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Synthesis of Benzyl Phenyl Sulfoxide from Benzyl Phenyl Sulphide using $[\text{Fe}(\text{Phen})_3]^{3+}$ By Kinetic Method

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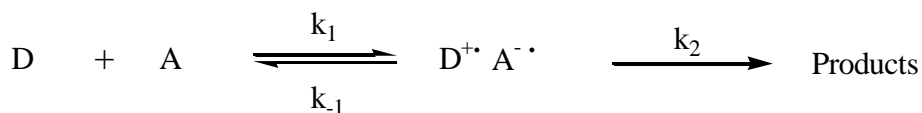
Abstract : The present work is on the selective synthesise of benzyl phenyl sulfoxide from benzyl phenyl sulfide without formation of sulfone using $[\text{Fe}(\text{Phen})_3]^{3+}$ as oxidant. Usually oxidation of sulphides produces mixture of sulfoxide and sulfone. But in this method only sulfoxide is identified as the product without further oxidation to sulfone. Benzyl phenyl sulfide (BPS) has been taken as a reactant and $[\text{Fe}(\text{Phen})_3]^{3+}$ as oxidant. The reaction was carried out at a p^{H} of 4-5 in aqueous methanol medium. The yield of the product sulfoxide formed was studied by varying the concentration of BPS, $[\text{Fe}(\text{Phen})_3]^{3+}$, Temperature, p^{H} and solvent composition. The optimum conditions for the maximum yield of sulfoxide. It has been observed that one mole of benzyl phenyl sulfide consumed two moles of $[\text{Fe}(\text{phen})_3]^{3+}$.¹⁻⁴ The maximum yield of sulfoxide achieved in the present study was approximately 92% while sulfone formation being only 2 % confirming selective oxidation of sulfoxide. The purification of the product performed using silica gel column chromatography with EtOAc/n-hexane (1/10). The product sulfoxide was characterized by IR and ¹H-NMR and GC-MS studies.

Introduction

Electron transfer (ET) reactions have long been a central focus in mechanistic inorganic chemistry. This interest stems partly from the fact that many transition metal complexes are versatile redox reagents. The electron exchange between an inorganic oxidant and a reductant is often a chemically reversible process owing to the common occurrence of thermodynamically stable redox pairs differing by a single electron. By contrast, the electron rich organic donors (D) generate transient cation radicals and the analogous electron attachment to electron poor organic acceptors (A) generally affords transient anion radicals. This leads to a mechanistic situation in which the stepwise formation of products via ET, is kinetically difficult to distinguish from a concerted single step process, especially when back electron transfer (k_{-1}) and the follow up step (k_2) are facile.

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However, ET concept has recently been accepted in the area of organic chemistry and the Marcus theory has been applied successfully to many organic redox reactions. The growth in the chemistry of organic sulfoxides during last decade was due to their importance as synthetic intermediates for the production of a wide range of biologically and chemically active molecules. The oxidation of sulfides to sulfoxides is the most straightforward synthetic route to the latter, and numerous reagents and oxidative procedures are available for this transformation. However, many of them cause over oxidation to the corresponding sulfones. Therefore, control of the reaction conditions, that is, time, temperature and the relative amount of oxidants, plays an important role in avoiding the formation of oxidation side products, but this is often hard to achieve and therefore there is still considerable interest in the development of selective oxidants for this transformation⁵⁻¹¹. Benzyl phenyl sulfide was selected as a model substrate, and the oxidation of this substrate with $[\text{Fe}(\text{Phen})_3]^{3+}$ in various effects were studied.

Experiments

The kinetic studies were carried out under pseudo first order conditions with BPS, $[\text{Fe}(\text{NN})_3]^{3+}$ complex ratio of at least 15:1 in perchloric acid medium. The substrate with all additives except the oxidant was allowed to attain the experimental temperature by keeping them separately in the constant temperature bath. A known volume of $[\text{Fe}(\text{NN})_3]^{3+}$ complex was then transferred to the reaction mixture at zero time and shaken well. The rate of formation of $[\text{Fe}(\text{NN})_3]^{2+}$ complex was followed using the UV-Vis spectrophotometer by measuring the change in the absorbance at wavelength 510 nm corresponding to $[\text{Fe}(\text{phen})_3]^{2+}$. The $[\text{Fe}(\text{NN})_3]^{2+}$ complex had molar extinction coefficients of the order of $\sim 1 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$ in the observed region while the corresponding iron(III) complex was practically transparent at this wavelength region. The reaction was followed at definite time intervals by following the increase in absorbance of $[\text{Fe}(\text{NN})_3]^{2+}$ till maximum absorbance (A_∞) was reached.

