# Quinones as Co-Catalysts and Models for the Surface of Active Carbon in the Phosphovanadomolybdate-Catalyzed Aerobic Oxidation of Benzylic and Allylic Alcohols: Synthetic, Kinetic, and Mechanistic Aspects

**Ronny Neumann,* Alexander M. Khenkin, and Inga Vigdergauz**[a]

**Abstract:** Quinones have been considered as reactive compounds present on the surface of active carbon. Thus, the co-catalytic use of quinones combined with the phosphovanadomolybdate polyoxometalate, $PV_2Mo_{10}O_{40}^{5-}$, has been studied as an analogue of the known $PV_2Mo_{10}O_{40}^{5-}$/C catalyst in oxidative dehydrogenation reactions. From the synthetic point of view both biphasic the quinone (org) – $Na_5PV_2Mo_{10}O_{40}$ – (aq) and monophasic quinone (org) – $^4Q_5PV_2Mo_{10}O_{40}$ – (org) [$^4Q = (nC_4H_9)_4N^+$] systems are effective for the selective oxidation of benzylic and allylic alcohols to their corresponding aldehydes. Kinetic measurements carried out on the model oxidative dehydrogenation of 4-methylbenzyl alcohol in the presence of *p*-chloranil, $^4Q_5PV_2Mo_{10}O_{40}$, and molecular oxygen showed that the reaction was non-elementary, although the 4-methylbenzyl alcohol oxydehydrogenation was the rate-determining step. ESR measurements showed the presence of the semiquinone of *p*-chloranil, probably as a complex with the polyoxometalate. This proposed complex was shown to be a more potent oxidant than *p*-chloranil. Thus, for the oxidation of 4-methoxytoluene the semiquinone complex was active, whereas *p*-chloranil alone was inactive. Beyond the importance of understanding quinone-phosphovanadomolybdate polyoxometalate-catalyzed reactions, insight gained from the formation of semiquinone active species can be applied for heterogeneous and aerobic oxidative transformations catalyzed by $PV_2Mo_{10}O_{40}^{5-}$ with carbon matrices as active supports.

**Keywords:** active carbon · oxidations · oxygen · polyoxometalates · quinones

## Introduction

Polyoxometalate-catalyzed (POM) oxidations[1] can be categorized by the principle mode of the catalytic reaction. Thus, one may distinguish between two major reaction modes. In the first reaction type an oxygen donor reacts with the polyoxometalate to form an activated intermediate capable of oxidizing, usually by oxygen donation, an organic substrate [Eq. (1)].

$$\text{Oxidant} + \text{POM}_{ox} \rightarrow [\text{POM-Ox}]_{activated} \quad (1a)$$

$$[\text{POM-Ox}]_{activated} + \text{Substrate} \rightarrow \text{POM}_{ox} + \text{Product} \quad (1b)$$

One can differentiate between a) reaction at an addenda position for example W, Mo, V or Nb, usually using peroxygen compounds as oxidants and b) reaction at positions substituted with low-valent transition metals leading to a "transition metal active oxygen" active intermediate species.

In the second reaction mode the catalytic cycle can be pictured as taking place in two main stages. For liquid-phase "homogeneous" systems, the reaction is often thought of as a redox interaction between a substrate and the oxidized form of the POM, leading to a oxidized (dehydrogenated) product and a reduced catalyst species. Typically, the catalytic cycle is completed by reoxidation of the reduced POM, preferably by molecular oxygen [Eq. (2)].[1]

$$\text{Substrate} + 2\,\text{POM}_{ox} \rightarrow \text{Product} + 2\,\text{POM}_{red} \quad (2a)$$

$$2\,\text{POM}_{red} + O_2 \rightarrow 2\,\text{POM}_{ox} + H_2O \quad (2b)$$

In the past, it has been found that mixed addenda vanadomolybdate Keggin type polyoxometalates, especially $PV_2Mo_{10}O_{40}^{5-}$, are most effective in the latter reaction mode. Therefore, others and ourselves have studied both synthetic applications and the catalytic cycle. Mechanistic research using the heteropoly acid $H_5PV_2Mo_{10}O_{40}$ as a dissolved catalyst in an organic liquid phase has revealed that the

---

[a] Prof. R. Neumann,[+] Dr. A. M. Khenkin, I. Vigdergauz
Casali Institute of Applied Chemistry
Graduate School of Applied Science
The Hebrew University of Jerusalem
91904 Jerusalem (Israel)
Fax: (+972)-2-6528250
E-mail: ronny@vms.huji.ac.il

[+] New address:
Department of Organic Chemistry
Weizmann Institute of Science
76100 Rehovot (Israel)
Fax: (+972) 8-9344142
E-mail: ronny.neumann@weizmann.ac.il

0947-6539/00/0605-0875 $ 17.50+.50/0

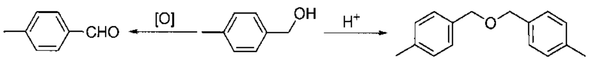
product formation occurred through a series of electron and proton transfers from the substrate to the POM.[2] POM reoxidation is less well understood and both inner sphere[2] and outer sphere mechanisms[3] have been suggested. Major synthetic applications for oxidation include the oxidative dehydrogenation of dienes,[4] alcohols and amines,[5] the formation of quinones from phenols,[6] and the oxidation of sulfides to sulfoxides.[7]

A closer look at the scope of the synthetic applications reveals that two basic techniques have been adopted. The first is to use the heteropoly acid $H_5PV_2Mo_{10}O_{40}$ as a dissolved (homogeneous) catalyst. Dissolution has been achieved either by complexation of $H_5PV_2Mo_{10}O_{40}$ by glymes in apolar solvents such as chlorohydrocarbons, or by using polar solvents such as acetonitrile, alcohols, acetic acid, and so forth.[4a, 6, 7a] In certain cases, however, the high acidity of $H_5PV_2Mo_{10}O_{40}$ is disadvantageous because of competing acid-catalyzed reactions. For example, in the oxidative dehydrogenation of benzyl alcohol, use of $H_5PV_2Mo_{10}O_{40}$ leads to formation of dibenzylether as major product instead of benzaldehyde. In order to avoid competing reactions due to the high acidity of heteropoly acid, neutral salts such as $[(C_nH_{2n-1})_4N]_5PV_2Mo_{10}O_{40}$ and $Na_5PV_2Mo_{10}O_{40}$ are acceptable alternatives. These neutral compounds in contrast to the protic forms are soluble, in organic solvents and water, respectively. Often, in order to increase surface area and for practical applications, supported POMs such as $Na_5PV_2Mo_{10}O_{40}$ have usually been employed as heterogeneous catalysts.[4b, 5, 6f, 7b–d] Significantly, in all reports *active carbon* in various forms has been used as the support.

