

# Partial Oxidation of Toluene in CH<sub>3</sub>COOH by H<sub>2</sub>O<sub>2</sub> in the Presence of VO(acac)<sub>2</sub> Catalyst

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The partial oxidation of toluene by hydrogen peroxide with catalytic amount of bis (acetylacetonato) oxovanadium (VO(acac)<sub>2</sub>) in acetic acid is studied in detail. Benzaldehyde is found to be the main product in the reaction, and V<sup>51</sup>NMR and ESI-MS are used to detect the possible intermediate species. The effect of reaction parameters, such as the amounts of catalyst and hydrogen peroxide used, the reaction temperature, and reaction time on the reaction are investigated. The mechanism of toluene partial oxidation is also studied, and the hydroxyl radical is found to be the key active species. The solvent acetic acid coordinates with vanadium atom, and the toluene partial oxidation passes through cage reaction to form the C<sub>6</sub>H<sub>5</sub>CH•(OOH) radical, which promptly decomposes to benzaldehyde and hydroxyl radical. C<sub>6</sub>H<sub>6</sub>CH<sub>2</sub>OOCH<sub>2</sub>C<sub>6</sub>H<sub>6</sub> is also found to be one possible intermediate.

## 1. Introduction

Benzaldehyde is an important intermediate in the production of perfumery, pharmaceutical, dyestuff, and agrochemicals. There are several problems such as environmental pollution, erosion of equipment, deep oxidation, and so on with traditional preparation techniques of benzaldehyde. The activation of the C–H bond is one of the challenging problems in catalysis research, and it is very important for the conversion of crude oil and natural gas constituents into oxygenated derivatives such as alcohols or carbonyl compounds. With the discovery of vanadium chloroperoxidase, vanadium complexes have received renewed attention.<sup>1</sup> Vanadium complexes<sup>2–23</sup> are known to be effective to catalyze hydrocarbon oxidation with molecular oxygen, hydrogen peroxide, and other oxygen donors. H<sub>2</sub>O<sub>2</sub> is an attractive oxidant not solely due to being more active than O<sub>2</sub>, but rather to being with H<sub>2</sub>O as the only byproduct. In the oxidation of hydrocarbons by the reagent “O<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>-vanadium derivative-pyrazine-2carboxylic acid”, Shul’pin et al. proposed a mechanism involving first the abstraction of hydrogen atom from alkane by HO• to form alkyl radical R•, which then reacts rapidly with an O<sub>2</sub> molecule to give the peroxy radical, ROO•. This radical is then transformed simultaneously into three products: alkyl hydroperoxide, ketone, and alcohol.<sup>3,5,6,11,18</sup> They brought forward an assumption that the rate-limiting step of the reaction is the monomolecular decomposition of the complex V<sup>V</sup>(PCA)(H<sub>2</sub>O<sub>2</sub>) to form the V(IV) species, which then reacts with H<sub>2</sub>O<sub>2</sub> to generate the hydroxyl radical.<sup>6,23</sup> Khaliullin et al. performed density functional theory on free radical generation in the vanadate/PCA/H<sub>2</sub>O<sub>2</sub> system, and their results showed that hydroxyl radical could not be generated via direct cleavage of the V-OOH bond for its high activation barrier; therefore, it may be formed via a sequence of steps involving lower activation barriers. However, according to this mechanism, the rate of V-OOH bond breakage is lower than the rate of the hydrogen transfer from the coordinated hydrogen peroxide molecule to a vanadyl group; thus, the rate-limiting step of the reaction is the latter.<sup>24</sup> Theoretical mechanistic study<sup>25</sup> on the

[MeReO<sub>3</sub>]/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O-CH<sub>3</sub>CN catalytic system and kinetics study of isopropanol oxidation<sup>19</sup> further support this viewpoint. Other authors have proposed that the reactive intermediate is diradical species V<sup>IV</sup>-OO• formed from a homolytic cleavage of the peroxidic ring.<sup>21,22</sup> Si et al. used [V(O)(Cl)(PBHA)<sub>2</sub>] (PBHA = *N*-phenyl benzohydroxamate) as catalyst for hydrocarbon oxidation and assumed a nonradical mechanism,<sup>16</sup> considering the monoperoxy vanadium(V) species as the reactive oxidant. Reis et al. also assumed that the peroxy-vanadium(V) species might be the oxygenating agent of the benzene ring carbon or the methyl group of mesitylene.<sup>15</sup>

To our knowledge, in the similar system, there is still a dearth of reports on the role of vanadium species in the formation of benzaldehyde with a detailed mechanism. In our previous study, selective catalytic oxidation of toluene with hydrogen peroxide over V-Mo based catalysts by hydrogen peroxide was investigated,<sup>26</sup> we also found that glacial acetic acid is the best solvent for toluene oxidation. Shijina et al.<sup>27</sup> have obtained the similar results. It will be very interesting to investigate the catalytic system using glacial acetic acid as solvent. In this article, we investigate the oxidation of toluene in glacial acetic acid, using VO(acac)<sub>2</sub> as catalyst precursor, hydrogen peroxide as oxidant with an emphasis on the detection of intermediate species.

## 2. Experimental Section

All chemicals were purchased commercially and used as received. VO(acac)<sub>2</sub> and VO(OAc)<sub>2</sub> were prepared according to the literature.<sup>28,29</sup>

The toluene oxidation was carried out in a two-neck glass reactor (50 mL) fitted with a condenser and a magnetic stirrer. In a typical oxidation experiment, 15 mL of glacial acetic acid, 2 mL of toluene, and 0.06 mmol VO(acac)<sub>2</sub> were filled in the reactor. When the temperature was raised up to 363 K, hydrogen peroxide was added to the reaction system dropwise within 1 h, and then the resulting mixture was refluxed for 3 h.

