Kinetics and catalysis of oxidation of phenol by ruthenium(IV)–oxo complex

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Abstract

Kinetics of oxidation of phenol by $[Ru^{IV}(tpy)(pic)(O)]^+$ (tpy = 2,2′,6′,2″-terpyridine; pic^- = picolinate) (**1**) has been studied in aqueous solution using a rapid scan stopped-flow spectrophotometer. Under pseudo-first order conditions of excess phenol concentrations, the rate of reaction was found to be first order in respect to both **1** and phenol concentrations. Quinones and $[Ru^{II}(tpy)(pic)(H_2O)]^+$ (**2**) were found to be the ultimate products of the reaction. Kinetic results were analyzed by using global kinetic analysis techniques and a working mechanism in agreement with the rate and activation parameters is presented. The experimental results are discussed in reference to data reported for the phenol oxidation by relevant $Ru^{IV}=O$ systems. Catalytic ability of **2** in effecting phenol oxidation in the presence of *t*-BuOOH has been explored.
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1. Introduction

The $[Ru^{IV}(tpy)(XY)O]$ type of complexes (where tpy = 2,2′,6′,2″-terpyridine; XY = bidentate ligands) are significantly important in studying the mechanism of oxo-transfer reaction in oxidation of organic substrates [1–8]. The coordinative stability of these ruthenium complexes and their easy accessibility to different oxidation states render themselves ideal for detailed kinetic and mechanistic studies under turnover conditions. For the past few years, we have been engaged [9–11] in developing the $[Ru(TDL)(XY)(H_2O)]$ type of ruthenium catalyst complex (where TDL = tridentate ligands; XY = bidentate ligands) that exhibits selectivity in hydrocarbon oxidation. The use of $[Ru^{III}(TDL)(XY)(H_2O)]$ complexes are fascinating due to the following reasons: (a) the TDL's could provide sites that can undergo stereogenic as well as chiral substitution, thus rendering promising chiral controlling shapes for asymmetric catalysis and (b) the electrophilicity of the ruthenium center could be tuned by changing the ancillary ligand (XY).

In a very recent paper [9] we have reported synthesis and catalytic ability of a new $[Ru^{II}(tpy)(pic)(H_2O)]^+$ (tpy = 2,2′,6′,2″-terpyridine; pic^- = picolinate) complex in the epoxidation of various alkenes in the presence of *t*-BuOOH as a terminal oxidant under ambient conditions. In this work we have taken phenol as a substrate. Phenol oxidation is important since quinone, the oxidation product of phenol, is of considerable synthetic importance in the synthesis of complex organic compounds [12]. In this work we describe kinetic results together with detailed mechanistic studies of oxidation of phenol by $[Ru^{IV}(tpy)(pic)O]^+$ based on a global kinetic analysis methodology. We also report the results of $[Ru^{II}(tpy)(pic)(H_2O)^+$ catalyzed oxidation of phenol using *t*-BuOOH as precursor oxidant under ambient conditions. The mechanism of the overall catalytic process has been discussed with regard to the intermediate identified in the oxidation of phenol by **1**.

2. Experimental

2.1. Materials

The $[Ru^{IV}(tpy)(pic)O]ClO_4$ (**1**) complex was prepared by oxidizing the $[Ru^{II}(tpy)(pic)H_2O]ClO_4$ (**2**) precursor complex [9] with ammonium cerium(IV) nitrate. To an hot aqueous

solution (10 ml) of **2** (57.5 mg) was added $(NH_4)_2[Ce(NO_3)_6]$ (200 mg in 5 ml of water), and the reaction mixture was stirred for 10 min under argon atmosphere. Addition of $NaClO_4$ to the pale yellow resultant solution caused precipitation of the desired product complex (**1**), which was collected on a frit, washed with a minimum amount of cold water and dried in vacuo. Yield: 60%. Anal. Calculated for $C_{21}H_{15}N_4O_7RuCl$: Calc. C, 44.1; H, 2.97; N, 9.8. Found: C, 44.5; H, 2.85; N, 10.1. UV–vis in H_2O: λ_{max} (ε_{max}): 361sh (7800), 284 (218,000), 268 (23,200); UV–vis in CH_3CN: λ_{max} (ε_{max}): 376 (6250), 240 (19,000); IR: ν_{COO^-} 1625 cm^{-1}, $\nu_{C=N}$ 1585 cm^{-1}, $\nu_{Ru=O}$ 790 cm^{-1}. Λ_M (Ω^{-1} M^{-1} cm^2) in $H_2O = 89.4$. The $E_{1/2}$ values for Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} redox couples are 0.4 and 0.23 V, respectively, at pH 7.0. $\mu_{eff} = 2.85$ B.M.

