



The oxidative cleavage of carbon–tin bond catalyzed by heteropolyacids of molybdenum

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Abstract

Heteropolymolybdoacids, $H_3[PMo_{12}O_{40}]$ and $H_6[P_2Mo_{18}O_{62}]$, catalyze the oxidative cleavage of C–Sn bond in the organotin derivatives of dibenzylchlorotin (**1**) and tribenzylchlorotin (**2**) in the presence of dioxygen. Benzaldehyde is the major reaction product, accompanied by smaller amounts of benzyl alcohol, benzyl chloride and dibenzyl. The results show that $H_6[P_2Mo_{18}O_{62}]$ as catalyst and ethanol (as solvent) produce the highest yield of benzaldehyde at 65 °C. Also, **1** produces a higher yield than **2**. The effects of catalyst type, temperature and solvent on the reaction time have been examined. In every case, $H_6[P_2Mo_{18}O_{62}]$ causes the C–Sn bond cleavage to be achieved in a shorter time than does $H_3[PMo_{12}O_{40}]$.

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1. Introduction

Among solid catalysts, heteropolyacids constitute a large class of compounds that are remarkable owing to their physicochemical properties. They include strong Bronsted acidity, reversible transformations, activation of molecular oxygen and hydrogen peroxide, high proton mobility and solubility in polar solvents. These properties have made them more and more popular in many fields, such as catalysis, biology, medicine, magnetism, photochemistry and material science [1–5].

Heteropolyacids are classified according to their structures. Two classes, the Keggin and the Wells–

Dawson structures, have been investigated more extensively than others [6–13].

Much attention has been devoted to the catalytic behavior of heteropolymolybdates. Several of these molybdates display redox characteristics and many reactions have been successfully demonstrated to proceed both in solution and heterogeneously with these catalysts [14–16]. We have worked on the synthesis and catalytic behavior of heteropoly compounds [17–19].

Due to the importance of C–Sn bond cleavage in biomimetic and enzymatic oxidations, in the present work, we report the oxidative-catalytic cleavage of C–Sn bond in (**1**) and (**2**) by heteropolyacids.

Very little is known about the reactivity and fate of tin derivatives in biomimetic or enzymatic oxidations, because most of the work has dealt with substrates that do not undergo any C–Sn bond scission

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[20]. Organotin compounds undergo oxidation to generate other functional groups, via C–Sn bond scission [21]. Among these reactions, conversion to the oxygen-containing group is one of the most important from a synthetic viewpoint. In particular, allylic and benzylic tin compounds are readily converted to the corresponding compounds by metallic or organic oxidants [22–24].

Recently, the oxidative cleavage of C–Sn bond in benzyltrialkyltins by iodobenzene (PhIO), has been investigated. The catalyst has been Iron-tetrakis (pentafluorophenyl) porphyrin chloride (TPFP)FeCl (a solid catalyst) with benzaldehyde as the main reaction product. However, the reported yield for this reaction is quite low [25]. We have been interested in studying C–Sn bond cleavage in the presence of other solid catalysts in order to obtain a higher yield of benzaldehyde. To this end, we looked beyond benzyltrialkyltins, and included di and tribenzyltins.

We have found that the Keggin, $H_3[PMO_{12}O_{40}]$, and the Wells–Dawson, $H_6[P_2Mo_{18}O_{62}]$, heteropolyacids, in an organic solvent, render effective oxidative cleavage of C–Sn bond in the presence of molecular oxygen with good yields.

2. Experimental section

2.1. Chemicals and apparatus

The deuterated solvents were purchased from Merck Company. The other solvents were prepared from commercial sources and were used without further purification. $H_6[P_2Mo_{18}O_{62}]$ was prepared according to the literature [26]. $H_3[PMO_{12}O_{40}]$ was a commercially available product. Di and tribenzylchlorotin were prepared with pure tin powder suspended in water and toluene in the presence of benzyl chloride at the boiling point as described in the literature [27].

1H NMR spectra were recorded on a FT-NMR Bruker 100 MHz ASPECT 3000 (with tetramethylsilane as an internal standard). IR spectra were obtained with a Buck 500 Scientific Spectrophotometer. GC analysis was performed on a PU 4500 gas chromatograph. Argon was used as carrier gas with a FID detector.

