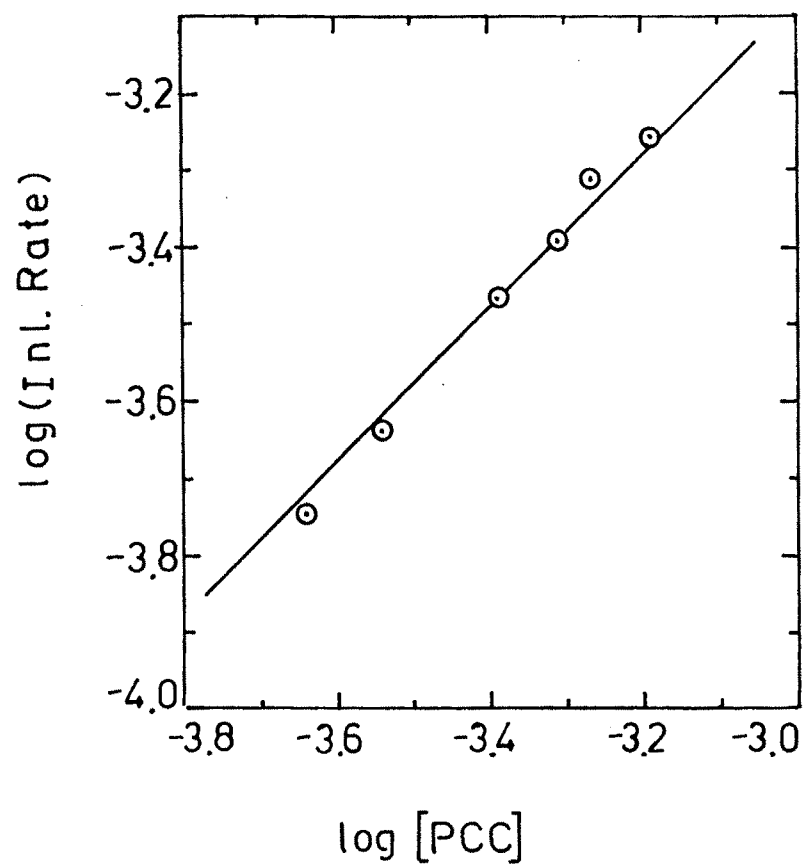


Table 4.2: Order in thallium(I)  
[PCC] =  $4.07 \times 10^{-4}$  M, [HCl] = 2.0 M,  
I = 2.1 M, Temp = 25°C

[Tl(I)] $\times 10^4$ M	Ini.Rate $\times 10^4$ s $^{-1}$	$-\log[\text{Tl(I)}]$	$-\log$ Int.Rate
2.70	1.37	3.5686	3.8643
3.60	1.83	3.4437	3.7367
4.50	2.42	3.3468	3.6168
4.95	2.88	3.3054	3.5401
5.85	3.43	3.2328	3.4643

\* Initial rates were determined from absorbance against time plots

Figure 4.2: Order in thallium(I) (conditions as in Table 4.2)