All chemicals used were of reagent grade, obtained from Aldrich Chemical Company and, where appropriate, degassed before use. Doubly distilled H_2O and HPLC grade acetonitrile were used throughout the studies.

2.2. Instrumentation

A PerkinElmer 240C elemental analyzer was used to collect microanalytical (C, H, N) data. The UV–vis and IR spectra were recorded on a PerkinElmer (Model Lambda 35) spectrophotometer and a PerkinElmer (Model 783) spectrometer using KBr pellets, respectively. Cyclic voltammetric experiments were performed using a CH Electrochemical Instruments (CHI-660B). A glassy carbon working electrode, platinum-wire auxiliary electrode and standard calomel electrode (SCE) as reference electrode were used for this purpose. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer.

2.3. Kinetic studies

The kinetics of the reaction of **1** with phenol was studied spectrophotometrically using a SF-61SX2 (HI-TECH) stopped-flow spectrophotometer coupled to a (KinetaScan) rapid scan spectral attachment. The solution temperature was maintained to within ± 0.1 °C using a circulating water bath (JEIO TECH RW-1025G). The rate of phenol oxidation was followed by monitoring 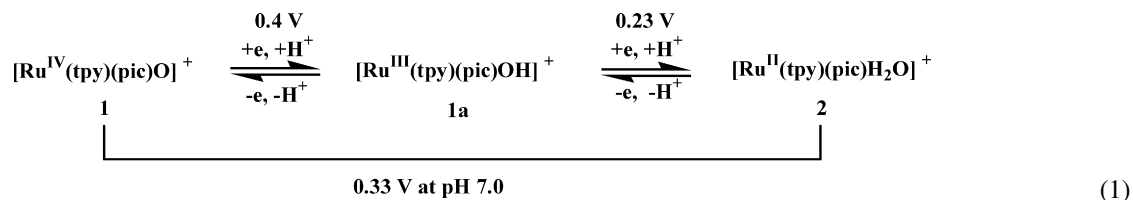the increase in absorbance of ruthenium(II) complex at 500 nm in water under pseudo-first order condition of excess phenol (10–100 times). The pH of the solutions was measured with a Mettler Delta 350 pH meter. Acetic acid-acetate and phosphate buffers were used to adjust the pH of the experimental solutions. In all cases spectral-kinetic data were processed by the use of the SPECFIT program. The results of such fit return both globally optimized rate constant and predicted spectra of

the colored species. Observed rate constants (k_{obs}) are presented as an average of several kinetic runs (at least 5–8) and were reproducible within $\pm 4\%$.

2.4. Product identification

For stoichiometric oxidation of phenol with **1**, the reaction product(s) was identified and analyzed by NMR and GC–MS studies. For this purpose **1** (1 mmol) was allowed to react with phenol (in 1:1 ratio) in H_2O (5 ml) for 1.0 h at room temperature. For catalytic experiments 0.01 mmol of **2**, 1.0 mmol of 70% aqueous t-BuOOH oxidant and 1.0 mmol of phenol in 5 ml of H_2O were rapidly magnetically stirred at room temperature (25 °C) for 4 h. For both cases the resultant mixture was severely shaken with CD_3Cl, and the organic layer was subjected to NMR and GC–MS analyses. GC parameters were quantified with authentic samples of the product prior to the analysis. NMR studies were performed on a Bruker 300AC NMR spectrometer. GC–MS analysis of the reaction product(s) was carried out on a GC–MS–MS equipment (Thermoelectron Corporation) equipped with a Polaris Q mass detector.

3. Results and discussion

The absorption spectrum of **1** in H_2O was found to be featureless in the visible region; however, it showed intra-ligand ($\pi \rightarrow \pi^*$) charge transfer bands in the UV region (see Section 2). The IR spectrum of **1** was found to be identical to that of the precursor aqua-complex (**2**) suggesting that the coordinated 'tpy' and 'pic$^-$' remain intact through out the synthesis. An intense band at 790 cm^{-1} in the IR spectrum of the **1** is assigned to the Ru^{IV}=O stretching band based on previous reports on other monoxoruthenium(IV) complexes [1–8]. This band was evidently absent in the IR spectrum of **1**. Conductance data (see Section 2) established the 1:1 electrolyte nature of **1**. The magnetic moments of **1** conform to the $(d_{xy})^2(d_{yz})^1(d_{zx})^1$ electronic configuration characteristic of the monoxoruthenium(IV) system [13]. The electrochemistry of **1** was found to be quite similar to that of its precursor aqua-complex (**2**) reported previously [9]. The reversibility of the Ru(IV)/(III)/(II) redox couples involving one electron, one proton transfer process is represented in Eq. (1):

