

## Kinetics and mechanism of Ru(III)-catalysed oxidation of organic sulphides and triphenylphosphine by N-methylmorpholine N-oxide

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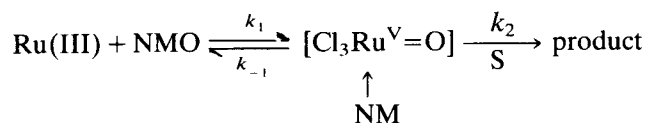
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**Abstract.** The selective oxidation of thioethers to sulphoxides and of PPh<sub>3</sub> to PPh<sub>3</sub>O can be effected by NMO in DMF as solvent in the presence of Ru(III) chloride as catalyst. Kinetic investigations indicate that the orders with respect to the catalyst and oxidant are one each. The order with respect to the substrate is variable being fractional order at low concentrations and zero at high concentrations. Spectrophotometric studies reveal the formation of a 1:1 complex between the substrate and the catalyst. A mechanism consistent with the above observations has been proposed and verified.

**Keywords.** Oxidation; sulphides; N-methylmorpholine N-oxide; catalysis by Ru(III); complex formation.

### 1. Introduction

The oxidation of thioethers R<sub>1</sub>-S-R<sub>2</sub> can yield either the corresponding sulphoxide R<sub>1</sub>-SO-R<sub>2</sub> or the sulphone R<sub>1</sub>-SO<sub>2</sub>-R<sub>2</sub> or both depending on the method used. Homogeneous catalysis by complexes of molybdenum and vanadium is one of the means of achieving selective oxidation of organic substrates (alkenes, amines, sulphides, triphenylphosphine, etc.) via oxygen transfer from hydroperoxides (Sheldon and Kochi 1980). Pyridinium chloro chromate (PCC) is used as a selective oxidant for the oxidation of sulphides to sulphoxides (Panigrahi and Mahapatro 1981). *cis*-RuCl<sub>2</sub>(DMSO)<sub>4</sub> and *trans*-RuBr<sub>2</sub>(DMSO)<sub>4</sub> are used as catalysts for the oxidation of sulphides to sulphoxides (Riley and Shumate 1984). Sharpless *et al* (1976) have carried out reactions using several N-oxides to oxidize cholestanol, geraniol, etc. Vijayasri *et al* (1987) have studied the kinetics and mechanism of the oxidation of secondary alcohols by N-methylmorpholine N-oxide using RuCl<sub>3</sub> as catalyst in DMF as the solvent and reported that N-methylmorpholine N-oxide (NMO) acts as an oxygen transfer agent in oxidizing secondary alcohols to ketones. The following mechanism has been proposed and verified (Vijayasri *et al* 1987):



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It was felt that the kinetics and mechanism could be different if one used a substrate capable of forming a complex with the catalyst.  $\pi$  donors like alkenes and soft bases (sulphur in thioether) might be expected to form complexes with a soft acid like Ru(III) (soft acid-soft base interaction). There are no significant reports on the kinetics of the Ru(III) chloride-catalysed oxidation of organic sulphides and  $\text{PPh}_3$  by NMO. The oxidation of dibutylsulphide, phenylmethylsulphide, dibenzylsulphide and triphenylphosphine is reported in this paper. A suitable mechanism has been proposed based on kinetic and spectral studies.

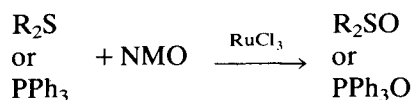
## 2. Experimental

N-methylmorpholine N-oxide (Fluka) was used as such. All the sulphides were prepared according to the standard procedure (Vogel 1971). Triphenylphosphine (KL) was recrystallised using methanol as solvent.  $\text{RuCl}_3$  (JM) was used as such. Solutions of  $\text{RuCl}_3$  in DMF were standardised by the method reported by Horiuchi and Ichiyyo (1970). DMF was purified according to the method of Faulkner and Bard (1968).

