

# Aromatization of Hydrocarbons by Oxidative Dehydrogenation Catalyzed by the Mixed Addenda Heteropoly Acid $H_5PMo_{10}V_2O_{40}$

Ronny Neumann\*

*Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel 91904*

Manfred Lissel\*

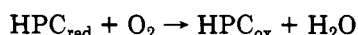
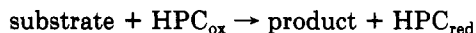
*Facultät für Chemie, Universität Bielefeld, 4800 Bielefeld 1, Federal Republic of Germany*

Received February 28, 1989

The mixed addenda heteropoly acid  $H_5PMo_{10}V_2O_{40}$  dissolved in 1,2-dichloroethane with tetraglyme, forming the (tetraglyme)<sub>3</sub>- $H_5PMo_{10}V_2O_{40}$  complex, catalyzes the aromatization of cyclic dienes at moderate temperatures in the presence of molecular oxygen. Dehydrogenations of exocyclic dienes such as limonene show that dehydrogenation is preceded by isomerization to their endocyclic isomers. Aromatization takes place by successive one-electron transfers and proton abstractions from the organic substrate to the heteropoly acid, the latter being reoxidized by dioxygen coupled with the formation of water.

## Introduction

Heteropoly acids and salts, especially those having a Keggin structure, have recently been increasingly reported as catalysts in both oxidative and acid-catalyzed transformations.<sup>1,2</sup> Heteropoly compounds as liquid-phase oxidation catalysts have been used in various systems which may be classified by the type of oxidant and whether the system has been photoactivated. One group of applications involves the use of oxidizing reagents such as hydrogen peroxide, *tert*-butyl hydroperoxide, or iodobenzene in the oxidation of alcohols, allyl alcohols, alkenes, and alkanes.<sup>3</sup> The use of molecular oxygen coupled with photochemical activation represents a second set of reactions as in the dehydrogenation of alcohols, alkenes, or alkanes.<sup>4</sup> The third area of research includes reactions where the heteropoly compound acts as an electron acceptor in what might be termed electron-transfer oxidations. In these transformations, oxidation of the substrate is achieved by successive one-electron transfers to the heteropoly anion. The reduced heteropoly compound is



reoxidized by oxygen coupled with the formation of water to complete the catalytic cycle. Substrates in the context of the above reaction may be organic molecules as in the

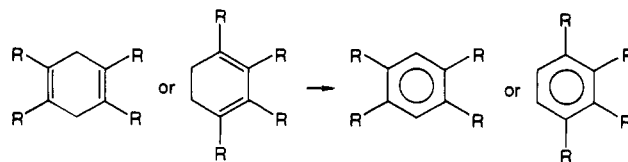
Table I. Oxidative Dehydrogenation of Hydrocarbons<sup>a</sup>

substrate	product	time, h	yield, <sup>b</sup> %
9,10-dihydroanthracene	anthracene	16	>98, 89 <sup>c</sup>
9,10-dihydroanthracene	anthracene	24	~1-2 <sup>d</sup>
9,10-dihydrophenanthrene	phenanthrene	5	>98
9,10-dihydrophenanthrene	phenanthrene	24	~1-2 <sup>d</sup>
1,2-dihydronaphthalene (75%)	naphthalene	5	>98
tetrahydronaphthalene	naphthalene	24	0
1,4-cyclohexadiene	benzene	18	>98
1,3-cyclohexadiene	benzene	6	>98
cyclohexene	benzene	24	0
4-vinyl-1-cyclohexene	ethylbenzene	24	22
limonene	<i>p</i> -cymene	20	>98, 70 <sup>c</sup>

<sup>a</sup> Reaction conditions: 5 mmol of substrate, 1 mmol of tetraglyme, 0.05 mmol of  $H_5PMo_{10}V_2O_{40}$ , 10 mL of 1,2-dichloroethane, temperature = 70 °C,  $P_{\text{oxygen}} = 1$  atm. <sup>b</sup> Yields as computed by GLC. <sup>c</sup> Isolated yields. <sup>d</sup> Reaction performed at 1 atm of nitrogen.

gas-phase dehydrogenation of aldehydes and carboxylic acids to form carbon-carbon double bonds  $\alpha$  to the functional group<sup>5</sup> or oxidation of sulfides to sulfoxides and sulfones.<sup>6</sup> In addition, substrates may be of an inorganic nature such as in the oxidation of bromide anions to molecular bromine.<sup>7</sup> The substrate may also be a primary catalyst such as Pd(0) (product is Pd(II)) in a Wacker type oxidation reaction.<sup>8</sup> Generally, the most effective catalysts for this electron-transfer type of oxidation are the mixed addenda heteropolyanions of the formula  $H_{3+n}PMo_{12-n}V_nO_{40}$ ,  $PMoV_n$ , where  $n = 2-6$ .