$$\underset{\textbf{1}}{[Ru^{IV}(tpy)(pic)O]^+} \underset{-e,\ -H^+}{\overset{\underset{+e,\ +H^+}{0.4\ V}}{\rightleftarrows}} \underset{\textbf{1a}}{[Ru^{III}(tpy)(pic)OH]^+} \underset{-e,\ -H^+}{\overset{\underset{+e,\ +H^+}{0.23\ V}}{\rightleftarrows}} \underset{\textbf{2}}{[Ru^{II}(tpy)(pic)H_2O]^+}$$

$$0.33\ V\ \text{at pH 7.0} \tag{1}$$

The complex **1** has been found to be an active oxidant capable of oxidizing phenol in aqueous solution. Organic products of the 1:1 stoichiometric reaction between **1** and phenol determined by NMR and GC–MS analyses were found to be *o*-quinone (9%) and *p*-quinone (71%). Spectral measurements of the resultant solution confirmed the formation of $[Ru^{II}(tpy)(pic)(H_2O)]^+$ (identified by its
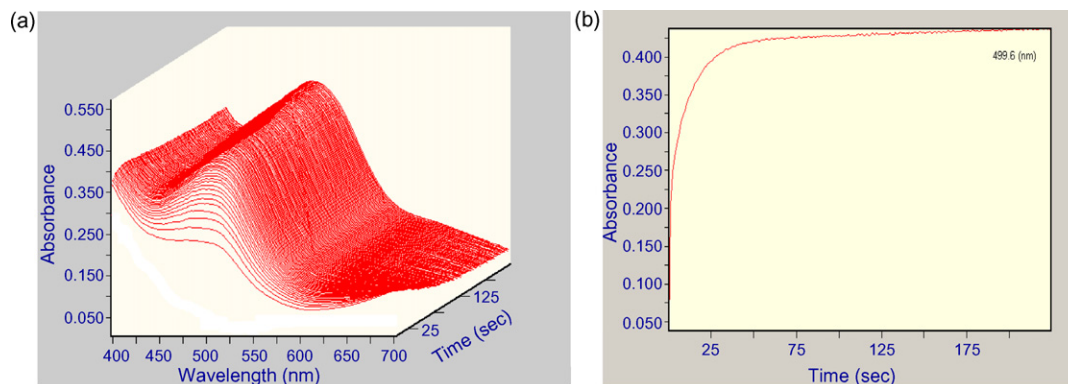
Fig. 1. (a) Spectral changes that occurs in the reaction of **1** (1.5×10^{-4} M) with phenol (1.5×10^{-3} M) in H_2O at 25 °C. (b) Kinetic trace at 500 nm.
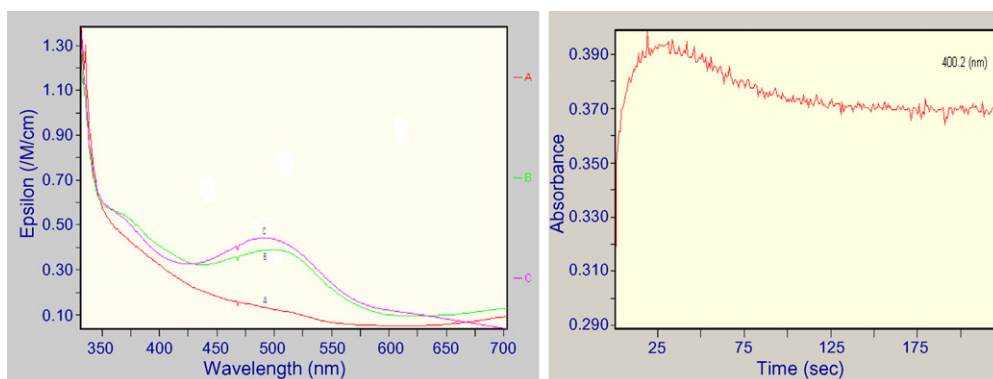

Fig. 2. (a) Spectra (A) **1**, (B) intermediate and (C) **2** generated by global SPECFIT analysis. (b) Kinetic trace for the reaction of **1** with phenol at 400 nm.

m.l.c.t band at 495 nm [9]) as the end product of the reaction.

