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ORIGINAL PAPER

Catalytic activity of iron-substituted polyoxotungstates in the oxidation of aromatic compounds with hydrogen peroxide

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Abstract The tetrabutylammonium (TBA) salts of Keggin-type polyoxotungstates of the general formula $[XW_{11}Fe^{III}(H_2O)O_{39}]^{n-}$, where $X = $ P, B or Si, were evaluated as catalysts in the oxidation, under mild conditions, of ethylbenzene, cumene, *p*-cymene and *sec*-butylbenzene with aqueous H_2O_2 in CH_3CN at 80 °C. The influence of various factors, such as the substrate/catalyst molar ratio, the amount of oxidant added or the reaction time, was investigated in a systematic way. Generally, the system exhibited moderate conversion, with good selectivity towards the corresponding acetophenone and hydroperoxide. In order to understand the reaction pathways, the oxidation of several products and presumed intermediates was also carried out in the presence of $TBA_4[PW_{11}Fe(H_2O)O_{39}]\cdot 2H_2O$. Under the conditions used, the oxidation of styrene and styrene derivatives gave rise mainly to carbon–carbon double-bond cleavage, affording the corresponding products in very high yields (81–87%). Possible reaction pathways are presented.

Keywords Polyoxometalates · Transition-metal compounds · Oxidations · Arenes · Peroxides · C=C cleavage

Introduction

Liquid-phase oxidation of arenes, namely alkyl-substituted benzenes, can be an important tool to obtain industrially valuable functionalized products. For example, the oxidation of cumene yields cumene hydroperoxide, which is an intermediate for both phenol and acetophenone production, and the oxidation of ethylbenzene to ethylbenzene hydroperoxide is a key step in the propylene oxide/styrene process [1]. The oxidation of *p*-cymene affords 4-methylacetophenone, an important precursor for the manufacture of perfumes, or 4-isopropylbenzaldehyde, used as a flavouring agent for food materials [2, 3].

Achievement of this type of transformation under catalytic conditions constitutes a challenging task to chemistry research and industry [4–7]. Facing the present environmental constraints, new catalytic approaches combining environmentally benign oxidants and catalysts are highly desirable. Many papers address the study of processes for the synthesis of value-added ketones by benzylic oxidation of alkylaromatics using oxidants such as O_2 or H_2O_2, a few of them quite recent [8–14]. These substitute the classic stoichiometric methods based on oxidations with $KMnO_4$ or $K_2Cr_2O_7$ or on Friedel–Crafts acylation catalysed by $AlCl_3$ [15, 16]. Aromatic ketones are important chemical intermediates in pharmaceutical, fragrance, flavour, dye and agrochemical industries [17, 18].

Polyoxometalates (POMs) are economically and environmentally attractive acid or oxidation catalysts in both academic and industrial processes [19–25]. Recently we have shown that Fe^{III}-substituted Keggin-type polyoxotungstates can be effective catalysts in the oxidation with H_2O_2 of compounds such as indane or indene in acetonitrile [26, 27]. Hydrogen peroxide has high effective oxygen content, low cost, safe storage and operation methods and,

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above all, an environmentally friendly nature [28–31]. The combination of iron polyoxotungstates and hydrogen peroxide seemed, thus, to be an interesting option to use in the catalytic oxidation of arenes, and this led us to extend our studies to less reactive substrates. The catalytic oxidation of aromatic hydrocarbons with hydrogen peroxide, namely ethylbenzene, has been investigated with POMs such as $K_8SiW_{11}O_{39}$ (covalently linked to Schiff base complexes) [32, 33], $Na_5PV_2Mo_{10}O_{40}$ (supported on MCM-41) [34], $TBA_3PW_{12}O_{40}$, $TBA_3PMo_{12}O_{40}$, $TBA_4H_3PW_{11}O_{39}$ [35], $H_6SiV_2Mo_{10}O_{40}$, $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ [36], $TBA_4PVMo_{11}O_{40}$, or $TBA_4HPW_{11}Fe(OH)O_{39}$ [37].

In this paper we report the oxidation of ethylbenzene, cumene, *p*-cymene and *sec*-butylbenzene with 30% aqueous H_2O_2 in acetonitrile, using the iron(III)-substituted polyoxotungstate anions $[XW_{11}Fe^{III}(H_2O)O_{39}]^{n-}$, $X =$ P, Si, or B, as homogeneous catalysts. The outcome of the reactions depended strongly on the catalyst and conditions used. The oxidation of some of the reaction products or possible intermediates was also studied, in order to define possible reaction routes.

Results and discussion

The tetrabutylammonium (TBA) salts of Keggin-type anions $[XW_{11}Fe^{III}(H_2O)O_{39}]^{n-}$, $X =$ P, Si, or B (abbreviated $XW_{11}Fe$), were used as catalysts in this study. The reactions were performed at 80 °C with H_2O_2/substrate molar ratios equal to 2.0, 4.0, or 9.8. All presented results were obtained after 24 h of reaction. No improvement in the outcome of the reaction was observed by maintaining the oxidation process during 36 h.

*Oxidation of ethylbenzene (**1**)*

The oxidation of ethylbenzene (**1**) (Scheme 1) occurs with moderate conversion (Table 1; Fig. 1), reaching the highest

Scheme 1

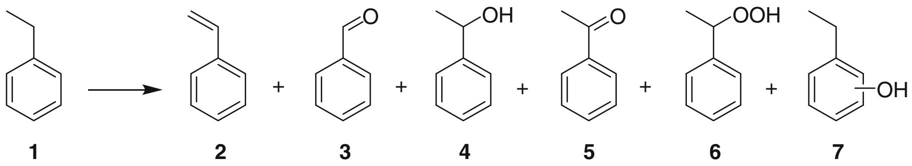


Table 1 Oxidation of ethylbenzene (**1**) by hydrogen peroxide catalysed by Fe^{III}-substituted polyoxotungstates after 24 h of reaction

Entry	Catalyst	Sub/cat	H_2O_2/sub	Conversion (%)[a]	TON[b]	H_2O_2 consumed (mmol)	Selectivity (%)[a]					
							2	**3**	**4**	**5**	**6**	**7**
1	$PW_{11}Fe$	667	2.0	17	114	0.54	4	10	10	27	41	8
2			4.0	18	120	1.92	5	12	9	33	40	1
3			9.8	20	132	3.22	5	14	9	32	37	3
4	$PW_{11}Fe$	333	2.0	21	69	0.85	6	10	13	13	42	16
5			4.0	25	85	2.61	6	9	8	18	47	12
6			9.8	26	87	6.28	6	9	7	21	48	9
7	$BW_{11}Fe$	667	2.0	17	115	1.97	7	16	20	39	18	–
8			4.0	18	120	3.94	6	15	17	46	16	–
9			9.8	19	137	9.65	7	13	17	50	13	–
10	$BW_{11}Fe$	333	2.0	15	49	1.97	1	12	14	59	12	2
11			4.0	16	53	3.96	4	11	13	59	6	7
12			9.8	17	56	9.64	3	8	16	67	4	2
13	$SiW_{11}Fe$	667	2.0	1	8	0.12	14	9	10	24	28	15
14			4.0	2	16	0.26	8	9	11	25	17	30
15			9.8	3	18	0.31	8	7	11	21	21	32
16	$SiW_{11}Fe$	333	2.0	10	33	0.19	4	5	6	10	29	46
17			4.0	10	33	0.48	2	4	4	10	30	50
18			9.8	11	36	0.70	2	5	5	12	25	51
19	None		9.8	–	–	n.d.	–	–	–	–	–	–

