ELSEVIER

Journal of Molecular Catalysis A: Chemical 165 (2001) 283–290

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

$H_{3+n}PMo_{12-n}V_nO_{40}$-catalyzed selective oxidation of benzoins to benzils or aldehydes and esters by dioxygen

Bassam El Ali*, Abdel Moneim El-Ghanam, Mohammed Fettouhi

Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Received 5 April 2000; accepted 20 September 2000

Abstract

Heteropolyacids $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*, $n = 1$–4) catalyze efficiently the oxidation and the oxidative cleavage of benzoin derivatives in the presence of dioxygen. HPA-2 gave the highest total yields in aldehydes and carboxylic esters by using primary alcohols as solvents. No oxidative cleavage products were obtained with secondary or tertiary alcohols. HPA-2 catalyzes the oxidation of benzoin to benzil in the presence of *t*-BuOH or other polar solvents such THF, CH_3CN, DME.

Keywords: Homogeneous reaction; Oxidation; Oxidative cleavage; Heteropolyacids; Vanadium; Benzoin; Benzil

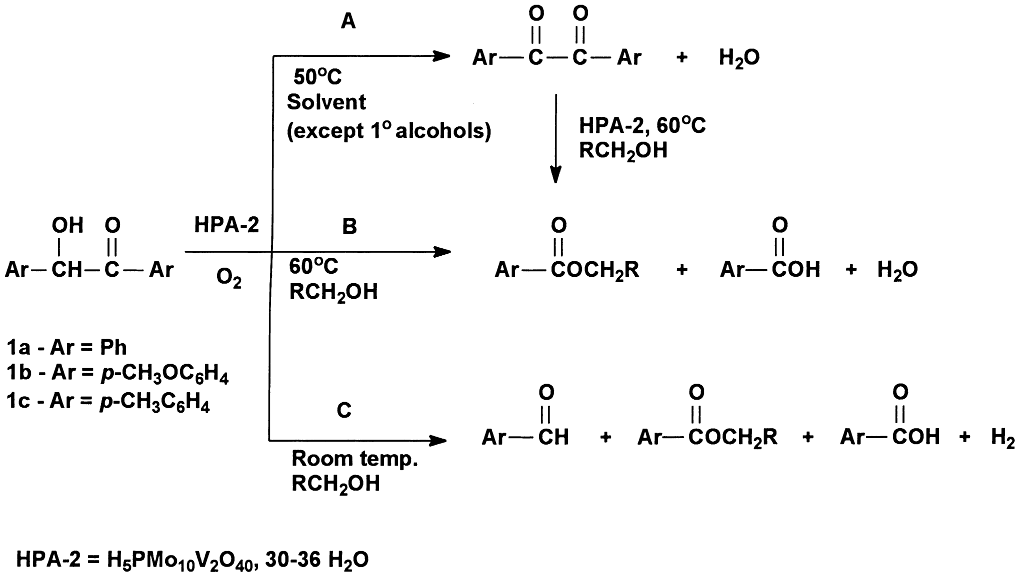
1. Introduction

Metal-catalyzed oxidative cleavage of C–C bond is widely used in organic synthesis in both academic research and industrial applications [1,2]. In fact, the catalytic oxidation of cyclohexane by V(V)–Cu(II) catalyst and nitric acid represents so far the best industrial method for the production of adipic acid [1,2]. The oxidative cleavage of ketones was previously examined using the heteropolyacid $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-2), as a catalyst affording carboxylic acid derivatives in high yields [3]. On the other hand, cyclic ketones in alcohols were oxidatively cleaved in the presence of stoichiometric amount of oxovanadium(V), $VO(OEt)Cl_2$ and dioxygen to give the corresponding ketoesters or diesters depending on the substituent at 2-position [4]. Recently, we have reported a new route to the catalytic synthesis of various saturated and unsaturated carboxylic esters via oxidative cleavage of benzil derivatives using heteropolyacids of series $H_{3+n}PMo_{12-n}V_nO_{40}$ ($n > 1$) and dioxygen [5]. The aromatic α-hydroxy ketones were also easily oxidized to the corresponding α-diketones under homogeneous and heterogeneous conditions in the presence of aldehyde or aldoacetal with catalytic amount of Co(II) or Fe(II) complexes and dioxygen [6]. In addition, the oxidation of benzoins to benzils was studied using *p*-benzoquinone or air in the presence of $(Fe^{II}(SPh)_4]^{2-}$ and $[Fe^{II}(SePh)_4]^{2-}$ [7], Fe(II)-cysteine peptide complexes [8] and *t*-butylperoxide [9,10]. Recently, ammonium chlorochromate adsorbed on alumina [11] or silica [12] was also used to oxidize benzoins to benzils. We now wish to report an efficient use of the heteropolyacids of the series $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*, $n > 1$) [13–15] in the oxidation and oxidative cleavage of benzoins to benzils or aldehydes and carboxylic esters under mild experimental conditions.