Kinetic studies were carried out at  $35 \pm 0.1^\circ\text{C}$ . The concentration of NMO remaining at any instant was determined titanometrically as reported earlier (Caroling *et al* 1986). In the low concentration region of sulphides the amount of sulphoxide formed was estimated according to the method of Barnard and Hargrave (1951). The initial rates in  $\text{mol l}^{-1} \text{min}^{-1}$  were obtained from the concentration time plots using the method of Pearlson and Simons (1945). Electronic spectra were recorded on a Hitachi 220-A Spectrophotometer. IR spectra were recorded on a Perkin Elmer 983G spectrometer. The formation of sulphoxide was confirmed by comparison of the retention times recorded gas chromatographically using an FFAP column, with those of authentic samples. The formation of the product was also confirmed by IR spectrum through the characteristic S-O and P-O stretching frequencies.

## 3. Results and discussion

Dibutylsulphide, phenylmethylsulphide and dibenzylsulphide were oxidized by NMO in the presence of  $\text{RuCl}_3$  to the corresponding sulphoxides and  $\text{PPh}_3$  to  $\text{PPh}_3\text{O}$ . The amount of the oxidation product corresponds to the amount of N-oxide consumed which gives a stoichiometry of 1:1 for the reaction between the substrate and NMO.



There is no significant oxidation of the sulphide and triphenylphosphine by NMO in the absence of the catalyst. The reaction in the presence of large excess of the sulphide showed first-order dependence on the oxidant (NMO) as evidenced by the

linearity of  $\log(a - x)$  vs. time as well as the constancy of the pseudo first-order rate constant. The order in the catalyst is found to be one whereas that in the substrate is zero at high concentration ( $[\text{sulphide}] > 0.5 \text{ M}$ ;  $[\text{PPh}_3] > 0.1 \text{ M}$ ) (table 1) and fractional at low concentrations ( $[\text{sulphide}] < 0.1 \text{ M}$ ;  $[\text{PPh}_3] < 0.05 \text{ M}$ ) (figure 1).

**Table 1.** Determination of the orders with respect to the reactants at high concentrations of the substrate.

Temperature =  $35 \pm 0.1^\circ\text{C}$ ; solvent = DMF

Substrate	$10^2[\text{NMO}]$	$[\text{S}]$	$10^4[\text{RuCl}_3]$	$10^3k_1$	$\frac{k_1}{[\text{Ru(III)}]}$	$\frac{k_2}{(\text{M}^{-1} \text{min}^{-1})}$
	(M)	(M)	(M)	( $\text{min}^{-1}$ )		
Dibutylsulphide	15.22	1.5	4.0	7.65		19.1
	9.45	1.5	4.0	7.55		18.9
	7.07	1.5	4.0	7.61		19.0
	4.45	1.5	4.0	7.58		18.9
	4.45	1.0	4.0	7.24		18.1
	4.45	0.7	4.0	7.40		18.5
	4.45	0.5	4.0	7.41		18.5
	4.45	0.5	5.0	10.10		20.2
	4.45	0.5	3.0	5.91		19.7
	4.45	0.5	2.0	3.85		19.2
				$k_2(\text{mean}) = 19.01 \pm 0.21 \text{ M}^{-1} \text{min}^{-1}$		
Phenylmethylsulphide	15.20	1.5	4.0	7.01		17.5
	10.16	1.5	4.0	6.61		16.5
	7.10	1.5	4.0	6.36		15.9
	5.25	1.5	4.0	6.54		16.3
	5.10	1.0	4.0	6.61		16.5
	5.10	0.7	4.0	6.56		16.4
	5.10	0.5	4.0	6.77		16.9
	5.10	0.5	5.0	8.69		17.4
	5.10	0.5	3.0	4.89		16.3
	5.10	0.5	2.0	3.32		16.6
				$k_2(\text{mean}) = 16.63 \pm 0.18 \text{ M}^{-1} \text{min}^{-1}$		
Dibenzylsulphide	10.60	1.0	4.0	7.44		18.6
	7.87	1.0	4.0	7.84		19.6
	4.82	1.0	4.0	7.37		18.4
	4.82	0.7	4.0	7.54		18.9
	4.82	0.5	4.0	7.40		18.5
	4.82	0.5	3.0	5.77		19.2
	4.82	0.5	2.0	3.66		18.3
				$k_2(\text{mean}) = 18.78 \pm 0.18 \text{ M}^{-1} \text{min}^{-1}$		
Triphenylphosphine	2.55	0.25	1.0	2.11		21.1
	1.94	0.25	1.0	2.04		20.4
	1.40	0.25	1.0	2.23		22.3
	1.10	0.25	1.0	2.17		21.7
	1.10	0.20	1.0	2.10		21.0
	1.10	0.15	1.0	2.17		21.7
	1.10	0.10	1.0	2.11		21.1
	1.10	0.10	2.0	4.25		21.3
	1.10	0.10	0.75	1.60		21.3
				$k_2(\text{mean}) = 21.32 \pm 0.18 \text{ M}^{-1} \text{min}^{-1}$		

