Polyoxometalates

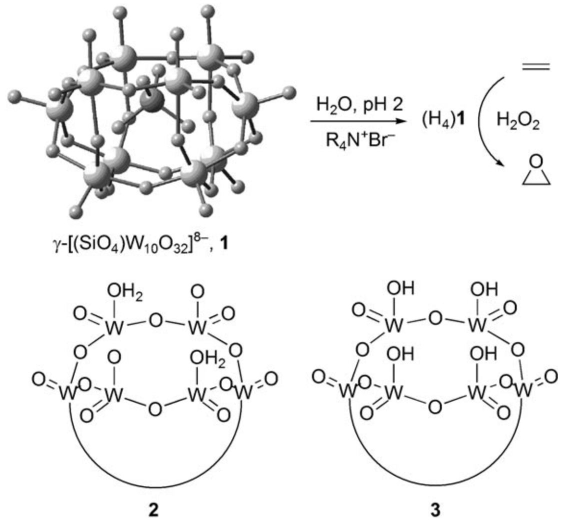
DOI: 10.1002/anie.200605120

Asymmetric Tetraprotonation of γ-[$(SiO_4)W_{10}O_{32}]^{8-}$ Triggers a Catalytic Epoxidation Reaction: Perspectives in the Assignment of the Active Catalyst**

Andrea Sartorel, Mauro Carraro, Alessandro Bagno, Gianfranco Scorrano, and Marcella Bonchio**

Polyoxometalates (POMs) are an inorganic alternative to classical transition-metal complexes. Their structural and solution chemistry is pivotal in the design of catalytically active sites with redox and acidic properties that can be tuned at the molecular level.[1,2] POMs with γ-Keggin decatungstosilicate structures catalyze the epoxidation of both terminal and internal double bonds, with quantitative conversion of H_2O_2, high regioselectivity, unique stereospecificity, and fast reaction times.[3,4] Since the first report on this epoxidation,[3] general consensus has emerged on the key role played by a reactive structural defect or "lacuna" on the POM surface.[3–5] The divacant complex γ-$[SiW_{10}O_{36}]^{8-}$ (**1**) features a tetraoxygenated lacunary site that is bordered with four W^{VI} atoms,[6] which are prone to H_2O_2 coordination.[5b,7] Moreover, the catalytic activity of **1** was found to be triggered by protonation.[3]

The active catalyst was isolated within a narrow pH range, and exhibited the highest reactivity when precipitated at pH 2 as the tetraalkylammonium salt (Scheme 1).[3] The generally accepted formulation envisaged a tetraprotonated complex, (H_4)**1** and a solid-state and solution structure with C_2 symmetry.[3] Notably, elongation of only two of the four W–O bonds at the lacunary site occurred upon protonation, with a difference in bond length $\Delta r(\text{W–O}_{\text{lacuna}})$ of 0.43 Å.[3] This is likely a key feature of the mechanism of catalysis that may affect the formation and reactivity of the active tungsten peroxide, and therefore access to fast and selective oxygen transfer. The distribution of the four protons on the lacunary site is a matter of current debate.[3,5] A bisaquo–bisoxo complex **2** or a tetrahydroxy isomer **3** have been considered (Scheme 1).[3,5] In the former case, regioselective double protonation of only two oxo groups of **1** leads to a localization of water molecules that are coordinated to the POM lacuna.[3] The second proposal stems from computational and Brønsted acidity studies that support the monoprotonation of all lacunary oxygen sites and the formation of four terminal hydroxo ligands.[5] However, the calculated geometry of **3** does not provide a conclusive description of the experimental structure, thus further attention is required.[5a]



Scheme 1. Synthesis of catalyst (H_4)**1** and schematic representation of the lacunary site in the postulated isomers **2** and **3**.

We present herein a combined kinetic, spectroscopic, and computational study to address the electronic and structural factors that dictate the protonation sites and equilibria of **1**, as well as their impact on the catalysis.

