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## **Kinetics and Mechanism of Oxidation of DMSO by Oxone Catalyzed by 12-tungstocobaltate(II)**

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### **ABSTRACT**

*The reaction between 12-tungstocobaltate(III) and dimethyl sulfoxide is reported to proceed with a very slow rate. In continuation of our interest in the polyoxometalate catalysis of oxidations, the present work of oxidation of dimethyl sulfoxide by Oxone in presence of 12-tungstocobaltate(II) was undertaken. The catalyst used in the present study acts as an outer-sphere reagent and the oxidant, Oxone, is the inner-sphere reagent.*

**Keywords:** *polyoxometalate, outer-sphere reagent, inner-sphere reagent.*

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### **INTRODUCTION**

Peroxo compounds like peroxydisulphate, perborate, peroxomonosulphate and organic peroxides are economically and environmentally preferred for oxidation of organic compounds [1] than conventional metal ions oxidants. Under ordinary conditions, oxidation by these reagents is slow and requires various metal ions as catalysts [2]. The preliminary step of catalysed path is oxidation of the metal ion to its higher oxidation state which then effects the oxidation of substrate. Such catalysis is more feasible if the redox potential of metal ion is 1.0V. Therefore, the metal ion having redox potential higher than 1.0 V can be reduced considerably by using different complexing agents. Transition metal substituted heteropolyoxometalates exhibit such diverse chemical and electrochemical properties [3] which make them attractive for catalytic applications. It has been known that tungsten and molybdenum compounds and their polyoxometalates [2] are efficient catalysts for oxidations by peroxo compounds. In continuation of our earlier work involving polyoxometalates [4-10], herein we report the kinetics of oxidation of DMSO by oxone catalysed by 12-tungstocobaltate (II).

## EXPERIMENTAL SECTION

Reagent grade chemicals and doubly distilled water were used throughout. The cobalt complex 12-tungstocobaltate(II) was prepared by literature method [11] and standardized spectrophotometrically [12] at 624nm using an Elico SL 159 UV-vis spectrophotometer. The solutions of oxone were freshly prepared and standardized iodometrically. The pH of the solutions is maintained by using buffer solution. The buffer of pH 4 was prepared by mixing quantity of  $0.2 \text{ mol dm}^{-3}$  sodium acetate and  $0.2 \text{ mol dm}^{-3}$  acetic acid. The pH of the solution was measured on Elico GL-10T pH meter. Dimethyl sulphoxide was fractionally distilled. The fraction boiling between  $75-76^\circ\text{C}$  was collected and used for preparation of solution.

### Kinetic procedure

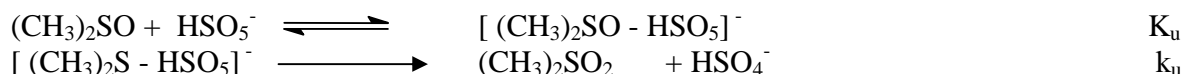
Kinetic runs were carried out in solution of pH = 4 under pseudo-first-order conditions keeping large excess of DMSO. The reaction was followed Iodometrically, by titrating 5 ml reaction mixture with standard sodium thiosulphate solution. The reaction product was found to be dimethyl sulphone. Dimethyl sulphone was identified by the spot test [13]. For the spot test the reaction mixture containing  $2.0 \text{ mol dm}^{-3}$  of DMSO,  $0.1 \text{ mol dm}^{-3}$  oxone and  $2 \times 10^{-4} \text{ mol dm}^{-3}$  of 12-Tungstocobaltate(II) was prepared in pH 4 solution and was kept for one day. The ether extraction was then carried out. The ether from extract was removed to obtain the solid product. The melting point of the solid was determined as  $108^\circ\text{C}$  (Lit. mp  $109^\circ\text{C}$  [14]). The solid was also used for the spot test. The solid was taken in a micro test tube and it was covered with  $\text{Ni}(\text{OH})_2$  paper. The green paper turns black, when the test tube was heated on a low flame, indicating the liberation of  $\text{SO}_2$  from dimethyl sulphone product. Therefore, the stoichiometry will be 1:1. The uncatalysed reaction also occurs to appreciable extent. Hence it also contributes to catalysed reaction.

