Int. J. Chem. Sci.: 12(1), 2014, 145-154
ISSN 0972-768X
www.sadgurupublications.com

KINETICS AND MECHANISM OF KEGGIN TYPE 12-TUNGSTOCOBALTATE (II) CATALYZED POTASSIUM IODIDE OXIDATION BY PERBORATE

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ABSTRACT

The oxidation of potassium iodide by perborate catalyzed by Keggin type $[Co(II)W_{12}O_{40}]^{6-}$ has been studied in sulphuric acid medium. The reaction proceeds by the oxidation of $[Co(II)W_{12}O_{40}]^{6-}$ to $[Co(III)W_{12}O_{40}]^{5-}$ by hydrogen peroxide, generated by the decomposition of perborate, which then oxidizes potassium iodide in a rate determining step. The reaction was found to be independent of $[H^+]$. Decreasing the relative permittivity of the medium increases the rate of the reaction, which is attributed to the formation of an outer-sphere complex between the catalyst and active oxidant. The activation parameters were also determined and the values support the proposed mechanism.

Key words: Kinetics, Mechanism, Potassium iodide, 12-tungtocobaltate (II), Perborate

INTRODUCTION

Transition metal substituted heteropolyoxometalates[1] are very good candidates for homogeneous outer-sphere electron transfer processes. They exhibit different chemical and electrochemical properties, which makes them attractive for catalytic[1-3] and electrocatalytic[4] applications.

Sodium perborate is widely used industrial chemical, mainly as a bleaching agent[5] with the empirical formula $NaBO_3.xH_2O$. It is also a very convenient source of hydrogen peroxide in solution and is less expensive, solid, and easily handled mild oxidizing agent which has been used for various organic functional group transformations[5]. The rates of oxidations by perborate are generally slow at normal temperatures thus requiring the presence of catalysts. Utilization of the polyoxometalates, as redox catalysts, in perborate oxidations may involve an outer-sphere path way without formation of a peroxo-metal

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intermediate. Therefore, in continuation of our earlier work[3] on the catalysis by polyoxometalates herein we report the 12-tungstocobaltate catalyzed oxidation of potassium iodide by perborate.

EXPERIMENTAL

Kinetic procedure

Reagent grade chemicals and doubly distilled H_2O were used throughout. The cobalt complexes $[Co(III)W_{12}O_{40}]^{5-}$ and $[Co(II)W_{12}O_{40}]^{6-}$ were prepared by literature method[6,7] and standardized spectrophotometrically[8] (at 388 nm for $[Co(III)W_{12}O_{40}]^{5-}$ and at 624 nm for $[Co(II)W_{12}O_{40}]^{6-}$, respectively) using an Elico SL 159 UV-vis spectrophotometer. The solutions of perborate (Lancaster) were freshly prepared and standardized iodometrically. The ionic strength was maintained using $NaClO_4$ and in order to vary hydrogen ion concentration, H_2SO_4 (BDH) was used. The solutions of potassium iodide (BDH) were prepared by dissolving calculated quantities of it in double distilled water. The stock solution was diluted to the required concentration and then used.

The reactions were studied under psuedo-first-order conditions by keeping large excess of potassium iodide over perborate and measuring the absorbance at 460 nm. The pseudo-first-order rate constants were calculated graphically by plotting log $(A_\infty - A_t)$ against time in case of both uncatalysed (k_u) and catalyzed (k_c) reactions. The absorbance at 460 nm at time 't' was A_t and A_∞ was measured after completion of the reaction. Thus the total rate constant (k_T) is equal to the sum of rate constant of the catalyzed (k_c) and uncatalyzed (k_u) reactions. The values of k_c were used to analyze the kinetic aspect of catalyzed path of the reaction. The rate constants were reproducible to within ± 4 %.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry for the reaction between perborate and potassium iodide in the presence of 2.0×10^{-5} mol dm^{-3} $[Co(II)W_{12}O_{40}]^{6-}$ was studied by keeping the concentration of perborate constant at 4.0×10^{-3} mol dm^{-3} and varying the potassium iodide concentration from 2.0×10^{-4} to 8.0×10^{-4} mol dm^{-3} in 1.0×10^{-2} mol dm^{-3} sulphuric acid. The reactants were mixed and the concentration of perborate was determined by titrating against standard sodium thiosulphate solution after 5 hrs. The stoichiometry was found to be 2 moles of potassium iodide per mole of perborate.