In Fig. 1a are shown the UV–vis spectral changes with time that occurred upon mixing aqueous solutions of **1** and phenol in the chamber of the stopped-flow instrument equipped with a rapid scan spectral attachment. Fig. 1b displays a typical kinetic trace at 500 nm generated from a number of spectra by using global kinetic analysis software (SPECFIT/32). The final spectrum of the reacting solution corresponds to the spectrum of the $[Ru^{II}(tpy)(pic)(H_2O)]^+$ species ($\lambda_{max} = 495$ nm, $\varepsilon_{max} = 5234\,M^{-1}\,cm^{-1}$) [9]. Further analysis of the spectra using SPECFIT software suggested that there is an intermediate being formed that can be observed at 510 nm (Fig. 2a). Formation of this intermediate could not be monitored clearly at 500 nm (Fig. 1b) due to the large absorbance increase at this wavelength associated with the formation of the final reaction product. However, at 400 nm reasonably good kinetic traces corresponding to the formation and subsequent decay of the intermediate could be recorded (Fig. 2b) and absorbance changes associated with the decay step were very small.

The step associated with the increase in absorbance was analyzed on a short time scale with a double exponential function since the subsequent absorbance decrease interferes with the absorbance increase at 400 nm. It may be noted here that the single exponential analysis of this step (growth) resulted in almost identical rate constant values, but it is a safer practice to analyze such kinetic traces (Fig. 2b) using a double exponential func-

tion in order to obtain rate constant for the first reaction step more accurately. Under the specified conditions the rate of the reaction was found to be first order with respect to [**1**], and the values of the observed rate constant for the first reaction step (k_{obs}^1) increased linearly with increasing [phenol] (Fig. 3), with an appreciable intercept that signifies the operation of a reverse aquation reaction of the intermediate species. The subsequent reaction (decay), which is slower than the first step, was evaluated separately on a longer time scale with a single exponential
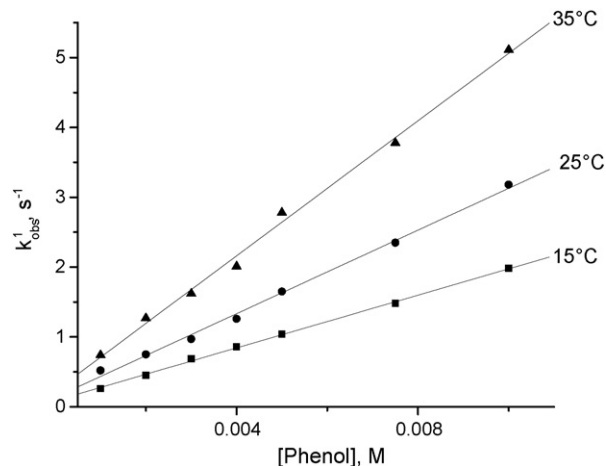

Fig. 3. Plot of (k_{obs}^1) *versus* [phenol] at different temperatures. [**1**] = 1.5×10^{-4} M.

Table 1
Kinetic and activation parameters for the oxidation of phenol by **1**

Temperature (°C)	$10^{-2} k_1$ ($M^{-1} s^{-1}$)	k_{-1} (s^{-1})	k_2 (s^{-1})	$\Delta H_1^{\neq}$ (kcal/mol)	$\Delta S_1^{\neq}$ (cal/deg mol)	$\Delta H_2^{\neq}$ (kcal/mol)	$\Delta S_2^{\neq}$ (cal/deg mol)
15	1.89 ± 0.03	0.09 ± 0.002	0.08 ± 0.005	7.7 ± 0.3	-20.0 ± 1	9.1 ± 0.3	-32.0 ± 1
25	2.99 ± 0.05	0.14 ± 0.02	0.14 ± 0.04				
35	4.83 ± 0.06	0.23 ± 0.06	0.24 ± 0.04				

function. The values of the observed rate constant (k_{obs}^2) were found to be independent of the phenol concentration. The rate constant values are tabulated in Table 1. Based on the above kinetic results, a working mechanism is proposed in Scheme 1. In the proposed scheme a quinone intermediate (**I**) is formed involving electrophilic attack of on the aromatic ring of the phenol. The intermediate (**I**) subsequently undergoes aquation in a pathway independent of phenol concentration to produce **2** and

quinone as ultimate reaction products. A similar mechanism was proposed for the oxidation of phenol by $[Ru^{IV}(bipy)_2(py)O]^{2+}$ [14].