Reaction conditions: substrate (1.0 mmol), catalyst (1.5 or 3.0 μmol), and 2.0, 4.0, or 9.8 mmol of aqueous 30% (w/w) H_2O_2 were stirred for 24 h in CH_3CN at 80 °C

n.d. Not determined

[a] Determined by gas chromatography-mass spectrometry (GC-MS)

[b] Turnover number (mol of products per mol of catalyst)

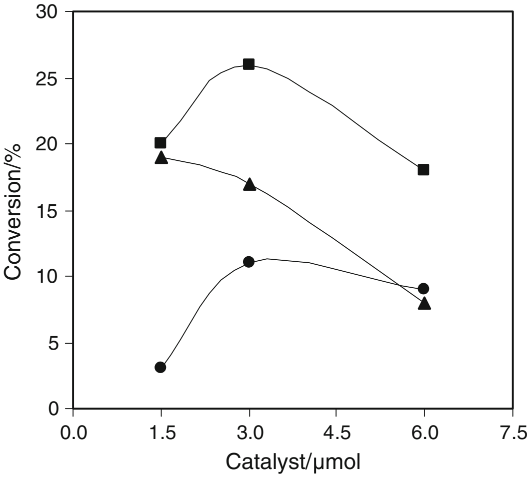


Fig. 1 Conversion of ethylbenzene in the presence of $PW_{11}Fe$ (*filled squares*), $SiW_{11}Fe$ (*filled circles*), or $BW_{11}Fe$ (*filled triangles*) after 24 h of reaction. Substrate: 1.0 mmol; H_2O_2: 9.8 mmol; acetonitrile: 3.0 cm^3; 80 °C

values (25–26%) in the presence of $PW_{11}Fe$ (molar ratio substrate/catalyst = 333) with excess of hydrogen peroxide (molar ratios H_2O_2/substrate = 4.0 and 9.8). For $BW_{11}Fe$, the conversions are in the range 15–19%, with the best results obtained when the oxidations are carried out with substrate/catalyst = 667. $SiW_{11}Fe$ was the least efficient catalyst, with conversion always lower than 11%.

Figure 1 illustrates how the conversion of ethylbenzene is affected by the amount of catalyst used, for the molar ratio H_2O_2/ethylbenzene of 9.8. Similar results were obtained with H_2O_2/ethylbenzene equal to 4.0. The maximum conversion of 26% is attained in the presence of 3.0 μmol of $PW_{11}Fe$ (per 1 mmol of substrate), and lower conversion values are obtained with 1.5 μmol or 6.0 μmol of $PW_{11}Fe$ (20% and 18%, respectively). This tendency is also observed with $SiW_{11}Fe$, but in the presence of $BW_{11}Fe$ the best performance is attained with the smallest amount of catalyst tested (1.5 μmol per mmol of substrate). The decreasing conversion with increasing amount of catalyst is not totally unexpected, due to the increase of iron concentration, which can assist H_2O_2 dismutation and inhibit the oxidation reaction [29].

The selectivity for the products varied with the catalyst added and also with the amounts of catalyst and oxidant used. In the presence of $PW_{11}Fe$, acetophenone (**5**) and ethylbenzene hydroperoxide (**6**) are, generally, the major products. Under the best conditions conversion wise (Table 1, entries 5 and 6), **6** is the main product (47–48%) followed by **5** (18–21%). Styrene (**2**), benzaldehyde (**3**), 1-phenylethanol (**4**) and ethylphenol (**7**) are obtained as minor products (≤9% for entry 6). In the reactions catalysed by $BW_{11}Fe$, the formation of acetophenone (**5**) is favoured and the best selectivity for this ketone (67%) is found for conditions of entry 12 in Table 1. Under these conditions, the second most abundant compound is **4** (16%), whereas the other products (**2**, **3**, **6**, and **7**) occur with minor abundances (selectivity ≤8%). The selectivity for **5** and **6**, in the presence of different amounts of oxidant, using 1.5 or 3.0 μmol of $BW_{11}Fe$, is presented in Fig. 2. With this catalyst, acetophenone (**5**) is always the major product and the selectivity for the hydroperoxide **6** decreases with increasing amount of catalyst and oxidant. In the presence of $SiW_{11}Fe$ (entries 16–18), oxidation of the aromatic ring is favoured, affording two phenol derivatives **7**, followed by **6** as the second most abundant product.

The consumption of H_2O_2 is higher in the presence of $BW_{11}Fe$ than for the other two polyoxotungstates, for the same H_2O_2/substrate molar ratio. The lowest consumption of H_2O_2 is observed with $SiW_{11}Fe$ (Table 1). For this catalyst and for $PW_{11}Fe$ the use of a higher amount of catalyst (6.0 μmol) induces a higher consumption of H_2O_2 without improving the conversion of ethylbenzene (results not shown). These results suggest that excess of catalyst in solution may lead to the decomposition of H_2O_2 and/or

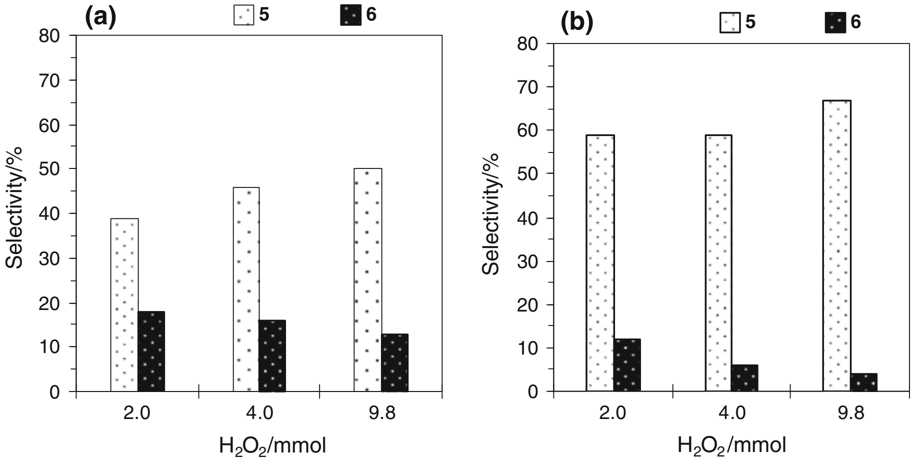


Fig. 2 Selectivity for acetophenone (**5**) and hydroperoxide (**6**) for ethylbenzene oxidation reaction with 2.0, 4.0, and 9.8 mmol of H_2O_2 catalysed by $BW_{11}Fe$, after 24 h. Substrate: 1.0 mmol; catalyst: **a** 1.5 μmol and **b** 3.0 μmol; acetonitrile: 3.0 cm^3 at 80 °C

hydroperoxide and that this effect is more pronounced in the presence of $BW_{11}Fe$.

