Kinetics of Transition Metal Ion Catalyzed Oxidation of Some Industrially Important Alcohols using Ammonium Metavanadate in Acidic Medium

By Harichandra A Parbat, D V Prabhu & Anna Pratima Nikalje

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2-Chloroethanol is used as a precursor for ethylene oxide and is useful in the manufacture of crop protection chemicals, and pharmaceuticals. 2-Butoxyethanol finds use in the making of paints, varnishes and industrial and household cleaners.

Keywords: alcohols, ammonium metavanadate, kinetics, ionic strength, thermodynamic activation parameters, the entropy of activation, transition metal ion catalysts, reaction mechanisms.

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Kinetics of Transition Metal Ion Catalyzed Oxidation of Some Industrially Important Alcohols using Ammonium Metavanadate in Acidic Medium

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Abstract- Oxidation of alcohols has industrial importance as it yields several useful products. Toxic and costly metal ions like Os(VIII), Cr(VI), and Ru in different oxidation states are widely used for the oxidation of a variety of organic compounds. We are reporting herein the oxidation of the industrially useful primary alcohols, 2-Chloroethanol, 2-Butoxyethanol and 2-Phenoxyethanol using Ammonium metavanadate in acidic medium. Relatively less toxic and cheaper transition metal ions of the first series are effectively used as homogeneous catalysts for the oxidation of the alcohols to the corresponding aldehydes.

2-Chloroethanol is used as a precursor for ethylene oxide and is useful in the manufacture of crop protection chemicals, and pharmaceuticals. 2-Butoxyethanol finds use in the making of paints, varnishes and industrial and household cleaners.

2-Phenoxyethanol serves as a perfume fixative. The oxidation is studied in the presence and absence of transition metal ions under first-order kinetic conditions concerning the inorganic oxidant. The dependence of the oxidation rate on alcohol and oxidant concentrations, ionic strength, and temperature is studied. The thermodynamic activation parameters of the oxidation reaction are evaluated from the variation of oxidation rate with temperature. The sequence of oxidation rates of the alcohols is explained based on their structural features.

Transition metal ions, Mn(II), Co(II), and Ni(II) are successfully used to catalyze the oxidation of alcohols, and the sequence of their catalytic efficiencies is determined for each substrate. A suitable reaction mechanism is suggested for the oxidation of the primary alcohols under study.

I. Introduction

The oxidation of alcohols to carbonyl compounds is extensively reported [1-5]. We have studied the kinetics of oxidation of a variety of alcohols and phenols using organic and inorganic oxidants [6-14]. This paper reports the oxidation of the primary alcohols, 2-Chloroethanol, 2-Butoxyethanol and 2-Phenoxyethanol by Ammonium metavanadate in acidic medium, using transition metal ions as catalysts.

The dependence of oxidation rate on alcohol and oxidant concentrations, ionic strength, and temperature is studied. The thermodynamic activation parameters of the oxidation reaction are evaluated from the variation of oxidation rate with temperature. The sequence of oxidation rates of the alcohols is explained based on their structural features.

Transition metal ions, Mn(II), Co(II), and Ni(II) are successfully used to catalyze the oxidation of alcohols, and the sequence of their catalytic efficiencies is determined for each substrate. A suitable reaction mechanism is suggested for the oxidation of the primary alcohols under study.

II. Materials and Methods

The alcohols were obtained from S H Kelkar & Co., Mumbai, and used after distillation. All other chemicals, solvents, and reagents were of Analytical Grade.

The oxidation of alcohol is studied under first-order kinetic conditions concerning the inorganic oxidant, ie [oxidant] << [alc.]. The progress of the reaction is monitored by arresting the reaction using ice and titrating the unreacted oxidant at regular time intervals against standard Na2S2O3 using starch as indicator. The first-order rate constants (k) are obtained from the slopes of the plots of log (unreacted oxidant) versus time. K2SO4 was used in the range µ = 0.05-0.25 mol dm−3 to find out the influence of ionic strength on oxidation rates of alcohol. The thermodynamic parameters are evaluated from the Arrhenius plots of log k versus T−1.
A similar procedure is adopted to study the catalytic impact of transition metal ions, Mn(II), Co(II) and Ni(II) on the oxidation of alcohols.

III. Results and Discussion

The primary alcohols, 2-Chloroethanol, 2-Butoxyethanol and 2-Phenoxyethanol are oxidized to the corresponding aldehydes in acidic medium. Their oxidation rates increased with [alc.] but decreased with increasing oxidant concentration (Table 1, Figure 1).