Effect of variation of reactant concentrations

The uncatalyzed oxidation of potassium iodide by perborate occurs with measurable rate under the experimental conditions. Therefore both catalyzed and uncatalyzed reactions were followed to calculate the overall rate constant of the reactions. The catalyzed reaction is understood to occur in parallel paths with contribution from both catalyzed and uncatalyzed paths. Thus the total rate constant (k_T) is equal to the sum of rate constant of the catalyzed (k_c) and uncatalyzed (k_u) reactions. So $k_C = k_T - k_U$. The effect of potassium iodide was studied between 1.0 x 10^{-3} to 10.0 x 10^{-3} mol dm^{-3} keeping concentration of perborate constant at 5.0 x 10^{-4} mol dm^{-3}, catalyst concentration constant at 2.0 x 10^{-5} mol dm^{-3} in 1.0 x 10^{-2} mol dm^{-3} sulphuric acid. The order with respect to iodide ion concentration was found to be unity as evidenced by constancy of the pseudo first-order rate constants of both uncatalyzed and catalyzed reactions. The effect of perborate concentration on the reaction was studied between 1.0 x 10^{-4} to 1.0 x 10^{-3} mol dm^{-3} by keeping the concentration of potassium iodide and sulphuric acid constant at 5.0 x 10^{-3} mol dm^{-3} and 1.0 x 10^{-2} mol dm^{-3}, respectively. In case of catalyzed reaction a constant amount of 12-tungstocobaltate (II) at 2.0 x 10^{-5} mol dm^{-3} was maintained. The pseudo-first-order rate constants increase with increase in [Perborate] in case of both uncatalyzed and catalyzed reactions indicating a positive order in [Perborate].

Table 1: Effect of reactant and catalyst concentration [H_2SO_4] = 1.0 x 10^{-2} mol dm^{-3}, Temp. = 298 K

10^3[KI] mol dm^{-3}	10^4[Perborate] mol dm^{-3}	10^5 $[Co^{II}W_{12}O_{40}]^{6-}$ mol dm^{-3}	10^3 k_{uncat} sec^{-1}	10^3k_T sec^{-1}	10^3k_{cat} sec^{-1}
1.0	5.0	2.0	0.23	1.73	1.50
3.0	5.0	2.0	0.24	1.75	1.51
5.0	5.0	2.0	0.26	1.76	1.50
7.0	5.0	2.0	0.24	1.76	1.52
10.0	5.0	2.0	0.24	1.76	1.52
5.0	1.0	2.0	0.043	0.59	0.447
5.0	3.0	2.0	0.11	1.0	0.89
5.0	5.0	2.0	0.26	1.76	1.50
5.0	7.0	2.0	0.32	2.32	1.98

Cont…

10^3[KI] mol dm^{-3}	10^4[Perborate] mol dm^{-3}	10^5 $[Co^{II}W_{12}O_{40}]^{6-}$ mol dm^{-3}	10^3 k_{uncat} sec^{-1}	10^3k_T sec^{-1}	10^3k_{cat} sec^{-1}
5.0	10.0	2.0	0.38	3.8	3.42
5.0	5.0	0.4	0.26	0.575	0.32
5.0	5.0	1.0	0.26	0.96	0.7
5.0	5.0	2.0	0.26	1.76	1.5
5.0	5.0	3.0	0.26	2.149	1.89
5.0	5.0	4.0	0.26	2.686	2.43

