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RESEARCH ARTICLE

Chromium(VI) oxidation of methyl phenyl sulfide—kinetic and mechanistic approach

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The kinetics and mechanism of oxidation of methyl phenyl sulfide (MPS) with bispyridinesilver(I) dichromate (BPSDC) leads to the formation of the corresponding sulfoxide. The reaction is first order with respect to (BPSDC) and a Michaelis–Menton type of kinetics followed with respect to (MPS). The reaction is catalysed by hydrogen ions. The decrease in dielectric constant of the medium increases the rate of the reaction. Addition of sodium perchlorate increases the rate of the reaction appreciably. Addition of acrylonitrile rules out the possibility of radical pathway mechanism. The reactions has been conducted at four different temperatures and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed.

Keywords: Methyl phenyl sulfide; Kinetics and mechanism; Kinetics; Oxidation; Bispyridinesilver(I) dichromate

1. Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds [1]. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups [2–4]. Studies on kinetics and mechanism of complexed Cr(VI) species, including that of sulfides have been already reported [5–7]. Recently Karunakaran *et al.* [8] have reported a common mechanism for the oxidation of diphenyl sulfide by various Cr(VI) reagents in acetic acid. Variety of new chromium(VI) oxidants together with special reaction conditions have been introduced for the chemospecific, regiospecific and stereospecific oxidative degeneration of functional groups in highly sensitive systems. Bispyridinesilver(I)

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dichromate is also one such recently developed Cr(VI) oxidant and has been found quite useful as an oxidant in organic synthesis [9]. Literature survey clearly reveals that the kinetics of oxidation of methyl phenyl sulfide by BPSDC has not been investigated so far. This prompted us to undertake the present investigation.

2. Results and discussion

2.1 Effect of varying oxidant concentration

The concentration of BPSDC was varied in the range, 7.5×10^{-4} to 1.75×10^{-3} mol dm⁻³ and keeping all other reactant concentrations as constant and the rates were measured (table 1). The non-variation in the pseudo-first-order rate constants at various concentrations of [BPSDC] indicates that the order with respect to [BPSDC] is unity. This was also confirmed from the linearity of plots of log [BPSDC] versus time ($r = 0.999$) upto 70% completion of the reaction.

2.2 Effect of varying substrate concentration

The substrate, MPS was varied in the range of 3.0×10^{-2} to 8.0×10^{-2} mol dm⁻³ at 30 °C and keeping all other reactant concentrations as constant and the rates were measured (table 1). The plot of log k_{obs} versus log [MPS] gave the slope of 0.50 ($r = 0.990$) shows that this oxidation reaction was fractional order with respect to [MPS]. Also the plot of $1/k_{\text{obs}}$ versus $1/[MPS]$ is linear ($r = 0.995$) with a positive intercept values indicated that the reaction mechanism is a Michaelis–Menton type.

Table 1. Effect of variation of [MPS], [BPSDC], [HClO₄], solvent composition and temperature on reaction rates.

[BPSDC]10 ³ (mol dm ⁻³)	[MPS] 10 ² (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	Solvent AcOH–H ₂ O (% v/v)	Temperature (K)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
0.75	6.00	0.22	60–40	303	8.44
1.25	6.00	0.22	60–40	303	8.34
1.50	6.00	0.22	60–40	303	8.23
1.75	6.00	0.22	60–40	303	8.16
1.25	4.00	0.22	60–40	303	5.49
1.25	5.00	0.22	60–40	303	6.36
1.25	6.00	0.22	60–40	303	7.21
1.25	7.00	0.22	60–40	303	8.64
1.25	8.00	0.22	60–40	303	9.45
1.25	6.00	0.17	60–40	303	6.01
1.25	6.00	0.28	60–40	303	11.07
1.25	6.00	0.33	60–40	303	13.07
1.25	6.00	0.39	60–40	303	15.40
1.25	6.00	0.22	55–45	303	6.52
1.25	6.00	0.22	65–35	303	9.74
1.25	6.00	0.22	70–30	303	16.76
1.25	6.00	0.22	80–20	303	45.65
1.25	6.00	0.22	60–40	298	7.13
1.25	6.00	0.22	60–40	308	9.99
1.25	6.00	0.22	60–40	313	11.77
1.25	6.00	0.22	60–40	318	14.76

2.3 Effect of perchloric acid concentration

The perchloric acid concentration was varied in the range of 0.165–0.385 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. 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 plot of log k_{obs} versus log $[\text{H}^+]$ is linear with a slope ($B = 1.10$, $r = 0.999$) indicating that first order dependence with respect to $[\text{H}^+]$.

2.4 Effect of ionic strength, MnSO_4 and solvent polarity

The effect of ionic strength was studied by varying the NaClO_4 concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.4 to 0.8 mol dm⁻³ and keeping all other reactant concentration as constant. It was found that the rate constants increased with increase in concentration of NaClO_4 (table 2). Further the rate of the reaction found to be increase with the decrease in the dielectric constant of the medium (table 2). The effect of ionic strength and solvent polarity suggesting that the participation of an ion and a neutral molecule in the mechanistic steps [10]. Addition of manganous sulphate enhances the rate of the reaction (table 2) shows that added Mn^{2+} shows catalytic activity in this oxidation reaction [10].

2.5 Polymerisation study

The possibility of radical formation and its involvement in the reaction had been ruled out as the addition of acrylonitrile in the reaction mixture developed no turbidity and hence the reaction rate was not affected even the $[\text{acrylonitrile}]$ was at 3.00×10^{-3} mol dm⁻³ (table 2).

