Catal Lett (2009) 128:281–289
DOI 10.1007/s10562-008-9718-8

Transition Metal Substituted Polyoxotungstates in the Catalytic Oxidation of 1*H*-Indene and 1,2-Dihydronaphthalene with Hydrogen Peroxide

Ana C. Estrada · Mário M. Q. Simões · Isabel C. M. S. Santos · M. Graça P. M. S. Neves · Artur M. S. Silva · José A. S. Cavaleiro · Ana M. V. Cavaleiro

Received: 10 July 2008 / Accepted: 29 September 2008 / Published online: 21 October 2008

Abstract The oxidation of 1*H*-indene and 1,2-dihydronaphthalene with hydrogen peroxide in the presence of Mn(III) or Fe(III) substituted Keggin-type polyoxotungstates is described. The products obtained depend on the catalyst and reaction conditions. Ring cleavage was observed, affording dialdehydes under mild and environmentally friendly conditions. Other main products were the α-hydroxy-ketones. The resulting epoxides seem to be intermediates to other oxygenated products.

Keywords 1*H*-indene · 1,2-dihydronaphthalene · Polyoxometalates · Polyoxotungstates · Hydrogen peroxide · Oxidation

1 Introduction

Keggin-type polyoxometalates have been used as catalysts or catalyst precursors in oxidative transformations, like epoxidation of olefins, hydroxylation of saturated hydrocarbons, alcohol oxidation and others [1–9]. In particular, transition metal mono-substituted Keggin-type heteropolytungstates $[XW_{11}M(H_2O)O_{39}]^{(n-m)-}$ (X = P, Si, etc.), in which a transition metal cation, M^{m+}, is coordinated to the binding sites of a lacunary heteropolyanion $[XW_{11}O_{39}]^{n-}$, have been used since the 1980s in the oxidation of several types of substrates with a variety of oxidants [9–11]. Following our interest on the use of polyoxotungstates as catalysts for oxidative transformations of organic compounds [12–18], we report here the oxidation of 1*H*-indene (**1**) and 1,2-dihydronaphthalene (**2**) with hydrogen peroxide, in acetonitrile, in the presence of tetrabutylammonium (TBA) salts of $[XW_{11}M^{III}(H_2O)O_{39}]^{n-}$, X = P, Si, B and M = Mn, Fe (abbreviated $XW_{11}M$). The hydrogen peroxide/acetonitrile system is an attractive option on environmental and economic basis. Hydrogen peroxide is considered a cheap, readily available reagent, giving water as the only by-product [19–21].

Among others, 1*H*-indene and 1,2-dihydronaphthalene have been thoroughly studied as model compounds in asymmetric epoxidation [22–26]. The described reactions usually do not proceed much further than the formation of the corresponding epoxides. Here we describe the formation of several oxygenated products, including those obtained through C–C or C=C bond cleavage in mild conditions. This type of ring opening cleavage is usually obtained with stronger oxidants like potassium permanganate, periodic acid, sodium or potassium periodate, and lead tetraacetate [27, 28]. To our knowledge, no previous studies on the oxidation of the chosen substrates have been reported in the presence of Keggin-type metal substituted polyoxotungstates.

A. C. Estrada · A. M. V. Cavaleiro (✉)
CICECO, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal
e-mail: anacavaleiro@ua.pt

M. M. Q. Simões · I. C. M. S. Santos · M. G. P. M. S. Neves · A. M. S. Silva · J. A. S. Cavaleiro
QOPNA, Department of Chemistry, University of Aveiro, Aveiro 3810-193, Portugal

2 Experimental

2.1 Reagents and Synthetic Procedures

Acetonitrile (Panreac), 30% (w/w) aqueous hydrogen peroxide (Riedel de-Häen), 1*H*-indene (Aldrich), and 1,2-dihydronaphthalene (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. The salts $TBA_4[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ ($n = 0$, 1), $TBA_4H[SiW_{11}M(H_2O)O_{39}]$ and $TBA_4H_2[BW_{11}M(H_2O)O_{39}] \cdot H_2O$, $M = Mn^{III}$ or Fe^{III}, were prepared and identified according to previously described procedures [12–14, 29]. 1,2-epoxyindane and 1,2-epoxy-1,2,3,4-tetrahydronaphthalene were prepared by the epoxidation of 1*H*-indene and 1,2-dihydronaphthalene, respectively, with hydrogen peroxide using Mn(TDCPP)Cl (TDCPP = *meso*-tetrakis-2,6-dichlorophenylporphyrin) as catalyst [30]. These epoxides were separated from the reaction media by extraction with dichloromethane and, after evaporation of the solvent, used directly in the catalytic experiments. The identification of the pure epoxides prepared by this process was done by ^1H and ^{13}C NMR.

2.2 General Oxidation Procedure

In a typical experiment, the substrate (1.0 mmol), the catalyst (3.0 μmol), the required amount of 30% (w/w) aqueous H_2O_2, and acetonitrile (3.0 mL) were stirred at 80 °C. The reactions were followed by GC analysis and were stopped when products yields remained constant after two successive GC analyses. The percentages of each compound in the reaction mixtures were estimated from the corresponding chromatographic peak areas, using 1-hexanol as internal standard. Blank reactions were carried out for both substrates, in the absence of polyoxotungstate, without the formation of products detectable by GC.

2.3 Instruments and Methods

^1H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions, using a Bruker Avance 300 spectrometer at 300.13 and 75.47 MHz, respectively. The chemical shifts are express as δ (ppm) relatively to tetramethylsilane (TMS) as internal reference. Thin layer chromatography was performed on silica gel (Merck silica gel 60 F_{254}, 70–230 mesh). GC–FID analysis were performed using a Varian 3900 chromatograph, whereas GC–MS analysis were performed using a Finnigan Trace GC/MS (Thermo Quest CE instruments) both using helium as the carrier gas (35 cm/s) and a fused silica Supelco capillary column SPB-5 (30 m × 0.25 mm i.d.; 25 μm film thickness). Gas chromatographic conditions were as follows: 70 °C (1 min); temperature rate: 18 °C/min; final temperature: 260 °C; injector temperature: 260 °C; detector temperature: 260 °C.