$k_1$  = Pseudo first-order rate constant ( $[\text{S}] \gg [\text{NMO}]$ ).

$k_2$  = Overall second order rate constant.

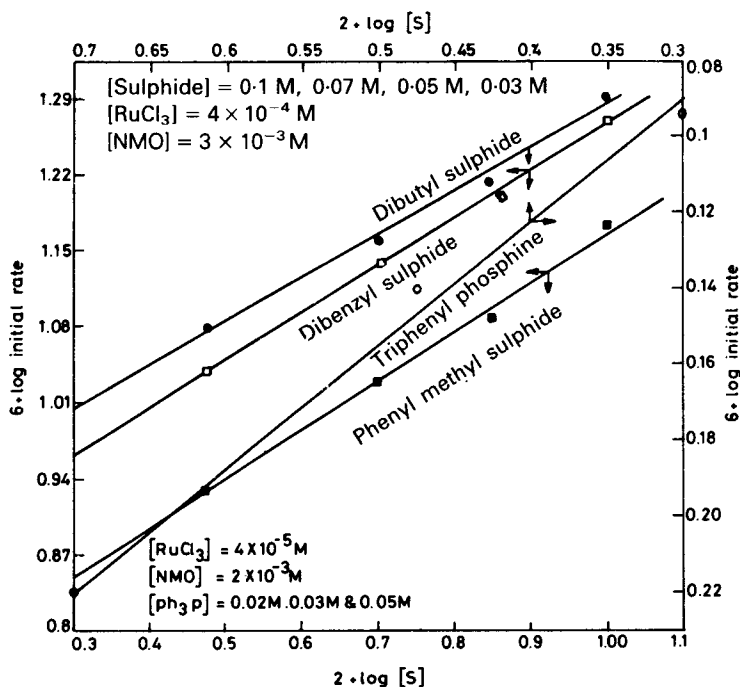


Figure 1. Order with respect to the substrate at low concentrations.

A fractional order in the substrate could arise as a result of complex formation. Spectral studies were undertaken to detect complex formation, if any. The absorption spectra recorded at high concentration of the substrate and low concentration of the catalyst are given in figure 2. The decrease in absorbance at 420 nm ( $\lambda_{\text{max}}$  of  $\text{RuCl}_3$ ) and increase in absorbance due to a new peak in the absorption spectrum indicate complex formation. The decrease in the absorbance at 420 nm was used to determine the equilibrium constant. The Scott equation (Foster and Hammick 1954) was employed to determine  $K$  in all the cases.

$$\frac{[D]_0[A]_0}{\Delta O \cdot D} = \frac{[D]_0}{\epsilon} + \frac{1}{K\epsilon}$$

$[D]_0$  = concentration of donor (sulphide or  $\text{PPh}_3$ );

$[A]_0$  = concentration of acceptor ( $\text{RuCl}_3$ );

$\epsilon$  = extinction coefficient;

$K$  = equilibrium constant.

