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# Catalysis of the oxone oxidation of some sulphoxides by Ru(III)

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Ru(III) catalyses the oxidation of some sulphoxides to sulphones in a clean irreversible process; a two-pathway mechanism–catalyst dependent and independent has been proposed to explain the kinetic behaviour.

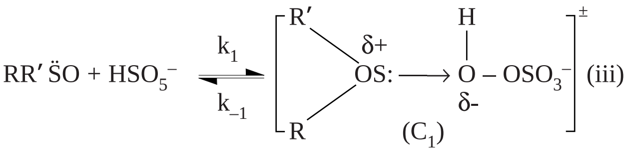
Low-valent ruthenium complexes catalyse the oxidation of various substrates in combination with various oxidants. The oxoruthenium species, formed by the reaction of low-valent ruthenium complex $Ru^{n+}L_n$ with oxidants, are believed to be the catalytic active species.[1] The catalyst enhances the electrophilic activity of the oxidant and the reaction proceeds with selectivity. The present work deals with the kinetics and mechanistic aspects of Ru(III) catalysed oxidation of several diaryl, dialkyl and alkyl aryl sulphoxides with $HSO_5^-$, a poor nucleophile.

Oxone ($2KHSO_5.KHSO_4.K_2SO_4$) was purchased from Aldrich. Its aqueous solutions are reasonably stable. A test using permanganate ensures the absence of free $H_2O_2$. Experiments were carried out under pseudo-first-order conditions by keeping the sulphoxides always in excess over the oxidant. Reactions were followed iodometrically. The amount of sulphone formed corresponds to the amount of $HSO_5^-$ consumed which gives a stoichiometry of 1:1 between the sulphoxide and $HSO_5^-$ in the presence of the catalyst. Sulphone was the only product and identified by m.p. and TLC.

The reaction exhibits first-order dependence each on oxidant and reductant. Ru(III) catalyses the reaction and a mixed order dependence on the concentration of Ru complex is observed. The rate of conversion did not change in acrylonitrile ruling out the possibility of radical mechanism. Studies on the solvent effect indicate that the transition state is more polar than the reactants in the initial state. The lack of solvent isotope effect excludes the rate-controlling participation of water as a nucleophile.

Substituent effects are used to probe into the reaction mechanism. Several *p,p′*-disubstituted diphenyl sulphoxides are employed and the kinetic studies reveal that electron-releasing groups enhance the reactivity while electron-withdrawing ones inhibit the rate. Experimental data are well correlated with $\rho(2\sigma)$ or $\rho(2\sigma°)$ relationships. The $\rho$ values ($\approx -0.3$) suggest an electron-deficient reaction centre in the transition state. The reaction constant values are inversely proportional to the temperature. The adherence to the Hammett equation shows that all the diaryl sulphoxides react by the same mechanism.

The very low reaction constant value suggests a mechanism in which sulphide suffers the electrophilic attack of $HSO_5^-$. The ionizing power of the solvent enhances the reactivity. Two-pathway mechanism has been proposed to explain the kinetic behaviour. The mixed order dependence on Ru(III) can be accounted for by considering that a fraction of the overall reaction proceeds *via* an alternative path independent of the involvement of catalyst.



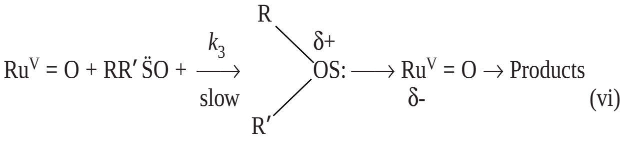
(forward step rate-limiting)

**Scheme 1**

$$C_1 \xrightarrow[\text{fast}]{k_2} RR'SO_2 + HSO_4^- \qquad \text{(iv)}$$

**Scheme 2**

$$Ru(III) + HSO_5^- \overset{K}{\rightleftharpoons} Ru^V = O + HSO_4^- \qquad \text{(v)}$$



Combined rate-law,

$$\frac{\text{Initial rate}}{[SO][Ox]} = k = k_1 + k_3 K'[Ru(III)] \qquad \text{(ix)}$$

where $K' = \dfrac{K}{[HSO_4^-]}$

Since the initial rates are determined, $[HSO_4^-]$ will be negligible and it is assumed as a constant. The good fit of the plot of initial rate/[SO][Ox] *vs* [Ru(III)] with a satisfactory correlation coefficient $r = 0.997$, favours the proposed mechanism. Complexation, if any, between substrate and ruthenium, as proposed in the oxidation of sulphides by NMO[16] can be excluded since the conversion follows clean first-order dependence on the concentration of sulphoxide.

The rate-coefficients are analysed using multiparameter extensions of the Hammett's equation. Goodness of the fit is judged by high $R$, low SE, small $f$ and $\psi$ values ($f$ = SD/RMS). The rate data fit well with all the triparametric equations including Swain–Lupton treatment. Yukawa–Tsuno equation is applied by plotting log $k_{obs}$ *vs* ($\sigma + r^+\Delta\sigma_R^+$). Quantity $r$, the enhanced resonance effect is $\approx 0.1$. The small $r^+$ value[17] probably indicates the small extent of bond breaking in the transition state.

The kinetic behaviours are similar in dialkyl and alkyl aryl sulphoxides. The linear Exner plot of log $k_{30°}$ *vs* log $k_{20°}$ ($r = 0.995$) favours a similar mechanism in all the sulphoxides studied. $\Delta G^{\#}$ values are nearly constant further confirming the above view. Activation parameters are of the same order of magnitude as observed for typical nucleophilic reactions.[3,4,21]

Techniques used: TLC, IR.

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Table 1: Effect of oxidant, substrate and catalyst on the reaction rates of DPSO at 303 K
Table 2: Dependence of ionic strength, solvent composition and acrylonitrile on the reaction rate at 303 K
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Table 4: Rate constants and activation parameters for the oxidation of sulphoxides
Table 5: Reaction constant values for different correlations at different temperatures

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