INTRODUCTION

Model systems that mimic catechol dioxygenase enzymes have attained considerable significance. The enzymes serve as a part of nature's strategy for degrading aromatic compounds in the environment. They catalyze the oxidation of catechol by breaking the carbon-carbon bond either at C1-C2 position (intradiol cleavage) or at C2-C3 position (extradiol cleavage). A substrate activation mechanism was proposed for the mechanism for the enzyme reaction wherein coordination of the catechol to the Fe(III) center generates a semiquinone radical which is susceptible for dioxygen attack. However, very few of the catechol complexes reported so far have attained considerable significance. The enzymes serve as a part of nature's strategy for degrading aromatic compounds in the environment.

RESULTS AND DISCUSSION

K[Ru(Salen)Cl] complex was dissolved in 2% SDS solution at pH 11 and the complex got converted into hydroxy species as [Ru(III)(Salen)(H2O)(OH)]10,11. This complex exhibits an irreversible reduction wave at -0.563V at this high pH value (i.e. pH 11). No oxidation wave is discernible. The irreversable reduction wave corresponds to the Ru(III)/Ru(II) potentials. On adding 1:1 equivalent DTBC to 1.0x10⁻⁶ mole/litre of [Ru(III)(Salen)(H2O)(OH)] complex, the solution turns green due to formation of [Ru(III)(Salen)(DTBC)]. The electronic spectrum of this complex exhibits band with λmax at 736 nm, 475 nm and 293 nm.

The model complex [Ru(III)(Salen)(H2O)(OH)] is coordinative unsaturated; the binding of DTBC is expected to occur without replacing the already bound donors of the Salen ligand. So, the changes in the absorption at 736 nm and 475 nm may be due to structural changes accompanying DTBC binding or to the overlap of ligand-Ru(III) charge transfer bands with phenolate-Ru(III) charge transfer one. The band at 293nm arises presumably from Salen-Ru(III) interaction, shifted to higher energy due to the chelation of the DTBCc.

The electronic spectra of [Ru(III)(Salen)(DTBC)]- comparable to those reported for [Fe(III)(DTBC)]. The visible electronic spectra of [Ru(III)(Salen)(DTBC)] and [Fe(III)(DTBC)] shows similarity to those of enzyme-substrate complexes. In the enzyme-substrate complexes the observed spectral change may correspond to displacement of coordinated water or imidazole and not the coordinated tyrosinate without changing in geometry.5,10,13

The cyclic voltammogram of Ru(III)-DTBC adduct in 2% SDS surfactant micelle (at pH 11) produce the cathodic peak at -0.273V and it is coupled with the anodic peak at -0.199V with a peak potential separation ΔE p = Epa – Epc = 0.078V; cathodic to anodic peak current ipc/ipa = 1.06 at potential scan rate 0.1V/s. Epa at -0.199V corresponds to the oxidation of coordinated DTBC ligand to coordinated semiquinone. Presence of tertiary butyl blocking groups on the catechol, aromatic ring makes it possible to oxidize DTBC reversibly to a stable semiquinone in basic media. The mid-point potential of the coordinated DTBSQ/DTBC is -0.234V (scan rate 0.1V/s). Scanning to positive potential, oxidizes the coordinated DTBSQ to DTBQ and as a result of an irreversible oxidation wave is observed near +0.204V. Cyclic voltammogram of free DTBC in aqueous 2% SDS surfactant micelle (pH = 11, scan rate 0.1V/s) shows DTBSQ/DTBC and DTBQ/DTBSQ redox potential at -0.172V and +0.524V respectively. The cathodic (i.e. negative) shift of mid-point potential (which is 0.062V cathodic shift) of the coordinated DTBSQ/DTBC redox couple with respect to free DTBSQ/DTBC redox couple indicates that the monodentate chelation of DTBSQ to ruthenium is more stable and reflect the
strong affinity of DTBSQ for ruthenium. The mid-point potential also reflects the Lewis acidity of the metal center as modulated by the tetradeutate ligand. Similarly, the cathodic shift of the irreversible oxidation wave (which is about 0.320V cathodic shift) of the coordinated DTBQ/DTBSQ with respect to free DTBQ/DTBSQ indicates the stability of DTBQ which does not reduce further. DTBQ formed in this reaction is a poor ligand which does not complex with Ru(II).

