Alkane oxidation with manganese substituted polyoxometalates in aqueous media with ozone and the intermediacy of manganese ozonide species

Ronny Neumann*† and Alexander M. Khenkin

Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Manganese substituted polyoxometalates (POMs), such as $Li_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$ were effective catalysts for the oxidation of alkanes to ketones with ozone in an aqueous reaction medium; a green intermediate compound observable by UV–VIS and ESR at −78 °C was postulated to be a reactive manganese ozonide species.

Transition metal substituted polyoxometalates have been studied as oxidatively resistant analogues of metalloporphyrins. The difference between the porphyrin ligand and the oxotungstate ligands when using peroxygen compounds is considerable because with polyoxometalates reaction can occur both at the transition metal center and the tungstate sites.[1] However, ‘metalloporphyrin type’ formation of stable Cr(v)=O species[2] and manganese catalyzed oxidation of alkenes has been observed using iodosylbenzene as oxidant.[3] A ruthenium substituted polyoxometalate has also been shown to activate dioxygen in a manner similar to a ruthenium porphyrin system.[4] Ozone is an environmentally benign (dioxygen is the co-product), single oxygen donor. The bond cleavage of alkenes with ozone[5] and the facile deactivation of organic ligands such as porphyrins[6] preclude the use of ozone for catalytic epoxidation of alkenes. The oxidative stability of polyoxometalates now presents an ideal opportunity for investigating the oxidation of alkanes with ozone catalyzed by manganese substituted polyoxometalates.

Catalysis with transition metal substituted polyoxometalates is commonly practiced by transferring the polyoxoanion into an organic solvent using a quaternary ammonium cation. With ozone such an approach is unacceptable due to self-oxidation of the counter cation. Use of lithium cations and 40–50% *t*-butyl alcohol–water allows formation of a neutral homogeneous reaction medium. Typically, 10 µmol $Li_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$ was dissolved in 2.5 mL 40% *t*-BuOH–water and 1 mmol substrate was added. The mixture was cooled to ≈ 2 °C and ozone as 2.5 mol% O_3/O_2 was bubbled at 30 mmol O_3 h^{-1} through the solution for 45 min. Ethylbenzene, 82 mol% conversion, yielded acetophenone (major product, ≈ 85 mol%) and 1-phenylethanol (minor product, ≈ 15 mol%). Conversion for a control reaction without catalyst was 15 mol% with similar selectivities. Other manganese containing polyoxometalates such as $K_5PMn^{II}W_{11}O_{39}$, $K_6SiMn^{II}W_{11}O_{39}$, $K_6H_6SiMn^{II}_2W_{10}O_{40}$ and $K_{10}[Mn_4(PW_9O_{34})_2]$ gave (based on manganese equivalents) similar (±3 mol%) conversions in 50% *t*-BuOH–water. All other polyoxometalates, $K_x[M_2ZnW(ZnW_9O_{34})_2]$ or $K_xSiMW_{11}O_{39}$, with M = Zn^{2+}, Co^{2+}, Cu^{2+}, Ru^{3+}, Cr^{3+} or Fe^{3+} showed essentially *no* catalytic activity. The reaction was general for alkylaromatics, and cyclic and acyclic alkanes as may be observed in Table 1. The reactivity was as expected, *i.e.* alkylaromatics > cyclic alkanes > acyclic alkanes. The selectivity of the oxidation to ketones as the major product is contrary to what has been observed in manganese porphyrin hydroxylations with ozone where 1-phenylethanol is the major product in ethylbenzene oxidation.[6,7] Also notable is the carbon–carbon bond scission in cumene. Oxidation of cyclohexanol yielded only 20% cyclohexanone under identical reaction conditions and both cumyl alcohol and *tert*-butyl alcohol were (< 1% conversion) inert. These results indicate that alcohols were not intermediate products.

Table 1 Oxidation of alkanes with ozone catalyzed by $Li_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$ in 40% *t*-BuOH–water[a]

Substrate	Product, mol%	Conversion, mol%
Ethylbenzene	Acetophenone, 85 1-Phenylethanol, 15	82 (15)
Diphenylmethane	Benzophenone, > 98	62
Tetrahydronapthalene	α and β-Tetralone,[b] > 98	56
Cumene	Acetophenone, > 98	38
Cyclohexane	Cyclohexanone, > 98	41
Cyclooctane	Cyclooctanone, > 98	38
n-Decane	2-, 3-, 4- and 5-Decanone,[b] > 98	28

[a] Reaction conditions: 1 mmol substrate, 10 µmol $Li_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$, 2.5 mL 40% *t*-BuOH–water, 45 min, 2 °C. [b] The amounts of ketone were not quantified.

