Aerobic Oxidation of Vicinal Diols Catalyzed by an Anderson-Type Polyoxometalate, $[IMo_6O_{24}]^{5-}$

Alexander M. Khenkin, Ronny Neumann*

Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel, 76100
Fax: (+972)-8-9344142, e-mail: Ronny.Neumann@weizmann.ac.il

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Dedicated to Professor Roger A. Sheldon on the occasion of his 60th birthday.

Abstract: An Anderson-type polyoxometalate, $[I^{VII}Mo_6O_{24}]^{5-}$, has been used as a catalyst for the aerobic oxidation at 80 °C of vicinal diols (glycols). This is the first report on the use of such a polyoxometalate as an oxidation catalyst. Reactivity and selectivity were dependent on the substrate. Thus, aryl-substituted diols yielded mostly the carbon-carbon bond cleavage products, while 1,2-cyclohexanediol yielded cyclohexanone-2-ol and 1,2-cyclohexanedione. Aliphatic diols were less reactive but yielded carbon-carbon bond cleavage products in the presence of additional acid. An abbreviated mechanistic study was carried out indicating that the polyoxometalate oxidizes the diol to the various products even under anaerobic conditions. The reduced polyoxometalates (heteropoly blues and heteropoly browns) formed in the oxidation of the diols are re-oxidized by the molecular oxygen.

Keywords: carbon-carbon bond cleavage; diols; homogeneous catalysis; oxidation; polyoxometalates

Introduction

Environmentally benign or “green” synthetic procedures are of key importance in the development of new chemical processes. In the area of oxidation, there is a special and very strong incentive to replace stoichiometric procedures that often use toxic oxidizing agents and result in the formation of copious amounts of dangerous by-products. In the area of research considered in this paper, the oxidation of vicinal diols, the classic stoichiometric oxidants are periodate[1] and lead tetraacetate[1] for carbon-carbon bond cleavage, and silver carbonate,[2] permanganate,[3] and also TEMPO-sodium hypochlorite[4] for diketone formation. Some research has been carried out using hydrogen peroxide as oxidant for both types of transformation.[5] In general, the activation of molecular oxygen and its use in a selective manner remains a very challenging goal for many catalytic transformations. Thus, an especially attractive catalytic and alternative method would be to oxidize vicinal diols with molecular oxygen. For vicinal diol oxidation there have been only a few reports of catalytic aerobic reactions using as catalysts $Ru(PPh_3)_3Cl_2$ on active carbon[6] or *N*-hydroxyphthalimide and $Co(acac)_3$.[7] We are interested in the application of polyoxometalates as catalysts for oxidation reactions, especially using molecular oxygen as oxidant or oxygen donor.[8] In the area of oxidative carbon-carbon bond cleavage there have been a few reports on the use of highly acidic $H_{3+x}PV_xMo_{12-x}O_{40}$ (x = 2, 3) Keggin-type polyoxometalate as catalyst for oxidation of cycloalkanones,[9] vicinal diols,[10] and α-hydroxyketones.[11]

In this manuscript, we report on the use of an Anderson-type polyoxometalate, $[I^{VII}Mo_6O_{24}]^{5-}$, Figure 1, as catalyst for the oxidation of vicinal diols.

This is the first report on the use of a polyoxometalate of such a structure as catalyst for an oxidation reaction. The rationale behind the use of this specific polyoxometalate as catalyst was as follows. Since periodate is a

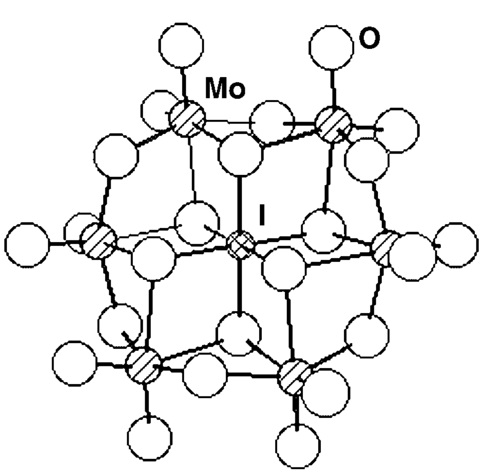


Figure 1. The Anderson-type $[IMo_6O_{24}]^{5-}$ polyoxometalate.

