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Aerobic Oxidation of Ethylbenzene Co-catalyzed by *N*-Hydroxyphthalimide and Oxobis(8-Quinolinolato) Vanadium (IV) Complexes

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Abstract: The mediation effect of vanadium compounds on the *N*-hydroxyphthalimide (NHPI)-catalyzed aerobic oxidation of ethylbenzene (EB) was investigated at 90 °C in benzonitrile. Among the vanadium mediators examined, a series of oxobis(8-quinolinolato) vanadium (IV) complexes ($V^{IV}OQ_2$), which were prepared by the coordination of 8-hydroxyquinoline or its derivatives with oxobis(2,4-pentanedionate) vanadium (IV) ($V^{IV}O(acac)_2$) showed a better mediation effect than $V^{IV}O(acac)_2$, NH₄VO₃, and V₂O₅ and they gave about 60%–69% EB conversion and 97% of acetophenone (AcPO) selectivity under optimum reaction conditions. This is due to the dual catalysis effects of these V mediators on the transformation of NHPI to the phthalimide-*N*-oxyl (PINO) radical and the decomposition of 1-phenylethyl hydroperoxide to AcPO, as supported by UV-Vis spectral characterization.

Key words: n-hydroxyphthalimide; oxobis(8-quinolinolato) vanadium (IV); aerobic oxidation; ethylbenzene; acetophenone

Acetophenone (AcPO) is an important intermediate and has been widely used for the synthesis of compounds such as perfumes, pharmaceuticals, resins, alcohols, and esters. Therefore, there has been considerable interest in the development of highly efficient processes for the production of AcPO from ethylbenzene (EB) [1]. For the oxidation of EB, t-butyl hydroperoxide (TBHP) [2,3] and H_2O_2 [4-6] are usually used as the oxidant because they provide a good yield of acetophenone under relatively mild conditions but the costly oxidants make these processes lack competitive capacity. From an economic and environmental viewpoint, air and molecular oxygen are more attractive than TBHP or H2O2 and they are considered to be the ultimate oxidants [7]. Many efficient catalysts have been developed for the catalytic partial oxidation of EB with molecular oxygen [8] but these processes generally need to employ harsh operating conditions because the triplet nature of molecular oxygen hampers the reaction with EB in its singlet state, which rarely leads to the chemistry being selective [9].

N-hydroxyphthalimide (NHPI) is usually used to improve the aerobic oxidation of hydrocarbons combined with mediators [10] such as metal compounds [11-20], hemin [21], anthraquinones [22], o-phenanthroline [23], alkaline-earth chlorides [24], oxime [25], azodiisobutyronitrile (AIBN) [26], Ce(IV) [27], I₂/HNO₃ [28], NO₂ [29], and quaternary ammonium salts [30]. Among these catalyst systems, NHPI combined with transition metal ions (e.g. cobalt and manganese) is well-known as the Ishii catalytic system, which has excellent catalytic activity for the aerobic oxidation of different kinds of organic substrates [8,11-20]. For example, Ishii et al. [31] and Sheldon et al. [32] reported that NHPI and Co(acac)₂ in an acetic acid medium could efficiently catalyze the aerobic oxidation of EB to the corresponding AcPO in good yield but the use of a corrosive acetic acid solvent hampers its industrial application. Vanadium and its derivatives are well known efficient catalysts for the oxidation of various organic substrates like alkenes, alcohols, aromatic, and aliphatic hydrocarbons

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halides [33] but few reports exist about the use of vanadium-containing compounds as mediators for NHPI-based aerobic oxidation [34]. Herein, we report initial results that we obtained upon using a small amount of oxobis(8-quinolinolato) vanadium (IV) ($V^{IV}OQ_2$) to significantly accelerate the NHPI-catalyzed aerobic oxidation of EB to AcPO in benzonitrile (PhCN) under 101.325 kPa O₂.