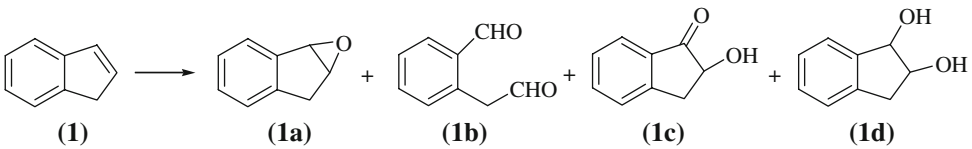
Aliquots were taken from the reaction mixtures, at regular intervals, for peroxide determination by titration with ceric sulfate [31]. The efficiency of usage of hydrogen peroxide was calculated by the following formula (see Schemes 1 and 2): [(amount of **1a** + amount of **1d** + 2 × (amount of **1b** + amount of **1c**)]/(amount of H_2O_2 used) or [(amount of **2a** + amount of **2b** + amount of **2e** + 2 × (amount of **2c** + amount of **2d**)]/(amount of H_2O_2 used).

2.4 Product Chromatographic Separation and Characterization

For the chromatographic separation of the oxidation products, final reaction mixtures were poured into water and extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate and concentrated using a rotary evaporator. The washed reaction mixtures were then separated by silica gel thin layer chromatography, using dichloromethane as eluent. By this procedure the pure compounds **1b–d** (Scheme 1), **2c–e** (Scheme 2) were obtained in separated fractions. Compounds **1b**, **1c**, **2c** and **2d** were identified by GC-MS and NMR analysis, whereas **1d** and **2e** were identified by GC-MS. The identity of the epoxides **1a** and **2b** was confirmed by comparing its mass spectrum with the information available from the GC-MS database and also by GC co-injection of samples of the compounds prepared by the process described in Sect. 2.1. Compound **2a** was identified by GC-MS analysis and by GC co-injection of a commercially available standard.

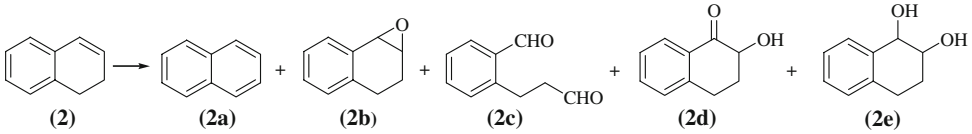
1,2-Epoxyindane (**1a**) [32–34]—^1H NMR ($CDCl_3$) δ (ppm): 2,99 (dd, 1H, H-3, J = 2.5 and 18.0 Hz), 3.23 (d, 1H, H-3, J = 18.0 Hz), 4.14 (t, 1H, H-2, J = 2.5 Hz), 4.27 (d, 1H, H-1, J = 2,5 Hz), 7.18–7.31 (m, 3H, H-4,5,6), 7.52 (d,

Scheme 1



(1) (1a) (1b) (1c) (1d)

Scheme 2



(2) (2a) (2b) (2c) (2d) (2e)

1H, H-7, $J = 7.2$ Hz). ^{13}C NMR δ: 34.6 (C-3), 57.6 and 59.1 (C-2, C-l), 125.1, 126.0, 126.2, 128.5, 140.8, 143.5 (C–Ar).

2-(2-Oxoethyl)Benzaldehyde (**1b**)—^{1}H NMR ($CDCl_3$) δ (ppm): 4,16 (d, 2H, CH_2, $J = 1.0$ Hz), 7.55–7.61 (m, 3H, H-3,4,5), 7.86 (dd, 1H, H-6, $J = 1.8$ and 7.2 Hz), 9.82 (t, 1H, Ar–CH_2–CHO, $J = 1.0$ Hz), 10.06 (s, 1H, Ar–CHO). MS (EI) *m/z* (rel. int., %): 148 ($M^{\bullet+}$, 8), 147 (9), 120 (98), 119 (93), 105 (5), 91 (100), 65 (36).

2-Hydroxyindan-1-one (**1c**) [35]—^{1}H NMR ($CDCl_3$) δ (ppm): 2.86 (s, 1H, OH), 3.02 (dd, 1H, H-3, $J = 5.0$ and 16.6 Hz), 3.60 (dd, 1H, H-3, $J = 7.9$ and 16.6 Hz), 4.54 (dd, 1H, H-2, $J = 5.0$ and 7.9 Hz), 7.42 (t, 1H, H-6, $J = 7.5$ Hz), 7.47 (d, 1H, H-4, $J = 7.5$ Hz), 7.65 (dt, 1H, H-5, $J = 1.0$ and 7.5 Hz), 7.78 (d, 1H, H-7, $J = 7.5$ Hz). MS (EI) *m/z* (rel. int., %): 148 ($M^{\bullet+}$, 100), 147 (57), 131 (22), 120 (30), 119 (77), 105 (38), 91 (88), 65 (28).

1,2-Dihydroxyindane (**1d**)—MS (EI) *m/z* (rel. int., %): 150 ($M^{\bullet+}$, 41), 132 (78), 131 (52), 119 (17), 107 (71), 104 (100), 103 (50), 91 (33), 77 (40), 65 (16).

1,2-Epoxy-1,2,3,4-Tetrahydronaphthalene (**2b**) [32, 36]—^{1}H NMR ($CDCl_3$) δ (ppm): 1.77 (dt, 1H, H-3, $J = 5.4$ and 14.1 Hz), 2.41 (dd, 1H, H-3, $J = 6.4$ and 14.1 Hz), 2.54 (dd, 1H, H-4, $J = 5.4$ and 14.9 Hz), 2.78 (dt, 1H, H-4, $J = 6.4$ and 14.9 Hz), 3.73 (s broad, 1H, H-2), 3.85 (d, 1H, H-1, $J = 2.7$ Hz), 7.09 (d, 1H, H-5, $J = 7.2$ Hz), 7.22–7.25 (m, 2H, H-6,7), 7.39 (dd, 1H, H-8, $J = 1.6$ and 7.1 Hz). ^{13}C NMR δ: 21.8 (C-3), 24.3 (C-4), 52.7 (C-1), 55.1 (C-2), 126.0 (C-6), 128.4 (C-7), 129.5 (C-5 e C-8), 132.5 (C-4a), 136.6 (C-8a).