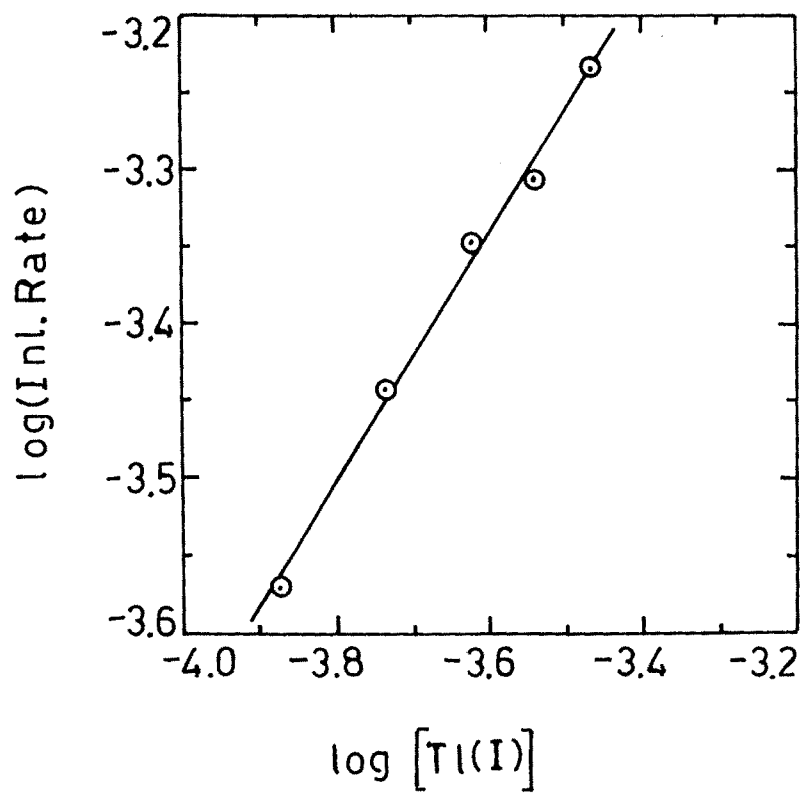


Table 4.3: Example run: pyridinium chlorochromate oxidation of thallium(I)

$[PCC] = 2.35 \times 10^{-4} M$ ,  $[Tl(I)] = 5.85 \times 10^{-4} M$

$[HCl] = 2.0 M$ ,  $I = 2.1 M$ , Temp. =  $25^{\circ}C$

Time in minutes	O.D.	$Cr^{VI} \times 10^4$	$Tl^I \times 10^4$	$\log \frac{b}{a} \left[ \frac{a-3x/2}{b-x} \right]$
00	0.165	2.35	5.85	0.0000
01	0.156	2.22	5.65	0.0096
02	0.149	2.12	5.50	0.0179
03	0.144	2.05	5.40	0.0245
04	0.138	1.97	5.28	0.0320
05	0.132	1.88	5.14	0.0407
10	0.102	1.45	4.50	0.0957
15	0.083	1.18	4.09	0.1437
20	0.066	0.94	3.73	0.2025
25	0.055	0.78	3.49	0.2546
30	0.045	0.64	3.28	0.3146

Figure 4.3: Example run; Pyridinium chlorochromate oxidation of thallium(I) (conditions as in Table 4.3)