Now, we have taken another look at *neutral* and supported $PV_2Mo_{10}O_{40}^{5-}$ as catalysts for reactions as described in Equation (2). Somewhat to our surprise, neutral forms of $PV_2Mo_{10}O_{40}^{5-}$ alone were catalytically inactive and of all the supports studied (silica, alumina, etc.) only use of an active-carbon support yielded catalytically active heterogeneous systems.[4b, 5a] This observation leads to two conclusions: either a) that the presence of protons was vital to sustain a catalytic cycle as in Equation (2), or b) that for non-protic, neutral $PV_2Mo_{10}O_{40}^{5-}$, active carbon was not an inert matrix, but played an integral part in the catalytic cycle.[8] As it is known that in the presence of oxidizing agents carbon surfaces are rich with oxygen-containing moieties,[9] the working hypothesis, for supported $PV_2Mo_{10}O_{40}^{5-}$, is that an intermediate or promoter, formed on the support surface, played a key part in the catalytic cycle. In this paper we discuss the possibility of quinones as being this active promoter. We show that catalytic systems consisting of neutral $PV_2Mo_{10}O_{40}^{5-}$ and quinone *together* are active for the oxidation of benzylic and allylic alcohols. In addition to the synthetic value of the methodology, this research sheds important and new light on the catalytic activity of $PV_2Mo_{10}O_{40}^{5-}$-type systems. Also an important insight into active carbon as a support in oxidative transformations is attained.

## Results and Discussion

The research was initiated by comparing various polyoxometalate catalytic systems for the catalytic dehydrogenation of 4-methylbenzyl alcohol, similar to those studied in the past,[5] [Table 1, Eq. (3)]



(3)

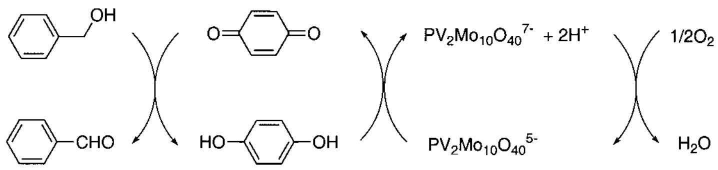
Table 1. Oxidation of 4-methylbenzyl alcohol under various conditions.

| Catalyst | Product Yield [mol %] | |
|---|---|---|
| | 4,4′-dimethyl-dibenzylether | 4-methylbenz-aldehyde |
| $H_5PV_2Mo_{10}O_{40}$[a] | 95 | 5 |
| $^4Q_5PV_2Mo_{10}O_{40}$[a,f] | 0 | 0 |
| $Na_5PV_2Mo_{10}O_{40}$[b] | 0 | 0 |
| $Na_5PV_2Mo_{10}O_{40}/C$[c] | 0 | 95 |
| $Na_5PV_2Mo_{10}O_{40}/SiO_2$[c] | 10 | 0 |
| $Na_5PV_2Mo_{10}O_{40}/Al_2O_3$[c] | 3 | 0 |
| $Na_5PV_2Mo_{10}O_{40}/Al_2O_3$ and C[d] | 1 | 6 |
| Active carbon[e] | 0 | < 1 |
| $(NH_4)_6H_3PMo_6V_6O_{40}/C$[c] | < 1 | 91 |

[a] 4-methylbenzyl alcohol (1 mmol), catalyst (0.014 mmol), acetonitrile (1 mL), 1 atm $O_2$, 110 ± 2 °C, 24 h. [b] 4-methylbenzyl alcohol (1 mmol) in decalin (1 mL), catalyst (0.018 mmol) in water (1 mL), 1 atm $O_2$, 100 ± 2 °C, 18 h. [c] 4-methylbenzyl alcohol (1 mmol), supported catalyst (0.01 mmol) at 10 wt % loading, toluene (3 mL), 100 ± 2 °C, 24 h. [d] as in [c] with the addition of active carbon (100 mg). [e] 4-methylbenzyl alcohol (1 mmol), active carbon (200 mg), toluene (3 mL), 100 ± 2 °C, 24 h. [f] $^4Q = (n\text{-}C_4H_9)_4N^+$.

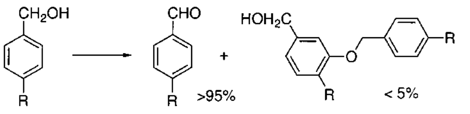
In single liquid-phase organic systems, one can observe that the use of acidic and protic $H_5PV_2Mo_{10}O_{40}$ led mainly to the acid-catalyzed formation of the dibenzylether, while non-acidic $^4Q_5PV_2Mo_{10}O_{40}$ ($^4Q = (n\text{-}C_4H_9)_4N^+$) was inactive. Similarly, in a water/organic biphasic system containing $Na_5PV_2Mo_{10}O_{40}$, no reaction was observed. In a third system with supported catalysts, the unique oxidative dehydrogenation activity of the carbon matrix is clearly observable. The silica and alumina supports were oxidatively inactive showing only some mild acid catalysis. Even separate addition of active carbon to an inactive $Na_5PV_2Mo_{10}O_{40}/Al_2O_3$ yielded some oxidation activity, although active carbon by itself showed practically no catalytic activity. The clear conclusion from these initial results is that use of non-protic (non-acidic) polyoxometalates does not lead to a oxidative dehydrogenation of benzylic alcohols in the absence of active carbon; the latter contains an active component necessary to promote the oxidative dehydrogenation reaction. This finding is not unique for the oxidative dehydrogenation of benzyl alcohols. For example, $\alpha$-terpinene in the presence of 0.01 equivalents of $H_5PV_2Mo_{10}O_{40}$ was quantitatively oxidized to *p*-cymene (acetonitrile, $P(O_2) = 1$ atm, 22 °C, 18 h), while $^4Q_5PV_2Mo_{10}O_{40}$ was inactive.

Quinones, particularly 2,3,-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), known for their ability to *stoichiometrically* dehydrogenate benzylic and allylic alcohols to the corresponding aldehydes[10] and known to exist on oxidatively treated carbon surfaces[9] were hypothesized to be the promoter of the POM/C-catalyzed reactions as discussed above. Therefore, a catalytic reaction that employs a quinone/neutral $PV_2Mo_{10}O_{40}^{5-}$ catalyst pair is now suggested and further investigated for the oxidative dehydrogenation of alcohols according to Scheme 1.



Scheme 1.

Similar quinone/$H_5PV_2Mo_{10}O_{40}$ systems have been used in the palladium-catalyzed oxidation of alkenes[11] and conjugated dienes.[12] There, however, the primary function of the quinone was to act as a coordinating and activating ligand to the palladium(II) center and as an electron transfer mediator. The use of quinones as co-catalyst was tested in two reaction modes. In the first mode (**A**), a biphasic liquid–liquid system was used, whereby $Na_5PV_2Mo_{10}O_{40}$ dissolved in water was treated with the substrate and quinone dissolved in an immiscible organic phase. The advantage of this method is the simple separation of $Na_5PV_2Mo_{10}O_{40}$ from the product in the reaction work up. In the second mode (**B**), the polyoxometalate $^4Q_5PV_2Mo_{10}O_{40}$, quinone, and substrate were all dissolved in a single solvent. This system is more practical for mechanistic and kinetic studies. The results for the oxidative dehydrogenation of a variety of benzylic [Eq. (4)] and allylic alcohols using 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil) as co-catalyst are presented in Table 2.



