

# Oxidation of toluene and nitrobenzene with 30% aqueous hydrogen peroxide catalyzed by vanadium(V)-substituted polyoxometalates

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## Abstract

Product distribution in the oxidation of toluene, as well as nitrobenzene, with 30% aqueous hydrogen peroxide catalyzed by Keggin- and Dawson-type selectively site-substituted vanadium(V) polyoxometalates (POMs) was carefully examined with GC and GC/MS measurements in order to clarify the mechanism of benzene oxidation catalyzed by them. The POMs used here as catalyst precursors were  $Y_4[PMo_{11}VO_{40}]$  ( $Y = Bu_4N$ , **1a**;  $K$ , **1b**;  $Na$ , **1c**),  $Y_4K[PW_{10}V_2O_{40}]$  ( $Y = Bu_4N$ , **2a**;  $K$ , **2b**) and  $K_7[P_2W_{15}Mo_2VO_{62}]$  **3b**.<sup>1</sup> As control experiments, radical reactions with  $[VO(O_2)(pic)(H_2O)_2] \cdot 2H_2O$  **4** (pic, picolinate) and Fenton reagent **5** ( $Fe^{II}SO_4/30\%$  aqueous  $H_2O_2$  plus 0.05 ml of 60% aqueous  $HClO_4$ ) for the toluene and nitrobenzene oxidations were also examined under our conditions; the hydroxylation of benzene by **4** has been proposed to be promoted by the radical species formed on the vanadium complexes, while that by **5** has been considered to be promoted by the hydroxy radical species  $\bullet OH$ . The GC/MS spectral patterns of toluene oxidation catalyzed by the POMs have suggested that there are four different reactions by the POM groups and at least three of them, i.e. (1), (3) and (4), proceed via different radical mechanisms: (1) the reaction by **2a** resembled that by Fenton reagent **5** closely in the preferential side-chain oxidation; (2) the reactions by **2b** and **3b** showed preferential ring-oxidation, in particular, the selective production of *o*-cresol, which were quite different from the radical reactions by **4** and **5**; (3) the reactions by **1b** and **1c** were very similar to the radical reaction by **4** showing comparably both the side-chain oxidation and the ring-oxidation; and (4) the reaction by **1a** showed low selectivity in side-chain oxidation, although the ring-oxidation was very similar to that by **1b** and **1c**. These facts will be also the case for benzene oxidation. The unique catalytic behavior of **2b** and **3b** has been also observed in nitrobenzene oxidation. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Oxidation; Toluene; Nitrobenzene; Hydrogen peroxide; Vanadium(V)-substituted polyoxometalates

## 1. Introduction

Catalytic hydroxylation of benzene is a very intriguing reaction, and many catalysts have so far been reported [1–17]. One of them, the Milas reagent which

consists of  $V_2O_5$  and aqueous  $H_2O_2$  [16,17], is indeed a very effective catalyst for hydroxylation of organic unsaturated substances such as benzene and many types of alkenes. Recently, the reactivity of vanadium(V) peroxide complexes is receiving renewed attention [18,19]. The formation of the red oxoperoxovanadium(V) ion and a variety of net two-electron oxidation reactions involving hydroxylation of benzene and other arenes and alkanes catalyzed by the peroxovanadium(V) complexes have been reviewed [18].

<sup>1</sup> In our previous paper [25], the counteranion described as  $K_8H$  for  $[P_2W_{15}Mo_2VO_{62}]^{7-}$  **3b** is erroneous, e.g. in part (c) of the fifth figure and summary (pp. 67, second column, line 18).

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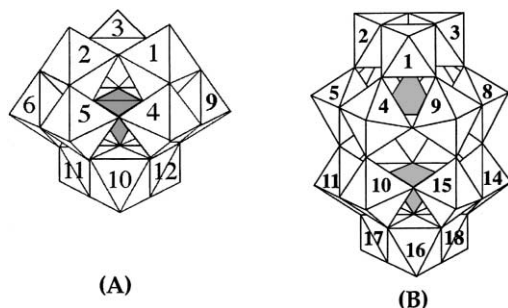


Fig. 1. (A) Polyhedral representation of the Keggin-type POM,  $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ , where one  $\text{PO}_4$  group is shown as the internal, black tetrahedron. In **1a–c**, **2a** and **2b**, the one and two vanadium octahedra are replaced by corner-shared  $\text{MO}_6$  octahedra in the one to three positions. (B) Polyhedral representation of the Dawson-type POM,  $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , where two  $\text{PO}_4$  groups are shown as the internal, gray tetrahedron. In **3a** and **3b**, the one vanadium and two molybdenum octahedra are replaced by three edge-shared  $\text{WO}_6$  octahedra in the one to three positions.