The change in voltammograms with increasing the scan rate and the plots of \( i_{pa} \) and \( i_{pc} \) versus the square root of scan rate (\( \sqrt{\nu} \)) are shown in figure 3(a) and figure 3(b).

The plots of \( i_{pa} \) and \( i_{pc} \) vs. the square root of scan rate produce a straight line passing through the origin, indicating that the electrode process is diffusion controlled. The ratio of cathodic to the anodic peak current \( i_{pa}/i_{pc} \) is almost unity.

This clearly indicates that the redox process associated with the coordinated DTBSQ/DTBC is quasi-reversible. A perusal of Table-1 shows that the mid-point potential \( (E_{1/2}) \) becomes more cathodic and \( \Delta E_p \) varies 0.071V to 0.099V with increasing scan rate. Both of these observations are indicative of the quasi-reversible one electron transfer process.

![Fig. 1: Electronic spectra of (a) [Ru(III)(salen)DTBC] in SDS micelle at pH 11.0 (b) Ru(III)(salen)(DTBSQ) in SDS micelle at pH 11.0 Spectra (b) was recorded of 20 minutes after addition of DTBC](image)

![Fig. 2: Cyclic Voltammogramm of [Ru(III)(salen)](DTBC)] in SDS micelle; Supporting electrolyte = NaNO₃, pH = 11, Temp. = 27°C](image)
Fig. 3(a) Cyclic Voltammogram variation for [Ru(III)(salen)(DTBC)] complex in aqueous SDS micelle with increasing the scan rate at pH 11.0; Scan rates are (i) 0.05 V/s (ii) 0.1 V/s (iii) 0.2 V/s (iv) 0.3 V/s (v) 0.4 V/s

Fig. 3(b): Plots of peak currents \(i_{pc}\) and \(i_{pa}\) versus the square root of the scan rate for [Ru(III)(salen)(DTBC)] complex in aqueous SDS micelle at pH 11.

Table 1: Cyclic Voltammetric parameters for [Ru(III)(salen)(DTBC)] in aqueous SDS micelle at micelle at pH 11.0, Temperature 25°C

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>(E_{pc}) (V)</th>
<th>(E_{pa}) (V)</th>
<th>(dE_p) (V)</th>
<th>(i_{pc}/i_{pa})</th>
<th>(E_{1/2}) (V)</th>
</tr>
</thead>
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<tr>
<td>0.05</td>
<td>-0.263</td>
<td>-0.192</td>
<td>0.071</td>
<td>0.99</td>
<td>-0.228</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.273</td>
<td>-0.195</td>
<td>0.078</td>
<td>1.06</td>
<td>-0.234</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.286</td>
<td>-0.202</td>
<td>0.084</td>
<td>1.04</td>
<td>-0.244</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.290</td>
<td>-0.204</td>
<td>0.086</td>
<td>1.09</td>
<td>-0.247</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.309</td>
<td>-0.210</td>
<td>0.099</td>
<td>1.31</td>
<td>-0.260</td>
</tr>
</tbody>
</table>

The EPR spectrum of DTBC adduct of Ru(III)(Salen) complex (figure-4) under anaerobic condition (at pH 11 and 27°C temperature) show two widely separated hyperfine lines (\(a = \text{ca.} 3.0 \text{G}\)) followed by further splitting of each of the lines (\(a_2 = 0.3 \text{G}\)). The EPR spectrum in water is typical of that reported for DTBSQ. The hyperfine coupling was largest for the proton attached to carbon containing the unpaired spin density and further splitting of each line was by interaction with protons of the nearest tertiarybutyl group. Splitting by the other protons is much smaller as was found for DTBSQ in 50% methanol. The hyperfine lines of the radical are much broader in the micellar solution as compared to that in water; all the lines due to the protons of the tertiary butyl groups are not properly resolved in SDS micelle. This effect could be due to restricted rotation of the entrapped radical in the micelles. On exposure to air the intensity of the EPR signal decreases and the green Ru(II)-DTBSQ complex turns to a brown coloured solution. The radical signal persists for a larger time in the micelles (1-2 hours) as compared to that in water (28 minutes). Similar results are also
obtained with analogous [Fe(III)(Salen)(DTBC)] complex in aqueous micellar solutions. The EPR lines are much broader in Fe(II)-DTBSQ complex presumably due to exchange interaction with unpaired electrons at the high-spin Fe(II) ion.