The oxidation rates follow the sequence:

2-Chloroethanol > 2-Butoxyethanol > 2-Phenoxyethanol (Table 1, Figure 1)

The Chlorine atom in 2-Chloroethanol facilitates the removal of hydrogen atoms making it most susceptible to oxidation.

The influence of ionic strength (µ) on the oxidation rates of alcohol is studied using K₂SO₄ in the range µ = 0.05 - 0.25 mol dm⁻³ at 313K (Table 2). The graphs of log k versus √µ are found to be straight lines parallel to the √µ axis, indicating that the rate of oxidation is independent of ionic strength due to the involvement of a nonionic species in the oxidation reaction (Figure 2).

The oxidation of alcohol is carried out in the temperature range 303-313K, and the thermodynamic activation parameters are determined from the Arrhenius plots of log k versus 1/T. The negative values of ΔS* indicate a decrease in entropy due to the formation of a short-lived activated complex, followed by the reorientation of solvent molecules around the activated complex [15, 16].

2-Chloroethanol Mn (II) > Ni(II) > Co(II) (Table 4a, Figure 3a)
2-Butoxyethanol Co(II) > Ni(II) > Mn(II) (Table 4b, Figure 3b)
2-Phenoxyethanol Co(II) > Ni(II) > Mn(II) (Table 4c, Figure 3b)

IV. Conclusions

1) The alcohols are oxidized as per the sequence, 2-Chloroethanol > 2-Butoxyethanol > 2-Phenoxyethanol.
2) The oxidation of alcohols is independent of ionic strength in dilute solution by the Bronsted – Bjerrum equation, log k = log k₀ + 1.02 ZAZB √µ.
3) There is a decrease in entropy of activation ΔS* during the oxidation of alcohols.
4) Transition metal ions, Mn(II), Co(II) and Ni(II) are effectively used to catalyze the oxidation of alcohols.

Transition metal ions are used to catalyze the oxidation of alcohol to aldehyde using Ammonium metavanadate in acidic medium. Mn(II), Co(II) and Ni(II) ions are used in the concentration range [M(II)] = 2.5 - 4.5 x 10⁻⁴ mol dm⁻³ at 303K. The rate constants of oxidation of alcohols are determined from the linear plots of log (unreacted oxidant) versus time. In each case, the rate (k) increased with [M(II)] (Tables 4a, 4b, and 4c, Figures 3a, 3b. and 3c).

The stability order for the complexes of the transition metal ions under study is expected to be Ni(II) > Co(II) > Mn(II) and hence the sequence of their catalytic efficiencies is expected to be Mn(II) > Co(II) > Ni(II) [17,18]. However, several discrepancies are observed and reported in literature [19,20]. In our study the sequences of catalytic efficiencies of transition metal ions are as follows:
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Table 1: Rate constant data for the oxidation of alcohols by Ammonium metavanadate In 0.1 M H₂SO₄ Temp.=303 K

| [alc.] x 10⁻¹ mol dm⁻³ | [NH₄VO₃] x 10⁻³ mol dm⁻³ | 2-Chloroethanol k x 10⁻⁴ s⁻¹ | 2-Butoxyethanol | 2-Phenoxyethanol |
|-------------------------|--------------------------|-----------------------------|-----------------|-----------------|
| 0.25                    | 5.00                     | 14.80                       | 12.43           | 11.80           |
| 0.50                    | 5.00                     | 17.00                       | 14.11           | 13.80           |
| 0.63                    | 5.00                     | 18.42                       | 16.39           | 15.00           |
| 0.75                    | 5.00                     | 20.72                       | 17.04           | 16.60           |
| 0.88                    | 5.00                     | 27.63                       | 18.42           | 17.45           |
| 1.00                    | 5.00                     | 32.24                       | 21.41           | 21.25           |
| 1.00                    | 2.50                     | 34.54                       | 29.90           | 20.95           |
| 1.00                    | 5.00                     | 25.33                       | 23.03           | 16.58           |
| 1.00                    | 10.00                    | 21.18                       | 20.72           | 9.21            |
| 1.00                    | 15.00                    | 18.42                       | 16.12           | 8.24            |
| 1.00                    | 20.00                    | 11.52                       | 13.81           | 7.44            |
| 1.00                    | 25.00                    | 9.90                        | 12.60           | 5.76            |

