Chromium(VI) Oxidation of Thallium(I) in Aqueous Acetic Acid & Effect of Added Vanadium(V) on the Reaction

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Chromium(VI) oxidation of thallium(I) in 60% acetic acid containing 1.25 mol dm^{-3} hydrochloric acid is a second order reaction, understood to be between CrO_3Cl^- and TlCl. Increase in $[H^+]$ and $[Cl^-]$ accelerates the reaction. Added V(V) accelerates the reaction till [V(V)] slightly exceeds [Tl(I)] because of a 1:1 interaction between V(V) and Tl(I). At higher [V(V)], the rate constant is lowered due to a specific cation effect. No interaction between added V(V) and Tl(I) is encountered in the case of the reaction in 40% aqueous acetic acid; however, in 80 and 90% aqueous acetic acid, 2:3 and 1:2 interactions between V(V) and Tl(I) are observed.

The oxidation of Tl(I) by Cr(VI) does not occur to any extent in aqueous perchloric and sulphuric acids but the reaction is facile in conc hydrochloric acid medium ($\geqslant 3$ mol dm^{-3}; the reaction is slow at [HCl] lower than 3 mol dm^{-3})[1]. The species in 3.0 mol dm^{-3} HCl solution[1] are reported to be thallium(I) chloride (TlCl) and chlorochromate (CrO_3Cl^-). The formation of chlorochromate is known to be greatly facilitated in aqueous acetic acid solutions as indicated by an equilibrium constant of 14 in water[2] rising to 1×10^5 in 86.5% acetic acid[3]. It was, therefore, worthwhile studying the reaction in 60% (v/v) aqueous acetic acid containing 1.25 mol dm^{-3} HCl. In view of the particular retarding effect of V(V), a product in the Cr(VI)-V(IV) reaction[4], the effect of added V(V) on the title reaction has also been studied.

Materials and Methods

Reagent grade chemicals were used. Doubly distilled water was used throughout this work. Chromium(VI) solution was obtained by dissolving potassium dichromate (BDH, AR) in water and standardised spectrophotometrically. Applicability of Beer's law at 360 nm was tested in the case of the 1.25 mol dm^{-3} HCl in 60% acetic acid solution containing 2.0×10^{-4} to 6.0×10^{-4} mol dm^{-3} Cr(VI) using matched 1 cm cells ($\varepsilon = 1250$). Concentrations of Cr(VI) higher than 6.0×10^{-4} mol dm^{-3} were not required in any of the kinetic runs, because of the limited solubility of Tl(I) in the reaction solution.

The Tl(I) solution was obtained by dissolving thallium(I) chloride (BDH) in water and standardising with bromate. Vanadium(V) solution was obtained by dissolving ammonium vanadate (BDH, AR) in water. Applicability of Beer's law was also tested for the latter solution at 360 nm ($\varepsilon = 75$). Hydrochloric acid

(Glaxo, AR) was used throughout this work. Acetic acid was purified by standard procedure.

Kinetic runs

These runs were carried out with solutions of 1.25 mol dm^{-3} HCl in 60% acetic acid at $\mu = 1.26$ mol dm^{-3}. In a typical run, [Cr(VI)] and [Tl(I)] were 2.0×10^{-4} and 3.0×10^{-4} mol dm^{-3} respectively and kinetics were followed spectrophotometrically at 360 nm by mixing the thermally equilibrated reactant solutions and transferring the reaction solution to a 1 cm cell kept in the thermostated cell compartment. The temperature was maintained at $25 \pm 0.1°C$. Kinetic results could be reproduced to $\pm 5\%$ and runs were usually followed upto 80% of the reaction.

Results

Since oxidation of HCl by Cr(VI) in the absence of Tl(I) was marginal (0.8% in 50 min), no correction for the oxidation of hydrochloric acid was made.