Effect of catalyst

The effect of catalyst was studied by varying catalyst concentration between 0.4 x 10^{-5} to 4.0 x 10^{-5} mol dm^{-3} keeping constant concentrations of potassium iodide (5.0 x 10^{-3} mol dm^{-3}), perborate (5.0 x 10^{-4} mol dm^{-3}) and sulphuric acid (1.0 x 10^{-2} mol dm^{-3}) at constant ionic strength of 0.01 mol dm^{-3}. The plot of k_T against concentration of catalyst is found to be linear without any intercept indicating the order in [catalyst] is also unity.

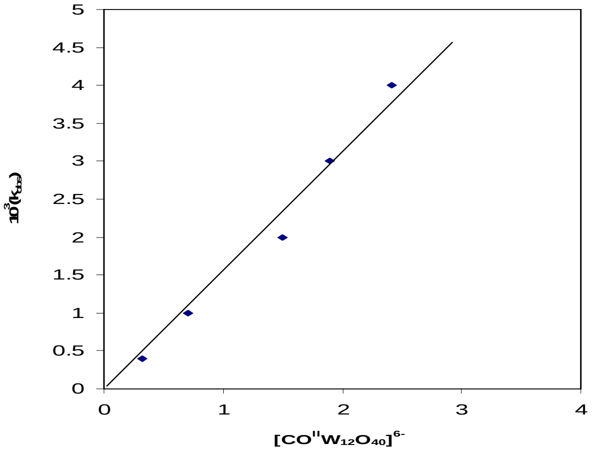

Fig. 1: Effect of catalyst variation plot of k_T against catalyst concentration (Conditions as in table 2)

Effect of hydrogen and sulphate ions

The effect of hydrogen and sulphate ions was carried out, in order to understand the nature of reactant species present the solution. The concentrations of $[H^+]$ and $[SO_4^{2-}]$ were varied between 0.007 to 0.07 mol dm^{-3}, keeping $[SO_4^{2-}]$ and $[H^+]$ constant at 0.01 mol dm^{-3} each, respectively. To vary the concentration of $[H^+]$ and $[SO_4^{2-}]$, sodium sulphate and perchloric acid were used, respectively. The kinetic data indicate that in case of both uncatalyzed and catalyzed reactions there is no change in the values of pseudo-first-order rate constants as $[H^+]$ and $[SO_4^{2-}]$ are varied. Therefore, the reaction is independent of the $[H^+]$ and $[SO_4^{2-}]$.

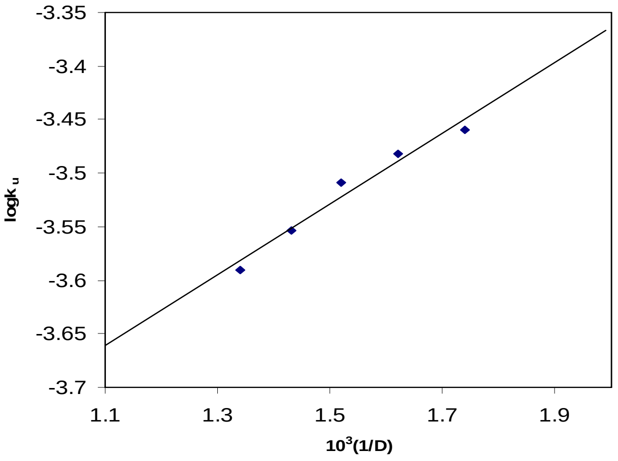

Fig. 2: Plot of log k_u against 1/D (Conditions as in Table 2)