(4)

We observed that the oxidative dehydrogenation reaction was possible using both methods. The two-phase method is preferable in terms of yield and recovery of the polyoxometalate. As expected electron-donating substituents in benzylic alcohols increased and electron-withdrawing groups decreased the yield, although the effect is rather small. Allylic alcohols are significantly less reactive than benzylic alcohols, except for the conjugated cinnamyl alcohol. The selectivity of the reactions is high, >95%. The only by-product formed is not the carboxylic acid produced by over oxidation of the aldehyde, but rather a ring-coupled product (especially for 4-methoxybenzyl alcohol). The reactivity of a series of quinones was also compared for the biphasic system and the water soluble $Na_5PV_2Mo_{10}O_{40}$ (Table 3). Clearly and quite simply the reactivity and yield in the benzyl alcohol oxidative dehydrogenation is a function of the oxidation potential of the quinone[13] and the presence of electron-withdrawing groups; the higher the oxidation potential and the more electron-withdrawing the substituents, the higher the yield.

Table 3. Oxidation of benzyl alcohol catalyzed by $Na_5PV_2Mo_{10}O_{40}$ and various quinones.[a]

| Quinone | Chemical yield [mol %][b] |
|---|---|
| 2,3,5,6-tetrachloro-1,4-benzoquinone | 84 |
| 2,3-dichloro-5,6-dicyano-1,4-benzoquinone | 81 |
| 1,4-benzoquinone | 69 |
| 1,4-naphthaquinone | 36 |
| 9,10-anthraquinone | 14 |
| 9,10-phenanthraquinone | 0 |

[a] Benzyl alcohol (1 mmol), quinone (0.05 mmol), decalin (1 mL), $Na_5PV_2Mo_{10}O_{40}$ (0.015 mmol), water (1 mL), 1 atm $O_2$, 90 ± 2 °C, 18 h. [b] The chemical yield was determined by GC with reference standards and calibrated mixtures.

After the initial studies demonstrating the synthetic utility of the neutral $PV_2Mo_{10}O_{40}^{5-}$/quinone catalytic system for the oxidative dehydrogenation of benzylic and allylic alcohols, we turned to investigate kinetic and mechanistic aspects. A model, single organic liquid-phase system was chosen with 4-methylbenzyl alcohol (**MBA**) as the substrate, *p*-chloranil (**TCBQ**) as the quinone, and $^4Q_5PV_2Mo_{10}O_{40}$ (**POM**) as the polyoxometalate. In this way, the catalytic cycle can be described according to Scheme 1 as a series of three reactions involving four components. An *empirical* rate equation for the entire benzylic alcohol oxidative dehydrogenation reaction scheme, taking into account all the components, is given in Equation (5).

$$-\,d[\mathrm{MBA}]/dt = k_{\mathrm{obs}}[\mathrm{MBA}]^a[\mathrm{TCBQ}]^b[\mathrm{POM}]^c P^d_{\mathrm{O_2}} \qquad (5)$$

A reaction profile for the oxidation of 4-methylbenzyl alcohol (Figure 1) clearly shows that the reaction *appears* to be zero order in 4-methylbenzyl alcohol ($a = 0$). The reaction rate under the (standard) conditions described in the caption for Figure 1 was $9.45 \times 10^{-6}\,\mathrm{M\,s^{-1}}$. An Arrhenius plot at temperatures between 80–120 °C (Figure 1, inset), yielded an observed energy of activation ($E_a$) of 13.8 Kcal mol$^{-1}$ ($\ln A = 14.74$, $\Delta H^{\neq}_{25} = 13.2$ Kcal mol$^{-1}$, $\Delta S^{\neq}_{25} = -31.1$ cal mol$^{-1}$K$^{-1}$).

The reaction order in oxygen pressure was found by measuring initial rates (constant oxygen pressure) for **MBA** oxidation at different initial pressures. A plot of the initial

Table 2. Oxidation of benzylic and allylic alcohols catalyzed by $PV_2Mo_{10}O_{40}^{5-}$/*p*-chloranil.

| Substrate | Product | Chemical yield [mol %][a] Method **A**[b] | Method **B**[c] |
|---|---|---|---|
| 4-methoxybenzyl alcohol | 4-methoxybenzaldehyde | 85 | 75 |
| 4-methylbenzyl alcohol | 4-methylbenzaldehyde | 82 | 63 |
| 4-chlorobenzyl alcohol | 4-chlorobenzaldehyde | 77 | 59 |
| benzyl alcohol | benzaldehyde | 81 | 62 |
| 4-nitrobenzyl alcohol | 4-nitrobenzaldehyde | 65 | 52 |
| cinnamyl alcohol | cinnamyl aldehyde | 85 | 80 |
| 1-phenylethanol | acetophenone | 87 | 80 |
| benzhydrol | benzophenone | 94 | 84 |
| *cis*-2-hexene-1-ol | *cis*-2-hexenal | 35 | 24 |
| *trans*-2-hexene-1-ol | *trans*-2-hexenal | 33 | 20 |
| 1-octene-3-ol | 1-octene-3-one | 76 | 34 |
| 2-cyclohexene-1-ol | 2-cyclohexene-1-one | 88 | 37 |

[a] The chemical yield was determined by GC with reference standards and calibrated mixtures. [b] Substrate (1 mmol), *p*-chloranil (0.05 mmol), decalin (1 mL), $Na_5PV_2Mo_{10}O_{40}$ (0.015 mmol), water (1 mL), 1 atm $O_2$, 90 ± 2 °C, 18 h. [c] Substrate (1 mmol), *p*-chloranil (0.05 mmol), $^4Q_5PV_2Mo_{10}O_{40}$ (0.015 mmol), acetonitrile (1 mL), 1 atm $O_2$, 110 ± 2 °C, 18 h.

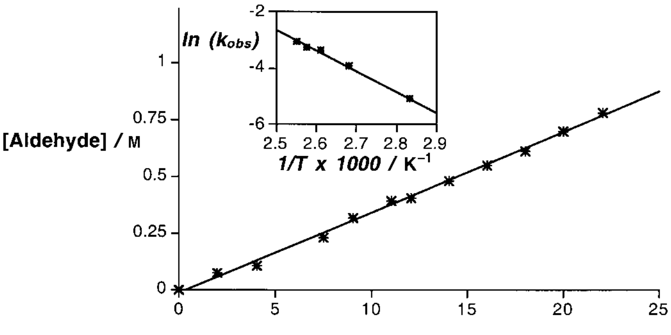


Figure 1. Reaction profile and Arrhenius plot (inset) for the oxidation of 4-methylbenzyl alcohol. Reaction conditions: 4-methylbenzyl alcohol (1M), *p*-chloranil (0.1M), and ${}^4Q_5PV_2Mo_{10}O_{40}$ (0.014M) in acetonitrile (5 mL), 1 atm $O_2$, 110 °C. Inset: the same conditions at different temperatures. The calculated zero-order rate constants were used.

oxygen pressure, between 1–4 atm, as a function of the initial reaction rate ($V_0$) is shown in Figure 2. The slope, $V_0/P_{O_2}$, was computed to be 0.01, which by a combination of statistical tests (t test, F test, and analysis of $r^2$) leads to the conclusion that the reaction rate was independent of the oxygen pressure.