$$\mathrm{POM_{ox}} + \text{Substrate} \longrightarrow \mathrm{POM_{red}} + \text{Product}$$

$$\mathrm{POM_{red}} + \mathrm{O_2} \longrightarrow \mathrm{POM_{ox}}$$

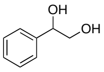
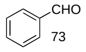
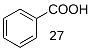
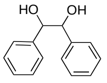
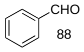
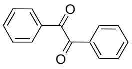
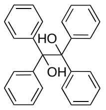
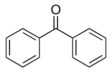
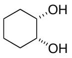
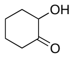
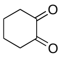
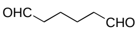
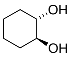
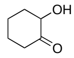
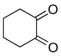
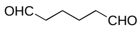
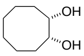
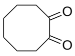
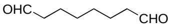
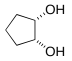
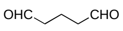
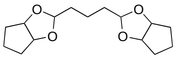
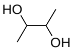
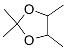
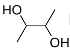
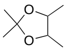
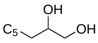
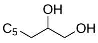
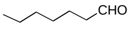
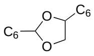
Scheme 1.

known stoichiometric oxidant of vicinal diols, it was hypothesized that periodate incorporated into a polyoxomolybdate matrix would lead to a catalytic reagent with similar reactivity. In the course of the oxidation of the diol, the polyoxometalate would be reduced. However, the latter are often known to undergo reoxidation in the presence of molecular oxygen, Scheme 1, enabling completion of a catalytic cycle.

Results and Discussion

The $[IMo_6O_{24}]^{5-}$ polyoxometalate was prepared first as $Na_5[IMo_6O_{24}] \cdot 3\,H_2O$ from sodium molybdate and sodium periodate according to the published literature procedure.[12] The tetrabutylammonium salt, $Q_3H_2[IMo_6O_{24}]$ where $Q = (n\text{-Bu})_4N^+$, was prepared by addition of a small excess of QBr to an aqueous solution of $Na_5[IMo_6O_{24}] \cdot 3\,H_2O$ brought to pH = 1.5 by addition of 1 N H_2SO_4. Cyclic voltammetry of $Q_3H_2[IMo_6O_{24}]$ in 0.1 N QBF_4 in acetonitrile yielded an irreversible oxidation potential of $E_a = +0.93$ V *versus* SCE. Vicinal diols were oxidized under 2 atm oxygen using pressure tubes in acetonitrile as summarized in Table 1.

Table 1. Aerobic oxidation of vicinal diols catalyzed by $Q_3H_2[IMo_6O_{24}]$.[a]

Substrate	Time [h]	Conversion [mol %]	Products [mol %]
	15	>99	 73  27
	3.5	>99	 88  12
	2	>99	 100
	5	>99	 64  31  5
	5	>99	 41  56  3
	5	>99	 70  30
	15	59	 17  83
	15	27	 100
 [b]	4	>99	 100
	15	0	
 [b]	15	>99	 17  83

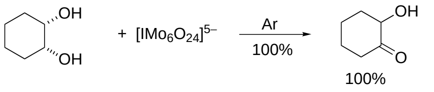
[a] Reaction conditions: 250 mM substrate, 10 mM $Q_3H_2[IMo_6O_{24}]$, 1 mL CH_3CN, T = 80 °C, P_{O2} = 2 atm.

[b] In the presence of 250 mM CH_3SO_3H.

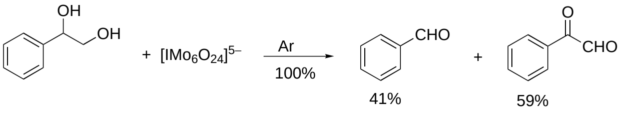
Depending on the substrate type various reaction products were observed. For vicinal diols substituted with a phenyl ring(s), products associated with carbon-carbon bond cleavage are dominant. Multiple substitution increases the reaction rate. For both *cis*- and *trans*-cyclohexanediol, only a small amount of carbon-carbon bond cleavage is observed and the dominant products are the cyclohexanone-2-ol and 1,2-cyclohexanedione. In the case of 1,2-cyclooctanediol, there is both carbon-carbon bond cleavage and formation of the α,β-diketone. Furthermore, for aliphatic diols and cyclopentanediol, only carbon-carbon bond cleavage is observed, coupled with significant acetal formation by reaction of the aldehyde product with the diol substrate. For improved reactivity, acidification, for example with methanesulfonic acid, of the reaction medium is to be preferred.

