Os(VIII) – catalysis on the oxidation of some diaryl sulphoxides with bromamine-B in alkaline medium

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The effect of substituents reveals the electronic character of Os(VII/)-catalysed N-bromobenzene sulphonamide (bromamine-B) oxidation of some diaryl sulphoxides to sulphones in a strongly alkaline (pH-11.5) t-butanol-water (1:1 v/v) medium and the conversion appears to be nucleophilic for bromamine-B (BAB). High dielectric constant of the medium favours the reactivity. The kinetic studies reveal that electron-withdrawing groups enhance the reactivity while electron-releasing ones inhibit the rate. It appears that the anion RNB⁺ is the reactive species of bromamine-B. The possibility of the formation of Os(VI)-BAB complex causing a retarding effect on the pseudo-first-order rate coefficients is discussed. Contrary to expectations there is a marked depression in the catalytic activity of Os(VIII) in the presence of other transition metals and pyridine bases such as 2,2’-bipyridyl and 1,10-phenanthroline. The probable reaction mechanisms are discussed on the basis of above results.

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The kinetics of redox reactions involving the platinum group metals such as osmium(VIII), ruthenium(III) and iridium(III) as homogeneous catalysts, have been studied extensively. OsO₄ is known to be an efficient catalyst in the oxidation of several organic compounds by various oxidants in aqueous alkaline as well as in acidic media. It is known to react across olefinic double bonds, as it is a well known agent for cis-hydroxylation. However, its ability to form complexes with compounds having no double bonds and thereby facilitating the oxidation in alkaline medium has been investigated.

We have reported the Os(VIII)-catalysed oxidation of sulphides by chloramine-B (CAB)² and methyl phenyl sulfides by bromamine-B (BAB)³ in alkaline medium. Despite intensive work on sulphoxide oxidations, conflicting reports have emerged regarding the electrophilic or nucleophilic nature of sulphoxide sites. It has been reported¹ that sulphoxides are known to be oxidised both electrophilically by peracids and nucleophilically by peracid anions. The present study has been undertaken to ascertain information concerning the electrophilic or nucleophilic nature of the sulphoxide site in this conversion using the effect of para-substituents on the reaction velocity. Also, this note analyses the rate retarding effects observed in this conversion in the presence of other transition metals and complexing bases using the available kinetic data.

Experimental

Osmium tetroxide (Johnson-Mathey) was dissolved in 0.001 mol dm⁻³ NaOH and analysed iodometrically. t-Butyl alcohol (BDH) was refluxed with quick lime for 6 h and distilled. The distilled alcohol was fractionated through a Dufton column. All the diaryl sulphoxides were obtained by the Friedel-Crafts reaction of substituted benzenes with thionyl chloride. All the sulphoxides were recrystallized from 95% ethanol and their purities were checked. Bromamine-B was prepared by the partial debromination of dibromamine-B⁸. The purity of the oxidant was checked iodometrically. Heavy water (99.4%) was supplied by Bhabha Atomic Research Centre, India. RuCl₃ (JM), PdCl₂ (Fluka), 2,2’-bipyridyl (Aldrich) and 1,10-phenanthroline (EM) were used as supplied without further purification. All the other chemicals used were of AnalR grade.

Caution: Osmic acid is highly toxic and poisonous. Care should be taken while preparing the solution.

The reactions were carried out in 50% aqueous-t-butanol (v/v). All the solutions were kept in a thermostat at constant temperature which was controlled using Gallenkemp thermostat to an accuracy of ± 0.1% and the measurements were made between 288 and 318 K. The required volumes of these solutions for each run were mixed and 2 ml aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 ml 2% potassium iodide solution and the liberated iodine was titrated against standard thiosulphate to a starch end point. The method of least-squares was adopted to evaluate the pseudo-first order rate coefficients. The rate constants determined were the average of two or more determinations.
Stoichiometry and product analysis

The amount of sulphone formed corresponds to the amount of BAB consumed which gives a stoichiometry of 1:1 of sulphoxide and BAB.

\[
\begin{align*}
\text{S} + \text{BAB} + \text{NaOH} & \rightarrow \text{SO}_2 + \text{PhSO}_2\text{NH}_2 + \text{Na}^+ + \text{Br}^- \\
\rightarrow & \text{OsSO}_4
\end{align*}
\]

The reaction mixtures containing excess BAB were kept aside at kinetic temperature for 48 h. Then it was extracted with ether. The ether extract was washed with a saturated solution of NaCl containing 1% NaOH to remove benzenesulphonamide and dried over anhydrous sodium sulphate. The solid obtained on removal of ether was recrystallized from ethanol, mp. 125-127°C. The melting point of its mixture with an authentic sample of diphenyl sulphone was not depressed.