Stoichiometry

Different reaction mixtures were prepared in 60% acetic acid containing 1.25 mol dm^{-3} HCl at $\mu = 1.26$ mol dm^{-3} and analysed after keeping them for over 3 hr at 25°C. Chromium(VI) was estimated spectrophotometrically at 360 nm while Tl(III) was found as difference of total oxidant titrated by iodometry with 2.0×10^{-3} mol dm^{-3} thiosulphate. The results indicate a 2:3 stoichiometry for Cr(VI) oxidation of Tl(I) in these solutions (see Eq. 1).

$$2Cr(VI) + 3Tl(I) = 2Cr(III) + 3Tl(III) \qquad \ldots(1)$$
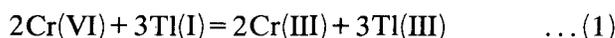
Order of reaction

The reaction followed second order rate law at [Tl(I)] in the range of 1.0×10^{-4} to 3.0×10^{-4} mol dm^{-3} and [Cr(VI)] in the range of 2.5×10^{-4} to

4.5×10^{-4} mol dm^{-3}. Since [Cr(VI)] was followed by spectrophotometry, its concentration was close to that of Tl(I). The kinetic study was restricted to the narrow range of reactant concentrations because of the low solubility of Tl(I) in 60% acetic acid containing 1.25 mol dm^{-3} HCl.

Effect of added products

The effect of added products, Cr(III) and Tl(III), was studied at $\mu = 1.26$ mol dm^{-3}, [HCl] = 1.25 mol dm^{-3}, [oxidant] = 2.0×10^{-4} mol dm^{-3} and [substrate] = 3.0×10^{-4} mol dm^{-3}. Under these conditions, no variation in second order rate constant was observed. In case of runs involving non-equivalent concentrations of reactants, the rate constant (k) was evaluated using Eq. (2) with a and b representing the initial [Tl(I)] and [Cr(VI)] respectively and x representing the decrease in reactant concentration in time t. Rate constants were determined graphically, the second order plots being linear over 80% of the reaction (Fig. 1).

$$k = \left\{ \frac{2.303}{t(a - 3b/2)} \right\} \log \left\{ \frac{b(a - 3x/2)}{a(b - x)} \right\} \qquad \ldots (2)$$

Effect of chloride and hydrogen ions

At fixed [reactant], [H$^+$] and [Cl$^-$] and $\mu = 1.26$ mol dm^{-3}, the second order specific rate constant (k) increased with increase in [Cl$^-$] and/or [H$^+$] (Table 1). The orders of reaction in [Cl$^-$] and [H$^+$] were 1.2 and 2.0 respectively.
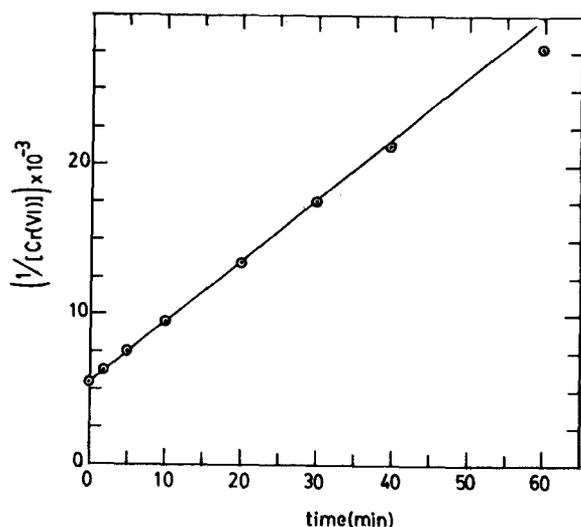

Fig. 1—Second order plot of chromium(VI)-thallium(I) reaction in 60% acetic acid containing 1.25 mol dm^{-3} hydrochloric acid at 25°C ([Cr(VI)] = 2.0×10^{-4} mol dm^{-3}, [Tl(I)] = 3.0×10^{-4} mol dm^{-3}, $\mu = 1.26$ mol dm^{-3})

Table 1—Effect of Varying [H$^+$] and [Cl$^-$] on Chromium(VI)-Thallium(I) reaction

[Cr(VI)] = 2.0×10^{-4} mol dm^{-3}; temp. 25°C;

[Tl(I)] = 3.0×10^{-4} mol dm^{-3}; solvent medium: 60% acetic acid.

