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Mechanistic study of quinoliniumdichromate (QDC) oxidation of mercury(I) in aqueous sulfuric acid in the presence of micro amounts of palladium(II) – Autocatalysis in catalysis

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Abstract

The kinetics of oxidation of mercury(I) with quinoliniumdichromate (QDC) in the presence of micro amounts of palladium(II) catalyst in aqueous sulfuric acid medium has been studied under varying conditions. The active species of oxidant, reductant and catalyst in the reaction medium were understood to be $HCrO_4^-$, $[Hg_2(SO_4)HSO_4]^-$ and $PdCl^+$, respectively. The autocatalysis by one of the products, chromium(III), was observed. A composite scheme and rate law were proposed. Reaction constants involved in the mechanism have been evaluated.

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1. Introduction

Nowadays the development of newer chromium(VI) reagents [1–4] for the oxidation of organic substrates continues to be a subject of interest. The reagent employed in these investigations, quinoliniumdichromate (QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, is a useful and versatile oxidant that deserves further evaluation. The literature survey reveals that although several organic compounds are oxidised by QDC and their mechanisms have been established, there are no reports on the oxidation of inorganic substrates by QDC, except in one case [5].

The oxidation of mercury(I) by different oxidants has received attention [6–9]. However, the QDC–mercury(I) reaction is immeasurably slow even though the redox potentials of the two couples, Hg(II)/Hg(I): +0.92 V and QDC, i.e. Cr(VI)/Cr(III): +1.33 V, permits a reasonable reaction in acid solution. No reports of the reaction, catalysed or uncatalysed seem to be available in the literature. However, the reaction is facile in the presence of palladium(II) as a catalyst and in aqueous sulfuric acid, but it does not takes place to any reasonable extent in other acid media. Furthermore, the usual redox type of catalysis seems to be precluded in this case as the QDC-palladium(II) reaction does not occur to any measurable extent, even at elevated temperatures (ca. 90 °C) in aqueous acid. Indeed palladium redox chemistry seems to be essentially limited to organic compounds, only a few studies of redox reactions with inorganic species being available [10,11]. Since the QDC-mercury(I) reaction is a non-complementary case, it has different mechanistic possibilities. Most studies using palladium(II) as a catalyst have employed it in the form of palladium(II) chloride [12,13], and the nature of its active form in such reactions remains obscure. We have investigated the effect of chloride as well as acid on palladium(II) catalysed oxidation of mercury(I) to determine the active species of the catalyst and the oxidant. The palladium(II) catalysed chromium(VI) oxidation of mercury(I) has been studied earlier [14], but the same reaction in the presence of quinoline base follows different kinetic parameters and effects. Hence to explore the mechanism, the title reaction was undertaken.

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2. Experimental

2.1. Materials

Reagent grade chemicals and doubly distilled water were used throughout this work. QDC was prepared by the reported method [2-4] and was characterised by IR spectra and m.p. -160 °C. The QDC solution was prepared by dissolving ODC in water and determining its concentration iodometrically [4]. The mercury(I) solution was obtained by dissolving mercury(I) nitrate (Fluka) in 1 mol dm^{-3} perchloric acid (70%) and the solution was standardised against potassium iodate solution [15a]. The palladium(II) solution was obtained by dissolving palladium chloride (Johnson Matthey) in 0.20 mol dm⁻ hydrochloric acid (AR) and assaying for palladium(II) by complexometric titration with EDTA [15b]. For some kinetic runs, chloride had to be absent and hence the chloride in the palladium(II) stock solution was removed by precipitation with silver nitrate, followed by repeated centrifugation. The resulting clear solution contained less than 1.0×10^{-6} mol dm⁻³ chloride and silver ions. Such extremely low concentrations of Ag⁺ and Cl⁻ were found to have no significant effect on the reaction. The required chloride concentration was maintained with sodium chloride. The chromium(III) solution was prepared by dissolving chromium(III) potassium sulfate (BDH, AR), $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ in water. The mercury(II) solution was obtained by dissolving mercuric oxide, HgO (BDH) in 0.50 mol dm^{-3} sulfuric acid. The ionic strength was kept constant with sodium sulfate. Use of sodium perchlorate was precluded since precipitation occurred under the reaction conditions.