1 Experimental

1.1 Preparation of V^{IV}OQ₂ complexes

The general preparation procedure for the V^{IV}OQ₂ complexes is as follows. Oxobis(2,4-pentanedionate) vanadium (IV) (V^{IV}O(acac)₂) was prepared as reported previously [35]. First, to a stirred mixture of CH₂Cl₂ (30 ml) and 8-hydroxyquinoline or its derivatives (10 mmol), a 5 ml of CH₂Cl₂ solution containing 5 mmol of V^{IV}O(acac)₂ was added dropwise within 15 min and the reaction mixture was refluxed for 2 h. The resulting precipitate was filtered and washed with CH₂Cl₂ at least three times. After air drying, a deep-black solid (yield: 85%–95%) was obtained and denoted **1a** to **1d** (see Scheme 1). The vanadium content of **1a** as measured by a UV-3310 spectrophotometer using 5-Br-PADAP and H₂O₂ as chromogenic agents [36] was 14.08 wt% and this was in good agreement with the calculated value (14.36 wt%) from the formula of **1a**.

1.2 UV-Vis spectral measurements

The solid and liquid UV-Vis spectral measurements of the $V^{IV}OQ_2$ complexes were recorded from 200 to 700 nm on a UV-3310 spectrophotometer (Hitachi).

1.3 Oxidation of EB

Catalytic oxidation was performed in a 100 ml of three-necked flask equipped with a water-cooled condenser. After the desired amount of substrate, the catalysts and PhCN were added into the reactor and the air in the reactor was replaced over three cycles with dioxygen (O_2). The reaction mixture was heated to an appropriate temperature under a pure O_2 atmosphere under magnetic stirring. After the desired reaction time had elapsed the reaction mixture was naturally cooled to room temperature and filtered to remove the catalyst. The



Scheme 1. Structures of the V^{IV}OQ₂ complexes.

filtrate was analyzed on an Agilent 6890N gas chromatograph (GC) with a HP-5 quartz capillary column (30 m \times 0.32 mm \times 0.25 µm) and flame ionization detector (FID) using ultra-pure nitrogen as a carrier gas with anisole as an internal standard. Both the injector and the detector were at 250 °C and the column temperature was 120 °C. The products AcPO and 1-phenylethanol (PEA) were satisfactorily identified by comparing the GC-MS spectra with those of authentic samples. The GC-MS contained a quartz capillary column HP-5 (30 m × 0.32 mm \times 0.25 µm) and the column temperature was initially 100 °C and held there for 2 min. It was then increased at a rate of 4 °C/min to 250 °C and held there for 1 min. The carrier gas was ultra-pure nitrogen and it was added at a constant flow of 1 ml/min. The injector, interface and ion-source were kept at 250, 250, and 200 °C, respectively. Electron impact mass spectra were obtained at a 70 eV standard electronic impact. The selectivity for alkyl hydroperoxide (PEHP) in the products was measured based on the change of selectivity for AcPO before and after the filtrate was treated with triphenylphosphine for 1 h [37]. A PhCN (18 ml) solution of EB (1272 mg, 12 mmol), NHPI (1.2 mmol), and V^{IV}OQ₂ (0.006 mmol) were placed in a three-necked flask equipped with a water-cooled condenser. The mixture was stirred at 90 °C for 12 h and then extracted with Et₂O. The organic layer was dried over MgSO₄. The products were separated from the solvent under reduced pressure and purified by column chromatography on silica gel (n-hexane:AcOEt = 20:1) to give the corresponding AcPO (748.9 mg, 52 mol%).

2 Results and discussion

2.1 Characterization of the V^{IV}OQ₂ complexes

Diffusion reflection UV-Vis spectra of the solid V^{IV}OQ₂ complexes (**1a–1d**) are very similar to each other (Fig. 1). They consist of two bands in the 230–350 nm region, which may be assigned to $\pi \rightarrow \pi^*$ transitions in the ligands. The complexes



Fig. 1. Diffusion reflectance UV-Vis spectra of solid $V^{IV}OQ_2$ complexes.

also exhibit a broad band at 370–470 nm probably as a result of ligand to metal V(IV) charge transfer (LMCT), as reported in literature^[38]. In addition, a weak and broad band in the 500–700 nm region may be attributed to a spin-allowed *d-d* transition of the central metal V(IV) ions [38]. The halogenated V^{IV}OQ₂ samples commonly result in a red shift of the LMCT band and this red shift effect gradually strengthens for the brominated and iodonated V^{IV}OQ₂ samples, which is most likely due to an increase in the electron-donating effect of the halogen substituents on the ligand's aryl ring.