2.2. General procedure

All reactions were carried out in a 100 ml three-necked round-bottom flask equipped with magnetic stirrer, inlet gas tube, thermometer and a reflux condenser. In a typical reaction, to 40 ml of ethanol, 0.25 mmol of benzyltin **1** and 0.010 mmol of $H_6[P_2Mo_{18}O_{62}]$ were added and the mixture was stirred under conditions mentioned in the Results and discussion. High purity oxygen gas (99.99%) was introduced to the stirred reaction mixture via an immersed inlet gas tube fitting at a flow rate of (0.5 l/min). At regular intervals, samples from the reaction mixture were taken and immediately injected into a gas chromatograph. The products were characterized by comparing their spectroscopic (IR, 1H NMR) properties, and their retention times with those of authentic standards.

3. Results and discussion

The oxidative cleavage of C–Sn bond in **1** and **2**, catalyzed by $H_3[PMO_{12}O_{40}]$ and $H_6[P_2Mo_{18}O_{62}]$, was studied. Cleavage of C–Sn bond in the presence of dioxygen leads to the formation of benzaldehyde, benzyl chloride, benzyl alcohol and traces of dibenzyl, as well as some minor (unknown) products. The study has been focused on the major product, which is benzaldehyde.

A series of control experiments have shown that no benzaldehyde is obtained from **1** and/or **2**, when either the catalyst or dioxygen is absent. Other experiments have shown that even for the higher concentrations of substrates **1** and **2**, no benzaldehyde is observed in the absence of dioxygen or the catalysts.

The effects of varying catalyst (structure and concentration), solvents and temperature were studied.

3.1. Effect of solvent

C–Sn bond cleavage of **1** and **2** in various solvents, such as acetonitrile, pyridine, tetrahydrofuran, dimethylformamide, ethanol, propanol, butanol and mixed solvent systems (methanol–acetonitrile, methanol–acetonitrile–ethanol, pyridine–methanol–acetonitrile) has been explored. We have found that alcohols are the most effective solvents. The results

Table 1
Yields (GC analysis) of oxidative-catalytic cleavage of C–Sn bond in **1** by H₃[PMo₁₂O₄₀] and H₆[P₂Mo₁₈O₆₂]^a

Catalyst	Solvent	Percentage yield of benzaldehyde ^b
H ₃ [PMo ₁₂ O ₄₀]	Ethanol	53.4
H ₃ [PMo ₁₂ O ₄₀]	Propanol	48.3
H ₃ [PMo ₁₂ O ₄₀]	Butanol	17.2
H ₃ [PMo ₁₂ O ₄₀]	Acetonitrile	Trace
H ₃ [PMo ₁₂ O ₄₀]	Tetrahydrofuran	Trace
H ₃ [PMo ₁₂ O ₄₀]	Dimethylformamid	Trace
H ₃ [PMo ₁₂ O ₄₀]	Other mixed solvents	Trace
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Ethanol	66.8
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Propanol	51.3
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Butanol	20.0
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Other solvents	Trace

^a Reaction conditions: catalyst: 0.015 mmol for H₃[PMo₁₂O₄₀] and 0.010 mmol for H₆[P₂Mo₁₈O₆₂], substrate: 0.250 mmol, solvent: 40 ml, 1 atm of O₂, 4 h.

^b Yield determined by GC (calibration by standard methods).

are shown in Tables 1 and 2. According to the results, the highly oxidative cleavage of C–Sn bond into benzaldehyde by dioxygen has been achieved for **1** at 65 °C in ethanol as solvent, and H₆[P₂Mo₁₈O₆₂] as catalyst. In the C–Sn bond cleavage, the reactivities of **1** and **2** in alcohols were lowered as the carbon chain of the alcohols grew longer. The yield of benzaldehyde increased in this order: butanol < propanol < ethanol. In addition, the study of the reaction progress

Table 2
Yields (GC analysis) of oxidative-catalytic cleavage of C–Sn bond in **2** by H₃[PMo₁₂O₄₀] and H₆[P₂Mo₁₈O₆₂]^a

Catalyst	Solvent	Percentage yield of benzaldehyde ^b
H ₃ [PMo ₁₂ O ₄₀]	Ethanol	41.3
H ₃ [PMo ₁₂ O ₄₀]	Propanol	27.9
H ₃ [PMo ₁₂ O ₄₀]	Butanol	11.6
H ₃ [PMo ₁₂ O ₄₀]	Acetonitrile	Trace
H ₃ [PMo ₁₂ O ₄₀]	Tetrahydrofuran	Trace
H ₃ [PMo ₁₂ O ₄₀]	Dimethylformamid	Trace
H ₃ [PMo ₁₂ O ₄₀]	Other mixed solvents	Trace
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Ethanol	43.9
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Propanol	33.9
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Butanol	15.4
H ₆ [P ₂ Mo ₁₈ O ₆₂]	Other solvents	Trace

^a Reaction conditions: catalyst: 0.015 mmol for H₃[PMo₁₂O₄₀] and 0.010 mmol for H₆[P₂Mo₁₈O₆₂], substrate: 0.250 mmol, solvent: 40 ml, 1 atm of O₂, 4 h.

