



Selective activation of C–H bonds on the ring of ethylbenzene catalyzed by several diperoxovanadate complexes

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ABSTRACT

The competitive oxidation of the C–H bonds on the aromatic ring and side-chain of ethylbenzene (EB) with hydrogen peroxide is investigated over four diperoxovanadate catalysts, that is, $K_3[VO(O_2)_2(ox)]$ (bpV(ox)), $K_2[VO(O_2)_2(pic)]$ (bpV(pic)), $K[VO(O_2)_2(bpy)]$ (bpV(bpy)), and $K[VO(O_2)_2(phen)]$ (bpV(phen)). The selectivity to ring C–H bonds activation is found to be affected by the polarity and acidity of the solvent. The electrophilicity of the diperoxovanadate complexes and their catalytic performance are tuned by different ligands. The high electrophilicity of the vanadium center shows preference for the ring C–H bonds activation. The HOAc molecule was involved not only in the ligand exchange around the vanadium center, but also in the stabilization of the diperoxovanadium species in the media. A polar intermediate mechanism by generating electrophilic catalytic species is proposed. The bpV(bpy)– H_2O_2 –HOAc system is found to be effective for the selective activation of the C–H bonds on aromatic ring of EB ($S = 68.3\%$). It shows promise for the direct one-step synthesis of substituted-phenols from alkylbenzene.

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1. Introduction

The selective activation and functionalization of various types of C–H bonds in hydrocarbons by a one-step method under mild conditions is an attractive subject for green and sustainable chemistry. The selective oxidation of the C–H bonds on aromatic ring is of particular interest, because it provides a one-step way to produce substituted mono- or diphenols that are valuable products or intermediates for the synthesis of resin, plastics, pharmaceuticals, agrochemicals, etc., most of which are currently manufactured via multi-step processes [1]. However, for those substrates possessing more than one type of C–H bond, the weakest one usually takes the priority over others to be activated. For example, with ethylbenzene (EB), the hydrocarbon possessing both benzylic and ring C–H bonds, the activation of the benzylic C–H bonds is preferential over the ring C–H bonds with selective formation of ethylbenzene hydroperoxide [2–6] or acetophenone [7–17]. Despite of the differences in the type of oxidant and the reaction temperatures employed, the competitive oxidation between benzylic and aromatic ring C–H bonds is affected by the reaction mechanism dominated by the interaction between the catalyst and the reactants. The attack of the weaker benzylic C–H bonds is favored by a free radical mechanism using molecular sieves or supported metal oxides as the catalysts [9,13,18,19]. The selective activation of the aromatic ring C–H

bonds is presumed to occur when electrophilic catalytic species is generated, as indicated in the oxidation of toluene [1,20–22]. However, no data are available on the parameters that affect the competitive oxidation between aromatic ring and side-chain C–H bonds of EB.

In this paper, the one-step catalytic oxidation of EB with H_2O_2 over several diperoxovanadate complexes is investigated, to explore the competitive activation of C–H bonds on aromatic ring and side-chain, as well as the influence of electronic and steric factors of the catalyst affecting these transformations.

2. Experimental

2.1. Preparation of the diperoxovanadate complexes

$K_3[VO(O_2)_2(ox)] \cdot 2H_2O$ [bpV(ox)] (ox = oxalic acid), $K_2[VO(O_2)_2(pic)] \cdot 2H_2O$ [bpV(pic)] (pic = picolinate), $K[VO(O_2)_2(bpy)] \cdot 5H_2O$ [bpV(bpy)] (bpy = 2,2'-bipyridine), and $K[VO(O_2)_2(phen)] \cdot 3H_2O$ [bpV(phen)] (phen = 1,10-phenanthroline) were prepared according to the reported methods [23,24], except that icy bath was used to prevent the fast decomposition of H_2O_2 . In a typical procedure, 4.5 g V_2O_5 and 3.3 g KOH were dissolved in 50 mL water, then 50 mL H_2O_2 (30 wt%) was added. The resulting solution was then added to 30 mL alcohol containing 8.0 g 2,2'-bipyridine with continuous stirring. When no color variation was observed, another 30 mL alcohol was added and the mixture was crystallized at 5 °C for 24 h. Then the crystal was filtered, washed with alcohol, and dried, obtaining the orange crystal bpV(bpy) (8.5 g).

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Table 1
Effect of the reaction media on the catalytic performance.^a

Solvent (polarity)	bpV(ox)		bpV(pic)		bpV(bpy)		bpV(phen)	
	C (%) ^b	S (%) ^c	C (%)	S (%)	C (%)	S (%)	C (%)	S (%)
CH ₃ COOC ₂ H ₅ (4.3)	0	0	0.3	0	0.4	10.0	0.4	10.0
C ₅ H ₅ N (5.3)	0	0	0	0	0	0	0	0
CH ₃ COCH ₃ (5.4)	0.5	0	2.1	0	4.2	20.0	2.4	41.0
CH ₃ COOH (6.2)	9.9	56.0	9.6	48.0	12.2	57.0	10.4	54.0
CH ₃ CN (6.2)	0 ^d	0	2.3	29.0	6.7	35.0	5.5	31.0
DMF (6.4)	0.1	0	0.2	0	0.2	0	0.2	0
DMSO (7.2)	0	0	0.1	0	0.1	0	0.1	0
H ₂ O (10.2)	0	0	0	0	0	0	0	0
HCOOH/H ₂ O	1.5	39.2	1.2	30.2	1.5	36.5	1.8	44.0
C ₂ H ₅ COOH	5.4	34.4	5.6	28.0	5.8	34.1	6.8	40.3
C ₃ H ₇ COOH	2.6	9.3	4.0	10.9	4.3	12.2	3.9	11.3

^a Reaction conditions: EB, 0.6 mL; H₂O₂ (30 wt%), 1.0 mL; catalyst, 0.05 mmol; solvent, 10 mL; 37 °C; 4 h.

