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KINETICS AND MECHANISM OF OXIDATION OF ALKYL PHENYL SULFIDES BY CETYLTRIMETHYLAMMONIUM DICHROMATE

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ABSTRACT

The oxidation kinetics of some alkyl phenyl Sulfides with Cetyltrimethylammonium dichromate(CTADC) as oxidizing agent was investigated in dichloromethane-acetic acid(80:20, V/V) at 30^0C and in aqueous acetic acid(60:40,50:50,V/V) at 30, 40 & 50^0C. The oxidation of alkyl Phenyl Sulfides followed a over all second order kinetics, first order each with respect to substrate and CTADC. It was found that the rate of reaction increases with electron donating power of the alkyl groups. A possible mechanism was also suggested for the oxidation process.

Key words: CTADC, Alkyl phenyl sulfides, oxidation, kinetics.

INTRODUCTION

A survey of literature revealed that there are number of oxidation reactions for organic Sulfides[1-6]. The rate and mechanisms of these sulfides are largely affected by the nature of the oxidant. Extensive studies on the oxidation of sulfides to sulfoxides by several oxidants like Morphonium chlorochromate[7], butyl triphenyl phosphonium dichromate(BTPPD)[8], EDTA catalyzed chromium (VI)[9], Chloramine – T[10], pyridinium chloro chromate[11], Ce(IV)[12], bromamine–B[13], chloramines–B[14], Mn(VII)[15] were reported and suitable mechanisms have been proposed. However, studies on the kinetics of oxidation of alkyl phenyl sulfides have received less attention and very few reports were observed which include the use of Tl(III)[16] and BTPPD[8] as oxidizing agents. In the present investigation an attempt was made on the oxidation of alkyl phenyl sulfides using CTADC as oxidizing agent. CTADC is a new, nonconventional, green and selective mild phase transferring oxidant. The results were analyzed according to Pavelich-Taft's equation and a possible mechanism was also proposed. The Taft equation is written as:

$$\log\left(\frac{k_s}{k_{\mathrm{CH3}}}\right) = \rho^*\sigma^* + \delta E_s$$

EXPERIMENTAL

Preparation of Cetyltrimethylammonium dichromate

CTADC was prepared according to the method reported by Sabitha Patel and Bijay Mishra[17]. It was observed that this reagent was appreciably stable for about more than 24hrs in the solvent systems used in the present investigation.

Preparation of Alkyl Phenyl Sulfides

Alkyl phenyl sulfides were prepared by standard procedures and they were purified by distillation or recrystallization from suitable solvents. The physical constants of each sulfide were found to be agree with literature values.

Other reagents

Dichloromethane (DCM) and Acetic acid used were of AR grade supplied by S.Merck. Doubly distilled water was used for all purposes.

Kinetic measurements

All the kinetic measurements were carried out at 350 nm, in a thermostated cell compartment of Elico SL-150 UV-Visible Spectrophotometer instrument. The measurements were performed in 60:40, 50:50 (V/V) acetic acid-water at 30, 40 & 50^0C; in 80:20 (V/V) DCM-acetic acid at 30^0C. The rate of disappearance of Chromium(VI) species in each run was followed spectrophotometrically by monitoring the absorption band at 350 nm.

Product analysis

Methyl phenyl sulfide (0.01 mol) and CTADC (0.01 mol) were dissolved in 60:40 acetic acid/water (50 ml) and the mixture was allowed to stand for approximately 24hrs. The product was extracted with ether. The ether layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation and the residue was analyzed by ^{1}H NMR spectroscopy. It was found that the spectra was supporting the peaks of methyl phenyl sulfoxide. The peaks characteristic of MeSPh and $MeSO_2Ph$ could not be detected. Similar experiments were performed with other alkyl phenyl sulfides (ethyl, propyl, isopropyl) also. In all cases, the products were found to be the corresponding sulfoxides only.

