Oxidation of palladium(II) by chromium(VI) in aqueous ethanoic acid and chloride media : a kinetic and mechanistic study

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A mechanism involving chlorochromate ($ClCrO_3^-$) and $[PdCl_4]^{2-}$ as oxidant and reductant respectively has been proposed. The activation parameters are computed and discussed.

Keywords: palladium(II) oxidation, chromium(III)

The kinetics of oxidation of palladium(II) by chromium(VI) in aqueous ethanoic acid containing large concentrations of hydrochloric acid at a constant ionic strength 4.1 mol/dm^3 has been studied spectrophotometrically. The oxidation is made possible by altering the redox potentials. The reaction is first order in oxidant and reductant concentrations and mearly second order each in acid and chloride concentrations under the experimental conditions. It has been found that as the ionic strength increases the rate of reaction increases. Similarly, as the ethanoic acid content increases in the reaction medium, the rate of reaction also increases. The initially added products Cr(III) and Pd(IV) did not show any significant effect on the rate of the reaction.

The results of rate increase with increase in chloride and acid concentrations suggest that equilibria of different Pd(II) complexes as in Eqns(2) to (5) and of Cr(VI) as in Eqns(8) and (9) are possible. Such equilibria have been well recorded in the literature.[14,18,19]

$$Pd^{2+} + Cl^- \rightleftharpoons PdCl^+ \qquad K_1 \quad (2)$$

$$PdCl^+ + Cl^- \rightleftharpoons PdCl_2 \qquad K_2 \quad (3)$$

$$PdCl_2 + Cl^- \rightleftharpoons PdCl_3^- \qquad K_3 \quad (4)$$

$$PdCl_3^- + Cl^- \rightleftharpoons PdCl_4^{2-} \qquad K_4 \quad (5)$$

and

$$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^- \qquad K_5 \quad (8)$$

$$HCrO_4^- + H^+ + Cl^- \rightleftharpoons ClCrO_3^- + H_2O \qquad K_6 \quad (9)$$
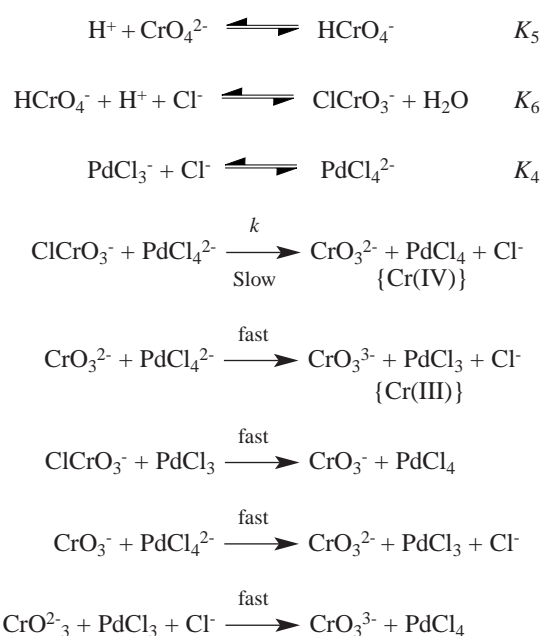
The stoichiometry of the title reaction is found to be 2:3. The chromium(VI) – palladium(II) reaction is facile only in the presence of large concentrations of hydrochloric acid and ethanoic acid due to altering the redox potentials. As the [H$^+$] concentration increases at constant chloride concentration the rate increases. The order in [H$^+$] is nearly two, and the active form of oxidant is found to be as in equilibrium(8) and (9). In chloride media the palladium(II) forms different chloride complexes[14] and are shown in equilibrium (2) to (5). As the [Cl$^-$] increases at constant [H$^+$] the reaction rate increases. The apparent order in [Cl$^-$] under experimental conditions is found to be nearly two. The variation of rate with chloride was shown to parallel the concentration of $PdCl_4^{2-}$ species (Table 4, Fig. 2). Hence $PdCl_4^{2-}$ is considered to be active palladium (II) species under the experimental conditions.

The reaction between chromium(VI) and palladium(II) in high acid and chloride concentration had unit order in chromium(VI) and palladium(II). No effect of products was observed. The experimental results can be accommodated in terms of Scheme 1.