These studies allow us to conclude that, in the reaction conditions studied, the maximum conversion of ethylbenzene attained is 26%. This is obtained in the presence of $PW_{11}Fe$ after 24 h of reaction, with good selectivity for ethylbenzene hydroperoxide (**6**). A moderate conversion of 18–19% is obtained with $BW_{11}Fe$ (with selectivity for acetophenone above 60%), while only 11% can be achieved with $SiW_{11}Fe$. The maximum conversions obtained are higher than those frequently observed for this substrate with published hydrogen peroxide/POM-based homogeneous systems [34–36].

*Oxidation of cumene (**8**)*

The oxidation of cumene (**8**) with H_2O_2 in the presence of the Fe^{III}-substituted polyoxotungstates affords the products shown in Scheme 2. The best conversions (34–37%) are attained in the presence of $PW_{11}Fe$ with excess of oxidant (substrate/catalyst = 333, Table 2, entries 5 and 6). The highest conversions attained with $BW_{11}Fe$ and $SiW_{11}Fe$ are 19% and 17%, respectively (Table 2, entries 9 and 18). As found with ethylbenzene, in the case of $PW_{11}Fe$ and $SiW_{11}Fe$ the conversion reaches a maximum at 3.0 µmol per mmol of substrate, and for $BW_{11}Fe$ the best values are observed with 1.5 µmol (Fig. 3a). Figure 3b illustrates how the conversion of cumene, in the presence of 3 µmol of each catalyst (cumene/catalyst molar ratio of 333), is affected by the amount of H_2O_2 added. In all cases, the increase of the H_2O_2/cumene molar ratio leads to an increase in the conversion.

In the presence of $PW_{11}Fe$, cumene hydroperoxide (**12**) is in general the major product, attaining selectivity higher than 71% for the best conversion conditions (Table 2, entries 4–6). Acetophenone (**5**) and 2-phenyl-2-propanol (**10**) are obtained with similar selectivity (7–12%) as the second most abundant products. In the presence of $BW_{11}Fe$, under the best conditions, the formation of **5** (46%) and **10** (31%) seems to be favoured (entry 9). Hydroperoxide **12**,

Scheme 2

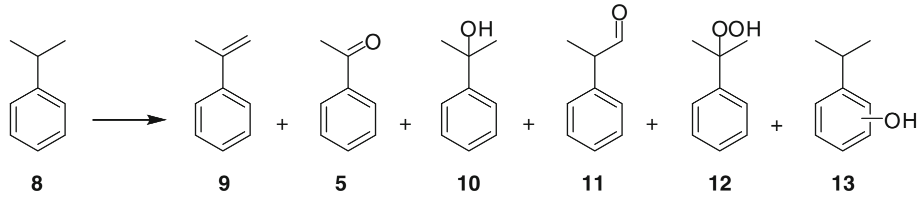


Table 2 Oxidation of cumene (**8**) by hydrogen peroxide catalysed by Fe^{III}-substituted polyoxotungstates after 24 h of reaction

Entry	Catalyst	Sub/cat	H_2O_2/sub	Conversion (%)[a]	TON[b]	H_2O_2 consumed (mmol)	Selectivity (%)[a]					
							9	5	10	11	12	13
1	$PW_{11}Fe$	667	2.0	3	20	1.46	11	16	15	10	27	21
2			4.0	10	70	2.71	4	13	12	2	68	1
3			9.8	17	112	3.62	6	23	3	1	67	–
4	$PW_{11}Fe$	333	2.0	30	100	1.87	2	8	7	2	78	3
5			4.0	34	113	3.08	2	10	7	3	72	6
6			9.8	37	122	6.24	3	12	12	2	71	–
7	$BW_{11}Fe$	667	2.0	10	67	1.89	6	40	30	2	22	–
8			4.0	15	100	3.91	10	37	27	4	22	–
9			9.8	19	126	9.61	8	46	31	5	10	–
10	$BW_{11}Fe$	333	2.0	7	23	1.89	4	25	25	2	44	–
11			4.0	12	39	4.00	4	30	29	2	35	–
12			9.8	16	53	9.58	5	43	31	3	18	–
13	$SiW_{11}Fe$	667	2.0	3	20	0.25	9	19	18	4	31	19
14			4.0	3	20	0.62	12	31	20	4	22	11
15			9.8	3	20	0.17	13	28	18	4	21	16
16	$SiW_{11}Fe$	333	2.0	13	44	0.29	3	10	10	4	38	35
17			4.0	16	54	0.75	9	15	13	9	25	29
18			9.8	17	58	0.57	11	15	13	10	22	29
19	None			–	–	n.d.	–	–	–	–	–	

Reaction conditions: substrate (1.0 mmol), catalyst (1.5 or 3.0 µmol), and 2.0, 4.0, or 9.8 mmol of aqueous 30% (w/w) H_2O_2 were stirred for 24 h in CH_3CN at 80 °C

n.d. Not determined

[a] Determined by GC-MS

[b] Turnover number (mol of products per mol of catalyst)

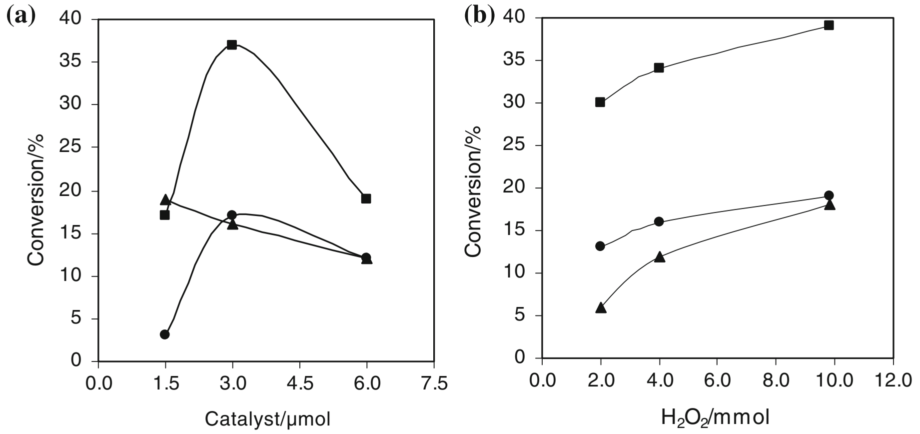


Fig. 3 Conversion of cumene (**8**) in the presence of $PW_{11}Fe$ (*filled squares*), $SiW_{11}Fe$ (*filled circles*), or $BW_{11}Fe$ (*filled triangles*) after 24 h of reaction. **a** H_2O_2: 9.8 mmol, different amounts of catalyst; **b** Catalyst: 3.0 μmol, different H_2O_2/substrate molar ratios. Substrate: 1.0 mmol; acetonitrile: 3.0 cm^3 at 80 °C