2.2 Oxidation of EB

Table 1 lists data for the oxidation of EB with O₂ upon co-catalysis by NHPI and various organic and inorganic V compounds at 90 °C in PhCN. Entries 1 and 2 show that the oxidation reaction hardly occurs without a catalyst or in the presence of the V^{IV}OQ₂ complex 1a. When 10 mol% NHPI was used as the catalyst (see entry 3) about 18% EB was oxidized to AcPO (selectivity, 46%), PEA (selectivity, 23%), and PEHP (selectivity, 31%) showing that NHPI plays an important role in this reaction. When NHPI was used with various V compounds to co-catalyze the reaction, EB conversion and AcPO selectivity improved significantly while PEHP selectivity decreased drastically (entries 4-10) and this is consistent with the results reported by Recupero et al. [10]. Among the V mediators examined the mediation effect of V₂O₅ was found to be the lowest most likely because of the poor solubility of V₂O₅ in the reaction medium (entry 4). Another inorganic mediator NH₄VO₃ promoted the reaction well and afforded about 46%

 Table 1
 Aerobic oxidation of EB catalyzed by the vanadium complexes/NHPI system

\bigcirc	$\frac{V \text{ complexes/NHP}}{O_{2}, PhCN}$	\rightarrow	+			
	-	AcPO	PEA		PEHP	
Entry	Catalyst	Conversion ^a	Selectivity ^a (%)			
		(%)	AcPO	PEA	PEHP	
1	blank	trace	_	_	_	
2	1 a	trace	_			
3	NHPI	18	46	23	31	
4	V ₂ O ₅ /NHPI	26	78	10	12	
5	NH ₄ VO ₃ /NHPI	46	90	8	2	
6	1a/NHPI	69	97	3	0	
7	1b/NHPI	64	97	3	0	
8	1c/NHPI	62	95	5	0	
9	1d/NHPI	60	96	4	0	
10	VO(acac) ₂ /NHPI	54	92	5	3	
11 ^b	Co(OAc) ₂ /NHPI	20	67	20	13	

Reaction conditions: PhCN 6 ml, EB 4 mmol, NHPI 0.4 mmol, catalyst 0.002 mmol, O_2 101.325 kPa, temperature 90 °C, time 12 h. ^aThe data were obtained by GC analysis using anisole as an internal standard. ^b0.002 mmol Co(OAc)₂.

EB conversion and 90% selectivity for AcPO (entry 5). Entries 6–10 show that all the organic V mediators gave a better promotion effect than both the inorganic mediators and the $V^{IV}OQ_2$ complexes were superior to $V^{IV}O(acac)_2$ in improving the conversion and selectivity (entries 6–9 vs entry 10). Among the $V^{IV}OQ_2$ complexes, **1a** was found to be the most efficient and about 69% EB conversion and 97% selectivity for AcPO was obtained when using 10 mol% NHPI-coupled with 0.05 mol% **1a** (entry 6). The three halogenated $V^{IV}OQ_2$ complexes gave about 60%–64% conversion and 92%–97% selectivity for the NHPI-catalyzed EB oxidation (entries 7–9). These NHPI-coupled V complex systems generally give higher catalysis efficiencies than the NHPI-coupled Co(OAc)₂ system (entry11) under the same reaction conditions. This is due to Co(OAc)₂ having poor solubility in PhCN.

2.3 Effect of temperature

The effect of reaction temperature on the aerobic oxidation of EB was determined using 10 mol% NHPI and 0.05 mol% **1a** as co-catalysts and the results are shown in Fig. 2. As expected, increasing the temperature from 60 to 90 °C resulted in a persistent increase in EB conversion and AcPO selectivity because of the accelerated effect of temperature on NHPI and **1a** co-catalyzed the oxidation of EB to AcPO. However, an attempt to further increase the temperature (100 °C) resulted in a slight decrease in EB conversion and AcPO selectivity. This was likely due to the partial degradation of NHPI in protic solvents at high temperature as reported by Saha et al. [39] after they studied the oxidation of *p*-xylene.

2.4 Effect of reaction time

The effect of reaction time on the aerobic oxidation of EB was investigated using 10 mol% NHPI and 0.05 mol% **1a** as co-catalysts. As shown in Fig. 3, EB conversion continuously increased with an increase in the reaction time from 2 to 8 h and, thereafter, it was mostly invariable. EB conversion increased sharply during the early to middle stages (2–8 h),



Fig. 2. Effect of reaction temperature on the aerobic oxidation of EB.