Stoichiometry

To determine the stoichiometry, a number reaction mixtures containing excess of CTADC (at least twice the concentration of the sulfide) were prepared in 60:40 acetic acid/water. The reaction mixtures were allowed to stand for 12h to ensure the completion of the reaction. The residual CTADC in all the mixtures was determined spectrophotochemically and was found that the reaction exhibited stoichiometry i.e. one mole of CTADC was consumed for one mole of sulfide.

RESULTS AND DISCUSSION

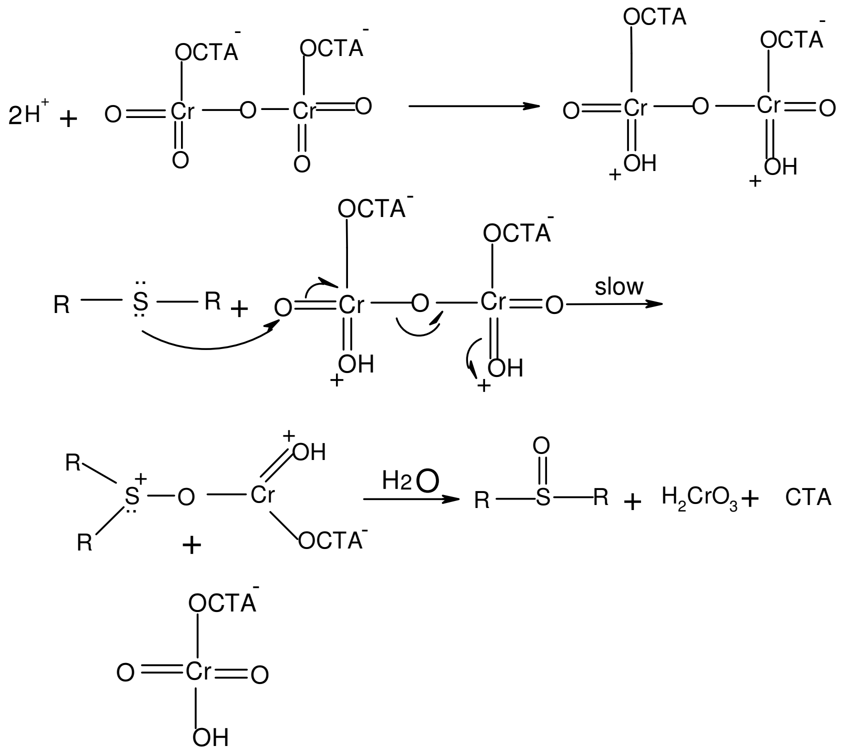
The rate constants of the oxidation of alkyl phenyl sulfides (alkyl = methyl, ethyl, propyl, isopropyl) with CTADC in acetic acid-water 60:40 and 50:50 V/V at 30, 40 and 50^0C were reported in Tables 1 and 2 respectively. The activation parameters ($\Delta H^\#$ and $\Delta S^\#$) for the above reactions were also presented in respective tables. The rate data clearly indicated that the reaction followed a over all second order kinetics, first order with respect to CTADC and the substrate. It is further observed that the rate of the reaction was found to decrease with increase in the size of the alkyl group. i.e. Ph-S-Me>Ph-S-Et>Ph-S-n-Pr>Ph-S-i-Pr. A similar trend was also observed in the oxidation of these sulfides by Cr(VI)[18], peroxy anions[19], diacetoxybenzene[20] and thalium(III)[16]. However, if the contribution of the +I effect of the alkyl groups predominates the steric effect exerted by the increasing bulkiness of the alkyl groups, one would expect a reverse order in the rate. But an inverse trend in going from n-propyl to iso propyl was observed in the oxidation of these sulfides with BTPPD[8].

An exellent correlation was observed between the enthalpies and entropies of activation of the oxidation(Fig 1, slope=0.354, r=0.998, sd=0.474) in acetic acid-water 60:40 and (Fig 2, slope=0.333, r=0.999, sd=0.206) in acetic acid-water 50:50 mixture.

