Pergamon

Tetrahedron Letters, Vol. 37, No. 36, pp. 6487-6490, 1996
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0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01418-9

Methyltrioxorhenium Catalyzed Oxidation of Saturated and Aromatic Hydrocarbons by H_2O_2 in Air

Ulf Schuchardt,* Dalmo Mandelli and Georgiy B. Shul'pin [†]

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154,
13083-970 Campinas (São Paulo), Brazil. Fax: + (55) 192 393 805. E-mail: ulf@iqm.unicamp.br

Abstract: Alkanes (cyclohexane, cyclooctane, *n*-heptane) and aromatic compounds (benzene, toluene, and ethylbenzene) are oxidized by anhydrous H_2O_2 in MeCN in air in the presence of catalytic amounts of MTO. The reaction is accelerated by addition of pyrazine-2-carboxylic acid. Alkanes give alkyl hydroperoxides as main products, as well as alcohols and ketones. Arenes yield predominantly phenols. Copyright © 1996 Elsevier Science Ltd

The oxidation of saturated and aromatic hydrocarbons with hydrogen peroxide and molecular oxygen catalyzed by transition metal complexes is of great importance since such reactions constitute a route for the direct transformation of these compounds into valuable products (alkyl peroxides, ketones, alcohols, phenols etc.).[1] Methyltrioxorhenium (MTO) is known to catalyze H_2O_2 oxidations of olefins,[2] amines,[3] substituted benzaldehydes,[4] electron-rich arenes (*e.g.*, phenols, anisols),[5] alcohols and some alkanes containing weak *tertiary* C–H bonds.[6] No information is available on MTO-catalyzed oxidations of more inert compounds, such as cyclohexane and normal alkanes.

We report here the oxidation of inert alkanes that do not contain a *tertiary* C–H bond (cyclohexane, *n*-heptane) as well as of several relatively electron-poor arenes (benzene, toluene). Anhydrous hydrogen peroxide [7] was used in all cases and the most appropriate solvent for these oxidations was acetonitrile. As shown earlier for vanadium-catalyzed oxidations of alkanes and arenes,[8] addition of pyrazine-2-carboxylic acid (PCA) accelerates the reaction catalyzed by MTO (the optimal ratio MTO:PCA is 1:4).[9] The results of the oxidation of alkanes are summarized in Table 1.[9] The rates of uncatalyzed autooxidation of cycloalkanes are *ca.* 20 times lower; those of the reactions catalyzed only by MTO are *ca.* 3 times lower. The oxidation of *trans*-decaline also shows that PCA accelerates the oxidation of the tertiary as well as of the secundary C-H bonds by

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[†] Permanent address: *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina, 4, Moscow 117977 Russia. Fax + (7095) 938 2156, E-mail: gb@shulpin.msk.ru*

Table 1. Oxidation of Alkanes by H_2O_2 Catalyzed by MTO–PCA.[a]

Substrate	Products, mmol L^{-1}				TON [b]
	-one	*-ol*	*ROOH*		
Cyclohexane	0.55	4.89	7.18		126
Cyclooctane	3.75	4.87	20.48		291
n-heptane	*C-1*	*C-2*	*C-3*	*C-4*	134
Ketone (aldehyde)	0.21	0.16	0.45	0.20	
Alcohol	0.04	0.85	1.15	0.54	
Hydroperoxide	0.54	3.62	3.90	1.71	
Selectivity [c] C-1 : C-2 : C-3 : C-4 = 1.0 : 8.8 : 10.4 : 9.3					

[a] The ratio MTO:PCA = 1:4.
[b] Turnover number in moles of all detected products per mole of MTO.
[c] Relative normalized reactivities of hydrogen atoms at carbon atoms 1, 2, 3 and 4 taking into account the number of hydrogen atoms at each of the carbon atoms.

ca. 3 time. For *n*-heptane the total yield of oxygenated products in the uncatalyzed reaction under the same conditions is 4 times lower.

The oxidation of cyclohexane in a vessel open to air gave cyclohexanone (**1**), cyclohexanol (**2**) and cyclohexyl hydroperoxide (**3**). The last product was identified by GC-MS and its concentration was determined both *directly* by its GC peak area and by comparing the data of GC analysis of the reaction solution *before* and *after* reduction with triphenylphosphine (which quantitatively reduces ROOH to ROH).[8,10] Using a Teflon-lined stainless-steel autoclave under an atmosphere of air, the oxidation ([MTO] : [PCA] = 1 : 10) also gave **1**, **2**, and **3** (concentrations after 3 h were 0.64, 5.07, and 5.46 mmol L^{-1}, resp.). However, when the air in the autoclave was replaced by argon, the product distribution was different (concentrations of **1**, **2**, and **3** after 3 h were 0.31, 2.20, and 3.81 mmol L^{-1}, resp.) and the total concentration of oxidized products was lower. This experiment indicates that atmospheric oxygen takes part in the oxidation. On the other hand, addition of α,α'-dipyridyl to the reaction solution completely inhibits the formation of products **1**, **2**, and **3**. If aqueous 30% H_2O_2 is used almost no oxidation occurs.

