Redirection of Oxidation Reactions by a Polyoxomolybdate: Oxydehydrogenation Instead of Oxygenation of Alkanes with *tert*-Butylhydroperoxide in Acetic Acid

Alexander M. Khenkin and Ronny Neumann*

Department of Organic Chemistry
Weizmann Institute of Science, Rehovot, Israel 76100

Received September 19, 2000

Selective oxidation of alkanes remains a very difficult but very important research goal. In this context many catalysts have been described that use hydroperoxides such as *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide as oxidants for *oxygenation* of alkanes to alcohols, ketones, and other or further oxygenated products. Among the many catalytic systems looked at in this area during recent years, there may be pointed out the somewhat mechanistically controversial iron-based biomimetic systems[1] and the metal-substituted zeolite catalysts.[2] Also in the area of our present interest, various transition metal-substituted polyoxometalates have been shown to effectively catalyze oxygenation of alkanes.[3] For oxidation of alkanes with TBHP and H_2O_2 it is now well-accepted by many researchers in the field that the reaction mechanism is of a radical nature and a Haber−Weiss type mechanistic scheme may be invoked (Scheme 1, reactions 1−4).

We have now found that in the presence of a Keggin-type polyoxomolybdate, $H_3PMo_{12}O_{40}$, as catalyst, the usual pathway to oxygenated products such as ketones, alcohols, and peroxides is strongly inhibited, and instead dehydrogenated products, alkenes, are formed with high selectivity.

A reaction was typically carried out by heating a solution of 1.8 M alkane, 0.6 M TBHP (70%, 30% H_2O) and 0.03 M $H_3PMo_{12}O_{40}\cdot 24H_2O$ in acetic acid at 80 °C in *air*. Reactions under argon gave practically the same results. Depending on the alkane used, the reaction time was about 20−60 min, that is until all of the TBHP is consumed. The catalyst was unchanged under the reaction conditions as measured by ^{31}P NMR. The completion of the reaction was easily observable. In the presence of TBHP, the polyoxometalate was in the yellow oxidized form; once the TBHP was used up the green reduced polyoxometalate appeared. The results showing the selectivity to the product types and the various dehydrogenated products are summarized in Figure 1 and Table 1, respectively. From Figure 1 one may observe that for a series of cyclic alkanes, the formation of the dehydrogenated product(s) dominates with typically 90 ± 5% selectivity. The minor products were (a) oxygenates such as alcohols, ketones, and peroxides, $(CH_3)_3COO{-}R$ (RH is the cyclic alkane) and (b) esters of acetic acid which, however, were probably not formed from intermediate alcohols (see below). For compounds with cyclohexyl moieties there was some tendency for aromatization. Thus, cyclohexane, methylcyclohexane, and 1,3-dimethylcyclohexane yielded some benzene, toluene, and *m*-xylene, respectively. *cis*-Decalin gave a broader product distribution with formation mainly of octahydronaphthalene and tetralin. In general, dienes were found only in small (decalin) or trace (other examples) amounts. Most interestingly, cycloalkenes were preferably formed at the less substituted positions. Thus, decalin was not dehydrogenated at the bridging position, and in the oxidation of methylcyclohexane, 1-methylcyclohexene was a minor product compared to 3- and 4-methylcyclohexene.

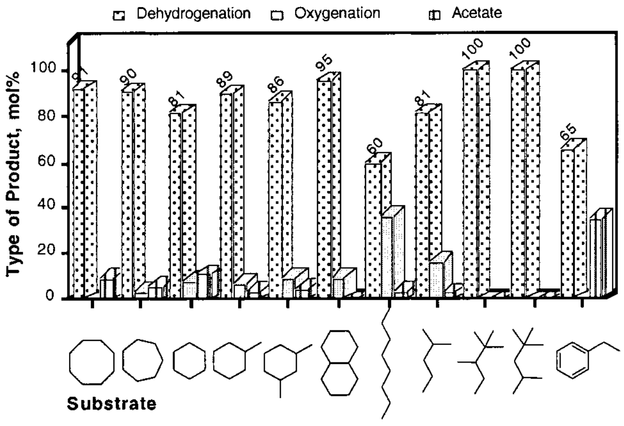
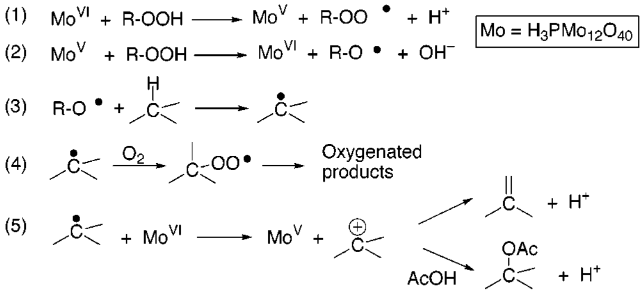