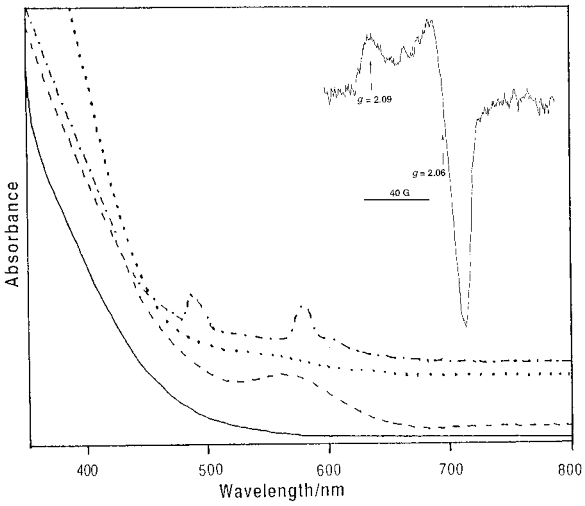
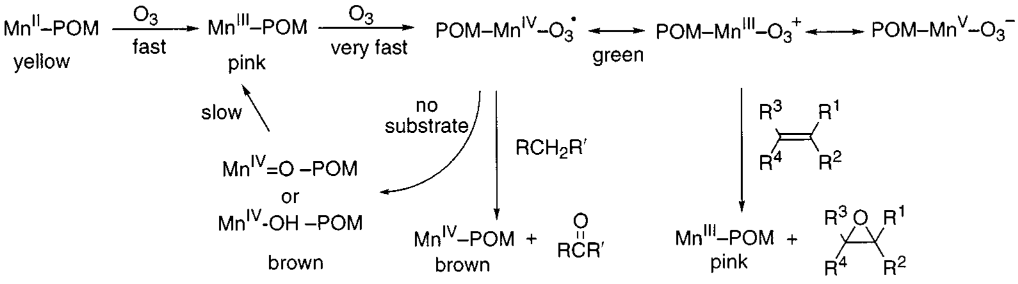


Fig. 1 UV–VIS spectra of various $[Mn_2ZnW(ZnW_9O_{34})_2]^{q-}$ species and the ESR spectrum of the active species. (a) —— $[Mn^{II}_2ZnW(ZnW_9O_{34})_2]^{12-}$, (b) - - - - $[Mn^{III}_2ZnW(ZnW_9O_{34})_2]^{10-}$, (c) ····· brown manganese(v) species, (d) -·-·- green manganese(v)–oxo species. The concentration of $[Mn_2ZnW(ZnW_9O_{34})_2]^{q-}$ was 5 × 10^{-4} M and the UV–VIS spectra are slightly offset for clarity. Spectra (a) and (b) were taken at ambient temperature, (c) was taken at 2 °C and (d) was taken immediately after removal from −78 °C using a diode array spectrometer. In (d), the optical density is a superposition of the light scattering because of condensation of water on the cuvette and the absorption from the manganese polyoxometalate. The peaks are distorted resulting in a truncated (from the bottom) appearance and with narrow peak widths. The ESR spectrum was taken at 120 K after purging the ozone with N_2.

The reactivity of alkanes was further probed by oxidation of *cis*-decalin. Oxidation at the tertiary position yielded a *trans*-decalol–*cis*-decalol ratio of ≈ 4 : 1 for both the catalysed and non-catalysed reaction.[8] Oxidation of 1 : 1 cyclohexane–cyclo-



Scheme 1

hexane-d_{12} gave a low kinetic isotope effect (KIE), $k_H/k_D = 1.2$.[9] The findings that cumene selectively formed acetophenone, *cis*-decalin gave *trans*-decalol as the major product and the low KIE in the oxidation of C_6H_{12}–C_6D_{12} all point to an alkyl radical intermediate in the oxidation of alkanes.

The reaction mechanism was further studied by UV–VIS, Fig. 1. The original catalyst, $Li_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$, is yellow. Upon addition of ozone at 2 °C, the solution within a minute turns pink, (Mn^{III}) $\lambda_{max} = 560$ nm, as is known for $[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$.[9–10] Further addition of ozone turns the solution brown forming a Mn^{IV}–oxo compound.[11] The later was inactive in a stoichiometric reaction with alkenes.[11] The brown compound was not stable slowly reverting within an hour to the pink manganese(III). In a further experiment, a solution of $Q_{12}[Mn^{II}_2ZnW(ZnW_9O_{34})_2]$ (Q = trioctylmethyl ammonium) in acetone was cooled to −78 °C and ozone was passed through the solution yielding a green solution, $\lambda_{max} = 486, 580$ nm, Fig. 1(d). Further characterization of the green solution by ESR, Fig. 1 (inset), showed an anisotropic spectrum with peaks at $g_{\parallel} = 2.09$ and $g_{\perp} = 2.06$.