Arenes are also oxidized by H_2O_2 when MTO–PCA is used as a catalyst.[9] In the case of alkylarenes products of aromatic ring hydroxylation (*o*- and *p*-isomers) are predominant (Table 2). Unsubstituted benzene is the least active compound. Thus it may be concluded that the catalytically active species exhibits strongly electrophilic character. In the absence of MTO the rates of aromatic ring hydroxylations are *ca.* 70 times less. The yield of benzaldehyde from the oxidation of toluene is 8 times less in the uncatalyzed reaction. The rates of oxidation of toluene and cyclohexane are lower when Et_4NReO_4 is used instead of MTO, but addition of PCA also accelerates the reactions.

The mechanism of the H_2O_2 oxidation of hydrocarbons catalyzed by MTO is unclear. However, one may assume that a rhenium peroxo complex [11] plays a crucial role in this process. Complexes **4** or **5** (Scheme 1) may produce radical species **6** (as has been proposed for oxidations by vanadium peroxo complexes [12]) which is capable of abstracting a H atom from the alkane, RH. The interaction of $R^{\bullet}$ with $Re^{VI}OOH$ or $Re^{VI}OH$ leads to

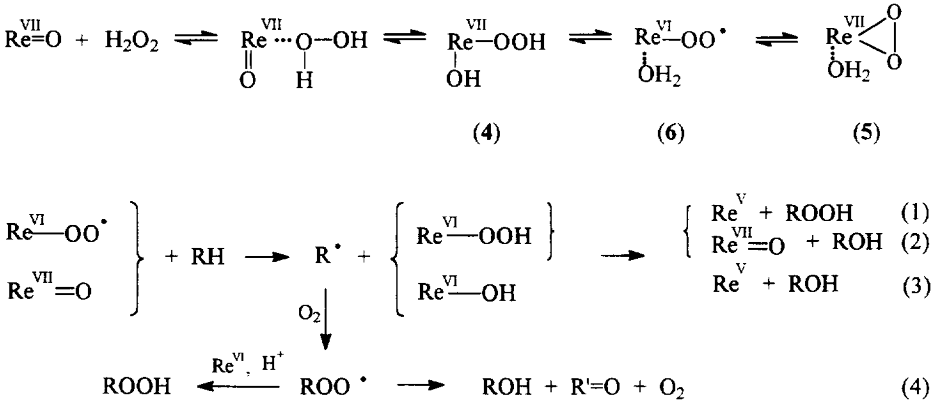
ROH (equations 2 and 3, resp.). Radicals $R^\bullet$ can also react with O_2 (eq. 4). Peroxo radicals $ROO^\bullet$ can be reduced by Re^{VI} or Re^{V}. Route (1) leading to ROOH is also possible (see [13]). In the oxidation of aromatic compounds, species **6** may add to the benzene ring with subsequent elimination of $Re^{VII}{=}O$ and formation of phenol.

Acknowledgments. This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) (grant No. 520678/94-0). One of us (G.B.Sh.) thanks CNPq (grant No. 360898/95-5) and the Instituto de Química, Universidade Estadual de Campinas (Brazil) for the invitation for a sabbatical stay during which this work was carried out. The authors are indebted to Dr. Carol Collins and Mr. Mário César Guerreiro for their help in this work.

Table 2. Oxidation of Arenes by H_2O_2 Catalyzed by MTO-PCA.

Substrate	Products (mmol L^{-1})	TON	*o* : *p* Ratio
Benzene	Phenol (3.04) Quinone (0.60)	31	-
Toluene	*o*-Cresol (9.05) *p*-Cresol (3.08) Benzaldehyde (0.50) Benzyl alcohol (1.10) Benzoic acid (0.39) Benzyl hydroperoxide (0.80)	149	74 : 26
Ethylbenzene	*p*-Ethylphenol (4.96) *o*-Ethylphenol (2.14) Acetophenone (1.06) 1-Phenylethanol (2.57) 1-Phenylethyl-hydroperoxide (5.35)	160	69 : 31

Scheme 1



REFERENCES AND NOTES

1. (a) Drago, R.S. *Coord. Chem. Rev.* **1992**, *117*, 185. (b) *Catalytic Selective Oxidation*, Oyama, S.T.; Hightower, J.W., Eds.; ACS: Washington, 1993. (c) *Catalytic Oxidations with H_2O_2 as Oxidant*; Strukul, G., Ed.; Kluwer: Dordrecht, 1992. (d) Schuchardt, U.: Carvalho, W.A.; Spinacé, E.V. *Synlett.* **1993**, 713. (e) *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Barton, D.H.R.; Martell, A.E.; Sawyer, D.T., Eds.; Plenum: New

York, 1993. (f) Crabtree, R.H. *Chem. Rev.* **1995**, *95*, 987. (g) Shilov, A.E.; Shul'pin, G.B. *Activation and Catalytic Reactions of Hydrocarbons*, Nauka: Moscow, 1995. (h) Barton, D.H.R.; Taylor, D.K. *Izv. Akad. Nauk, Ser. Khim.* **1995**, 595.