2.2. Kinetic procedure

Since the reaction was too fast to be monitored by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer (Tokyo, Japan) connected to a rapid kinetic accessory (HITECH SFA-12 unit). Kinetics were followed at 25 ± 0.1 °C and I = 1.60 mol dm^{-3} . The reaction was initiated by mixing the pre-equilibrated reactant solutions, which also contained known concentrations of sulfuric acid and sodium sulfate to give the required acidity and ionic strength. The reaction was followed under second order conditions by measuring the absorbance of QDC in the form of the monomer in the reaction mixture at 440 nm. Application of Beer's law under the reaction conditions had been verified earlier between 1.0×10^{-4} and 2.0×10^{-3} mol dm⁻³ of QDC at 440 nm with molar absorptivity, ε resulting as 395 \pm $10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The second order plots were nonlinear due to the autocatalytic effect of the one of the products, chromium(III). Hence the choice of initial rates at 5% completion of the reaction was made. The initial rates of the reaction were obtained from the slopes of concentrations versus time curves at the initial stages (5%) of the reaction by the plane mirror method. The initial rates were reproducible within $\pm 5\%$.

3. Results and discussion

3.1. Stoichiometry

Different sets of concentrations of reactants and catalyst, palladium(II), in 0.50 mol dm⁻³ sulfuric acid at constant ionic strength, 1.60 mol dm⁻³, were kept for over 8 h at 25 °C in a closed container. When [QDC] > [mercury(I)], the remaining QDC was assayed by measuring the absorbance at 440 nm, whereas under the conditions [mercury(I)] > [QDC], when QDC had fully reacted, the remaining mercury(I) concentration was determined by titration with potassium iodate [15a]. One of the products, the chromium(III) concentration, was determined by measuring the absorbance at 584 nm. The results showed that QDC reacted with mercury(I) in a 1:3 mole ratio. The catalyst concentration was unchanged at the end of the reaction as found by estimating it spectrophotometrically as the palladium(II) azide complex [16].

$$QDC + 3Hg(I) \xrightarrow{Pd(II)} Cr(III) + 3Hg(II)$$
(1)

3.2. Order of reaction

The reaction order was found from log–log plots of initial rates versus concentrations at constant ionic strength, $I = 1.60 \text{ mol } \text{dm}^{-3}$ and at constant sulfuric acid concentration (0.50 mol dm^{-3}). At constant palladium(II) concentration, $8.0 \times 10^{-6} \text{ mol } \text{dm}^{-3}$, the order with respect to QDC in the concentration range 5.0×10^{-5} – $5.0 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ was found to be unity. The order with respect to mercury(I), between 5.0×10^{-5} and $6.0 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ was less than unity, ca. 0.42 (Table 1). At constant reactant concentrations (3[QDC] = [Hg(I)] = $6.0 \times 10^{-4} \text{ mol } \text{dm}^{-3}$), constant acidity and ionic strength ([H₂SO₄] = 0.50 mol dm⁻³ and $I = 1.60 \text{ mol } \text{dm}^{-3}$), the palladium(II) concentration was varied between 1.0×10^{-6} and $1.0 \times 10^{-5} \text{ mol } \text{dm}^{-3}$ and the order was found to be unity (Table 1).

3.3. Effect of added products

The initially added products, chromium(III) and mercury(II), were studied in the $5.0 \times 10^{-5}-5.0 \times 10^{-4}$ and $1.0 \times 10^{-4}-5.0 \times 10^{-4}$ mol dm⁻³ concentration ranges, respectively, while keeping the reactant concentrations and all other conditions constant. It was observed that added chromium(III) enhances the reaction rate with an order of less than unity (0.73), whereas, the added mercury(II), does not change the rate appreciably (Table 2). This result indicates the autocatalytic nature of the product, chromium(III), which is also evident from the concentration of chromium(III) values versus *t* plot (Fig. 1) and a linear plot of (Initial rate) versus (rate)_{calc} for chromium(III) variations (Fig. 1, inset). However, in the case of the palladium(II) Table 1

Effect of QDC, Hg(I) and Pd(II) concentrations on Pd(II) catalysed oxidation of Hg(I) by QDC in acid medium: $[H_2SO_4] = 0.50$, $I = 1.60 \text{ mol dm}^{-3}$, 25 °C