Among the solvents tested (acetonitrile, 1,2-dichoroethane, nitroethane, acetic acid and ethanol), acetonitrile was the preferred solvent in terms of both activity and selectivity using the oxidation of phenyl-1,2-ethanediol as model substrate. For example, under the conditions given in Table 1, and acetic acid as solvent there was only 14% conversion and formation of mostly $PhC(O)CH_2OH$ and $PhCH(OH)CHO$. However, 10% $Na_5[IMo_6O_{24}]$ supported on active carbon with toluene as solvent were also an effective catalyst and reaction medium, respectively, yielding results similar to those reported in Table 1. 10% $Na_5[IMo_6O_{24}]$ on silica was significantly less effective. The stability of the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate catalyst was surveyed by IR and ^{127}I NMR spectroscopy. Thus, the IR spectrum of $Q_3H_2[IMo_6O_{24}]$ with peaks at 941, 913, 806, and 682 cm^{-1} attributable to the polyanion was compared to the IR spectrum of the polyoxometalate recovered from the reaction solution with peaks at 940, 912, 802, and 682 cm^{-1}. There was essentially no change in the IR spectrum for samples before and after the reaction. Furthermore, the ^{127}I NMR of the polyoxometalate prior to a reaction carried out in CD_3CN showed a singlet at 4084 ppm ($\Delta v1/2 = 250$ Hz, 5 M KI in D_2O as external standard) versus a broader peak at 3950 ppm ($\Delta v1/2 = 1000$ Hz) over the course of the reaction. Our conclusion from these IR and ^{127}I NMR experiments is that the structure of the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate remains unchanged during the oxidation reaction, however, the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate is slightly reduced, probably at a molybdenum atom, leading to a broadened and slightly shifted peak in the ^{127}I NMR due to formation of paramagnetic molybdenum(V).

We were also interested in the mechanism of the reaction, a subject or question that is often overlooked in recent catalytic examples and investigations of vicinal diol oxidation. First, stoichiometric reactions were carried out under anaerobic conditions (10 mM substrate, 10 mM $Q_3H_2[IMo_6O_{24}]$, 1 mL CH_3CN, T = 80 °C, 4 h), Eqs. 1–3. In all cases there was quantitative conversion of the organic substrate. For *cis*-cyclohexanediol as substrate there was formation only of the 2 electron oxidized product cyclohexanone-2-ol. The solution turned green indicating formation of a heteropoly blue polyoxometalate attributable to formation of molybdenum(V) centers.[13] For both 1-phenyl-1,2-ethanediol and the *meso*-1,2-diphenyl-1,2-ethanediol, there was multi-electron oxidation with formation of both the cleavage product, benzaldehyde (also formaldehyde) and the dicarbonyl product, β-ketophenylacetaldehyde and benzil, respectively, in similar ratios. Important also was the observation that the solution turned brown rather than green, indicating formation of heteropoly browns attributable to formation of highly reduced polyoxometalate species with multiple molybdenum(V) and probably also molybdenum(IV) atoms.[14] A second important observation was that α,β-diketones such as benzil and 1,2-cyclohexanedione, did not react in the presence of $Q_3H_2[IMo_6O_{24}]$ nor did simple alcohols such as cyclohexanol and benzyl alcohol. Benzoin, PhCH(OH)C(O)Ph, was more reactive than hydrobenzoin.



(1)



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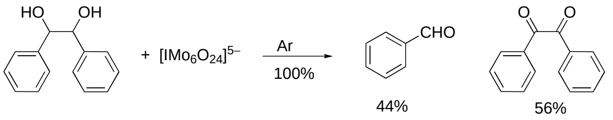


(3)

The kinetic profile of the vicinal diol oxidation reaction was also measured for *cis*- and *trans*-cyclohexanediol and *meso*- and *R,S*-hydrobenzoin, Figure 2.