---

* Corresponding author. Fax: +966-3-8604277.
E-mail address: belali@kfupm.edu.sa (B. El Ali).

PII: S1381-1169(00)00453-2



Scheme 1.

2. Results and discussion

The catalytic activity of the heteropolyacids, $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-*n*, $n = 1$–4), was explored using benzoins as substrates. HPA-*n* catalyze the oxidation of benzoins in the presence of dioxygen without cleavage of C–C bond leading to the formation of benzils, or with C–C bond cleavage forming aldehydes and carboxylic esters or mainly esters depending on the temperature of the reaction.

2.1. Oxidation of benzoin to benzil by HPA-2 and dioxygen

The heteropolyacids, HPA-*n* ($n > 1$), showed excellent catalytic activity in the oxidation of benzoin **1a** to benzil (Scheme 1, route A). The oxidation reaction was explored with various solvents such as THF, CH_3CN, DME and DMF at room temperature in the presence of the catalytic system HPA-2/O_2. At room temperature, only traces of benzil was formed with any of the mentioned solvents. However, the increase of the temperature to 50°C leads to a complete conversion of benzoin to benzil (except for DMF traces of benzil was found) (Table 1, entries 1–10). Excellent yields and selectivities were also observed with HPA-1, HPA-3 and HPA-4. However, traces of benzil were formed when $H_3PMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$ (with no vanadium) was used at room temperature or 50°C to catalyze the oxidation reaction.

2.2. Oxidative cleavage of benzoins by HPA-n and dioxygen

The oxidative cleavage of benzoin derivatives **1a–c** was examined in the presence of HPA-*n* ($n = 0$–4) and

Table 1
Oxidation of benzoin **1a** to benzil by HPA-2 and dioxygen[a]

Run	*T* (°C)	Solvent	% Yield[b] PhCOCOPh
1	25	*t*-Bu-OH	Traces
2	50	*t*-Bu-OH	100
3	25	THF	Traces
4	50	THF	100
5	25	CH_3CN	Traces
6	50	CH_3CN	100
7	25	DME	Traces
8	50	DME	100
9	25	DMF	Traces
10	50	DMF	Traces

[a] Reaction conditions: HPA-2 (0.02 mmol), benzoin (2.0 mmol), solvent (6 ml), 1 atm of O_2, 8 h.

[b] Yield determined by GC using anisol as internal standard, % yield = mmol of product/mmol substrate × 100.

Table 2
Oxidative cleavage of benzoin **1a** with dioxygen in 1-propanol. Effect of various types of catalyst[a]

Run	Catalyst[b]	T (°C)	Total yield[c] **(%)**	Products distribution[d] (%)		
				PhCHO	PhCOOR′	PhCOOH
1	HPA-2	25	96	45	48	7
2	NaHPA-2	25	Traces	–	–	
3	NH_4HPA-2	25	Traces	–	–	
4	HPA-1	25	31	50	48	2
5	HPA-3	25	78	46	48	6
6	HPA-4	25	82	48	48	4
7	HPA-Mo_{12}	50	Traces	–	–	–
8	HPA-W_{12}	50	Traces	–	–	–

[a] Reaction conditions: HPA (0.02 mmol), benzoin (2.0 mmol), 1-propanol (6 ml), 1 atm of O_2, 8 h.