In this paper we describe the use of  $H_5PMo_{10}V_2O_{40}$  dissolved in an apolar organic phase to catalyze the aromatization of cyclic dienes by oxidative dehydrogenation in the presence of dioxygen. In examples where the two double bonds are not endocyclic, e.g. limonene, aromati-



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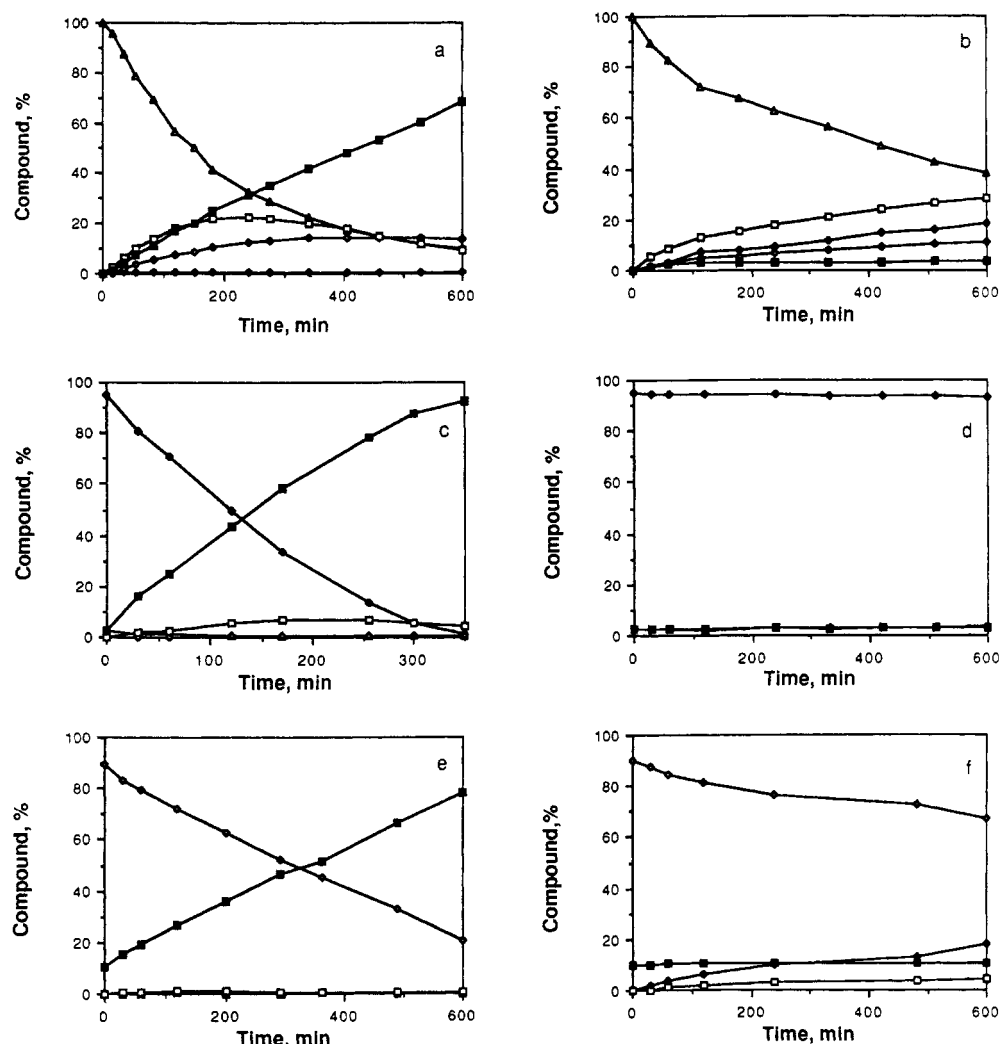
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**Figure 1.** Reaction profiles of the monoterpene dehydrogenation. Reaction conditions: 1 mmol of monoterpene substrate, 0.25 mmol of tetraglyme, 0.01 mmol of  $H_5PMo_{10}V_2O_{40}$ , 2 mL of 1,2-dichloroethane, temperature = 70 °C, dioxygen or nitrogen pressure = 1 atm. Monoterpene substrate: (a) limonene ( $O_2$ ), (b) limonene ( $N_2$ ), (c)  $\alpha$ -terpinene ( $O_2$ ), (d)  $\alpha$ -terpinene ( $N_2$ ), (e)  $\gamma$ -terpinene ( $O_2$ ), (f)  $\gamma$ -terpinene ( $N_2$ ). ( $\Delta$ ) Limonene; ( $\bullet$ )  $\alpha$ -terpinene; ( $\circ$ )  $\gamma$ -terpinene; ( $\square$ ) terpinolene; ( $\blacksquare$ ) *p*-cymene.