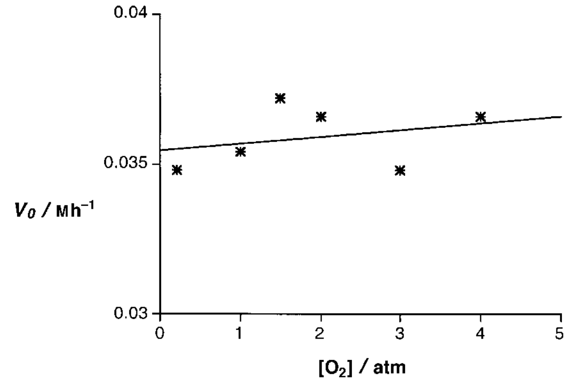


Figure 2. The initial rate as a function of the oxygen pressure. Reaction conditions: 4-methylbenzyl alcohol (1M), *p*-chloranil (0.1M), and ${}^4Q_5PV_2Mo_{10}O_{40}$ (0.014M) in acetonitrile (10 mL), 1–4 atm $O_2$, 110 °C.

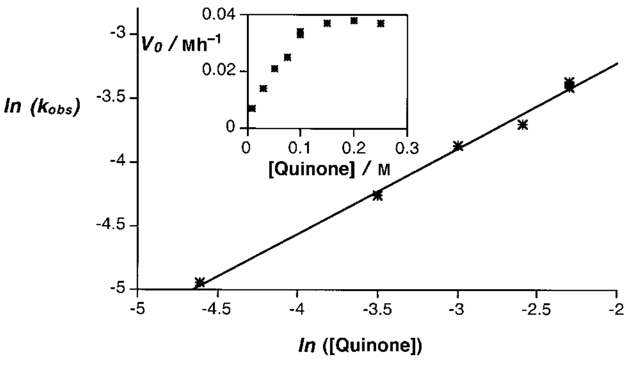


Figure 3. The rate constant as a function of *p*-chloranil concentration. Reaction conditions: 4-methylbenzyl alcohol (1M), *p*-chloranil (0.01–0.25M), and ${}^4Q_5PV_2Mo_{10}O_{40}$ (0.014M) in acetonitrile (5 mL), 1 atm $O_2$, 110 °C (line fit $y = 0.67x + 1.9$; $r^2 = 0.99$).

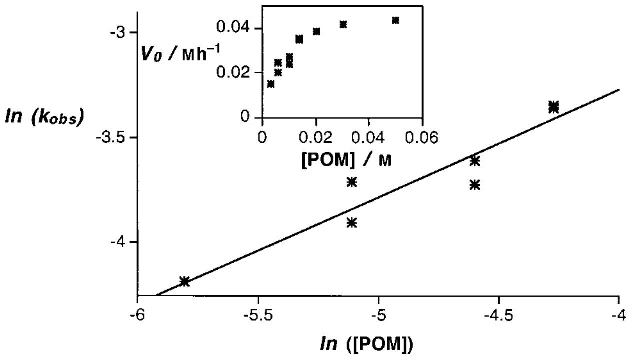
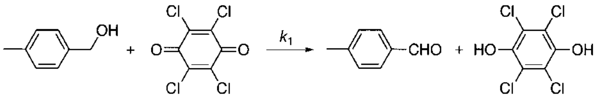


Figure 4. The rate constant as a function of ${}^4Q_5PV_2Mo_{10}O_{40}$ concentration. Reaction conditions: 4-methylbenzyl alcohol (1M), *p*-chloranil (0.1M), and ${}^4Q_5PV_2Mo_{10}O_{40}$ (0.003–0.05M) in acetonitrile (5 mL), 1 atm $O_2$, 110 °C (line fit $y = 0.51x + 1.22$; $r^2 = 0.91$).

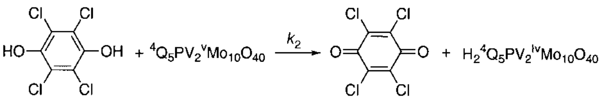
Logarithmic van't Hoff plots, for which rate constants were obtained from series of reaction profiles as presented in Figure 1, were used to find the reaction order in **TCBQ** (0–10 mol%; Figure 3) and **POM** (0–1.5 mol%; Figure 4). The given mol% amounts of **TCBQ** (up to 10 mol%) and **POM** (up to 1.5 mol%) were used because the kinetic profiles (initial rate as a function of **TCBQ** and **POM**) showed saturation effects (see insets in Figures 3 and 4) above these amounts of **TCBQ** and **POM**, respectively. The reaction orders calculated for **TCBQ** and **POM** (in nonsaturated systems, linear dependence) were 0.7 and 0.5, respectively. The following *empirical* rate equation (excess **MBA**) is therefore given by Equation (6) in which $k_{\mathrm{obs}} = 2.5 \times 10^6 \exp^{-13.2/RT}$.

$$-\mathrm{d}[\mathrm{MBA}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{TCBQ}]^{0.7}[\mathrm{POM}]^{0.5}P^{0}_{O_2} \qquad (6)$$

Conceptually, the entire catalytic oxidative dehydrogenation reaction cycle (Scheme 1) may *preliminarily* be divided into three separate reactions [Eqs. (7)–(9)].



(7)



(8)

$$2\,H_2{}^4Q_5PV^{IV}{}_2Mo_{10}O_{40} + O_2 \xrightarrow{k_3} 2\,{}^4Q_5PV^{V}{}_2Mo_{10}O_{40} + 2\,H_2O \qquad (9)$$

If the rate of the reaction is measured as $-\mathrm{d}[\mathrm{MBA}]/\mathrm{d}t$ and assuming that the rate-determining step is the bimolecular elementary reaction between **MBA** and **TCBQ** [Eq. (7)], then the reaction should theoretically be first order both in **MBA** and **TCBQ**. However, under the general reaction conditions used **MBA:TCBQ**$_0 \geq 10$, **TCBQ** is in a limited concentration, that is, catalytic. Therefore, the reaction instead *appears* to be zero order, as observed, in **MBA** and should be pseudo first order in **TCBQ**.[14] Even if the first step [Eq. (7)] is not rate determining, the fact that **MBA** is in *excess* to all other components means that the reaction is in any case observed, but not necessarily true zero order in

**MBA**. The fact, however, that the observed reaction order in **TCBQ** was only partial (0.7) and that the rate was also dependent on and of partial order in **POM** clearly argued for a more complicated kinetic scheme. Furthermore, the fact that the reaction was zero order in molecular oxygen indicates that the reoxidation step [Eq. (9)] is not rate determining.