[b] HPA-2 = $H_5PMo_{10}V_2O_{40}\cdot xH_2O$; NaHPA-2 = $Na_5PMo_{10}V_2O_{40}\cdot xH_2O$; NH_4HPA-2 = $(NH_4)_5PMo_{10}V_2O_{40}\cdot xH_2O$; HPA-1 = $H_4PMo_{11}V_1O_{40}\cdot xH_2O$; HPA-3 = $H_6PMo_9V_3O_{40}\cdot xH_2O$; $H_5PMo_{10}V_2O_{40}\cdot xH_2O$; HPA-4 = $H_7PMo_8V_4O_{40}\cdot xH_2O$.

[c] Yield determined by GC using anisol as internal standard, % yield = mmol of product/2 mmol substrate × 100.

[d] Determined by GC using anisol as internal standard, % = mmol of a product/Σ mmol products × 100.

dioxygen. The study includes the effect of varying the catalyst, the time of the reaction, and the temperature (Scheme 1, route B and C).

2.2.1. *Influence of the type of catalyst*

The oxidative cleavage of benzoin **1a** (Ar = C_6H_5) was studied with various heteropolyacids under atmospheric pressure of molecular oxygen at room temperature for 8 h by using 1-propanol as a solvent (Table 2, entries 1–8). Only traces of aldehyde and ester were observed when sodium or ammonium salt of the heteropolyacid HPA-2 was used (Table 2, entries 2, 3). Furthermore, the heteropolyacids that contain no vanadium entities such as $H_3PM_{12}O_{40}$ (M = Mo, W) showed no catalytic activity in the oxidative cleavage at room temperature (Table 2, entries 7, 8). However, the heteropolyacids of the series $H_{3+n}PMo_{12-n}V_nO_{40}\cdot xH_2O$ (HPA-n, n = 1–4) showed excellent catalytic behaviors in the oxidation of benzoin **1a** with dioxygen. For example, $H_5PMo_{10}V_2O_{40}$ (HPA-2) catalyzes efficiently the oxidation of benzoin **1a** giving a total yield of 96% (45% propylbenzoate, 48% benzaldehyde, and 7% benzoic acid) (Table 2, entry 1). In addition, HPA-1 (Table 2, entry 4), HPA-3 (Table 2, entry 5) and HPA-4 (Table 2, entry 6) gave a total yield of 31, 78 and 82%, respectively, and the excellent selectivities in benzaldehyde and propylbenzoate were always maintained high. It seems clear now that the presence of both Bronstëd acidity and vanadium in the structure of the heteropolyacids, $H_{3+n}PMo_{12-n}V_nO_{40}\cdot xH_2O$ (HPA-n), enhances their catalytic activity in the reaction of oxidative cleavage of benzoins. In fact, the catalytic system HPA-2/O_2 at room temperature appears as the most efficient system in the oxidation of benzoin **1a**.

2.2.2. *Effect of time*

The oxidative cleavage of benzoin **1a** was followed with time by considering methanol, 1-propanol and isopentanol as solvents in the presence of HPA-2/O_2 at room temperature. The reaction profiles (Fig. 1) showed clearly a different behavior of alcohols. The oxidation reaction is slower with isopentanol compared to methanol and 1-propanol. However, the maximum total yield of products (98%) was obtained in all cases between 6–8 h. These results indicate that the catalytic system HPA-2/O_2 is very active independent to type of primary alcohols.

2.2.3. *Effect of temperature*

The temperature effect on the oxidative cleavage of benzoin **1a** was also carefully investigated. The oxidation reaction was carried in the presence of HPA-2/O_2 and 1-propanol and the temperature was varied from room temperature to 70°C (Fig. 2). We have found that the yield of benzaldehyde decreases while the yield of propylbenzoate ester increases by elevating the temperature from 25 to 70°C. The reaction was accompanied by the formation of some benzil (5–15%) at temperatures between 45 and 70°C. We believe that the