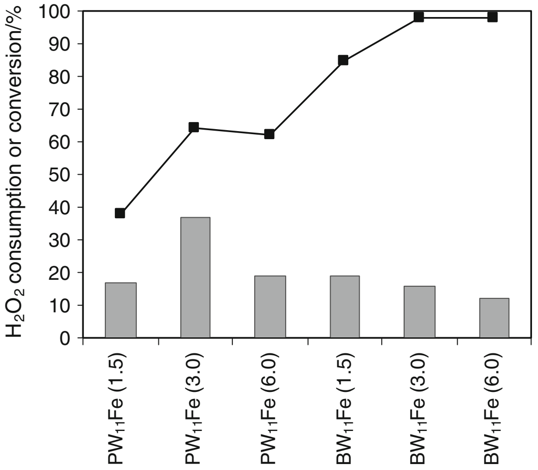


Fig. 4 H_2O_2 consumption (*filled squares*) and conversion (*bars*) for cumene (**8**) oxidation catalysed by $PW_{11}Fe$ and $BW_{11}Fe$ using 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 1.5, 3.0 or 6.0 μmol; acetonitrile: 3.0 cm^3 at 80 C

α-methylstyrene (**9**), and 2-phenylpropanal (**11**) occur with minor abundances (<10%). In the presence of $SiW_{11}Fe$ (entries 17 and 18), two phenol derivatives **13** and hydroperoxide **12** are the main products, although the oxidation of the aromatic ring is slightly favoured. The other products are obtained with comparable selectivity.

The hydrogen peroxide consumption in the oxidation of **8** is the highest (85–98%) in the presence of $BW_{11}Fe$. In the presence of 3.0 μmol or 6.0 μmol of $PW_{11}Fe$, H_2O_2 consumption is nearly the same (63%), but the best conversion is registered with 3.0 μmol (Fig. 4). Thus, the increase of the amount of catalyst possibly leads to nonproductive H_2O_2 decomposition. These results parallel those obtained with ethylbenzene.

Oxidation of *p*-cymene (**14**)

The oxidation of *p*-cymene (**14**) under the conditions studied gives *p*-methylacetophenone (**16**), *p*-isopropylbenzaldehyde (**17**), and hydroperoxide (**19**) as major products, along with *p*-isopropylbenzyl alcohol (**18**) and *p*,α-dimethylstyrene (**15**) as minor ones. Carvacrol (**20**) is observed only in the presence of $SiW_{11}Fe$ (Scheme 3; Table 3).

The best conversion (35%) is obtained in the presence of $BW_{11}Fe$ (Table 3, entry 9). With $PW_{11}Fe$ and $SiW_{11}Fe$, the highest conversions are 23% and 29%, respectively (Table 3, entries 5, 6 and 18). Figure 5 illustrates, in the case of H_2O_2/*p*-cymene molar ratio of 9.8, how the conversion of *p*-cymene is affected by the amount of catalyst used. These results are comparable to those found with the previous substrates.

With $PW_{11}Fe$ and for all the conditions studied, **16**, **17**, and **19** are always the major products. For $SiW_{11}Fe$ the main product is **19** and the compounds **16**, **17**, and **20** are obtained with similar selectivity (Table 3, entries 17 and 18); *p*,α-dimethylstyrene (**15**) occurs with minor abundance ($\leq$6%). *p*-Methylacetophenone (**16**) and *p*-isopropylbenzaldehyde (**17**) are always the major products in the presence of $BW_{11}Fe$ (Fig. 6). With this catalyst, hydroperoxide selectivity is lower than that observed with $PW_{11}Fe$ and $SiW_{11}Fe$, and decreases with increasing amount of catalyst. This behaviour can, again, be due to the apparent propensity of the anion with boron to decompose hydrogen peroxide or related species. Again, the consumption of hydrogen peroxide is always higher in the presence of $BW_{11}Fe$, when compared with $SiW_{11}Fe$ and $PW_{11}Fe$ in the same reaction conditions.

Oxidation of *sec*-butylbenzene (**21**)

sec-Butylbenzene (**21**) is the least reactive substrate tested (maximum conversion of 7%), and the oxidation is only detected when the substrate/catalyst molar ratio is equal to 333 in the presence of $PW_{11}Fe$ or $SiW_{11}Fe$, and 667 for $BW_{11}Fe$. Similar conversions are obtained using H_2O_2/substrate = 9.8 or 4.0. Acetophenone (**5**) and the hydroperoxide (**22**) were the products observed (Scheme 4).

Scheme 3

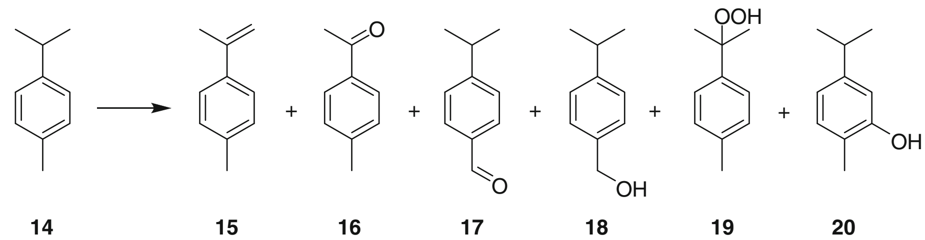


Table 3 Oxidation of *p*-cymene (**14**) by hydrogen peroxide catalysed by Fe^{III}-substituted polyoxotungstates after 24 h of reaction

Entry	Catalyst	Sub/cat	H_2O_2/sub	Conversion (%)[a]	TON[b]	H_2O_2 consumed (mmol)	Selectivity (%)[a]					
							15	**16**	**17**	**18**	**19**	**20**
1	$PW_{11}Fe$	667	2.0	14	93	1.00	9	22	19	–	50	–
2			4.0	20	132	1.81	10	22	23	–	45	–
3			9.8	20	132	3.45	19	36	25	–	20	–
4	$PW_{11}Fe$	333	2.0	18	59	1.56	9	20	26	–	45	–
5			4.0	23	77	2.59	13	20	24	–	43	–
6			9.8	23	77	4.79	13	29	27	–	31	–
7	$BW_{11}Fe$	667	2.0	15	98	1.95	15	43	25	–	17	–
8			4.0	23	150	3.99	9	40	23	6	22	–
9			9.8	35	235	9.67	8	48	32	8	4	–
10	$BW_{11}Fe$	333	2.0	18	60	1.93	15	46	28	–	11	–
11			4.0	20	65	3.94	17	48	27	–	8	–
12			9.8	25	83	9.71	15	55	27	–	3	–
13	$SiW_{11}Fe$	667	2.0	6	41	0.34	9	17	22	6	36	10
14			4.0	6	41	0.33	7	16	25	5	41	6
15			9.8	7	44	0.33	4	14	22	4	49	7
16	$SiW_{11}Fe$	333	2.0	17	55	0.36	6	19	19	12	25	19
17			4.0	28	94	0.37	5	16	19	14	29	17
18			9.8	29	95	0.40	6	14	18	13	33	16
19	None			–	–	n.d.	–	–	–	–	–	–