^b Conversion of EB.

^c Selectivity for ring activation.

^d bpV(ox) was undissolved in CH₃CN.

2.2. Oxidation of ethylbenzene

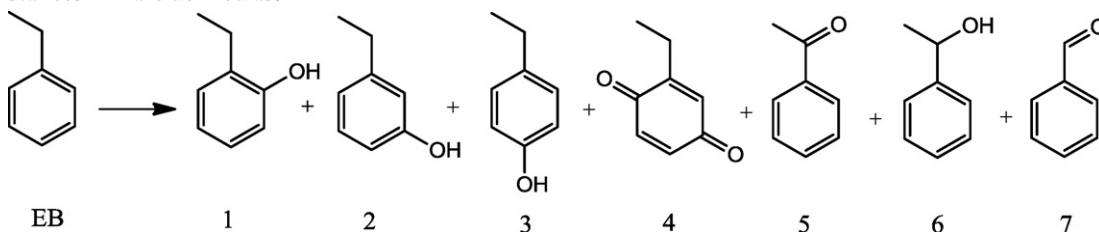
The oxidation of EB was carried out in a two-necked 50 mL round bottom flask placed in a water bath. A typical reaction procedure was as follows: 0.05 mmol catalyst was dissolved in 15 mL solvent, then 1.2 mL (9.8 mmol) ethylbenzene and designed amount of H₂O₂ (30 wt%) were added in turn. The reaction mixture was heated to designed temperature. The reaction was performed under intensive agitation and reflux in air for desired reaction time. After the reaction, the products were identified by GC–MS (Agilent, 5973 Network 6890N) and quantified by GC (FULI, GC-9790 equipped with FID detector and a capillary column) using nitrobenzene as an internal substance. The experiments were repeated at least for three times and the average of the data was presented. The inaccuracy in molar amount of the substance was evaluated to be the ±0.3% range.

The conversion of ethylbenzene and the selectivity to ring oxidation were defined as follows:

$$\text{Conversion of EB} = \frac{n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7}{n_{\text{EB}}} \times 100\%$$

$$\text{Selectivity to ring activation} = \frac{n_1 + n_2 + n_3}{n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7} \times 100\%$$

where n_i represents the molar amount of the substance i . The substances 1–7 are defined as:



2.3. UV–Vis spectra

The solution of the vanadium complexes with fixed concentration in water, or in glacial acetic acid, or in aqueous acetic acid, before or after the addition of H₂O₂, was studied by UV-vis spectroscopy with a TU-1901 UV-Vis spectrophotometer. The electronic spectra of the samples in the range of 200–800 nm were collected at 295 ± 0.5 K. The sample cells were quartz with a 10-mm path length. All the UV–Vis spectra were background-subtracted using the corresponding solvent as the reference sample.

3. Results and discussion

In this paper, we selected the selectivity towards different products as the major criterion whereby the diperoxovanadate catalysts, that is, bpV(ox), bpV(pic), bpV(bpy), and bpV(phen), are judged. The *o*-, *m*- and *p*-ethylphenols, 2-ethylcyclohexa-2,5-diene-1,4-dione, acetophenone, 1-phenylethanol and benzaldehyde were detected as the products in all cases. Neither tars nor polycondensed aromatic hydrocarbons were found to form during the oxidation reaction. The amount of the ring activation products over the amount of total products obtained was evaluated.

3.1. Effect of the solvent

The influence of the solvent on the catalytic performance of the as-prepared diperoxovanadate complexes were firstly explored in the oxidation of EB with H₂O₂ in ethyl acetate, pyridine, acetone, acetic acid, acetonitrile, DMF, DMSO and water.

As shown in Table 1, the four kinds of diperoxovanadate catalysts were inactive for the titled reaction in pyridine and water media, because no oxidation products from EB were detected. However, bpV(pic), bpV(bpy) and bpV(phen) catalysts exhibited catalytic performance for the reaction in the other six kinds of solvents. The bpV(ox) complex was active only in acetone, acetic acid and DMF. For a given diperoxovanadate complex, the ability to activate the C–H bonds of EB was found to be related to polarity of

the solvents. The conversion of EB increased firstly with increasing the polarity of the solvents, reached the maximum value in HOAc, and then dropped in the solvents with higher polarity. Notably, in acetonitrile and acetic acid, the two solvents with nearly equal polarity, the diperoxovanadate complexes bpV(pic), bpV(bpy) and bpV(phen) showed higher performance. The results suggested that higher or lower polarity of the solvents was unfavorable for the catalytic activation of the C–H bonds on EB. It was presumed that the generation of the catalytically active species by the interaction of vanadium complex with H₂O₂ was probably affected by the polarity