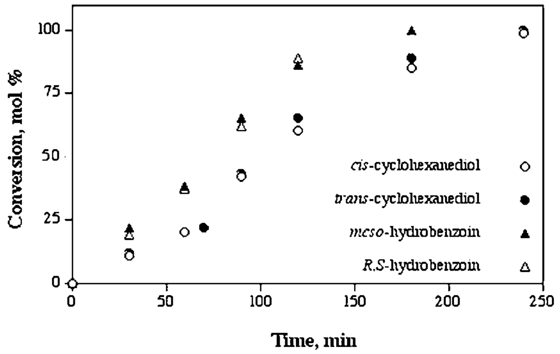
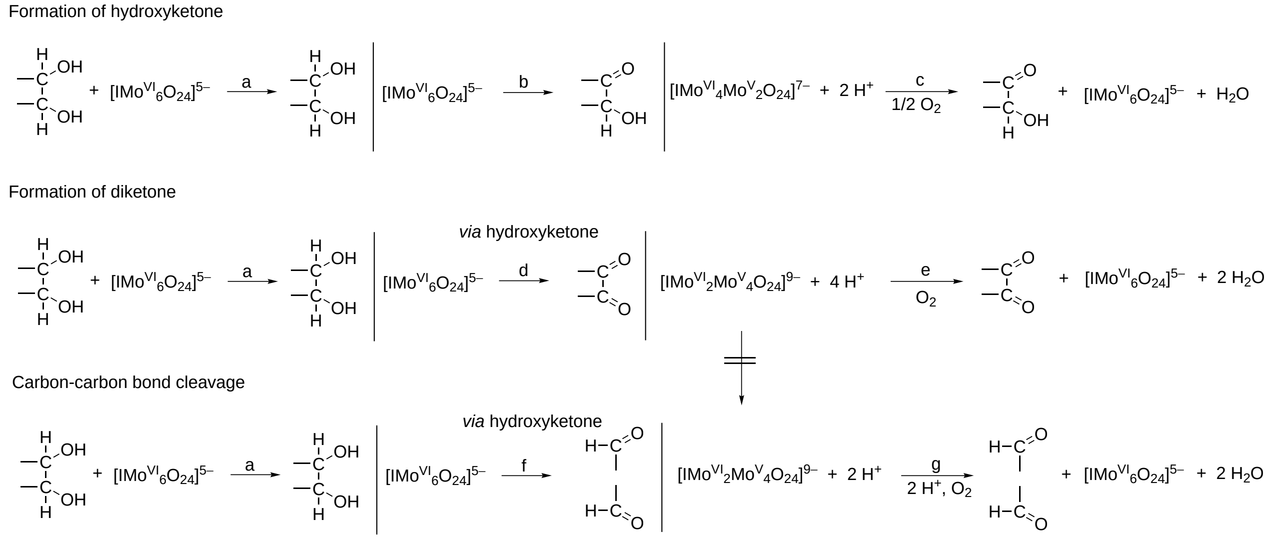


Figure 2. Kinetic profile of the oxidation of stereoisomers of 1,2-cyclohexanediol and 1,2-diphenyl-1,2-ethanediol. Reaction conditions: 250 mM diol, 10 mM $Q_3H_2[IMo_6O_{24}]$ in acetonitrile at 80 °C under 2 atm oxygen.

Clearly *cis*- and *trans*-glycols react at similar rates. This finding would tend to discount the possibility of a cyclic-intermediate mechanism as was suggested for periodic acid-catalyzed reactions.[15] The products of 1,2-cyclohexanediol are initially only cyclohexanone-2-ol, with increasing quantities of 1,2-cylohexanedione being formed as a function of time, that is the ratio 1,2-cylohexanedione/cyclohexanone-2-ol increases as a function of time. On the other hand in the hydrobenzoin oxidation, the benzaldehyde/benzil ratio is ~9 and more or less constant as a function of time. Since there was effective oxidation of diols under anaerobic conditions, radical-type mechanisms such as autooxidation or other direct involvement of oxygen in the oxidation of the diols may be discounted. Therefore, a preliminary but feasible mechanistic scheme to explain the results can be proposed as follows, Scheme 2.

First, there is complexation of the polyoxometalate to the glycol substrate (step a), which is followed by a two-electron oxidation of the vicinal diol to a hydroxyketone or hydroxy-aldehyde (step b). The hydroxyketone (aldehyde) is always observed either under anaerobic conditions or at low conversions. The association or complexation (step a) of the diol to the polyoxometalate seems to be critical since a simple alcohol such as benzyl alcohol with a lower (compared to cyclohexanediol) oxidation potential and C-H bond energy is not oxidized by the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate. After its formation, the hydroxy-ketone (aldehyde) may disassociate from the polyoxometalate and in the presence of oxygen the catalyst is re-oxidized with formation of water (step c). Alternatively, the hydroxy-ketone (aldehyde) will be further oxidized to yield the dicarbonyl product (steps d and e) or there will be oxidative cleavage of the carbon-carbon bond (step f). Dicarbonyl products, once formed, do not lead to carbon-carbon bond cleavage. In general and according to the results presented in Table 1, the specific pathway observed, that is the relative rate of each step is strongly substrate dependent. Another factor to consider concerns the aerobic re-oxidation of the polyoxometalate. The observation that under anaerobic conditions (argon) heteropoly blue and heteropoly brown