In the epoxidation of *cis*-cyclooctene catalyzed by (H_4)**1**, the turnover frequency (TOF) drops linearly upon addition of the first two equivalents of $(n\text{Bu}_4\text{N})\text{OH}$, then levels off to a plateau value (Figure 1). This result points out the major role in the promotion of oxygen transfer played by only two of the four acidic protons on the POM surface.

Therefore, the acid/base behavior of the catalyst in dimethyl sulfoxide (DMSO) was monitored to follow catalyst speciation. The ^{183}W NMR spectrum of (H_4)**1** exhibits five signals with equal intensity, which indicates a C_2 solution structure under slow proton-exchange conditions that is compatible with both **2** and **3**.[8] Titration of (H_4)**1** with

---

[*] Dr. A. Sartorel, Dr. M. Carraro, Prof. A. Bagno, Prof. G. Scorrano, Dr. M. Bonchio
ITM-CNR and Dipartimento di Scienze Chimiche
Università degli Studi di Padova
via Marzolo 1, 35131 Padova (Italy)
Fax: (+39) 049-827-5239
E-mail: a.sartorel@itm.cnr.it
marcella.bonchio@unipd.it

[**] Financial support from CNR, MIUR (FIRB CAMERE-RBNE03JCR5), the University of Padova (Progetto di Ricerca di Ateneo CPDA045589), and the ESF COST D26, D29 actions are gratefully acknowledged. The Cartesian coordinates of the X-ray structure of γ-$[(SiO_4)W_{10}O_{32}]^{8-}$ were provided by Prof. N. Mizuno.

Supporting information (full experimental procedures, computational methods, spectroscopic data (^{29}Si, ^{183}W, ^{1}H NMR, FTIR), oxidation kinetics, calculated geometries, energies and MEP surfaces) for this article is available on the WWW under http://www.angewandte.org or from the author.

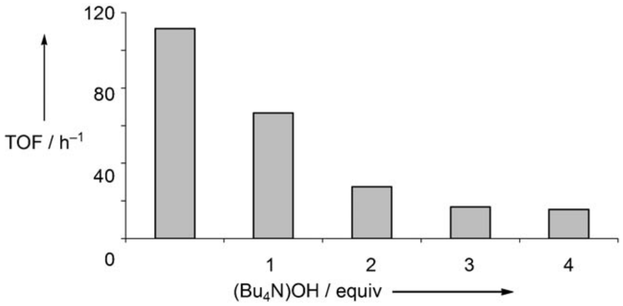


Figure 1. Dependence of the turnover frequency (TOF) of the epoxidation of *cis*-cyclooctene by (H_4)**1** and H_2O_2 upon titration with $(nBu_4N)OH$.

$(nBu_4N)OH$ causes the spectroscopic changes outlined in Figure 2. Addition of the first equivalent of base yields ten distinct resonance signals as expected for a nonsymmetric (H_3)**1** species under slow proton-exchange conditions. With a second equivalent of base, a C_{2v} structure ((H_2)**1**, three signals) is attained, which implies a fast exchange between the remaining protons if located on the lacunary site (see below). The NMR spectrum is not substantially modified by further additions of base.[9] Thus, the results from the NMR spectroscopic studies indicate that only two protons of (H_4)**1** are sufficiently acidic to be abstracted by $(nBu_4N)OH$, which accounts for the plateau of Figure 1.

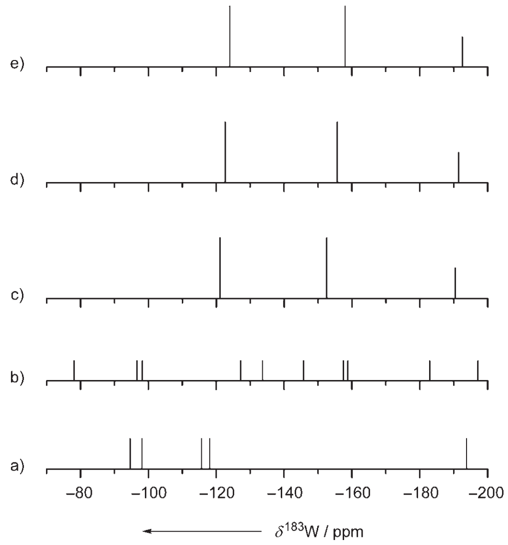


Figure 2. ^{183}W NMR spectra upon titration of (H_4)**1** (0.10 M) with $(nBu_4N)OH$ in DMSO at 25 °C; base added: a) 0 equiv, b) 1 equiv, c) 2 equiv, d) 3 equiv, e) 4 equiv.

