Palladium(II) Catalysed Oxidation of Tiemonium methylsulphate (TMS),by alkaline Diperiodatonickelate(IV)

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Abstract:

The kinetic runs of palladium(II) catalysed oxidation of Tiemonium methylsulphate (TMS),by Diperiodatonickelate(IV) (DPN) in aqueous alkaline medium were followed at different initial concentration of oxidant, substrate, catalyst and alkali in turn keeping all other concentrations constant. The reaction orders were determined from the slopes of log k_{obs} versus log concentration plots. The reaction is of first order with respect to [DPN]and of fractional order in substrate, [TMS]. The catalyst, palladium(II), was varied in the concentration range of 5.0 x 10^{-7} to 5.0 x 10^{-6} mol dm^{-3} at 25 ºC keeping all other [reactants] constant . The order in [Palladium(II)] was found to be unity. periodate has retarding effect on the rate of reaction. The rate of reaction increases with increase in alkali concentration. However, increasing ionic strength and decreasing dielectric constant of the medium increases the rate.

Key worlds: Diperiodatonickelate(IV), Tiemonium methylsulphate, Palladium(II) Oxidation, Kinetics

Studies of oxidation using nickel(IV) complexes as oxidants in the form of nickel(IV) oxime and nickel(IV) periodates[1-4] (DPN) are scanty and limited to a few cases. Reduction of nickel(IV) complexes has received considerable attention, in order to understand the nature of intermediate oxidation states of nickel such as nickel(III). Indeed, stable nickel(III) complexes are known[5]. The use of nickel(IV) periodate complex are limited by the fact that its solubility in aqueous medium is very low. Mechanistically oxidation with nickel(IV) are expected to involve the possibility of intervention of nickel(III) and this is not expected in case of complementary two equivalent reaction. Again multiple equilibria involving different nickel(IV) periodate complexes prevail in an alkaline solution[3] and it needs to know the active form of oxidant in the reaction.

Tiemonium methylsulphate (TMS), 4-[3-Hydroxy-3-phenyl-3-(2-thienyl) propyl]-4-methyl-morpholinium methyl sulphate is a colourless, crystalline, water soluble drug. It is used as antispasmodic, as antimuscarinic in the relief of visceral spasms with peripheral effects similar to those of atropine[5]. Some methods have been reported for the determination of TMS[6,7].However different kinetic observations were found in the title reaction. Hence, the present study of the title reaction was undertaken to investigate the redox chemistry of diperiodatonickelate(IV) in such media and to arrive at a plausible mechanism.

Palladium (II) acts as a catalyst in the oxidation of many reactions.[8] Most studies using palladium(II) as a catalyst have employed it in the form palladium(II) chloride[9] and the nature of its active form in such reactions remains obscure. Hence the effect of chloride on the reaction was studied in order to establish the active species of the catalyst. but very few

studies are available in alkaline medium[10]. Palladium(II) catalysis in redox reactions involve different degree of complexity, due to the formation of different intermediate complexes, free radicals and to different oxidation states of palladium. The oxidation of Tiemonium methylsulphate (TMS),by alkaline permanganate[11] then in presence of osmium(VIII) catalyst[12] and by alkaline diperiodatonickelate(IV)[13] have been studied earlier. The main oxidation products in all the cases were identified as aldehyde, further to know the changes in products and the scheme of the reaction this reaction has been studied.

The literature survey reveals that there are no reports on mechanistic studies of palladium(II) catalysed oxidation of Tiemonium methylsulphate (TMS),by alkaline diperiodatonickelate(IV). Thus in order to explore the mechanism of oxidation and to know the active species of palladium(II) and diperiodatonickelate(IV) in strongly alkaline medium the detail kinetic study of the title reaction is undertaken.

RESULTS AND DISCUISSION

3.1. *Stoichiometry and product analysis*

Different sets of reaction mixtures containing different amounts of reactants at constant alkalinity and ionic strength were allowed to react for 24 hours in an inert atmosphere, where, [Ni(IV)] > [TMS]. The remaining [DPN] was assayed spectrophotometrically by measuring the absorbance at 410 nm. The nickel(II) was analysed as the dimethylglyoxime by gravimetrically[17]. The results showed that two moles of Ni(IV) consumes one mole of Tiemonium methylsulphate (TMS),in accordance of the equation (1) Table: 3.1 (p.49). The main reaction products were identified as aldehyde[32] (α-formyl acetamide) by spot test, ammonia[18] by Nessler's reagent and Nickel(II) by its visible spectrum. CO_2 was qualitatively detected by bubbling N_2 gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water[19]. The quantitative estimation of aldehyde by 2,4-DNP derivative[20], yielded nearly 75%. The nature of the aldehyde, was confirmed by its IR spectrum[21] which showed a carbonyl stretching at 1729 cm^{-1} and a band at 2928 cm^{-1} due to aldehydic stretching thus confirming the presence of (α-formyl acetamide). It was further observed that the aldehyde does not under go further oxidation under the present experimental conditions. Test for corresponding acid was negative.

$$C_{19}H_{27}NO_6S_2 + 2Ni(IV) + 2OH^- \longrightarrow C_{19}H_{27}NO_7S_2 + Ni(II) + NH_3 + CO_2 + H_2 \quad (1)$$

Reaction Order

The kinetic runs of palladium(II) catalysed oxidation of Tiemonium methylsulphate (TMS),by Diperiodatonickelate(IV) in aqueous alkaline medium were followed at different initial concentration of oxidant, substrate, catalyst and alkali in turn keeping all other concentrations constant. The reaction orders were determined from the slopes of log k_{obs} versus log concentration plots.