On the other hand, there is also currently considerable interest in exploiting both the well-defined structure of the catalyst precursor and the multi-center active site to facilitate the catalysis by polyoxometalates (POMs) [20–22]. We have recently found that benzene oxidation with 30% aqueous hydrogen peroxide has been catalyzed by several vanadium(V)-substituted Keggin and Dawson POMs (Fig. 1) [23–26]. In these catalyses, the presence of a vanadium(V) center in the POMs is a key factor, but a coordination environment around it is essential [23]. The catalyses by  $[\alpha\text{-1,2-PW}_{10}\text{V}_2\text{O}_{40}]^{5-}$  and  $[\alpha\text{-PMo}_{11}\text{VO}_{40}]^{4-}$ , and the stability of these compounds as catalysts were strongly cation-dependent, i.e. the stabilities as catalysts of  $\text{CH}_3\text{CN}$ -soluble  $\text{Bu}_4\text{N}$  salts were superior to those of the water-soluble alkali metal salts [25]. Since benzene hydroxylation by these POMs was accompanied with simultaneous decomposition of hydrogen peroxide, the significant effect of the used amounts of hydrogen peroxide was observed. The reactions which occur on the vanadium species within the POMs have been proposed for the precursors such as  $\text{K}_6\text{H}[\alpha\text{-1,2,3-SiW}_9\text{V}_3\text{O}_{40}]$ ,  $\text{K}_5[\alpha\text{-1,2-PW}_{10}\text{V}_2\text{O}_{40}]$  **2b** (only for the first reaction),  $(\text{Bu}_4\text{N})_4\text{K}[\alpha\text{-1,2-PW}_{10}\text{V}_2\text{O}_{40}]$  **2a**,  $(\text{Bu}_4\text{N})_4[\alpha\text{-PMo}_{11}\text{VO}_{40}]$  **1a** and  $\text{K}_7[\alpha_2\text{-P}_2\text{W}_{15}\text{Mo}_2\text{VO}_{62}]$  **3b** (see footnote), while those which occur on the vanadium

species generated from the POMs have been proposed for the POMs,  $\text{K}_6\text{H}[\beta\text{-1,2,3-SiW}_9\text{V}_3\text{O}_{40}]$ ,  $\text{K}_6[\alpha\text{-1,2,3-PW}_9\text{V}_3\text{O}_{40}]$ ,  $\text{K}_4[\alpha\text{-PMo}_{11}\text{VO}_{40}]$  **1b**,  $\text{Na}_4[\alpha\text{-PMo}_{11}\text{VO}_{40}]$  **1c**,  $\text{K}_6[\alpha\text{-1,4,9-PW}_9\text{V}_3\text{O}_{40}]$ , and  $\text{K}_8[\alpha_2\text{-1,2-P}_2\text{W}_{16}\text{V}_2\text{O}_{62}]$  [25].

Yet, in benzene oxidation, it has remained to be elucidated if the reactions by the POMs are promoted by a radical mechanism or not. Thus, in this work, we examined the oxidations of toluene and nitrobenzene with 30% aqueous hydrogen peroxide using the POMs,  $\text{Y}_4[\text{PMo}_{11}\text{VO}_{40}]$  ( $\text{Y} = \text{Bu}_4\text{N}$ , **1a**;  $\text{K}$ , **1b**;  $\text{Na}$ , **1c**),  $\text{Y}_4\text{K}[\text{PW}_{10}\text{V}_2\text{O}_{40}]$  ( $\text{Y} = \text{Bu}_4\text{N}$ , **2a**;  $\text{K}$ , **2b**) and  $\text{K}_7[\text{P}_2\text{W}_{15}\text{Mo}_2\text{VO}_{62}]$  **3b**. As control experiments of the radical reactions, the oxidation of toluene, as well as nitrobenzene was also examined under our conditions using  $[\text{VO}(\text{O}_2)(\text{pic})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  **4** (pic, picolinate) [9–15] and Fenton reagent **5** ( $\text{FeSO}_4/30\%$  aqueous  $\text{H}_2\text{O}_2$  plus 0.05 ml of 60% aqueous  $\text{HClO}_4$ ) [3–5], which have promoted the oxidation of aromatic compounds by the radical species formed on the vanadium complexes (the diradical species  $\text{V}^{\text{IV}}\text{-O-O}^\bullet$  [10,18] or the radical anion of the vanadium complex [12,18] and the hydroxy radical  $\bullet\text{OH}$ , respectively. Product distributions of these oxidation reactions were evaluated by gas chromatographic (GC) and gas chromatography/mass spectra (GC/MS) analyses.