2-(3-Oxopropyl)Benzaldehyde (**2c**) [37]—^{1}H NMR ($CDCl_3$) δ (ppm): 2.80 (dt, 2H, Ar–CH_2–CH_2–CHO, $J = 0.9$ and 7.5 Hz), 3.36 (t, 2H, Ar–CH_2–CH_2–CHO, $J = 7.5$ Hz), 7.33 (d, 1H, H-3, $J = 7.7$ Hz), 7.44 (dt, 1H, H-5, $J = 1.3$ and 7.7 Hz), 7.53 (dt, 1H, H-4, $J = 1.6$ and 7.7 Hz), 7.82 (dd, 1H, H-6, $J = 1.6$ and 7.7 Hz), 9.83 (t, 1H, Ar–CH_2–CH_2–CHO, $J = 0.9$ Hz), 10,17 (s, 1H, Ar–CHO). ^{13}C NMR δ: 25.7 (Ar–CH_2–CH_2–CHO), 45.0 (Ar–CH_2–CH_2–CHO), 127.1 (C-3), 131.4 (C-5), 133.9 (C-4), 134.6 (C-6), 142.7 (C-1 and C-2), 193.1 (Ar–CH_2–CH_2–CHO), 201.2 (Ar–CHO). MS (EI) *m/z* (rel. int., %): 162 ($M^{\bullet+}$, 8), 144 (35), 133 (77), 118 (85), 116 (100), 105 (58), 103 (42), 91 (75), 77 (80), 65 (31).

2-Hydroxytetralin-1-one (**2d**) [38]—^{1}H NMR ($CDCl_3$) δ (ppm): 1.98–2.12 (m, 1H, H-3), 2.50–2.58 (m, 1H, H-3), 3.00–3.22 (m, 2H, H-4), 3.93 (s broad, 1H, OH), 4.39 (dd, 1H, H-2, $J = 5.4$ and 13.5 Hz), 7.28 (dd, 1H, H-5, $J = 0.9$ and 7.6 Hz), 7.35 (t, 1H, H-7, $J = 7.6$ Hz), 7.53 (dt, 1H, H-6, $J = 1.3$ and 7.6 Hz), 8.04 (dd, 1H, H-8, $J = 1.3$ and 7.6 Hz). ^{13}C NMR: 27.7 (C-4), 31.8 (C-3), 73.8 (C-2), 126.9 (C-7), 127.5 (C-8), 128.9 (C-5), 130.4 (C-4a), 134.1 (C-6), 144.3 (C-8a), 199.6 (C-1). MS (EI) *m/z* (rel. int., %): 162 ($M^{\bullet+}$, 76), 144 (66), 119 (30), 118 (100), 116 (75), 115 (43), 105 (23), 103 (25), 91 (41), 90 (90), 89 (73), 77(49).

1,2-Dihydroxytetralin (**2e**)—MS (EI) *m/z* (rel. int., %): 164 ($M^{\bullet+}$, 26), 148 (1), 147 (12), 146 (44), 145 (19), 131 (10), 119 (100), 115 (28), 91 (38), 77 (15), 65 (14).

3 Results and Discussion

The oxidation of 1*H*-indene and 1,2-dihydronaphthalene were carried out in homogeneous phase using an excess of hydrogen peroxide (molar ratio H_2O_2/substrate = 4.0 and 9.8), in acetonitrile at 80 °C, in the presence of catalytic amounts of the Keggin-type anions $[XW_{11}M^{III}(H_2O)O_{39}]^{n-}$ (X = P, Si, B, M = Fe, Mn). The obtained conversion of the substrates and the distribution of oxidation products depended on the catalyst and on the amount of hydrogen peroxide used.

3.1 Oxidation of 1*H*-Indene

The oxidation of 1*H*-indene **(1)** yielded the products shown in Scheme 1, namely the epoxide **1a,** the diol **1d**, the hydroxy-ketone **1c** and the dialdehyde **1b**. Some results are presented in Table 1. The best conversions obtained were found for H_2O_2/substrate = 9.8, and were obtained with $PW_{11}Mn$ (100%) after 5 h of reaction, followed by $BW_{11}Fe$ (91%), $BW_{11}Mn$ (88%) and $PW_{11}Fe$ (63%) after 7 h of reaction (Table 1, entries 7, 1, 3, and 5, respectively). With 4.0 mmol of oxidant per 1.0 mmol of substrate, those catalysts afforded 41–50% of conversion (Table 1, entries 2, 4, 6, and 8). The silicon polyoxotungstates, $SiW_{11}Fe$ and $SiW_{11}Mn$, were the less efficient catalysts (entries 9, 10, 11, and 12, respectively).

The experimental conditions selected for these studies were based on preliminary data obtained with $BW_{11}Fe$. Reactions carried out at room temperature in the presence of this catalyst (3.0 μmol), and using H_2O_2/substrate = 9.8, gave only 7% of substrate conversion after 24 h of reaction. Reactions with H_2O_2/substrate = 9.8 carried out at 80 °C but with lower amount of catalyst (1.5 μmol) yielded 65% of conversion (against the 91% of entry 1, Table 1). On the other hand, when H_2O_2/substrate = 2.0 and 3.0 μmol of catalyst were used, 45% of conversion was registered after 7 h.