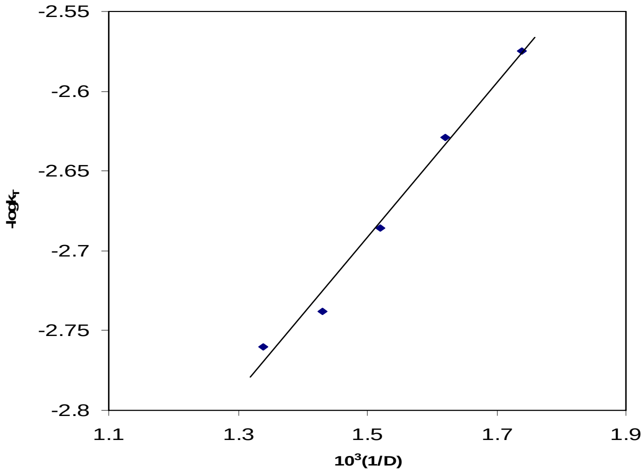

Fig. 3: Plot of log k_T against 1/D (Conditions as in Table 2)

Effect of ionic strength and solvent polarity

The effect of ionic strength on the reaction was studied by varying the concentration of sodium perchlorate (0.1 to 0.5 mol dm^{-3}) keeping potassium iodide, perborate and catalyst, $[Co(II)W_{12}O_{40}]^{6-}$, concentrations constants at 5.0 x 10^{-3} mol dm^{-3}, 5.0 x 10^{-4} mol dm^{-3} and 2.0 x 10^{-5} mol dm^{-3} in 0.01 mol dm^{-3} sulphuric acid, respectively. There was no effect of ionic strength on the reaction. The effect of solvent polarity on the reaction was studied by varying the percentage of acetonitrile from 0 to 50% v/v keeping potassium iodide, perborate and catalyst, $[Co(II)W_{12}O_{40}]^{6-}$, concentrations constants at 5.0 x 10^{-3} mol dm^{-3}, 5.0 x 10^{-4} mol dm^{-3} and 2.0 x 10^{-5} mol dm^{-3} in 0.01 mol dm^{-3} sulphuric acid, respectively. The relative permittivities of the reaction mixture were computed from the values of pure solvents. The plot of log k_{obs} against 1/D is shows that the decrease in the dielectric constant increases the rate of the reaction.

Table 2: Effect of solvent polarity on the reaction at 298K. [KI] = 5.0 x 10^{-3} mol dm^{-3} [Perborate] = 5.0 x 10^{-4} mol dm^{-3}, $[Co^{II}W_{12}O_{40}]^{6-}$ = 2.0 x 10^{-5} mol dm^{-3}, $[H_2SO_4]$ = 1.0 x 10^{-2} mol dm^{-3}

% of Acetontrile	10^3 k_u sec^{-1}	10^3 k_T sec^{-1}	10^3 k_c sec^{-1}
10	0.26	1.72	1.46
20	0.29	1.83	1.54
30	0.31	2.06	1.75
40	0.33	2.35	2.02
50	0.35	2.66	2.31

Effect of temperature

The effect of temperature on reaction was studied by measuring pseudo-first-order rate constants at 288, 293, 298 and 303 K by keeping the concentrations of potassium iodide, perborate and catalyst, $[Co(II)W_{12}O_{40}]^{6-}$, concentrations constants at 5.0 x 10^{-3} mol dm^{-3}, 5.0 x 10^{-4} mol dm^{-3} and 2.0 x 10^{-5} mol dm^{-3} in 0.01 mol dm^{-3} sulphuric acid, respectively.

Kinetics and mechanism of oxidation of iodide ion by perborate has been studied by Karunakaran and others[9]. They have studied catalysis of the reaction by zirconium(IV)[10], molybdenum(VI)[11], tungsten(VI)[12], iron(III)[13] and vanadium(V)[14]. The general mechanism proposed for the catalyzed oxidation of iodide ion by perborate involves formation of metal-peroxo species, which then effects the oxidation of iodide ion. The reactions were also found to be independent on the acid concentration except in case of vanadium(V) catalysis. Vanadium(V) catalyzes the perborate oxidation of iodide ion with negative order in acid concentration. The mechanism also involves prior formation of two peroxo-vanadium species thus making the order with respect to oxidant, perborate, more than unity. The inhibition of the reaction by acidity was explained due to formation of second peroxo-vanadium species.

