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RESEARCH ARTICLE

KINETICS AND MECHANISM OF OXIDATION OF DIPHENYL SULFOXIDE BY BISPYRIDINESILVER (I) DICHROMATE IN THE PRESENCE OF OXALIC ACID

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ABSTRACT

The kinetics of oxidation of diphenyl sulphoxide (DPSO) by bispyridinesilver (I) dichromate (BPSDC) has been studied in 50% (v/v) aqueous acetic acid medium at 308K. The reaction is first order with respect to [oxidant] and fractional order dependence with respect to [DPSO]. This reaction is catalysed by [H+] and oxalic acid. Decrease the dielectric constant of the medium increases the rate. The reaction has been conducted at four different temperature and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed and substantiated with the rate law.

INTRODUCTION

Chromium compounds have been used in a aqueous and non-aqueous medium for the oxidation of a variety organic compounds (Westheimer, 1949 and Muzart, 1992). Chromium compounds especially Cr (VI) reagents have been proved to be a versatile reagents capable of oxidising almost all the oxidisable functional groups (Rihter et al., 1988 and Sarasuat *et al.,* 2003). Bispyridinesilver (I) dichromate (BPSDC) is also one such reagent and has been used as an mild and selective oxidant (Firouzabadi *et al.,* 1984). Mo (VI) catalysis of pertorate oxidation of dimethyl and dibenzyl sulphoxide has been carried out by Karunakaran *et al.,* (2006). Kinetics and mechanism of oxidation of sulphides by Cr (VI) complexes has already been reported (Chellamani *et al.,* 1999). Kinetics and mechanism of the oxidation of organic sulphides by Cr (VI) has been studied by Shashi Vyas *et al.* (2002). Only few reports are available about the kinetics and mechanism of oxidation of sulfoxide with chromium (VI) complexes. However the kinetics and mechanism of oxidation of diphenylsulphoxide by BPSDC has not been reported. Hence we investigated the oxidation kinetics of diphenyl sulphoxide by BPSDC in aqueous acetic acid medium in the presence of oxalic acid and the corresponding mechanistic aspects are discussed in this research paper.

MATERIALS AND METHODS

Bispyridinesilver (I) dichromate was prepared by reported method (Firouzabadi *et al.,* 1984). Diphenyl sulphoxide, sodium perchlorate, oxalic acid, perchloric acid and other chemicals are all of analar grade samples and are used as such. All the kinetic reactions were carried out under pseudo first order conditions in 50 % (v/v) aqueous acetic acid medium at 308K unless otherwise mentioned and the reaction progress was followed by standard iodometric method. The required volume of these solutions for each run were mixed and 2 cm^3 aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10cm^3 of 5% KI solution and 10cm^3 of 2.5 N sulphuric acid. The liberated iodine was titrated against standard sodium thiosulphate solution to a starch end point. DPSO (0.2 mol dm^{-3}) and BPSDC (0.1 mol dm^{-3}) were mixed and kept at room temperature for 24 hours. The product was extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was evaporated and the product of this reaction was identified as diphenyl sulfone.

RESULTS AND DISCUSSION

Oxidation of diphenyl sulphoxide by BPSDC has been conducted in 50% (v/v) acetic acid – water medium in the presence of oxalic acid at 308 K under the pseudo first order conditions and the observed results were discussed in the subsequent pages.

Effect of varying BPSDC concentration

In this oxidation reaction, BPSDC concentration was varied in the range of 0.50 x 10^{-3} to 1.50 x 10^{-3} mol dm^{-3} and keeping the concentrations of all other reactant as constant and the rates were measured (Table 1). Non-variation in the pseudo –

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first order rate constants at various concentrations of [BPSDC] indicates that the order with respect to [BPSDC] is unity (Figure 1).

Effect of varying DPSO concentration

The substrate diphenyl sulphoxide (DPSO) was varied in the range of 1.50 x 10^{-2} to 4.00 x 10^{-2} mol dm^{-3} and keeping all other reactant concentrations as constant and the rates were measured. (Table 1) The plot of log k_{obs} versus log [DPSO] gave the slope of 0.7 (r=0.997, Figure 2) shows the Michaelis-Menton type of kinetics with respect to [DPSO].

Effect of perchloric acid concentration

In this oxidation reaction, perchloric acid concentration was varied in the range of 0.55 to 1.93 mol dm^{-3} and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increases with increase in perchloric acid concentration. This shows that added hydrogen ion had very significant effect on the protonation of the oxidant.