Results and discussion

Under pseudo-first-order conditions, it was observed that first order plots showed curvature after 40-45% conversion of BAB. Thereafter, the reaction becomes sluggish. Hence, the rate coefficients are evaluated on the basis of linear plots for the first 40-45% reactions. Under these conditions the results are reproducible. The inverse dependence of the rate on [BAB] (Table 1) is observed. The effect of sulphoxide on the rate coefficient at 303 K is listed in Table 1. The Michaelis-Menten dependence on [sulphoxide] is observed. It can be seen that the rate increases with increase in the concentration of the catalyt (Table 1). A simple plot of \( k_{\text{obs}} \) versus [OsO\(_4\)] is close to linear suggesting a unit order dependence on [OsO\(_4\)].

The pH dependent reaction shows no appreciable change in the rate with the change in the ionic strength of the medium affected by NaClO\(_4\) and Na₂SO₄. To verify the formation of radical as intermediates, a free radical scavenger, acrylonitrile (5% aqueous solution) was added to the reaction mixture. No turbidity was developed. Invariance of rate with acrylonitrile rules out a free radical process. Added chloride ion has no effect on the reaction velocity. Kinetic solvent isotope effect studies (\( k_{\text{D}}/k_{\text{H}} \sim 1 \)) do not indicate any significant solvent isotope effect.

Permittivity (\( D \)) values are approximately calculated from the values of pure solvents. The solvent effect on reactivity is quite significant. A plot of log \( k_{\text{A}} \) versus \( D^{-1} \) gives a negative slope suggesting the involvement of negative ion in the rate-limiting step.

The temperature dependence of this conversion is given in Table 2. The activation parameters were evaluated using an Eyring's plot of ln \( k_{\text{A}}/T \) versus. \( 1/T \) \( (r = 0.999; s = 0.757) \).

**Effect of substituents**

The effect of substituents on the reactivity has been investigated by employing some para-substituents in both the phenyl rings of sulphoxides. Even though there is a variation in the electronic properties of sulphoxides, the steric properties remain constant. Interestingly, the electron-withdrawing groups facilitate the rate of oxidation, while the electron-releasing ones retard the reaction (Table 2). Since there are only a very few substituents, we have not made attempts to do the complete correlation analysis. Anyway, the Hammett plot of log \( k_{\text{A}} \) versus \( \sigma \) indicated a small positive reaction constant (\( \rho \)) value (0.38).

Under the experimental conditions maintained the probable reactive species of BAB are \( \text{RNHB}r \) and \( \text{RNBr}^- \). Mahadevappa et al. have proposed \( \text{RNHCl} \) as the oxidising species in the Os(VIII)-catalysed oxidation of diphenyl sulphoxide by chloramine-T in alkaline medium. The effect of substituents in the present study very much reveals that sulphoxides are oxidised nucleophilically by the...
oxidant bromamine-B. It has been reported\textsuperscript{17} that sulfoxides are oxidised electrophilically by peracids and nucleophilically by peracid anions in peroxide oxidations. Ligand coupling between S and O\textsuperscript{-} will be more favourable if S is more electron-deficient which can be achieved by electron-withdrawers in the phenyl ring\textsuperscript{7}. Since the electron-withdrawing groups enhance the reactivity in the present investigations (Table 2), it is better to assume that the anion RNBr\textsuperscript{-} as the oxidising species under these conditions. The chloride ion catalysis\textsuperscript{10} can be explained through an interaction of RNH\textsubscript{X}...Cl\textsuperscript{3-}. No such catalysis is observed in the present study and this very much supports the RNBr\textsuperscript{-} as the only reactive species of BAB.

The inverse dependence of rate on [BAB] may be due to the formation of a less reactive species i.e., a dimer or N,N-dibromobenzene sulphonamide.