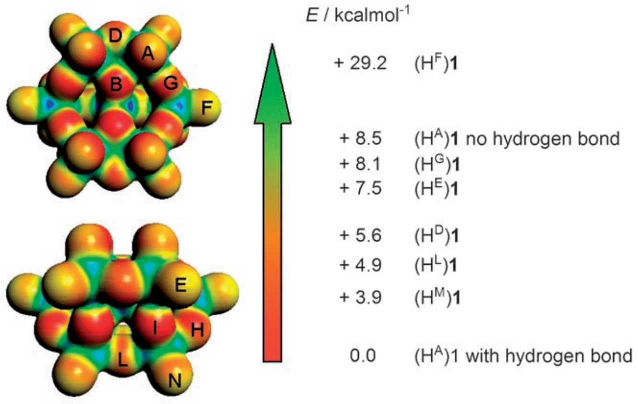


Figure 3. Calculated electrostatic potential surface of **1** (top and side views) and relative energies of selected monoprotonated isomers (H^X)**1** (X = A–N). Red and blue regions indicate negative and positive potential, respectively. Viable protonation sites are indicated with the letters A–N and include terminal W–O (A, E, F, N), bridging W–O–W (D, G, H, I, L, M), and Si–O (B) groups.

The location of these protons has been addressed by relativistic DFT calculations which included solvent effects.[10] The basicity of the oxygen sites of **1** was initially estimated in relation to their relative charge and the molecular electrostatic potential (MEP) surface (Figure 3). Inspection of the MEP surface and relative energies of the isomeric monoacids (H^X)**1** (X = A–N), indicates that the bridging oxygen atoms are the most favorable protonation sites compared with the terminal and lacunary oxygen atoms.[2,11]

While the low basicity of the lacunary site (O^A) apparently rules out its involvement in protonation equilibria, a completely reversed scenario is obtained when the geometry of (H^A)**1** is optimized to accommodate an intramolecular hydrogen bond. The formation of one hydrogen bond between two adjacent lacunary oxygen atoms provides a stabilization energy of 8.5 kcal mol^{-1} (Figure 3) which renders O^A the most favorable protonation site. Despite the polyanionic nature of **1**, such a value falls in the typical range for a neutral donor/acceptor hydrogen bond,[11] which is consistent with the low negative charge on the participating lacunary oxygen atoms.[12] This observation highlights the key role played by the strength and directionality of the hydrogen bond in the POM lacuna. Indeed, a second intramolecular hydrogen bond between the lacunary oxygen atoms ((H_2)**1**, Figure 4) involves an almost equal gain in energy, despite the former protonation on the vicinal site. The calculated structure of (H_2)**1** provides a basis with which to address the controversial assignment of the tetraprotonated isomers **2** and **3**.[3,5,13]

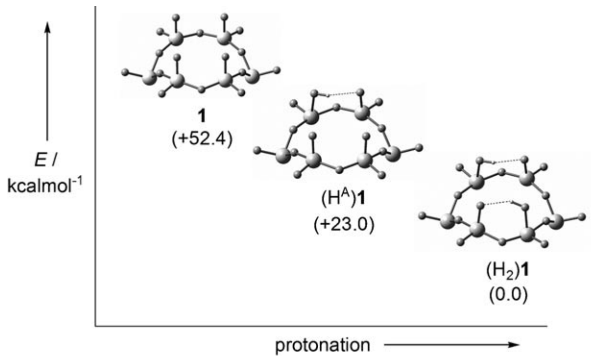


Figure 4. Calculated energies of hydrogen-bond formation for two sequential protonation steps in the lacunary site of **1**.

Inspection of the MEPs for $(H_2)\mathbf{1}$ (see the Supporting Information) shows that the monoprotonated lacunary oxygen atoms (HO^A) still retain significant electron density which does not prevent a regioselective double protonation of each site to form **2**.