Table 2
Catalytic performance over the diperoxovanadate catalysts in HOAc/H₂O media.^a

HOAc/H ₂ O (v/v)	bpV(bpy)		bpV(phen)	
	C (%)	S (%)	C (%)	S (%)
15:0	9.9	55.0	7.7	52.3
14:1	7.6	52.9	7.3	46.3
12:3	6.7	44.3	5.9	35.9
10:5	3.1	22.0	4.0	29.0
7.5:7.5	1.8	0	2.0	0
5:10	0.7	0	0.8	0
0:15	0	0	0	0

^a Reaction conditions: EB, 0.6 mL; H₂O₂, 1.0 mL; catalyst, 0.05 mmol; solvent, 15 mL; 30 °C; 4 h.

of the solvent. Such a solvent effect indicated a polar intermediate mechanism for the oxidation [25].

In addition, the competitive activation of C–H bonds between the ring and the side-chain occurred in different solvents. The ability for ring C–H bonds activation was enhanced in glacial acetic acid and acetonitrile media. Especially in glacial acetic acid, the preferential activation of aromatic ring C–H bonds was realized over the bpV(ox), bpV(bpy) and bpV(phen) catalysts, mainly obtaining the hydroxylated products (*S* > 50%).

To explore the possible influence of the acidity on the activation of EB, the oxidation was then comparatively carried out in formic acid, propionic acid, and *n*-butyric acid, in addition to acetic acid. It is known that the acidity of the used organic acids increased in the order of *n*-butyric acid < propionic acid < acetic acid < formic acid. It was interesting to find out that the conversion of EB increased with the acidity of the solvent, except for formic acid, indicating that the acidity of the solvent promoted the oxidation of EB. However, among the four kinds of organic acids investigated, the relative catalytic performance in formic acid was discrepant with the acidity. This may be due to the addition of water as co-solvent to formic acid for its fuming property.

3.2. Influence of water in HOAc on the activation of ring C–H bonds

To confirm the negative influence of water on the catalytic performance, the oxidation of EB was then studied over bpV(bpy) and bpV(phen) catalysts in aqueous acetic acid with different HOAc/H₂O volume ratios.

It was shown in Table 2 that both bpV(bpy) and bpV(phen) catalysts were inactive in water but active in HOAc/H₂O media. Both the conversion of EB and the selectivity to ring oxidation decreased with increasing the relative amount of water in the media. Whereas, the ring C–H bonds could not be activated when the volume of acetic acid was lower or equal to that of water. In terms of the polarity and acidity of the aqueous HOAc/H₂O media, the increased addition of water to HOAc increased the polarity of the media monotonically, but increased the acidity firstly and then lowered it. The results were consistent with the foregoing assumption that higher polarity and lower acidity of the solvent was disadvantageous for the activation of EB, especially for the activation of its aromatic C–H bonds. This may be why the activation of EB was relatively lower in aqueous formic acid than in glacial acetic acid.

3.3. Electronic and steric effect of the ligands on the catalytic performance

From Table 1, it was found that the four diperoxovanadate complexes with different ligands exhibited different ability to activate different types of C–H bonds of EB in glacial acetic acid. The catalysts bpV(bpy) and bpV(phen) were more active than bpV(ox) and bpV(pic) in terms of ring C–H bonds activation. In each case, the

amount of the *ortho*- and *para*-hydroxylated products formed was higher than that of the *meta*-ethylphenol. On account that the ethyl substituent is a weakly electron-donating group which renders the molecule more susceptible to an electrophilic attack at the *ortho*- and *para*-positions of the aromatic ring, a higher electrophilicity of the diperoxovanadates complex was deemed to be responsible for the higher selectivity towards ring C–H bonds activation. To confirm this assumption, the structures of the four diperoxovanadium complexes were optimized, and the electronic density around vanadium was evaluated by the TPSS//LANL2DZ method [26,27].

As indicated in Fig. 1, the electronic density around vanadium of the four diperoxovanadates complexes were 0.46, 0.42, 0.37, and 0.38, respectively, revealing the relative electrophilicity in the following order: bpV(ox) < bpV(pic) < bpV(phen) ≈ bpV(bpy). The higher electrophilicity of bpV(bpy) and bpV(phen) than that of bpV(ox) and bpV(pic) was responsible for their higher catalytic performance for ring activation. Furthermore, for the N, N-coordinated diperoxovanadates bpV(bpy) and bpV(phen), the steric hindrance of the ligand was also operative on the activation of the C–H bonds on EB. The ligand of phen had a planar structure with no twisting ability, which showed bigger steric hindrance than the flexible bpy ligand for the interaction of the vanadium center with the reactants or solvent molecules. As a result, bpV(bpy) was the most active catalyst for the activation of EB, especially for its aromatic ring C–H bonds activation.