Reaction conditions: substrate (1.0 mmol), catalyst (1.5 or 3.0 μmol), and 2.0, 4.0, or 9.8 mmol of aqueous 30% (w/w) H_2O_2 were stirred for 24 h in CH_3CN at 80 °C

n.d. Not determined

[a] Determined by GC-MS

[b] Turnover number (mol of products per mol of catalyst)

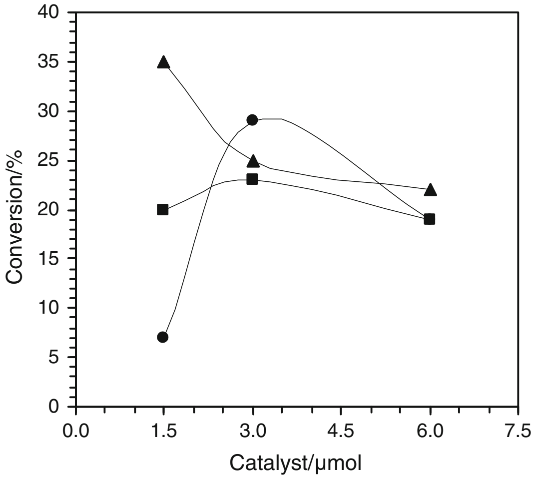


Fig. 5 Conversion of *p*-cymene (**14**) using 9.8 mmol H_2O_2 in the presence of $PW_{11}Fe$ (*filled squares*), $SiW_{11}Fe$ (*filled circles*), or $BW_{11}Fe$ (*filled triangles*) after 24 h of reaction. Substrate: 1.0 mmol; catalyst: 1.5, 3.0 or 6.0 μmol; acetonitrile: 3.0 cm^3 at 80 °C

$PW_{11}Fe$ affords **22** as the only product, and the other two catalysts give **22** (50% selectivity with $SiW_{11}Fe$) and **5** (77% selectivity with $BW_{11}Fe$) as the main products.

Catalyst stability

The reaction conditions used in this study were applied before in studies with other hydrocarbons [26], in which it was observed that no decomposition of $PW_{11}Fe$ took place during the reactions. In this study, the infrared spectra of the catalyst recovered from the solutions at the end of the reaction (24 h) presented the characteristic bands of $[PW_{11}Fe(H_2O)O_{39}]^{4-}$ or $[PW_{11}Fe(OH)O_{39}]^{5-}$ [38, 39], suggesting that no decomposition had occurred. The stability of the anion was also confirmed by the search for the possible existence of leached Fe^{III} in solution, using SCN^-. Preliminary tests showed that the addition of KSCN to a CH_3CN solution of $TBA_4[PW_{11}Fe(H_2O)O_{39}]$ did not noticeably change its yellow colour, while similar tests

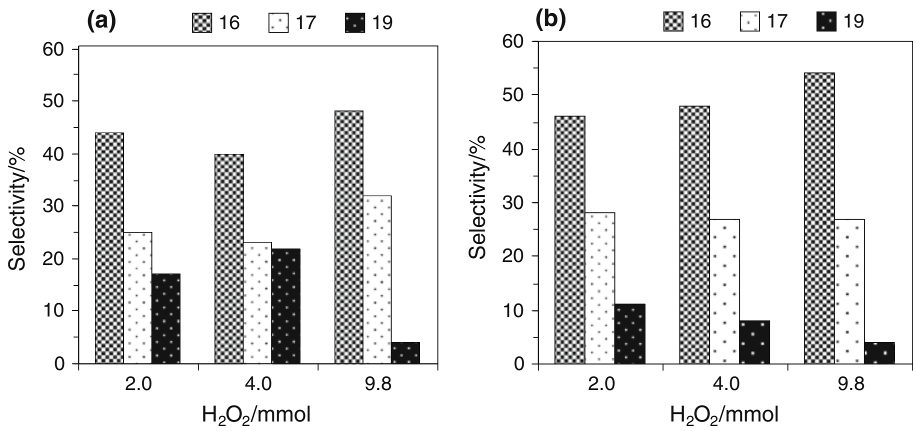
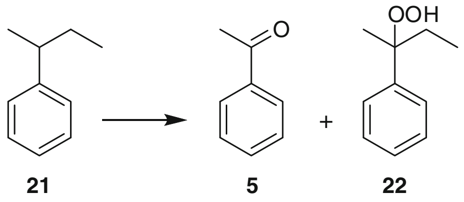


Fig. 6 Selectivity for reaction products **16**, **17**, and **19** for *p*-cymene (**14**) oxidation reactions in the presence of **a** 1.5 µmol or **b** 3.0 µmol of $BW_{11}Fe$ with 2.0, 4.0, or 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; CH_3CN: 3.0 cm^3 at 80 °C



Scheme 4

performed with $FeCl_3$ confer to the solution the common red colour of $[Fe(SCN)_x]^{3-x}$ complexes. Similar results were obtained with mixed CH_3CN/H_2O solvents (up to 30% volume water content). At the end of the catalytic reactions, a yellow solution was obtained after the addition of KSCN, in accordance with the absence of significant leaching of iron from the polyoxometalate to the reaction mixture. UV–Vis spectrophotometry was used to confirm the visual observations.

Mechanistic considerations

Taking into account the products obtained, the existence of concurrent reactions is clear, although dependent on the catalyst and reaction conditions used. When the reactions described herein were performed in the presence of iodine, a well-known radical trap [40], no products were detected, suggesting that the oxidations proceed mainly via a radical mechanism. In particular, the involvement of $R^{\cdot}$ and $ROO^{\cdot}$ is corroborated by the formation of the hydroperoxides. Scheme 5 illustrates a possible mechanism. The first step involves hydrogen abstraction from the substrate in the presence of the $HO^{\cdot}$ that is generated by the iron complexes through a Fenton-like process [29]. The resulting free radical can combine with oxygen to form a peroxy radical, $ROO^{\cdot}$, which abstracts a hydrogen atom from other substrate molecule to yield the hydroperoxide. The oxygen is possibly generated in situ through the reaction of Fe^{III} and H_2O_2, as proposed before [41]. The dismutation of the excess of H_2O_2 also contributes to the supply of O_2. The results of reactions performed in an inert atmosphere (oxidation of cumene with excess H_2O_2) are not significantly different from those obtained in air. Similar behaviour has already been described in our previous work on the oxidation of cycloalkanes in the presence of iron-substituted polyoxotungstates [41–43].