Figure 1 illustrates the conversion and yield versus time for all products during the oxidation of 1*H*-indene with H_2O_2/substrate = 9.8 in the presence of $BW_{11}Mn$ and $PW_{11}Fe$. The results obtained with $BW_{11}Mn$ are representative of what was found for other catalysts, that is, the di-aldehyde (**1b**) and hydroxyindanone (**1c**) are always the major products along the reaction course. The case of $PW_{11}Fe$ is particular in which there is only one major product, **1c**, which is obtained with 61% selectivity after 7 h. With H_2O_2/substrate = 4.0, there are, usually, three

Table 1 Oxidation of 1*H*-indene with hydrogen peroxide catalyzed by Mn(III) or Fe(III) substituted polyoxotungstates after 7 h of reaction[a]

Entry	Catalyst	Initial H_2O_2 (mmol)	Consumed H_2O_2 (mmol)	Conversion[b] (%)	Selectivity[b] (%)			
					1a	**1b**	**1c**	**1d**
1	$BW_{11}Fe$	9.8	8.0	91	8	38	47	7
2		4.0	3.3	50	6	30	34	30
3	$BW_{11}Mn$	9.8	6.1	88	8	40	43	9
4		4.0	3.9	44	10	24	35	31
5	$PW_{11}Fe$	9.8	4.6	63	10	19	61	10
6		4.0	1.7	41	10	14	58	18
7	$PW_{11}Mn$	9.8	6.9	100[c]	8	49	33	10
8		4.0	3.8	47	5	28	34	33
9	$SiW_{11}Fe$	9.8	3.3	33	16	31	31	22
10		4.0	0.5	11	21	39	20	20
11	$SiW_{11}Mn$	9.8	5.2	47	9	42	38	11
12		4.0	4.0	15	8	36	29	27
13	Without catalyst	9.8	n.d.[d]	–	–	–	–	–
14		4.0	n.d.[d]	–	–	–	–	–

[a] Reaction conditions: substrate (1.0 mmol), catalyst (3.0 μmol) and hydrogen peroxide (4.0 or 9.8 mmol) were stirred at 80°C in 3.0 mL of CH_3CN

[b] Determined by GC analysis

[c] Results obtained after 5 h of reaction

[d] Not determined

main products (**1b–d**) while the epoxide **1a** is always a minor product (Table 1). Again $PW_{11}Fe$ was different, affording **1c** as major product. It was found that, usually, the diol **1d** is obtained with higher selectivity when less oxidant was used.

According to the results presented in Table 1, higher values of conversion seem generally to be associated with a higher consume of oxidant. When 9.8 mmol of H_2O_2 were added per mmol of substrate, 100, 91 and 88% of 1*H*-indene conversion were registered for $PW_{11}Mn$, $BW_{11}Fe$ and $BW_{11}Mn$, corresponding to 70, 82 and 62% of hydrogen peroxide consumed (entries 7, 1 and 3, respectively), with 26, 21 and 26% peroxide efficiency. For H_2O_2/substrate = 9.8 the calculated efficiency of usage of hydrogen peroxide at the end of the reaction were in the range 16–27%. The highest value obtained (41%) corresponded to reactions with H_2O_2/substrate = 4.0 and $PW_{11}Fe$ (entry 6, Table 1). On average, the anions with Fe were associated with higher H_2O_2 efficiency than those with Mn.

In order to understand the formation of the reaction products and to identify possible reaction intermediates, the oxidation of 1,2-epoxyindane (**1a**) was carried out under the same conditions used for 1*H*-indene in the presence of $BW_{11}Mn$, using H_2O_2/substrate = 9.8. The epoxide **1a** was obtained through the previously reported highly selective oxidation of 1*H*-indene in the presence of a metalloporphyrin [30]. The catalytic oxidation of **1a** occurred

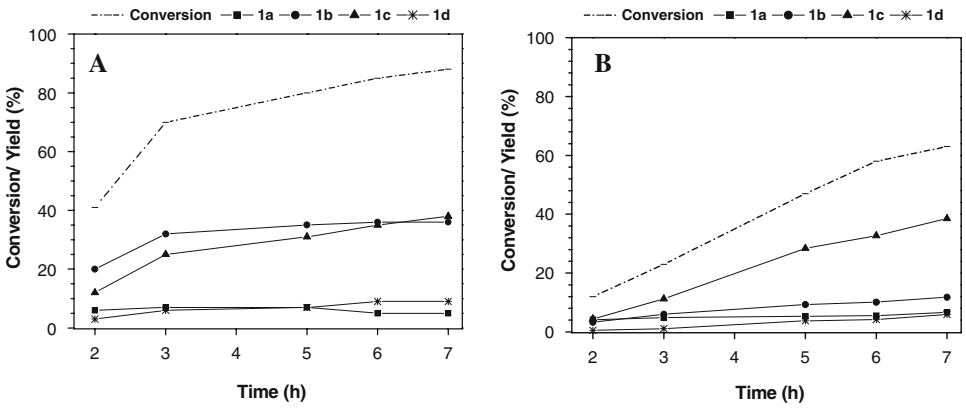


Fig. 1 Time dependence of the conversion and yield of all products for 1*H*-indene oxidation in the presence of (**a**) $BW_{11}Mn$ and (**b**) $PW_{11}Fe$ with 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

smoothly with high conversion (87%) after 3 h and afforded **1c** (76%) as the major product, followed by **1b** (9%) and **1d** (2%) (Fig. 2). These results suggest that, in the catalytic oxidation of **1**, **1a** is an important precursor of **1c**, which can be obtained through the oxidation of the benzylic position of **1d**, under the current conditions. Apparently, the formation of **1b** in the catalytic oxidation of **1** cannot be attributed only to the oxidative cleavage of **1d**, which arises from **1a** as an intermediate in 1*H*-indene oxidation (see Sect. 3.3); **1b** may also derive directly from 1*H*-indene by the oxidative cleavage of the carbon-carbon double bond. Oxidative cleavage of 1,2-diols, in order to afford aldehydes or ketones, is an important reaction in organic synthesis. In accordance with the literature [27], the dialdehyde **1b** can be obtained from the 1,2-diol **1d** with lead tetraacetate. Oxidative cleavage of carbon–carbon double bonds to carbonyl compounds is also a very frequently used method in synthetic organic chemistry [37, 39–42].