$[QDC] \times 10^4$ (mol dm ⁻³)	$[Hg(I)] \times 10^4$ (mol dm ⁻³)	$[Pd(II)] \times 10^{6}$ (mol dm ⁻³)	Initial rate $\times 10^7$ (mol dm ⁻³ s ⁻¹)
0.50	6.0	8.0	0.85
1.0	6.0	8.0	1.61
2.0	6.0	8.0	3.45
3.0	6.0	8.0	5.07
4.0	6.0	8.0	6.48
5.0	6.0	8.0	8.61
2.0	0.50	8.0	1.18
2.0	1.0	8.0	1.77
2.0	2.0	8.0	2.38
2.0	4.0	8.0	3.10
2.0	6.0	8.0	3.45
2.0	6.0	1.0	0.43
2.0	6.0	2.0	0.86
2.0	6.0	4.0	1.75
2.0	6.0	6.0	2.56
2.0	6.0	8.0	3.45
2.0	6.0	10.0	4.29

Table 2

Effect of initially added products, Cr(III) and Hg(II), on Pd(II) catalysed oxidation of Hg(I) in acid medium: $3[QDC] = [Hg(I)] = 6.0 \times 10^{-4}$; $[Pd(II)] = 8.0 \times 10^{-6}$; $[H_2SO_4] = 0.50$; I = 1.60 mol dm⁻³, 25 °C

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$\frac{[Cr(III)] \times 10^4}{(mol dm^{-3})}$	Initial rate $\times 10^{6}$ (mol dm ⁻³ s ⁻¹)	$[Hg(II)] \times 10^4$ (mol dm ⁻³)	Initial rate $\times 10^7$ (mol dm ⁻³ s ⁻¹)	
0.50	1.25	1.0	3.38	
1.0	2.31	2.0	3.48	
2.0	4.15	3.0	3.51	
3.0	5.77	4.0	3.41	
4.0	7.63	5.0	3.43	
5.0	8.95			

catalysed chromium(VI) oxidation of mercury(I) reaction [14] such autocatalysis was not observed.

3.4. Effect of acid

At constant reactant concentrations and other constant conditions (Table 3) the sulfuric acid concentration was varied between 0.20 and 1.0 mol dm⁻³ and the rate was found to increase with an order of ca. 0.51 in [H⁺]. The [H⁺] values calculated from the added sulfuric acid concentration and known equilibrium constant of the acid sulfate equilibrium [17] are shown in Table 3.

3.5. Effect of added chloride

For this purpose palladium(II) solutions, which did not contain chloride, were used. The initial rate increased with increase in $[Cl^-]$. This is ascribable to the formation of palladium(II) chloride complexes. The order in $[Cl^-]$ under the experimental conditions was close to unity (ca. 0.91). As with the dependence on mercury(I), the rate varies with



Fig. 1. Autocatalysis: [QDC] vs. *t* plots; 3[QDC] = [Hg(I)] = 6.0×10^{-4} , [H₂SO₄] = 0.50; *I* = 1.60 mol dm⁻³. (a) [Pd(II)] = 4.0×10^{-6} . (b) [Pd(II)] = 8.0×10^{-6} mol dm⁻³. Inset: Plot of (Initial rate)_{exptl} vs. (rate)_{calc}. (Rate)_{calc} = [QDC][Pd(II)][Hg(I)]^{0.42}[H⁺¹]^{0.51}[Cr(III)]^{0.73} for variation of Cr(III) (Table 2).

Table 3

Effect of sulfuric acid concentration on Pd(II) catalysed oxidation of Hg(I) by QDC: $3[QDC] = [Hg(I)] = 6.0 \times 10^{-4}; [Pd(II)] = 8.0 \times 10^{-6}; I = 3.70 \text{ mol dm}^{-3}, 25 \text{ °C}$

$[H_2SO_4] \\ (mol \ dm^{-3})$	$[H^+]$ (mol dm ⁻³)	Initial rate $\times 10^7$ (mol dm ⁻³ s ⁻¹)	
0.2	0.048	1.28	
0.4	0.139	2.73	
0.6	0.311	4.18	
0.8	0.579	5.21	
1.0	0.911	6.45	

[Cl⁻]. Palladium(II) is known to form chloride complexes [18] of the formula $Pd(Cl)_n^{+2-n}$, *n* having values 1–4, the cumulative stability constants β_1 to β_4 being 1.0×10^4 , 3.1×10^7 , 5.4×10^9 and 1.3×10^{11} , respectively, as shown in the following equilibrium:

 $Pd^{2+} + Cl^{-} \rightleftharpoons PdCl^{+} \qquad K_{1}$

 $PdCl^{+} + Cl^{-} \rightleftharpoons PdCl_{2} \qquad K_{2} \tag{3}$

 $PdCl_2 + Cl^- \rightleftharpoons PdCl_3^- \qquad K_3 \tag{4}$

$$PdCl_{3}^{-} + Cl^{-} \rightleftharpoons PdCl_{4}^{2-} \qquad K_{4}$$
(5)