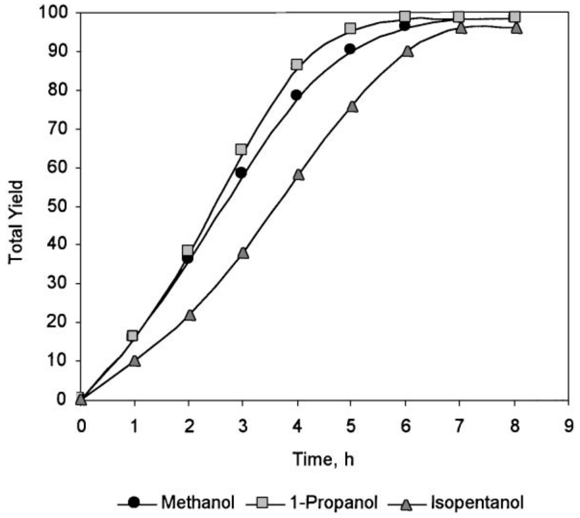


Fig. 1. Reaction profiles for the oxidative cleavage of benzoin by HPA-2/O_2 in the presence of different alcohols. Reaction conditions: HPA-2 (0.02 mmol), benzoin (2.0 mmol), alcohol (6 ml), 1 atm O_2, 8 h.

increase in ester formation by increasing the temperature comes mainly from the oxidative cleavage of benzil formed as intermediate in the reaction and partially from the esterification of benzoic acid in the presence of HPA-2 as catalyst and dioxygen (Scheme 1, route A) [5].

2.3. Oxidative cleavage of benzoins catalyzed by HPA-2/O_2 in the presence of various alcohols

The oxidative cleavage of benzoin derivatives **1a–c** catalyzed by HPA-2/O_2 was examined at room temperature for 8 h in the presence of different alcohols (Scheme 1, route C). The results are summarized in Table 3. Excellent total yields (76–96%) and excellent selectivity in aldehydes and carboxylic esters were obtained with various primary alcohols (Table 3, entries 1–21). However, almost no products were obtained when either 2-propanol or *t*-butyl alcohol was used as a solvent. In addition, a mixture of acetonitrile (2 ml) and primary alcohol (4 ml) was used with anizoin **1b** and 4,4′-dimethylbenzoin **1c** due to the low solubility of **1b** and **c** at room temperature in pure alcohol. Interestingly, the reaction of benzoins **1a–c** in the presence of allyl and benzyl alcohols leads to high total yields (74–92%) (Table 3, entries 22–27). This method represents an interesting and catalytic route to the synthesis of unsaturated and benzylic aldehydes and carboxylic esters. In all cases (Table 3, entries 1–27), the carboxylic acids (5–12%) are mainly formed by the

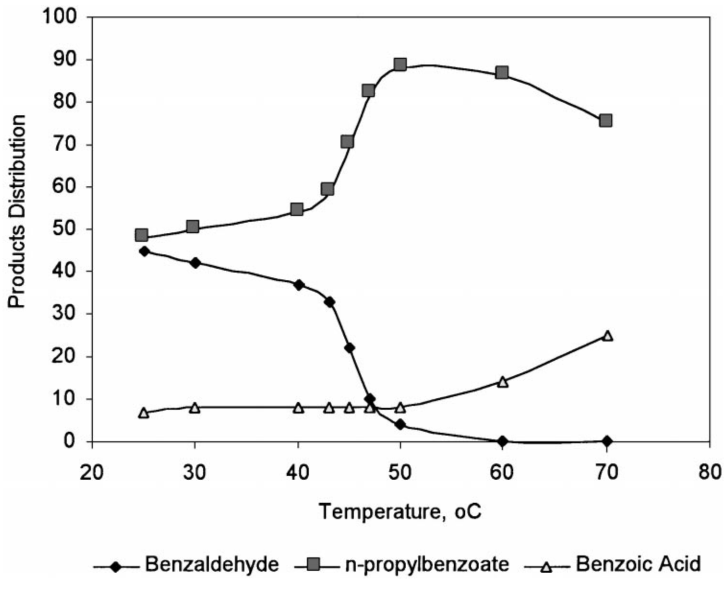


Fig. 2. Effect of temperature on the oxidative cleavage of benzoin by HPA-2/1-propanol/O_2. Reaction conditions: HPA-2 (0.02 mmol), benzoin (2.0 mmol), 1-propanol (6 ml), 1 atm O_2, 8 h.