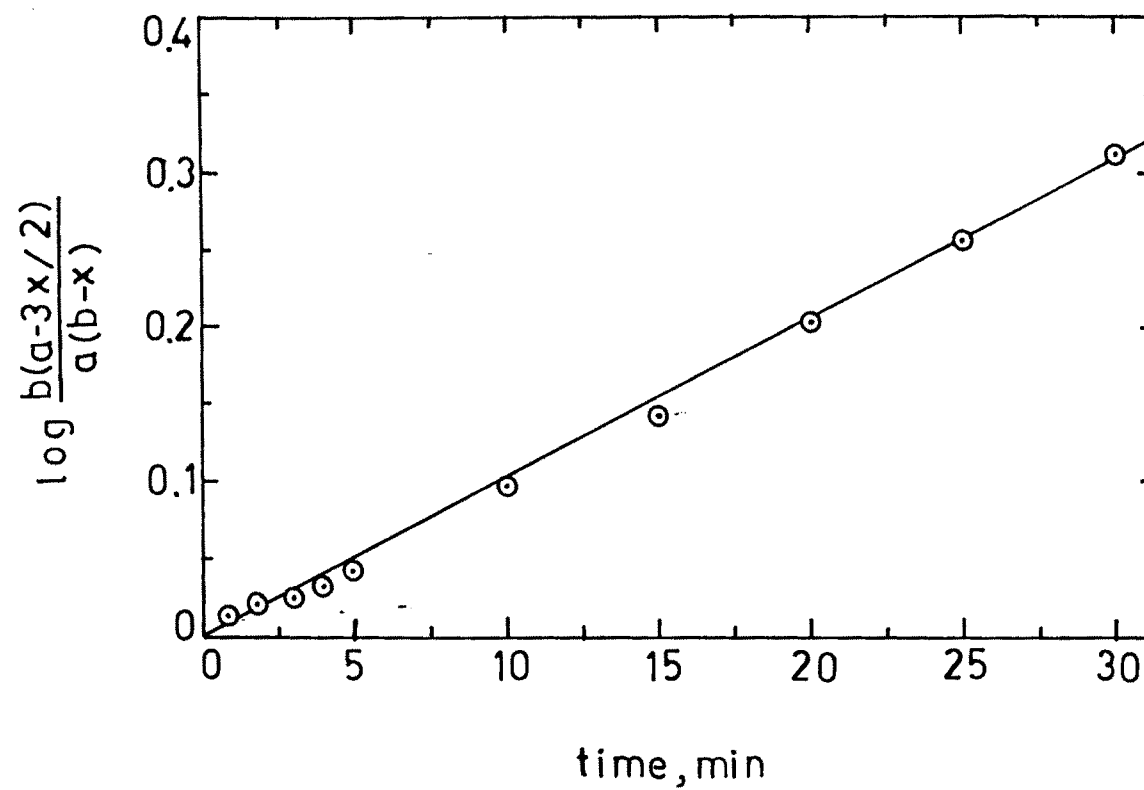




Table 4.4: Example run: pyridinium chlorochromate oxidation of thallium(I)

$[PCC] = 4.07 \times 10^{-4} M$ ,  $[Tl(I)] = 4.5 \times 10^{-4} M$

$[HCl] = 2.0 M$ ,  $I = 2.1 M$ , Temp. = 25°C

Time in minutes	O.D.	CrVI x 10 <sup>4</sup>	TlI x 10 <sup>4</sup>	$\log \frac{b}{a} \left[ \frac{a-3x/2}{b-x} \right]$
00	0.284	4.06	4.50	0.0000
01	0.272	3.88	4.23	0.0072
02	0.261	3.73	4.00	0.0141
03	0.253	3.61	3.82	0.0201
04	0.244	3.49	3.64	0.0264
05	0.237	3.36	3.45	0.0332
10	0.203	2.90	2.76	0.0662
15	0.180	2.57	2.26	0.1005
20	0.160	2.29	1.84	0.1397
25	0.145	2.07	1.51	0.1817
30	0.132	1.89	1.24	0.2277

Figure 4.4: Example run: Pyridinium chlorochromate oxidation of thallium(I) (conditions as in Table 4.4)