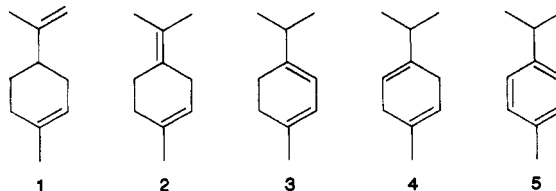
zation is preceded by double-bond isomerization to an endocyclic position.

### Results and Discussion

The reaction system for the oxidative dehydrogenation reaction consists of the substrate, the  $H_5PMo_{10}V_2O_{40}$  catalyst dissolved in the presence of tetraglyme,  $CH_3O-(CH_2CH_2O)_4CH_3$ , as complexing agent (see below), all in 1,2-dichloroethane as solvent. Reactions are typically carried out at 70 °C under 1 atm of dioxygen. The results describing the aromatization of several substrates are given in Table I. Perusal of the results leads to the following observations. First, the cyclic dienes are dehydrogenated to the corresponding aromatic derivatives whereas the cyclic monoenes and saturated compounds are inert to dehydrogenation. Second, dioxygen is essential for the catalytic cycle for there is no dehydrogenation (beyond the stoichiometric amount of catalyst) in reactions carried out under a nitrogen atmosphere. Third, the given catalyst is unable to oxygenate any substrates under the given conditions as no oxygenated products were found. This strongly indicates that dioxygen is not activated by the catalyst despite its being required for the reaction. Fourth, conjugated dienes dehydrogenate more quickly than non-conjugated dienes. From a preparative synthetic point of view this reaction enables a catalytic aromatization at mild

conditions with molecular oxygen in lieu of stoichiometric reagents such as quinones (DDQ and *p*-chloranil),<sup>9</sup> selenium, or sulfur<sup>10</sup> or a high-temperature catalytic dehydrogenation with palladium or platinum.<sup>11</sup>

Further insight into the dehydrogenation reaction is gained by more carefully investigating the dehydrogenation of several monoterpene isomers such as limonene, 1, terpinolene, 2,  $\alpha$ -terpinene, 3, and  $\gamma$ -terpinene, 4, to *p*-cymene, 5. The results of monoterpene dehydrogenation reaction

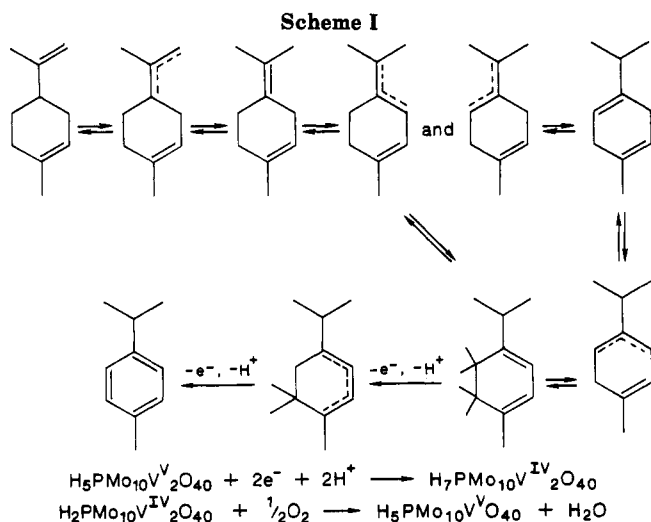


are given as reaction profiles in Figure 1. By examining the profiles one may make the following observations. As described above in the absence of dioxygen there is no dehydrogenation although isomerization of the exocyclic double bond occurs as can be seen in the isomerization of