A control experiment on the oxidation of EB over V₂O₅ was carried out at 50 °C in the absence of any ligands added. It was found that acetophenone, 1-phenylethanol, benzaldehyde, *ortho*-, *meta*-, *para*-ethylphenols, and 2-ethylcyclohexa-2,5-diene-1,4-dione formed, and the selectivity to side-chain oxidation was higher than that to ring. In addition, small amount of polycondensed aromatic hydrocarbons was detected. The products distribution and yield revealed that the presence of ligands in the diperoxovanadates complexes markedly affected the catalyst efficiency and selectivity to ring activation.

3.4. Optimization of the reaction conditions for ring activation

The selective oxidation of EB was then carried out by varying the amount of the diperoxovanadate catalysts used. The results plotted in Fig. 2 showed that the conversion of EB and the selectivity to ring activation were enhanced by increasing the amount of catalysts used. The elevated ability for ring activation suggested that the interaction of the diperoxovanadate complexes with H₂O₂ mainly led to the formation of the active species for aromatic C–H bonds activation.

Fig. 3 illustrates the effect of the amount of H₂O₂ on the selective oxidation of EB. As indicated, the EB conversion successively increased with the amount of H₂O₂ added, but the selectivity to ring activation decreased. Even in such case, no deep-oxidation products such as tars were produced.

The temperature effect was studied by varying the reaction temperature from 30 to 60 °C over bpV(bpy) catalyst in HOAc (Fig. 4). The conversion of EB increased from 10.6% at 30 °C to 15.6% at 50 °C but slightly dropped at higher temperature, presumably due to the accelerated non-productive decomposition of H₂O₂. The selectivity to ring oxidation increased with increasing reaction temperature. It was indicated that high temperature favored the generation of the catalytically active species which attacked the aromatic nucleus preferentially.

The effect of reaction time was investigated by varying the reaction time from 1 to 7 h over bpV(bpy) catalyst in HOAc, and the results were shown in Fig. 5. The conversion of EB increased from 5.4 to 20.6% with reaction time increasing from 1 to 4 h, and then kept almost constant. The selectivity to ring oxidation increased

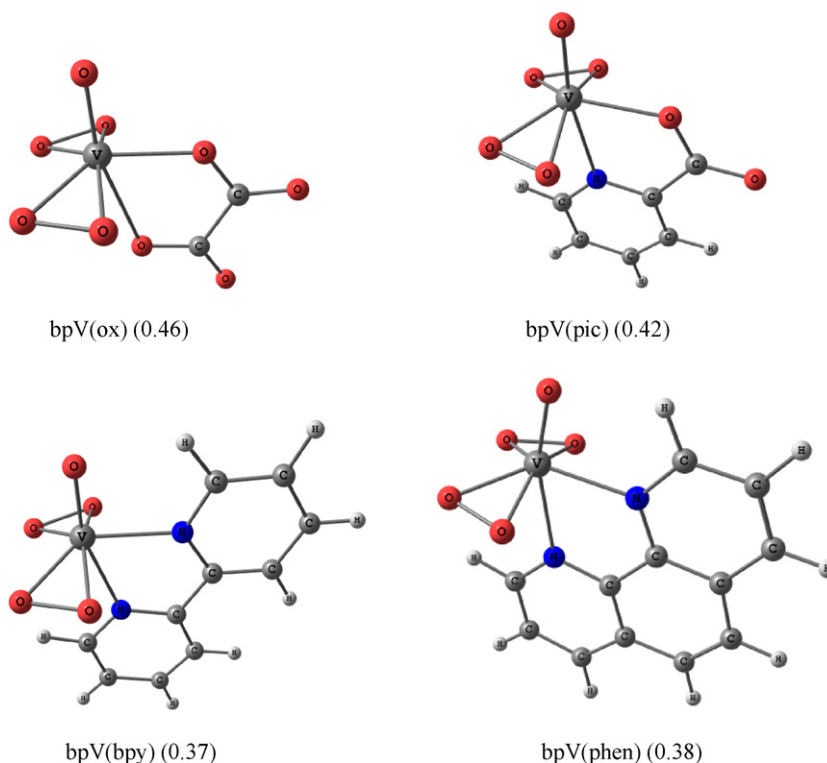


Fig. 1. The optimized structures and the electronic density around vanadium (by NBO analysis, shown in the bracket) for the diperoxovanadate complexes.

from 1 to 4 h, and kept almost unchanged with longer reaction time. The termination of oxidation reaction might be due to the used-up of H_2O_2 . It was indicated that 4 h reaction time at 50°C is proper.

The results under optimal reaction conditions for ring activation of EB over the four kinds of diperoxovanadate complexes are shown in Table 3. The preferential activation of the ring C–H bonds was realized in glacial acetic acid by adjusting the corresponding reaction conditions. The bpV– H_2O_2 –HOAc system was effective for the hydroxylation of EB without addition of any reducing agent such as hydroquinones, PhSH or tetrahydropterins in the medium [28]. An EB conversion of 20.6% with a selectivity to ring activation of 68.3% was obtained.

Table 3

Conversion of EB and selectivity to ring C–H bonds activation of EB over the diperoxovanadate catalysts under the optimal reaction conditions.