[Cl$^-$] (mol dm^{-3})	k (dm^{3}mol^{-1}s^{-1})	[H$^+$] (mol dm^{-3})	k (dm^{3}mol^{-1}s^{-1})
[H$^+$] = 1.25 mol dm^{-3}		[Cl$^-$] = 1.25 mol dm^{-3}	
0.25	0.91	0.50	1.0
0.50	1.6	0.75	2.3
0.75	2.9	1.00	3.5
1.00	5.0	1.25	6.3
1.25	6.3		

Effect of added vanadium(V)

The effect of added V(V) on the reaction was studied by taking into account the absorption due to both V(V) and Cr(VI) at 360 nm in runs where [Tl(I)] was greater (1.5 times) than [Cr(VI)]. Under the condition [Cr(VI)] > [Tl(I)], the absorption at 360 nm was regarded as due to the Cr(VI) exclusively, that due to V(V) being neglected in view of the very much higher ε of the former over that of V(V). In the presence of added V(V), the stoichiometry and the effect of added products remained the same as in the absence of V(V). Second order rate constant (k) in 60% acetic acid containing 1.25 mol dm^{-3} HCl in the presence of V(V) first increased till added [V(V)] exceeded that of the [Tl(I)] used; while, with further increase in [V(V)], the k-value progressively decreased. Hence, the order of reaction was determined in the two ranges of increasing and decreasing k in the presence of V(V). In the increasing range of k([V(V)] < [Tl(I)]), the orders in [Cr(VI)], [Tl(I)] and [V(V)] were 0.85, 1.0 and 0.60 respectively while in the decreasing range of k ([V(V)] > [Tl(I)]), the orders were 0.91, 0.90 and -1.0 respectively. In almost all runs, second order plots were linear practically throughout the 80% reaction range at all [V(V)] used. Such a behaviour of k was not observed in 40% acetic acid solution in the presence of 1.25 mol dm^{-3} HCl and k decreased continuously with increase in [V(V)].

In view of the distinctive effect of added V(V) on the reaction, the spectra of Tl(I) and V(V) were examined in 60% acetic acid containing 1.25 mol dm^{-3} HCl, individually and also together as mixed solution in the range of 250 to 350 nm. In the presence of both Tl(I) and V(V), there was a distinct change in the spectrum and the low intensity absorption bands of Tl(I) and V(V) were replaced by a high intensity band at 252 nm ($\varepsilon \sim 8200$), the latter being presumably due to the interaction between V(V) and Tl(I). Furthermore, a detailed study of the Job's curves[5] in respect of this sys-
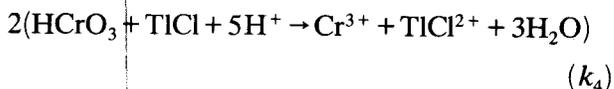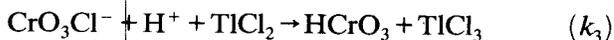
tem at 250, 260 and 270 nm each showed the composition of the V(V)-Tl(I) complex as 1:1, 1:1, 2:3 and 1:2 in 60, 70, 80 and 90% acetic acid solutions in the presence of 1.25 mol dm^{-3} HCl in each case.

Effect of Mn(II), Ce(III), Th(IV) and U(VI) on the reaction

Significantly, added Mn(II), Ce(III), Th(IV) and U(VI) in the concentration range of 0.5×10^{-3} to 1.5×10^{-3} mol dm^{-3} did not affect the reaction.