At this stage, each of the proposed reaction steps [Eqs. (7)–(9)], was investigated separately to measure the initial reaction rate and rate constant for each step. First, reaction of **MBA** and **TCBQ** (1 and 0.1M, respectively, in acetonitrile) at 110 °C yielded a rate constant $k_1 = 3.1 \times 10^{-5}\,\text{M}^{-1}\text{s}^{-1}$, derived from the initial reaction rate $-\text{d}[\text{MBA}]/\text{d}t = 3.1 \times 10^{-6}\,\text{M}\,\text{s}^{-1}$. Second, the reaction of equivalent amounts of 2,3,5,6-tetrachloro-1,4-dihydroxybenzene, **TCHQ**, and **POM**$_{ox}$ (0.01M each in acetonitrile) at *room temperature* under argon was followed by the appearance of heteropoly blue (**POM**$_{red}$) in the visible spectrum at 750 nm, Figure 5. The rate constant $k_2$, derived from the initial reaction rate $-\text{d}[\text{POM}_{ox}]/\text{d}t$,[15] was calculated to be $8.7 \times 10^{-1}\,\text{M}^{-1}\text{s}^{-1}$. Note that this rate constant is four orders of magnitude higher even at room temperature relative to the rate constant for the stoichiometric **MBA** oxidative dehydrogenation [Eq. (7)]. Finally, the reoxidation of **POM**$_{red}$ (0.01M in acetonitrile) with 1 atm $O_2$ (solution concentration ~0.01M, see above) was measured at 110 °C by the disappearance of **POM**$_{red}$ in the visible spectrum at 750 nm, Figure 6. The calculated rate constant $k_3$, derived from the initial reaction rate $-\text{d}[\text{POM}_{red}]/\text{d}t$, [15] was $1.3 \times 10^{-3}\,\text{M}^{-1}\text{s}^{-1}$. Therefore, since $k_2 \gg k_3 > k_1$, it would appear that the rate-determining step of the entire reaction sequence as broken down into three elementary reaction steps and represented by Equations (7)–(9) is the oxidative dehydrogenation of 4-methylbenzyl alcohol by *p*-chloranil. However, two anomalies must be noted: a) the reaction rate for the entire catalytic reaction sequence as determined from Figure 1 was $9.45 \times 10^{-6}\,\text{M}\,\text{s}^{-1}$ and is three times *faster* than the oxidative dehydrogenation of **MBA** by **TCBQ** as a separate step (rate $= 3.1 \times 10^{-6}\,\text{M}\,\text{s}^{-1}$) and b) the entire reaction sequence showed a complicated dependence in **TCBQ** and **POM** [Eq. (5)] rather than a simple first-order dependence in **TCBQ** only.

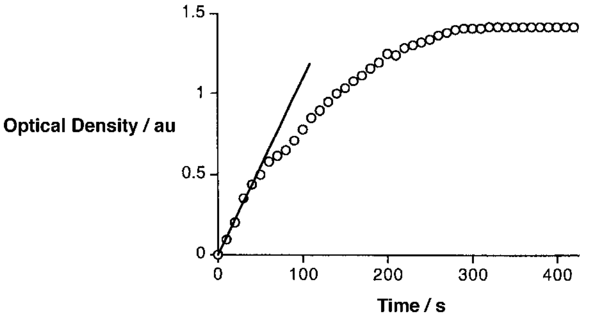


Figure 5. Reaction profile for the reduction of $^4Q_5PV_2Mo_{10}O_{40}$ with 2,3,5,6-tetrachloro-1,4-dihydroxybenzene. Reaction conditions: $^4Q_5PV_2Mo_{10}O_{40}$ (0.01M) and 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (0.01M) in acetonitrile (2 mL) at room temperature under argon, $\lambda = 750$ nm.

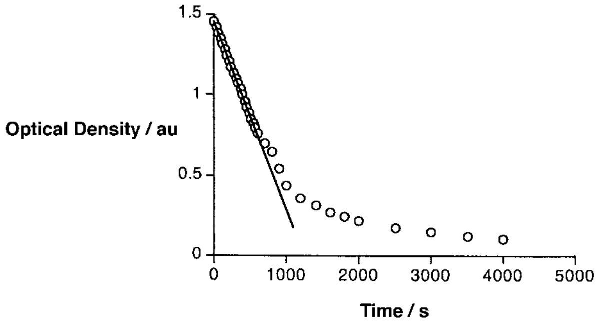


Figure 6. Reaction profile for aerobic oxidation of reduced $H_2{}^4Q_5PV_2Mo_{10}O_{40}$. Reaction conditions: $H_2{}^4Q_5PV_2Mo_{10}O_{40}$ (0.01M) in benzonitrile (2 mL) at 110 °C under $O_2$, $\lambda = 750$ nm.

The above described kinetic analysis was based on the assumption that the catalytic cycle (Scheme 1) could be divided into three *independent* reaction steps as shown in Equations (7)–(9). There is, however, much evidence from the literature that *o*-quinone compounds may insert[16] and carbonyl moieties in general may interact[17] with M–O bonds of polyoxometalates. In our case such an interaction between **TCBQ** and **POM** could lead to new "TCBQ-POM" species or complexes of catalytic significance. First, evidence for such a "TCBQ-POM" species was gained by using ESR spectroscopy. The mixing of 0.5 equivalents of **TCHQ** (a potential two-electron reductant) with one equivalent $^4Q_5PV^V{}_2Mo_{10}O_{40}$ yielded a 15-line ESR spectrum (Figure 7 top). This spectrum is attributable to the formation of mono-reduced

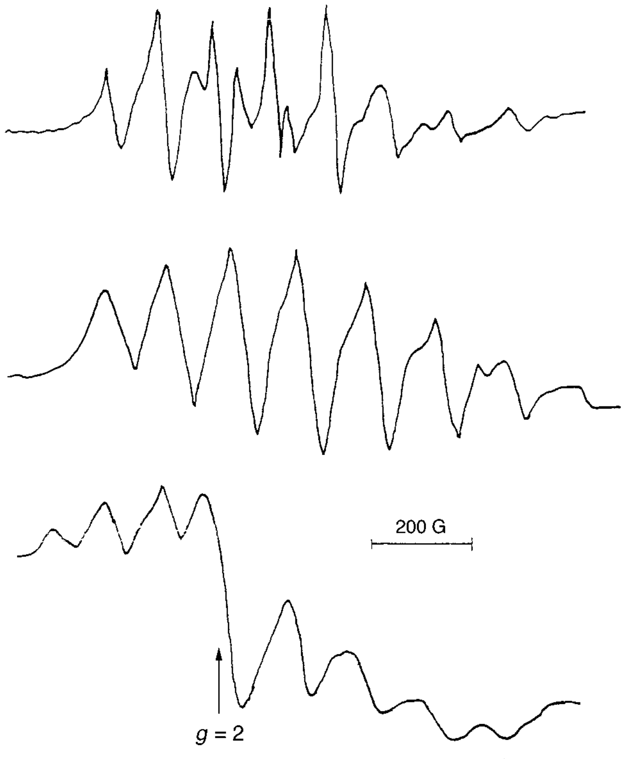
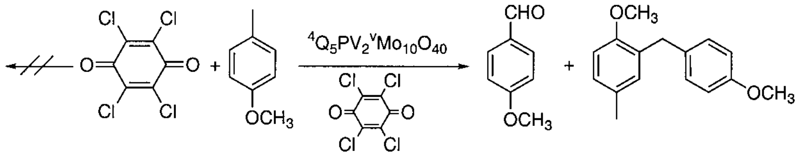


Figure 7. ESR spectra at room temperature of reduced $H_2{}^4Q_5PV_2Mo_{10}O_{40}$ in the presence of *p*-chloranil. Top:spectrum of polyoxometalate (2mM) after addition of 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (0.5 equiv). Middle: spectrum of polyoxometalate (2mM) after addition of 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (1.0 equiv). Bottom: spectrum of polyoxometalate (2mM) after addition of 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (1.0 equiv) followed by addition of *p*-chloranil (5.0 equiv).