A plot of the LHS against  $[D]_0$  is linear (figure 3). The ratio, slope/intercept gives the value of  $K$ . These reactions are not inhibited by N-methylmorpholine (reduction product of NMO) and so any prior step involving the formation of N-methylmorpholine is unlikely. There is no polymerisation of acrylamide when it is added to the reaction mixture. Hence a free radical mechanism is unlikely. Based on the kinetic and spectral studies the following mechanism is proposed.

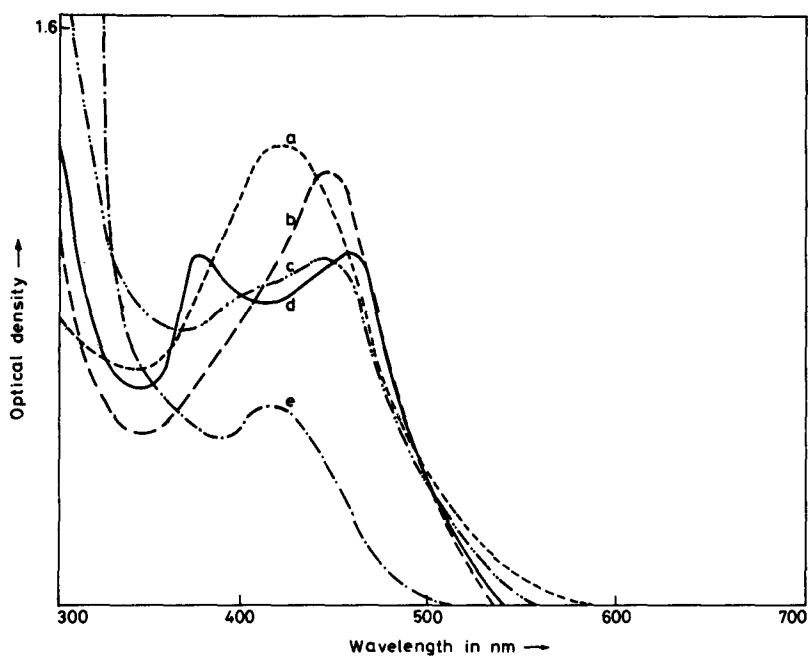


Figure 2. Absorption spectra of (a) RuCl<sub>3</sub> ( $2 \times 10^{-4}$  M) in DMF, (b) RuCl<sub>3</sub> ( $2 \times 10^{-4}$  M) and phenylmethylsulphide (0.2 M) in DMF, (c) RuCl<sub>3</sub> ( $2 \times 10^{-4}$  M) and dibenzylsulphide (0.2 M) in DMF, (d) RuCl<sub>3</sub> ( $2 \times 10^{-4}$  M) and dibutylsulphide (0.2 M) in DMF, (e) RuCl<sub>3</sub> ( $2 \times 10^{-4}$  M) and triphenylphosphine ( $2 \times 10^{-2}$  M) in DMF.

