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Authors: Meilin Tao, Yiming Li, Yurii V. Geletii, Craig L. Hill, Xiaohong Wang



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Aerobic oxidation of glycerol catalyzed by M salts of  $PMo_{12}O_{40}^{3-}(M = K^+, Zn^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+})$ 

Meilin Tao,<sup>a,b</sup> Yiming Li,<sup>a</sup> Yurii V. Geletii,<sup>b\*</sup> Craig L Hill,<sup>b\*</sup> and Xiaohong Wang <sup>a\*</sup>

<sup>a</sup>Key Lab of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun 130024, P. R. China, E-mail: wangxh665@nenu.edu.cn, Fax: 0086-431-85099759
<sup>b</sup>Department of Chemistry, Emory University, 1515 Dickey Dr., Atlanta, 30322 GA, USA

**Graphical Abstract** 



#### Highlights

- The mechanism of glycerol oxidation to lactic acid catalyzed by polyoxometalates (POMs) with different cations was studied.
- The reaction is a free radical chain process involving initiation, propagation and termination.
- After minimal optimization, the yield of LA was 88 % at glycerol conversion > 97 % within 6 h.

#### Abstract

Glycerol is a co-product in the manufacture of biodiesel from vegetable oil and animal fat. A significant increase in biodiesel production results in adramatic overproduction of glycerol. The oxidation of glycerol to lactic acid (LA) by O<sub>2</sub> is considered to be a promising technology to increase the value of glycerol. Studies on the fundamental reaction mechanism vary for different catalytic systems. In this work we have chosen Keggin polyoxometalates (POMs) as an exemplary family of water-soluble hydrolytically and oxidatively-stable, fully-inorganic complexes with

transition-metal and non-transition-metal counter-cations (M in the formula, MPMo<sub>12</sub>O<sub>40</sub>, where  $M = H^+$ ,  $K^+$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  in appropriate number to counterbalance the 3- charge of PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>). Reactions involving hydrogen peroxide, an intermediate during glycerol oxidation, produce free radicals. A kinetic analysis reveals that the radical chain length under typical conditions is about 20-30. After minimal optimization, the yield of LA was 88 % at glycerol conversion > 97% (1.0 M aqueous solution of glycerol, 4.0 mM of the Al salt of PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>, henceforth "AlPMo", 10 bar O<sub>2</sub> at 60 °C, reaction time 6.0 h).

Keywords: Glycerol oxidation; lactic acid; reaction mechanism; free radicals.

#### 1. Introduction

Global energy consumption is quickly increasing because of population and economic growth. Fossil energy resources are sufficient to cover most of the increasing demand, but lead to increased atmospheric CO<sub>2</sub> levels. Fuel derived from biomass, or biofuel, is an appealing renewable alternative to fossil fuels. The two most common types of biofuels are ethanol and biodiesel [1, 2]. The production of 100 kg of biodiesel from vegetable oils and animal fats creates about 10 kg of crude glycerol. In 2013 the domestic production of biodiesel was 9.0 million barrels per day with a projected 13 million barrels per day by 2020 [3]. Thus, about  $10^4$  tons of glycerol is produced daily creating a large surplus of this by-product. This huge amount entering into the market significantly impacts its commodity price. Crude glycerol from biodiesel plants has low commercial value, and its disposal and utilization has become a serious financial problem and environmental liability for the biodiesel industry [4, 5]. Thus, biodiesel producers are seeking new, value-added uses for voluminous triol. One of the most attractive alternatives for glycerol utilization is as a feedstock for production added-value compounds such as bioplastic, platform chemicals, and fuel [4]. From chemical point of view, this by-product is a highly versatile molecule with two primary OH groups and a secondary OH group, which offer a range of possibilities for synthetic modification. The high-added-value oxygenated products derived from glycerol oxidation include dihydroxyacetone, hydroxypyruvic acid, glyceric acid, tartaric acid, oxalic acid, mesoxalic acid, glyoxylic acid, glyceraldehydes, and glycolic acid [4]. Numerous catalytic systems for  $O_2$ -dependent oxidation are reported in the literature [6]. Surprisingly, the fundamental reaction mechanism was not a focus of the glycerol-based publications. Commonly, the oxidation of organic materials by  $O_2$  at elevated temperature (60-120 °C) proceeds through