^b Yield determined by GC (calibration by standard methods).

by GC indicates that reaction time is shortest for cleavage of C–Sn bond in ethanol.

3.2. Effect of catalyst structure

The oxidative cleavage of C–Sn bond in **1** and **2** in ethanol by dioxygen with H₃[PMo₁₂O₄₀] and H₆[P₂Mo₁₈O₆₂] as catalyst, was studied. The progress of the reaction was monitored by GC and yielded the highest concentration of benzaldehyde when the oxidation of **1** is carried out with H₆[P₂Mo₁₈O₆₂] as catalyst at 65 °C. The results indicate that employing **1** as substrate, the highest concentration of benzaldehyde is obtained after 120 min with H₃[PMo₁₂O₄₀] as the catalyst, but it is reached after only 20 min when H₆[P₂Mo₁₈O₆₂] is the catalyst. In other words, for the catalyst with a Wells–Dawson structure the reaction time is decreased.

3.3. Effect of catalyst concentration

The oxidative cleavage of C–Sn bond under optimum conditions (**1**) as substrate, ethanol as solvent, and H₆[P₂Mo₁₈O₆₂] as catalyst at 65 °C was investigated in solutions with 4.17×10^{-6} , 8.33×10^{-6} , 8.33×10^{-5} , 1.66×10^{-4} , and 2.50×10^{-4} molar H₆[P₂Mo₁₈O₆₂]. The reaction progress was followed by GC and the results indicate that the reaction time and rate were affected by changing the catalyst concentration. The concentration effects on the C–Sn bond cleavage rate, with in situ generated benzaldehyde, were studied. The results show that the rate increases with that of the catalyst concentration up to 8.33×10^{-5} M. Any further increasing of the catalyst concentration does not have any effect on the reaction rate (Fig. 1). The GC studies indicate that, for the lowest catalyst concentration, there is a competition between benzaldehyde and benzyl chloride formation.

3.4. Effect of temperature

From the GC data, it is established that (Fig. 2) the C–Sn bond cleavage rate is a function of temperature. The maximum concentration of benzaldehyde in optimum conditions is reached at 65 °C after 20 min and as temperature decreased to room temperature, the maximum concentration of benzaldehyde is reached in 180 min.