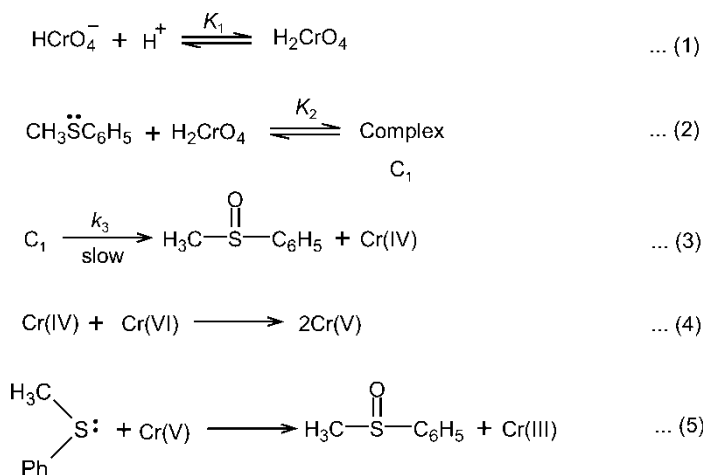
2.6 Effect of temperature

This oxidation reaction was conducted at five different temperatures viz., 298, 303, 308, 313 and 318 K and measured rates were given in (table 1). Eyring's plot of $\ln k_{\text{obs}}/T$ versus $1/T$

Table 2. Effect of variation of $[\text{NaClO}_4]$, $[\text{Acrylonitrile}]$ and $[\text{MnSO}_4]$ on reaction rates.

$[\text{NaClO}_4]$ (mol dm ⁻³)	$[\text{Acrylonitrile}] 10^3$ (mol dm ⁻³)	$[\text{MnSO}_4]$ (mol dm ⁻³)	$k_{\text{obs}} \times 10^4$ (s ⁻¹)
0.20	–	–	8.96
0.40	–	–	9.78
0.60	–	–	10.76
0.80	–	–	11.72
–	1.00	–	8.30
–	2.00	–	8.36
–	3.00	–	8.28
–	–	1.00	19.97
–	–	2.00	21.42
–	–	2.50	23.24
–	–	3.00	34.48

$[\text{MPS}] = 6.00 \times 10^{-2}$ mol dm⁻³; $[\text{HClO}_4] = 0.22$ mol dm⁻³; $[\text{BPSDC}] = 1.25 \times 10^{-3}$ mol dm⁻³; $\text{AcOH-H}_2\text{O} = 60\text{--}40$ (% v/v); Temperature = 303 K



SCHEME 1

were linear ($r = 0.995$) and the activation parameters $\Delta H^\ddagger = 26.10 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -217.82 \text{ J K}^{-1} \text{ mol}^{-1}$ were obtained from the slope and intercept of the Eyring's plot.

2.7 Mechanism and rate law

In the aqueous acetic acid medium the oxidant BPSDC dissociates to give pyridinium ions and chromate ions (HCrO_4^-) [11]. The literature survey reveals that the species HCrO_4^- is the active species in Cr(VI) oxidation reactions [12]. Initially the HCrO_4^- forms a complex (C_1) with MPS in an equilibrium step. This complex then dissociates to give methyl phenyl sulfoxide in a slow and rate determining step (scheme 1).

The proposed mechanism was substantiated by the following rate law.

$$\text{Rate law} = \frac{K_1 K_2 k_3 [\text{Cr(VI)}][\text{H}^+][\text{S}]}{1 + K_2[\text{S}]} \quad (6)$$

$$k_{\text{obs}} = \frac{K_1 K_2 k_3 [\text{H}^+][\text{S}]}{1 + K_2[\text{S}]} \quad (7)$$

3. Conclusion

Oxidation of methyl phenyl sulfide by BPSDC is an acid catalysed reaction and follows a Michaelis–Menton type of kinetics. The oxidation of MPS yields the corresponding sulfoxide as the product. The effects of ionic strength and solvent polarity suggest the participation of an ion and a neutral molecule in the mechanistic steps. Addition of Mn^{2+} shows catalytic activity in this oxidation reaction. The negative value of entropy adds additional support for the formation of the intermediate complex (C_1).

4. Experiment

Bispyridinesilver(I) dichromate was prepared by the standard method. Methyl phenyl sulfide (Lancaster) and other chemicals used in this studies are of AnalaR grade and used as such. Doubly distilled water was used for the entire work.

All kinetic reactions were carried out under pseudo first-order conditions in 60% aqueous acetic acid medium at 303 K unless otherwise mentioned. The course of the reaction was followed by spectrophotometric method. In this method a known volume of BPSDC is transferred 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 accessories.

5. Product analysis and stoichiometry

Methyl phenyl sulfide (0.2 mol dm^{-3}) and BPSDC (0.1 mol dm^{-3}) were mixed and kept at room temperature for 24 h. The product was extracted with chloroform and dried over anhydrous sodium sulfate. The chloroform layer was evaporated. The product of this reaction was identified as methyl phenyl sulfoxide.

Reaction mixture containing an excess of oxidant (BPSDC) over methyl phenyl sulfide in the presence of perchloric acid were kept at room temperature for the sufficient length of time. Estimation of unchanged oxidant showed that one mole of methyl phenyl sulfide consumed one mole of BPSDC.

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