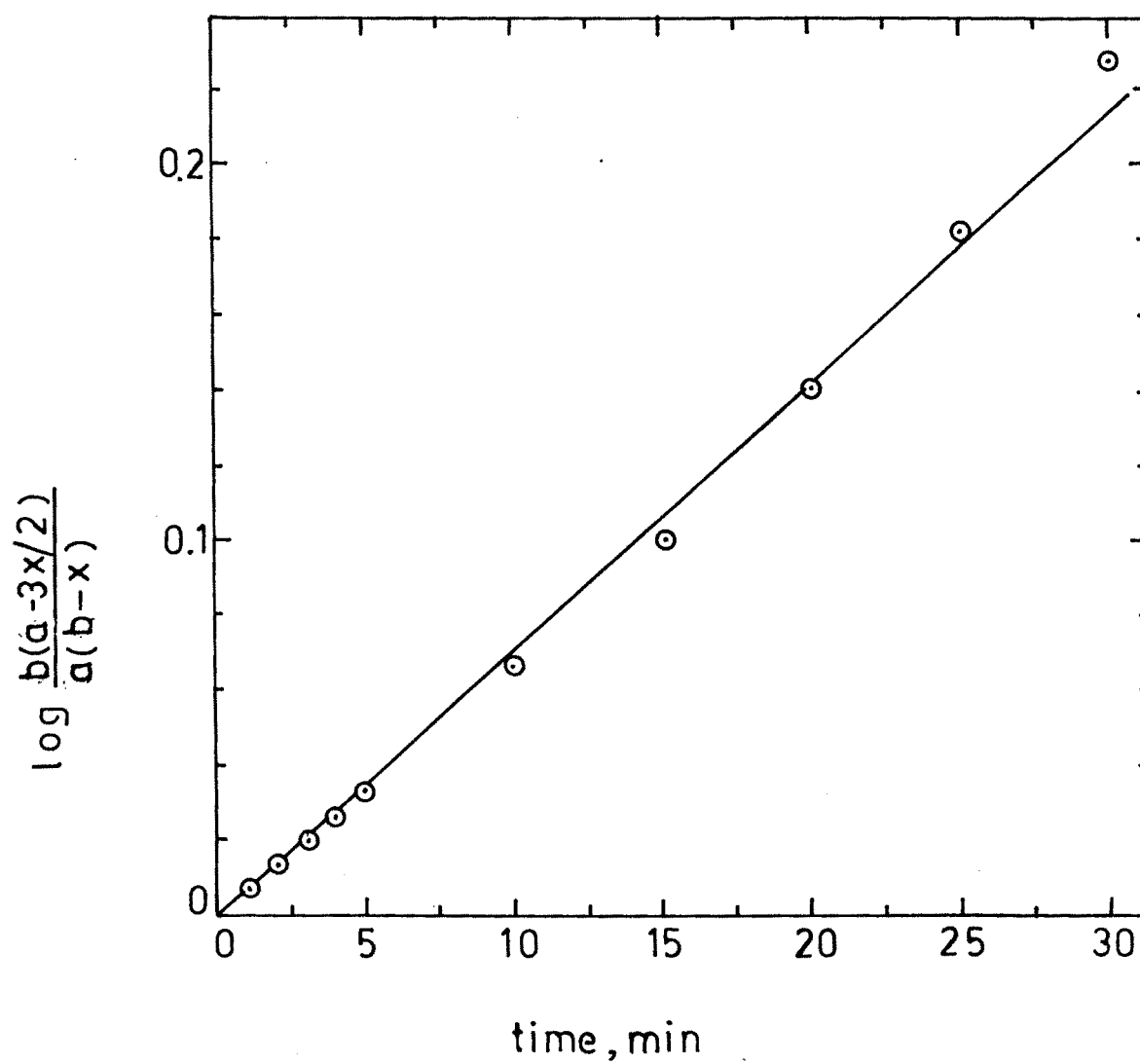


Table 4.5: Effect of reactant concentration on the second order rate constant  $k_s$ .

[HCl] = 2.0 M, EI = 2.1 M, Temp = 25°C

$[Tl(I)] \times 10^4$ M	$[PCC] \times 10^4$ M	$k_s$ M <sup>-1</sup> s <sup>-1</sup> M
2.70	4.07	1.75
3.60	4.07	1.73
4.50	4.07	1.77
4.95	4.07	1.77
5.85	4.07	1.76
5.85	2.35	1.77
5.85	2.89	1.73
5.85	4.92	1.75
5.85	5.42	1.74
5.85	6.35	1.74

Table 4.6: Effect of hydrogen and chloride ion concentration on second order rate constant,  $k_s$ .

$$[\text{Tl(I)}] = 5.85 \times 10^{-4} \text{M}, [\text{PCC}] = 4.07 \times 10^{-4} \text{M},$$

$$I = 2.1 \text{ M}, \text{Temp} = 25^\circ \text{C}$$

$[\text{H}^+] = 2.0 \text{ M}$		$[\text{Cl}^-] = 2.0 \text{ M}$	
$[\text{Cl}^-] \text{ M}$	$k_s \text{ M}^{-1} \text{ s}^{-1}$	$[\text{H}^+] \text{ M}$	$k_s, \text{ M}^{-1} \text{ s}^{-1}$
1.0	0.37	1.0	0.38
1.2	0.44	1.2	0.45
1.4	0.69	1.4	0.85
1.6	0.90	1.6	0.98
1.8	1.53	1.8	1.36
2.0	1.76	2.0	1.76

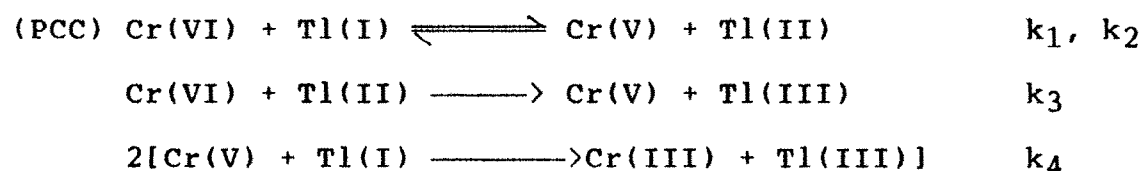
are also given in Table 4.7 and 4.8 with respective second order plots in Figure 4.5 and 4.6. From table 4.6 it can be seen that both hydrogen and chloride ions accelerate the reaction considerably.

#### EFFECT OF ADDED PRODUCT

The effect of added product, thallium(III) was studied between the concentration range of  $1.0$  to  $5.0 \times 10^{-4}$  M by keeping PCC ( $4.07 \times 10^{-4}$  M), thallium(I) ( $5.85 \times 10^{-4}$  M) and hydrochloric acid (2.0 M) concentrations constant at an ionic strength of 2.1 M. The results are given in Table 4.9 and indicate no effect of added product on the reaction.