After reaction, the products were directly analyzed by GC (FULI, GC-9790 equipped with a hydrogen flame ionization detector and a capillary column) using chlorobenzene as internal standard and/or identified by GC-MS analyses (Agilent, 5973 Network 6890N). While the reaction mixture was analyzed twice

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**TABLE 1: Effect of VO(acac)<sub>2</sub> Amount on the Distribution of Products Obtained from Toluene Oxidation<sup>a</sup>**

VO(acac) <sub>2</sub> (mmol)	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
0	1.3	23.6	0.3	5.4	0.5	9.1	0	0	3.4	61.8	5.4
0.01	6.8	67.3	0.8	7.9	0.3	3.0	0	0	2.2	21.8	10.1
0.03	9.9	72.8	0.7	5.1	0.8	5.9	trace	0	2.2	16.2	13.6
0.06	9.7	61.8	0.7	4.4	0.4	2.5	3.4	21.6	1.5	10.0	15.7
0.10	9.9	50.0	1.2	6.1	0.3	1.5	4.4	22.2	4.0	20.2	19.8
0.15	8.0	53.7	0.9	6.0	trace	0	2.9	19.5	3.1	20.8	14.9
0.20	7.5	55.6	0.7	5.2	0.2	1.5	1.6	11.9	3.5	25.9	13.5

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; hydrogen peroxide (30%), 12 mL; reaction time, 4 h; temperature, 363 K, adding hydrogen peroxide within 1 h.

**TABLE 2: Catalytic Performance of VO(acac)<sub>2</sub> in Toluene Oxidation as a Function of Reaction Time<sup>a</sup>**

reaction time/h	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
0.25	2.7	39.1	0.2	2.9	0	0	0	0	4.0	58.0	6.9
0.5	3.6	41.4	0.4	4.6	0	0	0	0	4.7	54.0	8.7
1.3	6.6	60.0	0.1	0.9	0.1	0.9	1.3	11.8	2.9	26.4	11.0
2	7.5	53.6	0.8	5.7	0.2	1.4	2.4	17.1	3.1	22.1	14.0
4	9.3	56.0	0.8	4.8	0.1	0.6	4.3	25.9	2.1	12.6	16.6
6	9.4	55.3	0.8	4.7	0.3	1.8	3.9	22.9	2.6	15.3	17.0

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; hydrogen peroxide (30%), 12 mL; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; temperature, 363 K, adding hydrogen peroxide within 1 h.

before and after reduction by triphenylphosphine, both alcohol and peroxide yields can be obtained from the quantified alcohol concentration before and after reduction.<sup>7</sup> It is revealed that the yield of peroxide is neglectable.

Yields were calculated as follows: the amount of product (mol)/the amount of toluene added. Selectivity was calculated as follows: the amount of target product (mol)/the sum of all products (mol).

V<sup>51</sup>NMR was used to characterize vanadium species in the reaction solution. Samples for the V<sup>51</sup>NMR characterization were prepared by dissolving 0.06 mmol catalyst in 15 mL of glacial acetic acid, and then 6 mL of 30% hydrogen peroxide was added. The V<sup>51</sup>NMR spectra of the samples were recorded on a Bruker DRX-400 spectrometer operating at 105.2 MHz using a 5-mm broadband probe in H<sub>2</sub>O–D<sub>2</sub>O solution. The probe temperature was maintained at 295.5 K. Chemical shifts were referred to external VOCl<sub>3</sub> (0 ppm). The <sup>51</sup>V NMR acquisition parameters were 104 kHz of spectral width, 0.31 s of acquisition time, and 1 Hz of line broadening.

The ESI-MS measurements were carried out using an LCQ instrument (thermoquest, San Jose, CA). Solution flow rate, 20 μL/min; capillary temperature, 298 K; spray voltage, 2.2 kV; capillary voltage, 15 V; tube lenses offset, –55 V; nebulizing gas, N<sub>2</sub> (40 units flow rate). The reaction mixture is acquired after 80 min of reaction at 363 K using 0.06 mmol catalyst, 2 mL of toluene, and 12 mL of H<sub>2</sub>O<sub>2</sub>. The anionic ion mode mass spectrum of the reaction mixture, using water–methanol as infusion solvent, showed the presence of different ionic species.

### 3. Results and Discussion

**3.1. Effect of Catalyst Amount.** The above-mentioned partial oxidation of toluene gives rise to benzaldehyde, benzyl alcohol, benzyl acetate, benzoic acid, and other oxidized products. The results are shown in Table 1. From Table 1, we observed that side-chain oxidation is the main reaction. With increased amount of catalyst used, a maximum yield of benzaldehyde of 9.9% at 0.03 mmol catalyst used with a maximum selectivity of 72.8% is observed. When the amount

of catalyst varies from 0.03 mmol to 0.10 mmol, the yield of benzaldehyde keeps almost unchanged, but the selectivity to benzaldehyde decreases. It is noted that when the amount of catalyst used is greater than 0.03 mmol, significant amount of benzoic acid is detected to form without any increase of benzaldehyde. It is well known that VO(acac)<sub>2</sub> is prone to association with itself and the solvent molecule. Csanyi et al. investigated the oxidation of hydrocarbon by O<sub>2</sub> in the presence of the VO(acac)<sub>2</sub> catalyst<sup>8</sup> and found the aggregation tendency of VO(acac)<sub>2</sub> in carbon tetrachloride, benzene, chlorobenzene, acetonitrile, and toluene; thus, two conversion maxima were observed. In our system, only one maximum benzaldehyde yield is observed; however, benzoic acid is detected when more than 0.03 mmol catalyst is used. This may be caused by the unstable characteristics of benzaldehyde capable of being further oxidized or the ignition of catalytic activity for benzoic acid formation. The yield of benzoic acid increases from trace to 4.4% with the catalyst amount increasing from 0.03 to 0.10 mmol, then falls with further increase of catalyst. Except benzyl acetate, the yields of other oxidized products reach maxima at 0.10 mmol catalyst with the highest toluene conversion of 19.8%. The maximum yield of benzyl acetate is obtained at 0.03 mmol catalyst similar to that of benzaldehyde. This phenomena of activity decrease at high catalyst amount can be identified as the so-called catalyst inhibitor conversion known for transition metal catalyzed oxidation.<sup>30–32</sup>

**3.2. Effect of Reaction Time.** The results in Table 2 show the conversion of toluene, the yields, and selectivities of products as a function of reaction time. It can be seen from Table 2 that benzaldehyde and benzyl alcohol form almost immediately, but benzoic acid and benzyl acetate form after an interval of reaction time. It seems that both benzoic acid and benzyl acetate form via secondary reactions. This implies that benzoic acid might be formed from the oxidation of benzaldehyde. To confirm this speculation, a control experiment in which benzaldehyde is directly used as starting material is carried out, and benzoic acid is obtained with 100% selectivity. It is shown that the catalyst is also active for the oxidation of benzaldehyde to