The values of activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) determined by temperature dependence studies of the rate constant values, k_1 and k_2 are summarized in Table 1. The overall negative values found for the entropy is ascribed to an associative character of the concerned reaction steps in the overall oxi-
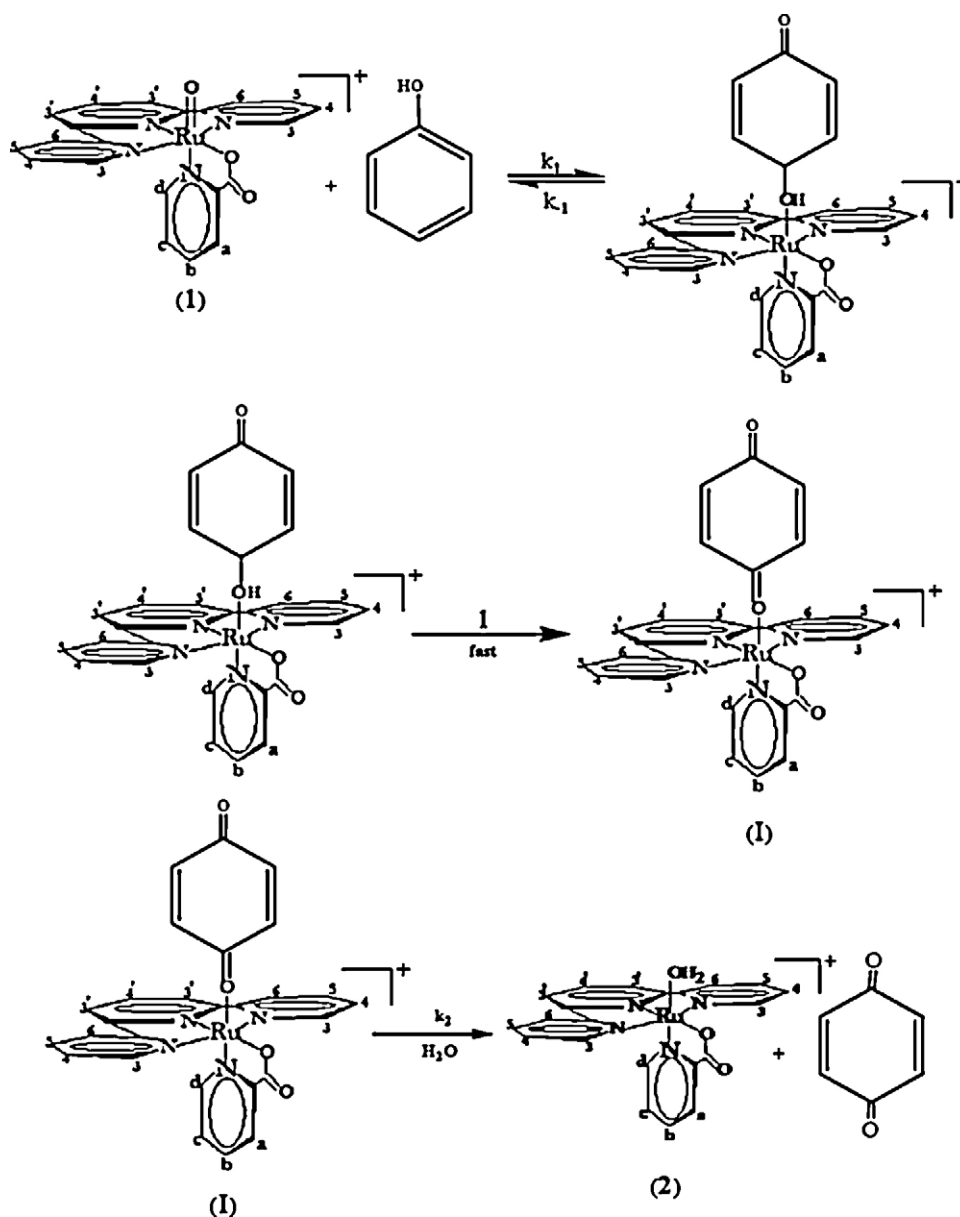
Scheme 1. .