Herein we report full details of the product distributions of toluene and nitrobenzene oxidations with 30% aqueous hydrogen peroxide catalyzed by the POMs described above.

## 2. Experimental

### 2.1. Apparatus and instrumentation

Gas chromatographic measurements were carried out on a Shimadzu GC-17AAT, which was equipped with a capillary column (column: DB-FFAP; column length: 15 m; inner diameter: 0.53 mm; film: 1 mm; column temperature: 90–150°C with a temperature ramp of 20°C  $\text{min}^{-1}$ ). GC/MS measurements were carried out by ThermoQuest (Tokyo, Japan) using TRACE MS (Quadrupole Mass Spectrometer) equipped with TRACE GC 2000 system (column: DB-FFAP). ESR spectra were recorded on a JEOL JES-RE2X spectrometer using a flat quartz cell for solutions (LABOTEC, LLC-04B).

## 2.2. Preparation and characterization of catalyst precursors of polyoxometalates

Fenton reagent **5** ( $\text{Fe}^{\text{II}}\text{SO}_4/30\%$  aqueous  $\text{H}_2\text{O}_2$  [0.1 mmol/2.0 ml] plus 0.05 ml of 60% aqueous  $\text{HClO}_4$ ) [3] and  $[\text{VO}(\text{O}_2)(\text{pic})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  **4** [10] were prepared according to the literature, and the latter was characterized with FT-IR,  $^1\text{H}$  NMR and TG/DTA. The POMs as catalyst precursors ( $\text{Bu}_4\text{N}$ ) $_4$  $[\text{PMo}_{11}\text{VO}_{40}]$  **1a**,  $\text{K}_4[\text{PMo}_{11}\text{VO}_{40}]\cdot 5\text{H}_2\text{O}$  **1b**,  $\text{Na}_4[\text{PMo}_{11}\text{VO}_{40}]\cdot 8\text{H}_2\text{O}$  **1c**, ( $\text{Bu}_4\text{N}$ ) $_4\text{K}[\text{PW}_{10}\text{V}_2\text{O}_{40}]$  **2a**,  $\text{K}_5[\text{PW}_{10}\text{V}_2\text{O}_{40}]\cdot n\text{H}_2\text{O}$  ( $n = 5-7$ ) **2b**, ( $\text{Bu}_4\text{N}$ ) $_7[\text{P}_2\text{W}_{15}\text{Mo}_2\text{VO}_{62}]$  **3a** and  $\text{K}_7[\text{P}_2\text{W}_{15}\text{Mo}_2\text{VO}_{62}]\cdot n\text{H}_2\text{O}$  ( $n = 11-19$ ) **3b** were prepared as previously described [23–26], and their compositions including hydrated water and their higher purities were confirmed by FT-IR, TG/DTA,  $^{31}\text{P}$  and  $^{51}\text{V}$  NMR spectroscopies.

Infrared spectra were recorded on a Jasco 300 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of  $4^\circ\text{C min}^{-1}$  between 20 and  $500^\circ\text{C}$ .

The  $^{31}\text{P}$  NMR (161.70 MHz) and  $^{51}\text{V}$  NMR (104.95 MHz) were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and JEOL EX-400 NMR data-processing system.  $^{31}\text{P}$  NMR spectra were referenced to an external standard of 25%  $\text{H}_3\text{PO}_4$  in  $\text{H}_2\text{O}$  in a sealed capillary and the  $^{51}\text{V}$  NMR spectra referenced to an external standard of  $\text{VOCl}_3$  by a substitution method. The chemical shifts were reported on the  $\delta$  scale with resonances upfield of  $\text{H}_3\text{PO}_4$  ( $\delta = 0$ ) as negative and with resonances upfield of  $\text{VOCl}_3$  ( $\delta = 0$ ) as negative, respectively.

