Catalytic effect of a second H_3PO_2 in the mechanism of stabilisation of the unstable pyramidal tautomer of H_3PO_2 coordinated at $[Mo_3S_4M']$ clusters (M′ = Ni, Pd)†

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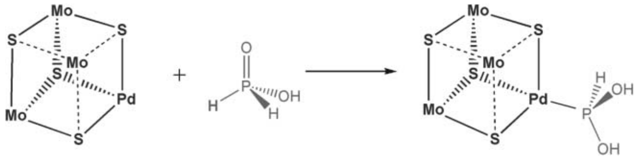
Kinetic and DFT studies indicate that the stabilization of a single pyramidal H_3PO_2 molecule at the M′ site of $[Mo_3S_4M']$ clusters requires the participation of two tetrahedral H_3PO_2 molecules, the role of the second one being assisting tautomerization of a previously coordinated tetrahedral H_3PO_2.

Phosphinic acid (H_3PO_2), also called hypophosphorous acid, is known to exist as a tetrahedral (*tet*) $H_2PO(OH)$ molecule with a P=O group.[1] However, there is an alternative unstable pyramidal form (*pyr*), $HP(OH)_2$, for which quite different chemical properties must be reasonably expected. Thus, the existence of a lone pair of electron on the phosphorus atom of *pyr*-H_3PO_2 can provide an entry into a coordination chemistry with evident parallelisms to the rich chemistry of the phosphine complexes, with the additional advantages of the water solubility of the complexes and the existence of OH groups able to promote additional hydrogen bonding and proton transfer processes. Phosphorous acid, H_3PO_3, and other acids of phosphorus in low oxidation states also show the possibility of *tet* and *pyr* tautomeric forms, so that unraveling the way and conditions in which tautomerization occurs in these low-valent phosphorus compounds is fundamental for understanding some basic aspects in the chemistry of phosphorus.

Although tautomerization to the *pyr* form was proposed decades ago to explain the kinetics of H/D exchange and oxidation of H_3PO_2,[2] it has not been until recent years that the occurrence of this process has been unequivocally demonstrated. Actually, there are now several well-characterized metal complexes containing the *pyr* forms of H_3PO_2 and related acids, P-coordinated to the soft metal centers of $[M_3M'Q_4(H_2O)_9]^+$ clusters (M = Mo, W; M′ = Ni, Pd; Q = S, Se)[3] and other mononuclear complexes.[4] As a continuation of our interest in the mechanistic aspects of reactions of M_3Q_4 and $M_3M'Q_4$ clusters, we decided to carry out kinetic studies on the reaction shown in Scheme 1, where the $[Mo_3PdS_4(H_2O)_{10}]^+$ cluster[5] (**1**) reacts with H_3PO_2 to give complex **2**, which contains *pyr*-H_3PO_2 coordinated at the Pd site.[3c,d]



Scheme 1 The reaction of H_3PO_2 with **1** occurs with tautomerization. The water molecules are not shown for simplicity.

The reaction of **1** with an excess of H_3PO_2 in aqueous solution (25.0 °C, 2 M Hpts/Lipts, pts$^-$ = *p*-toluenesulfonate) occurs with biphasic kinetics, thus showing the existence of a reaction intermediate **I**. The electronic spectrum calculated for **I** (Fig. 1) resembles that of the starting complex, which suggests that the coordination environments around the metal centers do not change significantly in the first kinetic step and makes reasonable the assumption that this step is a simple substitution leading to a complex (**I**) containing O-coordinated H_3PO_2. Monitoring the reaction with $^{31}P\{^1H\}$ NMR confirmed that the only reaction product is **2**, characterized by a singlet at 122.0 ppm that converts to a doublet ($^1J_{P,H}$ = 414 Hz) in the proton-coupled phosphorus spectrum. The appearance of a single signal for the reaction product indicates that tautomerization only occurs at Pd, *i.e.* the Mo centers are ineffective for this process, in agreement with the lower lability of the Mo centres in **1**[5b] and with all reported crystal structures for these compounds.[3] Unfortunately, no NMR signal