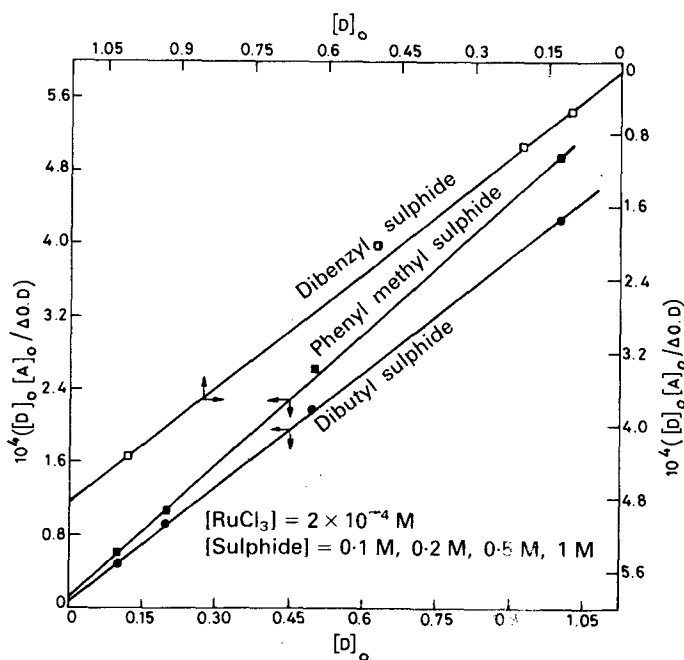
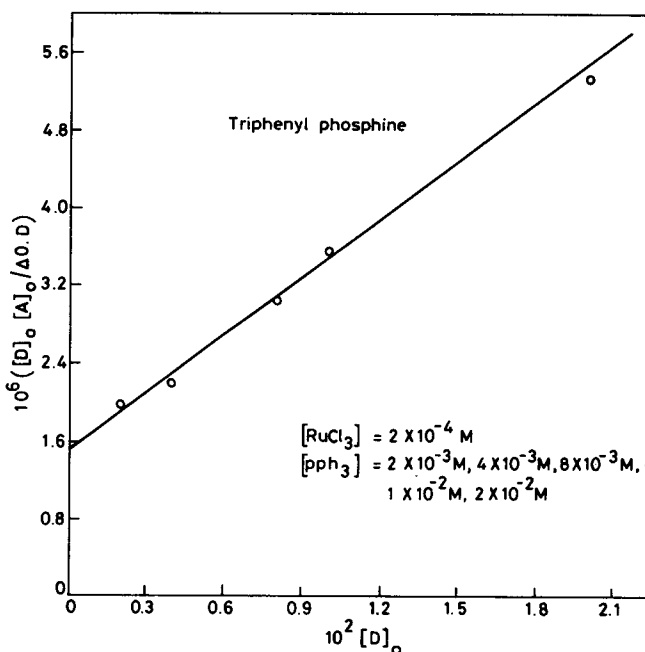
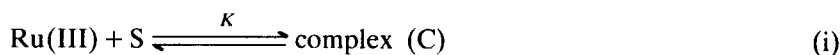


Figure 3a. Linear plots according to the Scott equation for the determination of the equilibrium constant.



**Figure 3b.** Linear plots according to the Scott equation for the determination of the equilibrium constant.



In the above scheme for the mechanism of the reaction step (ii) or (iii) can be considered rate determining. If step (iii) is taken to be rate determining, in order to account for the observed orders it will be necessary to consider that the equilibrium constants for steps (i) and (ii) are very small. There is no evidence to justify this. Therefore step (ii) is considered the rate determining step. This mechanism leads to the following rate expression (1) where  $[\text{Ru(III)}]_i$  is the initial concentration of the catalyst

$$\text{initial rate} = \frac{k_2 K [\text{Ru(III)}]_i [\text{S}] [\text{NMO}]}{1 + K [\text{S}]} \quad (1)$$

which can be rearranged to give (2).

$$\frac{1}{\text{initial rate}} = \frac{1}{K k_2 [\text{Ru(III)}]_i [\text{NMO}] [\text{S}]} + \frac{1}{k_2 [\text{Ru(III)}]_i [\text{NMO}]} \quad (2)$$