## 2.3. Typical oxidation procedures and products analysis

The oxidation reactions of toluene and nitrobenzene were carried out at  $25^\circ\text{C}$  in a 50 ml round-bottom flask. The reaction system consisted of two liquid phases: an organic layer containing substrate and acetonitrile, and an aqueous layer containing acetonitrile and 30%  $\text{H}_2\text{O}_2$ . In a typical experiment, 0.10 mmol of catalyst precursor, 10 ml (93.99 mmol of toluene and 97.80 mmol of nitrobenzene) of

substrate, 2 ml (25.4 mmol) of aqueous 30%  $\text{H}_2\text{O}_2$ , and varied amounts (2, 5 and 10 ml) of acetonitrile in a 50 ml round-bottom flask with a serum cap were employed. A magnetic stirrer was provided to stir the reaction medium.

The nitrobenzene oxidation was examined by GC analysis of the organic layer. The organic solution of toluene oxidation was evaporated to ca. 1 ml volume by a rotary evaporator after separating the organic layer with a separatory funnel from the reaction solution. For both reaction systems, 1.5  $\mu\text{l}$  of the organic phase was sampled using a microsyringe and analyzed. The reaction products (*o*-, *m*-, *p*-cresol, benzaldehyde and benzyl alcohol in toluene oxidation and *o*-, *m*- and *p*-nitrophenol in nitrobenzene oxidation) were quantitatively analyzed using the calibration curve based on the relative area of each of authentic samples relative to an acetonitrile. In toluene oxidation, the reactions with excess diazomethane of the organic layers of the reaction solutions with all POMs showed no formation of methyl benzoate, suggesting that benzoic acid was not formed. Identification of products of toluene oxidation was also carried out by GC/MS analysis. Catalytic turnovers were estimated as a ratio of product (mmol)/catalyst precursor (mmol).

## 3. Results and discussion

### 3.1. Toluene oxidation

Conversion of toluene oxidation with 30% aqueous hydrogen peroxide catalyzed by POMs (**1a–c**, **2a**, **2b** and **3b**) was comparable to that of benzene oxidation under the same conditions. These reactions lack true synthetic value because of the relatively low yields. Major products of toluene oxidation were *o*-, *m*- and *p*-cresol, benzaldehyde and benzyl alcohol, which have been identified with GC and GC/MS analyses. In these reactions, benzoic acid was not formed. It should be, however, noted that only a reaction by **1a** was a lower-selective reaction as described below. The relative ratio (%) of major products at low conversion (0.2–0.9% of substrate) was estimated by GC and GC/MS analysis as listed in Table 1.

The GC/MS spectral patterns (Fig. 2) of the reaction solutions showed that the catalysis by the POMs can be classified into four groups as follows.

Table 1

Relative ratio of oxidation products of toluene with 30% aqueous H<sub>2</sub>O<sub>2</sub> catalyzed by vanadium(V)-substituted POMs and reference materials<sup>a</sup>

Catalyst precursor	Compound	Group	<i>o</i> -Cresol (turnover)	<i>m</i> -Cresol	<i>p</i> -Cresol	Benzyl alcohol	Benzaldehyde	Reaction time (h)
(Bu <sub>4</sub> N) <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	<b>1a</b> <sup>b</sup>	IV	30 (0.7)	14	3	15	38	480
K <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	<b>1b</b>	III	42 (2.0)	24	7	4	23	480
Na <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	<b>1c</b>	III	40 (1.7)	20	3	3	34	168
(Bu <sub>4</sub> N) <sub>4</sub> K[PW <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	<b>2a</b>	I	6	9 (0.3)	1	8	76	288
K <sub>5</sub> [PW <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	<b>2b</b>	II	50 (4.5)	11	11	7	21	480
K <sub>7</sub> [P <sub>2</sub> W <sub>15</sub> Mo <sub>2</sub> VO <sub>62</sub> ]	<b>3b</b>	II	53 (2.5)	9	10	8	20	288
[VO(O <sub>2</sub> )(pic)(H <sub>2</sub> O) <sub>2</sub> ]	<b>4</b>	III	32 (0.5)	27	9	4	28	48
Fenton reagent	<b>5</b>	I	8 (trace)	6	1	9	76	144

<sup>a</sup> Conditions: 0.20 mmol of catalyst precursor, 4 ml (50.8 mmol) of 30% aqueous H<sub>2</sub>O<sub>2</sub>, 20 ml (189.2 mmol) of toluene, room temperature, amounts of CH<sub>3</sub>CN; 20 ml for (**1a** and **2a**), 10 ml for (**1b**, **1c** and **3b**) and 4 ml for (**2b**, **4** and **5**).