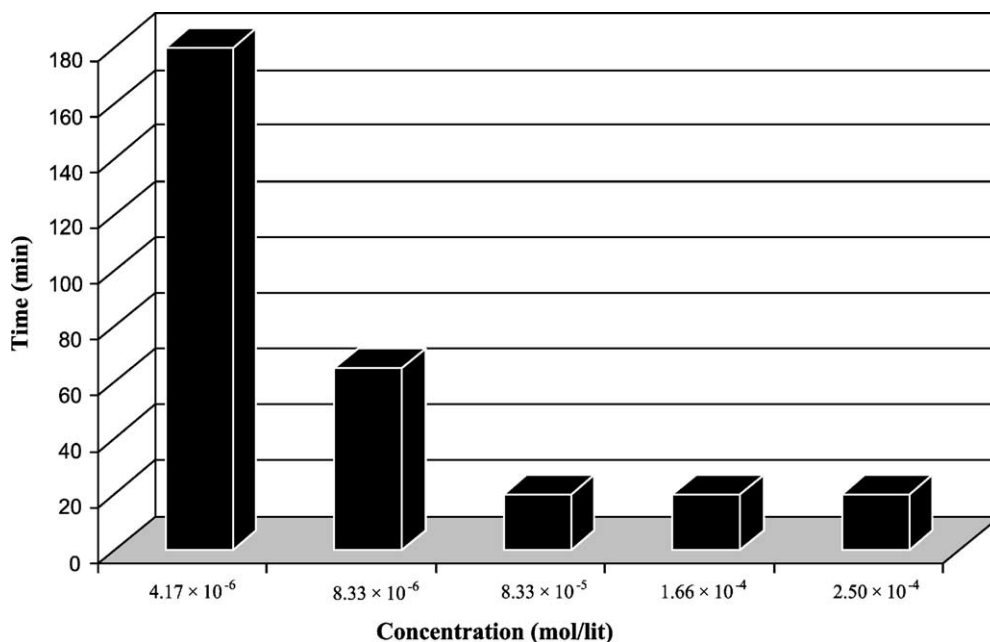


Fig. 1. Dependence of reaction time on catalyst concentration for C–Sn bond cleavage. Substrate: **1**; solvent: ethanol; catalyst: $\text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$; major product: benzaldehyde.

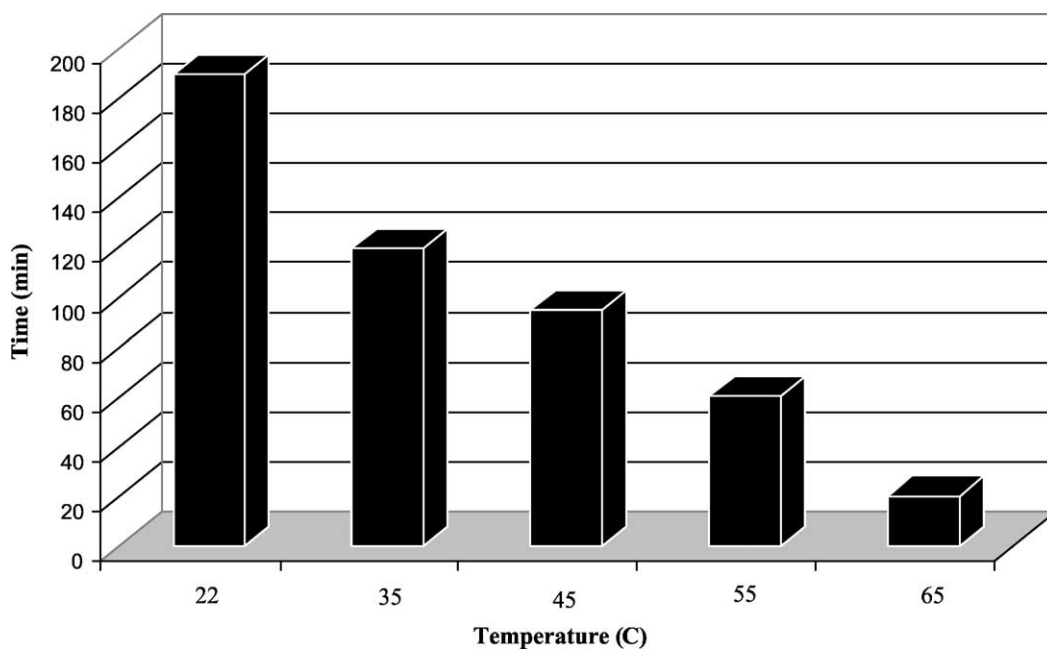


Fig. 2. Dependence of reaction time on temperature for C–Sn bond cleavage. Substrate: **1**; solvent: ethanol; catalyst: $\text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$; major product: benzaldehyde.

Thus reaction time for the oxidative cleavage of C–Sn bond in **1**, decreased as the reaction temperature was raised. In other words, at higher temperatures, the rate is increased. This was expected since most reactions, where breaking of a bond is their most likely rate-determining step, would behave the same way.

4. Conclusions

The oxidative catalytic cleavage of the C–Sn bond was studied in different solvents. Among the different solvents that were studied, ethanol was found to produce the highest yield of benzaldehyde. The results also suggest that the catalyst concentration, as well as temperature, are important factors. While in most oxidative catalytic reactions, heteropolymolybdoacids with the Keggin structure are thought to be better catalysts, our results suggest that $H_6[P_2Mo_{18}O_{62}]$, with a Dawson structure, is a more effective catalyst (Tables 1 and 2). Furthermore, they point out that the catalytic effectiveness may be enhanced as the number of molybdenum atoms (or the number of protons) per molecule is increased. Both possibilities stand to reason. The larger number of metal atoms provides more “sites” for the production of peroxide intermediates that are likely to be involved in the reaction. Likewise, the larger number of protons per catalyst molecule may lower the activation barrier to the redox reaction. Our studies point to the importance of this heteropolyacid as a catalyst in the chemistry of oxidation. Finally, as described above, a useful synthetic method for direct catalytic oxidation of benzyltins to the corresponding aldehydes was achieved by the heteropolyacids. These findings are considered to provide a versatile catalytic system for oxidative conversions of organometallic compounds.