**TABLE 3: Catalytic Performance of VO(acac)<sub>2</sub> in Benzyl Alcohol Oxidation with Different Amounts of Hydrogen Peroxide<sup>a</sup>**

H <sub>2</sub> O <sub>2</sub> /(mL)	benzaldehyde		benzyl acetate		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	
1	18.0	32.0	38.3	68.0	56.3
0.5	9.0	22.1	31.7	77.9	40.7
0	2.6	8.7	27.3	91.3	29.9

<sup>a</sup> Conditions: benzyl alcohol, 1 mL; glacial acid, 15 mL; temperature, 363 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol, adding hydrogen peroxide for one time.

benzoic acid, and benzoic acid might originate from the primarily formed benzaldehyde. The yield of benzaldehyde increases with reaction time within the initial 4 h and then keeps constant, while its selectivity increases with time to reach a maximum at 4 h and then decreases. This may be caused by benzoic acid formation from benzaldehyde oxidation, and both the yield and selectivity of benzoic acid increase with reaction time.

It can be observed that the yields of the main products, that is, benzaldehyde and benzoic acid, reach maxima at 4 h, and the conversion of toluene also reaches its maximum simultaneously. The yields of benzyl alcohol and benzyl acetate keep almost constant after 80 min. It seems that both of them are intermediates for benzaldehyde and benzoic acid formation. Another control experiment is carried out under the same reaction conditions, where benzyl alcohol and benzyl acetate instead of toluene are used as substrate separately. No conversion of benzyl acetate is observed when it is used as reaction feed, while benzyl alcohol is oxidized to benzaldehyde and benzyl acetate, the latter being the main product as shown in Table 3. That is to say, the esterification of benzyl alcohol has precedence over its further oxidation and protects it from being further oxidized. From the results mentioned above, it can be concluded that benzoic acid may form from the oxidation of benzaldehyde, but benzyl alcohol may not be the main intermediate for benzaldehyde formation because the amount of benzaldehyde formed is much greater than that of benzyl acetate. Thus, benzaldehyde may form via a direct route other than via the benzyl alcohol intermediate under the present reaction conditions.

**3.3. Optimization of Reaction Conditions.** The results in Table 4 show the influence of temperature on oxidation. We observed that higher temperature is beneficial to side-chain oxidation of toluene. Over the temperature range from 323 to 363 K, the yield of side-chain oxidation products increases with elevated temperature, and so does the conversion of toluene. It is worthy of note that the temperature effect from 343 to 363 K for the toluene conversion and for the yield of benzaldehyde is more obvious than that from 323 to 343 K. It seems that temperature has a significant effect on toluene conversion and benzaldehyde yield. An optimal yield of benzaldehyde is obtained at 363 K since further increase in temperature will cause evaporation of the reactant. It is well known that high temperature is beneficial to the decomposition of hydrogen peroxide. From this point of view, it seems that the decomposition of hydrogen peroxide is important for toluene oxidation.

The results in Table 5 show the effect of the amount of hydrogen peroxide used on toluene oxidation. We observed that side-chain oxidation is dominating in this reaction system. The yield of benzaldehyde meets the maximum with 12 mL of hydrogen peroxide used. Further increase of H<sub>2</sub>O<sub>2</sub> causes further oxidation of benzaldehyde to benzoic acid. When 16 mL of

hydrogen peroxide is used, the system becomes biphasic. Two layers were obviously observed, and the increase of the toluene conversion is slowed down.

The consumption of hydrogen peroxide is caused competitively by its self-decomposition and the oxidation of toluene. Therefore, a necessary prerequisite for the effective use of hydrogen peroxide in this system is to inhibit its self-decomposition. In order to probe the effect of instantaneous concentration of hydrogen peroxide on the above-mentioned two competitive reactions, we added the same amount of hydrogen peroxide into the reaction system at different times within 4 h to vary its instantaneous concentration. The results are shown in Table 6. From Table 6, it is likely that instantaneous hydrogen peroxide concentration has prodigious influence on toluene oxidation in this catalytic system. The more times H<sub>2</sub>O<sub>2</sub> is added, the higher the yields of oxidized products from side-chain oxidation, but when more than 24 times of H<sub>2</sub>O<sub>2</sub> addition is applied, both the yield of benzaldehyde and the conversion of toluene decreased. The rate of bromide oxidation by hydrogen peroxide catalyzed by *cis*-dioxovanadium(V), *cis*-VO<sub>2</sub><sup>+</sup> in acidic, aqueous, and aqueous/ethanol solution is slow at low H<sub>2</sub>O<sub>2</sub> concentration, increases to a maximum, and then decreases at high H<sub>2</sub>O<sub>2</sub> concentration.<sup>33</sup> It means that there is a best instantaneous hydrogen peroxide concentration for the formation of benzaldehyde.

The results in Table 7 show the influence of different catalyst precursors on toluene oxidation. It can be observed that the highest benzaldehyde yield and toluene conversion are obtained over vanadium pentoxide, while those obtained over VO(OAc)<sub>2</sub> are the lowest. Bonchio et al. found that the oxidation of V(IV) to V(V) proceeds through a radical chain mechanism which causes more decomposition of H<sub>2</sub>O<sub>2</sub> than the stoichiometric oxidation of V(IV) to V(V).<sup>34</sup> Previously, it has been reported that the reduction of vanadium by H<sub>2</sub>O<sub>2</sub> is the first step of the catalytic cycle.<sup>6,35</sup> The better catalysis of vanadium pentoxide than VO(acac)<sub>2</sub> and VO(OAc)<sub>2</sub> can be explained as follows: at initial reaction time, hydrogen peroxide consumption is less, and the establishment of catalytic cycle is faster in the presence of vanadium pentoxide than VO(acac)<sub>2</sub> and VO(OAc)<sub>2</sub>.