<sup>b</sup> In this reaction, many other compounds are produced (see the text). These compounds were disregarded in calculating the numerical value.

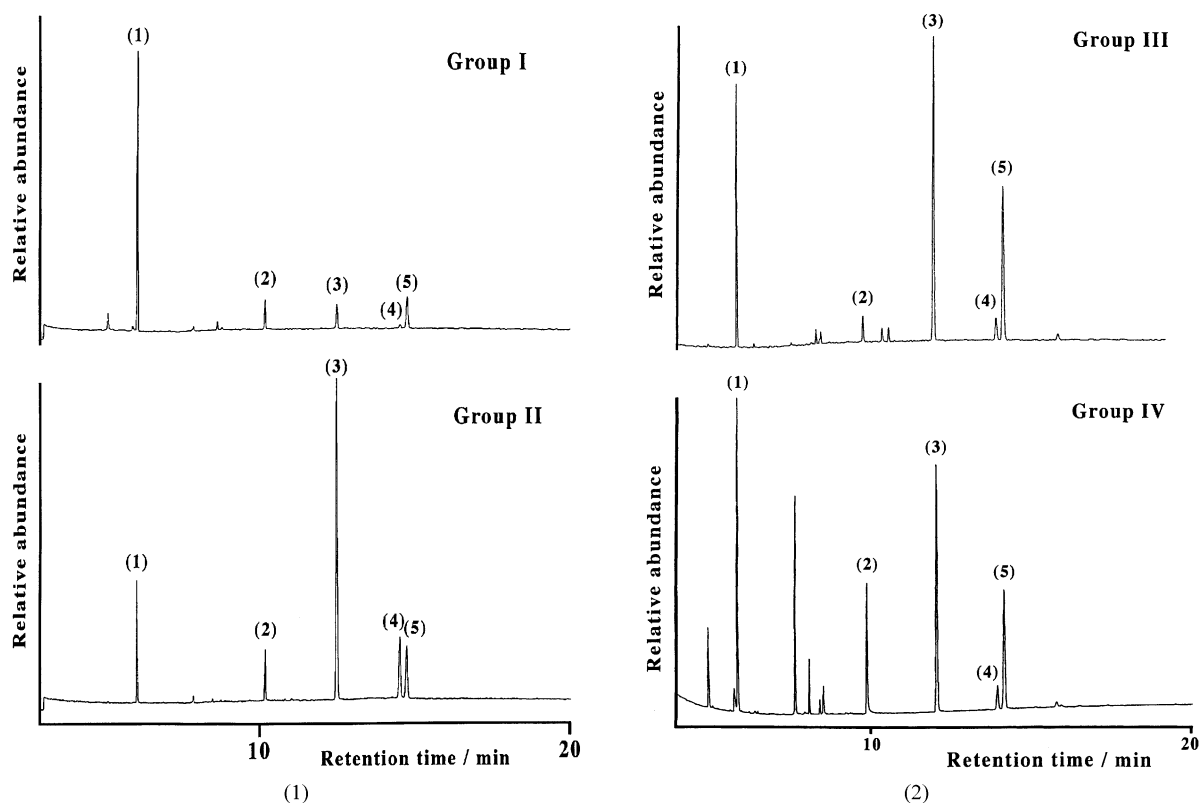


Fig. 2. Typical spectral patterns in GC/MS of toluene oxidation with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by the POMs and the reference materials; group I (**2a** and **5**), group II (**2b** and **3b**), group III (**1b**, **1c** and **4**) and group IV (**1a**). The parenthesized number of each peak in the GC/MS spectrum designates the products: (1) benzaldehyde; (2) benzyl alcohol; (3) *o*-cresol; (4) *p*-cresol; and (5) *m*-cresol.