2BAB $\leftrightarrow$ (BAB\textsubscript{2}) or C\textsubscript{6}H\textsubscript{5}SO\textsubscript{2}NBr\textsubscript{2}

The idea that N-halo-compounds\textsuperscript{11} existing in equilibrium with the corresponding N,N-dihalo-compounds is well known. The curvature in the first order plots may also be due to the influence of products on the reaction velocity. The possibility of Os(VI)-sulphoxide/Os(VI)-BAB complex causing a retarding effect on reactivity is not ruled out. Mayell\textsuperscript{12} has given spectrophotometric evidence for the formation of Os(VI) species.

Effect of substituents observed in the present investigations is not uncommon. Ph\textsubscript{3}SO is oxidised 3.5 times faster than DMSO by potassium t-butyld peroxide\textsuperscript{15}. No polymerisation is observed with acrylonitrile. Acrylonitrile has no retarding effect on the rate of oxidation, ruling out a free radical mechanism. The positive $\rho$ value can be accounted for by the possible cleavage of O-O bond in the transition state in peroxybenzoic acid oxidation\textsuperscript{7}. It is very difficult to visualize such a type of situation in the present study. Also, O-O linkage break involves the formation of free radicals which is not well supported by experimental observations. The sulphur cation radical-like transition state is ruled out because it can be stabilized by both electron-releasing and electron-withdrawing groups resulting in a concave upward Hammett plot, contrary to experimental observations. Generally, in acidic medium sulphur behaves as a better nucleophile. In the present study, under alkaline conditions, the experimental results very much favour an electrophilic sulphone site.

\[
\text{Plot of } \frac{1}{k_1} \text{ against } \frac{1}{[SO]} \text{ is linear with positive intercept. This clearly gives the kinetic evidence for intermediate complex formation. The complex formation couldn't be confirmed spectrophotometrically and it is quite likely due to the very low value of formation constant. The cyclic nature of the complex is very much supported by large negative entropy values.}
\]

**Mechanism**

The zero order dependence on the concentration of the oxidant was observed in the Os(VIII)-catalysed oxidation of substrates with BAB\textsuperscript{14}, CAT\textsuperscript{9} and hexacyanoferrate(III)\textsuperscript{15}. The general mechanism of the reaction involves the oxidation of substrate by Os(VIII) and the subsequent oxidation of Os(VI) which was formed during the intramolecular electron transfer by the oxidant in a fast step. First-order dependence on [oxidant] observed in the present study suggests the possibility of the reaction routed through a ternary intermediate. Similar types of intermediates have been proposed in the Os(VIII)-catalysed oxidation of hypophosphite by CAT,\textsuperscript{10} EDTA catalysed chloramine-B oxidation of $\alpha$-phenylpyropanoic acids\textsuperscript{16} and the scheme is analogous to general features of Rocek's cooxidation mechanism proposed for the Cr(VI) oxidation of some substrates\textsuperscript{17-19}.

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**Table 2—Rate constants and activation parameters for the oxidation of sulfoxides**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_1 \times 10^3$ (s$^{-1}$)</th>
<th>$\Delta H^\circ$</th>
<th>$-\Delta S^\circ$</th>
<th>$\Delta G^\circ$</th>
<th>$r$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>6.5</td>
<td>25.5</td>
<td>19.4</td>
<td>4.4</td>
<td>0.999</td>
<td>0.707</td>
</tr>
<tr>
<td>$p,p'\text{-Me}$</td>
<td>5.5</td>
<td>23.5</td>
<td>16.0</td>
<td>9.5</td>
<td>0.999</td>
<td>0.693</td>
</tr>
<tr>
<td>$p,p'\text{-Cl}$</td>
<td>7.5</td>
<td>28.2</td>
<td>27.5</td>
<td>10.0</td>
<td>0.999</td>
<td>0.849</td>
</tr>
<tr>
<td>$p,p'\text{-Br}$</td>
<td>12.5</td>
<td>28.6</td>
<td>41.4</td>
<td>10.4</td>
<td>0.999</td>
<td>0.778</td>
</tr>
</tbody>
</table>

**NOTES**
Octahedral complexes of trans-[OsO$_4$(OH)$_2$]$_{2}^{2-}$ and [OsO$_4$(OH)(H$_2$O)]$^-$ have been reported by Griffith$^{20}$. In the alkaline solutions employed, OsO$_4$ seems to be completely converted into [OsO$_3$(OH)$_2$]$^-$$. Further combination with OH$^-$ yields the reactive form [OsO$_4$(OH)$_2$]$^{2-}$. Neither BAB nor Os(VIII) is an effective oxidant in this conversion of sulphoxides in alkaline medium. But in the presence of OsO$_4$, bromamine-B smoothly catalyses the oxidation of sulphoxides to sulphones. The kinetic data can be described by the following mechanism.

