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Kinetics and Mechanism of the Oxidation of Diphenyl Sulphides by *Bis*-pyridinesilver(I) Dichromate

K. KRISHNASAMY*, V. VENKATESWARAN† and M. SHANMUGAM‡
Department of Chemistry, Annamalai University, Annamalai Nagar-608 002, India
E-mail: krishbala56@yahoo.co.in

The kinetics of oxidation of diphenyl sulphide (DPS) by *bis*-pyridinesilver(I) dichromate (BPSDC) have been studied in 70 % aqueous acetic acid medium. The reaction is first order with respect to [oxidant] and fractional order with respect to [substrate]. The reaction has been found to be catalyzed by H^+ ions. Decrease the dielectric constant of the medium increases the rate. Activation parameters have been evaluated from the Eyring's plot. The stoichiometric studies reveal that the reactants react in 1:1 mole ratio *via* the formation of a complex. Mechanism consistent with the observed kinetics results has been proposed and the related rate law was derived.

Key Words: Kinetics, Oxidation, Biphenyl sulphides, Chromium(VI) oxidation.

INTRODUCTION

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds[1-3]. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents capable of oxidizing almost all the oxidizable organic functional groups[4-7]. *Bis*-pyridinesilver(I) dichromate (BPSDC) is also one such reagent. However, the studies on kinetics and mechanism reactions of complexed Cr(VI) species, including that of sulphides have already been reported[8,9]. Recently, Karunakaran *et al.*[10] have reported a common mechanism for the oxidation of biphenyl sulphide by various Cr(VI) reagents in acetic acid medium. Further, the oxidation of sulphides by quinolinium dichromate has been carried out by Sharma *et al.*[9] kinetics of oxidation of biphenyl sulphide by BPSDC has not been investigated. Hence, here we report the kinetics of oxidation of biphenyl sulphide by BPSDC in aqueous acetic acid medium and the corresponding mechanistic aspects are discussed.

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†Department of Chemistry, Erode Arts College, Erode-638 009, India.

‡Department of Chemistry, Muthayammal College of Arts & Science, Rasipuram-637 408, India.

EXPERIMENTAL

Bis-pyridinesilver(I) dichromate was prepared by standard method[11]. Biphenyl sulphide (Lancaster), perchloric acid and other chemicals are of AnalR grade and used as such. Doubly distilled water was used for the entire work.

All the kinetic reactions were carried out under pseudo first-order conditions in 70 % aqueous acetic acid medium at 308 K unless otherwise mentioned. The course of the reaction was followed by spectrophotometric method. In this method a known volume of BPSDC is transfered to the reaction mixture at zero time and shaken well. The rate of disappearance of BPSDC was followed by monitoring the decrease in absorption of BPSDC at 347 nm employing Elico-BL-198-UV-Visible spectrophotometer with a variable temperature accessory.

RESULTS AND DISCUSSION

The kinetic results of the oxidation of diphenyl sulphide by BPSDC along with the experimental conditions are given in Tables 1-4.

TABLE-1
EFFECT OF THE CONCENTRATION OF DPS, BPSDC AND PERCHLORIC ACID ON REACTION RATE
Acetic acid = 70 % (v/v), Temp. = 308 K

[BPSDC] × 10^4 (mol dm^{-3})	[DPS] × 10^2 (mol dm^{-3})	[HClO$_4$] × 10^2 (mol dm^{-3})	k_{obs} × 10^4 (s^{-1})
5.00	8.00	2.00	4.21
10.00	8.00	2.00	4.27
12.25	8.00	2.00	4.36
15.00	8.00	2.00	4.38
12.25	4.00	2.00	2.84
12.25	5.00	2.00	3.05
12.25	6.00	2.00	3.55
12.25	7.00	2.00	4.08
12.25	8.00	2.00	4.36
12.25	10.00	2.00	5.03
12.25	8.00	1.20	1.92
12.25	8.00	1.60	2.74
12.25	8.00	2.40	5.57
12.25	8.00	2.80	8.31

Under the pseudo first order conditions, the plots of log [BPSDC] *vs.* time were linear indicating first order dependence with respect to [BPSDC]. This was further confirmed by the constancy in the pseudo-first order rate

TABLE-2
EFFECT OF SOLVENT POLARITY ON REACTION RATE
[DPS] = 8.00×10^{-2} mol dm^{-3}; [BPSDC] = 12.25×10^{-4} mol dm^{-3}
Temp. = 308 K; [$HClO_4$] = 2.00×10^{-2} mol dm^{-3}

AcOH-H_2O (% v/v)	60	65	70	75	80
Dielectric constant	35.76	32.07	28.37	24.68	20.98
$k_{obs} \times 10^4$ (s^{-1})	2.77	3.64	4.36	15.94	28.54