Catalyst	Conversion of EB (%)	Selectivity to ring activation (%)	TON
bpV(ox) ^a	10.9	60.2	4.3
bpV(pic) ^b	15.6	63.1	7.6
bpV(bpy) ^b	20.6	68.3	10.1
bpV(phen) ^c	16.1	61.3	7.9

^a Reaction conditions: EB, 1.2 mL; catalyst, 0.25 mmol; H_2O_2 , 1.0 mL (dropped in once); HOAc, 15 mL; 30°C ; 10 h.

^b Reaction conditions: EB, 1.2 mL; catalyst, 0.20 mmol; H_2O_2 , 1.0 mL (dropped in five runs); HOAc, 15 mL; 50°C ; 4 h.

^c Reaction conditions: EB, 1.2 mL; catalyst, 0.20 mmol; H_2O_2 , 1.0 mL (dropped in five runs); HOAc, 15 mL; 50°C ; 7 h.

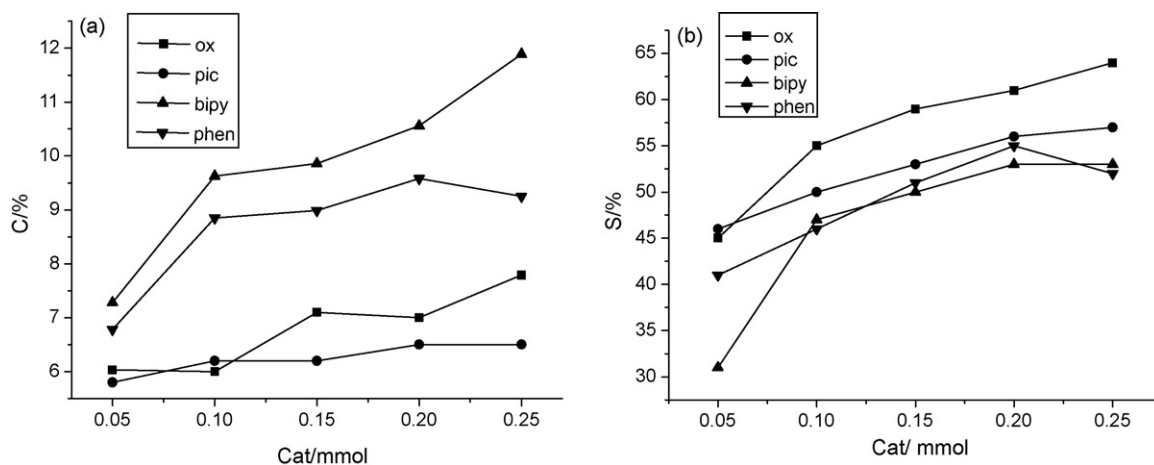


Fig. 2. The conversion of ethylbenzene (a) and the selectivity to ring C–H bonds oxidation (b) as a function of the catalyst amount. Reaction conditions: EB, 1.2 mL; H_2O_2 , 1.0 mL; HOAc– H_2O (v/v=9:1), 15 mL; 30°C ; 4 h.

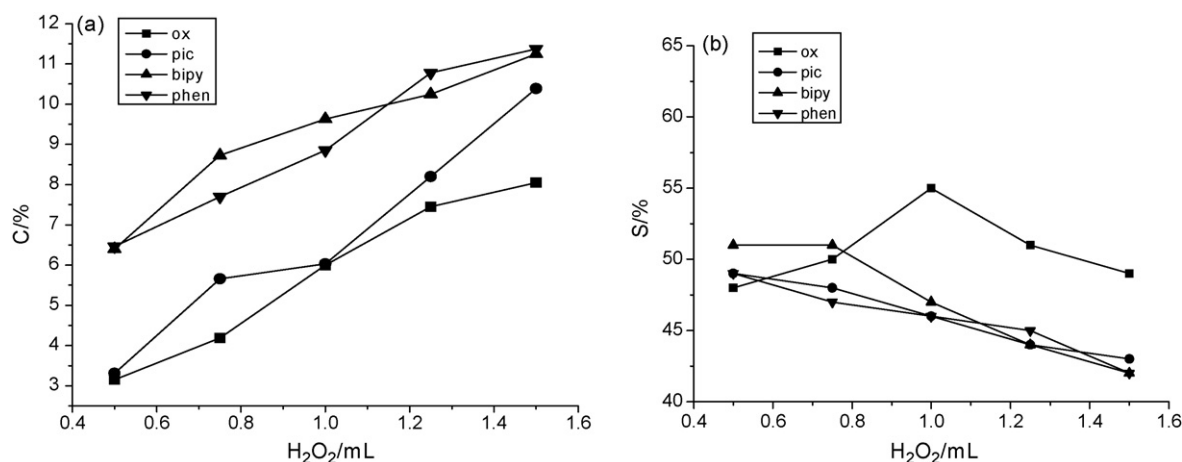


Fig. 3. Effect of the amount of H₂O₂ on the conversion of ethylbenzene (a) and the selectivity to ring C–H bonds oxidation (b). Reaction conditions: EB, 1.2 mL; catalyst, 0.1 mmol; HOAc–H₂O (v/v=9:1), 15 mL; 30 °C; 4 h.