The approximate concentrations of such species may be calculated based on the following equation:

$$\left[Pd(II) \right]_{T}$$

$$= [Pd(II)]_{f} \left\{ 1 + \beta_{1} [CI^{-}] + \beta_{2} [CI^{-}]^{2} + \beta_{3} [CI^{-}]^{3} + \beta_{4} [CI^{-}]^{4} \right\}$$
(6)

from the concentrations of the dissolved palladium(II) and chloride, with their competing equilibria [19,20]. Variation in the concentrations of such species with increase in $[Cl^-]$ is shown in Table 4, along with the rates of the respective

Table 4

$[Cl^{-}] \times 10^{5} (mol dm^{-3})$	α0	$10^2 \alpha_1$	$10^2 \alpha_2$	$10^4 \alpha_3$	$10^4 \alpha_4$	Initial rate $\times 10^7 \pmod{\text{dm}^{-3} \text{s}^{-1}}$
0	1.0					0.09
0.5	0.96	4.8	0.074	0.0064	0.0008	0.52
1.0	0.91	9.1	0.28	0.049	0.0126	1.17
1.5	0.86	13.0	0.60	0.158	0.0569	2.36
2.5	0.79	19.7	1.53	0.665	0.4003	3.82
4.0	0.69	26.5	3.42	2.38	2.300	5.75
5.0	0.63	31.7	4.91	4.28	5.148	6.50
6.0	0.58	35.0	6.52	6.81	9.837	7.98
8.0	0.50	40.0	9.91	13.8	26.61	9.83
10.0	0.43	43.2	13.4	23.3	56.15	11.2
15.0	0.31	46.7	21.7	56.7	204.7	12.5

Variation of different Pd(II) species^a with [Cl⁻] on Pd(II) catalysed oxidation of Hg(I) by QDC in acid medium: $3[QDC] = [Hg(I)] = 6.0 \times 10^{-4}$; $[Pd(II)] = 8.0 \times 10^{-6}$; $[H_2SO_4] = 0.50$; $I = 1.60 \text{ mol dm}^{-3}$, 25 °C

^a α_0 , α_1 , α_2 , α_3 and α_4 are the fractions of total Pd(II) of the species Pd_f²⁺, PdCl⁺, PdCl₂, PdCl₃⁻ and PdCl₄²⁻, respectively. The stability constants of the different Pd(II) complexes are from Ref. [15].

catalysed reactions, and it is found that there is a parallelism only between rates and $[PdCl^+]$ (Fig. 2).

Rates of reaction with 30 different sets of concentrations of QDC, mercury(I), palladium(II) and H^+ ion at constant ionic strength were found to obey the rate law (7) shown in Fig. 3.

Rate
$$\propto$$
 [QDC][Pd(II)][Hg(I)]^{0.42}[H⁺]^{0.51} (7)

3.6. Effect of dielectric constant and ionic strength

When the acetic acid content (V/V) in the reaction medium was increased, keeping the reactant concentrations and other conditions constant, the reaction rate increases. Since the dielectric constants of aqueous acetic acid are not available in the literature, they were computed from the values for pure liquids [21]. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. A plot of log(Initial rate) versus 1/D is linear with positive slope (Fig. 4, $(r \ge 0.999, \sigma \le 0.015)$). Variation of ionic strength between 1.6 and 4.0 mol dm⁻³, using sodium sulfate, caused a decrease in the rate of reaction. A



Fig. 2. Effect of chloride concentrations on different palladium(II) species and also on the rates of reaction (conditions as in Table 4).



Fig. 3. Plot of the initial rate of the QDC–Hg(I) reaction vs. the product of reactant concentrations at 25 °C and $I = 1.60 \text{ mol dm}^{-3}$.

plot of log(Initial rate) versus $I^{1/2}$ is linear with negative slope as shown in Fig. 4 ($r \ge 0.998$, $\sigma \le 0.021$).

3.7. Effect of added ions

In this case, the palladium(II) used contain chloride concentrations less than 1.0×10^{-6} mol dm⁻³ as stated in Section 2. When the reactant concentrations and other conditions were kept constant, ions such as Cu²⁺, Na⁺ and NO₃⁻ did not have any significant effect on the rate of the reaction, whereas added Mn²⁺ decreases the rate.