Table 2: Effect of Ionic strength on the oxidation rates of alcohols by Ammonium metavanadate in 0.1M H₂SO₄. [alc.] = 0.1M, [NH₄VO₃] = 2.5 x 10⁻³M, Temp.=313 K

| µ mol dm⁻³ | √µ | 2-Chloroethanol k x 10⁻⁴ s⁻¹ | 2-Butoxyethanol | 2-Phenoxyethanol |
|------------|----|-----------------------------|-----------------|-----------------|
| 0.00       | 0.00| 6.82                        | 4.54            | 2.24            |
| 0.05       | 0.22| 6.72                        | 4.27            | 2.28            |
| 0.10       | 0.32| 6.64                        | 4.64            | 2.31            |
| 0.15       | 0.39| 6.53                        | 4.50            | 2.21            |
| 0.20       | 0.45| 6.50                        | 4.07            | 2.39            |
| 0.25       | 0.50| 6.58                        | 5.00            | 2.35            |
Table 3: Thermodynamic activation parameters of the oxidation of alcohols by Ammonium metavanadate in 0.1M H$_2$SO$_4$

| Temp.(K) | k x 10$^4$ s$^{-1}$ | E (kJ mol$^{-1}$) | K* x 10$^{16}$ | ∆G* (kJ mol$^{-1}$) | ∆H* (kJ mol$^{-1}$) | ∆S* (kJ K$^{-1}$ mol$^{-1}$) |
|----------|---------------------|-----------------|----------------|-------------------|-------------------|-------------------|
| 2-Chloroethanol |
| 303      | 18.42               | 14.24           | 2.92           | 90.13             | 11.72             | -0.2588           |
| 308      | 20.58               | 14.24           | 3.21           | 91.37             | 11.68             | -0.2587           |
| 313      | 27.95               | 14.24           | 4.29           | 92.10             | 11.64             | -0.2571           |
| 2-Butoxyethanol |
| 303      | 16.12               | 6.23            | 2.55           | 90.46             | 3.71              | -0.2863           |
| 308      | 17.27               | 6.23            | 2.69           | 91.82             | 3.67              | -0.2862           |
| 313      | 19.34               | 6.23            | 2.97           | 93.06             | 3.62              | -0.2857           |
| 2-Phenoxyethanol |
| 303      | 8.24                | 18.08           | 1.31           | 92.15             | 15.56             | -0.2528           |
| 308      | 12.34               | 18.08           | 1.92           | 92.68             | 15.52             | -0.2505           |
| 313      | 13.95               | 18.08           | 2.14           | 93.91             | 15.48             | -0.2506           |

Table 4: Catalytic effect of transition metal ions on the oxidation of alcohols by Ammonium metavanadate in 0.1M H$_2$SO$_4$ [alc.]=0.1M, [NH$_4$VO$_3$] = 2.5 x 10$^{-3}$M, Temp. = 303K

| [M(II)] x 10$^4$ mol dm$^{-3}$ | k x 10$^4$ s$^{-1}$ |
|--------------------------------|---------------------|
|                                | Mn(II) | Co(II) | Ni(II) |
| Table 4a. 2-Chloroethanol      |
| 0.00                           | 4.84    | 4.84   | 4.84   |
| 2.50                           | 16.09   | 7.84   | 9.95   |
| 3.50                           | 22.22   | 8.24   | 11.75  |
| 4.50                           | 27.18   | 9.21   | 14.11  |
| Table 4b. 2-Butoxyethanol      |
| 0.00                           | 3.93    | 3.93   | 3.93   |
| 2.50                           | 6.63    | 14.96  | 9.90   |
| 3.50                           | 7.46    | 16.74  | 13.35  |
| 4.50                           | 11.67   | 18.42  | 16.35  |
| Table 4c. 2-Phenoxyethanol     |
| 0.00                           | 4.34    | 4.34   | 4.34   |
| 2.50                           | 5.76    | 8.70   | 6.91   |
| 3.50                           | 8.61    | 14.73  | 9.30   |
| 4.50                           | 9.21    | 16.42  | 18.65  |
Fig. 1: Variation of rate constant of oxidation of alcohols by Ammonium metavanadate in acidic medium with [alc.]

Fig. 2: Effect of ionic strength on the rate constant of oxidation of alcohols by Ammonium metavanadate in acidic medium
**Fig. 3a:** Variation of rate constant of transition metal ion catalyzed oxidation of 2-Chloroethanol with [M(II)] Sequence of catalytic efficiencies: Mn(II) > Ni(II) > Co(II)

**Fig. 3b:** Variation of rate constant of transition metal ion catalyzed oxidation of 2-Butoxyethanol with [M(II)] Sequence of catalytic efficiencies: Co(II) > Ni(II) > Mn(II)
Fig. 3c: Variation of rate constant of transition metal ion catalyzed oxidation of 2-Phenoxyethanol with [M(II)]
Sequence of catalytic efficiencies: Co(II) > Ni(II) > Mn(II)