Table 1. Effect of Variation of [DPSO], [BPSDC], [$HClO_4$], [Oxalic], Solvent Composition and temperature on the reaction rates

[DPSO] 10^2 mol dm^{-3}	[BPSDC] 10^3 mol dm^{-3}	Solvent AcOH–H_2O%	[$HClO_4$] mol dm^{-3}	[Oxalic] 10^4 mol dm^{-3}	Temperature K	k_{obs} x 10^4 s^{-1}
1.50	1.00	50-50	1.38	2.50	308	2.55
2.00	1.00	50-50	1.38	2.50	308	2.74
2.50	1.00	50-50	1.38	2.50	308	3.09
3.00	1.00	50-50	1.38	2.50	308	3.57
3.50	1.00	50-50	1.38	2.50	308	3.97
4.00	1.00	50-50	1.38	2.50	308	4.43
3.00	0.50	50-50	1.38	2.50	308	4.68
3.00	0.75	50-50	1.38	2.50	308	4.15
3.00	1.00	50-50	1.38	2.50	308	3.57
3.00	1.25	50-50	1.38	2.50	308	3.20
3.00	1.50	50-50	1.38	2.50	308	2.87
3.00	1.00	45-55	1.38	2.50	308	2.46
3.00	1.00	50-50	1.38	2.50	308	3.57
3.00	1.00	55-45	1.38	2.50	308	3.84
3.00	1.00	60-40	1.38	2.50	308	4.95
3.00	1.00	65-35	1.38	2.50	308	7.98
3.00	1.00	70-30	1.38	2.50	308	17.09
3.00	1.00	50-50	0.55	2.50	308	1.12
3.00	1.00	50-50	0.83	2.50	308	1.72
3.00	1.00	50-50	1.10	2.50	308	2.73
3.00	1.00	50-50	1.38	2.50	308	3.57
3.00	1.00	50-50	1.65	2.50	308	5.89
3.00	1.00	50-50	1.93	2.50	308	7.48
3.00	1.00	50-50	1.38	2.50	303	2.83
3.00	1.00	50-50	1.38	2.50	308	3.57
3.00	1.00	50-50	1.38	2.50	313	4.29
3.00	1.00	50-50	1.38	2.50	318	5.30

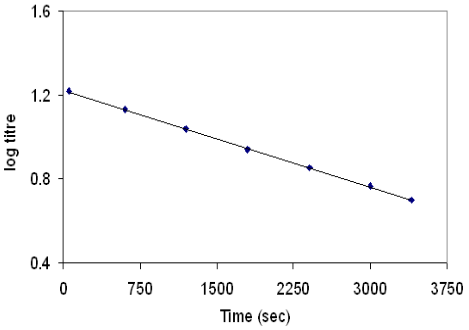

Fig.1. Plot of log titre *versus* time (sec)

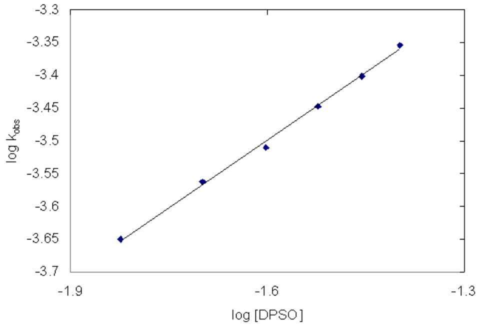

Fig. 2. Plot of log k_{obs} *versus* log [DPSO]

Effect of perchloric acid concentration

In this oxidation reaction, perchloric acid concentration was varied in the range of 0.55 to 1.93 mol dm^{-3} and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increases with increase in perchloric acid concentration. This shows that added hydrogen ion had very significant effect on the protonation of the oxidant.

Effect of ionic strength, $MnSO_4$, acrylonitrile and solvent polarity

The rate of the reaction has been found to increases with the decrease in the dielectric constant of the medium. Addition of neutral salt like sodium perchlorate increases the rate of the reaction shows that ion and a neutral molecule may be involved in the rate-determining step (Krishnasamy *et al.,* 2007). Also there is no visible polymerization occurs due to the added acrylonitrile. Added Mn^{2+} decreases the rate of the reaction considerably. This shows the involvement of two electron changes in the rate determining step (Krishnasamy *et al.,* 2007).

Effect of oxalic acid

The oxalic acid concentration was varied in the range of 1.25 x 10^{-4} to 10.00 x 10^{-4} mol dm^{-3} and keeping all other reactant concentrations as constant and the rates were measured. The rate of the reaction increases with increase the concentration of oxalic acid. Further a plot of log k_{obs} versus log [oxalic acid] gives a straight line (B = 0.8, r = 0.997) with integral slope value.