It has been reported that in the presence of a reducing agent, for example, ascorbic acid, vanadium compounds can efficiently catalyze aerobic hydroxylation of hydrocarbons. We also studied the effect of ascorbic acid in this system, and the results are shown in Table 8. It is shown that, the existence of ascorbic acid is beneficial to toluene oxidation, particularly for side-chain oxidation. It is noteworthy that ascorbic acid does not take part in further reactions in the catalytic cycle owing to higher activity of ascorbic acid than toluene. According to the literature,<sup>10,36</sup> ascorbic acid plays a role in catching molecular oxygen in reaction solution, then more hydroxyl radical is formed. On the basis of this statement, it is reasonable to propose that the hydroxyl radical is the active species in our system. The acetylacetonato ligand is irreversibly oxidized to acetic acid according to the literature,<sup>37</sup> and the better catalysis of VO(acac)<sub>2</sub> compared to that of VO(OAc)<sub>2</sub> may be caused by the acetylacetonato ligand as reducer.

**3.4. Role of Solvent.** In this system, the catalytic circle may pass through the one-electron redox process, in which vanadium is in oxidation states ranging from +4 to +5. The redox potential of this couple varied with acidity.<sup>38</sup> Therefore, the effect of proton on oxidation is investigated. Perchloric acid is used to provide proton, and acetonitrile instead of glacial acid is used as solvent. The results are shown in Table 9.

**TABLE 4: Catalytic Performance of VO(acac)<sub>2</sub> at Different Reaction Temperatures<sup>a</sup>**

temperature /K	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
303	2.4	27.0	0.4	4.5	trace	0	1.7	19.1	4.4	49.4	8.9
323	3.3	35.5	0.3	3.2	0.2	2.2	1.4	15.1	4.1	44.1	9.3
343	5.5	49.5	0.6	5.4	0.1	0.9	2.8	25.2	2.1	18.9	11.4
363	9.7	63.0	0.7	4.5	0.1	0.9	3.4	22.1	1.5	9.7	15.4

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; hydrogen peroxide (30%), 12 mL; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol, adding hydrogen peroxide within 1 h.

**TABLE 5: Catalytic Performance of VO(acac)<sub>2</sub> with Different Amounts of Hydrogen Peroxide in Toluene Oxidation<sup>a</sup>**

H <sub>2</sub> O <sub>2</sub> (mL)	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
4	4.4	47.8	0.4	4.3	0.4	4.3	0.4	4.3	3.6	39.1	9.2
8	7.1	59.7	0.5	4.2	0.4	3.4	1.6	13.4	2.3	19.3	11.9
12	9.7	63.0	0.7	4.5	0.1	0.6	3.4	22.1	1.5	9.7	15.4
16	9.7	56.7	0.9	5.3	0.4	2.3	4.3	25.1	1.8	10.5	17.1

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; temperature, 363 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol, adding hydrogen peroxide within 1 h.

**TABLE 6: Catalytic Performance of VO(acac)<sub>2</sub> in Toluene Oxidation with Different Times of Hydrogen Peroxide Addition<sup>a</sup>**

times of addition	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
1	4.8	61.8	0.3	3.9	0.1	1.3	0.5	6.6	2.0	25.9	7.7
2	5.4	62.1	0.5	5.7	0.3	3.4	0.9	10.3	1.6	18.4	8.7
4	8.0	47.9	0.8	4.8	0.4	2.4	4.4	26.3	3.1	18.6	16.7
8	11.7	60.6	1.2	6.2	0.3	1.6	4.5	23.3	1.6	8.3	19.3
12	13.8	62.4	1.3	5.9	0.4	1.8	4.9	22.2	1.7	7.7	22.1
24	11.7	65.6	1.1	6.2	0.44	2.5	3.3	18.5	1.3	7.3	17.8

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; temperature, 363 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; hydrogen peroxide (30%), 12 mL.

**TABLE 7: Effect of Different Catalyst Precursors on the Catalytic Performance in Toluene Oxidation<sup>a</sup>**

catalyst	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
V <sub>2</sub> O <sub>5</sub>	8.7	53.0	1.0	6.1	0.5	3.0	3.3	20.1	2.9	17.7	16.4
VO(OAc) <sub>2</sub>	7.5	52.1	0.7	4.9	0.4	2.8	2.5	17.4	3.3	22.9	14.5
VO(acac) <sub>2</sub>	8.0	53.1	0.8	5.3	0.3	2.0	3.3	21.9	2.6	17.6	15.0

<sup>a</sup> Conditions: toluene, 2 mL; glacial acid, 15 mL; temperature, 363 K; reaction time, 4 h; catalyst, 0.06 mmol; hydrogen peroxide (30%), 12 mL, adding hydrogen peroxide within 1 h.

**TABLE 8: Effect of Ascorbic Acid on Catalytic Performance in Toluene Oxidation<sup>a</sup>**

amount of ascorbic acid/g	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
0	9.1	56.5	0.7	4.3	1.7	10.6	1.1	6.8	3.5	21.7	16.1
0.1	10.5	58.3	0.9	5.0	2.0	11.1	2.0	11.1	2.6	14.4	18.0
0.2	10.1	55.2	0.6	3.3	1.6	8.7	3.2	17.5	2.8	15.3	18.3
0.4	11.6	62.0	0.5	2.7	1.6	8.6	2.9	15.5	2.1	11.2	18.7
0.8	13.0	59.9	0.7	3.2	2.3	10.6	3.6	16.6	2.1	9.7	21.7

<sup>a</sup> Conditions: toluene, 1 mL; glacial acid, 15 mL; temperature, 343 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; hydrogen peroxide (30%), 6 mL, adding hydrogen peroxide within 1 h.

From Table 9, we could observe that there is a maximum conversion as a function of proton concentration, so does the yield of benzaldehyde. This is consistent with the literature<sup>33</sup> for bromide oxidation by hydrogen peroxide and the literature<sup>39</sup> for methane oxidation in an aqueous solution. The presence of proton has accelerated the side-chain oxidation, particularly for benzoic acid and benzaldehyde formation, but there is no substantial increase of activity with further increase of perchloric acid concentration, and this is close to the results reported in the literature.<sup>40</sup> Such an effect might be related to the anionic

nature of the active species in solution, tentatively described as a radical anion.<sup>41</sup>

Acetic acid is a kind of weak acid, and in this catalytic system, it may provide protons to active species. To check this proposal, we studied the toluene oxidation by H<sub>2</sub>O<sub>2</sub> in the CH<sub>3</sub>CN–CH<sub>3</sub>COOH mixture with different volume ratios of CH<sub>3</sub>CN/CH<sub>3</sub>COOH ranging from 15:0 to 0:15, and the results are shown in Table 10. We can observe from Table 10 that the toluene oxidation does not increase monotonically with acetic acid concentration and that there are two maxima at the ratio