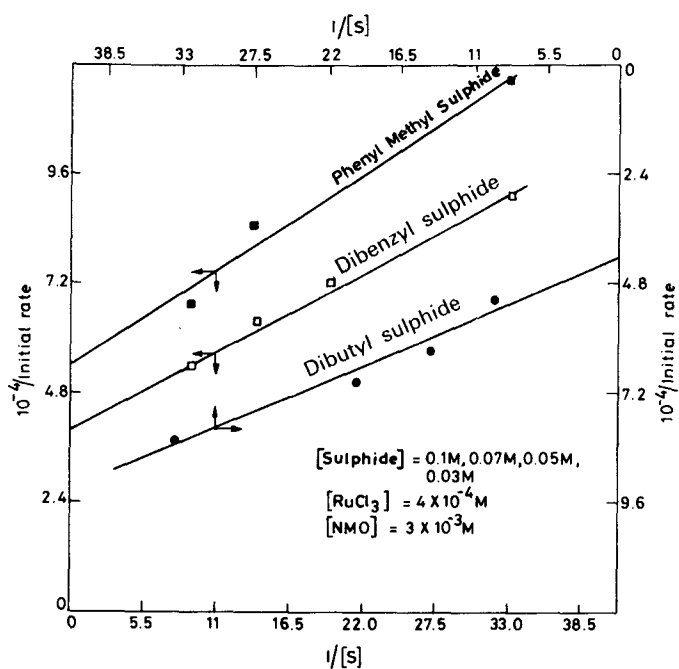


Figure 4a. Double reciprocal plot verifying the rate expression.

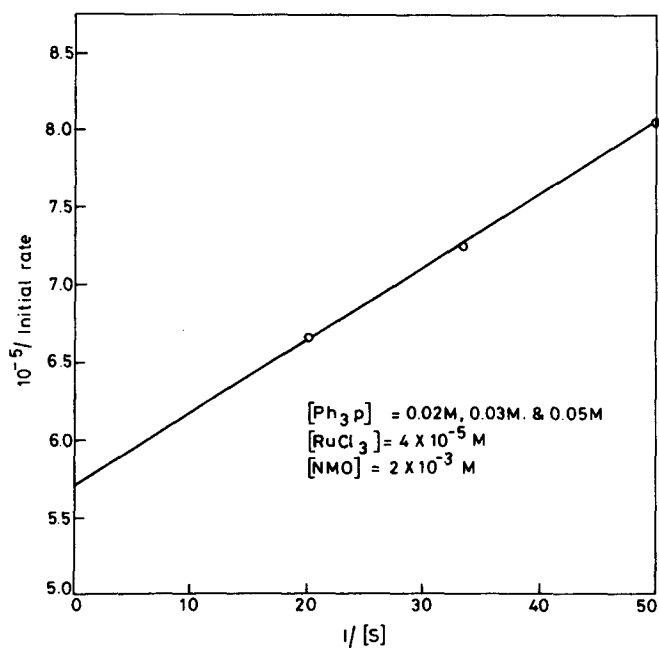


Figure 4b. Double reciprocal plot verifying the rate expression.

**Table 2.** Evaluation of  $K$  and  $k_2$  from the double reciprocal plot.

Substrate	$K/l \text{ mol}^{-1}$		$k_2/M^{-1} \text{ min}^{-1}$	
	From double reciprocal plot	Spectrophotometric measurements	From double reciprocal plot	Under zero order conditions with respect to [S]
Dibutylsulphide	30.7	29.8	19.9	$19.01 \pm 0.21$
Phenylmethylsulphide	27.7	26.9	15.4	$16.63 \pm 0.18$
Dibenzylsulphide	27.7	23.9	18.6	$18.78 \pm 0.18$
Triphenylphosphine	121.0	122.0	21.9	$21.32 \pm 0.18$

According to (2) a plot of  $1/\text{initial rate}$  against  $1/[\text{substrate}]$  (figure 4) should be linear. One can evaluate  $k_2$  from the intercept and  $K$  from the slope of this double reciprocal plot. From table 2 it is seen that there is good agreement between the values of  $K$  determined spectrophotometrically and kinetically. The values of  $k_2$  determined under zero order conditions with respect to the substrate agree well with the value of  $k_2$  obtained from the double reciprocal plot. At high concentration of substrate ( $[\text{sulphide}] > 0.5 \text{ M}$  and  $[\text{PPh}_3] > 0.1 \text{ M}$ ),  $1$  is negligible when compared to  $K[\text{S}]$  which explains the zero order in the substrate, while at low concentrations of substrate ( $[\text{sulphide}] < 0.1 \text{ M}$ ;  $[\text{PPh}_3] < 0.05 \text{ M}$ ),  $K[\text{S}]$  is not negligible as compared to  $1$  which explains the fractional order in the substrate. Thus in the case of substrates capable of complex formation, the mechanism is quite different though the kinetic behaviour is the same as reported earlier for secondary alcohols (Vijayasri *et al* 1987).

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