Fig. 3. Effect of reaction time on the aerobic oxidation of EB.

which matches the expected chain propagation process during radical oxidation. AcPO selectivity increased slowly with a reaction time up to 12 h after which it remained almost unchanged.

2.5 Effect of V^{IV}OQ₂ concentration

The effect of $V^{IV}OQ_2$ concentration was investigated using **1a** as an example at a NHPI concentration of 10 mol% and a reaction temperature of 90 °C. As shown in Fig. 4, EB conversion and AcPO selectivity increased drastically with an increase in the concentration of **1a** from 0 to 0.05 mol%. After that the conversion decreased slightly and the selectivity for AcPO remained almost constant with a further increase in $V^{IV}OQ_2$ concentration.

2.6 Effect of NHPI concentration

Table 2 lists the effect of NHPI concentration on the reaction. By maintaining a **1a** concentration of 0.05 mol%, an increase in NHPI concentration from 5 to 10 mol% resulted in a continuous increase in EB conversion from 47% to 69% and an increase in selectivity for AcPO from 93% to 97%, respectively (Table 2, entries 1–3). However, when the concentration was



Fig. 4. Effect of $V^{IV}OQ_2$ concentration on the aerobic oxidation of EB.

Table 2 Effect of NHPI concentration on the aerobic oxidation of EB

Entry	NHPI	$V^{IV}OQ_2$	Conversion	Selectivity ^a (%)		
	(mol%)	(mol%)	(%)	AcPO	PEA	PEHP
1	5.0	0.05	47	93	7	0
2	7.5	0.05	65	96	4	0
3	10.0	0.05	69	97	3	0
4	12.5	0.05	63	97	3	0
5	12.5	0.04	61	97	3	0
6	12.5	0.1	68	97	3	0
7	10.0	0.1	64	97	3	0
8	7.5	0.1	56	95	5	0

Reaction conditions: PhCN 6 ml, EB 4 mmol, O_2 101.325 kPa, temperature 90 °C, time 12 h. ^aThe data were obtained by GC analysis using anisole as an internal standard.

increased to 12.5 mol% the conversion was reduced to 63% (entry 4). Interestingly, at a high NHPI concentration (12.5 mol%) the conversion was improved by increasing the concentration of the V mediator **1a** (entries 4–6) but the opposite was found when using a low concentration of NHPI (entries 7–8). The existence of an optimal NHPI/V^{IV}OQ₂ molar ratio (about 125–200) implies that a synergistic catalysis effect exists between NHPI and V^{IV}OQ₂.

2.7 Reaction mechanism

The NHPI/V^{IV}OQ₂ co-catalyzed EB oxidation process was further monitored by UV-Vis spectroscopy. Figure 5 shows a stepwise overlay of the UV-Vis spectra for NHPI and the V^{IV}OQ₂ complex **1a** in acetonitrile at room temperature. The UV-Vis spectrum of NHPI has an absorption band with a λ_{max}



Fig. 5. Liquid UV-Vis spectra of the mixture of NHPI and V^{IV}OQ₂(**1a**) in acetonitrile treated with O₂ at 80 °C. (1) A solution of NHPI in acetonitrile $(2.0 \times 10^{-4} \text{ mol/L}, 8 \text{ ml})$; (2) After the addition of a solution of V^{IV}OQ₂ in acetonitrile (1 mol/L, 0.2 µl); (3) After treatment with O₂ at 80 °C for 20 min; (4) For 40 min; (5) For 60 min. Inset is the liquid UV-Vis spectra of NHPI in acetonitrile after treatment with O₂ at 80 °C. (6) A solution of NHPI in acetonitrile $(2.0 \times 10^{-4} \text{ mol/L}, 8 \text{ ml})$; (7) After treatment with O₂ for 20 min; (8) For 40 min; (9) For 60 min.