$H^4Q_5PV^VV^{IV}Mo_{10}O_{40}$ species. The 15-line spectrum is due to additional splitting of the eight lines at the $V^{IV}$ center ($I = 7/2$ for $^{51}V$) by a nearest neighbor vanadium atom.[17d] After addition of another 0.5 equivalents of **TCHQ**, an eight-line spectrum is observed (Figure 7 middle). This is explained by formation of both doubly reduced $H_2{}^4Q_5PV^{IV}{}_2Mo_{10}O_{40}$ with vanadium in vicinal positions, which are ESR silent due to antiferromagntic coupling and doubly reduced $H_2{}^4Q_5PV^{IV}{}_2Mo_{10}O_{40}$ with vanadium in distal positions, which lead to typical eight-line spectra.[17d] Now, addition of five equivalents of **TCBQ** (ratio **TCBQ**:**POM** = 6), clearly shows the previously observed eight-line spectrum ($g = 1.98$) with an overlapping singlet at $g = 2.00$ (Figure 7 bottom). This singlet is easily attributed to the formation of the 2,3,5,6-tetrachloro-1,4-benzosemiquinone[18] (**SQ**) by electron transfer from the doubly reduced **POM** to **TCBQ** [Eq. (10)].



Scheme 2.

$$POM^{2-} + Q \xrightarrow{K_1} POM^{1-}\text{-}SQ \xrightarrow{K_2} POM^{1-} + SQ \qquad (10)$$

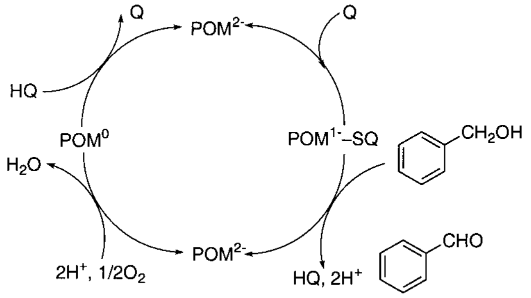
The observation of **SQ** or **SQ-POM** species at ratios of **TCBQ**:$\mathbf{POM_{red}} = 6$ is significant, because these are quite typical of ratios used in the catalytic reactions as described above. It is not entirely clear if **SQ** exists on its own in solution or as a complex, **SQ-POM**. Although, we were not successful in isolating any such intermediate, there is certainly precedent for such complexes.[16, 17]

Further support for an **SQ** or **SQ-POM** species was obtained by using cyclic voltammetry (CV).[19] The CV of **TCBQ** showed two reversible wave with oxidation potentials of −0.12 V and 0.6 V with a silver electrode,[10e] whereas a 1:1 mixture of **TCBQ** and **POM** showed a new reversible wave at 0.8 V. This indicates the formation of a strong oxidant for the **TCBQ/POM** system relative those of **TCBQ** and **POM** (0.68 V) alone. Additionally, UV-visible measurements showed no significant decrease in the optical density at 750 nm, that is, oxidation of $\mathbf{POM_{red}}$ upon addition of the quinone oxidant. This clearly indicates that $K_2$ [Eq (10)] is low as it would be expected that $\mathbf{POM^{1-}}$ would have a ~50% lower optical density relative to $\mathbf{POM^{2-}}$ or $\mathbf{POM^{1-}}$/**SQ**, as optical densities at 750 nm are proportional to the degree of reduction.[2] The existence of a **SQ-POM** intermediate complex is reasonable.

After showing the existence of **SQ-POM** intermediate species under catalytically relevant conditions, it, of course, remains to be ascertained if such species are in fact catalytically relevant oxidants. In order to differentiate between the oxidative activity of **TCBQ** and **SQ-POM**, conditions should be preferably found for which one is active and the other is not or vice versa. Such a system was sought and we turned our attention to the oxidation of methyl aromatics to aldehydes or ketones. Such stoichiometric oxidations that use 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are known.[10a, 20] Thus, treatment 4-methoxytoluene (1 mmol) with DDQ (3 mmol) in benzonitrile (8 mL) at 140 °C for 3 h resulted in the selective formation of 4-methoxybenzaldehyde with 84% conversion. Importantly, the same reaction with *p*-chloranil, **TCBQ**, instead of DDQ yielded only a small amount of product, ~0.5%. In contrast, the reaction of 1 mmol 4-methoxytoluene with *catalytic* amounts of *p*-chloranil (0.1 mmol) and polyoxometalate (0.01 mmol) in benzonitrile (8 mL) at 140 °C and 1 atm $O_2$ led to a 16% conversion of 4-methoxytoluene to 75% 4-methoxybenzaldehyde and 25% ring-coupled by-product. The experiment is summarized in Scheme 2.

Significantly, the ring-coupled product can be expected to be formed with the use of only a one-electron oxidant, in this case the semiquinone, whereas the aldehyde can be formed by the use of both one- and two-electron oxidants. Clearly **SQ** or **SQ-POM** are catalytically relevant oxidants.

The fact that semiquinone intermediates are catalytically relevant oxidants, which are stronger oxidants than the original quinone, makes it necessary to reformulate the catalytic cycle. In the proposed reaction scheme, initial amounts of two-electron reduced polyoxometalate, $\mathbf{POM^{2-}}$ are produced by the reactions as described by Equations (7) and (8), that is, stoichiometric oxidative dehydrogenation of the benzylic alcohol with **TCBQ**. The reaction between the **TCHQ** formed and **POM** gives $\mathbf{POM^{2-}}$. Once the reduced polyoxometalate is formed, the catalytic cycle may proceed as indicated in Scheme 3.



Scheme 3.

In the first step, the benzylic alcohol dehydrogenation, the presence of a *sufficient* concentration of **TCBQ** is required so as to allow the formation of the proposed polyoxometalate-semiquinone complex, $\mathbf{POM^{-1}}$-**SQ**. This complex, in a two-electron oxidation, dehydrogenates the benzylic alcohol to yield the benzaldehyde and **TCHQ** in the rate-determining step. Determination of this step as rate limiting is also supported by the results of a competitive reaction between benzyl alcohol and [D$_7$]benzyl alcohol, for which a $k_H/k_D$ ratio of 4.3 was observed. A breaking of the C–H benzylic bond is certainly involved in the rate-determining step for the oxidation of benzylic alcohol with **POM$^{-1}$-SQ**. In a second relatively faster reaction, the oxidized polyoxometalate **POM$^0$** is aerobically regenerated.[2] The oxidized polyoxometalate then can regenerate the quinone, allowing again for formation of the **POM$^{-1}$-SQ** oxidant. The fact that the reduced polyoxometalate may a) react with quinone to produce semiquinone and b) be aerobically oxidized accounts for the non-elementary rate equation [Eq. (6)] obtained for this reaction.