Table 3
Catalytic oxidation of benzoin derivatives **1a–c** by HPA-2/O_2/25°C in the presence of various alcohols[a]

Run	Benzoin (**1a–c**)	Alcohol[b]	Total yield[c] (%)	Products distribution[d] (%)		
				PhCHO	PhCOOR	PhCOOH
1	**1a**	CH_3OH	90	46	45	8
2	**1b**	CH_3OH	83	48	47	5
3	**1c**	CH_3OH	81	47	45	7
4	**1a**	CH_3CH_2OH	96	45	46	9
5	**1b**	CH_3CH_2OH	85	48	46	6
6	**1c**	CH_3CH_2OH	86	47	46	7
7	**1a**	$CH_3CH_2CH_2OH$	96	45	48	7
8	**1b**	$CH_3CH_2CH_2OH$	76	46	45	9
9	**1c**	$CH_3CH_2CH_2OH$	96	47	44	9
10	**1a**	$CH_3CH_2CH_2CH_2OH$	90	46	47	7
11	**1b**	$CH_3CH_2CH_2CH_2OH$	90	47	45	8
12	**1c**	$CH_3CH_2CH_2CH_2OH$	90	48	44	8
13	**1a**	$CH_3(CH_2)_3CH_2OH$	88	46	48	6
14	**1b**	$CH_3(CH_2)_3CH_2OH$	79	45	46	9
15	**1c**	$CH_3(CH_2)_3CH_2OH$	81	47	45	8
16	**1a**	$CH_3CH(CH_3)CH_2CH_2OH$	90	47	48	5
17	**1b**	$CH_3CH(CH_3)CH_2CH_2OH$	82	46	44	10
18	**1c**	$CH_3CH(CH_3)CH_2CH_2OH$	80	45	47	8
19	**1a**	$CH_3(CH_2)_5CH_2OH$	87	45	46	9
20	**1b**	$CH_3(CH_2)_5CH_2OH$	78	45	43	12
21	**1c**	$CH_3(CH_2)_5CH_2OH$	80	44	46	10
22	**1a**	$CH_2{=}CHCH_2OH$	90	45	44	11
23	**1b**	$CH_2{=}CHCH_2OH$	92	46	42	12
24	**1c**	$CH_2{=}CHCH_2OH$	76	45	46	9
25	**1a**	$PhCH_2OH$	74	44	46	10
26	**1b**	$PhCH_2OH$	74	46	45	9
27	**1c**	$PhCH_2OH$	74	47	44	9

[a] Reaction conditions: HPA-2 (0.02 mmol), benzoin (2.0 mmol), 1 atm of O_2, room temperature (25°C), 8 h. For **1a**: alcohol (6 ml), for **1b** and **c**: alcohol (4 ml), CH_3CN (2 ml).

[b] **1a** = C_6H_5-CO-CHOH-C_6H_5, **1b** = *p*-CH_3O-C_6H_4-CO-CHOH-C_6H_4-*p*-OCH_3, **1c** = *p*-CH_3-C_6H_4-CO-CHOH-C_6H_4-*p*-CH_3.

[c] Yield determined by GC using anisol as internal standard, % yield = mmol of product/2 mmol substrate × 100.

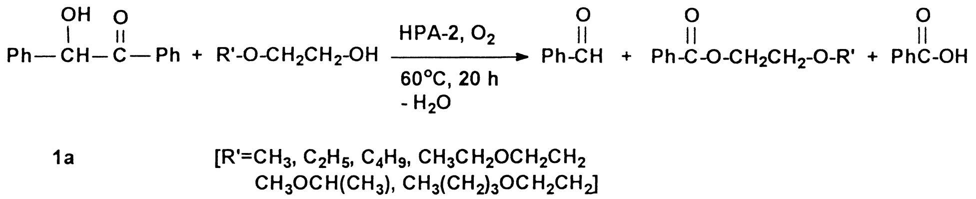
[d] Determined by GC using anisol as internal standard, % = mmol of a product/Σ mmol products × 100.

hydrolysis of esters or by the cooxidation of aldehydes formed.