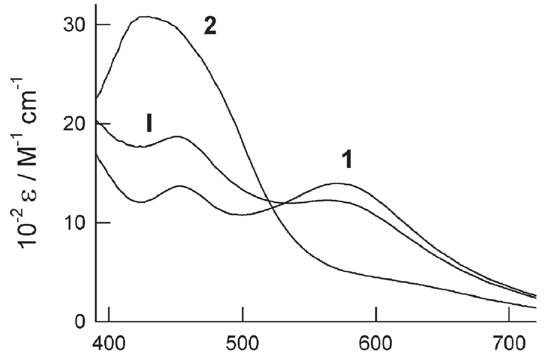


Fig. 1 Calculated electronic spectra for the species involved in the reaction of cluster **1** with H_3PO_2.

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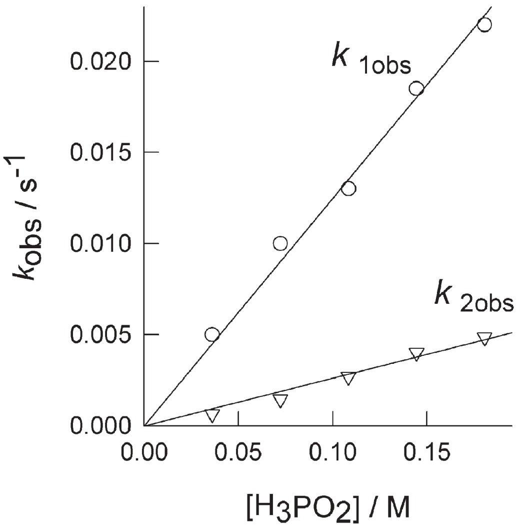

Fig. 2 Plots of the dependence with the H_3PO_2 concentration of the observed rate constants for the reaction of cluster **1** with H_3PO_2. The circles and triangles correspond to the first and second steps, respectively.

could be observed for the intermediate, probably because of rapid exchange between coordinated and free H_3PO_2. However, the proposal that **I** contains O-coordinated *tet*-H_3PO_2 is also supported by the fact that reaction of **1** with H_3PO_4, which can not exist in the *pyr* form, occurs with spectral changes quite similar to those observed for the first step in the reaction with H_3PO_2.

Surprisingly, the rate constants for both steps show a first-order dependence with respect to H_3PO_2 (Fig. 2), which indicates that stabilization of a single *pyr*-H_3PO_2 requires the participation of two H_3PO_2 molecules, one in each step. The values of the second-order rate constants are $k_1 = (12.5 \pm 0.3) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_2 = (2.6 \pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$, and they do not change with the H^+ concentration (0.5–2.0 M range), which suggests that the only species that contribute significantly to the reaction rate are **1** and H_3PO_2.‡ The reaction of the related $[Mo_3NiS_4(H_2O)_{10}]^+$ complex (**1**Ni) with H_3PO_2 shows similar kinetics, although the second step occurs under conditions of reversible equilibrium, in agreement with the reported lower reactivity of **1**Ni.[3d] The values of the rate constants for **1**Ni are $k_1 = (2.38 \pm 0.05) \times 10^{-2}\ M^{-1}\ s^{-1}$, $k_{2forw} = (1.00 \pm 0.06) \times 10^{-4}\ M^{-1}\ s^{-1}$ and $k_{2rev} = (1.76 \pm 0.05) \times 10^{-5}\ s^{-1}$.

These kinetic data can not be explained with simple mechanisms involving tautomerization of free H_3PO_2 followed by coordination of the resulting *pyr* form. Thus, a fast pre-equilibrium between both tautomeric forms followed by rate-determining reaction of *pyr*-H_3PO_2 with **1** would lead to a single kinetic step. Although slow tautomerization of H_3PO_2 followed by coordination of the *pyr* form could result in biphasic kinetics, the rate of the first step should be independent of the nature of the cluster. Alternative mechanisms involving coordination at the Mo centers in the first step also appear unlikely because substitutions at these centres are several orders of magnitude slower than at Pd,[5b] and because coordination at M′ (= Pd, Ni) in the second step should be then unreasonably accompanied by the rapid dissociation of the H_3PO_2 previously coordinated at Mo. In contrast, the interaction of two molecules of an acid with a single metal site has been found to be relevant in other reactions of this kind of cluster.[6] For this reason we decided to look for additional mechanistic information by carrying out DFT calculations,§ which proved to be very useful for understanding the way in which a second H_3PO_2 molecule assists tautomerization of the previously coordinated one.