**TABLE 9: Effect of Proton Concentration on Catalytic Performance in Toluene Oxidation (Perchloric Acid)<sup>a</sup>**

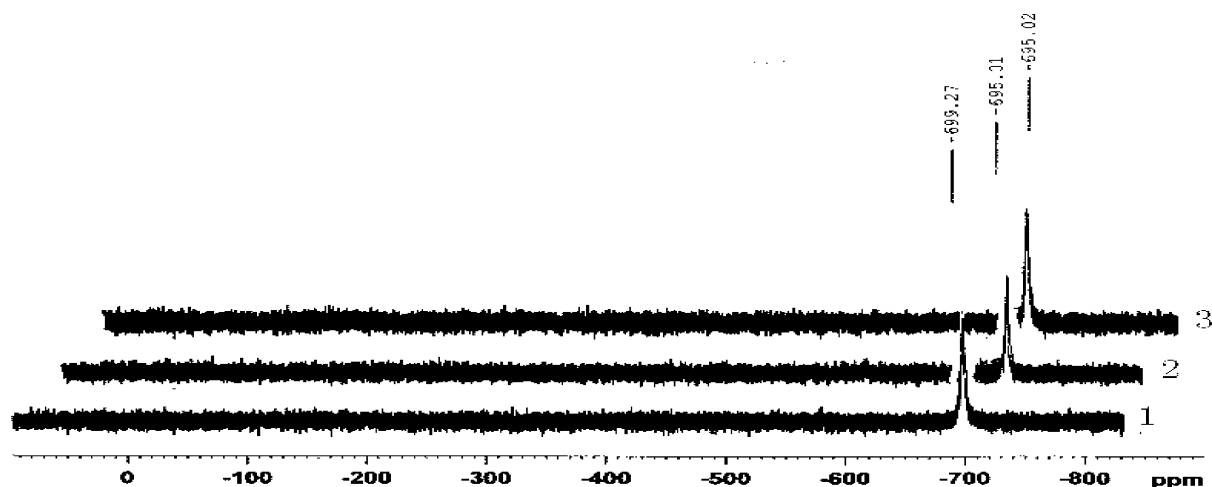
amount of perchloric acid/mmol	benzaldehyde		benzyl alcohol		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
0	7.0	70.7	0.5	5.1	0	0	2.4	24.2	9.9
1	10.2	71.3	0.5	3.5	2.1	14.7	1.5	10.5	14.3
2	10.5	72.4	0.4	2.8	2.5	17.2	1.1	7.6	14.5
3	12.8	72.7	0.7	4.0	2.6	14.8	1.5	8.5	17.6
4	11.5	70.1	0.5	3.0	3.4	20.7	1.0	6.1	16.4

<sup>a</sup> Conditions: toluene, 1 mL; acetonitrile, 15 mL; temperature, 343 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; hydrogen peroxide (30%), 6 mL, adding hydrogen peroxide within 0.5 h.

**TABLE 10: Effect of Acetic Acid Concentration on Catalytic Performance in Toluene Oxidation<sup>a</sup>**

ratio of CH <sub>3</sub> CN/CH <sub>3</sub> COOH	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
15:0	6.5	60.7	0.4	3.7	0	0	0	0	3.8	35.5	10.7
14:1	7.7	60.1	0.4	3.1	trace	0	2.0	15.6	2.7	21.1	12.8
12:3	7.1	55.5	0.4	3.1	0.6	4.7	0.8	6.2	3.9	30.5	12.8
10:5	5.7	66.3	0.3	3.5	0.3	3.5	0.6	7.0	1.7	19.8	8.5
5:10	5.7	63.3	0.3	3.3	0.3	3.3	0.6	6.7	2.1	23.3	9.0
0:15	8.3	43.0	0.6	3.1	trace	0	5.4	28.0	5.0	25.9	19.3

<sup>a</sup> Conditions: toluene, 1 mL; mixed solvent, 15 mL; temperature, 343 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; hydrogen peroxide (30%), 6 mL, adding hydrogen peroxide within 0.5 h.



**Figure 1.**  $V^{51}$ NMR spectrum of different catalyst precursors after oxidation by hydrogen peroxide without substrate. 1 is  $V^{51}$ NMR spectrum of VO(acac)<sub>2</sub>, 2 is  $V^{51}$ NMR spectrum of V<sub>2</sub>O<sub>5</sub>, and 3 is  $V^{51}$ NMR spectrum of VO(OAc)<sub>2</sub>.

of 14:1 and 0:15 for benzaldehyde formation along with the toluene conversion. It can be seen from the results that acetic acid is beneficial to toluene conversion, but with further increase in acetic acid concentration, the toluene oxidation is suppressed, passing through a rock bottom 10:5 with 8.5% toluene conversion and 5.7% benzaldehyde yield, reaching a maximum at pure acetic acid with 19.3% toluene conversion and 8.3% benzaldehyde yield. Thus, the function of acetic acid cannot merely be explained as proton provider. It is reasonable to propose that acetic acid may take part in toluene oxidation in other ways, such as complexing with the catalytic active center at high acetic acid concentration or forming peroxyacetic acid.

Kozlov et al. have suggested that in an organic solvent, because of the higher reactivity of organic compounds toward hydroxyl radical in comparison with the reactivity of H<sub>2</sub>O<sub>2</sub>, chain processes of hydrogen peroxide decomposition will be accompanied with conjugated solvent oxidation reactions because solvent molecules usually react with hydroxyl radicals.<sup>18</sup> For example, acetonitrile and trichloroacetonitrile were oxidized to peroxy-carboximidic acids under basic conditions.<sup>42,43</sup> It is reasonable to assume that peroxyacetic acid can be generated

