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DFT Study on the Five Isomers of $PW_{12}O_{40}^{3-}$: Relative Stabilization upon Reduction

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The electronic characteristics and the redox properties of each isomer of $PW_{12}O_{40}^{3-}$ depend on the arrangement adopted by the metal–oxide framework. At the DFT/BP86 level, we computed the structures of the five isomers of $PW_{12}O_{40}^{3-}$ in oxidized form. The energy scale fits the experimental findings as well as the number of rotated triads of the metal–oxide core since the energy grows as follows: $\alpha < \beta < \gamma < \delta < \epsilon$. The reduced clusters behave differently as long as the β form becomes the most stable isomer after the second reduction. The γ isomer also gains stability upon reduction, but not enough to be competitive with β. For the 4-fold reduced PW_{12} cluster, the energy difference computed between β and γ in solution is 11 kcal mol^{-1}. This large difference proves that the $\beta \rightarrow \gamma$ isomerization is not favored upon simple reduction. The other isomers, δ and ϵ, are much more unstable than α or β in any reduction state.

Polyoxometalates[1] (POMs) are medium/large-sized molecular metal−oxides, made up of clusters of MO_6 octahedra, mostly with $M^{z+} = W^{6+}$, Mo^{6+}, and V^{5+}. Because of the high oxidation state of M^{z+}, POMs are, typically, good electron acceptors. The Keggin phosphotungstate, $PW_{12}O_{40}^{3-}$, and its derivatives have been the most largely studied systems among POMs. In PW_{12},[2] a $W_{12}O_{36}$ core, formally composed of corner- and edge-sharing WO_6 units, surrounds the internal PO_4^{3-} anion. In fully oxidized form, the external core is neutral, and the electronic configuration of tungstens (d^0) allows them to accept electrons. The electronic structure of most POMs may be viewed as a set of occupied orbitals, the highest ones pertaining to oxo ligands, and a set of unoccupied levels that are symmetry-adapted combinations of the d-metal orbitals.[3] The metal orbitals accommodate the incoming electrons, thus giving the heteropoly blues[4] due to the characteristic color of the reduced species. Many groups have investigated the redox properties of several $XM_{12}O_{40}^{q-}$ anions.[5−9] In 1970, Baker and Figgis[10] postulated the existence of five isomers with that formula based on the arrangement of the metal−oxide core (see Figure 1).

Although the molecular formula remains the same in all cases, the redox properties do not. Experimental[5,11] and theoretical[12] data prove that the redox properties vary from isomer to isomer. For many years, it was established that the oxidized Keggin anions always preferred to adopt the α arrangement,[13] but recent studies[12,14] have shown that the α/β-$XW_{12}O_{40}^{q-}$ equilibrium is gradually displaced toward the β form for X = Si and, especially, for Al. The α-PW_{12} form is the most stable oxidized Keggin anion, but after a few reduction steps, the β isomer becomes more stable than α. It was proposed from DFT calculations[12] that the origin of this inversion is the different energy of the LUMO of α and β, which governs the reduction potentials. Furthermore, cyclic voltammetry data showed a direct relationship between the reduction potential of SiW_{12} and the number of rotated triads in the $M_{12}O_{36}$ framework with growing oxidizing power in the order $\alpha < \beta < \gamma$. However, the oxidizing

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(2) The abbreviated formula PW_{12} stands for the $PW_{12}O_{40}^{3-}$ oxidized anion, whereas $PW_{12}ne$ indicates the $PW_{12}O_{40}^{(3+n)-}$, *n*-fold-reduced, cluster.

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(4) The blue color of reduced POMs is characteristic of delocalized metal electrons. Systems such as the monoreduced $SiVW_{11}$ anion are brown because the metal electron is localized in a single vanadium atom.

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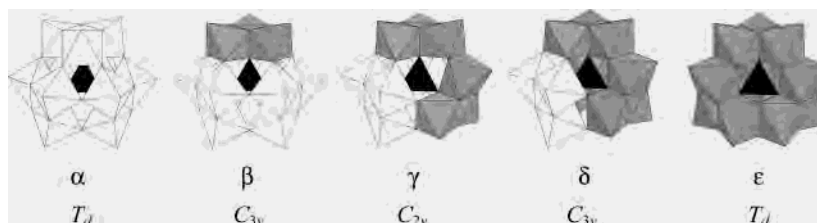
Figure 1. The five isomers of $PW_{12}O_{40}^{3-}$ in polyhedral representation, showing the labeling and the symmetry point group of each structure. The α isomer is characterized by an assembly of four edge-sharing triads, W_3, which share corners to each other in a tetrahedral fashion. By successive 60°-rotations of 1−4 triads (shaded octahedra), one gets the β, γ, δ, and ϵ isomers.