- Group I includes  $(\text{Bu}_4\text{N})_4\text{K}[\text{PW}_{10}\text{V}_2\text{O}_{40}]$  **2a** and Fenton reagent **5** (Fig. 2). These compounds showed preferentially the side-chain oxidation (benzaldehyde as a major product and benzyl alcohol as a minor product) to the ring-oxidation ( $o$ -  $\sim$   $m$ -  $\gg$   $p$ -cresol). The amount of benzyl alcohol produced was comparable to those of  $o$ - and  $m$ -cresol. This product distribution was not seen in the reactions catalyzed by other POMs. Benzene oxidation catalyzed by **2a** has been shown to be promoted by the vanadium species within the POMs [25]. In analogy to the catalysis by **5** which generates the hydroxy radical  $\bullet\text{OH}$  as an active species, the catalytic reaction by **2a** will be probably promoted by a mono-radical species such as the hydroxy radical, which will be formed by the reaction of  $\text{H}_2\text{O}_2$  with the vanadium atoms in the POMs. In fact, the reaction of **2a** in  $\text{CH}_3\text{CN}$  with 30% aqueous  $\text{H}_2\text{O}_2$  in the presence of 5,5-dimethyl-1-pyrroline  $N$ -oxide (DMPO) as the spin trap resulted in the formation of the  $\text{DMPO-OH}\bullet$  radical, which was detected by ESR measurements.
- Group II includes the POMs,  $\text{K}_5[\text{PW}_{10}\text{V}_2\text{O}_{40}]$  **2b** and  $\text{K}_7[\text{P}_2\text{W}_{15}\text{Mo}_2\text{VO}_{62}]$  **3b** (Fig. 2). Benzene oxidation catalyzed by **2b** and **3b** has been shown to be promoted by the vanadium species within the POMs [25]. These compounds showed the preferential ring-oxidation to the side-chain oxidation. The amounts of products of the ring-oxidation decreased in the order;  $o$ -  $\gg$   $m$ -  $\sim$   $p$ -cresol. The high selectivity of  $o$ -cresol produced is noteworthy. It should be also noted that the catalysis by the alkali metal salt **2b** of  $[\text{PW}_{10}\text{V}_2\text{O}_{40}]^{5-}$  is in contrast to that by the  $\text{Bu}_4\text{N}$  salt **2a**. The catalysis by this group is unique; the product distribution by this group is quite different from those by the radical reactions by groups I, III and IV, thus suggesting that the reaction by group II may proceed through an ionic mechanism by the  $\text{OH}^+$  species.
- Group III includes  $\text{K}_4[\text{PMo}_{11}\text{VO}_{40}]$  **1b**,  $\text{Na}_4[\text{PMo}_{11}\text{VO}_{40}]$  **1c** and  $[\text{VO}(\text{O}_2)(\text{pic})(\text{H}_2\text{O})_2]$  **4** (Fig. 2). These compounds showed comparably the side-chain oxidation (benzaldehyde as a major product and benzyl alcohol as a minor product) and the ring-oxidation ( $o$ -  $>$   $m$ -  $\gg$   $p$ -cresol). Regarding the catalysis by **4** for benzene hydroxylation, Mimoun et al. have proposed a mechanism through

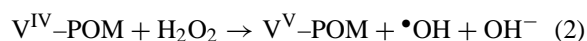
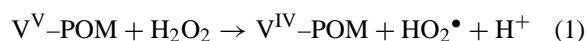
the diradical species  $\text{V}^{\text{IV}}-\text{O}-\text{O}\bullet$  as an active species [10,18], while Mondena et al. have suggested an alternate mechanism through the radical anion of the vanadium complex [12,18]. Benzene oxidation catalyzed by **1b** and **1c** has been shown to be promoted by the vanadium species generated from the POMs [25]. Thus, toluene oxidation by **1b** and **1c** will be promoted by the radical species formed on such free vanadium species.

- Group IV includes  $(\text{Bu}_4\text{N})_4[\text{PMo}_{11}\text{VO}_{40}]$  **1a**. This compound also showed both the side-chain oxidation and the ring-oxidation. Although the product distribution of the ring-oxidation is very similar to those in group III, i.e.  $o$ -  $>$   $m$ -  $\gg$   $p$ -cresol, group IV is quite different from all other groups with regard to the side-chain oxidation. The reaction by **1a** showed the formation of benzaldehyde, benzyl alcohol and benzyl formate as major products (the order was benzaldehyde  $>$  benzyl formate  $>$  benzyl alcohol), and also the formation of many other minor products such as acetic acid, formic acid, benzyl acetate, 3-acetyl-2,5-dimethylfuran and acetamide which may come from  $\text{CH}_3\text{CN}$  oxidation. Thus, the catalysis by **1a** showed a lower selectivity of products. Benzene oxidation catalyzed by **1a** has been shown to be promoted on the vanadium species within the POM [25]. Thus, toluene oxidation by **1a** also probably proceeds through a radical species formed on the vanadium atom in the POM. These results show that there are at least three different radical mechanisms in the toluene oxidation catalyzed by the POMs.