2

radical chain processes. The oxidation mechanism can be different for different catalytic systems. Recently, radical chain mechanism was suggested for the oxidation of propylene glycol to hydroxyacetone over the UiO-66 metal-organic framework [7]. Prati and Rossi demonstrated that gold could catalyze the oxidation of alcohols to acid in basic solutions [8-10] through the reduction-oxidation mechanism. High selectivity toward carboxylic acids is not a rare phenomenon even for radical chain oxidation. A homogeneous catalytic mechanism of para-xylene to terephthalic acid based on free radical generation being catalyzed through cobalt catalyst was studied by Fadzil group [11]. Glycerol is the most likely oxidized through this mechanism, but no evidence has been reported. Here, we report that glycerol oxidation also proceeds through a radical chain mechanism.

#### 2. Experimental

#### 2.1. Instruments

Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES. IR spectra (4000-500 cm<sup>-1</sup>) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. X-ray diffraction (XRD) patterns of the sample were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ = 0.154178 nm). The measurements were obtained in steps of 0.04° with an account time of 0.5 s and 20 values ranging 5-90°. <sup>31</sup>P MAS NMR spectra were obtained using a Bruker AM500 spectrometer at 202.5 MHz. UV–vis spectra were recorded with an Agilent 8453 spectrophotometer equipped with a diode array detector using a 1.0 cm optical-path-length quartz cuvette.

#### 2.2. Synthesis and characterization of polyoxometalate (POM) derivatives

The MPMo catalysts were synthesized by an ion-exchange method, eqs 1 and 2, following a procedure described previously [12]. Initially, 9.1 g (5.0 mmol) of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (HPMo) was dissolved in 10 mL of vigorous stirred deionized water at room temperature. Then, the appropriate amount of metal salt was added (chlorides for K, Cr and Zn; sulfates for Al, Cu and Fe). The solutions were stirred for 2 hours at room temperature (for CuPMo, the color was light green, and for CrPMo the color was dark green). The solutions were placed in the refrigerator (-4 °C) for 2 days, and the yields of crystalline material were  $\approx$  76 %.

$$M^{3+} + H_3 PMo_{12}O_{40} \longrightarrow 3H^+ + M_{1,0} PMo_{12}O_{40} \quad (M = Fe^{\underline{m}}, Al^{\underline{m}}, Cr^{\underline{m}})$$
(1)

$$1.5 \text{ M}^{2+} + \text{H}_3\text{PMo}_{12}\text{O}_{40} \longrightarrow 3\text{H}^+ + \text{M}_{1.5}\text{PMo}_{12}\text{O}_{40} \quad (\text{M} = \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}})$$
(2)

The resulting complexes were characterized by ICP-ES, FTIR, XRD, and <sup>31</sup>P NMR (see Table S1 and Fig S1-2 for details).

#### 2.3. General Procedure

Glycerol oxidation was performed in a high-pressure stainless-steel autoclave with a polytetrafluoroethylene insert (10 mL) at a constant temperature of 60 °C. The autoclave was connected to the O<sub>2</sub> supply system, which kept the pressure constant. The solution was stirred magnetically. Typically, 5.0 mL of 1.0 M glycerol in water was oxidized in the presence of 4.0 mM catalyst at 60 °C at aconstant pressure of 10 bars of O<sub>2</sub>. After desired time, the reactor was quickly cooled down, depressurized and the catalyst was removed by extraction with diethyl ether. The stability of the catalysts after reaction was tested by FTIR and XRD, which did not change compared with the fresh ones [Fig. S3]. The remaining solution was diluted 10 times with distilled water and analyzed by high performance liquid chromatography (HPLC) using a Shimadzu LC10A-VP chromatograph equipped with SPB-10A UV and RID-10A R.I. detectors, and a Prevail TM C18 (4.6 mm × 250 mm) column. A solution of H<sub>2</sub>SO<sub>4</sub> (0.1 % w/w) in H<sub>2</sub>O/acetonitrile (1/2 v/v) was used as the eluent at a flow rateof 1.0 mL min<sup>-1</sup> at 50 °C. The glycerol conversion,  $\alpha$ , and the selectivity for lactic acid (LA), S<sub>LA</sub>, were calculated using eqs 3-4:

(3) 
$$\alpha = \frac{[Gly]_0 - [Gly]}{[Gly]_0} \times 100 \%$$

(4) 
$$S_{LA} = \frac{[LA]}{[Gly]_0 - [Gly]} \times 100 \%$$

### 3. Results and discussion

#### 3.1. Main results

The main glycerol oxidation reaction is presented on Scheme 1 [13]. The primary products of oxidation are dihydroxyacetone (DHA) and glyceraldehyde (GCA), which can isomerically interconvert. The dehydration of DHA produces pyruvaldehyde (PRA), which then reacts with water to form lactic acid (LA).

#### Scheme 1

The catalytic activity and product distribution using different MPOMs are summarized in Table

1. The total amount of the four products is close to 100 % based on consumed glycerol. The conversion of glycerol and the product distribution are strongly dependent on counter cation of the POM ("M" in MPOM). The activity of MPMo with non-transition-metal counter cations correlates with a charge of these cations, with AlPMo, the complex with the highest charged counter cation, Al<sup>3+</sup>, having the highest conversion and selectivity to LA. KPMo has the lowest activity. The transition metal cations definitively show their own activity. Cu<sup>2+</sup> completely inhibits the reaction, i.e. there is no reaction when CuPMo is used.

### Table 1

No reaction occurs in the absence of any catalyst, confirming that the ability of  $O_2$  in oxidation of glycerol is limited. In an essential control reaction, free radicals are generated by 2, 2'-azobis (2-amidinopropane) dihydrochloride under otherwise the same reaction conditions; in this case, the reaction becomes unselective and 40 % side products are generated. This supports the idea that the POM catalyst is involved in free radical production.

Since AlPMo showed the best results, we studied the effects of  $O_2$  pressure and AlPMo concentration on the product yields in glycerol oxidation (Fig. 1), as well as the reactivity of the individual oxidized organic intermediates under  $N_2$  (Table 2). In the overall production of LA, only the first step involves oxidation; isomerization and dehydration/hydration reactions complete the overall transformation (Scheme 1). In order to better clarify key relative rates of processes during complete conversion of glycerol to LA, we examined, individually, the reactions of all three principal intermediates, DHA, GCA and PRA, under the same conditions excepting the  $O_2$ being instead by  $N_2$  in the same pressure (Table 2).

### Table 2

#### Fig. 1

As seen from Tables 1-2, PRA quickly undergoes hydration to form LA. GCA isomerizes to DHA with a moderate rate, but GCA remains in low concentration as an intermediate to high conversions of glycerol. These data indicate that DHA is the main intermediate in glycerol oxidation to LA. The degree of the glycerol conversion after 2 hours (Fig. 1) represents the average reaction rate. The reaction rate increases linearly with the O<sub>2</sub> pressure, but then reaches a plateau. A similar trend was also observed while varying the catalyst concentration.

3.2. Reaction mechanism

It is commonly assumed that POM-catalyzed air-based oxidation processes proceed through a general two-step reaction mechanism: oxidation of the substrate by the oxidized POM followed by the reoxidation of the reduced POM by  $O_2$  [14], while  $O_2$  only oxidizes reduced POM to fulfil one cycle. In this case, the reaction between a substrate and oxidized POM under Ar should be the same or faster than the overall catalytic process. We used UV-Vis spectroscopy to follow the reduction of 4.0 mM of AlPMo by 1.0 M glycerol in water at 60 °C under anaerobic conditions. The reaction rate was very slow (only a few percent conversion after 15 hours), which is not consistent with the two-step reaction mechanism. Alternatively, the reaction may proceed through a radical chain mechanism with a low initiation rate but a long chain length. To confirm the radical producer is  $H_2O_2$  not  $O_2$ , the generation of  $H_2O_2$  was determined by reaction with potassium iodide in the presence of starch (S1). It could be seen that the solution of KI and starch changed from white to blue gradually as in the mixture of 4.0 mM of AlPMo by 1.0 M glycerol in water at 60 °C with oxygen, which determined  $H_2O_2$  was generated during this reaction acting as the true active oxidant.