3.8. Effect of temperature

The rate constants (k_1) of the slow step of Scheme 1 were obtained from the intercepts of [QDC][Pd(II)]/(Initial rate)versus 1/[Hg(I)] plots at four different temperatures, by



Fig. 4. Plot of log(Initial rate) vs. $I^{1/2}$ and log(Initial rate) vs. 1/D.

employing the values of K_5 . The activation parameters for the rate determining step were obtained by the least-square method and from a plot of $\log k_1$ versus 1/T ($r \ge 0.987$, $\sigma \le 0.019$). The values of $k_1 \times 10^2$ (dm³ mol⁻¹ s⁻¹) are 3.88, 5.02, 6.94 and 9.42 at 298, 303, 308 and 313 K, respectively, which lead to the activation parameters $E_a = 23 \pm$ 1 kJ mol⁻¹, $\Delta H^{\#} = 21 \pm 1$ kJ mol⁻¹, $\log A = 6.7 \pm 0.5$, $\Delta S^{\#} =$ -126 ± 10 J K⁻¹ mol⁻¹ and $\Delta G^{\#} = 58 \pm 5$ kJ mol⁻¹.

Thermodynamic quantities of first step of Scheme 1 are evaluated from the slope of the plot of [QDC][Pd(II)]/(Initial rate) versus 1/[H⁺] at different temperatures. The values of K_5 at 298, 303, 308 and 313 K are 4.24, 4.65, 4.91 and 5.28 dm³ mol⁻¹, respectively. The Van't Hoff plot was drawn for the variation of K_5 with temperature (log K_5 versus 1/T; $r \ge 0.996$, $\sigma \le 0.023$). The values of the thermodynamic quantities are $\Delta H = 11.0 \pm 0.5$ kJ mol⁻¹, $\Delta S = 49. \pm 3$ J K⁻¹ mol⁻¹ and $\Delta G = -4.0 \pm 0.2$ kJ mol⁻¹. A comparison of these values with those values obtained for the slow step shows that the reaction before the ratedetermining step is fairly rapid [22].

The oxidation of mercury(I) by QDC is not observed in the absence of palladium(II) and, in the presence of latter, occurs with measurable speed only in aqueous sulfuric acid. Furthermore, since QDC does not oxidise palladium(II), even at the higher temperature (ca. 90 °C) of the aqueous acid, it is unlikely that any higher oxidation states, such

$$\begin{array}{rcl} QDC + H^{+} & & HCrO_{4}^{-} + Q \mbox{ (quinoline)} & K_{5} \\ Hg(I) + Pd(II) & & Complex \mbox{ (C}_{1}) & K_{6} \\ C_{1} + HCrO_{4}^{-} & & Slow \\ C_{1} + HCrO_{4}^{-} & & 2 \ Hg(II) + Cr(V) \ + Pd(I) & k_{1} \\ Cr(V) + Pd(I) & & fast \\ Cr(V) + Pd(I) & & fast \\ Hg(I) + Cr(IV) & & fast \\ Hg(II) \ + Cr(III) \\ Scheme \ 1. \end{array}$$

as palladium(III) or palladium(IV), are involved in the reaction. In the presence of perchloric acid and nitric acid, the palladium(II) catalyst is inefficient, possibly due to active species of palladium as palladium chloride complexes, which are not possible in such media. Hence the study was undertaken in sulfuric acid and chloride medium.

The reaction between mercury(I) and QDC in sulfuric acid in the presence of palladium(II) has a stoichiometry of 1:3 with an apparent less than unit order in mercury(I) and H^+ and first order dependence on ODC, palladium(II) and Cl⁻. It was observed that one of the products, chromium(III), increases the reaction rate, whereas another product, mercury(II), does not affect the rate of the reaction. However, in the palladium(II) catalysed chromium(VI) oxidation of mercury(I) an apparent less than unit order in mercury(I) and Cl⁻, and first order dependence on Cr(VI), palladium(II) and H⁺ concentrations were obtained. In this study, the initially added products have no effect on the rate of the reaction. The different behaviour in the palladium(II) catalysed oxidation of mercury(I) by chromium(VI) and QDC might be due to the presence of the quinolinium moiety. There are reports [23] that the reactivities of substituted pyridine, quinoline and isoquinoline complexes of chromium(VI) resemble one another. Such complexes show no dimerisation or polymerisation in solutions [24a]. In aqueous solution, QDC and chromium(VI) behave in different manners. Quinoline acts as an electron donor. Due to this, considerable quantities of QDC are reduced to chromium(III) [24b]. The thus formed chromium(III) immediately forms a weak complex with QDC, which is responsible for autocatalysis.