The metal ion catalysis of perborate oxidation of iodide ion proceeds with prior interaction of the catalyst and hydrogen peroxide generated in solution by the decomposition of perborate in solution. The interaction leads to formation of metal-peroxo[9-14] reactive species of the reaction. The mechanism in all the cases (except vanadium catalysis) proposed to be of acidity independent as no probable protonation equilibria were involved. The inhibition by acidity was observed in case of vanadium(V) catalysis due to involvement of deprotonation step during formation of second vanadium(V)-peroxo species.

Table 3: Variation of rate constants with temperature and activation parameters (Conditions as in Table 2)

Temperature	**10^3 k_T sec^{-1}**	**10^3 k_u sec^{-1}**	**10^3 k_c sec^{-1}**
288	0.39	0.03	0.36
293	0.88	0.12	0.76
298	1.76	0.26	1.50
303	2.22	0.36	1.86

Activation parameters	**E_a KJmol^{-1}**	**$\Delta H^{\neq}$ KJmol^{-1}**	**$\Delta S^{\neq}$ JK^{-1}mol^{-1}**	**$\Delta G^{\neq}$ KJmol^{-1}**
Values for catalyzed reactions	76.59	68.93	-49.62	83.72

The results of the study show that the order with respect to oxidant is unity each in case of both uncatalyzed and 12-tungstocobaltate(II) catalyzed reactions as the pseudo-first-order rate constants were linear. The order with respect to iodide ion was also found to be unity as the k_u and k_c values remain unchanged even after changing concentration of iodide ion by tenfold at constant concentration of all other constituents. The plots k_c of against concentration of catalyst was also found to be linear indicating an order of unity in concentration of catalyst. The reaction is independent of hydrogen ion concentration, sulphate ion concentration and as well as ionic strength in case of both uncatalyzed and catalyzed reaction.

The mechanism of uncatalyzed reaction, as the kinetic results obtained, suggest, is occurring through the interaction of oxidant and iodide ion in a rate determining step. Since neither of hydrogen peroxide or iodide are known to be involved any protonation equilibria, there is no possibility of its dependence on the hydrogen ion concentration. One of the reactant, hydrogen peroxide, is neutral therefore the ionic strength also did not affect the reaction. The mechanism of uncatalyzed reaction can now be represented by **Scheme 1** in accordance with the results obtained.

$$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$$

$$IO^- + I^- + 2\,H^+ \xrightarrow{\text{Fast}} I_2 + H_2O$$

Scheme 1

The corresponding rate law would be a simple second order rate law as given by Equation 1. Since the reaction is studied under

$$\text{Rate} = k_1\,[H_2O_2]\,[I^-] \qquad \ldots(1)$$

pseudo-first-order conditions Equation (1) can be written as Equation (2) with $k_1' = k_1\,[I^-]$.

$$\text{Rate} = k_1'\,[H_2O_2] \qquad \ldots(2)$$

The pseudo-first-order rate constant k_u is now given by Equation (3).

$$K_u = \frac{\text{Rate}}{[H_2O_2]} = k'_1 = k_u = k_1\,[I^-] \qquad \ldots(3)$$

The catalyzed path of the reaction would differ by the first step of the **Scheme 1**, which has to be replaced by the step involving the catalyst and oxidant. The catalyst, 12-tungstocobaltate(II), is an outer-sphere reagent therefore formation of an intermediate peroxo species is less probable. The probable way of their interaction would be a redox step in which 12-tungstocobaltate(II) would be oxidized to its higher oxidation state 12-tungstocobaltate(III) in a prior equilibrium. In the next rate determining step the oxidized form of catalyst reacts with iodide and regenerating the catalyst. The catalyzed mechanism can now be represented as in **Scheme 2**.