2. (a) Herrmann, W.A.; Fischer, R.W.; Rauch, M.U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (b) Adam, W.; Mitchell, C.M. *Angew. Chem.* **1996**, *108*, 578.
3. (a) Zhu, Z.; Espenson, J.H. *J. Org. Chem.* **1995**, *60*, 1326. (b) Murray, R.W.; Iyanar, K.; Chen, J.; Wearing, J.T. *Tetrahedron Lett.* **1996**, *37*, 805.
4. Yamazaki, S. *Chem. Lett.* **1995**, 127.
5. (a) Adam, W.; Herrmann, W.A.; Lin, J.; Saha-Möller, C.R. *J. Org. Chem.* **1994**, *59*, 8281. (b) Adam, W.; Herrmann, W.A.; Lin, J.; Saha-Möller, C.R.; Fischer, R.W.; Correia, J.D.G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2475. (c) Adam, W.; Herrmann, W.A.; Saha-Möller, C.R.; Shimizu, M. *J. Mol. Catal. A: Chem.* **1995**, *97*, 15. (d) Karasevich, E.I.; Nikitin, A.V.; Rubailo, V.L. *Kinetika i Kataliz*, **1994**, *35*, 878.
6. Murray, R.W.; Iyanar, K.; Chen, J.; Wearing, J.T. *Tetrahedron Lett.* **1995**, *36*, 6415.
7. A stock solution of anhydrous H_2O_2 was prepared by the following method: 20 mL of commercial 30% hydrogen peroxide (Merck, Brazil) was concentrated under vacuum to 82.6%. 2.77 g was dissolved in 63.6 mL of MeCN and anhydrous $MgSO_4$ (3 g) was added to the solution. After 3 h the solution was filtered and used in further oxidations.
8. (a) Shul'pin, G.B.; Attanasio, D.; Suber, L. *Russ. Chem. Bull.* **1993**, *42*, 55. (b) Shul'pin, G.B.; Attanasio, D.; Suber, L. *J. Catal.* **1993**, *142*, 147. (c) Shul'pin, G.B.; Druzhinina, A.N.; Nizova, G.V. *Russ. Chem. Bull.* **1993**, *42*, 1326. (d) Nizova, G.V.; Shul'pin, G.B. *Russ. Chem. Bull.* **1994**, *43*, 1146. (e) Shul'pin, G.B.; Süss-Fink, G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1459.
9. In most experiments, a solution of 0.1 mmol L^{-1} of MTO, 0.4 mmol L^{-1} of PCA, 0.47 mol L^{-1} of substrate, and 0.2 mol L^{-1} of H_2O_2 in acetonitrile [7] was refluxed (80 °C) in air during 6 h. The reaction solution was analyzed by GC (each sample was analyzed twice, *i.e.* before and after the addition of an excess of solid triphenylphosphine, see [8, 10]). For the analysis, a Hewlett Packard Series II 5890 gas chromatograph equipped with a FID and outfitted with Carbowax 20M, 25 m × 0.2 mm × 0.2 μm film thickness or 100% dimethylpolysiloxane, 25 m × 0.2 × 0.33 μm columns was used. The carrier gas was helium. A Shimadzu CR3A integrator was employed. For the identification of the peaks by GC-MS, a Shimadzu GC-17A-QP 5000 instrument was used (INNOWAX, 25 m × 0.2 mm × 0.4 μm). All peaks were attributed by comparison of their MS with those from the Wiley 139 Database library.
10. (a) Shul'pin, G.B.; Nizova, G.V. *Mendeleev Commun.* **1995**, 143. (b) Shul'pin, G.B.; Bochkova, M.M.; Nizova, G.V. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1465. (c) Shul'pin, G.B.; Nizova, G.V.; Kozlov, Yu.N. *New J. Chem.* **1996**, in press. (d) Guerreiro, M.C.; Schuchardt, U.; Shul'pin, G.B. to be published.
11. (a) Herrmann, W.A.; Fischer, R.W., Rauch, M.U.; Scherer, W. *Angew. Chem.* **1993**, *105*, 1209. (b) Herrmann, W.A.; Fischer, R.W., Rauch, M.U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (c) Pestovsky, O.; van Eldik, R.; Huston, P.; Espenson, J.H. *J. Chem. Soc., Dalton Trans.* **1995**, 133.
12. Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.
13. Shul'pin, G.B.; Druzhinina, A.N.; Shul'pina, L.S. *Neftekhimiya* **1993**, *33*, 335.

(*Received in USA* 13 *June* 1996; *revised* 15 *July* 1996; *accepted* 17 *July* 1996)