It is well known that in aqueous acid solution, QDC exists mainly in the form of the acid chromate ion [25,26], $HCrO_4^{-}$. The results suggest that mercury(I) reacts with palladium(II) to give a complex, which then reacts with $HCrO_4^{-}$ in a rate determining step to give the mercury(II) product, the intermediates chromium(V) and palladium(I) being generated. The intermediate chromium(V) reacts in further fast steps to give the products, palladium(II) being regenerated. The results can be accommodated by Scheme 1.

The evidence for complex formation was obtained from UV-Vis spectra of both palladium(II) and mercury(I)-palladium(II) mixtures, in which a hypsochromic shift of palladium(II) from 320 to 300 nm and hyperchromicity at 300 nm, occurred (Fig. 5). This was also evident from the Michaelis-Menten plot and such complex formation between substrate and catalyst has also been observed in other studies [27,28]. Since oxidation of mercury(I) by QDC is a non-complementary reaction, it may occur by the intervention of reactive chromium(V) and chromium(IV) species. The intervention of chromium(V) is evident from the induction experiment with iodide [25,26]. The induced oxidation of iodide yields two equivalent of iodine for each equivalent of the inductor oxidised. In any induced oxidation the inductor factor is defined as the ratio of the number of equivalents of reducing agent oxidised to



Fig. 5. UV–Vis spectra showing the formation of complex between Pd(II) and Hg(I) in the Pd(II) catalysed QDC oxidation of mercury(I) reaction in aqueous sulfuric acid at 25 °C. $[H_2SO_4] = 0.5 \text{ mol } dm^{-3}$ in all spectra. (I) Spectra of $[Hg(I)] = 2.0 \times 10^{-4} \text{ mol } dm^{-3}$. (II) Spectra of a mixture of $[Hg(I)] = 2.0 \times 10^{-4} \text{ and } [Pd(II)] = 0.5 \times 10^{-4} \text{ mol } dm^{-3}$. (IV) Spectra of a mixture of $[Hg(I)] = 2.0 \times 10^{-4} \text{ and } [Pd(II)] = 2.0 \times 10^{-4} \text{ mol } dm^{-3}$. (V) Spectra of a mixture of $[Hg(I)] = 2.0 \times 10^{-4} \text{ and } [Pd(II)] = 2.0 \times 10^{-4} \text{ mol } dm^{-3}$. (VI) Spectra of a mixture of $[Hg(I)] = 2.0 \times 10^{-4} \text{ and } [Pd(II)] = 4.0 \times 10^{-4} \text{ mol } dm^{-3}$.

the number of equivalents of inductor oxidised. The induction factor for iodide oxidation is nearly two, which indicates that the active oxidising agent is pentavalent chromium. The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of increasing amounts of added manganese(II), the decrease reaching a limit of about one half of the rate found in the absence of manganese(II). Such results have also been obtained for chromium(VI) oxidation of 2-propanol in aqueous acetic acid [29,30].

Scheme 1 leads to the rate law (8)

$$Rate = \frac{-d[QDC]}{dt} = \frac{k_1 K_5 K_6 [QDC] [Hg(I)] [Pd(II)] [H^+]}{1 + K_5 [H^+] + K_6 [Hg(I)] + K_5 K_6 [Hg(I)] [H^+]}$$
(8)

Rate law (8) accommodates all the experimental results except the autocatalytic effect of chromium(III). The rate law (8) may be rearranged to Eq. (9), which is suitable for verification.

$$\frac{[\text{QDC}][\text{Pd}(\text{II})]}{\text{Rate}} = \frac{1}{k_1 K_5[\text{H}^+]} + \frac{1}{k_1 K_6[\text{Hg}(\text{I})]} + \frac{1}{k_1 K_5 K_6[\text{Hg}(\text{I})][\text{H}^+]} + \frac{1}{k_1}$$
(9)

According to Eq. (9), a plot of the LHS versus $1/[H^+]$ and LHS versus 1/[Hg(I)] should be linear, and are found to be

so (Fig. 6; $r \ge 0.999$, $\sigma \le 0.018$ and $r \ge 0.998$, $\sigma \le 0.018$). The slopes and the intercepts of such plots leads to values of k_1 , K_5 and K_6 of $(3.88 \pm 0.15) \times 10^2$ dm³ mol⁻¹ s⁻¹, 4.24 ± 0.21 dm³ mol⁻¹ and $(8.23 \pm 0.38) \times 10^3$ dm³ mol⁻¹, respectively. The modest activation energy and sizeable



Fig. 6. Verification of rate law (8) in the form of (9) (conditions as in Tables 1 and 3).

entropy of activation supports a complex transition state in the reaction.