powers of the latter two forms were found more alike compared to that of α.[15] The present note was motivated by a recent study by Antonio and co-workers,[16] who reported new insights into the isomerization of the PW_{12} anion upon reduction. Their results show that $\alpha \rightarrow \beta$ isomerization commences at the third reduction of α, associating the fourth reduction to the β isomer exclusively. These authors consider the possibility of obtaining the γ form upon reduction, claiming a lack of comparative studies of α, β, and γ reduced forms. To the best of our knowledge, the only thorough theoretical study on the γ-Keggin anion was performed by Rohmer et al.[17−18] In that work, they investigated and rationalized the localization of metal electrons. The present report compares the electronic structure and relative stability of the rotational isomers of PW_{12} in different reduction states. It is part of the ongoing theoretical research into the electronic properties of POMs.[9,19]

We carried out DFT calculations (ADF2003.01 package[20]) characterized by the local density approximation featuring the Xα model with Becke's functional[21] for exchange, and the VWN parametrization[22] with Perdew's correction[23] for correlation. The basis functions for describing the valence electrons of the atoms are Slater-type orbitals of TZP quality. The internal or core electrons (O, 1s; P, Si, Al, 1s−2s; W, 1s−4d) were frozen and described by single Slater functions. We applied scalar relativistic corrections to them, zeroth-order regular approximation (ZORA), via the core potentials

Table 1. Binding Energies Computed, Relative to the α Form, and HOMO−LUMO Gaps for the Five Isomers of $PW_{12}O_{40}^{3-}$ in Oxidized Form[a]

| isomer (no. rotated triads)	M−M close contacts	relative energy (kcal mol^{-1})			HOMO−LUMO gap (eV)		
		P	Si	Al	P	Si	Al
α	0	0.0	0.0	0.0	2.73	2.76	2.79
β (1)	0	+4.57	+3.82	+2.37	2.56	2.60	2.62
γ (2)	1	+13.9	+13.8	+13.3	2.59	2.64	2.63
δ (3)	3	+30.7			2.83		
ϵ (4)	6	+55.9			2.73		

[a] For the Si and Al derivatives, only isomers α−γ were computed.

generated with the program DIRAC.[20] The optimized structures were obtained in the presence of the conductor-like screening model (COSMO)[24] for the solvent (water, $\epsilon = 78$). Our group has shown recently[25] that the charge and size of the anions computed in this paper are also well described in a vacuum.

Table 1 shows the relative energies and HOMO−LUMO (H−L) gaps of the fully optimized isomers of PW_{12} in oxidized form. We also optimized the structures for the α, β, and γ isomers of SiW_{12} and AlW_{12} for comparison. For all the heteroatoms, X, the close energies of α and β highlight the fact that both isomers have very similar geometries and electronic structures, and that they are the most stable forms of the Keggin anion. Compared to our previous study performed in a vacuum,[12] the energy differences between isomers herein reported with COSMO are smaller. In that study, we reported a β/α energy difference in a vacuum of 6.5 and 6.0 kcal mol^{-1} for PW_{12} and SiW_{12}, respectively. In the present work, accounting for the solvent effects reduces each of these differences by ~2 kcal mol^{-1}. As a matter of fact, $\Delta E_{\beta - \alpha} = 2.37$ kcal mol^{-1} for AlW_{12}, very close to the experimental value of 2.1 kcal mol^{-1} found by Weinstock and co-workers.[14] When two or more triads have been rotated, additional edge-sharing contacts appear between the W_3 units rotated. The γ, δ, and ϵ forms, of substantial higher energy, feature 1, 3, and 6 more edge-sharing octahedra, respectively, than α or β. Some authors[26] have attributed the instability of γ, δ, and ϵ forms to the electrostatic contributions arising from the $W^{6+}-W^{6+}$ short contacts. Table 1 shows an increase in energy of 8−9 kcal mol^{-1} for each

(15) Data corresponding to the TBA salts of α-, β-, and γ-SiW_{12} in acetonitrile solution follow. The half-wave reduction potentials (vs SCE) are $E_{1/2}(\alpha) = -0.73$ V; $E_{1/2}(\beta) = -0.62$ V; $E_{1/2}(\gamma) = -0.58$ V. Tézé, A.; Canny, J.; Gurban, L.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1996**, *35*, 1001.
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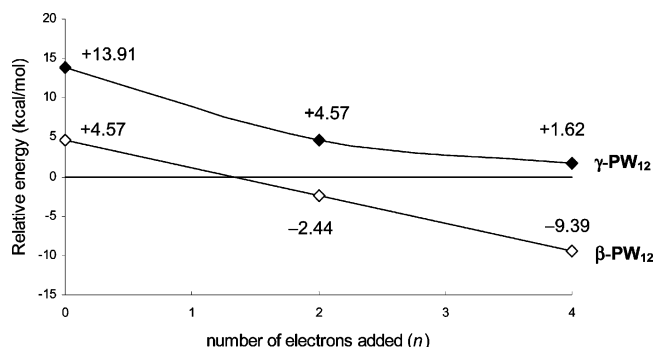
Figure 2. Relative energies (in kcal mol^{-1}) for β-PW$_{12}n$e ($\diamond$) and γ-PW$_{12}n$e ($\blacklozenge$), as a function of the number of electrons added, n. The energy of α-PW$_{12}n$e was taken as zero at each point.