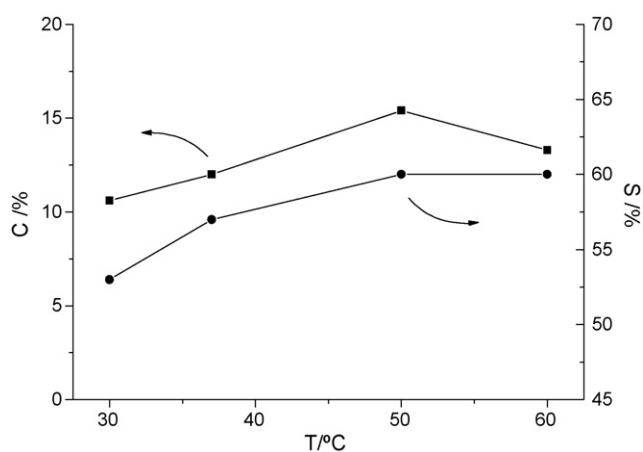


Fig. 4. Effect of temperature on the conversion and selectivity. Reaction conditions: EB, 1.2 mL; bpV(bpy), 0.2 mmol; H₂O₂, 1.0 mL; HOAc–H₂O (v/v=9:1), 15 mL; 4 h.

3.5. UV–Vis characterization

To get more information on the interaction between the catalyst, the solvent, and the oxidant in bpV(bpy)–H₂O₂–HOAc system, the UV–Vis spectra of the reaction mixture were monitored.

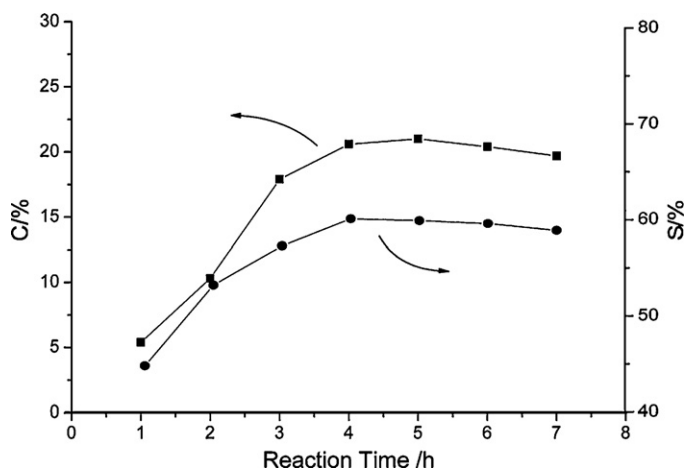
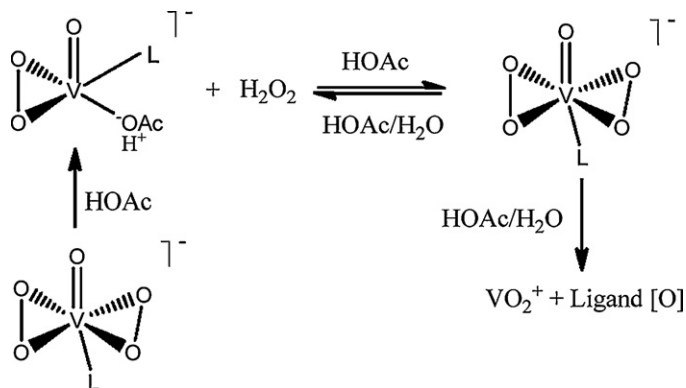


Fig. 5. Effect of reaction time on the conversion and selectivity. Reaction conditions: EB, 1.2 mL; bpV(bpy), 0.2 mmol; H₂O₂, 1.0 mL; HOAc–H₂O (v/v=9:1), 15 mL.

As shown in Fig. 6, characteristic electronic absorption of diperoxovanadate structure (320–350 nm) was observed in the UV–Vis spectra [29–31], indicating that the vanadium center was coordinated with two peroxy groups in water for all the four complexes. Whereas in acetic acid, a ligand exchange of peroxy group with one solvent molecule occurred with the formation of a stable six-coordinated monoperoxovanadate complex that exhibited electronic absorption at 400–450 nm [29,31–33]. The variation in color from yellow in water to red in acetic acid confirmed this structure change [29]. Notably, these peroxovanadate complexes were all stable in water or acetic acid. Immediately after the addition of hydrogen peroxide into acetic acid, no obvious variation in peroxovanadate structure was observed, except for the appearance of the electronic absorption of H₂O₂ at 249 nm.

The structural variation of bpV(bpy) complex after addition of H₂O₂ in the substrate-free glacial acetic acid and aqueous acetic acid was then monitored with time evolution (Fig. 7). In glacial acetic acid, as shown in Fig. 7(a), the appearance of the broad 320–500 nm absorption peak at 1 h indicated the transformation of monoperoxy to diperoxy. The structure of the resulting diperoxovanadate complex was stable in glacial acetic acid. However, in aqueous acetic acid (Fig. 7(b)), the structure of the diperoxovanadate complex was quickly destroyed by H₂O₂ within 90 min, as indicated by the disappearance of 320–370 nm bands for diperoxy structure and the observation of 270 nm band for VO₂⁺. The possible structural variation of the peroxovanadate species in glacial and aqueous acetic acid is schematically shown in Scheme 1. On account that the performance of the peroxovanadate complexes



Scheme 1. Structure variation of the peroxovanadate species in glacial or aqueous acetic acid.