After purging the solution of excess ozone with N_2, stoichiometric amounts of alkenes were added. The solution was brought to −40 °C and turned pink after a few minutes. 2,3-Dimethyl-2-butene and cyclooctene, 80 and 63% conversion respectively, reacted selectively to give epoxides as sole products whereas norbornene (74% conversion) gave 94% *exo* epoxide and 6% 2-norbornanone. *cis*-Stilbene was epoxidized 95% stereoselectively with no formation of the cleavage product, benzaldehyde. An identical experiment carried out with stoichiometric addition of ethylbenzene gave a darkish brown solution and yielded (28 mol% based on manganese) acetophenone–1-phenylethanol, $\approx 20:1$.

Our interpretation of the results of the catalytic and stoichiometric oxidation reactions, and the UV–VIS and ESR spectra is summarized in Scheme 1. The initial yellow Mn^{II}–POM is first oxidized to the pink Mn^{III}–POM. The catalytic cycle begins by reaction of Mn^{III}–POM with ozone to give the stipulated active intermediate, the green manganese species. Based on the spectra and the reactivity profile, we assign the green compound as a manganese ozonide complex. The ESR spectrum is attributable to an anisotropic oxygen centered radical species[12] formulated here as POM–Mn^{IV}–O–O–O$^{\bullet}$, formed by reaction of Mn^{III}–POM and O_3. Other canonical forms, POM–Mn^{III}–O–O–O^+ or POM–Mn^V–O–O–O^- are possible. The UV–VIS spectrum is supportive of this assignment, since peaks at 450–480 nm are typically observed for ozonides.[12] In the absence of a substrate and/or at higher temperatures the compound quickly decays by reduction or disproportionation to a brown manganese(IV) oxo or hydroxy species (a typical ESR spectrum with peaks at $g = 2$ and 4 was also observed)[11] and then more slowly to Mn^{III}–POM. The formulation of the green species as an ozonide is consistent with the oxidation reaction profiles observed. In alkane oxidation non-catalytic and catalytic reactions showed practically identical selectivity with a preponderance of the ketones as products, a low KIE, formation of acetophenone from cumene and the formation of an equilibrium mixture of *trans*-decalol–*cis*-decalol from *cis*-decalin. This reactivity clearly supports a reaction occuring through a free alkyl radical intermediate[13] as opposed to a oxygen-rebound mechanism often invoked in metalloporphyrin oxidation.[14] Epoxidation of alkenes with retention of stereochemistry is explainable through reaction of the ozonide, POM–Mn^{III}–O–O–O^+ canonical form, as an electrophile with the nucleophilic alkene with co-formation of molecular oxygen and Mn^{III}–POM.

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

Notes and References

† E-mail: ronny@vms.huji.ac.il

1 R. Neumann and M. Gara, *J. Am. Chem. Soc.*, 1995, **117**, 5066.
2 D. E. Katsoulis and M. T. Pope, *J. Chem. Soc., Chem. Commun.*, 1986, 1186; A. M. Khenkin and C. L. Hill, *J. Am. Chem. Soc.*, 1993, **115**, 8178.
3 C. L. Hill and R. B. Brown, *J. Am. Chem. Soc.*, 1986, **108**, 536; D. Mansuy, J.-F. Bartoli, P. Battioni, D. K. Lyon and R. G. Finke, *J. Am. Chem. Soc.*, 1991, **113**, 7222.
4 R. Neumann and M. Dahan, *Nature*, 1997, **388**, 353.
5 P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978.
6 S. Camperstrini, A. Robert and B. Meunier, *J. Org. Chem.*, 1991, **56**, 3725; Z. Gross, S. Nimri and L. Simkhovich, *J. Mol. Catal. A: Chem.*, 1996, **113**, 231; Z. Gross and L. Simkhovich, *J. Mol. Catal. A: Chem.*, 1997, **117**, 243.
7 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
8 J. R. Lindsay Smith and P. R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1165.
9 J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 6243.
10 C. M. Tourné, G. F. Tourné and F. Zonnevijlle, *J. Chem. Soc., Dalton Trans.*, 1991, 143.
11 X. Zhang, M. T. Pope, M. R. Chance and G. B. Jameson, *Polyhedron*, 1995, **14**, 1381; X. Zhang, G. B. Jameson, C. J. O'Connor and M. T. Pope, *Polyhedron*, 1996, **15**, 917; X. Zhang, C. J. O'Connor, J. B. Jameson and M. T. Pope, *Inorg. Chem.*, 1996, **35**, 30; X. Zhang and M. T. Pope, *J. Mol. Catal. A: Chem.*, 1996, **114**, 201.
12 S. Schlick, *J. Chem. Phys.*, 1972, **56**, 654; J. Steffen, W. Hesse, M. Jansen and D. Reinen, *Inorg. Chem.*, 1991, **30**, 1923; W. Hesse, M. Jansen and W. Schnick, *Prog. Solid State Chem.*, 1989, **19**, 47.
13 E. T. Denisov and T. G. Denisova, *Kinet. Catal.* (*Engl. Transl.*), 1996, **37**, 46.
14 J. T. Groves, *J. Chem. Educ.*, 1985, **62**, 928.

Received in Cambridge, UK, 10th June 1998; 8/04396E