The active species involved in the mechanism can be understood as follows. In aqueous acid media, QDC is known to exist mainly as $HCrO_4^{-}$. Mercury(I) has been shown to exist [31] as the complex $[Hg_2(SO_4)HSO_4]^{-}$. Oxidation of mercury(I) is greatly facilitated in sulfuric acid solution and the reason may be that mercury(I) sulfate complexes are actively involved. The variation of rate with chloride ion was shown in Section 3. Except PdCl⁺ species, the remaining species of palladium(II) do not parallel the rate From the second equilibrium of Scheme 2

$$[Hg_{2}(SO_{4})HSO_{4}]^{-} = K_{7}[Hg_{2}^{2+}][SO_{4}^{-2}][HSO_{4}^{-}]$$
(11)

But total [Hg(I)] is given by

$$[Hg(I)]_{T} = [Hg(I)]_{f} + [Hg_{2}(SO_{4})HSO_{4}]$$

$$\therefore [Hg(I)]_{f} = \frac{[Hg(I)]_{T}}{1 + K_{7}[SO_{4}^{2-}][HSO_{4}^{-}]}$$
(12)

Substituting Eq. (12) in Eq. (11), the following equation is obtained:

$$[Hg_{2}(SO_{4})HSO_{4}]^{-} = \frac{K_{7}[Hg(I)]_{T}[SO_{4}^{2-}][HSO_{4}^{-}]}{1 + K_{7}[SO_{4}^{2-}][HSO_{4}^{-}]}$$
(13)

From the third step of Scheme 2

$$[PdCl^+] = K_1[Pd^{2+}][Cl^-]$$
(14)

Substituting Eq. (6) in Eq. (14)

$$\therefore \quad [PdCl^+] = \frac{K_1 [Pd^{2+}]_T [Cl^-]}{1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \beta_3 [Cl^-]^3 + \beta_4 [Cl^-]^4}$$
(15)

Substituting Eqs. (13) and (15) in Eq. (10) and omitting subscripts, we obtain the following equation:

$$Rate = \left\{ \frac{k_1 K_1 K_5 K_6 K_7 [Hg(I)] [QDC] [Pd(II)] [CI^-] [SO_4^{2-}] [HSO_4^{-}] [H^+]}{(1 + K_7 [SO_4^{2-}] [HSO_4^{-}]) (1 + \beta_1 [CI^-] + \beta_2 [CI^-]^2 + \beta_3 [CI^-]^3 + \beta_4 [CI^-]^4)} \right\} \\ \times \left\{ 1 + K_5 [H^+] + \frac{K_6 K_7 [Hg(I)] [SO_4^{2-}] [HSO_4^{-}]}{1 + K_7 [SO_4^{2-}] [HSO_4^{-}]} + \frac{K_5 K_6 K_7 [Hg(I)] [SO_4^{2-}] [HSO_4^{-}] [H^+]}{1 + K_7 [SO_4^{2-}] [HSO_4^{-}]} \right\}^{-1}$$
(16)

(Table 4 and Fig. 2). Hence $PdCl^+$ is considered as the active species of palladium(II) in acid medium. In the same way, $PdCl^+$ is considered as the active species of palladium(II) in aqueous alkaline medium, since $PdCl^+$ species parallel the rate [32]. In both cases, the role of the medium is not very significant compared to the complexation of the ligand, chloride ion, with palladium. The mechanism of Scheme 1 will therefore involve the species shown in Scheme 2.

The probable structure of the complex (C_2) is as follows:



Therefore in terms of the active species, rate law (8) takes the following form:

The reaction is accelerated in media of low polarity, which can be qualitatively explained by the involvement of oppositely charged ions, as in Scheme 1. However, the decrease in rate with increase in ionic strength is not easy to interpret. This might be due to the presence of various ionic reactions. The negative value of $\Delta S^{\#}$ (-126 ± 10 J K⁻¹ mol⁻¹) suggests that the two ionic species combine in a rate determining step to give one intermediate complex which is more ordered than the reactants [33]. The negative value of $\Delta S^{\#}$ might be due to changes in vibrational frequencies and internal rotations of the reactants and complex [34]. The observed modest entropy of activation and higher rate constant of the slow step indicate that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by the results of earlier work [35–37].