3.2 Oxidation of 1,2-Dihydronaphthalene

The oxidation of 1,2-dihydronaphthalene (**2**) with H_2O_2 in the presence of the Mn(III) or Fe(III) substituted polyoxotungstates afforded the products depicted in Scheme 2. As for 1*H*-indene oxidation, it was studied the influence of the different reaction conditions (polyoxotungstate used, amount of oxidant added and reaction time) upon the percentages of conversion and the distribution pattern of the oxidation products (Table 2).

As found for the 1*H*-indene, conversions obtained in the oxidation of 1,2-dihydronaphthalene increased when the oxidant/substrate molar ratio passed from 4.0 to 9.8. By

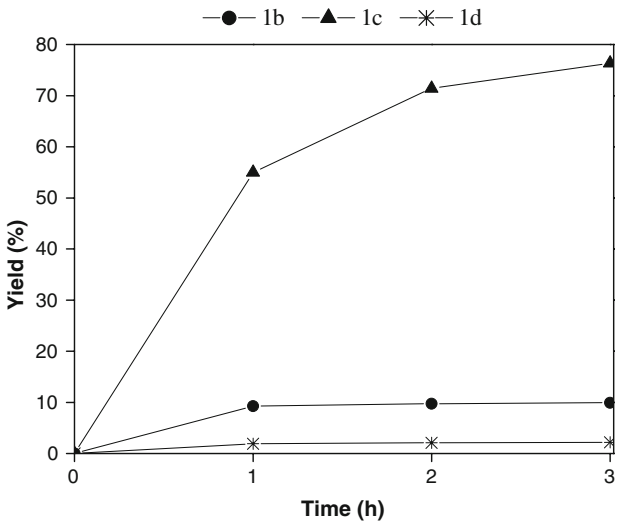


Fig. 2 Yield of products **1b**, **1c** and **1d** in 1,2-epoxyindane (**1a**) oxidation in the presence of $BW_{11}Mn$ with 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

comparing the results obtained with catalysts with the same heteroatom X, it is clear that the Mn polyoxotungstates usually gave higher values of conversion than the corresponding Fe complexes (Table 2).

In fact, in the presence of 9.8 mmol of hydrogen peroxide per mmol of substrate, the $BW_{11}Mn$ and $PW_{11}Mn$ anions were the more active catalysts, affording total conversion of the substrate after 5 and 4 h of reaction (entries 3 and 7, Table 2, respectively) and $SiW_{11}Mn$ reached 91% of conversion after 7 h of reaction (entry 11, Table 2). When H_2O_2/substrate = 4.0, the more active catalysts were again $BW_{11}Mn$ and $PW_{11}Mn$, which gave 97 and 90% of conversion after 7 h of reaction (Table 2, entries 4 and 8). Note that, in all cases, the values of conversion are almost unchanged after 12 h of reaction. In the case of the iron polyoxotungstates, the boron complex gives the higher conversion of **2**, independently of the quantity of H_2O_2 used.

Figures 3 and 4 illustrate the conversion and/or yield of all products during the oxidation of **2** with H_2O_2/substrate = 9.8, in the presence, respectively, of iron and manganese polyoxometalates (X = P, B). Iron complexes (Fig. 3) clearly favor the formation of **2d** (selectivity: 46–51%), whereas manganese complexes (Fig. 4) give rise to high yields of naphthalene **2a**, resulting from the oxidative dehydrogenation of **2**. For instance, in the case of $BW_{11}Mn$ (Fig. 4b), the oxidative dehydrogenation product **2a** is always the major one, whereas $BW_{11}Fe$ (Fig. 3b) originates **2d** as the main product in the same reaction conditions. It should be noted that for H_2O_2/substrate = 9.8 the yields of the epoxide **2b** and of the 1,2-diol **2e** are always low.

The catalytic oxidation of **2b**, prepared by the method referred for the 1*H*-indene, in the presence of $PW_{11}Mn$, occurred with high conversion (90% after 3 h), affording **2d** (49%) as the major product, followed by **2c** (22%) and **2e** (20%) (Scheme 2, Fig. 5). Based on these results, we may presume that epoxide **2b** is an important precursor in the catalytic oxidation of **2**, under the current conditions. Formation of **2c** apparently proceeds from the oxidative cleavage of **2e**, which arises from **2b** as an intermediate in 1,2-dihydronaphthalene oxidation. Finally, **2d** can be obtained through oxidation of the benzylic position of **2e**.

3.3 Comparison of Reaction Pathways

Comparison of the oxidation of 1,2-epoxyindane (**1a**) and 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**2b**) indicated a possible common reaction course (Scheme 3) in the oxidation of 1*H*-indene (**1**) and 1,2 dihydronaphthalene (**2**). Based on the results, it can be concluded that the dialdehydes obtained (**1b** and **2c**) presumably proceed from the oxidative cleavage of the corresponding diol, which arises

Table 2 Oxidation of 1,2-dihydronaphthalene with hydrogen peroxide catalyzed by Mn(III) or Fe(III) substituted polyoxotungstates after 7 h of reaction[a]