#### DISCUSSION

The stoichiometry of 2;3 for pyridinium chlorochromate (PCC) and thallium(I) reaction and the results can be accommodated by scheme I and II. In scheme I the reactant



#### SCHEME - I

Cr(VI) (PCC) and Tl(I) are involved in a first reversible step giving reactive intermediates Cr(V) and Tl(II) and the latter species are involved in further steps. A steady state treatment of Cr(V) and Tl(I) gives equation 1 and 2.

Table 4.7: Example run: Pyridinium chlorochromate oxidation of thallium(I)

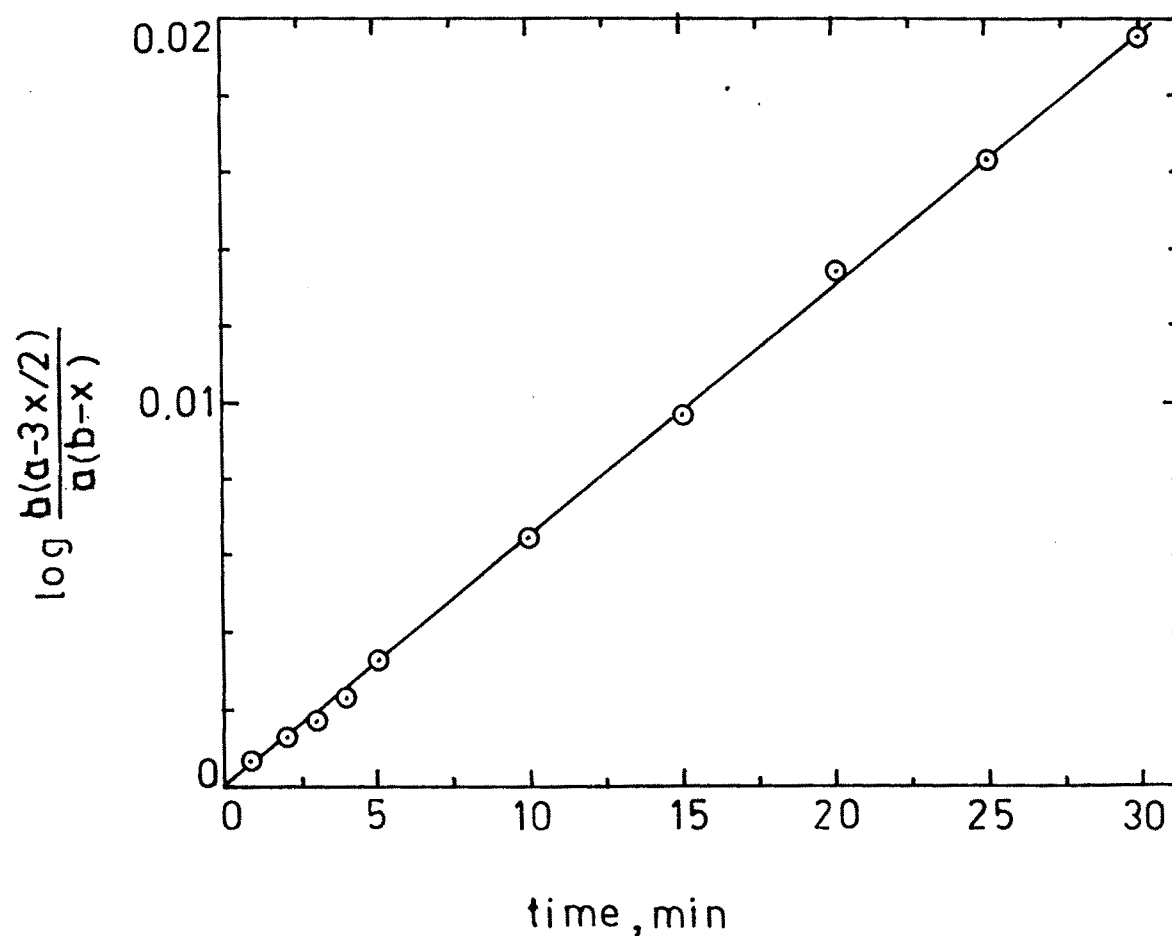
$$[\text{PCC}] = 4.07 \times 10^{-4} \text{M}, [\text{Tl(I)}] = 5.85 \times 10^{-4}$$