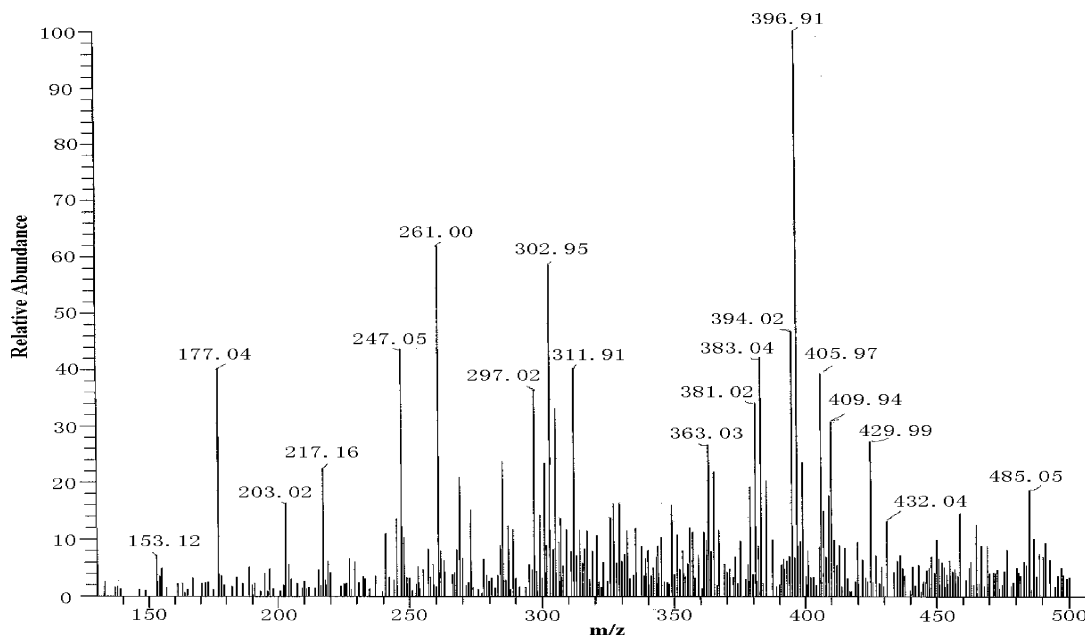
in situ by mixing solutions of acetic acid and hydrogen peroxide in the reaction process. To check this proposal, we studied toluene oxidation by peroxyacetic acid in acetic acid and acetonitrile. The results are shown in Table 11. From Table 11, we observe that, when peroxyacetic acid is used as oxidant, different solvents have no obvious influence on selectivity and activity of the reactions. However, the solvent used has an awful effect on the selectivity of benzaldehyde and benzoic acid using hydrogen peroxide as oxidant. It seems that peroxyacetic acid is not the key factor for the formation of benzaldehyde in our system.<sup>14</sup>

**3.5.  $V^{51}$ NMR Results.**  $V^{51}$ NMR is used to investigate the change of vanadium species, and the results are shown in Figure 1. The color of the solution becomes red immediately after the addition of H<sub>2</sub>O<sub>2</sub> but soon transforms to yellow. The  $V^{51}$ NMR spectra of all catalyst precursors show a chemical shift at around 695 ppm. The red color of the solution may be caused by the formation of monoperoxo vanadium.<sup>37</sup> In the literature,<sup>33,44,45</sup> the NMR spectrum at 691 ppm was assigned to [VO(O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O]<sup>-</sup> species. The magnetic shielding increases with the electron donation properties of the ligands.<sup>44,46</sup> Therefore,

**TABLE 11: Catalytic Performance of VO(acac)<sub>2</sub> in Toluene Oxidation by Peroxyacetic Acid<sup>a</sup>**

solvent	benzaldehyde		benzyl alcohol		benzyl acetate		benzoic acid		others		conversion (%)
	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)	
CH <sub>3</sub> CN	7.6	70.4	0.5	4.6	0.2	1.9	1.1	10.1	1.4	13.0	10.7
CH <sub>3</sub> COOH	7.1	65.4	0.2	1.8	0.5	4.6	1.8	16.5	1.3	11.9	10.8

<sup>a</sup> Conditions: toluene, 2 mL; solvent, 15 mL; temperature, 343 K; reaction time, 4 h; catalyst VO(acac)<sub>2</sub>, 0.06 mmol; peroxyacetic acid (18%), 12 mL, adding peroxyacetic acid within 0.5 h.

**Figure 2.** ESI-MS spectrum of reaction solution.

acetic acid coordinated peroxy vanadium species  $[\text{VO}(\text{O}_2)_2\text{-OAc}]^{2-}$  may form and show chemical shifts around 695 ppm.

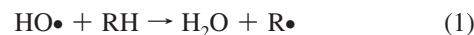
**3.6. ESI-MS Results.** ESI-MS experiments are carried out in order to obtain the direct experimental information about different vanadium species formed in the reaction. The results are shown in Figure 2. The ESI-MS spectrum in anionic shows the formation of a single vanadium peroxy species identified as  $[\text{OV}(\text{O}_2)(\text{OAc})_2]^-$  at  $m/z$  217.16. The peak at  $m/z$  = 177.04 is assigned to  $[\text{VO}_2(\text{OH})(\text{OAc})]^-$  with one water molecule. The peak at  $m/z$  = 383.04 is assigned to  $[\text{OV}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2]^-$  with one acetic acid molecule. The peak at  $m/z$  = 297.02 corresponds to  $[\text{OV}(\text{O}_2)(\text{OAc})(\text{C}_6\text{H}_5\text{CH}_2\text{O})]^-$  species with one methanol molecule. The peak at  $m/z$  = 261.00 is assigned to  $[\text{OVO}(\text{OAc})_2]^-$  with one acetic acid molecule. It is a direct evidence for the coordination of acetic acid to vanadium atom.

**3.7. Mechanism of the Reaction.** It is well known that the decomposition of hydrogen peroxide under the action of transition metals occurs as a radical chain process.<sup>47</sup> Chain transfer agents are hydroxyl and the hydroperoxyl radical. At the initial reaction stage, the catalyst precursor VO(acac)<sub>2</sub> is immediately oxidized to red vanadium(V) species and then oxidized to the diperoxy vanadium complex with hydroxyl radical production at simultaneously. These reactions in acetic acid are much less efficient.<sup>48</sup>

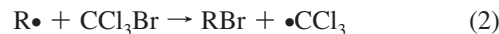
Hydrogen peroxide could reduce vanadium(V) to vanadium(IV) and produce the  $[\text{V}^{\text{IV}}\text{O}(\text{O}_2)]^-$  species in solution.<sup>49,50</sup> Mimoun et al. have proposed a mechanism through the diradical species  $\text{V}^{\text{IV}}\text{-O-O}\cdot$  as an active species,<sup>21</sup> but this compound shows the preferential ring-oxidation to the side-chain oxidation in toluene oxidation.<sup>47</sup> Bonchio et al. reported vanadium picolinate peroxy complexes could oxidize nitrobenzene to the corresponding phenol.<sup>52</sup> If  $[\text{V}^{\text{IV}}\text{O}(\text{O}_2)]^-$  species were the main

oxidative species in our system, (*o*, *p*, *m*), then nitrophenol would be obtained. However, in the control experiment under the same reaction conditions, using nitrobenzene instead of toluene as substrate, only trace *m*-nitrophenol is obtained. It seems that  $[\text{V}^{\text{IV}}\text{O}(\text{O}_2)]^-$  species may not be the main active species in our system.

