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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.

Keywords: Oxidation; Mercury(I); Quinoliniumdichromate; Palladium(II); Catalysis; Autocatalysis

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 QDC 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^{-3} 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 ± 10 dm^3 mol^{-1} 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 ±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].

$$\mathrm{QDC} + 3\mathrm{Hg(I)} \overset{\mathrm{Pd(II)}}{\rightarrow} \mathrm{Cr(III)} + 3\mathrm{Hg(II)} \qquad (1)$$

3.2. Order of reaction

The reaction order was found from log–log plots of initial rates versus concentrations at constant ionic strength, $I = 1.60$ mol dm^{-3} and at constant sulfuric acid concentration (0.50 mol dm^{-3}). At constant palladium(II) concentration, 8.0×10^{-6} mol dm^{-3}, the order with respect to QDC in the concentration range 5.0×10^{-5}–5.0×10^{-4} mol dm^{-3} was found to be unity. The order with respect to mercury(I), between 5.0×10^{-5} and 6.0×10^{-4} mol dm^{-3} was less than unity, ca. 0.42 (Table 1). At constant reactant concentrations (3[QDC] = [Hg(I)] = 6.0×10^{-4} mol dm^{-3}), constant acidity and ionic strength ($[H_2SO_4] = 0.50$ mol dm^{-3} and $I = 1.60$ mol dm^{-3}), the palladium(II) concentration was varied between 1.0×10^{-6} and 1.0×10^{-5} mol 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 5.0×10^{-5}–5.0×10^{-4} and 1.0×10^{-4}–5.0×10^{-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 $(\mathrm{rate})_{\mathrm{calc}}$ for chromium(III) variations (Fig. 1, inset). However, in the case of the palladium(II)