In toluene oxidation, the POMs with different counter-cations have shown different catalysis ( $\text{Bu}_4\text{N}$  versus alkali metal). This fact is more informative than benzene oxidation. The stability in solutions in the presence of hydrogen peroxide of the polyoxoanions used here is strongly cation-dependent as shown in benzene oxidation [25] and, consequently, the active species participating in the reaction will be also different for the same polyoxoanion.

In relation to the present reactions, oxidation of alkylaromatics including toluene and ethylbenzene catalyzed by " $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ " in 15 ml acetic acid solvent proceeded under the conditions; 2.5 mmol substrate, 0.02 mmol catalyst precursor, 25 mmol of 30%  $\text{H}_2\text{O}_2$  at  $80^\circ\text{C}$  for 3 h should be noted [27].

At 9.8 mol% conversion of toluene reacted, the selectivity of products of 85% benzaldehyde, 11% benzyl acetate and other unknown products has been reported. This catalyst precursor, which has been prepared by the so-called ether-extraction method, actually consists of Keggin-type  $H_4[PMo_{11}VO_{40}]$  and many non-Keggin-type unstable peroxy species consisting of P, V and Mo atoms, but does not contain divanadium(V)-substituted Keggin species [26]. However, the reaction mechanism proposed is useful, which has been based on the initial formation of hydroperoxy radical  $HO_2^\bullet$  and  $V^{IV}$ -POM by homolytic cleavage of  $H_2O_2$  at the vanadium atom within POM (Eq. (1)), the subsequent formation of hydroxy radical  $\bullet OH$  and  $V^V$ -POM by reaction of  $H_2O_2$  with  $V^{IV}$ -POM (Eq. (2)), and ethylbenzene oxidation through the reaction of the radicals  $HO_2^\bullet$  or  $\bullet OH$  with substrate forming a benzyl radical [27].



This mechanism may be applicable to our results of the preferred side-chain oxidation to the ring-oxidation observed in the catalysis by the POM of group I.

### 3.2. Nitrobenzene oxidation

Conversion of nitrobenzene oxidation with 30% aqueous hydrogen peroxide catalyzed by the POMs was much lower than those of toluene and benzene. Products of nitrobenzene oxidation catalyzed by **1–3** were *o*-, *m*- and *p*-nitrophenol, and *m*-nitrophenol was

a major product. The relative ratio (%) of products at very low conversion (0.2–1.0% of substrate) was estimated by GC analysis as listed in Table 2.

The results show the following several points.

1. In the reactions with the POMs of groups I, III and IV (**2a**, **1b** and **1a**), which caused toluene oxidation by the different radical mechanisms, the amounts of the products decreased in the order; *m*- > *p*- > *o*-nitrophenol, as is the case of reference materials (**4** and **5**). On the other hand, in the reactions with group II (**2b** and **3b**) which may promote toluene oxidation through the ionic mechanism, a different order was found; *m*- > *o*-  $\gg$  *p*-nitrophenol. Thus, the catalysis by group II (**2b** and **3b**) is also unique in nitrobenzene oxidation and different from those of other POMs.
2. The effect of counteranions was also observed in the nitrobenzene oxidation. The difference between **2a** and **2b** is more remarkable than that between **1a** and **1b**.

### 3.3. Relation to benzene oxidation

In benzene oxidation, it has been found by the  $^{31}P$  and  $^{51}V$  NMR measurements that the catalyses by  $[\alpha\text{-}1,2\text{-PW}_{10}\text{V}_2\text{O}_{40}]^{5-}$  and  $[\alpha\text{-}PMo_{11}VO_{40}]^{4-}$ , and their stabilities as catalysts are strongly cation-dependent ( $Bu_4N$  versus alkali metal) [25]. The benzene oxidation which occurs on the vanadium species within the POMs has been suggested for the catalyst precursors  $(Bu_4N)_4[\alpha\text{-}PMo_{11}VO_{40}]$  **1a**,  $(Bu_4N)_4K[\alpha\text{-}1,2\text{-PW}_{10}\text{V}_2\text{O}_{40}]$  **2a**,  $K_5[\alpha\text{-}1,2\text{-PW}_{10}$