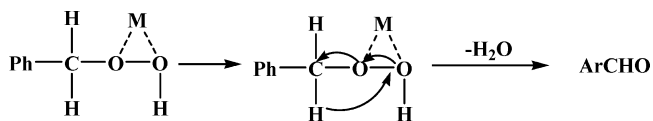
Fenton reagent is well known to generate the hydroxyl radical  $\cdot\text{OH}$  as an active species. Kenji Nomiya used this reagent for toluene oxidation, and the results showed that the hydroxyl radical is preferential for side-chain oxidation.<sup>51</sup> Hydroxyl radicals can be generated from hydrogen peroxide under the action of various transition metal ions involving vanadium.<sup>53,54</sup> Diphenylamine is an efficient radical trap for the hydroxyl and hydroperoxyl radical. When it is added into the reaction solution, the distribution of products is changed to those when the reaction occurred on the benzene ring. It is reasonable to assume the hydroxyl and hydroperoxyl radical as active species for toluene side-chain oxidation in this system. The hydroxyl radical easily abstracts hydrogen atoms from alkanes according to eq 1:



$\text{CCl}_3\text{Br}$  is an efficient C-centered radical trap as a donor of the bromine atom.



In order to determine the intermediate of toluene oxidation,  $\text{CCl}_3\text{Br}$  is added to the reaction solution. Benzyl bromide and benzyl chloride are obtained confirming the existence of the

**SCHEME 1: Mechanism of the Metal Catalyzed Dehydration of the Benzyl Hydroperoxide**

benzyl radical, but the main products are benzoyl chloride and benzoyl bromide. It has been reported that in the vanadium-mediated oxidation process, the proposed mechanism involves ketyl radical formation. The ketyl radical can lead to a chain process where ketone and  $\text{H}_2\text{O}_2$  are the products, but the ketyl radical is usually formed from alcohol oxidation.<sup>2,55</sup> Because we have already proved that benzaldehyde does not mainly form from benzyl alcohol, the formation of benzoyl chloride and benzoyl bromide may be key clues for benzaldehyde formation in our system.

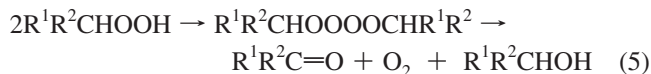
Alkyl radicals  $\text{R}\cdot$  react rapidly with the molecular oxygen obtained from hydrogen peroxide decomposition present in the solution, according to eq 3, to produce the corresponding alkylperoxy<sup>1,6,56–58</sup>



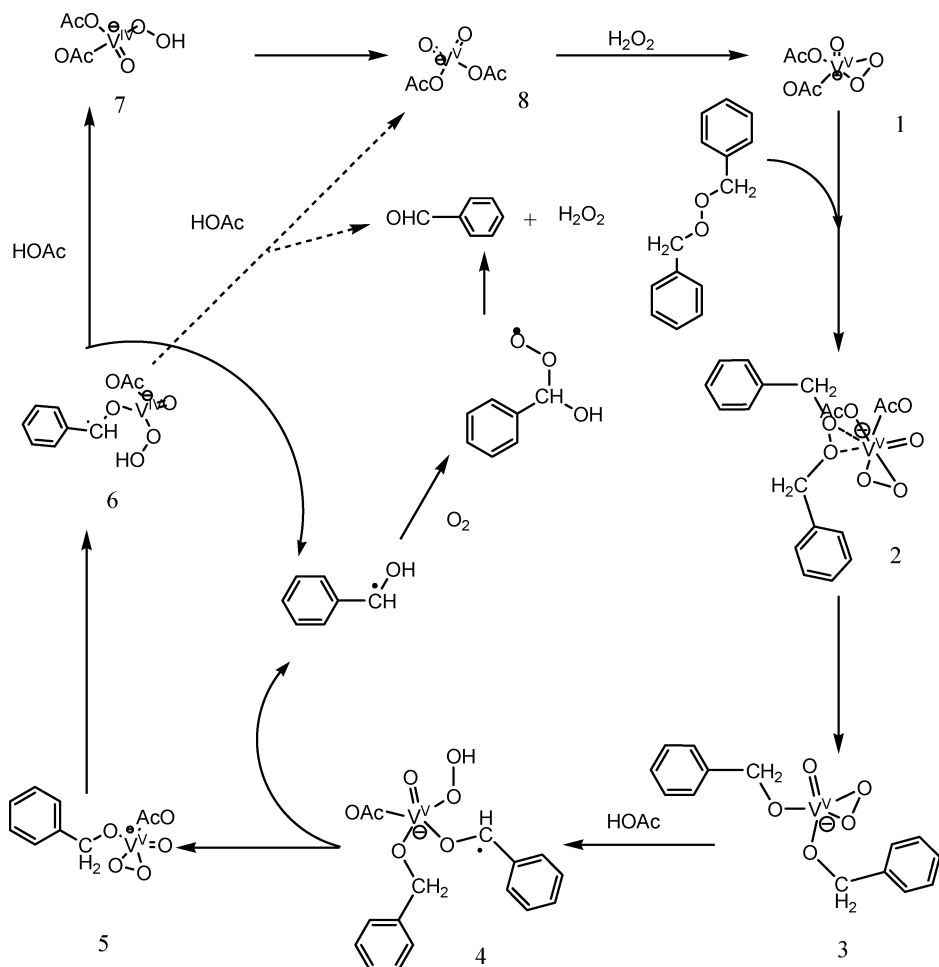
Alkyl radicals  $\text{R}\cdot$  can also react with hydroperoxyl radical to form benzyl hydroperoxide (eq 4).