$$[\text{H}^+] = 1.6 \text{ M}, [\text{Cl}^-] = 2.0 \text{ M},$$

$$[\text{I}^-] = 2.1 \text{ M}, \text{Temp.} = 25^\circ\text{C}$$

Time in minutes	O.D.	CrVI x 10 <sup>4</sup>	TlI x 10 <sup>4</sup>	$\log \frac{b}{a} \left[ \frac{a-3x/2}{b-x} \right]$
00	0.285	4.07	5.85	0.0000
01	0.275	3.93	5.64	0.0007
02	0.267	3.81	5.46	0.0013
03	0.260	3.71	5.31	0.0018
04	0.254	3.63	5.19	0.0023
05	0.248	3.54	5.05	0.0033
10	0.217	3.10	4.39	0.0064
15	0.193	2.76	3.88	0.0096
20	0.171	2.44	3.40	0.0134
25	0.155	2.21	3.06	0.0162
30	0.142	2.03	2.79	0.0194

Figure 4.5: Example run: Pyridinium chlorochromate oxidation of thallium(I) (conditions as in Table 4.7)



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Table 4.8: Example run: pyridinium chlorochromate oxidation of thallium(I)

$[PCC] = 4.07 \times 10^{-4} M$ ,  $[Tl(I)] = 5.85 \times 10^{-4} M$

$[HCl] = 2.0 M$ ,  $[Cl^-] = 1.8 M$ ,

$I = 2.1 M$ , Temp. =  $25^\circ C$

Time in minutes	O.D.	$CrVI_x \times 10^4$	$TlI \times 10^4$	$\log \frac{b}{a} \left[ \frac{a-3x/2}{b-x} \right]$
00	0.280	4.00	5.85	0.0000
01	0.270	3.85	5.62	0.0008
02	0.260	3.71	5.41	0.0013
03	0.250	3.57	5.20	0.0017
04	0.240	3.42	4.98	0.0019
05	0.232	3.31	4.81	0.0028
10	0.195	2.78	4.02	0.0049
15	0.165	2.35	3.37	0.0085
20	0.141	2.01	2.86	0.0119
25	0.124	1.77	2.50	0.0151
30	0.110	1.57	2.20	0.0186



Figure 4.6: Example run: Pyridinium chlorochromate oxidation of thallium(I) (conditions as in Table 4.8)