Results & Discussion

The investigation was first carried out with the oxidant, tris(1,10-Phenanthroline)iron(III) and the BPS. A known excess of $[\text{Fe}(\text{Phen})_3]^{3+}$ was mixed with a known concentration of BPS under the experimental conditions of $[\text{H}^+] = 1.5\text{M}$ in 50% aqueous CH_3OH at 305K. The reaction was followed by measuring the change of absorbance of $[\text{Fe}(\text{phen})_3]^{2+}$ at 510nm. After the reaction was complete, the concentration of the product, $[\text{Fe}(\text{phen})_3]^{2+}$ was calculated from its absorbance maximum and the known value of molar extinction coefficient and this gave the amount of $[\text{Fe}(\text{phen})_3]^{3+}$ consumed in the reaction. The reaction of $[\text{Fe}(\text{phen})_3]^{3+}$ with BPS follows simple second order kinetics first order each in iron(III) complex and the BPS- first order in the BPS and first order in the oxidant.

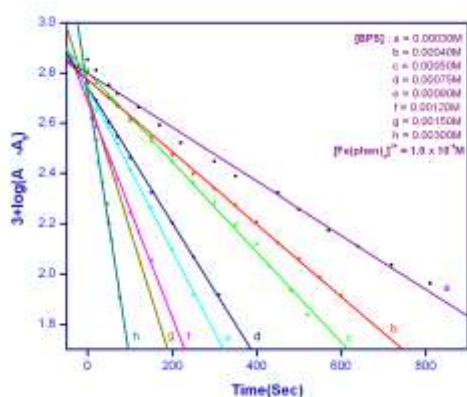


Figure. 1: Plot of $\log (A_\infty - A_t)$ vs time

The rate of oxidation is accelerated by an increase in methanol content of the medium and this has been accounted for the formulation of a charge separated complex in the rate determining step. The electron transfer mechanism has been confirmed from the linear plots observed, when $\log k_2$ values are plotted against oxidation potentials of sulfide. When the concentration of oxidant is varied, the pseudo first rate constants remain constant. Further, straight lines are obtained when $\log (A_\infty - A_t)$ are plotted against time for different concentrations of oxidant. A sample plot for the oxidation of BPS with $[\text{Fe}(\text{phen})_3]^{3+}$ is given in Figure 2. These facts confirm that the order with respect to oxidant is one (Table 1).

Table 1: Pseudo first order rate constant (k_1) and second order rate constant (k_2) values for the oxidation of benzyl phenyl sulfide by $[\text{Fe}(\text{NN})_3]^{3+}$

[BPS] $\times 10^3, \text{M}$	$[\text{Fe}(\text{phen})_3]^{3+}$ $\times 10^4, \text{M}$	$k_1 \times 10^3, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$	[BPS] $\times 10^3, \text{M}$	$[\text{Fe}(\text{bpy})_3]^{3+}$ $\times 10^4, \text{M}$	$k_1 \times 10^3, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$
$[\text{H}^+] = 1.0 \text{ M}, \mu = 1.2 \text{ M}, \text{Temp.} = 25^\circ \text{ C}, \text{MeOH} = 70\% \text{ (v/v)}$							
0.15	1.0	1.23± 0.09	8.23± 0.58	0.15	1.0	1.02±0.13	6.83± 0.86
0.3	1.0	2.46± 0.14	8.21± 0.46	0.3	1.0	2.05± 0.13	6.84± 0.43
0.4	1.0	3.32± 0.09	8.29± 0.22	0.6	1.0	4.10± 0.23	6.83± 0.38
0.5	1.0	4.12± 0.14	8.24± 0.27	0.75	1.0	5.14± 0.22	6.85± 0.29
0.75	1.0	6.20± 1.95	8.26± 2.60	0.9	1.0	6.17±0.18	6.86± 0.20
0.9	1.0	7.44± 0.27	8.27± 0.30	1.2	1.0	8.24± 0.59	6.87±0.49
1.2	1.0	9.90± 0.69	8.25± 0.58	1.5	1.0	10.3± 0.71	6.86± 0.47
1.5	1.0	12.4± 0.87	8.26± 0.58	3.0	1.0	20.5±0.11	6.85±0.38
3.0	1.0	24.9±1.93	8.31± 0.64				
$[\text{H}^+] = 3.0 \text{ M}, \mu = 3.2 \text{ M}, \text{Temp} = 30^\circ \text{ C}, \text{MeOH} = 30\% \text{ (v/v)}$							
1.5	0.6	3.14± 0.10	2.09± 0.07	1.5	1.0	3.29± 0.25	2.19± 0.17
1.5	0.8	3.11± 0.10	2.07± 0.07	1.5	1.2	3.29± 0.25	2.19± 0.17
1.5	1.0	3.13± 0.09	2.09± 0.06	1.5	1.3	3.34± 0.16	2.23± 0.11
1.5	1.2	2.97± 0.10	1.98± 0.07	1.5	1.4	3.34± 0.19	2.23± 0.13
1.5	1.4	3.10± 0.09	2.07± 0.06	1.5	1.5	3.29± 0.23	2.19± 0.15
				1.5	1.6	3.30± 0.19	2.20± 0.13

The rate constant increases at lower concentration of perchloric acid and at higher concentrations the rate constant remains constant.