Figure 1. Type of product distribution in the oxidation of alkanes with TBHP catalyzed by $H_3PMo_{12}O_{40}$. Reaction conditions: 1.8 M alkane, 0.6 M TBHP, 0.03 M $H_3PMo_{12}O_{40}$ in acetic acid, 80 °C in air. The reaction time was 20−60 min (until all TBHP was used up). The type of product is given as mol % specific product type out of all product types. Control experiments (a) without $H_3PMo_{12}O_{40}$ the reactions were very slow, 72 h, 9% conversion, and only oxygenated products were observed. (b) In oxidation of 1.8 M cyclooctane with 0.03 M mononuclear $MoO_2(acac)_2$ the reaction was slower, 5 h, the conversion was lower, 14%, and selectively to cyclooctene was only 14%. (c) In other solvents such as acetonitrile, nitromethane and *tert*-butyl alcohol, the selectivity in cyclooctane oxidation was only ~40% to dehydrogenation, and a significant amount of epoxide was formed. Acetic acid was unique in that no epoxidation was observed.

Scheme 1. Mechanism for Formation of Alkenes and Acetates



Acylic alkanes as substrates also showed that the dehydrogenated products were dominant. The relative percentage of dehydrogenation was a function of the linearity of the alkane. Thus, as the branching of the alkane is increased, the selectivity toward dehydrogenation increased from 60% for *n*-octane to 100% for 2,2,4-trimethylpentane. It is notable, however, that this increased selectivity is at the expense of reduced yield on TBHP (Table 1). As was observed in the oxidation of cyclic alkanes, the formation of the double bond at the less substituted carbon centers was preferred. Thus, in the oxidation of 2,2,4-trimethylpentane, the terminal alkene, 2,2,4-triMe-4-pentene, was formed in 4-fold excess relative to the internal alkene, 2,2,4-triMe-3-pentene. An exemplary alkyl aromatic compound, ethylbenzene, showed only the formation of styrene and α- and *β*-phenylethyl acetate. The acetates were obtained in a ~5:1 ratio.

As noted in the literature, reactions with TBHP invariably proceed with initial formation of *tert*-butylperoxy and *tert*-

---

[1] (a) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *Acc. Chem. Res.* **1998**, *31*, 159. (b) Walling, C. *Acc. Chem. Res.* **1998**, *31*, 155.

[2] (a) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144. (b) Huybrechts, D. R. C.; De Bruycker, L.; Jacobs, P. A. *Nature* **1994**, *345*, 240.

[3] (a) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487. (b) Neumann, R.; Khenkin, A. M. *Inorg. Chem.* **1995**, *34*, 5753. (c) Cramarossa, M. R.; Forti, L.; Fedotov, M. A.; Detusheva, L. G.; Likholobov, V. A.; Kuznetsova, L. I.; Semin, G. L.; Cavani, F.; Trifiró, F. *J. Mol. Catal.* **1997**, *127*, 85. (d) Matsumoto, Y.; Asami, M.; Hashimoto, M.; Misono, M. *J. Mol. Catal.* **1996**, *114*, 161.

10.1021/ja005620e CCC: $20.00

Table 1. Distribution of Oxidative Dehydrogenation Products in the Oxidation of Alkanes with TBHP Catalyzed by $H_3PMo_{12}O_{40}$

substrate	yield[b]	distribution of dehydrogenation products, mol %[c]
cyclooctane	30	cyclooctene (>99)
cycloheptane	22	cycloheptene (>99)
cyclohexane	15	cyclohexene (94), benzene (6)
Me-cyclohexane	12	3- & 4-Me-cyclohexene[d] (83), 1-Me-cyclohexene (11), toluene (6)
1,3-diMecyclohexane	12	1,3-diMe-5-cyclohexene (91), 1,3-diMe-3 & 4-cyclohexene[c] (8), 3-xylene (2)
cis-decalin	43	octahydronaphthalene[e] (32), hexahydronaphthalene (4), tetralin (53), dehydronaphthalene (8), naphthalene (3)
octane	27	1-octene (23), 2-octene (27), 3-octene (27), 4-octene (23)
2-Me-pentane	14	2-Me-4-pentene (43), 2-Me-3-pentene (45), 2-Me-2-pentene (5), 2-Me-1-pentene (7)
2,2,3-triMe-pentane	7	2,2,3-triMe-3-pentene (50), 2,2,3-triMe-4-pentene (50)
2,2,4-triMe-pentane	4	2,2,4-triMe-4-pentene (79), 2,2,4-triMe-3-pentene (21)
ethylbenzene	6	styrene (100)

[a] Reaction conditions: 1.8 M alkane, 0.6 M TBHP, 0.03 M $H_3PMo_{12}O_{40}$ in acetic acid, 80 °C in air. The reaction time was 20−60 min (until all TBHP was used up). [b] Yield based on TBHP assuming 1 equiv needed per formation of one double bond and oxygenated product. [c] The amount of product is given as mol % specific product out of all dehydrogenated products. [d] Mixtures, the components of which were not separated by GC. [e] Dehydrogenation at the 1,2 and 3,4 positions not at the 9,10 position.