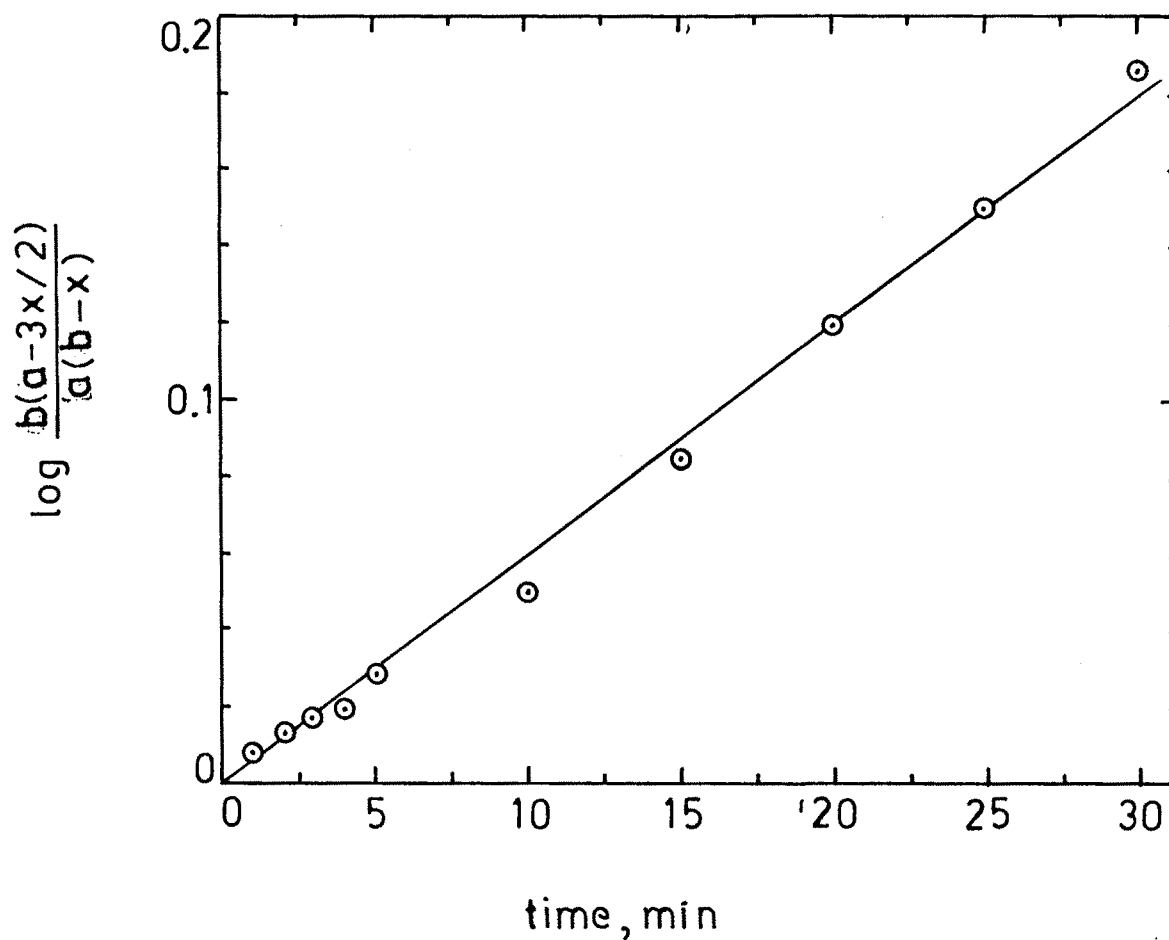


Table 4.9: Effect of added product on the second order rate constant,  $k_s$ .

$[Tl(I)] = 5.85 \times 10^{-4} \text{ M}$ ,  $[PCC] = 4.07 \times 10^{-4} \text{ M}$

$[HCl] = 2.0 \text{ M}$ ,  $I = 2.1 \text{ M}$ , Temp =  $25^\circ\text{C}$

$[Tl(III)] \times 10^4 \text{ M}$	$k_s \text{ M}^{-1} \text{ s}^{-1}$
0.0	1.76
1.0	1.77
2.0	1.73
3.0	1.75
4.0	1.74
5.0	1.74

$$\begin{aligned} \text{Cr(V)} : & k_1[\text{Cr(VI)}] [\text{Tl(I)}] - k_2 [\text{Cr(V)}] [\text{Tl(II)}] \\ & + k_3 [\text{Cr(VI)}] [\text{Tl(II)}] - 2k_4 [\text{Cr(V)}] [\text{Tl(I)}] = 0 \dots\dots\dots(1) \end{aligned}$$

$$\begin{aligned} \text{Tl(II)} : & k_1[\text{Cr(VI)}] [\text{Tl(I)}] - k_2 [\text{Cr(V)}] [\text{Tl(II)}] \\ & - k_3 [\text{Cr(VI)}] [\text{Tl(II)}] = 0 \dots\dots\dots(2) \end{aligned}$$

Subtracting 1 from 2 and simplifying for [Cr(V)] we have

$$[\text{Cr(V)}] = \frac{k_3 [\text{Cr(VI)}] [\text{Tl(II)}]}{k_4 [\text{Tl(I)}]} \dots\dots\dots(3)$$

Substituting for [Cr(V)] in 2 and simplifying, the quadratic equation in [Tl(II)] is obtained.

$$k_2k_3[\text{Tl(II)}]^2 + k_3k_4[\text{Tl(I)}] [\text{Tl(II)}] - k_1k_4[\text{Tl(I)}]^2=0 \dots(4)$$

The solution of equation 4 yields [Tl(II)] as

$$[\text{Tl(II)}] = \frac{k_4}{2k_2} \left\{ \left[ 1 - \frac{4k_1k_2}{k_3k_4} \right]^{\frac{1}{2}} - 1 \right\} [\text{Tl(I)}] \dots\dots\dots(5)$$