Fig. 3 includes the optimized geometries of the products resulting from coordination of H_3PO_2 to the Pd site of cluster **1**. As expected, P-coordination of *pyr*-H_3PO_2 in **2** was found to stabilize the system by 13.8 kcal mol^{-1} more than O-coordinated *tet*-H_3PO_2 in **I**,§ so that tautomerization is thermodynamically favored. Although both structures show the existence of an intramolecular hydrogen bond, additional calculations, to be reported elsewhere, showed that it does not play a significant role in the tautomerization process. Similar calculations using the $H_2PO_2^-$ anion instead of H_3PO_2 resulted in proton abstraction from a water molecule coordinated to an adjacent Mo, thus showing that **I** contains O-coordinated *tet*-H_3PO_2 independently of the $H_3PO_2/H_2PO_2^-$ protonation state. The second step thus consists in tautomerization of the coordinated H_3PO_2 molecule, which according to the kinetic results requires the participation of a second H_3PO_2. The reaction pathway proposed for this tautomerization on the basis of DFT calculations is included in Fig. 4.

Attack to **I** by the second H_3PO_2 molecule results initially in proton abstraction from a P–H bond to yield $H_4PO_2^+$ and a complex (I_2) containing O-coordinated *pyr*-$H_2PO_2^-$. Interestingly, other reactions involving the P–H bond of H_3PO_2, such as H/D exchange and oxidations with several reagents, have been also proposed to occur with formation of $H_4PO_2^+$.[2] Proton abstraction

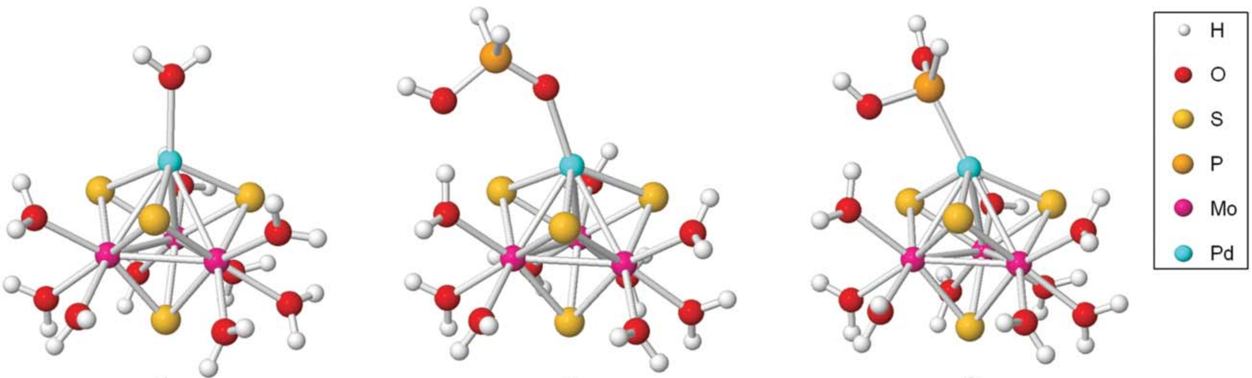

Fig. 3 Optimized geometries for the starting complex **1**, the reaction intermediate **I** and the reaction product **2**.