Discussion

The rate data in 60% acetic acid containing 1.25 mol dm^{-3} HCl parallel the results of an earlier study[1b] in 3 mol dm^{-3} HCl solution with respect to reaction order, effect of added products and the influence of Cl$^-$ ions. However, with respect to H$^+$ ions, the order in the present case is two as against one found in the earlier study[1b]. In the presence of large [Cl$^-$] and [H$^+$], Cr(VI) and Tl(I) mainly exist in the form of chlorochromate[2], CrO$_3$Cl$^-$, and thallium(I) chloride, TlCl, respectively[1b]. These species may be expected to form in prior equilibria in the present case. The experimental results lead to the mechanism shown in Scheme 1

$$HCrO_4^- + Cl^- + H^+ \rightleftharpoons CrO_3Cl^- + H_2O \qquad \dots (K_1)$$

$$Tl^+ + Cl^- \rightleftharpoons TlCl \qquad \dots (K_2)$$

$$CrO_3Cl^- + H^+ + TlCl \rightleftharpoons HCrO_3 + TlCl_2 \qquad (k_1, k_2)$$

$$CrO_3Cl^- + H^+ + TlCl_2 \rightarrow HCrO_3 + TlCl_3 \qquad (k_3)$$

$$2(HCrO_3 + TlCl + 5H^+ \rightarrow Cr^{3+} + TlCl^{2+} + 3H_2O) \qquad (k_4)$$

Scheme 1

Chromium(VI) in acid solutions exists mainly as acid chromate ion[6] (HCrO$_4^-$) and chlorochromate (CrO$_3$Cl$^-$) is formed from this species in a preequilibrium. The latter and TlCl, also formed in a preequilibrium, react in a one equivalent reversible step (k_1, k_2) yielding the reactive Cr(V) and Tl(II) species. The Tl(II) interacts (k_3) with a second Cr(VI) ion giving a second Cr(V). The Cr(V) formed oxidises Tl(I) subsequently in a two-equivalent step (k_4). Scheme 1 does not involve any Cr(IV) species but includes Cr(V). However, no direct evidence for Cr(V) could be obtained. While induction experiments[6] with iodide could not be performed to show the intermediacy of Cr(V) as one of the products, Tl(III), also oxidises iodide along with Cr(VI). The Cr(V)-Tl(I) reaction, being a complementary reaction, is also expected to be fast and, as a result, Cr(V) is expected to be present in very low concentrations. In this respect, it is noteworthy that the evidence for the involvement of Cr(IV) in the reaction is negative. Added Mn(II) ions

do not influence the reaction to any significant extent. If Cr(IV) was implicated in the mechanism, the presence of Mn(II) ions in the reaction solution would have caused substantial changes[6] in stoichiometry and rate constant.

The application of the steady state approximation to the reactive intermediates, Tl(II) and Cr(V), of Scheme 1 leads to the rate equation (3) which is in agreement with the experimental results and the experimental second order rate constant (k) may be identified with the constant factors in Eq. (3) at fixed [H$^+$] and [Cl$^-$]. In Eq. (3), K_1 and K_2 are the equilibrium constants of formation of CrO$_3$Cl$^-$ and TlCl respectively and k_0 is a constant given by Eq. (4), k_1, k_2, k_3 and k_4 in Eq. (4) being the rate constants of the

$$-\frac{d[Cr(VI)]}{dt} = \left\{ \frac{k_0 K_1 K_2 [H^+]^2 [Cl^-]^2}{(1 + K_1[H^+][Cl^-])(1 + K_2[Cl^-])} \right\}$$
$$\times [Cr(VI)][Tl(I)] \qquad \dots (3)$$

$$k_0 = (k_3 k_4 / k_2)[\{1 - (4k_1 k_2 / k_3 k_4)\}^{1/2} - 1] \qquad \dots (4)$$

different steps shown in Scheme 1. An alternative pathway, almost identical to that of Scheme 1, except that the reactive intermediates, Cr(V) and Tl(II), are formed in an irreversible step in contrast to the reversible step of Scheme 1, can also be conceived. However, both Cr(V) and Tl(II) are usually formed in reversible steps[7] in noncomplementary electron transfer reactions of Cr(VI) and Tl(I) and Scheme 1 is therefore preferred.