Entry	Catalyst	Initial H_2O_2 (mmol)	Consumed H_2O_2 (mmol)	Conversion[b] (%)	Selectivity[b] (%)				
					2a	**2b**	**2c**	**2d**	**2e**
1	$BW_{11}Fe$	9.8	9.2	96	16	7	19	51	7
2		4.0	3.8	86	31	8	15	29	16
3	$BW_{11}Mn$	9.8	4.4	100[c]	39	6	22	28	5
4		4.0	3.6	97	26	5	20	37	12
5	$PW_{11}Fe$	9.8	3.7	85	19	7	19	46	8
6		4.0	1.4	63	18	9	20	48	5
7	$PW_{11}Mn$	9.8	5.2	100[d]	32	6	19	34	8
8		4.0	3.8	90	27	4	20	28	22
9	$SiW_{11}Fe$	9.8	3.8	75	17	12	23	36	13
10		4.0	0.8	36	23	12	23	27	15
11	$SiW_{11}Mn$	9.8	5.8	91	17	7	24	42	10
12		4.0	4.0	20	23	5	20	31	20
13	Without catalyst	9.8	n.d.[e]	–	–	–	–	–	–
14		4.0	n.d.[e]	–	–	–	–	–	–

[a] Reaction conditions: substrate (1.0 mmol), catalyst (3.0 μmol) and hydrogen peroxide (4.0 or 9.8 mmol) were stirred at 80 °C in 3.0 mL of CH3CN

[b] Determined by GC analysis

[c] Results obtained after 5 h of reaction

[d] Results obtained after 4 h of reaction

[e] Not determined

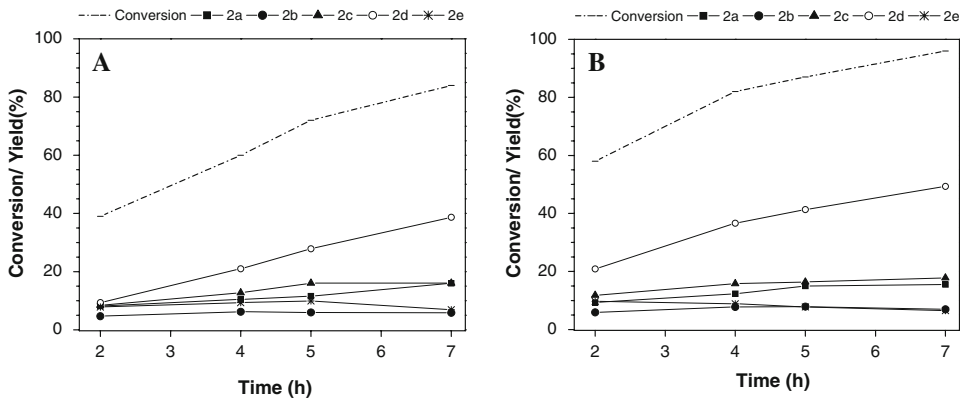


Fig. 3 Conversion and yield of all products for the oxidation of 1,2-dihydronaphthalene (**2**) in the presence of (**a**) $PW_{11}Fe$ and (**b**) $BW_{11}Fe$, using 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

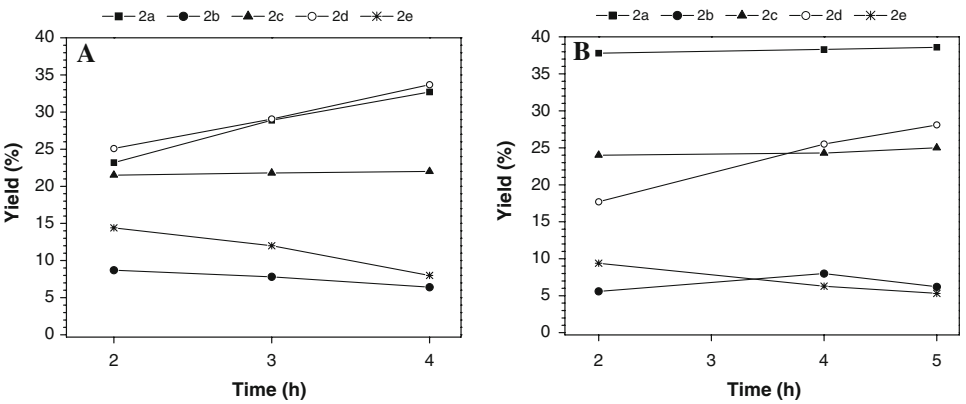


Fig. 4 Yield of all products during the oxidation of 1,2-dihydronaphthalene (**2**) in the presence of (**a**) $PW_{11}Mn$ or (**b**) $BW_{11}Mn$, using 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

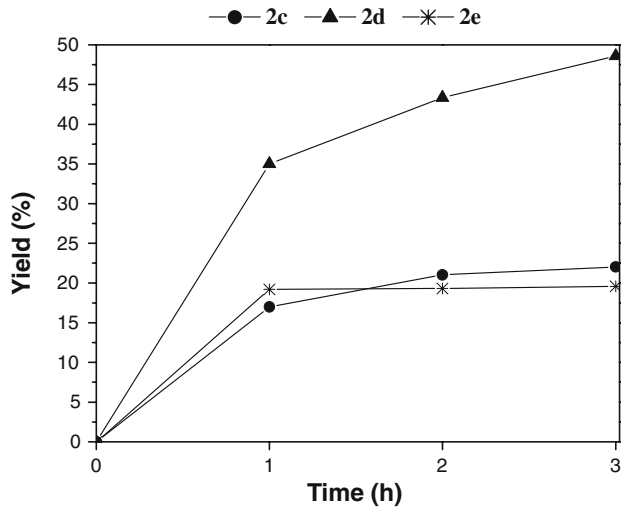


Fig. 5 Yield of products **2c**, **2d** and **2e** in the oxidation of 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**2b**) in the presence of $PW_{11}Mn$ with 9.8 mmol of H_2O_2. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