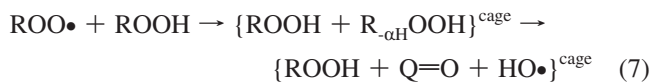


There are two kinds of reactions between peroxy radicals at low temperature affording corresponding intermediate or final products, that is, the so-called Russell termination (eq 5)<sup>59</sup> and Vaughan termination (eq 6).<sup>60</sup>



According to Russell termination, benzaldehyde and benzyl alcohol would be the main products of this reaction system. Owing to further oxidation of benzyl alcohol, benzyl acetate and benzaldehyde are the main products. At the end of the reaction, the amount of benzyl acetate would be more in our system. According to the product distribution, Vaughan termination might not be happening in our system. Concerning the products configuration and the formation of benzoyl chloride and benzoyl bromide, it seems that  $\text{C}_6\text{H}_5\text{CH}_2\text{OO}\cdot$  and benzyl hydroperoxide pass through a solvent cage reaction to form the  $\text{C}_6\text{H}_5\text{CH}(\text{OOH})\cdot$  radical,<sup>61</sup> which promptly decomposes to benzaldehyde and the hydroxyl radical (eq 7).

**SCHEME 2: Mechanism of Benzaldehyde Formation from  $\text{C}_6\text{H}_5\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_5$** 



Partenheimer has reported the mechanism of the metal catalyzed dehydration of the benzyl hydroperoxide in Scheme 1.<sup>62</sup> Vanadium species may play the same role in benzaldehyde formation in our system since benzyl hydroperoxide is not detected during the toluene reaction. According to our ESI-MS results, the peaks at  $m/z = 297.02$  and  $m/z = 383.04$  suggest the formation of  $[\text{OV}^{\text{V}}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})(\text{OAc})]^-$ , which is usually formed in alcohol oxidation,<sup>55,63,64</sup> and the formation of  $[\text{OV}^{\text{V}}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2]^-$ , which indicates a different way of benzaldehyde formation. The appearance of the peak at  $m/z = 432.04$  suggests that  $\text{C}_6\text{H}_6\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_6$  may be one possible intermediate for benzaldehyde formation. On the basis of this hypothesis, we propose the formation of benzaldehyde from  $\text{C}_6\text{H}_6\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_6$  as shown in Scheme 2.

After Vaughan termination forming  $\text{C}_6\text{H}_6\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_6$ , as shown in Scheme 2,  $\text{C}_6\text{H}_6\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_6$  reacts with  $[\text{V}^{\text{O}}(\text{O}_2)(\text{OAc})_2]$  species 1, then passes through complex 2 to form complex 3  $[\text{OV}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2]^-$ . Complex 3  $[\text{OV}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2]^-$  passes through intermolecular radical transfer to form complex 4. There is a peak at  $m/z = 432$  assigned to complex 4 with one acetic acid molecule in the ESI-MS spectrum. Then the solvent acetic acid acts on complex 4 to produce complex 5  $[\text{OV}(\text{O}_2)(\text{OAc})(\text{C}_6\text{H}_5\text{CH}_2\text{O})]^-$  and the ketyl radical, which can further react with  $\text{O}_2$  to form a new radical, and the new radical can give rise to benzaldehyde and  $\text{H}_2\text{O}_2$ .  $[\text{OV}(\text{O}_2)(\text{OAc})(\text{C}_6\text{H}_5\text{CH}_2\text{O})]^-$  can further intramolecularly transform to complex 6, which further decomposes to give complex 7 and the ketyl radical or directly gives benzaldehyde and complex 8. Complex 7 can further transform to complex 8  $[\text{OVO}(\text{OAc})_2]^-$ .

In our catalytic system, the products of the ring oxidation are mainly *ortho*- and *para*-cresol plus trace quinone. Hermans et al.<sup>61</sup> suggested that oxy radicals generated from the reaction of benzaldehyde and benzylperoxy radicals could abstract aromatic hydrogen atoms from toluene forming cresol. The reaction of  $\text{O}_2$  and  $\text{MePh}\cdot\text{OH}$  to form cresol and benzoquinone has been reported.<sup>65,66</sup> In the above-mentioned experiment, while  $\text{CCl}_3\text{Br}$  is added and *o*- and *p*-chlorotoluene and *o*- and *p*-bromotoluene are obtained, it seems that the reaction of  $\text{MePh}\cdot$  radicals and  $\cdot\text{OH}$  gives rise to cresol.

#### 4. Conclusions

In the partial oxidation of toluene in glacial acetic acid, using  $\text{VO}(\text{acac})_2$  as catalyst precursor and hydrogen peroxide as oxidant, side-chain oxidation is the main reaction with benzaldehyde as the main product. There is a best catalyst amount for toluene oxidation at 0.10 mmol with 19.8% conversion and an optimal catalyst amount for benzaldehyde formation at 0.03 mmol with 72.8% selectivity. Reaction temperature has a crucial effect on toluene oxidation, and the best catalysis is obtained at 363 K. The reaction is almost accomplished within 4 h. If more than 12 mL of hydrogen peroxide is added, the conversion of toluene does not increase as expected. The hydroxyl radical is an important active species for benzaldehyde formation, and the instantaneous concentration for  $\text{H}_2\text{O}_2$  has significant effect on its formation. Solvent acetic acid coordinates with the vanadium atom during toluene oxidation. Hydroxyl radical abstracts the H atom of toluene to form the benzyl radical, which then reacts with  $\text{O}_2$  to form the peroxy radical.  $\text{C}_6\text{H}_6\text{CH}_2\text{OO}\cdot$  and benzyl

hydroperoxide pass through a solvent cage process to form the  $\text{C}_6\text{H}_5\text{CH}\cdot(\text{OOH})$  radical, which promptly decomposes to benzaldehyde and the hydroxyl radical. During toluene oxidation,  $[\text{OV}(\text{O}_2)(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2]^-$  species may form from the reaction of  $[\text{V}^{\text{V}}\text{O}(\text{O}_2)(\text{OAc})_2]$  with  $\text{C}_6\text{H}_6\text{CH}_2\text{OOCH}_2\text{C}_6\text{H}_6$ , which is derived from Vaughan termination of the peroxy radical.

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