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limonene whereas isomerization of  $\alpha$ - and  $\gamma$ -terpinene with two endocyclic double bonds is more limited.  $\alpha$ -Terpinene is more reactive than limonene or  $\gamma$ -terpinene. This is indicated both by the faster rate in Figure 1c and by its virtual absence in Figure 1, parts a and e. Another manifestation of the greater reactivity of the  $\alpha$ -terpinene is the fact that its addition at room temperature to the catalytic solution immediately yields the reduced heteropoly blue with the simultaneous formation of *p*-cymene, whereas limonene and  $\gamma$ -terpinene reduce the catalyst at higher ( $\sim 50^\circ\text{C}$ ) temperatures only. UV-vis spectra of 0.5 mM  $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{q-}$  ( $q = 5, 6, \text{ or } 7$ ) dissolved in 1,2-dichloroethane with 20 mM tetraglyme were taken after the addition of the various terpenes. Addition of  $\alpha$ -terpinene at room temperature yields a blue solution with an optical density of 0.978 ( $\epsilon = 1956$ ) at  $\lambda_{\text{max}}$  756 nm. On the other hand addition of limonene or  $\gamma$ -terpinene at  $50^\circ\text{C}$  gives a green solution with an optical density of 0.472 ( $\epsilon = 944$ ) at  $\lambda_{\text{max}}$  774 nm. Since the intensity of the intervalence charge-transfer band is proportional to the number of electrons introduced and reduction beyond the one-electron stage causes a blue shift,<sup>12</sup> it is clear that in the case of  $\alpha$ -terpinene the heteropolyanion undergoes a two-electron reduction whereas limonene or  $\gamma$ -terpinene transfer one electron.

A plausible reaction scheme that satisfactorily explains all the results above may be as represented in Scheme I. This scheme implies that the isomerization takes place through reversible electron transfer between the substrate and heteropoly compound (perhaps through a charge-transfer complex) as is indicated by the one-electron reduction of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  by both limonene and  $\gamma$ -terpinene. Alternatively, the monoterpene isomerizations could be explained by the well-known acid catalysis.<sup>13</sup> In fact, similar isomerizations of linear alkenes catalyzed by heteropoly acids have been recently reported.<sup>14</sup> However, in the past acid-catalyzed isomerization of limonene has been shown to yield in addition to polymeric tars dimethylbicyclo[3.2.1]octenes,  $\alpha$ -terpinene, *p*-menthenes, and *p*-cymene, the latter compounds being formed by intermolecular proton transfer.<sup>15</sup> We have repeated such a procedure using the conditions in the footnote of Table I with polyphosphoric acid instead of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  as

catalyst and received similar results. These results differ from the results as given in Figure 1a and point to an electron-transfer mechanism, although acid-catalyzed isomerization cannot be ruled out.

The dehydrogenation to the aromatic product is mostly through the more reactive  $\alpha$ -terpinene (Figure 1c). Support for this pathway can be found by the virtual absence of  $\alpha$ -terpinene in the dehydrogenation of limonene and  $\gamma$ -terpinene (Figure 1a,e) despite its significant but slower formation in the absence of dioxygen (Figure 1b,f). Therefore, in the dehydrogenation of limonene and  $\gamma$ -terpinene the rate-determining step is the formation of  $\alpha$ -terpinene, whereas in the  $\alpha$ -terpinene dehydrogenation it appears the rate-determining step is the heteropoly acid reoxidation, otherwise one cannot explain the formation of 5–7% terpinolene in the latter case. Based on literature precedent<sup>2a,b</sup> dehydrogenation occurs by two (as shown by the UV-vis) successive electron transfers and proton abstractions from the endocyclic diene to the heteropoly acid forming the aromatic product and the reduced heteropoly blue.<sup>16</sup> The reduced heteropoly acid is reoxidized by dioxygen with formation of water.

At the beginning of our discussion we stated that the heteropoly acid catalyst was dissolved into the 1,2-dichloroethane solvent by complexation with tetraglyme. We wish to elaborate on this point and describe the isolation of the tetraglyme- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  complex. The complexation of heteropoly acids by crown ethers<sup>17</sup> has been previously reported, so it is not surprising that an analogous linear polyether will also ligate the heteropoly acid. Thus, addition of tetraglyme to a mixture of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  and 1,2-dichloroethane solubilizes the  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ . Addition to the solution of an apolar hydrocarbon such as hexane causes precipitation of the tetraglyme- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  complex. This complex as identified by elementary analysis and  $^1\text{H}$  NMR spectroscopy (see Experimental Section) contains three tetraglyme ligands per heteropoly acid and may be formulated as (tetraglyme)<sub>3</sub>- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ . As for the  $^1\text{H}$  NMR spectra it is informative to note that the peaks of the methylene moieties were broadened (singlets were observed) and the AA'-BB' coupling expected and observed in the  $^1\text{H}$  NMR spectra of pure tetraglyme is lost. A probable explanation is the interaction of the acidic protons from  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  with the oxygen atoms of the tetraglyme causing line broadening. It may therefore, be concluded that the actual catalytic species is not the free  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  but the complexed heteropoly acid (tetraglyme)<sub>3</sub>- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ . Work is under way to crystallize this compound in order to characterize the molecular structure.