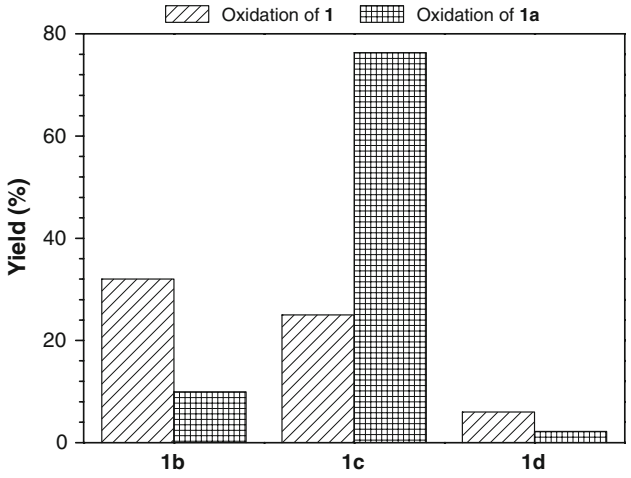


Fig. 6 Comparative yield of products **1b**, **1c** and **1d** in 1*H*-indene (**1**) and 1,2-epoxyindane (**1a**) oxidation reactions in the presence of $BW_{11}Mn$ with 9.8 mmol of H_2O_2 after 3 h. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

from the related epoxide as an intermediate in 1*H*-indene or 1,2-dihydronaphthalene catalytic oxidation (Scheme 3). Additionally, 2-(2-oxoethyl)benzaldehyde (**1b**) seems to be formed mainly by the oxidative cleavage of 1*H*-indene (**1**) carbon–carbon double bond. In fact, when the independent oxidation reactions of **1** and **1a** are compared (Fig. 6), we can conclude that the oxidation of **1a** contributes less to the yield of **1b** than the oxidation of **1**. So, **1b** seems to be the result of two reaction pathways: (a) the oxidative cleavage of **1d**, which arises from **1a** as an intermediate in 1*H*-indene oxidation and (b) directly from 1*H*-indene by the oxidative cleavage of the carbon–carbon double bond (Scheme 3). Both reaction pathways have also to be considered for the formation of 2-(3-oxopropyl)benzaldehyde (**2c**), as may be deduced from the comparison of the outcome of the oxidation of **2** and **2b**, in separate reactions (Fig. 7). In this case, in the conditions of Fig. 7, the most important pathway seems to be the oxidative cleavage of the carbon–carbon bond of 1,2-dihydroxytetralin (**2e**).

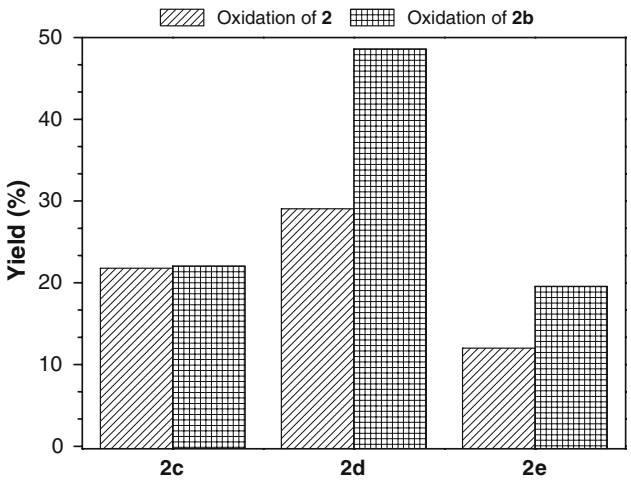
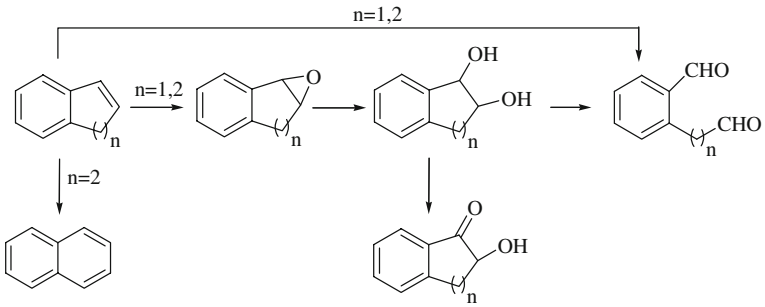


Fig. 7 Comparative yield of products **2c**, **2d** and **2e** in 1,2-dihydronaphtalene (**2**) and 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**2b**) oxidation reactions in the presence of $PW_{11}Mn$ with 9.8 mmol of H_2O_2 after 3 h. Substrate: 1.0 mmol; catalyst: 3.0 μmol; acetonitrile: 3.0 mL; 80 °C

Scheme 3



Finally, hydroxy-ketones **1c** and **2d** can be obtained through the oxidation of the benzylic position of the corresponding diol. In the catalytic oxidation reaction of **2**, the oxidative dehydrogenation product **2a** was also observed, as a competitive pathway in the oxidation of 1,2-dihydronaphthalene (Scheme 3).

4 Conclusions

The oxidation of 1*H*-indene, 1,2-dihydronaphthalene, 1,2-epoxyindane and 1,2-epoxy-1,2,3,4-tetrahydronaphthalene with hydrogen peroxide, in the presence of catalytic amounts of tetrabutylammonium salts of manganese(III) or iron(III) substituted Keggin-type polyoxotungstates was studied. The percentages of conversion and selectivity for 1*H*-indene and 1,2-dihydronaphthalene oxidation reactions were found to be dependent on the polyoxotungstate used, on the amount of oxidant added and on the reaction time. In general, polyoxotungstates studied gave rise to relatively high conversions and the formation of several oxygenated products was observed.

The oxidation of **1** and **2**, respectively, yielded two or three main products after 5–7 h of reaction, when a 5-fold excess of H_2O_2 (in relation to the stoichiometric amount needed for the most oxidized products) was used. These were, respectively, the hydroxy-ketones **1c** and **2d** and the di-aldehydes **1b** and **2c**, together with naphthalene (**2a**), obtained by oxidative dehydrogenation of substrate **2**. Through the study of the oxidation of the epoxides **1a** and **2b**, it was possible to understand the sequential formation of the diverse products found and propose the series of oxidative steps depicted in Scheme 3.

The oxidative cleavage of carbon–carbon bonds of 1,2-diols and the oxidative cleavage of C=C bonds of olefins to afford carbonyl compounds, that originated the formation of **1b** and **2c**, are very important reactions in synthetic organic chemistry. Here we report the oxidative cleavage of 1,2-diols carbon–carbon bond and the oxidative cleavage of carbon–carbon double bond of olefins to carbonyl compounds under mild and environmentally friendly conditions, using hydrogen peroxide as oxidant.

