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Letter

Oxidation of benzene with *tert*-butylhydroperoxide catalyzed by a novel $[Ru^{III}(amp)(bipy)(H_2O)]^+$ complex: first report of homogeneously catalyzed oxo-transfer reaction in benzene oxidation

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Abstract

$[Ru^{III}(amp)(bipy)(H_2O)]^+$ complex (**1**) has been synthesized and characterized by physico-chemical methods. The complex **1** is found to be an effective catalyst in the oxidation of benzene to phenol by using *tert*-butylhydroperoxide (*t*-BuOOH). A high valent Ru(V)-oxo species as catalytic intermediate formed in the reaction of **1** with *t*-BuOOH is proposed to be the source of oxygen atom in the oxidized product. A mechanism involving stacking of benzene followed by the O atom insertion seems to be operative in the formation of phenol from benzene. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

We have been engaged in studying oxo-transfer reactions catalyzed by transition metal complexes of non-porphyrinic ligands [1–5]. We wish to communicate a very significant observation on the oxidation of benzene to phenol and subsequently to quinones via oxo-transfer reaction catalyzed by a novel Ru(III)-complex. Direct oxidation of benzene to phenol is of great interest not only for its industrial importance, but also from pure scientific point of view. Apart from the reports [6–10] on the oxidation of benzene to phenol by hydroxyl radicals generated by the reaction of Fe^{2+} salt (Fenton reagent) with H_2O_2, not much is known about the homogeneously catalyzed oxo-functionalization of aromatic C–H bond through oxo reactions. Although a number of ruthenium complexes in presence of O_2 [11–13], H_2O_2 [14], iodosylbenzene [15–18], hypochlorite [19,20], pyridine-*N*-oxide [5] *t*-BuOOH [21] and oxone [22,23] have proved to be useful catalysts for oxidation of a myriad of organic substrates, reports on benzene oxidation is conspicuous by its absence. The lack of studies is largely owing to the fact that the activation of C–H bond in benzene is difficult due to its resonanc stability. Nonetheless, we report herein that oxidation of benzene to phenol and benzoquinones by *t*-BuOOH can be effected in presence of novel $[Ru^{III}(amp)(bipy)(H_2O)]^+$ mixed-ligand complex (**1**) at ambient conditions

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(H_2amp = N-(hydroxyphenyl)salicyldimine; bipy = $2,2'$-bipyridyl). Catalytic activity of **1** towards oxo-functionalization of C–H bond of various organic substrates using *t*-BuOOH was demonstrated in our earlier paper [4].

2. Experimental

2.1. Materials

The $[Ru^{III}(amp)(bipy)\ H_2O]Cl\cdot 2H_2O$ (**1**) was prepared (by interacting $RuCl_3$ with *N*-(2-hydroxyphenyl)-salicyldimine (H_2amp) [24] and 2,2′-bipyridyl (bipy) in a stoichiometric ratio) and characterized following the published procedure [4]. Anal. Calculated for $RuC_{23}N_3O_5H_{23}Cl$: C, 49.51; H, 4.13; N, 7.53. Found: C, 49.32; H, 4.18; N, 7.43. Λ_M in CH_3CN, $118\,\Omega^{-1}\,mol^{-1}\,cm^2$ at 25°C. UV–VIS data in H_2O (λ_{max}, nm (ε_{max}, $M^{-1}cm^{-1}$): 243 (7062), 288 (10,242), 468 (2066), 562 (1703)). IR (cm^{-1}): 1580 ($\nu_{C=N}$), 1230 (ν_{C-O}). $\mu_{eff} = 1.98$ BM. FAB mass data ($m/z = 486$) is consistent to the formation of cationic $[Ru^{III}(amp)(bipy)(H_2O)]^+$ species. The pK_a value corresponding to $[Ru^{III}(amp)(bipy)(H_2O)]^+ = [Ru^{III}(amp)(bipy)(OH)] + H^+$ acid dissociation estimated titrimetrically is 6.87 at 25°C. All other chemicals and solvents were of AR grade and used as obtained. Doubly distilled water was used throughout the experiments.

2.2. Instrumentation

A GBC Cintra 10 spectrophotometer was used to record the UV–VIS spectra. Infrared spectra were obtained on a Perkin Elmer (Model 783) spectrometer (using KBr pellets). A PAR Electrochemical equipment (Model 174A) equipped with a platinum working electrode and standard calomel electrode (SCE) as reference was used for electrochemical studies. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer and microanalysis (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer.

2.3. Procedure of catalytic studies

In a typical catalytic experiment, 0.01 mmol of **1**, 0.1 mmol of benzyltributylammoniumchloride (phase transfer catalyst, PTC) and 10 mmol benzene (or phenol) in 10 ml of CH_2Cl_2 were magnetically stirred with 10 mmol *t*-BuOOH at room temperature. Aliquots of the CH_2Cl_2 layer were withdrawn at chosen interval of time and subjected to gas chromatographic (GC) analysis for product(s). GC analyses were performed with a Carlo Erba GC 8000^{Top} series on a Tenax column connected with a FID detector. GC parameters were quantified by the authentic product samples prior to the analysis.