The geometries and energies of both postulated isomers **2** and **3** were assessed at different computational levels, either with a hybrid density functional (B3LYP), an augmented ECP Gaussian basis set and the PCM solvent model, followed by single-point energy calculation with a larger basis,[5] or with scalar relativistic effects at the B3LYP-ZORA level with Slater basis sets and the COSMO solvent model (Table 1; see the Supporting Information for details). Thus, we have used the most sophisticated computational tools viable for a system of this size.

Table 1: Calculated relative energies and bond lengths of structures **2** and **3**.

Calculation protocol[a]	$E(\mathbf{2})-E(\mathbf{3})$ [kcal mol^{-1}][b]	Δr(W−O$_{lacuna}$) (**2**) [Å][c]	Δr(W−O$_{lacuna}$) (**3**) [Å][c]
ZORA-BP86/S-I// ZORA-BP86/S-I	−4.66	0.58	0.06
B3LYP/G-II// B3LYP/G-I	−2.90	0.38	0.08
ZORA-B3LYP/S-I// B3LYP/G-I	+1.14	0.38	0.08
ZORA-B3LYP/S-II// B3LYP/G-I	+0.63	0.38	0.08

[a] All calculations include solvent effects (see the Supporting Information). [b] Absolute energies are reported in the Supporting Information. [c] Experimental Δr(W−O$_{lacuna}$) = 0.43 Å, see text.

The resulting energies of **2** and **3** are so close, as to be very sensitive to the combination of method/basis set adopted, with the energy gap $E(\mathbf{2})-E(\mathbf{3})$ between −5 and +1 kcal mol^{-1}. However, the optimized geometry of **2** fits better with the X-ray structure.[3,5] In all cases, modeling of **2** gave a calculated Δr(W−O$_{lacuna}$) value in the range 0.58–0.38 Å, which closely matches the experimental value of 0.43 Å. Conversely, a substantial deviation is obtained in the case of **3** (Δr(W−O$_{lacuna}$) < 0.10 Å, Table 1). Furthermore, the calculated structure of **2** reproduces the well-known Pfeiffer effect, whereby nonsymmetric protonation of alternate MO_6 octahedra leads to a chiral distortion of the polyanion.[14] This effect results in an alternate sequence of long and short *trans* O−W−O bond lengths,[14] as observed theoretically (PCM-B3LYP/G-I level) and experimentally along the two sequences O1−W1−O3−W3−O5 and O2−W2−O4−W4−O6, highlighted in Figure 5, to give respectively (experimental distances in brackets): 2.16 (2.16), 1.84 (1.82), 2.03 (2.05), 1.87 (1.85) and 1.79 (1.72), 2.13 (2.20), 1.83 (1.79), 2.05 (2.08) Å. Such structural analysis speaks in favor of **2** as the active epoxidation catalyst.

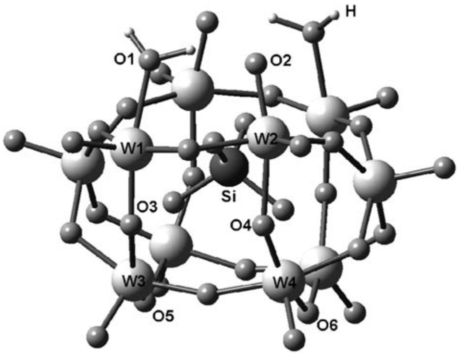


Figure 5. Calculated optimized structure of **2** at the PCM-B3LYP/G-I level.

In conclusion, the structure **2** explains the solution behavior of the competent catalyst with this evidence:

- The calculated relative energies (kcal mol^{-1}) along the protonation pathway to **2** are in the order: **1** (58.6), $(H^A)\mathbf{1}$ (29.2), $(H_2)\mathbf{1}$ (6.2), $(H_3)\mathbf{1}$ (−1.8), **2** (0), and support the different acidity of the two types of protons that is dictated by the intramolecular hydrogen bonds.
- The fast catalysis with **2** is probably aided by the two W−OH_2 functions which carry an incipient leaving group, thus fostering ligand exchange within the coordination sphere of each independent catalytic site.[7,15,16]
- The switch to a fast proton-exchange regime observed upon deprotonation of **2** may be attributable to the release of the Pfeiffer compression,[14] which alters the *trans* push/pull effect along the POM skeleton, thus modifying the hydrogen-bond-donor/acceptor properties of lacunary W−O sites.