According to scheme I the rate of reaction is given by equation (6) substituting [Tl(II)]

$$\frac{-d[\text{Cr(VI)}]}{dt} = 2 k_3 [\text{Cr(VI)}] [\text{Tl(II)}] \dots\dots\dots(6)$$

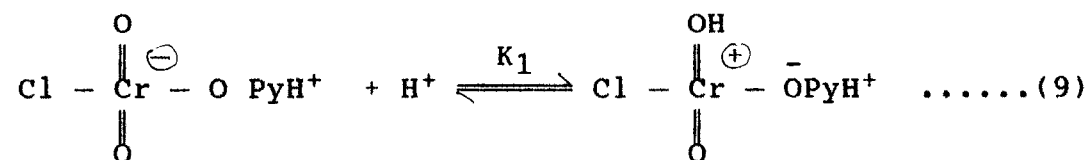
we get

$$\frac{-d[\text{Cr(VI)}]}{dt} = \left[ \frac{k_3k_4}{k_2} \right] \left\{ \left[ 1 - \frac{4k_1k_2}{k_3k_4} \right]^{\frac{1}{2}} - 1 \right\} [\text{Cr(VI)}][\text{Tl(I)}] \dots(7)$$

Scheme II is essentially the same as scheme I except for the fact that the intermediates Cr(V) and Tl(II) are forming in a rate determining and irreversible step. While this mechanism is in agreement with the results, more often than not, in non-complementary reactions involving chromium(VI) and thallium(III), the formation of Cr(V) and Tl(II) occurs in a reversible step<sup>57</sup>. However, in view of the fact that both Cr(V) and Tl(II) are reactive and are likely to be present in very low concentrations it is difficult to distinguish between schemes I and II. According to scheme II, the constant factors on the right hand side of the rate law (7) will then simplify to the rate constant  $k_1$  of the first irreversible and rate determining step of formation of intermediates Cr(V) and Tl(II) which is given by equation (8).

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_1 [\text{Cr(VI)}] [\text{Tl(I)}] \quad \dots(8)$$

The accelerating effect of hydrogen and chloride ions on the reaction may be due to the conversion of reactants into different species. The effect of hydrogen ion can be explained due to the formation of protonated pyridinium chlorochromate<sup>58</sup> ion in acid solutions as represented in equilibria (9). Therefore the catalytic effect of hydrogen



#### Pyridinium Chlorochromate

ion on the reaction may be attributed to the formation of protonated pyridinium chlorochromate which is more reactive<sup>58</sup> than the pyridinium chlorochromate itself. Since exact equilibrium constant for protonated species is not available and involvement of pyridinium chlorochromate in other possible equilibria, like further protonation, are not known, it is difficult to analyse the effect of hydrogen ion on the reaction accurately.

The effect of chloride ion on the reaction can be due to the formation of different thallium(I) chloro complexes which is described in chapter 3. In order to know which of the thallium(I) chloro complexes is reactive the order with respect to chloride was determined from  $\log(\text{Inl. Rate})$  Vs.  $\log$  concentration plots. The order was found to be 1.8 (Figure 4.7) between the concentration range of 1.0 to 2.0 M while keeping the hydrogen ion concentration constant at 2.0 M at an ionic strength of 2.1 M (Table 4.10). The order of 1.8 indicate involvement of  $\text{TlCl}_2^-$  as the reactive species of the reductant thallium(I).

Table 4.10: Order in chloride ion concentration  
 $[PPC] = 4.07 \times 10^{-4} \text{ M}$ ,  $Tl(I)] = 5.85 \times 10^{-4} \text{ M}$ ,  
 $[H^+] = 2.0 \text{ M}$ ,  $I = 2.1 \text{ M}$ , Temp =  $25^\circ\text{C}$

$[Cl^-] \times 10^4 \text{ M}$	Inl. Rate* $\times 10^7 \text{ s}^{-1}$	$-\log[Cl^-]$	$-\log[\text{Inl. Rate}]$
1.0	0.86	0.0000	7.0633
1.2	1.29	0.0792	6.8883
1.4	1.62	0.1461	6.7896
1.6	1.86	0.2041	6.7309
1.8	2.38	0.2553	6.6232
2.0	2.91	0.3010	6.5355

\* Initial rates were determined from  $[PCC]$  Vs time plots

Figure 4.7: Order in chloride ion concentration (conditions as in Table 4.10)