## Conclusion

The research presented above has produced several important results. On the synthetic level, a method to use quinones and the $PV_2Mo_{10}O_{40}^{5-}$ polyoxometalate as co-catalysts for the aerobic oxidative dehydrogenation of benzylic and allylic alcohols has been forwarded. The use of quinones as co-catalyst was derived from the observation that previous systems that employed *neutral* $PV_2Mo_{10}O_{40}^{5-}$ entities were catalytically inactive unless active carbon was used as a support. The kinetic and mechanistic investigation carried out leads to the conclusion that the $PV_2Mo_{10}O_{40}^{5-}$ polyoxometalate can interact with quinones to yield semiquinone intermediates or complexes. The latter is a more potent oxidant than the quinone itself and participates in the catalytic cycle. Beyond the deductions made concerning the specific polyoxometalate/quinone system investigated, this research could be important in the understanding and use of active carbon alone or as a support in oxidative transformations, wherein the carbon surface containing oxygenated species plays a role as catalyst or promoter.

## Experimental Section

**Materials**: The $H_5PV_2Mo_{10}O_{40} \times 32\,H_2O$ polyoxometalate was prepared by a standard technique.[21] The hydration state was determined by thermogravimetric analysis (Mettler 50). Elemental analysis: calcd P 1.34, V 4.41, Mo 41.56; found P 1.31, V 4.38, Mo 41.32. $Na_5PV_2Mo_{10}O_{40} \times 42H_2O$ was prepared[21] from the acid by ion exchange using Amberlite-120 ($Na^+$ form). Elemental analysis: calcd Na 4.41, P 1.19, V 3.91, Mo 36.85; found Na 4.52, P 1.04, V 4.05, Mo 36.29. $^4Q_5PV_2Mo_{10}O_{40}$ ($^4Q = (n\text{-}C_4H_9)_4N^+$) was prepared by adding an aqueous solution $H_5PV_2Mo_{10}O_{40} \times 32\,H_2O$ (0.25 M, 20 mL) dropwise into a stirred solution of $(n\text{-}C_4H_9)_4N^+Cl^-$ (25 mmol) in water (50 mL). The precipitated product was collected and thoroughly washed with water. Elemental analysis: calcd C 32.63, H 6.16, N 2.38; found C 32.48, H 6.32, N 2.43. Solvents were of analytical grade (Frutarom), and benzylic and allylic alcohols and quinones were reagent grade from Fluka and Aldrich and were used without purification. Supported catalysts were prepared at a 10 wt% loading by wet impregnation. In other words, solutions ($Na_5PV_2Mo_{10}O_{40}$ in water and $^4Q_5PV_2Mo_{10}O_{40}$ in acetone) were mixed with gentle stirring with the desired support for 1 h at room temperature. The solvent was then removed by vacuum evaporation, and the supported catalyst was dried at 100 °C for six hours. 2,3,5,6-Tetrachloro-1,4-dihydroxybenzene was prepared by reduction of *p*-chloranil in Zn/acetic acid and recrystallized from ethanol.

**Instrumentation**: Oxidation reaction products were characterized by using reference compounds when available by use of GLC (Hewlett-Packard 5890 gas chromatograph) with a flame-ionization detector and a 15 m × 0.32 mm 5% phenylmethylsilcone (0.25 μm coating) capillary column and helium carrier gas. Products whose initial identity was questionable were unambiguously identified by using a gas chromatograph equipped with a mass-selective detector (GC-MS Hewlett-Packard GCD) and with the same column described above. UV/Vis spectra and redox kinetic measurements were measured on a Hewlett-Packard 8452A diode array spectrometer equipped with a thermostated bath for variable temperature measurements. ESR spectra (X-band) were taken with a Varian E-12 spectrometer at room temperature; DPPH was used as standard.

**General procedure for oxidative dehydrogenation**: Reactions were carried out in glass pressure tubes (20 mL) equipped with a magnetic stirring bar. Typically, the tube was loaded with polyoxometalate (supported or dissolved), quinone, and solvent(s). See footnotes of Tables 1–3 for quantities. The tube was purged by gently bubbling molecular oxygen through the reaction solution for 5 min and then closed. The solution was then brought to the appropriate temperature in a thermostated oil bath. Every 3–4 hours oxygen was added to bring the pressure to 1 atm. After the reaction was completed and the mixture cooled, GLC analysis was performed on aliquots withdrawn directly from the reaction mixture.

**Kinetic measurements**: The kinetic analysis for the 4-methylbenzyl alcohol/*p*-chloranil/$^4Q_5PV_2Mo_{10}O_{40}/O_2$ catalytic system was carried out in a 50 mL Buchi glass autoclave. The autoclave was loaded with the appropriate amounts of compounds (see legends of Figures 1, 3, and 4), and the tube was purged by gently bubbling molecular oxygen through the reaction solution for 5 min and then closed. The autoclave was brought to the desired pressure and then brought to the appropriate temperature in a thermostated oil bath. At the desired time intervals a 2 μL sample was removed from the solution and analyzed directly by GLC. Upon a noticeable drop in pressure, additional oxygen was added. For measurements on the dependence on oxygen pressure, the reaction were carried out in a 300 mL glass lined Parr autoclave containing 4-methylbenzyl alcohol (1 M), *p*-chloranil (0.1 M), and $^4Q_5PV_2Mo_{10}O_{40}$ (0.014 M) in acetonitrile (10 mL), 1–4 atm $O_2$, 110 °C. Rates were measured as initial rates only, that is, only until a discernible decrease in the oxygen pressure was observed.

The stoichiometric reaction between 4-methylbenzyl alcohol (0.5 M) and *p*-chloranil (0.5 M) in acetonitrile (1 mL) was measured in a 10 mL pressure tube under nitrogen. At the desired time intervals a 2 μL sample was removed from the solution and analyzed directly by GLC.

The reaction of $^4Q_5PV_2Mo_{10}O_{40}$ (0.01 M) and 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (0.01 M) in acetonitrile (2 mL) was measured under argon. The increased absorption at 750 nm observed due to the reduction of $^4Q_5PV_2Mo_{10}O_{40}$ was taken as a measure of the conversion to the final absorption. The initial slope was used to measure the initial reaction rate. Similarly, a reduced polyoxometalate (0.01 M) in benzonitrile (2 mL) obtained by the addition of 2,3,5,6-tetrachloro-1,4-dihydroxybenzene (1 equiv) under argon. When no further change in the optical density was observed at 750 nm, the solution was heated to 110 °C and oxygen was added by bubbling through the solution; the decrease in the absorption was measured as a function of time. Again the slope was used to measure the initial reaction rate.

## Acknowledgements

This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities.

---

[1] a) R. Neumann, *Prog. Inorg. Chem.* **1998**, *47*, 317; b) C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev.* **1995**, *143*, 407; c) T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* **1996**, *41*, 113; d) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.