POMs provide discrete, homogeneous models of solid metal–oxides and therefore the interplay of a spectroscopic/computational approach, as outlined in this study, has a great potential to gain new insight into the structural and mechanistic effects induced by multiple proton transfer on extended inorganic surfaces.

Received: December 19, 2006
Revised: January 30, 2007

Keywords: density functional calculations · epoxidation · homogeneous catalysis · polyoxometalates · tungsten

---

[1] *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T.Yamase, M. Pope), Kluwer Academic, Plenum Publishers, New York, **2002**, pp. 1–232.
[2] J. M. Poblet, X. López, C. Bo, *Chem. Soc. Rev.* **2003**, *32*, 297–308.
[3] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964–966.
[4] M. Carraro, L. Sandei, A. Sartorel, G. Scorrano, M. Bonchio, *Org. Lett.* **2006**, *8*, 3671–3674.
[5] a) D. G. Musaev, K. Morokuma, Y. V. Geletii, C. L. Hill, *Inorg. Chem.* **2004**, *43*, 7702–7708; b) R. Prabhakar, K. Morokuma, C. L. Hill, D. G. Musaev, *Inorg. Chem.* **2006**, *45*, 5703–5709.
[6] J. Canny, A. Tézé, R. Thouvenot, G. Hervé, *Inorg. Chem.* **1986**, *25*, 2114–2119.
[7] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, *Chem. Eur. J.* **2007**, *13*, 639–648.

[8] In the optimized structure of **3**, hydrogen bonding between the four terminal hydroxo ligands leads to overall C_2 symmetry. ^{1}H NMR resonances at $\delta = 7.36$ and 6.72 ppm can be assigned to non-equivalent protons on the POM surface. The slow-exchange behavior was confirmed by variable-temperature NMR experiments (see the Supporting Information, Figure S4) and was not modified by addition of water. On titration with base (2 equiv), the signal at $\delta = 7.36$ ppm disappears (Figure S5).

[9] ^{29}Si NMR and by FTIR spectroscopy provide direct evidence of the POM integrity on titration with base (see the Supporting Information, Figures S6 and S8).

[10] a) A. Bagno, M. Bonchio, *Angew. Chem.* **2005**, *117*, 2059–2062; *Angew. Chem. Int. Ed.* **2005**, *44*, 2023–2026; ; b) A. Bagno, M. Bonchio, J. Autschbach, *Chem. Eur. J.* **2006**, *12*, 8460–8471.

[11] F. Hibbert, J. Emsley, *Adv. Phys. Org. Chem.* **1990**, *26*, 255–379.

[12] a) X. López, C. Bo, J. M. Poblet, *J. Am. Chem. Soc.* **2002**, *124*, 12574–12582; b) D. Laurencin, R. Villanneau, H. Gerard, A. Proust, *J. Phys. Chem. A* **2006**, *110*, 6345–6355.

[13] Higher energies were found for other (H_4)**1** isomers (see the Supporting Information, Table S2)).

[14] a) M. T. Pope, *Inorg. Chem.* **1976**, *15*, 2008–2010; b) J. F. Garvey, M. T. Pope, *Inorg. Chem.* **1978**, *17*, 1115–1118; c) U. Kortz, S. S. Hamzeh, N. A. Nasser, *Chem. Eur. J.* **2003**, *9*, 2945–2952.

[15] J. O. Edwards, *Inorganic Reaction Mechanisms*, Benjamin, New York, **1964**.

[16] Titration of one W–OH_2 group was expected to halve the oxidation rate from consideration of the statistical factor, as experimentally observed. The calculated energy associated with the loss of a water ligand (ZORA-BP86/S-I//ZORA-BP86/S-I) was found to be +8.4 kcal mol^{-1}.