Acknowledgments Thanks are due to the University of Aveiro, FCT (Fundação para a Ciência e a Tecnologia) and FEDER for funding the Organic Chemistry Research Unity and CICECO. A.C.E. and I.C.M.S.S. also thank FCT for their grants.

References

1. Griffith WP (1991) Trans Met Chem 16:548
2. Hill CL (1992) In: Strukul G (ed) Catalytic oxidations with hydrogen peroxide as oxidant Ch. 8. Kluwer, Dordrecht
3. Mizuno N, Misono M (1994) J Mol Catal 86:319
4. Okuhara T, Mizuno N, Misono M (1996) Adv Catal 41:113
5. Kozhevnikov IV (1998) Chem Rev 98:171
6. Vazylyev M, Sloboda-Rozner D, Haimov A, Maayan G, Neumann R (2005) Topics Catal 34:93
7. Mizuno N, Yamaguchi K, Kamata K (2005) Coord Chem Rev 249:1944
8. Hill CL (2007) J Mol Catal A Chem 262:2
9. Kozhevnikov IV (1995) Catal Rev Sci Eng 37:311
10. Hill CL, Prosser-McCartha CM (1995) Coord Chem Rev 143:407
11. Neumann R (1998) Progr Inorg Chem 47:317
12. Simões MMQ, Conceição CMM, Gamelas JAF, Domingues PMDN, Cavaleiro AMV, Cavaleiro JAS, Ferrer-Correia AJV, Johnstone RAW (1999) J Mol Catal A Chem 144:461
13. Santos ICMS, Simões MMQ, Pereira MMMS, Martins RRL, Neves MGPMS, Cavaleiro JAS, Cavaleiro AMV (2003) J Mol Catal A Chem 195:253
14. Santos ICMS, Simões MMQ, Neves MGPMS, Cavaleiro JAS, Cavaleiro AMV (2003) Synlett 1643
15. Simões MMQ, Santos ICMS, Balula MSS, Gamelas JAF, Cavaleiro AMV, Neves MGPMS, Cavaleiro JAS (2004) Catal Today 91–92:211
16. Balula MSS, Santos ICMS, Simões MMQ, Neves MGPMS, Cavaleiro JAS, Cavaleiro AMV (2004) J Mol Catal A Chem 222:159
17. Cavaleiro AMV (2005) In: Paquette LA (ed) Tungstoboric acid, tetrakis(tetrabutylammonium) Salt, e-EROS encyclopedia of reagents for organic synthesis. Wiley, New York
18. Santos ICMS, Gamelas JAF, Balula MSS, Simões MMQ, Neves MGPMS, Cavaleiro JAS, Cavaleiro AMV (2007) J Mol Catal A Chem 262:41
19. Sanderson WR (2000) Pure Appl Chem 72:1289
20. Grigoropoulou G, Clark JH, Elings JA (2003) Green Chem 5:1
21. Jones CW (1999) Applications of hydrogen peroxide and derivatives. The Royal Society of Chemistry, Cambridge
22. Adolfsson H (2004) In: Bäckvall J-E (ed) Modern oxidation methods Ch. 2. Wiley-VCH, Weinheim
23. Shi Y (2004) In: Bäckvall J-E (ed) Modern oxidation methods Ch. 3. Wiley-VCH, Weinheim
24. Canali L, Cowan E, Deleuze H, Gibson CL, Sherrington DC (2000) J Chem Soc Perkin Trans 1:2055
25. Abdi SHR, Kureshy RI, Khan NH, Jasra RV (2004) Catal Surv Asia 8:187
26. Kureshy RI, Ahmad I, Khan NH, Abdi SHR, Pathak K, Jasra RV (2006) J Catal 238:134
27. Haines AH (1988) Methods for the oxidation of organic compounds. Academic Press, New York, pp 277–292
28. Hudlický M (1990) Oxidations in organic chemistry. American Chemical Society, Washington
29. Balula MS, Gamelas JA, Carapuça HM, Cavaleiro AMV, Schlindwein W (2004) Eur J Inorg Chem 619
30. Rebelo SLH, Simões MMQ, Neves MGPMS, Silva AMS, Tagliatesta P, Cavaleiro JAS (2005) J Mol Catal A Chem 232:135
31. Vogel AI (1961) A text-book of quantitative inorganic analysis including elementary instrumental analysis, 3rd edn. Longmans, London
32. Pedragosa-Moreau S, Archelas A, Furstoss R (1996) Tetrahedron 52:4593
33. Palucki M, Finney NF, Pospisil PJ, Güler ML, Ishida T, Jacobsen EN (1998) J Am Chem Soc 120:948
34. Choi OK, Cho BT (2001) Tetrahedron Asymmetr 12:903
35. Resnick SM, Torok DS, Lee KY, Brand JM, Gibson DT (1994) Appl Environ Microb 60:3323
36. Smith K, Liu C-H, El-Hiti GA (2006) Org Biomol Chem 4:917
37. Mang H, Gross J, Lara M, Goessler C, Schoemaker HE, Guebitz GM, Kroutil W (2007) Tetrahedron 63:3350

38. Chai W, Takeda A, Hara M, Jib S, Horiuchia CA (2005) Tetrahedron 61:2453
39. Berglund RA (1995) In: Paquette LA (ed) Encyclopedia of reagents for organic synthesis. Wiley, New York, pp 3837–3843
40. Dhakshinamoorthy A, Pitchumani K (2006) Tetrahedron 62:9911
41. Mang H, Gross J, Lara M, Goessler C, Schoemaker HE, Guebitz GM, Kroutil W (2006) Angew Chem Int Ed 45:5201
42. Miyamoto K, Tada N, Ochiai M (2007) J Am Chem Soc 129:2772