Effect of [Diperiodatonickelate(IV)]

The oxidant, [diperiodatonickelate(IV)] was varied in the range of 2.0 x 10^{-5} to 2.0 x 10^{-4} mol dm^{-3} keeping all other conditions constant (Table: 3.2, Linearity of plots of log[DPN] versus

time indicates the order in [DPN] as unity Figure: 3.1 This was also confirmed by varying [DPN] which did not show any change in pseudofirst order rate constants, k_{obs}

Effect of [Tiemonium methylsulphate]

The substrate, Tiemonium methylsulphate, was varied in the concentration range of 5.0×10^{-4} to 5.0×10^{-3} mol dm^{-3} at 25 ºC keeping all other [reactants] constant Table: 3.3 The order in [TMS] was found to be less than unity. The plot of log k_{obs} verses log[TMS] reveals the order of less than unity figure 3.2

Effect of [Palladium(II)]

The catalyst, palladium(II), was varied in the concentration range of 5.0×10^{-7} to 5.0×10^{-6} mol dm^{-3} at 25 ºC keeping all other [reactants] constant Table: 3.4 The order in [Palladium(II)] was found to be unity. The plot of log k_{obs} verses log[Pd(II)] reveals the order as unity figure 3.3.

Effect of added periodate and Chloride

The reaction was studied by varying the periodate concentration in the range of 2.0×10^{-4} to 2.0×10^{-3} mol dm^{-3} keeping all other conditions constant (Table. 3.5). It was found that the periodate has retarding effect on the rate of reaction.

Although, the stock solution of palladium(II) contained chloride, for this series of runs a palladium(II) solution which did not contain Cl$^-$

was used. When the chloride content of the reaction mixture containing palladium(II) was increased, the rate of reaction also increased.

Effect of [alkali]

The effect of alkali on the reaction was studied at constant [DPN] [Pd(II)], and [TMS] keeping constant ionic strength of 1.50 mol dm^{-3} at 25 ºC. The rate constant increased with the increase in [OH$^-$] as given in Table: 3.6 and order was found to be less than unity from the slopes of log k_{obs}. verses log [OH$^-$] plots as shown in Figure 3.4

Effect of ionic strength

The effect of ionic strength was studied by varying the concentration of KNO$_3$ from 0.5 to 2.0 mol dm^{-3} at constant concentration of oxidant, reductant, catalyst and alkali. It was found that the rate constant decreases with increase in concentration of KNO$_3$ as given in Table 3.7. and the plot of log k_{obs} verses I$^{1/2}$ was linear with positive slope which is given in Fig.3.5.

Dielectric constant

The dielectric constant of (D) of the reaction medium was studied by varying the *t-butanol-water* (Baker sample) content in the reaction mixture.

Earlier the inertness of the *t-butanol* towards the oxidant in the reaction mixture had been confirmed. The rate constant increased with decrease in the dielectric constant of the medium, with the increase of *t-butanol* content from 1 to 5% (v/v), Table: 3.8 .The plot of log k_{obs} verses 1/D was linear with positive slop as shown in figure 3.6

Effect of initially added products

The initially added products such as Ni(II) in the form of Nickel sulphate, aldehyde and ammonia were studied by varying concentration of each product to ten times as shown in table. The results did not show any significant effect on the rate of the reaction Table: 3.9a, Table 3.9b and Table 3.9c.

Test for free radicals

To study the intervention of free radical in the reaction, the reaction mixture, to which a known amount of acrylonitrile scavenger had been added initially, was kept for 24 hours in an inert atmosphere. On diluting the reaction mixture with methanol white precipitate formed indicating the presence of free radical intervention in the reaction.

Effect of temperature

The effect of temperature was studied at 25, 30, 35 and 40 ºC at constant concentration of Diperiodatonickelate(IV) and ionic strength by varying [OH⁻]. The rate constants, k of the slow step of the mechanism. were calculated from the intercepts of plots of[Pd(II)] / k_{obs} versus 1/[OH⁻] Figure: 3.8. For different temperatures the data is subjected to least square analysis which is given in Table: 3.9 T_1. From the plot of log k versus 1/T Figure: 3.7, the energy of activation corresponding to these constants was evaluated and other activation parameters have calculated and are tabulated in Table:3.9

  The activation parameters for the reaction were studied by using linear regression analysis (also known as the method of least square). In generalized notation, the formula for the straight line is y = ax + b. the most tractable form of linear regression analysis assumed that values of the independent variables 'x' are known without error and that experimental error is manifested only in values of the dependent variable 'y'. Most sets of kinetic data approximate this situation, in as much as times of observations are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by common linear regression analysis is that which minimizes the sum of squires of deviations of the y variable from the line.

The slope 'a' and intercept 'b' parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different looking experiments. Most familiar are.

Slope: $a = \dfrac{n\Sigma xy - \Sigma x\Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$ Intercept : $b = \dfrac{\Sigma y\Sigma x^2 - \Sigma x\Sigma xy}{n\Sigma x^2 - (\Sigma x)^2}$

Where n is the no. of data point and the summation are for all data points in the set. These data were subjected to least squire analysis and are given in Table. 3.9 T_1. The activation parameters were evaluated from the plots of logk verses 1/T as shown in figure.

The activation energy of the reaction was calculated by,

$$Ea = -2.303 \times R \times Slope$$

The entropy of activation is calculated by

$$\frac{\Delta S^{\#}}{4.576} = logk - 10.753 - log\,T + \frac{Ea}{4.576\,T}$$

Where k is in sec^{-1}, temperature in absolute and Ea in calories.

    The enthalpy of activation is calculated by

$$\Delta H^{\#} = Ea - RT$$

And the free energy of activation was calculated by

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$