Scheme 6 illustrates how some of the reaction products may result from the decomposition of the hydroperoxides formed [4, 44, 45]. This seems to be an important pathway to justify many of the products obtained, whereas the oxidative dehydrogenation of the substrates may account for the formation of **2**, **9** and **15**. Even so, in order to identify other possible contributions for the distribution of reaction products, the oxidation of several commercially available products was conducted under one of the reaction conditions used, namely 3.0 µmol of $PW_{11}Fe$ per 1.0 mmol of substrate using H_2O_2/substrate = 9.8. The results obtained are summarized in Table 4.

The catalytic oxidation of the secondary alcohol 1-phenylethanol (**4**) occurs at total conversion, affording acetophenone (**5**) as the main product (95% selectivity) and **2** as a minor component (Table 4, entry 1). The oxidation of styrene (**2**) occurs also with full conversion and affords **3** (52%) and **23** (29%) as major products (Table 4, entry 2). On the other hand, the oxidation of styrene oxide (**26**) gives the corresponding diol **27** as main product (60% selectivity), followed by benzaldehyde (**3**) and benzoic acid (**23**) (16% and 20%, respectively; Table 4, entry 3). These results suggest that oxidative cleavage of carbon–carbon double bond has an important contribution for the formation of the styrene oxidation products.

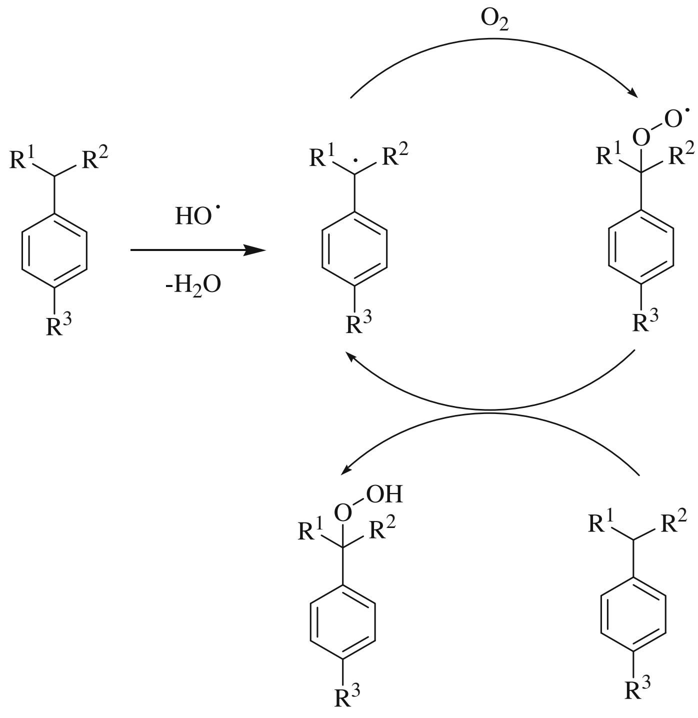
The carbon–carbon double-bond cleavage seems to be also the main catalytic oxidation pathway for the other two vinyl derivatives **9** and **15**. These are oxidized with high efficiency (Table 4, entries 4 and 5), reaching 86% and 88% conversion, respectively, affording the corresponding ketones **5** and **16** with high selectivity (87% and 82%,

Scheme 5

$$XW_{11}Fe^{III} + H_2O_2 \longrightarrow XW_{11}Fe^{II} + HOO^{\cdot} + H^+$$

$$XW_{11}Fe^{III} + HOO^{\cdot} \longrightarrow XW_{11}Fe^{II} + O_2 + H^+$$

$$XW_{11}Fe^{II} + H_2O_2 \longrightarrow XW_{11}Fe^{III} + HO^{\cdot} + OH^-$$



ethylbenzene (**1**) $R^1 = CH_3$; $R^2 = R^3 = H$; cumene (**8**) $R^1 = R^2 = CH_3$, $R^3 = H$;

p-cymene (**14**) $R^1 = R^2 = R^3 = CH_3$; *sec*-butylbenzene (**21**) $R^1 = CH_3$, $R^2 = CH_2CH_3$, $R^3 = H$

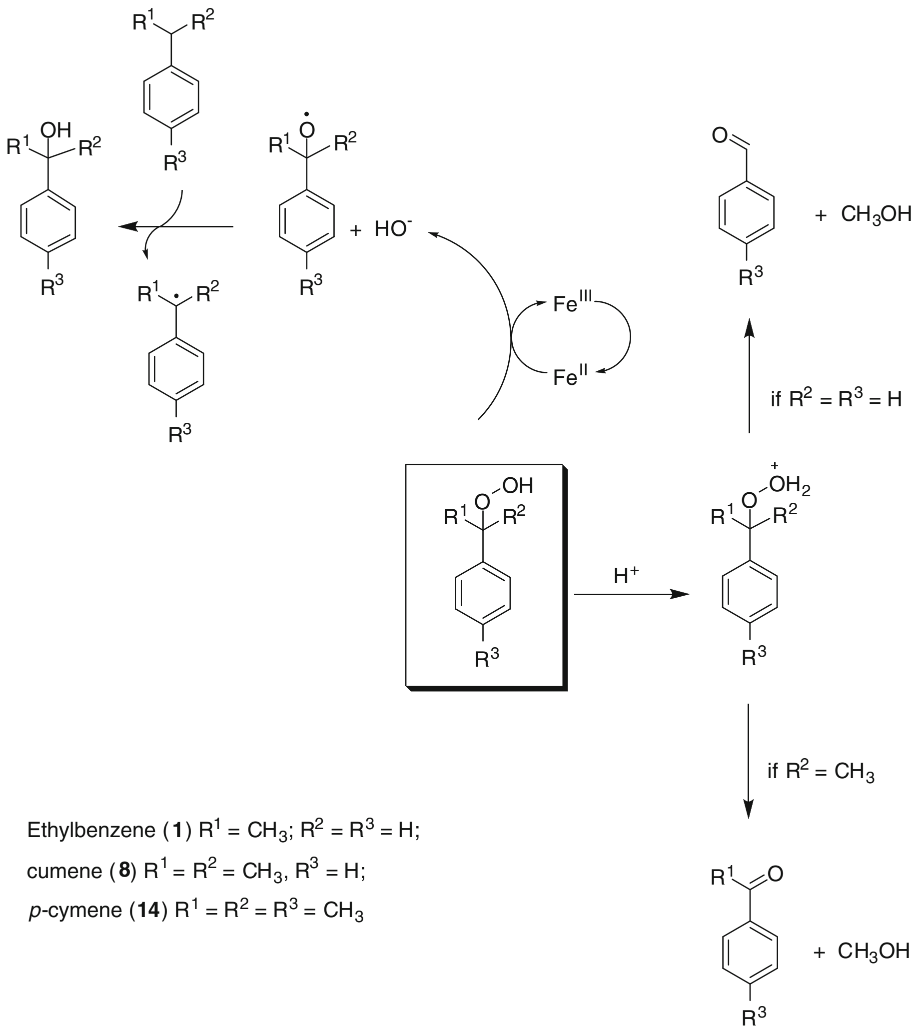
respectively). Again, a minor contribution of epoxide ring-opening is detected.