Table 2
Kinetic and activation parameters for the oxidation of phenol by Ru(IV)-complexes

Rate and activation parameters	Ru(IV)-complex	
	$[Ru^{IV}(tpy)(pic)O]^+$	$Ru^{IV}(bipy)_2(py)O]^{2+}$
k_1	$2.99 \times 10^2\,M^{-1}\,s^{-1}$	$5.6 \times 10^2\,M^{-1}\,s^{-1}$
k_2 (s^{-1})	$0.14\,s^{-1}$	$0.26\,s^{-1}$
$\Delta H_1^{\neq}$	7.7 kcal/mol	6.4 kcal/mol
$\Delta S_1^{\neq}$	−20.0 cal/deg mol	−24 cal/deg mol
$\Delta H_2^{\neq}$	9.1 kcal/mol	14.7 kcal/mol
$\Delta S_2^{\neq}$	−32.0 cal/deg mol	−11 cal/deg mol

dation process. Unfortunately there exists only one report on the kinetics of the phenol oxidation by Ru(IV) complex [14]. The values of rate data and activation parameters reported for the phenol oxidation by $[Ru^{IV}(bipy)_2(py)O]^{2+}$ [14] seem to be quite comparable to those obtained in the present case (Table 2). Further, *p*-quinone was found to be the major oxidation product for both oxidants, $[Ru^{IV}(bipy)_2(py)O]^{2+}$ and $[Ru^{IV}(tpy)(pic)O]^+$ in phenol oxidation. Although presence of two 'bipy' ligands makes $[Ru^{IV}(bipy)_2(py)O]^{2+}$ species thermodynamically more stronger oxidant ($E_{1/2}$ for Ru(IV/III) redox couple at pH 7.0 = 0.53 V) than $[Ru^{IV}(tpy)(pic)O]^+$ ($E_{1/2}$ for Ru(IV/III) redox couple at pH 7.0 = 0.40 V), the results in Table 2 reveal that the change in the electrophilicity of the Ru^{IV}=O species by changing the coordinated ligand ('tpy' to 'bipy') does not find chemical expression significantly either in the rate of phenol oxidation or in product selectivity. The findings taken collectively with those on $[Ru^{IV}(bipy)_2(py)O]^{2+}$ strongly suggest that the mechanistic pattern for the oxidation of phenol remains the same in both cases, wherein access of phenol towards the Ru=O bond is sterically favored in both of the cases as the nearly planner tri-coordinated 'tpy' or two 'bipy' ligands coordinated in the trans position in $[Ru^{IV}(bipy)_2(py)O]^{2+}$ open an avenue for O-atom insertion through the electrophilic interaction of the strong Ru=O bond of Ru(IV)–oxo species with the C–H bond of phenol.

We have also examined catalytic oxidation of phenol using the precursor aqua-complex **2** using *t*-BuOOH as primary oxidant. Negligible oxidation products were detected in the absence of **2**. The catalytic oxidation of phenol was found to be very efficient. For phenol oxidation the total turnover of quinone (37% *p*-quinone and 8% *o*-quinone) was found to be 90 under specified conditions (see Section 2). The recovery of the catalyst studied spectrophotometrically revealed about 96% of the **2** was regenerated even after stirring the complex under catalytic conditions. This indicates the robustness of the catalyst complex, thus being capable of affording the advantage of a higher product turnover number. We found that the rate of phenol oxidation (monitored by product analysis with time) by the **2**/*t*-BuOOH system is in

good agreement with that we have recently reported for the reaction of **2** with *t*-BuOOH in aqueous solution [9], and slower than the rate that observed for the oxidation of phenol by Ru^{IV}=O complex (**1**). Based on the above fact we propose herein the intermediacy of a [Ru–O(*t*–Bu)–O]$^{\bullet}$ type of radicaloid intermediate for oxidation of phenol species by the **2**/*t*-BuOOH system as proposed for alkene oxidation by the **2**/*t*-BuOOH system [9].

4. Conclusions

The detailed kinetic and mechanistic study of the oxidation of phenol by $[Ru^{IV}(tpy)(pic)(O)]^+$ (**1**) as a stoichiometric reaction is elucidated in this work. The initial stage involves formation of a $[Ru^{II}(tpy)(pic)quinone]^+$ intermediate (**I**) that was identified by spectral analysis using SPECFIT software. This intermediate releases quinone and undergoes aquation to form aqua-complex **2** back in the reacting system. Formation of a radical type intermediate which subsequently undergoes solvation leading to the formation of epoxide and $[Ru^{II}(TDL)(XY)H_2O]$ species as the end products. The catalysis of phenol oxidation by the **2**/*t*-BuOOH system proceeds involving the intermediacy of a radicaloid species, [Ru–O(*t*Bu)–O$^{\bullet}$] as suggested for the alkene oxidation [9].

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