3.2.1 Overview of alcohol oxidation via a radical chain mechanism

Two types of peroxyl radicals are involved in the chain oxidation of alcohols,

 $\alpha$ -hydroperoxyl, >COO•(OH), and hydroperoxyl, HO<sub>2</sub>• [15], which are in equilibrium, eq 5.

$$>C(OH)OO \rightarrow \rightleftharpoons >C=O + HO_2 \bullet$$
 (5)

We considered two extreme cases of equilibrium, namely one completely shifted either to the right and one shifted to the left of eq 5. The data best fit equilibrium is shifted to the left. Glycerol has two primary and one secondary hydroxyl groups, and two different peroxyl radicals. Since the intermediate concentrations of GCA are lower, the oxidation of the secondary alcohol is the dominant step.

For glycerol of extra high purity, a primary radical, e.g.COO•(OH), can form very slowly via a different pathway. Then, the C-H bond alpha to COO•(OH) cleaves forming a carbon centered radical >C•(OH), which reacts with O<sub>2</sub> regenerating>COO•(OH), eqs 6-7. Most carbon-based radicals are well documented to react with O<sub>2</sub> at essentially diffusion-controlled rates [16]. Here, we assume that the >CHOO•(OH) radical is the chain carrying species, eq 7.

$$>C\bullet(OH) + O_2 \rightleftharpoons >COO\bullet(OH)$$

$$>$$
COO•(OH) +  $>$ CH(OH)  $\rightarrow$   $>$ C(OOH)(OH) +  $>$ C•(OH) (7)

(6)

Since the rate of glycerol oxidation depends on  $O_2$  pressure, the termination step is probably eq 8.

$$>COO \bullet (OH) + >C \bullet (OH) \longrightarrow >C(OOH)(OH) + >C=O$$
(8)

The hydroperoxide intermediate >C(OOH)(OH) is in equilibrium with  $H_2O_2$ . For simplicity, we assume that for glycerol the equilibrium in eq 9 is shifted to the right,

$$>C(OOH)(OH) \rightleftharpoons >C=O + H_2O_2$$
 (9)

During a storage of glycerol under air or in the beginning of reaction, the

peroxides, >C(OOH)(OH) and  $H_2O_2$ , accumulate in the solution and become a main source of free radicals [17]. As a result, glycerol undergoes autoxidation through the branching radical-chain mechanism [15]. However, at moderately elevated temperature, 50-100 °C, autoxidation is commonly slow. Transition metal complexes tend to catalytically decompose peroxides via intermediate formation of free radicals resulting in an increase of overall oxidation rate [18, 19]. Thus, glycerol oxidation via radical chain mechanism is not an unexpected process.

We applied several tests to confirm the presence of the radical chain pathway and then showed that this pathway is dominant. The efficient inhibition of glycerol oxidation by Cu<sup>2+</sup> ions (6.0 mM in 4.0 mM CuPMo, Table 1, entry 5) through the reactions in eqs 10-11 confirm the radical chain nature of process [20].

$$>C\bullet(OH) + Cu^{2+} \longrightarrow >C=O + Cu^{+} + H^{+} \qquad k_{10}\approx 5 \times 10^{7} \text{ M}^{-1} \text{s}^{-1} \text{ at } \text{RT}$$
(10)

$$Cu^{+} + \frac{1}{4}O_{2} + H^{+} \rightarrow Cu^{2+} + \frac{1}{2}H_{2}O$$
(11)