In addition, the oxidative cleavage of benzoin **1a** was also carried out at room temperature in the presence of various alcoxyalcohols. The reaction was catalyzed by HPA-2/O_2 to form, in addition to benzaldehyde, some interesting functionalized carboxylic esters (Eq. (1)) (Table 4, entries 1–6).

3. Proposed mechanism

The proposed mechanism for the oxidative cleavage of benzoin by HPA-*n* and dioxygen is described (Scheme 2). Many studies have shown that VO_2^+ is formed in isolated form or within heteropolyacids (Eq. (2)) [16–21]. Recently, the ^{13}P and ^{51}V NMR spectra of the reaction of benzene hydroxylation with



$$\underset{\mathbf{1a}}{\text{Ph—CH(OH)—C(=O)—Ph}} + \text{R'-O-}CH_2CH_2\text{-OH} \xrightarrow[60^{\circ}C,\ 20\ h,\ -H_2O]{HPA\text{-}2,\ O_2} \text{Ph-CH(=O)} + \text{Ph-C(=O)-O-}CH_2CH_2\text{-O-R'} + \text{PhC(=O)-OH} \quad (1)$$

$$[R' = CH_3,\ C_2H_5,\ C_4H_9,\ CH_3CH_2OCH_2CH_2,\ CH_3OCH(CH_3),\ CH_3(CH_2)_3OCH_2CH_2]$$

Table 4
Catalytic oxidation of benzoin **1a** by HPA-2/O_2 in the presence of various alcoxyalcohols[a]

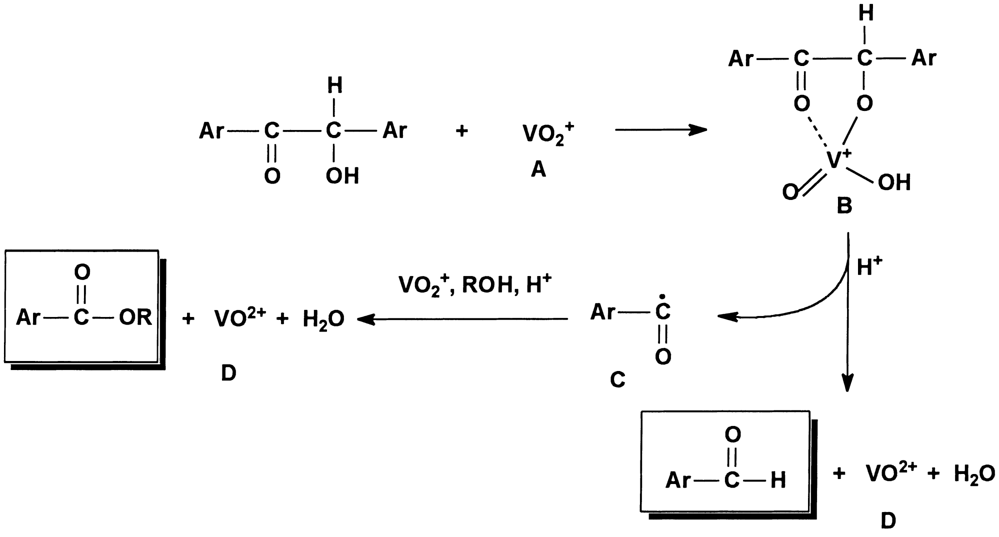
Run	Alcohol	Products distribution[b] (%)			
		Total yield[c] (%)	PhCHO (%)	PhCOOR″ (%)	PhCOOH (%)
1	$CH_3OCH_2CH_2OH$	87	45	46	9
2	$CH_3CH_2OCH_2CH_2OH$	78	45	43	12
3	$CH_3CH_2OCH_2CH_2OCH_2CH_2OH$	80	44	46	10
4	$CH_3OCH(CH_3)OCH_2CH_2OH$	90	45	44	11
5	$CH_3CH_2CH_2CH_2OCH_2CH_2OH$	92	46	42	12
6	$CH_3(CH_2)_2CH_2OCH_2CH_2OCH_2CH_2OH$	76	45	46	9

[a] Reaction conditions: HPA-2 (0.02 mmol), alcohol (6 ml), benzoin (2.0 mmol), 1 atm of O_2, room temperature (25°C), 20 h.
[b] Determined by GC using anisol as internal standard, % = mmol of a product/Σ mmol products × 100.
[c] Yield determined by GC using anisol as internal standard, % yield = mmol of product/2 mmol substrate × 100.