of ~295 nm, which is due to a $\pi \rightarrow \pi^*$ transition (see curve (1)). When a trace amount of **1a** in acetonitrile $(1 \text{ mol/L}, 2 \mu \text{l})$ was added to solution (1) its spectrum did not show any change (see curve (2)). When solution (2) was treated for 20 min in the presence of O₂ at 80 °C, a new shoulder peak appeared at a λ_{max} of \sim 328 nm (see curve (3)) and it became more obvious when the treatment time was increased to 40 or 60 min (see curves (4) and (5)). This shoulder peak was also observed by Figiel et al. [34] in the UV-Vis analysis of NHPI solutions in the presence of [n-Bu₄N] VO₃ and they attributed it to the formation of PINO· radical species by ESI-MS characterization. Moreover, Yoshino et al. [13] and Sheldon et al. [32] also proved the existence of PINO by EPR after the exposure of NHPI to dioxygen in benzonitrile at 80 °C over 45 min. The inset in Fig. 5 shows that the cleavage of NHPI to PINO. in the absence of 1a, as reported in Refs. [13,32] could also occur in acetonitrile in the presence of O_2 at 80 °C (see curves (6)–(9)) but its cleavage rate was slower than that in the presence of 1a (curves (6)-(9) vs (3)-(5)). This accounts for 1a promoting this cleavage process.

Figure 6 shows the spectral change of complex **1a** in acetonitrile before and after treatment with O_2 at 80 °C. A strong adsorption band with a λ_{max} of ~378 nm and a very weak band with a λ_{max} of ~302 nm were observed in the UV-Vis spectrum of fresh **1a** (see (1)) and this is attributed to oxovanadium (IV) and oxoperoxovanadium (V) species, respectively [38,40]. After **1a** was treated for 30 min with O_2 at 80 °C, the oxovanadium (IV) band decreased obviously with a concomitant increase in the oxoperoxovanadium (V) band (see curve (2)) indicating that the present reaction conditions can lead to the transformation of oxovanadium (IV) to oxoperoxovanadium (V), as reported by Maurya et al. [38,40] upon studying the interaction between V(IV) and H₂O₂. Moreover, this trans-



Fig. 6. Liquid UV-Vis spectra of the mixture of $V^{IV}OQ_2$ (**1a**) in acetonitrile treated with O_2 at 80 °C. (1) A solution of $V^{IV}OQ_2$ in acetonitrile (1×10⁻⁶ mol/L, 8 ml); (2) After treatment with O_2 at 80 °C for 30 min; (3) For 60 min; (4) For 90 min; (5) For 120 min. The inset is UV-Vis spectra obtained after adding a solution of NHPI in acetonitrile (0.16 mol/L, 1 µl to solution (5). (6) 60 min later; (7) 120 min later; (8) 180 min later.



Scheme 2. Catalytic cycle of the $V^{IV}OQ_2/NHPI$ system for EB oxidation.

formation reaction continuously proceeded when the treatment time was increased from 30 to 120 min, as shown by the spectral curves (3)–(5) in Fig. 6. Interestingly, when solution (5) was treated with a solution of NHPI in acetonitrile (0.16 mol/L, 1 μ l) for 1 h at 80 °C, a comeback phenomenon of the oxovanadium (IV) band was observed (see curve (6) in the inset), and this comeback trend became more obvious with an increase in the treatment time (see curves (7) and (8)). This spectral change supports the assertion that the oxoperoxovanadium (V) species participates in the cleavage process of NHPI to PINO by reduction to the oxovanadium (IV) species.

Based on the results given here as well as those in previous studies [10–30], it is apparent that the above experimental data are better explained according to the reaction pathway given in Scheme 2. First, NHPI may be cleaved to form a PINO· free radical under an O_2 atmosphere and with heating. This cleavage process can be accelerated significantly by the transfer of its hydrogen atom to the V(V) species that is generated in situ from the reaction of V^{IV}OQ₂ with O_2 , as supported by the above UV-Vis spectral characterization. The next step involves the abstraction of a secondary H atom from EB by PINO· and the resulting hydrocarbon radical is trapped by dioxygen through a well-known reaction pathway [41]. Another effect of the V^{IV} OQ₂ mediator, as reported in many papers, is the ability to catalyze the decomposition of the in situ produced PEHP, which can lead to a significant increase in AcPO selectivity.

3 Conclusions

An oxobis(8-quinolinolato) vanadium (IV) complex was developed to efficiently promote the aerobic oxidation of ethylbenzene to acetophenone upon catalysis by NHPI. This catalytic system has some distinct characteristics: (a) noncorrosive benzonitrile can be used as a medium; (b) small amounts of $V^{IV}OQ_2$ catalyst (0.05 mol %) are required; and (c) excellent AcPO selectivity (97%) is obtained. Improving this catalytic system by reducing the required amount of NHPI and by enhancing its catalytic efficiency will provide a promising strategy for the industrial synthesis of acetophenone from ethylbenzene.

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