We also examined the effect of the water-soluble inhibitor, sodium phenolsulfonate, on this POM-initiated O<sub>2</sub>-based glycerol oxidation. The kinetics of this oxidation catalyzed by AlPMo in the presence of 5.0 mM inhibitor is shown on Fig. 2. An induction period of 1 h is clearly seen. In such cases, the initiation rate is usually calculated as  $2 \times [inhibitor]/(induction period)$ . Under the conditions in Fig. 2, the calculated initiation reaction rate is around  $3 \times 10^{-6}$  Ms<sup>-1</sup>. The maximum rate of glycerol consumption in Fig. 2 is about  $7 \times 10^{-5}$  Ms<sup>-1</sup>, indicating that the radical chain length L = (reaction rate)/(initiation rate) is about 20.

#### Fig. 2

#### 3.2.2 Radical formation initiated by MPMo

To check the hypothesis that MPMo can produce free radicals, we used Pyrogallol Red (PGR) as a model radical scavenger; the UV-Vis spectrum of this indicator dye changes considerably

upon oxidation (Fig. 3). Earlier, PGR was used as a probe molecule to assess the antioxidant activity of peroxynitrite (O=NO-OH) to generate free HO• and NO<sub>2</sub>• radicals via homolytic cleavage of the O-O bond [21, 22]. Here, we note that peroxynitrite is a very active oxygen atom donor, a typical property of peroxides. However, PGR does not react with peroxynitrite as an oxygen atom donor. In addition, we confirmed that each PGR molecule scavenges two radicals using ABTS• as a model radical (Fig S4).

#### Fig. 3

Free radicals are formed when H<sub>2</sub>O<sub>2</sub>, AlPMo and glycerol are all present in the solution. The solution of 50  $\mu$ M PGR in slightly acidified water (pH ~ 2) was placed in a thermostat cell of a spectrophotometer and the kinetics of PGR consumption were measured at 60 °C (Fig. 3). PGR absorbs light at 468 nm with  $\varepsilon_{468} = 2 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> (at pH > 7,  $\lambda_{max} = 548$  nm). No changes were observed for the first 10 min. Then, when 5.0  $\mu$ L of H<sub>2</sub>O<sub>2</sub> (30% w/w, 10.0 M in molar concentration) was injected into the cell and the spectra were recorded every 30 s. Again, no significant spectral changes were observed. However, after addition of 5.0  $\mu$ L of aqueous AlPMo solution (150 mM), the absorbance at 468 nm and 280 nm decreased with time, while the absorbance at 320 nm increased (Fig. S5). The presence of an isosbestic point indicates the quantitative conversion of PGR to a single product with an absorbance in the range 350- 410 nm. PGR was completely consumed after 7-8 min (Fig. 4), confirming that the mixture of AlPMo and H<sub>2</sub>O<sub>2</sub> in the presence of glycerol generates free radicals.

### Fig. 4

In order to determine the rate of radical generation, the PGR spectral changes were recorded after addition of the desired quantity of AAPH (see Table 1 and Fig. 4). The decrease of absorbance at 468 nm with time is shown in Fig. 4. The initial rate of PGR consumption in the presence of 10 mM AAPH is about  $1 \times 10^{-7}$  M<sup>-1</sup>s<sup>-1</sup>. AAPH undergoes thermal decomposition to free radicals with the rate constant  $k_i \sim 3 \times 10^{-6}$  s<sup>-1</sup> at 60 °C [23]. Under conditions in Fig. 4, the expected rate of radical generation is  $1 \times 10^{-7}$  M<sup>-1</sup>s<sup>-1</sup>, which is in excellent agreement with the experimental number.