The primary alcohol **18**, when submitted to the same reaction conditions as *p*-cymene (**14**), gives, at excellent conversion, the corresponding aldehyde **17** as the major product with 86% selectivity (Table 4, entry 7). The oxidation of the tertiary alcohol **10** occurs with full conversion and affords hydroperoxide **12** (44%) and phenol (42%) as major products (Table 4, entry 6). The other compounds detected are α-methylstyrene (10%) and acetophenone (4%). The unexpected formation of the hydroperoxide from the tertiary alcohol was confirmed by comparing its mass spectrum with that obtained from an authentic commercially available sample (Fig. 7) and also by GC co-injection of the two samples. The oxidation of the commercially available hydroperoxide **12** occurs with 76% conversion and gives **5** (40%) as the main product, followed by **10** (24%) and **9** (22%) as the next most abundant products. Phenol (**24**) is obtained with 14% selectivity. As expected, ketones **5** and **16** do not react when submitted to the reaction conditions under study (entry 9).

In summary, the main products obtained in the oxidation of alkylbenzenes are the corresponding ketones and hydroperoxides. Aldehyde **3** and ketones **5** and **16** may arise from C=C cleavage of the corresponding styrene derivatives, along with the contribution from the C–C cleavage of the corresponding hydroperoxide, which is formed by a radical mechanism.

Acetophenone (**5**) is one of the major products in ethylbenzene (**1**) oxidation and seems to arise via further oxidation of the secondary alcohol (**4**). Acetophenone is also observed in the products of cumene oxidation and, as a minor component, in the oxidation of **10**, which is formed during cumene oxidation. Therefore, we believe that

Scheme 6



acetophenone arises from cumene hydroperoxide C–C cleavage, according to Scheme 6. In the ethylbenzene oxidation, ethylbenzene hydroperoxide C–C cleavage leads to benzaldehyde (Scheme 6).

These studies show that ketones **5** and **16** also arise from carbon–carbon double-bond cleavage of the corresponding alkene [27]. In fact, the oxidation of styrene (**2**) and styrene derivatives (**9** and **15**) in the presence of $PW_{11}Fe$ afford the corresponding carbon–carbon double-bond cleavage products in very high yields. In the oxidation of **2**, C=C cleavage products **3** and **23** sum 81%, whereas for the oxidation of **9** and **15** the ketones obtained by C=C cleavage represent 87% (**5**) and 82% (**16**), respectively.

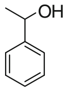
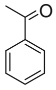
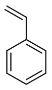
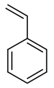
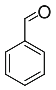
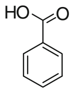
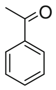
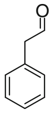
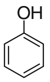
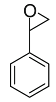
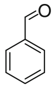
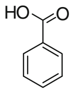
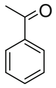
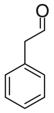
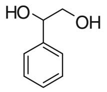
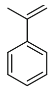
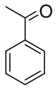
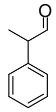
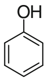
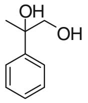
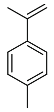
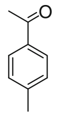
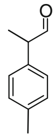
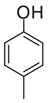
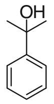
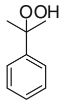
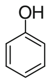
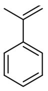
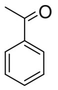
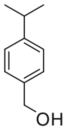
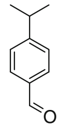
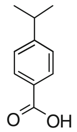
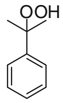
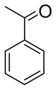
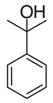
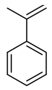
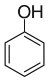
Compounds **2** and **9** do not seem to arise from the dehydration of alcohols **4** and **10**, respectively, since only minor amounts of **2** and **9** are obtained in the oxidation of these alcohols. Thus, the oxidative dehydrogenization of **1** and **8** is considered more probable. The oxidation of **14**, where alkene **15** is also obtained without detection of the alcohol, seems to confirm this fact.

Finally, the type of products obtained shows that in most of the cases the reactions occur preferentially in the more reactive benzylic positions.

Conclusions

The results presented reveal a significant catalytic system based on iron(III) POMs for the oxidation of alkylbenzenes and other benzene derivatives, using environmentally benign H_2O_2 under mild conditions. The solvent used (acetonitrile) is comparatively benign, and no co-catalysts are needed. The oxidation of ethylbenzene, cumene, *p*-cymene, and *sec*-butylbenzene was studied with three different catalysts at different substrate/catalyst and H_2O_2/substrate molar ratios. The oxidation of ethylbenzene and cumene occurred with maximum conversion of 26% and 37%, respectively, in the presence of $PW_{11}Fe$, both after 24 h of reaction, whereas the maximum conversion of *p*-cymene (35%) was found when $BW_{11}Fe$ was used. These

Table 4 Oxidation of products and presumed intermediates with H_2O_2 catalysed by $PW_{11}Fe$

Entry	Substrate	Conversion (%)[a]	Products Selectivity (%)[a]
1	 **4**	100	 **5** [95]  **2** [5]
2	 **2**	100	 **3** [52]  **23** [29]  **5** [13]  **25** [4]  **24** [2]
3	 **26**	100	 **3** [16]  **23** [20]  **5** [2]  **25** [2]  **27** [60]
4	 **9**	86	 **5** [87]  **11** [4]  **24** [6]  **28** [3]
5	 **15**	88	 **16** [82]  **29** [11]  **30** [7]
6	 **10**	100	 **12** [44]  **24** [42]  **9** [10]  **5** [4]
7	 **18**	89	 **17** [86]  **31** [14]
8	 **12**	76	 **5** [40]  **10** [24]  **9** [22]  **24** [14]
9	**5** and **16**	0	No products

Reaction conditions: substrate (1.0 mmol), catalyst (3.0 μmol), and 9.8 mmol of aqueous 30% (w/w) H_2O_2 were stirred for 24 h in CH_3CN at 80 °C

[a] Determined by GC

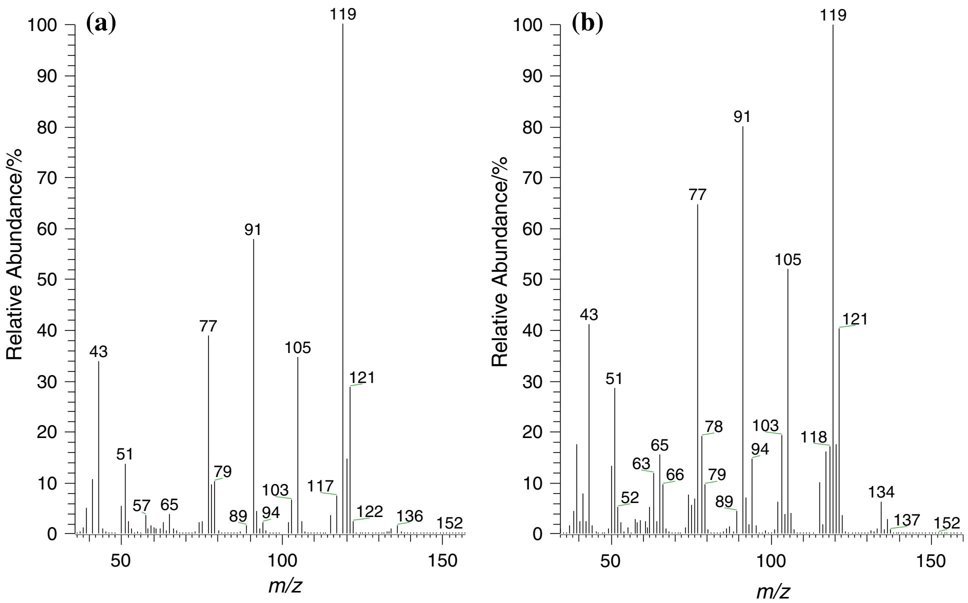


Fig. 7 MS spectra of **a** commercial sample of cumene hydroperoxide (**12**) and **b** cumene hydroperoxide (**12**) in the oxidation of 2-phenyl-2-propanol (**10**)