[2] R. Neumann, M. Levin, *J. Am. Chem. Soc.* **1992**, *114*, 7278.

[3] C. L. Hill, D. C. Duncan, *J. Am. Chem. Soc.* **1997**, *119*, 243.

[4] a) R. Neumann, M. Lissel, *J. Org. Chem.* **1989**, *54*, 4607; b) R. Neumann, I. Dror, *Appl. Catal. A* **1998**, *172*, 67.

[5] a) R. Neumann, M. Levin, *J. Org. Chem.* **1991**, *56*, 5707; b) K. Nakayama, M. Hamamoto, Y. Nishiyama, Y. Ishii, *Chem. Lett.* **1993**, 1699; c) M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* **1993**, *58*, 6421.

[6] a) O. A. Kholdeeva, A. V. Govin, I. V. Kozhevnikov, *React. Kinet. Catal. Lett.* **1992**, *46*, 107; b) O. A. Kholdeeva, A. V. Govin, R. A.

Maksimovskaya, I. V. Kozhevnikov, *J. Mol. Catal.* **1992**, *75*, 235; c) M. Lissel, H. Jansen van de Wal, R. Neumann, *Tetrahedron Lett.* **1992**, *33*, 1795; d) H. Orita, M. Shimizu, T. Hayakawa, K. Takehira, *React. Kinet. Catal. Lett.* **1991**, *44*, 209; e) K. I. Matveev, E. G. Zhizhina, V. F. Odyakov, *React. Kinet. Catal. Lett.* **1995**, *55*, 47; (f) R. J. J. Jansen, H. M. van Veldhuizen, H. van Bekkum, *J. Mol. Catal.* **1996**, *107*, 241.

[7] a) R. D. Gall, M. Faraj, C. L. Hill, *Inorg. Chem.* **1994**, *33*, 5015; b) R. D. Gall, C. L. Hill, J. E. Walker, *J. Catal.* **1996**, *159*, 473; c) R. D. Gall, C. L. Hill, J. E. Walker, *Chem. Mater.* **1996**, *8*, 2523. d) R. D. Gall, C. L. Hill, *J. Mol. Catal.* **1996**, *114*, 103.

[8] a) F. Cavani, F. Trifirò, *Appl. Catal. A* **1995**, *133*, 219; b) G. C. Grunewald, R. S. Drago, *J. Mol. Catal.* **1990**, *58*, 227; c) A. Hershman, D. J. Bauer, US Patent 4,264,776, **1976**; [*Chem. Abs.* **1981**, *95*, 80117]; d) D. Riley, M. Stern, J. Ebner, in *The Activation of Dioxygen and Homogenous Catalytic Oxidation* (Eds.: D. H. R. Barton, A. E. Martell, D. T. Sawyer), Plenum, New York, **1993**, p. 31.

[9] D. W. van Krevelen, *Coal: Typology, Chemistry, Physics, Constitution*, Elsevier, Amsterdam, **1961**.

[10] a) H.-D. Becker, A. B. Turner, in *The Chemistry of Quinoid Compounds, Vol 2* (Eds.: S. Patai, Z Rappoport), Wiley, New York, **1988**; b) A. Ohki, T. Nishiguchi, K. Fukuzumi, *Tetrahedron*, **1979**, *35*, 1737; c) H.-D. Becker, A. Björk, E. Adler, *J. Org. Chem.* **1980**, *45*, 1596; d) B. A. McKittrick, B. Ganem, *J. Org. Chem.* **1985**, *50*, 5897. e) A. L. Jorgenson, R. A. Nadeau, V. G. Young, W. L. Gladfelter, *J. Organomet. Chem.* **1998**, *563*, 1.

[11] H. Grennberg, K. Bergstad, J.-E. Bäckvall, *J. Mol. Catal.* **1996**, *113*, 355; b) T. Yokota, S. Fujibayashi, Y. Nishiyama, S. Sakaguchi, Y. Ishii, *J. Mol. Catal.* **1996**, *114*, 113.

[12] K. Bergstad, H. Grennberg, J.-E. Bäckvall, *Organometallics* **1998**, *17*, 45.

[13] D. Walker, J. D. Heibert, *Chem. Rev.* **1967**, *67*, 153.

[14] The *true* reaction order in **MBA** can be determined by using the method of initial rates for **MBA** at concentrations between 0.3–2 M. The reaction was first order in **MBA**. Reaction conditions: 4-methylbenzyl alcohol (0.3–2 M), *p*-chloranil (0.1 M), and $^4Q_5PV_2Mo_{10}O_{40}$ (0.014 M), in acetonitrile (5 mL), 1 atm $O_2$, 110 °C. The slope from the van't Hoff plot was 0.97, $r^2 = 0.98$.

[15] Only the initial rate was considered because since the $PV_2Mo_{10}O_{40}^{5-}$ polyoxometalate is a mixture of five different isomers with different reactivity for each isomer. The most reactive vicinal isomers are only those that are catalytically significant and the initial changes and rate define their reactivity. This question is discussed in detail in A. M. Khenkin, A. Rosenberger, R. Neumann, *J. Catal.* **1999**, *182*, 82.

[16] a) S. Liu, S. N. Shaikh, J. Zubieta, *Inorg. Chem.* **1987**, *26*, 4303; b) S. Liu, S. N. Shaikh, J. Zubieta, *Inorg. Chem.* **1988**, *27*, 3064.

[17] a) G. A. Popova, A. A. Budneva, T. V. Andrushkevich, T. V. *React. Kinet. Catal. Lett.* **1997**, *61*, 353; b) M. Misono, K. Sakata, Y. Yoneda, W. Y. Lee, in *Proc. 7th Int. Cong. Catal. Tokyo* (Eds.: T. Seiyama, K. Tanabe), Elsevier, Amsterdam, **1981**, p. 1047; c) Y. Konishi, K. Sakata, M. Misono, Y. Yoneda, *J. Catal.* **1982**, *77*, 169; d) A. M. Khenkin, A. Rosenberger, R. Neumann, *J. Catal.* **1999**, *182*, 82.

[18] J. E. Wertz, J. L. Vivo, *J. Chem. Phys.* **1955**, *23*, 2441.

[19] CV measurements were made using a silver working electrode and a silver chloride reference electrode with concentrations of 0.5 mM **TCBQ** and **POM** in 0.1 M tetrabutylammonium perchlorate in acetonitrile at a scan rate of 100 mV sec$^{-1}$.

[20] a) M. Bouquet, A. Guy, M. Lemaire, J. P. Guette, *Synth. Commun.* **1985**, *15*, 1153; b) L. Eberson, L. Jönsson, L.-G. Wistrand, *Acta Chem. Scand.* **1979**, *B33*, 413; c) H. Lee, R. G. Harvey, *J. Org. Chem.* **1983**, *48*, 749.

[21] G. A. Tsigdinos, C. J. Hallada, *Inorg. Chem.* **1968**, *7*, 437.

Received: January 21, 1999

Revsied version: August 4, 1999 [F1559]