hydrogen peroxide confirm the formation of $VO_2{}^+$ which is probably converted into $VO(O_2)^+$ in the presence of H_2O_2 [24,25]. We also believe that $VO_2{}^+$ (**A**) is the key and active species formed under dioxygen in the oxidative cleavage of benzoin derivatives in the presence of alcohols. $VO_2{}^+$ is added to benzoin to form the alcoxyvanadium(V) intermediate **B**. The homolytic cleavage of **B** in the presence of H^+ gives aldehyde, the radical **C** and H_2O and the vanadium(IV) intermediate VO^{2+} (**D**). The formation of radical in this reaction was confirmed by the addition of the radical inhibitor, 2,6-di-*tert*-butyl-*p*-cresol, to the reaction mixture of HPA-2/O_2/1-propanol/benzoin; the total yield decreased from 96 to 12%. The vanadium(V) cation $VO_2{}^+$ reacts with radical **C** in the presence of alcohol (ROH) to form the carboxylic ester, H^+, and VO^{2+} (**D**). The vanadium(IV) species VO^{2+} returns into the heteropolyanions either by an electron transfer (Eq. (3)) or by association with the lacunary species HPA $(n-1)$ (Eq. (4)) [16–21]. Eventually, VO^{2+} is reoxidized by O_2 inside HPA-n (Eq. (5)).

$$\text{HPA-}n \rightleftarrows VO_2{}^+ + \text{HPA-}(n-1) \qquad (2)$$

$$VO^{2+} + \text{HPA-}n + H_2O \rightleftarrows VO_2{}^+ + \text{H(HPA-}n) \qquad (3)$$



Scheme 2.

$$VO^{2+} + HPA\text{-}(n-1) + H^+ \rightleftarrows H(HPA\text{-}n) \quad (4)$$

$$4HPA\text{-}(n-1) + O_2 \rightleftarrows 4HPA\text{-}n + H_2O \quad (5)$$

4. Experimental

Alcohols, alcoxyalcohols and benzoins (**1a** and **b**) are commercially available materials and were used without further purification. The benzoin **1c** was prepared according to the literature method [22]. The heteropolyacids $H_4PMo_{11}V_1O_{40}$, $H_5PMo_{10}V_2O_{40}$, $H_6PMo_9V_3O_{40}$ and $(NH_4)_5PMo_{10}V_2O_{40}$ were prepared according to the literature method [13–15], however, $H_7PMo_8V_4O_{40}$, was prepared according to Brégeault method [13–15]. The solid FT-IR of the synthesized heteropolyacids did not show clear differences and the bands between 800 and 1100 cm^{-1} confirmed the presence of the Keggin-type structure [23]. The analysis of the prepared heteropolyacids is as follows:

$Na_{0.5}H_{3.5}PMo_{11}VO_{40}$, $30H_2O$. Calculated: P, 1.33; Mo, 45.25, V, 2.18; Na, 0.49. Found: P, 1.35; Mo, 46.1; V, 2.26; Na, 0.45 ($Mo/P = 11.02$, $V/P = 1.02$, $Mo/V = 10.8$).

$Na_{0.5}H_{4.5}PMo_{10}V_2O_{40}$, $30H_2O$. Calculated: P, 1.35; Mo, 41.95; V, 4.45; Na, 0.50. Found: P, 1.31; Mo, 41.61; V, 4.35; Na, 0.20 ($Mo/P = 10.25$, $V/P = 2.02$, $Mo/V = 5.08$).

$Na_{0.5}H_{5.5}PMo_9V_3O_{40}$, $15H_2O$. Calculated: P, 1.75; Mo, 43.74; V, 7.74; Na, 0.58. Found: P, 1.58; Mo, 44.7; V, 7.5; Na, 0.11 ($Mo/P = 9.14$, $V/P = 2.88$, $Mo/V = 3.17$).