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$$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^- \qquad K_5$$

$$HCrO_4^- + H^+ + Cl^- \rightleftharpoons ClCrO_3^- + H_2O \qquad K_6$$

$$PdCl_3^- + Cl^- \rightleftharpoons PdCl_4^{2-} \qquad K_4$$

$$ClCrO_3^- + PdCl_4^{2-} \xrightarrow[\text{Slow}]{k} CrO_3^{2-} + PdCl_4 + Cl^-$$
$$\{Cr(IV)\}$$

$$CrO_3^{2-} + PdCl_4^{2-} \xrightarrow{\text{fast}} CrO_3^{3-} + PdCl_3 + Cl^-$$
$$\{Cr(III)\}$$

$$ClCrO_3^- + PdCl_3 \xrightarrow{\text{fast}} CrO_3^- + PdCl_4$$

$$CrO_3^- + PdCl_4^{2-} \xrightarrow{\text{fast}} CrO_3^{2-} + PdCl_3 + Cl^-$$

$$CrO_3^{2-} + PdCl_3 + Cl^- \xrightarrow{\text{fast}} CrO_3^{3-} + PdCl_4$$

Scheme 1

The evidence for formation of intermediate Pd(III) is in accordance with earlier work[22] and its existence cannot be determined since it is in low concentration and unstable. The intervention of chromium(V) is evident from the induction experiment with iodide. The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of increasing amount of added manganese(II). Such results have also been obtained from chromium(VI) oxidation of 2-propanol in aqueous ethanoic acid. [9,10,23]

Scheme 1 leads to the rate law (10).

$$\text{Rate} = -\frac{d [Pd(II)]}{dt} = \qquad (10)$$

$$\frac{k K_4 K_5 K_6 [Cr(VI)] [Pd(II)] [H^+]^2 [Cl^-]^2}{1 + K_5[H^+] + K_5 K_6[H^+]^2 [Cl^-] + K_4 [Cl^-] + K_4 K_5 [H^+] [Cl^-] + K_4 K_5 K_6 [H^+]^2 [Cl^-]^2}$$

The rate law (10) may be rearranged to Eqn (11), which is suitable for verification.

$$\frac{[Cr(VI)] [Pd(II)]}{\text{Rate}} = \frac{1}{k_2} = \qquad (11)$$

$$\frac{1}{k K_4 K_5 K_6 [H^+]^2 [Cl^-]^2} + \frac{1}{k K_4 K_6 [H^+] [Cl^-]^2} + \frac{1}{k K_4 [Cl^-]}$$
$$+ \frac{1}{k K_5 K_6 [H^+]^2 [Cl^-]} + \frac{1}{k K_6 [H^+] [Cl^-]} + \frac{1}{k}$$

According to Eqn (11), the plots of LHS *versus* $1/[H^+]^2$ and $1/[Cl^-]^2$ should be linear and this is verified in Fig. 7. The effect of ionic strength on the rate qualitatively accounts for the reaction between two negatively charged ions in the rate determining step as seen in Scheme 1. The effect of solvent on the reaction rate has been described in detail elsewhere.[24,27] The increase in the ethanoic acid content in the reaction medium leads to an increase in the rate of the reaction, contrary to the expected slower reaction between like ions in the media of lower dielectric constant (D). Perhaps this effect is countered substantially by the formation of active reactant species to a greater extent in low dielectric constant media, leading to the net increase in the reaction rate.[29] This also supports the enhancement of reduction potentials of the Cr(VI) / Cr(III) couple.[20] The moderate values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ both favour electron transfer processes.

Techniques used : Spectrophotometry.

References : 29

Tables : 4

Figure 1: Plot of $k_2/[H^+]$ *versus* $[H^+]$ (conditions as in Table 3).

Figure 2: Effect of chloride concentration of different palladium(II) species and also on the rates of reaction (conditions as in Table 4). The concentration of PdII chloride species except $PdCl_4^{2-}$, decreases steadily and are not shown.

Figure 3: Spectrum of palladium(II) with different chloride concentrations: (1) Zero, (2) 1.0, (3) 2.0, (4) 3.0 and (5) 4.0 mol/dm^3 at constant [H+] = 4.0 mol/dm^3.

Figure 4: Plot of the initial rate of the Cr^{VI} – Pd^{II} reaction *versus* the product of reactant concentrations at 25°C and I = 4.1 mol/dm^3.

Figure 5: Plot of log k_2 *versus* $I^{1/2}$ and log k_2 *versus* $1/D$.

Figure 6: Spectrum of $HCrO_4^-$ (1) and $ClCrO_3^-$ (2).

Figure 7: Verification of rate law (11) (conditions as in Table 3 and 4)

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