Fig. 4: EPR spectra for Ru(II)(salen)(DTBSQ) in SDS micelle under anaerobic condition at pH 11 and temperature 27°C, Modulation amplitude = 0.16, receive signal = 1.6x10^3, microwave power = 5 mW. Time constant =0.008

Scheme 1: Proposed mechanism for the extradiol cleavage of DTBC

Reactivity with 3,5-diteritarybutyl catechol
Spectrophotometric study showed that absorbance at 736 nm band [Fe(III)(Salen)(DTBC)]: adduct gradually decreases on exposure of the solution to air and solution colour turns to red-brown. After complete oxygenation, the micellar solution was acidified with HCl to pH=3. Organic products were extracted from aqueous micellar solution with hexane and dried over anhydrous Na_{2}SO_{4} and chromatographed on silica gel using chloroform as the eluent. The colorless product was identified by using electronic, infra-red, mass and NMR spectral techniques. The product was identified as 4,6-ditet-butyl-2-pyrene in 55% yield along with DTBQ as a minor product. In a previously study, cleavage of catechol to give 2-pyrene was possible with Cu(II), Fe(III), Ru(II), V(III or IV) complexes.

UV-Vis (in methanol): \( \lambda_{\text{max}} \) 276 nm (sharp) and \( \lambda_{\text{max}} \) 398 nm.

IR: The compound shows peaks 1741 cm\(^{-1}\), 1666 cm\(^{-1}\), 1569 cm\(^{-1}\) and 1240 cm\(^{-1}\). The first of these is assigned to the \( \delta \)-lactone carbonyl group, the second to the conjugated \( \nu \) \( \text{C} = \text{C} \) double bonds, third to the frequency originating in the highly conjugated \( \alpha \)-pyrone ring.

Mass(C.I. methane): \( m/e=208(\text{MH}^{+}) \).

\( ^{1}H \) NMR (CDCl\(_3\)): 8.13, 8.095((CH\(_3\))C); 8.63((CH\(_3\))C=CH-CO), 8.69(CH\(_3\))C=CH-C(CH\(_3\))\(_3\).

M.P. =110°C.

The probable binding mode of the Ru(III) complex with 3,5-diteritarybutyl catechol is depicted in scheme 1. The first step appears to involve the binding of the substrate (state a) followed by formation of semiquinone character of the bound DTBC\(^{2-}\) (state b). The Lewis acidity of the ruthenium center enhances the covalence of
the Ru-catecholate interaction and enhances the semiquinone character of the bound DTBC. This increased semiquinone character renders DTBC more prone to oxygen attack and accelerates the redox process of catechol dioxygenases. The attack of O2 on the activated substrate yields alkyl peroxy radical (state c) which combines with the equally short-lived Ru(II) center to generate an alkyl peroxy-Ru(II) species. Electron transfer from metal to O2 in Ru(II)-O2 species results in a superoxide-like moiety (state d) which combines with the equally short-lived Ru(II) center to generate an alkyl peroxo-Ru(II) species. Electron transfer from metal to O2 in Ru(II)-O2 species results in a superoxide-like moiety (state d) and combines with the equally short-lived Ru(II) center to generate an alkyl peroxo-Ru(II) species. The Ru(II)-DTBSQ/DTBC redox process is diffusion-controlled quasi-reversible.

CONCLUSION

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REFERENCES

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