The order in DMSO was found to be unity for uncatalysed reaction whereas it was fractional (0.63) for the catalysed reaction. The pseudo-first-order rate constant remain unchanged for both uncatalysed and catalysed reaction therefore the reaction is first order in oxidant concentration. The values of pseudo-first-order rate constants increase with increase in concentration of catalyst. The order in catalyst was found to be 0.54. The relative permittivities of the reaction mixtures were computed from the values of the pure liquids using the equation  $D = V_1D_1 + V_2D_2$ ,  $V_1$  and  $V_2$  are the volume fractions and  $D_1$  and  $D_2$  are the dielectric constants of water and acetic acid respectively. The rate of reaction in the uncatalysed reaction decreases while it increases in the catalysed reaction with decrease in dielectric constant of the reaction medium. The effect of temperature was studied at 15,20,25,30C and rate constants for uncatalysed reaction were  $3.4 \times 10^{-4}$ ,  $4.8 \times 10^{-4}$ ,  $6.7 \times 10^{-4}$ ,  $12.4 \times 10^{-4} \text{ s}^{-1}$  respectively. The values of activation parameters  $\Delta H^\ddagger = 60.14 \pm 5 \text{ K J mol}^{-1}$  and  $\Delta S^\ddagger = -102.87 \pm 4 \text{ K J mol}^{-1}$

For catalysed reaction, ( $[\text{Co}^{\text{II}}\text{W}^{12}\text{O}^{40}]^{6-} = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ) the rate constants at 15,20,25,30 C were  $1.18 \times 10^{-3}$ ,  $1.4 \times 10^{-3}$ ,  $2.2 \times 10^{-3}$ ,  $3.5 \times 10^{-3} \text{ s}^{-1}$  respectively. The values of activation parameters  $\Delta H^\ddagger = 56.8 \pm 5 \text{ K J mol}^{-1}$  and  $\Delta S^\ddagger = -102.8 \pm 4 \text{ K J mol}^{-1}$

**Mechanism of the reaction****Uncatalysed reaction**

The oxidant is an inner-sphere reagent therefore the reaction is initiated by the prior interaction of the catalyst with the substrate to form a complex. Under the conditions of the pH utilized to study the reaction the oxidant exists mainly as  $\text{HSO}_5^-$ . The Michealis-Menten plots of  $1/k_{\text{obs}}$  versus  $1/[\text{DMSO}]$  was linear without an intercept. Therefore, in agreement with the results obtained the mechanism of the reaction can be represented as in Scheme 1.

**Scheme 1**

$$\text{Rate} = k_u[\text{Complex}] = k_u K_u [\text{DMSO}] [\text{Oxone}] \quad (1)$$

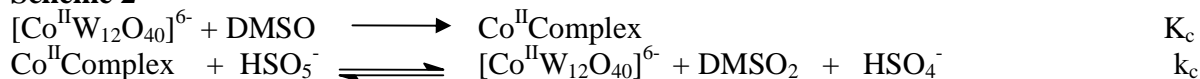
$$\text{Rate} / [\text{Oxone}] = k_{\text{uncat}} = k_u K_u [\text{DMSO}] \quad (2)$$

pseudo-first-order rate constant by equation 3

**Catalyzed reaction**

The initiation of the reaction occurs through the interaction between the catalyst and the substrate in a prior rapid equilibria to form a complex which then is oxidized by the oxidant in a slow step. The formation of the complex was kinetically verified by Michealis-Menten plot of  $1/k_{\text{cat}}$  against  $1/[\text{DMSO}]$ .

The mechanism on the basis of the kinetic data can be represented by Scheme 2 and the corresponding rate law was derived as follows.

**Scheme 2**

The rate of the reaction is given by

$$\text{Rate} = k_c [\text{Co}^{\text{II}}\text{Complex}] [\text{Oxone}] \quad (3)$$

From the complex formation equilibria of Scheme 2 we get

$$K_c = [\text{Co}^{\text{II}}\text{Complex}] / [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]_{\text{free}}^{6-} [\text{DMSO}]_{\text{free}} \quad (4)$$

Since the catalyst is in small concentration in comparison with the substrate we have

$$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]_{\text{total}}^{6-} = [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]_{\text{free}}^{6-} + [\text{Co}^{\text{II}}\text{Complex}] \quad (5)$$

from equation 5 we get for  $[\text{Co}^{\text{II}}\text{Complex}]$

$$[\text{Co}^{\text{II}}\text{Complex}] = K_c [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]_{\text{free}}^{6-} [\text{DMSO}]_{\text{free}} \quad (6)$$

therefore, from equations 6 and 7 we get

$$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} = [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{free}} \{ 1 + K_c [\text{DMSO}] \} \quad (7)$$

as  $[\text{DMSO}]_{\text{free}} = [\text{DMSO}]_{\text{total}}$  and now

$$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{free}} = [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} / \{ 1 + K_c [\text{DMSO}] \} \quad (8)$$

therefore,

$$[\text{Co}^{\text{II}}\text{Complex}] = K_c [\text{DMSO}] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} / \{ 1 + K_c [\text{DMSO}] \} \quad (9)$$