The rate of radical generation depends on the nature of cations,  $Al^{3+} > Zn^{2+} > K^+$ , as well as  $Fe^{3+} > Cr^{3+} > Cu^{2+}$  (Fig. 5). For the transition metal cations, the order of activity,  $Fe^{3+} > Cr^{3+}$ , is directly related to their catalytic H<sub>2</sub>O<sub>2</sub> decomposition activity [24]. Copper ions are well known to

be efficient inhibitors of alcohol oxidation by a radical chain mechanism [18]. In control experiments, we looked at the kinetics of PGR consumption in the presence of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or ZnSO<sub>4</sub> and 10 mM H<sub>2</sub>O<sub>2</sub> but without POM. No acceleration of PGR consumption by Al<sup>3+</sup> or Zn<sup>2+</sup> was observed. So far, the role of non-transition metal cations remains unclear. If PRG and glycerol are both present, the rate of PGR consumption drops by about 20 %. In this case, about 20 % of all generated radicals react with glycerol, implying that these radicals react with glycerol about 5 orders of magnitude slower than with PGR. For the less selective HO<sub>2</sub>• radical, the ratio of the reaction rate constants for 2-propanol (~3 M<sup>-1</sup>s<sup>-1</sup>) [15] and Trolox (10<sup>5</sup> M<sup>-1</sup>s<sup>-1</sup>) is  $\approx 3 \times 10^4$  [25].

#### Fig. 5

#### 3.2.3 General discussion

In order to confirm that the radical chain process is dominant, we built a simplified kinetic model for the catalytic oxidation of glycerol by  $O_2$ . First, we assumed that the main chain carrier is  $HO_2$ •. However, this model was not consistent with the experimental data. Therefore, the >COO•(OH) radical was considered as the main chain carrier.

The rate constant for the reaction in eq 7 was taken to be, similar to that of 2-propanol:  $k_7 \approx 1$   $M^{-1}s^{-1}$  [25]. Again, the reaction of carbon centered radicals with O<sub>2</sub>, i.e.  $k_6$ , usually approaches  $10^9$   $M^{-1}s^{-1}$ . The same rate constant is assigned for the termination step,  $k_8 = 10^9 M^{-1}s^{-1}$ . POMs are known to react with hydrogen peroxide to form peroxy-species [26]. For simplicity we ignore the speciation of PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> at pH 1.6-2.0, and write the reaction in eq 12:

$$H_2O_2 + PMO_{12}O_{40}^{3-} \longrightarrow H_2O + PMO_{12}O_{39}(OO)^{3-}$$
 (12)

 $PMo_{12}O_{39}(OO)^{3-}$ , a two-electron oxidizing agent, is expected to react with glycerol, eq 13  $PMo_{12}O_{39}(OO)^{3-} + >CH(OH) \longrightarrow PMo_{12}O_{40}^{3-} + >C=O + H_2O$  (13)

We assume that a small fraction of  $PMo_{12}O_{39}(OO)^{3-}$  reacts through a one-electron mechanism oxidizing two glycerol molecules to two radicals, eqs 14-15, thus initiating the radical chain

$$PMo_{12}O_{39}(OO)^{3-} + >CH(OH) + H^{+} \rightarrow PMo_{12}O_{39}(O)^{2-} + >C\bullet(OH) + H_{2}O$$
(14)

$$PMo_{12}O_{39}(O)^{2-} + >CH(OH) \longrightarrow PMo_{12}O_{40}^{3-} + >C\bullet(OH) + H^{+}$$
(15)

The reaction rate constants  $k_{13}$  and  $k_{14}$  were the variable parameters, and  $k_{15}$  was assumed to be fast,  $k_{15} > 10^6 \text{ M}^{-1}\text{s}^{-1}$ . The dehydration reaction is known to be catalyzed by  $\text{Al}^{3+}$  [13] and is written for simplicity as eq 16

### $>C=O + Al^{3+} \longrightarrow PRA + Al^{3+}$

(16)

(18)

