Kinetics & Mechanism of Oxidation of Dipentyl & Diphenyl Sulphoxides with Nitric Acid in Acetic Acid-Water Medium

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The title reaction shows first order dependence each in [substrate] and [oxidant] and the active oxidant species is found to be HNO₃. The reaction involves an electron transfer from the sulphoxide to the oxidant resulting in the formation of a radical cation in the rate-determining step, which gives rise to a dication in a fast step followed by hydrolysis and deprotonation to form the sulphone.

Solvent extraction of uranium, thorium, protactinium, zirconium and their fission products from acid solutions using dimethyl sulphoxide, diphenyl sulphoxide etc. as extractants has been reported. The sulphoxides have also been successfully employed for the extraction of actinides, lanthanides and transition elements and it has been reported that extraction of americium(III) and neptunium(IV) from nitric acid solution is poor at higher acid concentration due to probability to the oxidation of sulphoxides to sulphones. The present investigation has been undertaken to ascertain the nitric acid concentration which can be used satisfactorily in the solvent extraction process. It is pertinent to mention that considerable work has been done on the oxidation of sulphoxides with various oxidants.

All the chemicals and solvents used were of AR (BDH) grade and doubly distilled water was used for preparing the solutions. Dipentyl and diphenyl sulphoxides, synthesized in the laboratory were purified by repeated recrystallization from warm pet ether (60-80°C) and were characterized by their melting points and IR spectra. Purified acetic acid was used.

For kinetic measurements solutions (equal volumes) of the sulphoxide in acetic acid-water and nitric acid were equilibrated separately at the desired temperature and mixed. Aliquots, withdrawn at definite time intervals were poured into excess of ceric sulphate solution in dil. H₂SO₄. The amount of ceric sulphate remaining unreacted was titrated with standard ferrous ammonium sulphate solution using N-phenylanthranilic acid as indicator.

The kinetics were studied under pseudo-first order conditions ([substrate] > > [oxidant]) and the rate constants were calculated from the slopes of the linear plots of log [oxidant] versus time.

The stoichiometric runs indicated that 1 mol of sulphoxide consumes 1 mol of the oxidant to give the corresponding sulphone viz. dipentyl and diphenyl sulphones which were characterized by their IR and analytical data.

**Dependence on [substrate] and [oxidant]**

The pseudo-first order rate constant (k₁) increases with increase in [substrate] (between 0.5 and 1.5 x 10⁻⁴ mol dm⁻³) indicating first order dependence in [substrate]. The second order rate constant k₂ (= k₈/[sulphoxide]), which is invariant, also supports the above view. The reaction shows first order dependence in [oxidant] (in the range of 0.5 to 1.25 x 10⁻³ mol dm⁻³) until 35% completion of the reaction as shown by the constancy of k₈ in any single run; the agreement between replicate runs is within 3-5%.

Oxidation of both dipentyl and diphenyl sulphoxides induce polymerization of added acrylamide indicating that the reaction proceeds by a radical mechanism, in confirmity with the literature observations on the oxidation of sulphoxides.

Increase in concentration of acetic acid in the solvent mixture increases the rate in the case of dipentyl sulphoxide while the reaction rate is decreased in the case of diphenyl sulphoxide. The plots of log k₁ versus 1/T are linear in both the cases, with positive and negative slopes respectively in the former and latter cases. The dipole moment is lower in dipentyl sulphoxide as it is restricted to only s-o bond and it results in positive slope. The higher dipole moment in the case of diphenyl sulphoxide is due to partial development of charges in the aromatic rings resulting in negative slope.

The thermodynamic parameters evaluated by least squares method from the linear plots of log k₁ versus 1/T in the temperature range of 303-318K are given in Table 1, and it is seen that the activation parameters are similar to those obtained for bimolecular displacement processes.

Though the presence of a number of species in nitric acid has been reported, under the present experimental conditions and at low concentration, HNO₃ is the active species. Based on the results, we believe that electron transfer from the sulphoxide to oxidant takes place in the rate-determining step, resulting a cation radical, which in the subsequent steps gives rise to a di-
Table 1—Activation Parameters for Oxidation of Dipentyl and Diphenyl Sulphoxides by Nitric Acid

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kJ mol$^{-1}$ at 308K)</th>
<th>$\Delta F^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J k$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentyl Sulphoxide</td>
<td>35.42</td>
<td>32.84</td>
<td>93.99</td>
<td>-198.00</td>
</tr>
<tr>
<td>Diphenyl Sulphoxide</td>
<td>53.84</td>
<td>51.26</td>
<td>94.22</td>
<td>-140.00</td>
</tr>
</tbody>
</table>

The rate law, in accord with Scheme 1, is given by Eq. (1)

$$- \frac{d[\text{HNO}_3]}{dt} = \frac{-d[\text{substrate}]}{dt} = k_2[R_2\text{SO}][\text{HNO}_3] = k_{\text{obs}}[\text{HNO}_3]$$  \( (1) \)

where $k_{\text{obs}} = k_2[R_2\text{SO}]$, and it is valid only when $[R_2\text{SO}] >> [\text{HNO}_3]$.

The suggested bimolecular process is supported by the negative entropies of activation (Table 1). Maruthamuthu and Santappa\textsuperscript{16} have reported a dication mechanism for the oxidation of dimethyl sulphone by peroxymonophosphate.

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References