results were obtained with excess of hydrogen peroxide (molar ratio H_2O_2/substrate $\geq$ 4). The reactions occurred by a radical mechanism, and the formation of hydroperoxides (compounds **6**, **12**, **19**, and **22**) was observed for all substrates studied. The highest selectivity (yield) values for the hydroperoxides were obtained with $PW_{11}Fe$. In the presence of $BW_{11}Fe$, the oxidation of ethylbenzene and cumene yielded acetophenone (**5**) with moderate selectivity, while *p*-methylacetophenone was generally the major product obtained in the oxidation of *p*-cymene.

The systems described herein show good catalytic efficiency associated to a different product distribution when compared with other systems using hydrogen peroxide and POMs [34–36]. In fact, the conversions obtained here are higher than frequently observed for this kind of substrates, accompanied by an unusual formation of high amounts of the corresponding hydroperoxides, which are detected for the first time in catalysis with POMs. It should be noted that the outcome of the oxidation of the alkylaromatics may possibly be tuned through the choice of catalyst and reaction conditions.

In order to understand the reaction pathways, other organic compounds, namely styrenes (**2**, **9**, and **15**), alcohols (**4**, **10**, and **18**), cumene hydroperoxide and styrene oxide, were oxidized with H_2O_2 in the presence of $PW_{11}Fe$. In the condition used, all reacted with high conversion and, for some of them, with high selectivity. Examples are the oxidation of α-methylstyrene (**9**), *p*,α-dimethylstyrene (**15**) and *p*-isopropylbenzyl alcohol (**18**), which occurred with conversions between 86% and 89% after 24 h, leading respectively to the formation of acetophenone (**5**), *p*-isopropylbenzaldehyde (**17**), and *p*-methylacetophenone (**16**), all with selectivity above 80%. These results suggest that the catalytic system H_2O_2/iron polyoxotungstates can be used with good results in the oxidation of alcohols and vinyl aromatic derivatives.

Experimental

Reagents and synthetic procedures

Acetonitrile (Panreac), 30% (w/w) aqueous hydrogen peroxide (Riedel-de-Haën), ethylbenzene (**1**), styrene (**2**), benzaldehyde (**3**), α-methylstyrene (**9**), 2-phenyl-2-propanol (**10**), 2-phenylpropanal (**11**), cumene hydroperoxide (**12**), *p*,α-dimethylstyrene (**15**), *p*-methylacetophenone (**16**), *p*-isopropylbenzaldehyde (**17**), *p*-isopropylbenzyl alcohol (**18**), carvacrol (**20**), and styrene oxide (**26**) (all from Aldrich), and 1-phenylethanol (**4**), acetophenone (**5**), cumene (**8**), *p*-cymene (**14**), and *sec*-butylbenzene (**21**) (all from Fluka) were used as received. All other reagents and solvents obtained from commercial sources were used as received or distilled and dried using standard procedures. $TBA_4[PW_{11}Fe(H_2O)O_{39}]\cdot 2H_2O$, $TBA_4H[SiW_{11}Fe(H_2O)O_{39}]$, and $TBA_4H_2[BW_{11}Fe(H_2O)O_{39}]\cdot H_2O$ were prepared and identified according to previously described procedures [46–48]. The obtained compounds were characterized by elemental analysis, thermogravimetry, and infrared spectroscopy [38, 47].

Typical procedure for the oxidation reactions

Typical oxidation reactions were carried out as follows: 1.5, 3.0, or 6.0 μmol of catalyst, 1.0 mmol of substrate, the required amount of 30% (w/w) aqueous H_2O_2 and 3.0 cm^3 acetonitrile were stirred at 80 °C in a closed vessel. The reactions were followed by GC-MS and were stopped when conversion remained constant after two successive GC-MS analyses. The percentages of each compound in the reaction mixtures were estimated from the corresponding chromatographic peak areas, using 1-hexanol as internal standard (added after the reaction). When experiments (oxidation of cumene with excess H_2O_2) were repeated under an inert atmosphere, the air was purged from the reaction vessel and substituted by argon. Blank reactions were performed for all substrates, confirming that no oxidation products were obtained unless the catalyst and H_2O_2 were present.

Instruments and methods

GC-MS analysis was performed using a Finnigan Trace GC-MS (Thermo Quest CE instruments) with helium as carrier gas (35 cm^3/s) and a fused silica capillary column with 5% phenyl methylpolysiloxane (30 m × 0.25 mm i.d.; 25 μm film thickness). Gas chromatographic conditions were as follows: ethylbenzene [initial temperature: 90 °C (2 min); first temperature rate: 5 °C/min until 140 °C; second temperature rate: 50 °C/min until 250 °C]; cumene [initial temperature: 90 °C (2 min); first temperature rate: 2.5 °C/min until 130 °C; second temperature rate: 50 °C/min until 220 °C]; *p*-cymene and *sec*-butylbenzene [initial temperature: 100 °C (2 min); first temperature rate: 3 °C/min until 160 °C; second temperature rate: 50 °C/min until 260 °C]. The injector and interface temperatures were 250 and 270 °C, respectively. Aliquots were taken from the reaction mixtures at regular intervals for peroxide determination, as described elsewhere [26, 42].

All products, except **6**, **19**, and **22**, were identified by GC-MS analysis and by co-injection of commercially available standards. The hydroperoxides were identified by their mass spectrum and by the triphenylphosphine test, following a method described in the literature [49, 50]. An excess of triphenylphosphine was added to the solutions at the end of the reactions, and the reduction of the hydroperoxides to the corresponding alcohols was detected by GC-MS analysis. This test was performed for all substrates.

The possibility of formation of peroxyimidic acid, which would function as the oxidizing agent, was discarded because acetamide was never observed in the products.

At the end of the reactions with $[PW_{11}Fe(H_2O)O_{39}]^{4-}$, a drop of the reaction mixture was dried on a KBr pellet and the infrared spectrum measured in order to assess the stability of the catalyst. Solutions with POM or $FeCl_3$ concentrations in the range 2×10^{-5}–5×10^{-4} M were used for the tests with KSCN.

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