Similar reactions should be written for oxidation of the primary alcohol groups in glycerol. To avoid the complexity, we simply considered that the reaction product GCA is in equilibrium with >C=O (DHA), eq 17

$$GCA = >C = 0 \tag{17}$$

The transformation of PRA to LA was described by a simple pseudo-first-order reaction in eq

$$d[LA]/dt = -k_{18} [PRA]$$

The reaction rate constants in eqs 16-18 were the variable parameters. The concentration of  $O_2$ at 60 °C and at pressure10 bar is 8 mM [27]. Since the initiation of radicals involves the reaction product  $H_2O_2$ , the shape of kinetic curves in the beginning of the reaction depends on initial  $H_2O_2$ concentration. The theoretical curves of glycerol consumption barely exhibit an induction period at 1 mM  $[H_2O_2]_o$ . In our calculations, we used  $[H_2O_2]_o = 1$  mM, which is a reasonable value for not freshly purified glycerol [17]. In order to choose the best set of parameters, the data in Fig. 1, the dependences of glycerol conversion and product yields on  $[O_2]$  and  $[PMo_{12}O_{40}^{3-}]$ , were also taken into account. This kinetic model is over-parameterized and does not give a single set of variable parameters. We were mostly interested in whether the radical chain process is feasible at a low rate of radical initiation. The radical chain length, L, is the ratio of the propagation and initiation rates, and was estimated earlier to be  $\approx 20$ . Therefore, only the sets of parameters with L in the range 20-30 were considered. In addition, we calculated the product yields after 2 hours at different concentrations of O<sub>2</sub> and catalyst, and compared them with experimental data (Fig. 1). The fitting of AlPMo data with the best sets of variable parameters are presented in Fig. 6. The kinetic modelling confirmed that all available experimental data can be described by a classical branching radical chain mechanism, in which the peroxide intermediate generates free radicals in the presence of a transition metal complex.

#### Fig. 6

Contrary to a common belief that radical reactions are not selective, in this work a selectivity of 92 % for lactic acid formation was achieved at 95 % glycerol conversion. This can be explained by several factors. Aldehyde, PRA, forms LA quickly and selectively (entry 3 in the Table 2), and PRA concentration remains low in the course of the reaction. Carboxylic acid, including LA, has a

very low oxidizability. The first step, the oxidation of glycerol is not selective, it gives two products, ketone (DHA) and aldehyde (GCA). Hypothetically, the primary alcohol groups in DHA could be further oxidized to give a broad spectrum of products. At the same time, GCA reversibly isomerizes to DHA faster than it is further oxidized (entry 2 in the Table 2). Formally, the pathway  $GLY \rightarrow GCA \rightarrow DHA$  makes an unselective oxidation of glycerol to a single selective  $GLY \rightarrow$ DHA pathway. The isomerisation GCA  $\rightarrow$  DHA is the key reaction for the high selectivity. The DHA  $\rightarrow$  PRA reaction is known to be catalysed by Al<sup>3+</sup>cation [13]. This is likely a key function of that counter cation in our case. Thus, the efficient generation of free radicals from H<sub>2</sub>O<sub>2</sub> by LPMo combined with a relatively high efficiency GCA  $\rightarrow$  DHA isomerization make the overall process fast and selective.

### 4. Conclusions

A series of homogeneous phosphomolybdate catalysts MPMo<sub>12</sub>O<sub>40</sub> (M =H<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>) have been synthesized and characterized by several techniques. The POM complexes with different counter cations show different catalytic activities. Of the 7 complexes reported here, AlPMo had the highest efficiency: 92 % for LA at 95 % glycerol conversion within 6 h. Inhibition of the reaction by AAPH and by Cu<sup>2+</sup> (from CuPMo) and the generation of free radicals from H<sub>2</sub>O<sub>2</sub> catalyzed by MPMo confirm the branching-radical-chain mechanism of the process. Despite the involvement of free radicals, the reaction is selective due to isomerization of GCA to DHA, followed by catalytic dehydration of DHA to PRA. This work demonstrates that a classical radical chain oxidation can result in the selective oxidation of glycerol to lactic acid.

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**Fig. 1.** The effect of  $O_2$  pressure and initial [AlPMo] on glycerol consumption and product yields after 2 hours at 60 °C. (a) Dependence on  $O_2$ ; conditions: glycerol (1 M) and AlPMo (4 mM). (b) Dependence on catalyst (AlPMo) concentration; conditions: glycerol (1 M) and  $O_2$  (5 bar). Code: glycerol, black; DHA, red; GCA, blue; PRA, green; and LA, pink. The open circles are experimental and solid circles are calculated based on the proposed kinetic model.