3.9. Autocatalysis

Autocatalysis by one of the products, chromium(III), is interesting. The apparent order of significantly less than

$$Rate = \frac{k_1 K_5 K_6 [HCrO_4^{-}] [Hg_2(SO_4) HSO_4]^{-} [PdCl^+] [H^+]}{1 + K_5 [H^+] + K_6 [Hg_2(SO_4) HSO_4]^{-} + K_5 K_6 [Hg_2(SO_4) HSO_4]^{-} [H^+]}$$



unity (0.73) in [Cr(III)], when [Cr(III)] is initially present, may be attributed to the weak complex formation between the product chromium(III) and oxidant, since chromium(III) is well known as a good complexing agent [38]. This is followed by the interaction of the weak complex with the reductant as in Scheme 3. The steps shown in Scheme 1 will form part of Scheme 1.

Evidence for the weak complex (C₃) was obtained by comparing UV–Vis spectra of chromium(III) with the mixture of QDC and chromium(III). There is a hypsochromic shift of chromium(III) from 584 to 580 nm, nearly 4 nm in the spectra of chromium(III) and the mixture of QDC and chromium(III). However, weak complex formation between chromium(III) and palladium(II) is disregarded due to our experimental rate law and lack of spectral evidence. Indeed such weak complex formation between QDC and chromium(III) has been observed in the literature [39–41].

Thus, when chromium(III) is initially present, a composite scheme involving all the steps of Schemes 1 and 3 operates and the rate law is given by the sum of the catalysed and autocatalysed rates.

$$Rate_{(gross)} = Rate_{(cat)} + Rate_{(autocat)}$$
(17)

Thus, the rate law for the autocatalytic path can be obtained as:

$$Rate_{(autocat)} = Rate_{(gross)} - Rate_{(cat)}$$
$$= \frac{k_2 K_8 [QDC] [Hg(I)] [Cr(III)]}{1 + K_8 [Cr(III)] + K_8 [QDC] + K_8^2 [QDC] [Cr(III)]}$$
(18)

Eq. (18) can be rewritten as:



Fig. 7. Verification of rate law (19) in the form (20) (conditions as in Table 2).

Scheme 3. The k_2 and K_8 values found from the intercepts and slope of such a plot were $(2.44 \pm 0.12) \times 10^2$ dm³ mol⁻¹ s⁻¹ and $(1.10 \pm 0.04) \times 10^3$ dm³ mol⁻¹, respectively. Using these values, the experimental rates for the added [Cr(III)] at constant concentrations of QDC and mercury(I) can be regenerated (Table 2).

4. Conclusion

The reaction between mercury(I) and QDC is very slow in sulfuric acid. Palladium(II) is known to catalyse the reaction with a measurable velocity at 10^{-6} mol dm⁻³, especially in a sulfuric acid medium; which is not the case in perchloric acid and nitric acid media. The active species involved in the mechanism play an important role in the

$$\frac{[\text{QDC}][\text{Hg}(\text{I})]}{\text{Rate}_{(\text{autocat})}} = \frac{1 + K_8[\text{Cr}(\text{III})] + K_8[\text{QDC}] + K_8^2[\text{QDC}][\text{Cr}(\text{III})]}{k_2 K_8[\text{Cr}(\text{III})]} = \frac{1}{k_2 K_8[\text{Cr}(\text{III})]} + \frac{1}{k_2} + \frac{[\text{QDC}]}{k_2[\text{Cr}(\text{III})]} + \frac{K_8[\text{QDC}]}{k_2}$$
(19)

Thus, Eq. (19) can be rearranged to the form (20) which is suitable for verification.

$$\frac{[\text{QDC}][\text{Hg}(\text{I})]}{\text{Rate}_{(\text{autocat})}} = \frac{1}{k_2[\text{Cr}(\text{III})]} \left\{ \frac{1}{K_8} + [\text{QDC}] \right\} + \frac{1}{k_2} \{1 + K_8[\text{QDC}]\}$$
(20)

At constant concentrations of oxidant and reductant, a plot of LHS versus 1/[Cr(III)] of Eq. (20) should be linear and this was found to be so (Fig. 7; $r \ge 0.999$, $\sigma \le 0.021$). Indeed it is to be noted that the plot shows an intercept which is in agreement with the complex formation, as in

reaction. It is interesting to note that autocatalysis has taken place in the catalysed reaction, making a composite reaction scheme and rate law. The overall mechanistic sequence described here is consistent with the product, mechanistic and kinetic studies.

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