TABLE-3
EFFECT OF [$MnSO_4$], [$NaClO_4$] AND [ACRYLONITRILE] ON THE REACTION RATE
[DPS] = 8.00×10^{-2} mol dm^{-3}; [BPSDC] = 12.25×10^{-4} mol dm^{-3}
[$HClO_4$] = 2.00×10^{-2} mol dm^{-3}; Temp. = 308 K

[$MnSO_4$] 10^4 (mol dm^{-3})	[$NaClO_4$] 10^1 (mol dm^{-3})	[Acrylonitrile] 10^4 (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})
10.00	-	-	5.81
15.00	-	-	7.72
20.00	-	-	9.07
-	2.00	-	6.21
-	3.00	-	4.20
-	4.00	-	3.88
-	-	10.00	4.29
-	-	15.00	4.37
-	-	20.00	4.35

TABLE-4
EFFECT OF TEMPERATURE ON REACTION RATE
[DPS] = 8.00×10^{-2} mol dm^{-3}; [BPSDC] = 12.25×10^{-4} mol dm^{-3}
[$HClO_4$] = 2.00×10^{-2} mol dm^{-3}; Solvent: AcOH-H_2O 70 % (v/v)

Temp. (K)	k_{obs} 10^4 (s^{-1})
303	2.66
308	4.36
313	8.96
318	11.75

(k_{obs}) constants, for varying [BPSDC]. The plot of log k_{obs} *vs.* log [DPS] gave the slope of 0.67 shows that this oxidation reaction was fractional order with respect to [substrate]. The plot of 1/k_{obs} *vs.* 1/[DPS] is linear with good correlation coefficient. The positive intercept value obtained in this plot indicated that the reaction mechanism is a Michaelis-Menton type. The rate of oxidation increases with increase in perchloric acid concentration. The plot of log k_{obs} *vs.* log $[H^+]$ is linear with the slope of 1.72. It was noticed that the added hydrogen ions had very significant effect on the rate of reaction showing that the hydrogen ions provided by the solvent molecules were not adequate for the protonation of the oxidant.

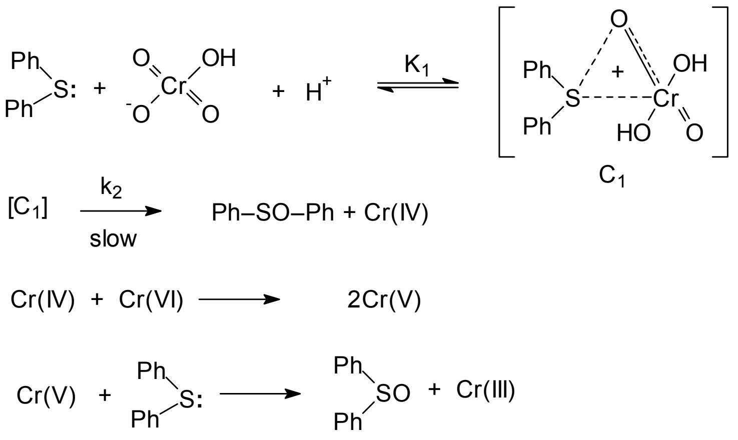
The effect of dielectric constant on the reaction rate of this oxidation reaction was investigated. It was found that the rate constants increased with increase in composition of acetic acid or decrease in dielectric constant shows that the involvement of an ion and the neutral molecule in the rate determining step[12].

The reaction rate increases with increasing concentration of manganous sulphate shows that the addition of Mn^{2+} having a catalytic effect[13]. The rate constant decreases with increasing concentration of sodium perchlorate suggesting that the reaction may be between an ion or ions and dipole molecule[14]. Further the addition of acrylonitrile has no effect on the reaction rate showing the absence of free radical pathway mechanism[15].

The oxidation reaction were conducted at four different temperatures and the corresponding reaction rates were given in Table-4. The Eyring's plot, ln k_{obs}/T *vs.* $1/T$ were linear and the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were obtained from this plot. The value of $\Delta H^{\#} = 83.68$ KJ mol^{-1} and $\Delta S^{\#} = -37.34$ JK^{-1} mol^{-1}. The product was identified as diphenyl sulphoxide and the stoichiometry analysis shows that one mole of BPSDC consumed one mole of DPS.

Mechanism: In the aqueous acetic acid medium the oxidant BPSDC dissociates to give pyridinium ions and chromate ions. The literature survey reveals that $HCrO_4^-$ is the active oxidizing species in the Cr(VI) oxidation reactions[15].

In the light of all the experimental results obtained in the present investigation and the evidences from other investigations the following mechanistic steps have been proposed.



$$\text{Rate law} = \frac{K_1k_2[HCrO_4^-][H^+][DPS]}{1+K_1[DPS]}$$

$$k_{obs} = \frac{K_1k_2[H^+][DPS]}{1+K_1\left([DPS][H^+]\right)}$$

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