butyloxy radicals. The importance of the formation of these radicals in this case could also be demonstrated using two accepted probe reactions.[1a] Addition of an effective radical scavenger, *tert*-butylcatechol, in the oxidation of cyclooctane totally inhibited formation of any product. Also when using a probe hydroperoxide, $PhCH_2C(CH_3)_2OOH$ instead of TBHP no cyclooctane conversion was noticeable, since the corresponding tertiary alkoxy radical undergoes a very fast β-scission prior to hydrogen abstraction from cyclooctane. The initially formed *tert*-butylperoxy and *tert*-butyloxy radicals were also trapped and observed by ESR (Supporting Information) using two spin traps, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and *N*-*tert*-butyl-α-phenylnitrone (PBN). The use of DMPO allows one to differentiate between carbon- and oxygen-centered radicals. The spectrum shows that only oxygen-centered radicals were trapped. The kinetic profile of the reaction at 55 °C (Supporting Information) indicates that there was no induction period, autocatalysis, or other complex behavior.

Our explanation of these results, Scheme 1, is that first the alkyl radical is formed by reaction with the *tert*-butyloxy radical. The alkyl radical is then oxidized by electron transfer to the polyoxomolybdate to yield a carbocation.[4] The latter may then yield the alkene by loss of a proton or an acetate after nucleophilic attack by the solvent. It is clear that the capture of the alkyl radical by the polyoxomolybdate must be *very fast* because alkyl radicals react with molecular oxygen at diffusion-controlled rates. Such electron-transfer oxidation of alkyl radicals is rather unique; it has mostly been described in the past using Cu(II) salts, preferably $Cu^{II}(OAc)_2$.[5] Also, in related research Cu salts have been shown to decompose alkyl hydroperoxides in macrocycles with intramolecular formation of a double bond,[6] and TBHP in the presence of copper chelates and iron compounds have been reported to dehydrogenate *cyclooctane* with low selectivity in air.[7] It is also very worthwhile mentioning that polyoxotungstates have been shown to partially dehydrogenate photochemically formed alkyl radicals to alkenes under *anaerobic* conditions.[8] In air oxygenated products dominated.

A more complete discussion of the reaction mechanism is beyond the scope of this paper, but some initial comments that would explain the product selectivity toward the formation of less substituted alkenes is worthwhile. A competitive oxidation at 75 °C of C_6H_{12}/C_6D_{12} showed an isotope effect of $k_H/k_D = 3.5 \pm 0.3$. This would seem to indicate that the rate-determining step of the reaction is hydrogen abstraction of the alkane by the *tert*-butyloxy radical. In a substrate with 3°, 2°, or 1° H atoms, radical formation at the more substituted carbon is preferred, but perhaps not exclusive. The formation of less substituted alkenes can be explained using 2,2,4-triMe-pentane as an example.[9] A carbocation at the 4-position would lead to a 3/1 mixture of 2,2,4-triMe-4-pentene/2,2,4-triMe-3-pentene from strictly statistical considerations. However, results are skewed in consideration of the likelihood of the formation of other carbocations and their relative stability. Also, it is likely that since 3° carbocations are more stable to further reaction (alkene formation), the yield based on TBHP consumption is reduced in 2,2,4-triMe-pentane compared to that based on *n*-octane since TBHP is decomposed in a parallel reaction.

A polyoxometalate compound has been shown to catalyze an alkane to alkene oxydehydrogenation with **TBHP** as oxidant by a mechanism proposed to be a combination of *tert*-butoxy radical formation and electron transfer oxidation of an intermediate alkyl radical.

Acknowledgment. This research was supported by the Basic Research Foundation administered by the Israeli Academy of Science and Humanities. Dr. Lev Weiner is thanked for the ESR measurements.

Supporting Information Available: The ESR spectrum of the trapped radicals and the reaction profile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA005620E

---

(4) Papaconstantinou, E. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2769.

(5) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.

(6) (a) Cekovic, Z.; Green, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 3000. (b) Schreiber, S. L. *J. Am. Chem. Soc.* **1980**, *102*, 6163.

(7) (a) Barton, D. H. R.; Bévière, S. D.; Hill, D. R. *Tetrahedron* **1994**, *50*, 2665. (b) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Tetrahedron Lett.* **1993**, *34*, 567. (c) Launay, F.; Patin, H. *New J. Chem.* **1997**, *21*, 247.

(8) Renneke, R. F.; Hill, C. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1526. (b) Renneke, R. F.; Hill, C. L. *New J. Chem.* **1987**, *11*, 763. (c) Renneke, R. F.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6585.

(9) Disproportionation as an explanation for formation of less substituted alkenes is not likely under *aerobic* conditions, because relatively long-lived radicals would have to be postulated. In ref 8 such a mechanism has been proposed for anaerobic conditions, but in air there is autooxdiation.