### Conclusion

A methodology has been developed for the liquid-phase catalytic oxidative dehydrogenation at moderate temperatures of cyclic dienes to the corresponding aromatic derivatives by use of (tetraglyme)<sub>3</sub>- $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  dissolved in 1,2-dichloroethane in the presence of dioxygen. Aromatization is preceded by isomerization for dienes with an exocyclic double bond.

### Experimental Section

**Materials and Instruments.** All reagents and solvents used were obtained commercially and were used without further pu-

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rification. The heteropoly acid  $H_5PMo_{10}V_2O_{40}$  was prepared by the common literature procedure.<sup>18</sup> The catalyst is in fact a hydrated mixture of stereoisomers and was identified<sup>19</sup> by its  $^{51}V$  NMR spectrum at 78.864 MHz with  $VOCl_3$  as external standard on a Bruker WH-300 spectrometer.  $\delta$  ppm (integration) -527.9 (1), -533.6 (4), -536.4 (4), and -543.2 (1). From the  $^{51}V$  NMR data there is no evidence of impurities. GLC measurements were made with a HP-5890 equipped with FID detector and helium carrier gas. Peaks were quantified by a HP-3396A integrator after calibration with known amounts of the compounds analysed. Elementary analysis were performed at the Hebrew University microanalytical center. Atomic absorption was performed using a GBC single-beam spectrometer.  $^1H$  NMR spectroscopy was performed on a Bruker WP-200-SY spectrometer.

**Typical Procedure for the Oxidative Dehydrogenation Reactions.** The heteropoly catalyst  $H_5PMo_{10}V_2O_{40}$  (0.05 mmol, 100 mg) was dissolved in 10 mL of 1,2-dichloroethane by addition tetraglyme (1.0 mmol, 220  $\mu$ L). After the solution was brought to the reaction temperature of 70 °C, the reaction substrate (5.0 mmol) was added and dioxygen was slowly bubbled through the solution. At the end of the reaction the organic phase was extracted with water to remove the catalyst and analysed by GLC. The columns used were HP-5 (cross-linked 5% phenylmethyl silicone) or cross-linked FFAP. Both columns have a column i.d.

of 530  $\mu$ m and length 10 m. Reactions on a preparative scale were performed using 10 times the amounts quoted above.

**Dehydrogenation of the Monoterpenes: Reaction Profiles.** The heteropoly catalyst  $H_5PMo_{10}V_2O_{40}$  (0.01 mmol, 20 mg) was dissolved in 2 mL of 1,2-dichloroethane by addition tetraglyme (0.25 mmol, 55  $\mu$ L) in a Wheaton reaction vial. The monoterpene substrate (1 mmol, 136 mg) was added, and the vial was closed with an air-tight Teflon septum. The reaction mixture was then purged with dioxygen (or nitrogen where applicable) and kept under 1 atm of pressure and heated to 70 °C. Reaction samples were taken at the various intervals and analyzed by GLC. The column used was a 10 m (length)  $\times$  530  $\mu$ m (i.d.) cross-linked FFAP at a column temperature of 50 °C. Retention times were limonene 1.55 min, terpinolene 2.70 min,  $\alpha$ -terpinene 1.30 min,  $\gamma$ -terpinene 2.05 min, and *p*-cymene 2.40 min. Other isomers in trace amounts were also detected. All peaks were base-line separated.

**Preparation of the (Tetraglyme)<sub>3</sub>-H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> Complex.** The heteropoly  $H_5PMo_{10}V_2O_{40}$  (0.025 mmol, 50 mg) was dissolved in 5 mL of 1,2-dichloroethane by addition of tetraglyme (1.0 mmol, 220  $\mu$ L). Hexane (5 mL) was added to the warmed solution (50 °C), and the mixture was slowly cooled. The precipitated complex was collected (yield was 40 mg, ~65%) and analyzed by elementary analysis and atomic absorption. The calculated (found) percentages for (tetraglyme)<sub>3</sub>-H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> are C, 14.98 (15.15); H, 3.06 (3.33); P, 1.29 (1.13); V, 4.23 (4.08); Mo, 39.87 (39.56). The  $^1H$  NMR spectra in  $CD_3COCD_3$  at 200 MHz:  $\delta$  3.27 (3 H, s, terminal methyl), 3.47 (2 H, broad s, terminal methylene), and 3.55 (6 H, s, internal methylene).

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