In the presence of added V(V), it is observed that the Cr(VI)-Tl(I) reaction is accelerated till the added [V(V)] is slightly greater than [Tl(I)]. Thereafter, further addition of V(V) lowers the rate constant. In view of the rate law of Scheme 1, the nature of the distinctive effect of V(V) on the reaction needs to be understood. The experimental kinetic and spectroscopic results confirm the formation of a 1:1 V(V)-Tl(I) species and it is this species which is responsible for the initial rate acceleration in 60% acetic acid containing 1.25 mol dm^{-3} HCl. The active reductant under these conditions is a (VO$_2$TlCl)$^+$ species. Once the latter is completely formed, the rate constant is lowered on the further addition of V(V) because the latter manifests a specific cation effect on the CrO$_3$Cl$^-$-TlCl reaction. Perhaps the V(V)-V(IV) cycle is now involved. That the influence of V(V) on the reaction is specific and limited to this ion is shown by the fact that the reaction is unaffected by ions of different valences and sizes such as Mn^{2+}, Ce^{3+}, Th^{4+} and UO$_2^{2+}$ in a range of concentrations from one to four times that of the reductant. Because of the specific cation effect,

Table 2—Effect of Added Vanadium(V) on Chromium(VI)-Thallium(I) Reaction at 25°C

$[V(V)] \times 10^4$ (mol dm^{-3})	$k^{a,b}$ (dm^{3}mol^{-1}s^{-1})	$k^{a,c}$ (dm^{3}mol^{-1}s^{-1})	k^d (dm^{3}mol^{-1}s^{-1})
0.0	6.9	5.0	1.9
1.0	8.3	7.7	1.8
2.0	10	8.7	1.7
3.0	12	9.6	1.5
4.0	14	8.8	1.4
5.0	11	8.3	1.3
7.5	8.3		

(a) $[Cr(VI)] = 2.0 \times 10^{-4}$ mol dm^{-3}; $[HCl] = 1.25$ mol dm^{-3}; 60% acetic acid solution.

(b) $[Tl(I)] = 3.0 \times 10^{-4}$ mol dm^{-3}.

(c) $[Tl(I)] = 2.0 \times 10^{-4}$ mol dm^{-3}.

(d) $[Cr(VI)] = 2.0 \times 10^{-4}$ mol dm^{-3}; $[Tl(I)] = 3.0 \times 10^{-4}$ mol dm^{-3}; $[HCl] = 1.25$ mol dm^{-3}; 40% acetic acid solution.

there are two paths now for the reaction: one involving the reductant, $(VO_2TlCl)^+$, and the other, involving TlCl itself. It is noteworthy that the order of reaction in added V(V) is fractional (0.60) in the range of increasing rate constant and 1.0 for the range of decreasing rate constant. While excess V(V) is needed to drive the equilibrium towards complex formation, after the complex is fully formed, all added V(V) contributes to retardation of reaction. It is also possible that the V(V)-V(IV) cycle, marginally involved during catalysis, might be more active during retardation.

However, there has been no evidence of any V(IV) during the reaction under a variety of conditions but it is also true that any V(IV) formed will be short-lived in the presence of several powerful oxidants in the reaction.

In 40% acetic acid containing 1.25 mol dm^{-3} HCl, there is no evidence of any V(V)-Tl(I) complex formation and hence the rate decreases with increase in [V(V)] (Table 2), again reinforcing the specificity of V(V) effect. As would be expected, there is no initial acceleration of reaction because no complex is formed in these solutions of higher dielectric constant. It is also apparent from the results of Table 2 that added V(V) decreases the rate much more efficiently in the absence of complex formation in 40% acetic acid solution than in solutions where the complex formation is facilitated.

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