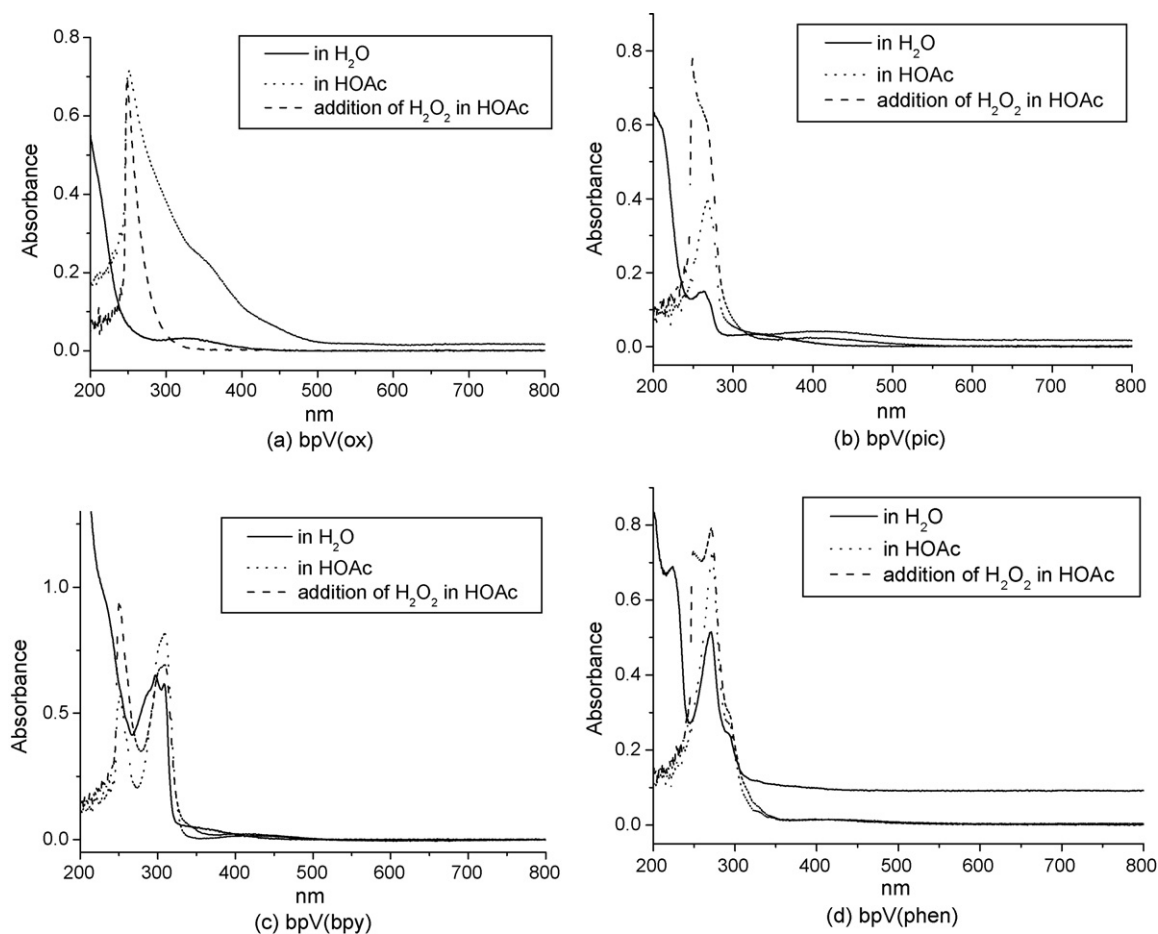


Fig. 6. UV-Vis spectra of the diperoxovanadate complexes in water and acetic acid solvents. (a) bpV(ox), (b) bpV(pic), (c) bpV(bpy), (d) bpV(phen).

for ring activation of EB was relatively higher in glacial acetic acid, we assumed that a stable diperoxovanadate structure in acetic acid is essential for obtaining an effective catalyst for ring oxidation of EB.

Based on the electronic spectra of the bpV(bpy)-H₂O₂-HOAc system, it was found that the HOAc molecule was involved in the ligand exchange around the vanadium center, and also in the stabilization of the diperoxovanadium species in the media. The coordination of HOAc molecule to the vanadium center was deemed to affect the generation of the active species by a polarization process. The presence of water in the system made the

peroxovanadium species unstable, and then lowered the selectivity to ring activation of EB. This could explain the fact that a higher concentration of HOAc in the media was essential for ring C-H bonds activation. In addition, a higher concentration of HOAc provided a higher pH value of the media. A protonation may contribute to the involvement of the catalytically active vanadium species [34].