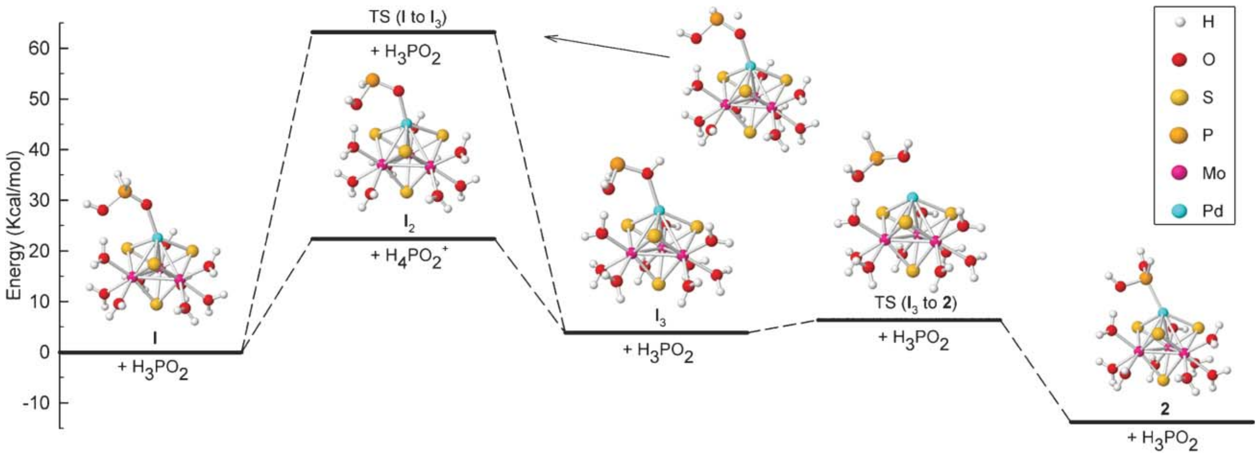

Fig. 4 Energy profile and optimized geometries for the intermediates and transition states found for the H_3PO_2-assisted tautomerization of a molecule of H_3PO_2 O-coordinated to the Pd centre of cluster **1**.

from a P–H bond has been also found to be relevant in the mechanism of the Atherton–Todd reaction of oxidation of dialkyl phosphonates with chlorocarbons.[7] The calculations show that conversion of **I** to $\mathbf{I}_2$ has a moderate energy cost (22.4 kcal mol^{-1}) and occurs without any additional activation barrier. The energy profile in Fig. 4 indicates that this is the most energy-demanding step, so that it will be the rate determining step in the tautomerization process. The mechanism continues with protonation of $\mathbf{I}_2$ by $H_4PO_2^+$ to form intermediate $\mathbf{I}_3$, which contains O-coordinated *pyr*-H_3PO_2. This process is favored by 18.5 kcal mol^{-1} and it also occurs without an activation barrier. The net effect of the first two steps in Fig. 4 is a hydrogen shift from phosphorus to oxygen, the second H_3PO_2 acting as a catalyst for the process because of its capability to act as a base forming $H_4PO_2^+$, which then acts as an acid and transfers the proton to the oxygen in coordinated *pyr*-$H_2PO_2^-$. Although a transition state was found for direct conversion of **I** to $\mathbf{I}_3$, the activation barrier (63.2 kcal mol^{-1}, see Fig. 4) is quite high and close to that found for the H-shift in free H_3PO_2 (65.3 kcal mol^{-1}), so that the assisted pathway is much more effective. The reaction is completed with isomerization of $\mathbf{I}_3$ to **2**, which leads to a stabilization of 17.7 kcal mol^{-1} through a transition state with a very low activation barrier of only 2.5 kcal mol^{-1}.

This mechanism accounts for the experimental kinetic findings and indicates that the role of the second H_3PO_2 molecule consists in catalyzing the hydrogen shift, which is made possible by its capability for accepting a proton from a P–H bond. Nevertheless, a similar proton transfer from one P–H bond of free *tet*-H_3PO_2 is not favored because it requires previous activation, which is achieved in the present case through coordination to Pd. Although the actual solution behavior can be complicated by the existence of other proton-transfer and hydrogen-bonding processes competitive with those in Fig. 4, those alternative processes do not prevent tautomerization through the proposed mechanism, which provides a pathway less energy-demanding than those operating in the absence of metal complex.

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Notes and references

‡ The absence within that pH range of hydroxo complexes derived from **1** had been confirmed previously,[5b] but the pK_a of H_3PO_2 is close to 1 and significant amounts of $H_2PO_2^-$ can exist in the solutions used for the kinetic studies. However, participation of this anion in any of both kinetic steps can be reasonably ruled out because it would lead to a significant increase in the rate constants when [H^+] decreases.

§ Calculations were carried out with Gaussian 03 following the procedure detailed in the ESI. All the energy values are given in aqueous solution.

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