Substituting the value of  $[\text{DMSO}]_{\text{free}}$  and  $[\text{Co}^{\text{II}}\text{Complex}]$  in the rate equation 4 we get

$$\text{Rate} = k_c K_c [\text{Oxone}] [\text{DMSO}] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} / \{ 1 + K_c [\text{DMSO}] \} \quad (10)$$

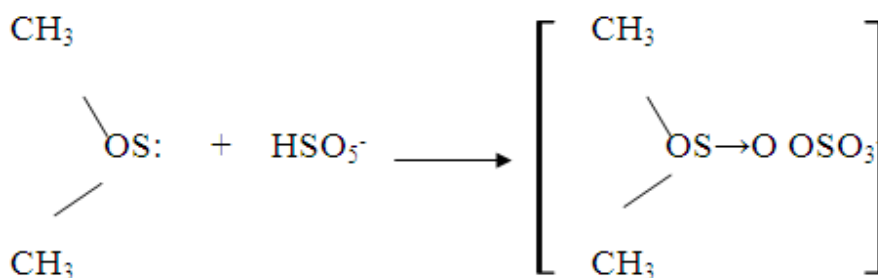
$$\text{Rate} / [\text{Oxone}] = k_{\text{cat}} = k_c K_c [\text{DMSO}] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} / \{ 1 + K_c [\text{DMSO}] \} \quad (11)$$

The uncatalyzed reaction also occurs to considerable extent in presence of the catalyst therefore, the total rate law for the catalyzed reaction would be combination of equation 3 and 12 which is given by equation 13.

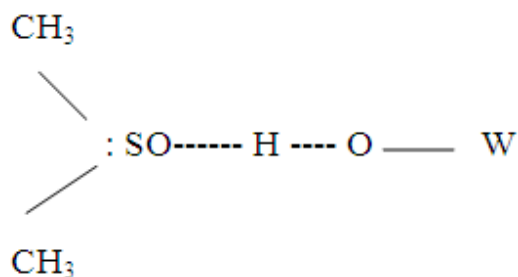
$$k_{\text{obs}} = k_u K_u [\text{DMSO}] + k_c K_c [\text{DMSO}] [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}_{\text{total}} / \{ 1 + K_c [\text{DMSO}] \} \quad (12)$$

$$k_{\text{obs}} = (k_u K_u + k_c K_c [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{\text{6-}}) [\text{DMSO}] / \{ 1 + K_c [\text{DMSO}] \} \quad (13)$$

The overall rate law 14 explains satisfactorily the order in catalyst, substrate and the oxidant. The probable structures of the complexes formed in the uncatalyzed and catalyzed reactions may be assumed to be formed by respective interaction of the substrate, DMSO, with Oxone and the catalyst and their justification is as follows. In the uncatalyzed reaction electrophilic attack of  $\text{HSO}_5^-$  on the sulphide group of DMSO forming an unstable complex as Shown in below Figure.



The fractional order dependence on the catalyst suggests that the overall reaction proceeds through an alternative mechanism involving catalyst. Since the catalyst is an outer-sphere reagent containing coordinated water molecules the possibility of forming an outer-sphere complex by the replacement of one of the coordinated water molecule by the substrate is most probable as shown below,



Since both the mechanisms have more ordered transition state due to coordination of DMSO with oxone in uncatalyzed reaction and 12-tungstocobaltate(II) catalysed reaction. Both the reactions were expected to have same decrease in entropy as observed.

**Table 1: Effect of [DMSO],[OXONE], [Co<sup>II</sup>W<sup>12</sup>O<sup>40</sup>]<sup>6-</sup> on oxidation of DMSO by oxone at 15<sup>o</sup> C and pH=4**

10 <sup>2</sup> [DMSO]	10 <sup>3</sup> [OXONE]	10 <sup>4</sup> [Co <sup>II</sup> W <sub>12</sub> O <sub>40</sub> ] <sup>6-</sup>	10 <sup>3</sup> k <sub>un</sub>	10 <sup>3</sup> k <sub>cat</sub>
0.5	1	2	0.34	1.18
1	1	2	0.9	2.08
3	1	2	2.19	4.16
5	1	2	3.48	5.69
7	1	2	4.61	7.12
0.5	0.25	2	0.34	1.28
0.5	0.5	2	0.349	1.4
0.5	1.0	2	0.349	1.18
0.5	1.5	2	0.35	1.13
0.5	2.5	2	0.355	1.13
0.5	1	1	0.35	0.82
0.5	1	2	0.35	1.18
0.5	1	3	0.35	1.44
0.5	1	4	0.35	1.76
0.5	1	5	0.35	2.08

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