Table 2. Effect of variation of [$MnSO_4$], [$NaClO_4$] and [acrylonitrile] on reaction rates.

[$MnSO_4$] 10^3 mol dm^{-3}	[$NaClO_4$]10^2 mol dm^{-3}	[Acrylonitrile] 10^4 mol dm^{-3}	k_{obs} x $10^4 s^{-1}$
0	-	-	3.57
2.50	-	-	3.29
5.00	-	-	2.58
7.50	-	-	1.68
10.00	-	-	1.62
-	5.00	-	4.43
-	10.00	-	4.93
-	15.00	-	5.27
-	20.00	-	5.66
-	-	2.50	3.50
-	-	7.50	3.59
-	-	10.00	3.64

Condition [BPSDC] = 1.00 x 10^{-3} mol dm^{-3} , [DPSO] = 3.00 x 10^{-2} mol dm^{-3} AcoH – H_2O = 50 – 50 (v/v), [Oxalic] = 2.50 x 10^{-4} mol dm^{-3}

Table 3. Effect of [Oxalic acid] and different catalyst on the reaction rates*

[Oxalic acid] 10^4 mol dm^{-3}	k_{obs} x $10^4 S^{-1}$
0.00	0.51
1.25	1.67
2.50	3.57
5.00	5.51
7.50	7.41
10.00	9.23
2.50^a	0.77
2.50^b	0.43

*Condition: [BPSDC] = 1.00 x 10^{-3} mol dm^{-3}, [DPSO] = 3.00 x 10^{-2} mol dm^{-3} ACOH – H_2O = 50 – 50 (v/v) : Temperature : 308 K, a = 1,10-Phenanthroline, b=Imidazole

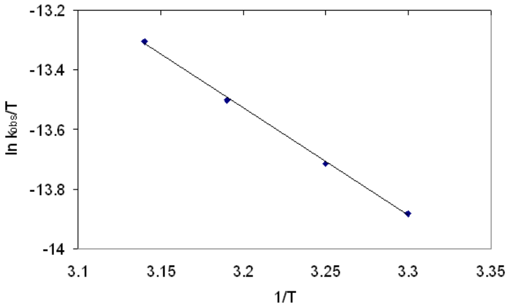

Fig.3. Plot of ln k_{obs}/T *versus* 1/T

Effect of various complexing agents

To know the catalytic activity of various complexing agents, we have used the various catalysts Viz., 1, 10-phenanthroline and imidazole under identical experimental conditions and the reactivities are compared. The order of catalytic efficiency is Oxalic acid > 1,10 – phenanthroline > Imidazole. More pronounced activity in the presence of oxalic acid as a catalyst is observed. This may probably due to the formation of more reactive electrophile in between oxidant and oxalic acid and the corresponding transition state is well established (Islam *et al.,* 2005 and Dharmaraja *et al.,* 2008).

Effect of temperature

This oxidation reaction was conducted at four different temperatures viz., 303, 308, 313 and 318K and the corresponding rate constant values were given in Table 1. Eyring's plot of ln $k_{obs/T}$ versus 1/T was linear (r=0.999, Fig 3) and the corresponding activation parameters are $\Delta H^{\#}$ =31.26 kJ mol^{-1} and $\Delta S^{\#}$ = - 209.72 kJ mol^{-1}.

Mechanism and Rate law

From the observed kinetic results the following possible mechanism was proposed for this oxidation reaction.

$$\text{Cr(VI)} + H^+ + \text{Oxalic acid} \xrightleftharpoons{K_1} \text{complex -1}$$

$$\text{Complex – 1 + DPSO} \xrightleftharpoons{K_2} \text{complex -2}$$

$$\text{Complex -2} \xrightarrow[K_3]{\text{slow}} \text{product + Cr(IV)}$$

The proposed mechanism was substantiated by the following rate law.

$$\text{Rate} = \frac{K_1 K_2 k_3 [\text{DPSO}]\,[H^+]\text{Cr(VI)}[\text{Oxalic}]}{\{1 + K_2[DPSO]\}}$$

Conclusion

Oxidation of diphenyl sulphoxide by BPSDC is first order dependence with respect to [BPSDC] and [Oxalic acid]. Michaelis-Menton type kinetics was observed with respect to [DPSO]. This oxidation kinetics is an acid catalysed reaction. Diphenyl sulfone is identified as the product. The effect of ionic strength and solvent polarity suggest the participation of an ion and a neutral molecule in the rate determining step. The negative value of entropy adds additional support for the formation of the intermediate complex C_1 and C_2. More pronounced catalytic activity in the presence of oxalic acid as a catalyst is observed.

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