Figure 3. Electronic structure of the fully oxidized α-, β-, and γ-PW$_{12}$ anions. The scheme shows the symmetry of the virtual orbitals and their absolute energy at the BP86 level within the solvent (in eV).

new W−W contact. We computed a distance between neighboring tungsten atoms of 3.02 Å in γ-PW$_{12}$, which is very close to the distance of 2.99 Å reported for the homologous γ-SiW$_{12}$ system by Tézé et al.[27] The dependence of the H−L gap with X is also remarkable. Although the variation found is small (2.73−2.79 eV for α-XW$_{12}$ with X = P, Si, and Al), we reproduced the experimental separation between the oxo and the metal bands from P to Al. The values of H−L gap for isomers α to γ are also reproduced.[14−15,28]

The relative energies of α-, β-, and γ-PW$_{12}$ are shown in Figure 2 for different reduction states. The energy of the fully oxidized α-PW$_{12}$ anion is the lowest as expected. At this point, β-PW$_{12}$ is +4.57 kcal mol^{-1} higher in energy. However, successive reductions of PW$_{12}$ change the relative energies of the isomers, and inversion of stability in the α/β pair occurs after the second reduction, leaving β-PW$_{12}$2e 2.4 kcal mol^{-1} lower in energy than its 2-fold-reduced α counterpart. For γ-PW$_{12}$, the addition of 2 electrons reduces $\Delta E_{\gamma-\alpha}$ from +13.9 to +4.57 kcal mol^{-1}; thus, it is not sufficient to fully balance the difference existing in oxidized form. However, in the process PW$_{12}$ → PW$_{12}$2e the γ form gains more stability (−9.34 kcal mol^{-1}) than β (−7.01 kcal mol^{-1}). The next two reductions allow the β-PW$_{12}$2e form to increment its relative stabilization since its energy in the 4-fold-reduced form is 9.39 and 11.01 kcal mol^{-1} below the α and γ arrangements, respectively.

In the oxidized form, the energy of each LUMO may be considered as a signal of the ability of each form to be reduced.[29] The values in Figure 2 exemplify this point given that they might be expected from the energies of the LUMOs in Figure 3.[12] In β-PW$_{12}$O$_{40}{}^{3-}$, the energy of the LUMO is 0.14 eV (3.23 kcal mol^{-1}) below the homologous orbital of the α isomer (Figure 3). Therefore, the energy difference
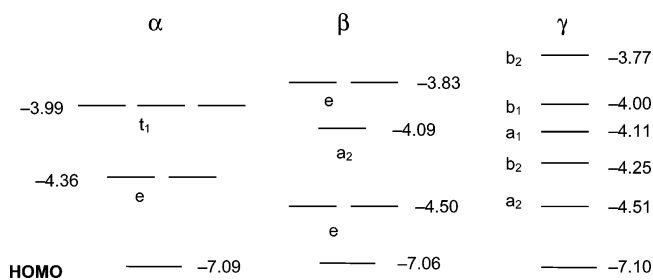
between these isomers, $\Delta E_{\beta-\alpha}$, decreases ~0.14 eV per electron added up to the fourth reduction. The LUMO of γ-PW$_{12}$ is also lower than that of α and very close to the LUMO of β. The experimental data available for SiW$_{12}$ compounds reveal that γ is a stronger oxidant than β,[15] an ambiguous fact if one observes their molecular orbitals in the oxidized form. However, reduction by 2 electrons of γ and β provides the experimental trend since the former is further stabilized by 2.33 kcal mol^{-1}. The slightly different behavior between β and γ isomers must be attributed to a greater relaxation of the geometry in the γ form after reduction. Going further up to the fourth reduction, γ-PW$_{12}$ still remains higher in energy than the other two isomers in the PW$_{12}$4e state. It only gained ~3 kcal mol^{-1} of additional relative stability with respect to PW$_{12}$2e, which is one-third of the energy gained with the first two reductions. The explanation for this fact may be found in the energy of the orbitals filled upon reduction in each isomer. α and β isomers have LUMOs that formally accept 4 electrons each, as shown in Figure 3. On the other hand, γ-PW$_{12}$ is forced to occupy a relatively high-lying metal orbital to form the 3- and 4-fold-reduced clusters, thus preventing γ-PW$_{12}$ from becoming more stable than α in the PW$_{12}$4e form.

In summary, the stability of the five isomers of PW$_{12}$O$_{40}{}^{3-}$ follows the trend $\alpha < \beta < \gamma < \delta < \epsilon$. However, by successive reductions, this ordering may be altered. After the second reduction, the process $\alpha \rightarrow \beta$ is favored, and the stability of the β form is even increased with further reduction. The stabilization of the γ isomer is also favored in relation to α when going from the oxidized form to PW$_{12}$2e, but there is no inversion of stability.[29b] The fourth reduction of the anion leaves $\Delta E_{\gamma-\alpha} = 1.62$ kcal mol^{-1}, which is a very small value. However, since $\Delta E_{\beta-\gamma}$ and $\Delta E_{\beta-\alpha}$ are −11.01 and −9.39 kcal mol^{-1} in the 4-fold reduced state, the β isomer is the most abundant form in such a reduction state.

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