**Fig. 2.** Study of phenolsulfonate inhibition during the glycerol oxidation process. Glycerol consumption, black; yields of DHA, red; GCA, blue; PRA, green; LA, pink. Conditions: 1 M glycerol, 4 mM of AlPMo, 10 bar O<sub>2</sub>, 60 °C plus sodium phenolsulfonate (5 mM) as an inhibitor.

![](_page_14_Figure_2.jpeg)

**Fig. 3.** UV-visible spectra of PGR under varying conditions: initial spectra of 50  $\mu$ M PGR, black; after 10 min, red; 10 min after 10 mM H<sub>2</sub>O<sub>2</sub> addition, blue; after 0.25 mM AlPMo addition for 5 min, green; 10 min, pink; and 15 min, brown. Conditions: 50 mM sodium sulfate buffer (pH 1.6) at 60 °C.

![](_page_15_Figure_2.jpeg)

**Fig. 4.** Oxidation of 50  $\mu$ M PGR by 10 mM H<sub>2</sub>O<sub>2</sub> in the presence of 1.0 M glycerol, 0.125 mM FePMo, black; 0.125 mM AlPMo, red; 0.125 mM ZnPMo, blue; and in the presence of 0.5 mM AAPH, green ; 10 mM AAPH, pink. Reaction conditions: 50 mM sodium sulfate buffer pH 1.6, 60 °C.

![](_page_16_Figure_2.jpeg)

**Fig. 5.** Oxidation of 50  $\mu$ M PGR by 10 mM H<sub>2</sub>O<sub>2</sub> in the presence of 0.125 mM FePMo, black; AlPMo, red; and CrPMo, blue. Reaction conditions: 50 mM sodium sulfate buffer (pH=1.6), 60 °C.

![](_page_17_Figure_2.jpeg)

**Fig. 6.** The kinetics of 1.0 M glycerol oxidation by  $O_2$  (10 bar) at 60 °C catalyzed by 4 mM AlPMo. Open circles are experimental data and solid lines are the theoretical curves. Code: glycerol, black; DHA, red; GCA, blue; PRA, green; LA, pink.

![](_page_18_Figure_2.jpeg)

Entry	Catalyst	α, %	Yields, %				Mass
			DHA	GCA	PRA	LA	balance (%)
1	AIPMo	52	14.5	4.1	6.2	25	95.8
2	FePMo	45	13.9	4.9	4.5	19.8	95.8
3	CrPMo	33	8.6	5.9	3.0	12.9	92.1
4	ZnPMo	16	5.4	4.5	1.6	3.6	94.4
5	CuPMo	0	0	0	0	0	
6	КРМо	12	4.8	4.2	0.7	1.4	92.5
7	HPMo	44	16.0	14.9	8.4	4.5	99.5

**Table 1.** Oxidation of glycerol by  $O_2$  in the presence of homogeneous MPMo catalysts.

Scheme 2. Structures of ABTS and PGR

8	none	2	0	0	0	0	
9	AAPH <sup>a</sup>	20	8	4	0	0	60.0

Reaction conditions: 5.0 mL of 1.0 M aqueous solution of glycerol, 4.0 mM of POM, 10 bar  $O_2$  at 60 °C, reaction time 2.0 h.

<sup>a</sup>In the presence of a radical initiator, 4.0mM of 2,2'-azobis(2-amidinopropane)

dihydrochloride (AAPH).

Substrates	α,%	Yields %				
Substrates		DHA	GCA		PRA	LA
DHA	44		1		25	15
GCA	41	25			9	5
PRA	91					87

Reaction conditions: 5.0 mL of 1.0 M aqueous solution of substrate, 4.0 mM of POM, 10 bar  $N_2$  at 60 °C, reaction time 0.5 h.