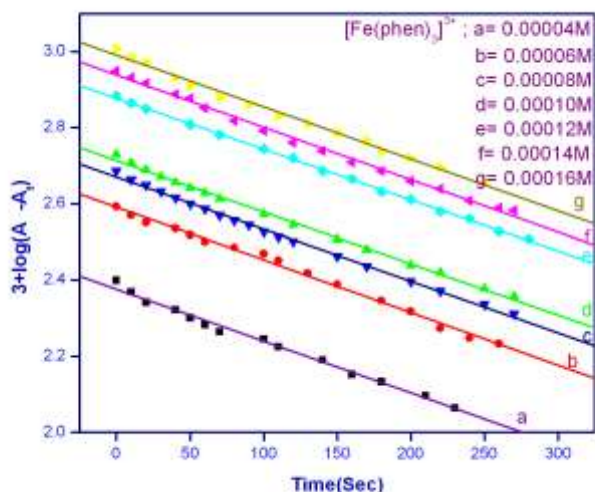


Figure. 2 Plot of $\log (A_{\infty} - A_t)$ vs time for $[\text{Fe}(\text{phen})_3]^{3+}$ oxidation of BPS

The reaction has been found to be first order with respect to BPS and $[\text{Fe}(\text{phen})_3]^{3+}$ complex. The reaction was found to be decreased with increase in concentration of H^+ ion while acceleration effect was found with decrease in polarity of the medium. The observed stoichiometry of 2:1 between $[\text{Fe}(\text{phen})_3]^{3+}$ and BPS. The involvement of single ET has been proved from the mechanism. Further the ET mechanism was confirmed by the double logarithmic plot of oxidation potential of BPS and Iron(III) complex against the rate constant.

Activation parameters were determined from the k_2 values obtained at the temperatures 293 K, 298 K, 308 K, 313 K. The enthalpy of activation ΔH^\ddagger and the entropy of activation ΔS^\ddagger are evaluated from the linear Eyring's plot of $\log k_2/T$ vs $1/T$. The activation parameters are presented in Table 1. The positive ΔH^\ddagger value and negative ΔS^\ddagger value show that the reaction is thermodynamically feasible.

Substrate	$k_2, \text{M}^{-1}\text{s}^{-1}$					ΔH^\ddagger kJ mol^{-1}	$-\Delta S^\ddagger$ $\text{Jmol}^{-1} \text{K}^{-1}$
	293K	298K	303K	308K	313K		
BPS	0.740 ± 0.06	1.17 ± 0.06	2.07 ± 0.04	2.76 ± 0.35	4.51 ± 0.34	64.3 ± 4.40	27.8 ± 15.0

Conclusion

The oxidation of sulfides to sulfoxides is of significant importance in organic chemistry, both for fundamental research and for a wide range of applications.¹²⁻¹⁴ The present study was carried out on BPS with 1,10-phenanthroline iron(III) complexes. The reaction is found to be first order in the substrate and first order in the oxidant. The kinetic study was carried out in aqueous CH_3OH (v/v) under pseudo first-order conditions. The second order rate constant remains constant at different concentration of substrates. Further $\log k_1$ vs $\log [\text{substrate}]$ plots give straight lines with unit slope. The constancy of k_2 values along with the unit slopes obtained indicate the first order dependence of the reaction on $[\text{BPS}]$. The plots of k_1 vs $[\text{substrate}]$ are linear and pass through the origin. This result excludes the formation of complex between substrate and $[\text{Fe}(\text{Phen})_3]^{3+}$.

Retardation by $[\text{H}^+]$ may be attributed to the conversion of the more reactive species to the less reactive species in the mixture. Thus decrease in the rate with increase in $[\text{H}^+]$ can be attributed to the formation of more and more $[\text{HFe}(\text{NN})_3]^{4+}$ with rise in $[\text{H}^+]$. The rate is independent of ionic strength. This may presumably be due to the attack of an ion on a neutral molecule in the rate determining step. The rate of oxidation is accelerated by an increase in methanol content of the medium. This may be due to decrease in polarity of the medium.

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