$$[\mathrm{Co(II)W_{12}O_{40}}]^{6-} + [\mathrm{H_2O_2}] \xrightleftharpoons{k_1} [\mathrm{Co(III)W_{12}O_{40}}]^{5-} + \mathrm{OH}^- + {}^{\bullet}\mathrm{OH}$$

$$[\mathrm{Co(III)W_{12}O_{40}}]^{5-} + \mathrm{I}^- \xrightarrow{k_2} [\mathrm{Co(II)W_{12}O_{40}}]^{6-} + \mathrm{I}$$

$$\mathrm{H}^+ + {}^{\bullet}\mathrm{OH} + \mathrm{I}^- \longrightarrow \mathrm{H_2O} + \mathrm{I}$$

$$2\mathrm{I} \longrightarrow \mathrm{I_2}$$

$$\mathrm{OH}^- + \mathrm{H}^+ \longrightarrow \mathrm{H_2O}$$

Scheme 2

According to Scheme 2, the rate of reaction is given by Equation (4)

$$\text{Rate} = k_2\,[\mathrm{Co(III)W_{12}O_{40}}]^{5-}\,[\mathrm{I}^-] \qquad \ldots(4)$$

and considering the formation equilibria of first step of Scheme 2 as rapid, as the concentration of hydrogen peroxide is quite in large excess in comparison with that of the catalyst concentration as we get for $[\mathrm{CO^{III}W_{12}O_{40}}]^{5-}$ as,

$$[\mathrm{Co(III)W_{12}O_{40}}]^{5-} = K_1\,[\mathrm{H_2O_2}]\,[\mathrm{Co(II)W_{12}O_{40}}]^{6-} \qquad \ldots(5)$$

Substituting Equation (5) in Equation (4), we get Equation (6) for the rate of the catalyzed reaction.

$$\text{Rate} = K_1\,k'_2\,[\mathrm{Co(II)W_{12}O_{40}}]^{6-}\,[\mathrm{H_2O}]\,[\mathrm{I}^-] \qquad \ldots(6)$$

Since the reaction was carried out under pseudo-first-order conditions Equation (6) can be rearranged to get Equation (7).

$$\text{Rate} = K_1\,k_2'\,[\mathrm{Co(II)W_{12}O_{40}}]^{6-}\,[\mathrm{H_2O_2}] \qquad \ldots(7)$$

The pseudo-first-order rate constant of the catalyzed reaction, k_c, is given by Equation (8).

$$\frac{\text{Rate}}{[\mathrm{H_2O_2}]} = k_c = K_1\,k_2'\,[\mathrm{Co(II)W_{12}O_{40}}]^{6-} \qquad \ldots(8)$$

The overall rate constant, k_T, of the reaction which was determined experimentally can be obtained by combining Equation (8) and (3) to get Equation (9) for k_T.

$$k_T = k'_1 + K_1 k'_2\,[\mathrm{Co(II)W_{12}O_{40}}]^{6-} \qquad \ldots(9)$$

or

$$k_T = k_u + K_c \qquad \ldots(10)$$

The rate laws Eq. (3) and (9) for uncatalyzed and 12-tungstocobaltate(II) catalyzed reactions explain all the kinetic results obtained in the present study satisfactorily. The ionic strength did not affect the rate of reaction as one of the reactant in both the reactions is neutral species. The effect of solvent polarity[15] is also due to the interaction of a neutral molecule with a negative ion. The activation parameters were also determined for both uncatalyzed and catalyzed reactions. The activation energy for the uncatalyzed reaction is comparatively greater than that of catalyzed reaction because of availability of an alternate low energy path. The low entropy of activation in both the cases supports the outer-sphere path of the reaction without any rigid transition state formation.

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Accepted : 02.01.2014