\[
[\text{OsO}_3(\text{OH})_2]^- + \text{OH}^- \xrightarrow{K} [\text{OsO}_4(\text{OH})_2]^{2-} \quad \text{(Os(VIII))}
\]

[OsO$_4$(OH)$_2$]$^{2-}$ is simply represented as OsO$_4$.\n
\[
\text{BAB} + \text{SO} \rightleftharpoons \text{C}_1
\]

where SO stands for Ph$_2$SO

\[
\text{C}_1 + \text{OsO}_4 \rightarrow \text{C}_2
\]

\[
\text{C}_2 \rightarrow \text{OsO}_4 + \text{Ar}_2\text{SO}_2 + \text{RNH}_2 + \text{Na}^+ + \text{Br}^-
\]

A plot of $[\text{OsO}_4]/k_{\text{obs}}$ versus $1/[\text{SO}]$ is fairly linear ($r = 0.995$) which very much supports the proposed mechanism. From the intercept and slope $k_2$ and $K_1$ values can be calculated. Rate equation (6) well describes the experimental observations.

Since the ternary intermediate (C$_2$) is bulky and disorganised, it will decompose in a fast step (step 4) and the formation of C$_2$ (step 3) is assumed to be slow and rate-limiting.

DMSO interacts with peroxy anions with its electrophilic sulphur site$^{21}$.

\[
\text{ROO}^- + \text{OS(CH}_3)_2 \rightleftharpoons \text{ROO}--\text{S}--(\text{CH}_3)_2
\]

Under alkaline conditions, a similar type of interaction between sulphoxides and the anion RNBr$^-$ can be envisaged.

\[
\text{RNBr}^- + \text{OS(Ph)}_2 \rightleftharpoons \text{RNBr}--\text{S}--(\text{Ph})_2
\]

Low positive $\rho$ value very much suggests that the negative polarisation is not very much high. Hence structure of C$_1$ could be a cyclic structure. In the EDTA catalysed chloramine-B oxidation of $\alpha$-phenoxypyranoic acids$^{15}$, low positive $\rho$ value was accounted for by envisaging a moderate degree of charge separation in the transition state.

This intermediate closely resembles the cyclic transition state proposed in the oxidation of sulfides by Cr(VI)$^{22}$. Electron-rich transition state (C$_1$) is favoured by electron withdrawers.

Even though D$_2$O has no effect on the reaction velocity, the participation of water molecule in the reaction sequence is not ruled out and well supported by pH dependence on the reaction rate$^{23}$. High dielectric constant favours the rate indicating that the transition state is more polar than the reactants.

**Binary mixtures of transition metals as catalysts**

It has been shown that a mixture of two metal ions such as Os(VIII) and Ru(III) functions as an efficient catalyst in the oxidation of organic substrates$^{24,25}$. In the present investigations, we have observed no such rate accelerative effects with Os(VIII)-Ru(III).
Os(VIII)-Hg(II) and Os(VIII)-Pd(II) binary mixtures. Interestingly, the added metals reduce the catalytic activity of Os(VIII). The retardative effect is very small in the case of Hg(II). It appears that the reaction is not routed through the formation of a termolecular complex involving both metals, as the most favourable pathway; steric factor plays a dominant role. We believe that Ru(III) and Pd(II) compete with Os(VIII) in forming a complex with reactants and thereby depressing the reactivity.

We have also analysed the effects of 1,10-phenanthroline and 2,2’-bipyridyl in the present study. Contrary to expectations, there is a marked decrease in the rate of oxidation. Quite likely, Os(VIII) forms an inactive complex with these pyridine bases and as such, its effective concentration is reduced resulting in a depressed reactivity. The results of this study are very much in agreement with earlier observations.

Near constancy of $\Delta G^\circ$ values implies that a common mechanism is operating in all the sulphoxides studied. Entropies of activation in this series do not remain constant. The variation in $\Delta S^\circ$ is linearly related to changes in $\Delta H^\circ$ ($r = 0.990; s=6.91$). The linear Exner plots of log $k_1$ ($T_2$) versus log $k_1$ ($T_1$) with excellent correlation coefficient ($r=0.987; s=0.032$) further support a similar mechanism in all the listed sulphoxides. The kinetics looks much more complex than expected.

Acknowledgement

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References