$Na_{0.1}H_{6.9}PMo_8V_4O_{40}$, $10H_2O$. Calculated: P, 1.69; Mo, 41.91; V, 11.13; Na, 0.13. Found: P, 1.73; Mo, 42.5; V, 11.36; Na, 0.25 ($Mo/P = 7.92$, $V/P = 3.99$, $Mo/V = 1.98$).

*4.1. General procedure for the oxidative cleavage of benzoin derivatives **1a–c***

HPA-2 (0.02 mmol) was added to a mixture of benzoin **1a** (2.0 mmol) and 1-propanol (6 ml) and the reaction mixture was stirred under 1 atm of dioxygen for 8 h at room temperature. The progress of reaction was monitored by GC by using anisol as internal standard. The conversion and the total yield of products were determined by GC and GC-MS. All products gave excellent ^1H and ^{13}C NMR spectra.

5. Conclusion

The results show a new and potential use of the heteropolyacids, $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-n, n = 1–4), as catalysts in the chemistry of oxidation. The benzoins are easily oxidized with or without C–C bond cleavage. The reaction provides a simple and highly efficient catalytic method for synthesis of aldehydes and carboxylic esters in the presence of primary alcohols under very mild conditions.

Acknowledgements

We would like to thank KFUPM — Saudi Arabia for financial support.

References

[1] D.E. Danly, C.R. Campbell, in: M. Grayson (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 1, Wiley, New York, 1978, p. 510.
[2] J.R. Lindsay Smith, D.I. Richards, C.B. Thomas, M. Whittaker, J. Chem. Soc., Perkin Trans. 2 (1985) 1677.
[3] B. El Ali, J.-M. Bregeault, J. Mercier, J. Martin, C. Martin, O. Convert, J. Chem. Soc., Chem. Commun. (1989) 825.
[4] T. Hiro, M. Mori, Y. Oshiro, Bull. Chem. Soc., Jpn. 62 (1989) 2399.
[5] B. El Ali, A.M. El-Ghanam, M. Fettouhi, Arabian J. Chem., submitted for publication.
[6] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, L. Lopez, J. Mol. Catal. 111 (1996) 33.
[7] W.-Y. Sun, N. Ueyama, A. Nakamura, J. Mol. Catal. 71 (1992) 391.
[8] W.-Y. Sun, N. Ueyama, A. Nakamura, Tetrahedron 48 (1992) 1557.
[9] J. Muzart, Tetrahedron Lett. 28 (1987) 2131.
[10] J. Muzart, Syn. Commun. 19 (1989) 2061.
[11] G.-S. Zhang, Q.-Z. Shi, M.-F. Chen, K. Cai, Syn. Commun. 27 (1997) 953.
[12] G.-S. Zhang, Q.-Z. Shi, M.-F. Chen, K. Cai, Syn. Commun. 27 (1997) 3691.
[13] G.A. Tsigdinos, C.J. Hallada, Inorg. Chem. 7 (1968) 437.
[14] P. Courtin, Rev. Chim. Min. 8 (1971) 75.
[15] A. Atlamsani, M. Ziyad, J.M. Bregeault, J. Chim. Phys. 92 (1995) 1344.

[16] I.V. Kozevnikov, K.I. Matveev, Appl. Catal. 5 (1983) 135.

[17] O.A. Kholdeeva, A.V. Golovin, R.I. Maksimovskaya, I.V. Kozhevnikov, J. Mol. Catal. 75 (1992) 235.

[18] I.V. Khozhenvikov, Catal. Rev.-Sci., Eng. 37 (1995) 311.

[19] I.V. Khozhenvikov, J. Mol. Catal. 117 (1997) 151.

[20] N. Mizuno, M. Misono, J. Mol. Catal. 86 (1994) 319.

[21] R. Neumann, M. de la Vega, J. Mol. Catal. 84 (1993) 93.

[22] J.E.T. Corrie, Tetrahedron 54 (1998) 5407.

[23] C. Rocchiccioli-Deltcheff, R. Thouvenot, M. Dabbabi, Spectrochim. Acta A 33 (1977) 143.

[24] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, J. Mol. Catal. 156 (2000) 143.

[25] K. Nomiya, K. Yagishita, Y. Nemoto, T. Kamataki, J. Mol. Catal. 126 (1997) 43.