Scheme 2.

species are obtained, while under aerobic conditions, the polyoxometalate is observed to be largely in its oxidized form would indicate that the aerobic re-oxidation of the polyoxometalate is relatively fast compared to the diol oxidation steps. In this context, it is important to note the following: (a) the oxidation of the diol to the hydroxyketone (aldehyde) is a two-electron oxidation with formation of two protons (step b), (b) the oxidation to the dicarbonyl is a four-electron oxidation with formation of four protons (step), and (c) the carbon-carbon bond cleavage reaction is a four-electron reaction with however formation of two protons, (step f). Since the re-oxidation of the polyoxometalate with molecular oxygen is a four-electron oxidation requiring four protons, the absence of sufficient acid may inhibit the re-oxidation reaction, (step g). This may explain the positive effect of the addition of an acid on the diol oxidation reaction.

Conclusions

Catalytic aerobic oxidation of vicinal alcohols is possible using an Anderson-type polyoxometalate, $[IMo_6O_{24}]^{5-}$ as catalyst. Reactivity and selectivity varied depending on the substrate. Thus, aryl-substituted diols yielded mostly the carbon-bond bond cleavage products, while 1,2-cyclohexanediol yielded cyclohexanon-2-ol and 1,2-cyclohexanedione. Aliphatic diols were less reactive but yielded carbon-carbon bond cleavage products in the presence of additional acid.

Experimental Section

Materials

Reaction substrates and solvents were obtained from commercial sources and were used without further purification. $Na_5[IMo_6O_{24}] \cdot 3\,H_2O$ was prepared according to the literature procedure[12] by dissolving 13.5 g $Na_2MoO_4 \cdot 2\,H_2O$ in 50 mL water and heating the solution to ~95 °C. 6.2 mL of 12 N HCl were added slowly, followed by dropwise addition of a hot solution of sodium periodate (2 g in 10 mL water). The clear solution was reduced to 25 mL and upon cooling, white platelet type crystals precipitated from the solution. $Q_3H_2[IMo_6O_{24}]$ was prepared by mixing 0.75 g (0.6 mmol) $Na_5[IMo_6O_{24}] \cdot 3\,H_2O$ in 5 mL water with 1.28 g (4 mmol) QBr dissolved in 5 mL water. 1 N H_2SO_4 was added until a pH = 1.5 was obtained. The resulting precipitate was filtered and washed successively with water, absolute ethanol and ether and then recrystallized from acetonitrile to yield very light yellow crystals; yield: 0.75 g. Elemental analysis: found (calculated): C 31.53 (31.7), H 6.30 (6.06), N 2.73 (2.31); IR: $\nu = 941, 913, 806, 721$ and $681\ cm^{-1}$; UV-vis: $\lambda_{max} = 250$ nm (log $\varepsilon = 4.18$); ^{127}I NMR (CD_3CN): $\delta = 4084$ ppm (KI in D_2O external standard).

General Oxidation Procedures

Reactions were carried out in 20-mL glass pressure tubes. Typically, the tubes were loaded with the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate (20 µmol), diol (500 µmol) and acetonitrile (2 mL) and degassed by three successive "freeze-pump-thaw" cycles and pressurized with O_2 to 2 atm. The solution was brought to 80 °C in a thermostatted oil bath. After the reaction was completed the mixture was cooled. Reactions were quantified by GLC (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID 0.32 mm and 0.25 µm coating (Restek 5MS) and products were identified by GC-MS (HP 5973) with the same column and conditions. Analysis was preformed on aliquots directly withdrawn from the reaction mixture. Mass balances were verified by addition of an external standard (*n*-decane).

Reactions under anaerobic conditions were carried out in 20-mL Schlenk flasks. The flasks were loaded with the $Q_3H_2[IMo_6O_{24}]$ polyoxometalate (100 μmol), diol (100 μmol) and acetonitrile (2 mL) and degassed by three successive "freeze-pump-thaw" cycles and loaded with Ar. Further reaction and analysis was as for described for aerobic reactions.

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