References

- [1] C. Hu, M. Hashimoto, T. Okuhara, M. Misono, *J. Catal.* 143 (1993) 437.
- [2] C.L. Hill, *Chem. Rev.* 98 (1998) 1.
- [3] Y. Guo, Y. Wang, C. Hu, Y. Wang, E. Wang, *Chem. Mater.* 12 (2000) 3501.
- [4] T. Yamase, M. Suzuki, K. Ohtaka, *J. Chem. Soc., Dalton Trans.* (1997) 2463.
- [5] C. Hu, Q. He, Y. Zhang, Y. Liu, T. Tang, J. Zhang, *Chem. Commun.* (1996) 121.
- [6] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [7] K. Nomiya, Y. Nemoto, T. Hasegawa, S. Matsuoka, *J. Mol. Catal.* 152 (2000) 55.
- [8] Y. Ono, in: J. M. Thomas, K. I. Zamarayev (Eds.), *Perspectives in Catalysis*, Blackwell Scientific Publications, Oxford, 1992.
- [9] M. Langpape, J.C.M. Millet, *Appl. Catal. A: Gen.* 89 (2000) 200.
- [10] T. Nakato, Y. Toyoshi, M. Kimura, T. Okuhara, *Catal. Today* 52 (1999) 23.
- [11] R. Neumann, A.M. Khenkin, *J. Mol. Catal.* 114 (1996) 169.
- [12] D. Mansuy, J.F. Bartoli, P. Battioni, D.K. Lyon, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7222.
- [13] C. Rong, F.C. Anson, *Inorg. Chem.* 33 (1994) 1064.
- [14] A. Mamoru, *J. Catal.* 71 (1981) 88.
- [15] O.I. Goncharova, T.M. Yureva, *Kinet. Katal.* 28 (1997) 380.
- [16] N. Mizuno, W. Han, T. Kudo, M. Iwamoto, *Stud. Surf. Sci. Catal.* 101 (1996) 1001.
- [17] M.H. Alizadeh, H. Razavi, F. Mohammadi Zonoz, M.R. Mohammadi, *Polyhedron*, submitted for publication.
- [18] M.H. Alizadeh, H. Razavi, F.F. Bamoharram, M. Hasanzadeh, *Kinetics and Catalysis*, submitted for publication.
- [19] M.H. Alizadeh, S.P. Harmalker, Y. Jeanenin, J. Martin-Frere, M.T. Pope, *J. Am. Chem. Soc.* 107 (1985) 2662.
- [20] (a) P.W.M.N. Van Leeuwen, R. Kaptein, R.I. Huis, W. Kalisvaart, *J. Organomet. Chem.* 93 (1975) C5–C7;
(b) R.H. Fish, E.K. Kimmel, J.E. Casida, *J. Organomet. Chem.* 118 (1976) 41;
(c) R.H. Fish, J.E. Casida, E.C. Kimmel, *Tetrahedron Lett.* 40 (1977) 3515;
(d) R.H. Fish, R.T. Price, *Organometallics* 8 (1989) 225.
- [21] (a) P.G. Harrison, *Chemistry of Tin*, Blackie, New York, 1989.;
(b) M. Pereyre, J.P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987.
- [22] W.C. Still, *J. Am. Chem. Soc.* 99 (1977) 4186.
- [23] E. Baciocchi, T. Del Giacco, C. Rol, G.V. Sebastiani, *Tetrahedron Lett.* 30 (1989) 3573.
- [24] (a) M. Ochiai, E. Fujita, M. Arimoto, H. Yamaguchi, *Chem. Pharm. Bull.* 32 (1984) 887;
(b) M. Ochiai, E. Fujita, M. Arimoto, H. Yamaguchi, *Chem. Pharm. Bull.* 32 (1984) 507.
- [25] E. Baciocchi, M. Ioelle, *J. Org. Chem.* 60 (1995) 5504.
- [26] (a) R. Massart, R. Contant, J.-M. Fruchart, J.-P. Ciabrini, M. Fournier, *Inorg. Chem.* 16 (1977) 2916;
(b) M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, 1983.
- [27] K. Sisko, Y. Takeda, Z. Kinugawa, *J. Am. Chem. Soc.* 83 (1961) 538.