3.6. Nature of the catalytically active species

To obtain more information on the characteristics of the catalytically active species for the aromatic ring activation of EB,

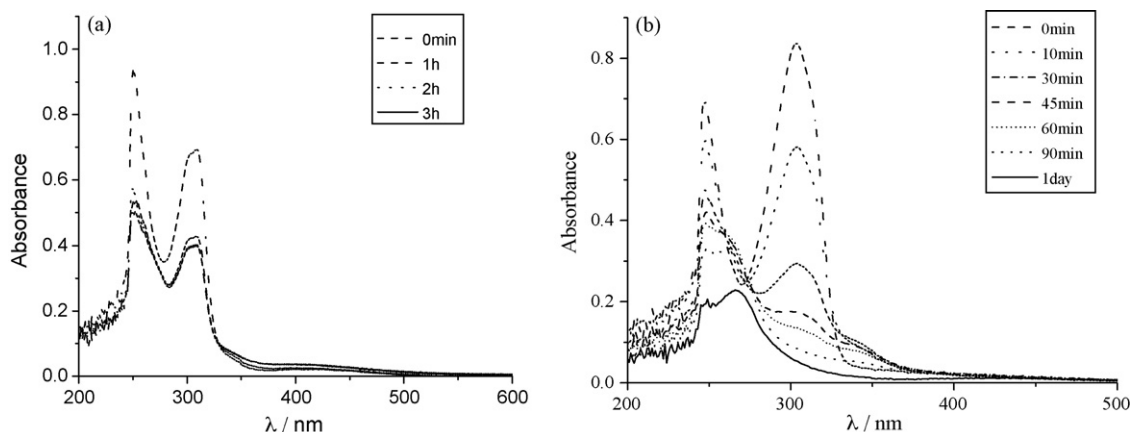


Fig. 7. Time variation of bpV(bpy) complex in glacial HOAc (a) and HOAc/H₂O (b) after addition of H₂O₂.

Table 4
Effect of the addition of radical scavenger on the catalytic performance.^a

Additive	Molar ratio of additive to substrate	Conversion of ethylbenzene (%)	Selectivity to ring activation (%)
<i>t</i> -Butyl alcohol (TBA)	1/2	18.4	63.2
	1/1	16.5	59.3
	2/1	12.7	58.4
2,6-Di- <i>t</i> -butyl-4-methylphenol (BHT)	1/2	11.6	69.8
	1/1	8.0	81.7
	2/1	6.3	96.5

^a Reaction conditions: bpV(bpy), 0.20 mmol; EB, 1.2 mL; H₂O₂, 1.0 mL (dropped in five runs); glacial HOAc, 15 mL; 50 °C; 4 h.

tert-butyl alcohol (TBA) or 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) were added into the reaction system to scavenge the possible radical species. The results are shown in Table 4.

A blank experiment without any additives revealed that the selectivity to ring oxidation of EB over bpV(bpy) catalyst reached 68.3% under the optimal reaction condition (Table 3, in glacial HOAc, 50 °C, 4 h). As expected, the conversion of EB was lowered after the addition of TBA or BHT, suggesting that the reactive oxygen species generated from H₂O₂ was consumed by TBA or BHT. These reactive oxygen species included the free radicals such as superoxide anion radicals (O₂^{•-}) or hydroxyl radicals (OH[•]), and non-radical species such as H₂O₂. It was found that the selectivity to ring oxidation was decreased when TBA, an effective hydroxyl radical scavenger, was added. Because the presence of free OH[•] in the oxidation mainly led to the preferential activation of the benzylic C–H bond, the addition of TBA in the system would enhance the selectivity to ring C–H bond activation if free OH[•] existed in the system. The decreased selectivity to ring oxidation indicated that OH[•] was rarely formed in the investigated reaction system. In addition, benzaldehyde was detected by GC–MS as a main product. This result revealed that O₂^{•-} radicals existed in the medium, which oxidized TBA to *tert*-butylhydroperoxide (TBHP) and the latter captured the weakest benzylic C–H bond easily resulting in the formation of benzaldehyde. When O₂^{•-} radicals were scavenged by BHT [35], the selectivity to ring oxidation was enhanced significantly, even to 96.5%. This means that the selectivity for ring oxidation was enhanced by scavenging the free oxygen radical species in the reaction system. The active species for attacking the ring C–H bond was deemed to be an electrophilic vanadium species which had preferential reactivity towards the aromatic rings but not too reactive towards the phenol products. They acted mainly as an electrophilic oxygen-transfer reagent under the investigated reaction conditions. The complex vanadium-containing species play a key role in control of the selective oxidation.

4. Conclusions

The competitive oxidation of C–H bonds between aromatic ring and side-chain of ethylbenzene was influenced considerably by the polarity and acidity of the solvent, the steric and electronic nature of the ligands of the peroxovanadate complexes, the amounts of catalyst and H₂O₂, as well as the reaction temperature. The ligand tuned the electrophilicity of the vanadium center and then tuned the catalytic performance. The bpV(bpy) and bpV(phen) with stronger electrophilicity than bpV(ox) and bpV(pic) made them more effective

to activate the ring C–H bonds. The smaller steric hindrance of 2,2'-bipyridine than 1,10-phenanthroline made bpV(bpy) the most efficient catalyst for ring C–H bond activation of EB. The HOAc molecule was involved not only in the ligand exchange around the vanadium center, but also in the stabilization of the diperoxovanadium species in the media. Primary experimental results revealed a polar intermediate mechanism by generating electrophilic catalytic species. The bpV(bpy)–H₂O₂–HOAc system was found to be an effective system for the preferential activation of the aromatic ring C–H bond (*S* = 68.3%).

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