The same oxidation process was also extended to DCM-acetic acid mixture (80:20, V/V) at 30^0C. The results were given in Table 3 and it was found that all the oxidation kinetics were followed a second order kinetics, first order each with respect to substrate and reagent. Similar observation in the rate was alsofound in going from smaller alkyl group to bulky alkyl groups. i.e. the decrease in the rates of oxidation of substrates, Ph-S-Me>Ph-S-Et>Ph-S-n-Pr>Ph-S-i-Pr.

Mechanism

Following the analysis of the observed results, a suitable mechanism was proposed(Scheme 1). It is considered that the first step of the reaction involved the diprotonation of CTADC. The protonated species was proposed to form transition state with the substrate. The ρ^+ value obtained for the plot of Hammet's σ^+ constants against the logarithms of rate constants is -0.521 (r = 0.966 and S.D = 0.07). The negative ρ^+ value indicates that the nucleophilic sulfur atom of the sulfide is more positively charged in the transition state of the rate determining step of the oxidation. Such small ρ values are commonly observed in most studies of other electrophilic reactions at sulfur centre ($\rho^+ = -0.56$ for peroxy disulfate)[19]. An excellent correlation is observed with Taft's Es values against log K/K_{Me} ($\rho = 0.004$, r = 0.999, S.D = 0.006). But the correlation coefficients were with σ_0 vs log k/k_{Me} (r = 0.898). These results show that the reaction is sensitive to steric congetion at the reaction centre. Similar results have been observed in the oxidation of thiourea with CTADC[21]. This support the existance of relatively less polar transition state during the oxidation.



Scheme-1

Table-1: Rate constants and activation parameters for the oxidation of sulfides by CTADC.
Solvent = Acetic acid: H_2O, 60:40

Sulfide	$[C_6H_5SCH_3]$ $X10^{-2}$	[CTADC] $X10^{-4}$	k_2 x 303 K	10^2 313 K	dm^3 mol^{-1} sec^{-1} 323 K	$\Delta H^\#$ ($KJmol^{-1}$)	$-\Delta S^\#$ ($Jmol^{-1}K^-$)
Methyl	0.7471	3.6175	1.73	2.52	3.12	21.44	169.45
Ethyl	0.7465	3.4137	1.48	2.25	2.85	24.12	161.79
Propyl	0.9904	3.6175	1.28	1.99	2.77	31.40	139.39
Isopropyl	1.3714	3.2608	0.69	0.90	1.90	38.40	122.15

Table-2: Rate constants and activation parameters for the oxidation of sulfides by CTADC.
Solvent = Acetic acid: H_2O, 50:50

Sulfide	$[C_6H_5SCH_3]$ $X10^{-2}$	[CTADC] $X10^{-4}$	k $x10^2$ 303 K	dm^3 mol^{-1} sec^{-1} 313 K	323 K	$\Delta H^\#$ ($KJmol^{-1}$)	$-\Delta S^\#$ ($Jmol^{-1}K^{-1}$)
Methyl	0.7471	3.4132	1.66	2.38	3.05	22.18	167.39
Ethyl	0.7465	3.0570	1.32	2.10	2.67	26.13	156.23
Propyl	0.9904	3.3118	1.16	1.68	2.53	29.09	147.90
Isopropyl	1.3714	3.6175	0.55	1.10	2.09	51.72	79.32

Table-3: Rate constants for the oxidation of sulfides by CTADC.
Solvent = Acetic acid: DCM, 20:80

Alkyl phenyl sulfide	[$C_6H_5SCH_3$] X10^{-2}	[CTADC] X 10^{-4}	Kx10^3 dm^3 mol^{-1} sec^{-1} 303 K
Methyl	1.2850	3.6170	0.73
Ethyl	1.6841	3.2608	0.265
Propyl	1.1349	3.5156	0.258
Isopropyl	1.3766	3.3627	0.124
n-butyl	1.2533	3.0570	0.115

CONCLUSION

The oxidation of aryl methyl sulfides in aqueous acetic acid medium and in dichloromethane leads to the formation of sulfoxides. The reaction follows a simple second order kinetics. The suggested mechanism was in accordance with the observed kinetic data.

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