Table 2

Relative ratio of oxidation products of nitrobenzene with 30% aqueous  $H_2O_2$  catalyzed by vanadium(V)-substituted POMs and reference materials<sup>a</sup>

Relative ratio (%)						
Catalyst precursor	Compound	Group	<i>o</i> -Nitrophenol	<i>m</i> -Nitrophenol (turnover)	<i>p</i> -Nitrophenol	Reaction time (h)
$(Bu_4N)_4[PMo_{11}VO_{40}]$	<b>1a</b>	IV	22	46 (2.6)	32	480
$K_4[PMo_{11}VO_{40}]$	<b>1b</b>	III	20	54 (1.4)	26	264
$(Bu_4N)_4K[PW_{10}V_2O_{40}]$	<b>2a</b>	I	18	55 (1.7)	27	480
$K_5[PW_{10}V_2O_{40}]$	<b>2b</b>	II	38	44 (3.3)	18	360
$K_7[P_2W_{15}Mo_2VO_{62}]$	<b>3b</b>	II	43	42 (1.0)	15	120
$[VO(O_2)(pic)(H_2O)_2]$	<b>4</b>	III	17	53 (1.3)	30	120
Fenton reagent	<b>5</b>	I	25	44 (1.7)	31	120

<sup>a</sup> Conditions: 0.10 mmol of catalyst precursor, 2 ml (25.4 mmol) of 30% aqueous  $H_2O_2$ , 10 ml (97.80 mmol) of nitrobenzene, room temperature, amounts of  $CH_3CN$ ; 10 ml for (**1a** and **2a**), 5 ml for (**1b** and **3b**) and 2 ml for (**2b**, **4** and **5**).

V<sub>2</sub>O<sub>40</sub>] **2b** and K<sub>7</sub>[α<sub>2</sub>-P<sub>2</sub>W<sub>15</sub>Mo<sub>2</sub>VO<sub>62</sub>] **3b**, whereas that catalyzed by the vanadium species generated from the POM has been suggested for K<sub>4</sub>[α-PMo<sub>11</sub>VO<sub>40</sub>] **1b** and Na<sub>4</sub>[α-PMo<sub>11</sub>VO<sub>40</sub>] **1c**. Strangely, the Bu<sub>4</sub>N salt **3a** of [α<sub>2</sub>-P<sub>2</sub>W<sub>15</sub>Mo<sub>2</sub>VO<sub>62</sub>]<sup>7-</sup> has shown no activity for benzene oxidation, although the potassium salt **3b** has exhibited considerable activity.

Toluene oxidation catalyzed by the POMs is much more informative. In toluene oxidation catalyzed by the vanadium-substituted POMs, there are at least three different radical mechanisms via a hydroxy radical (group I), and a radical species formed on the free vanadium atoms generated from the POM (group III) and on the vanadium atom within the POM (group IV). The most unique reaction is catalyzed by group II (**2b** and **3b**) which may proceed through an ionic mechanism driven by a reactive cationic species such as OH<sup>+</sup> or other radical mechanism different from groups I, III and IV. It should be also noted that these reactions are cation-dependent. These mechanisms are also the case for benzene oxidation.

#### 4. Summary

Oxidation of substituted benzene with 30% aqueous H<sub>2</sub>O<sub>2</sub> catalyzed by the vanadium(V)-substituted POMs has given more suggestive information than benzene oxidation. The catalysis by the POMs for toluene oxidation has been classified into four groups on the basis of GC/MS spectral patterns of the side-chain oxidation and/or the ring-oxidation: group I (**2a**) showing preferential side-chain oxidation (major benzaldehyde plus minor benzyl alcohol), the catalysis of which is very similar to that by Fenton reagent **5**, group II (**2b** and **3b**) showing preferential ring-oxidation to side-chain oxidation, the catalysis of which is characteristic of highly selective production of *o*-cresol, group III (**1b** and **1c**) showing comparably both the side-chain oxidation and the ring-oxidation (*o*- > *m*- >> *p*-cresol), the catalysis of which is very similar to that by [VO(O<sub>2</sub>)(pic)(H<sub>2</sub>O)<sub>2</sub>] **4**, and group IV (**1a**); although the product distribution of the ring-oxidation in group IV is very similar to that in group III, the product distribution of the side-chain oxidation is quite different from those of groups I–III. The unique catalytic behavior

of group II (**2b** and **3b**) has been also observed in nitrobenzene oxidation. The reactions by groups I, III and IV proceed through three different radical mechanisms.

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