3. Results and discussion

Spectral and electrochemical data obtained for $[Ru^{III}(amp)(bipy)(H_2O)]^+$ (**1**) species is virtually identical to that reported earlier [4]. The addition of *t*-BuOOH to the precursor complex (**1**) resulted in the formation of high-valent $[Ru^{V}(amp)(bipy)O]^+$ complex (**2**) [4]. Formation of **2** has been further evidenced by FAB mass data ($m/z = 484$, supplementary).

The results of the **1**-catalyzed reaction are summarized in Table 1. Blank experiments established that each component is essential for an effective catalytic transformation and the oxidation did not take place under O_2 in absence of *t*-BuOOH. Although, ruthenium complexes are well-established to oxidize organic substrates via high-valent Ru-oxo intermediate, the results (Table 1) appear to be the first time for activation C–H bond in benzene (albeit one report exists with regards to the oxidation of benzene involving some not fully characterized ruthenium-oxo intermediate species, formed in the reaction of $BaRuO_3(OH)_2$ in TFA–CH_2Cl_2 containing bipyridine ligand [25]). The results may be explicable, at least conceptually, in terms of the formation of a weak intermediate complex as represented in Fig. 1. Access of benzene towards Ru=O bond is sterically favored as the coordinated ‘amp^{2-}’ ligand is *flat*. A stacking of benzene (through O atom of coordinated amp^{2-} and oxo atom of $[Ru^{V}(amp)(bipy)O]^+$) above the flat ‘amp^{2-}’ should put C–H bond of the benzene across the Ru=O axis (Fig. 1). This affords an avenue for O atom insertion through the interaction of very strong electrophilic Ru=O bond of $[Ru^{V}(amp)(bipy)O]^+$ with C–H sigma bond of benzene. Oxidation of phenol to benzoquinone was found to be rapid. A similar mechanism as proposed by Meyer and Seok [26]

Table 1
Results of the **1**-catalyzed oxidation of aromatic hydrocarbons with *t*-BuOOH[a]

Substrate	Oxidant	Product(s)[b]	Yield (%)[c]	Yield (%)[d]	Turnover[e]
Benzene	*t*-BuOOH[a]	Phenol	8	91	890
		Benzoquinones[f]	27		
Phenol		Benzoquinones[f]	46	95	920

[a] See experimental for reaction condition.

[b] After 6 h of reaction.

[c] Based on substrate concentration.

[d] Combined products yield based on *t*-BuOOH consumed. For mass balance between substrate converted and *t*-BuOOH consumed the benzoquinones yield is to be multiplied by 3, since 3 moles of *t*-BuOOH are required to make one mole of quinone from benzene.

[e] Moles of products (phenol + 3 × benzoquinones) formed per mole of catalyst.

[f] Total yield of *o*- and *p*-benzoquinones.

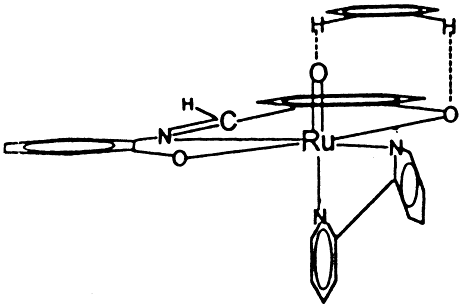

Fig. 1. Schematic representation of the stacking of benzene above ‘amp^{2-}’.

involving direct electrophilic attack on the aromatic ring (*o*-/*p*-position) leading to ultimate reaction products *o*- and *p*-benzoquinones seems to be operative in the present case. The decrease in the catalytic activity observed at the end of the reaction is probably associated with the formation of a catalytically inactive μ-oxo dimer $[\{Ru^{IV}(amp)(bipy)\}_2O]^{2+}$ complex. Formation of μ-oxo dimer perhaps takes place through the following reaction ($[Ru^{V}(amp)(bipy)O]^{+}$ + $[Ru^{III}(amp)(bipy)H_2O]^{+} \rightarrow [\{Ru^{IV}(amp)(bipy)\}_2O]^{2+}$). No appreciable conversion was observed upon addition of benzene (or cyclohexene) to the resultant solution.

4. Conclusion

In conclusion the results of the present studies convincingly demonstrate the catalytic ability of the reported complex (**1**) for oxidizing benzene to phenol with *t*-BuOOH. A high-valent Ru(V)-oxo complex is proposed to be the active species in the catalytic process. A mechanism involving stacking of benzene followed by the O atom insertion seems to be operative in the oxidation process. Ongoing studies include heterogenization of present system by immobilizing the catalyst complex (**1**) on solid support in order to increase the catalytic efficiency (as the immobilized catalyst complex cannot form catalytically inactive μ-oxo dimer species) and obtain the benefit of easy catalyst separation.

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