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The mechanism of CO_2 hydration: a porous metal oxide nanocapsule catalyst can mimic the biological carbonic anhydrase role†‡

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The mechanism for the hydration of CO_2 within a Keplerate nanocapsule is presented. A network of hydrogen bonds across the water layers in the first metal coordination sphere facilitates the proton abstraction and nucleophilic addition of water. The highly acidic properties of the polyoxometalate cluster are crucial for explaining the catalysed hydration.

Concerns about global warming, together with the incoming necessity to find alternative feedstocks to fossil fuels,[1] have boosted interest in the capture and use of CO_2 as a chemical starting material.[2–5] Living organisms having the carbonic anhydrase enzyme carry out the simplest CO_2 transformation, *i.e.* hydration to carbonic acid, in an easy manner. The presence of an electrophilic Zn center together with a network of water molecules in the proximity of the enzyme site makes the hydration reaction possible, which is rather slow in the absence of a catalyst. The exploration of carbonic anhydrase[6–9] and related analogues[10] has afforded major bio-inspired catalytic routes for CO_2 fixation over the past few decades. On the other hand, synthetic chemistry afforded new transition metal based catalysts that can convert CO_2 into other chemical entities, for instance CO_2 reduction to methanol,[11] coupling with oxiranes to produce cyclic carbonates,[12–14] or other value added chemicals.[15,16]

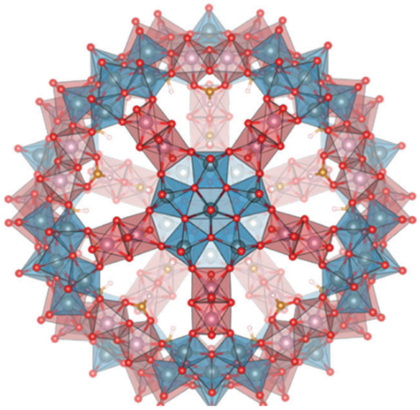

Fig. 1 The pictorial representation of the $\{Mo_{132}\}$ Keplerate capsule.

Some of us reported recently[17] a novel way to sequestrate and transform CO_2 into carbonate by encapsulation within unique molybdenum oxide nanocapsules. This novelty hinges on the fact that the approach uses only aqueous, room temperature and open air chemistry. These capsules, belonging to the Keplerate family, are nano-sized molecular metal oxide spheres with the general formula $[\{(M^{VI})M^{VI}_5O_{21}(H_2O)_6\}_{12}\{M'^{V}_2O_2X_2(\mu^2\text{-}Y)\}_{30}]^{n-}$ (M = Mo, W; M′ = Mo; X = O, S; Y = bridging ligand, *e.g.* $RCOO^-$, $SO_4{}^{2-}$).[18] This sort of capsule contains 12 pentagonal $\{Mo^{VI}_6\}$ units placed at the vertices of an icosahedron and linked by 30 binuclear $\{Mo^{V}_2\}$ units. This arrangement leads to the formation of capsules (Fig. 1) with twenty $\{M_3Mo_6O_9\}$-type pores and a cavity where a large quantity of water molecules, anions or other species can be confined.[19,20] By bubbling CO_2 in an aqueous solution of $(NH_4)_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(\mu^2\text{-}CH_3COO)\}_{30}]\cdot$*ca.* 10 $CH_3COONH_4\cdot$*ca.* 300 $H_2O \equiv (NH_4)_{42}\cdot$Anion **1a**·*ca.* 10 $CH_3COONH_4\cdot$*ca.* 300 $H_2O \equiv$ Compound **1**[21] at pH 7 the carbonate derivative $(NH_4)_{72}$ $[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(\mu^2\text{-}CO_3)\}_{30}]\cdot$*ca.* 260 $H_2O \equiv (NH_4)_{72}$ anion **2a**·*ca.* 260 $H_2O \equiv$ Compound **2** was obtained.[17] The pictorial representation of the $\{Mo_{132}\}$ Keplerate capsule is displayed in Fig. 1. The characterisation of Compound **2** prompted the major question of whether the carbonate anion formed in solution (in minute amounts at pH 7) was captured by the Keplerate cluster by diffusion into the inner cavity or, more interestingly, whether the carbonate anion formation took place *in situ* inside the capsule, either at the Mo^{V} or Mo^{VI} coordination sites, by a metal catalysed nucleophilic addition of water to a solubilised CO_2 molecule, likewise the accepted mechanism of carbonic anhydrase.

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† Dedicated to the memory of Tom Ziegler (1945–2015).

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The CO_2 transformation is also reversible *via* acidification of the aqueous solution of Compound **2**.[17] The results of the theoretical study presented herein suggest that this transformation of CO_2 to carbonate is actually the third example[22,23] known to date of a catalytic process occurring inside the $\{Mo_{132}\}$ capsule, where the Mo^{V} and also the Mo^{VI} sites play a role.

The mechanism of the hydration of CO_2 to form the carbonic acid has been a subject of theoretical studies over the past few decades.[24,25] The challenge lies in the accurate description of the explicit water molecules participating in the reaction as was shown by the latest work of Yamabe and Kawagishi.[26] The uppermost energy barrier of carbon dioxide hydration is always the initial step of water addition.[27] The arrangement of this initial transition state[24–26,28] is a cyclic three water molecular arrangement as depicted in Fig. 2. We will adopt this model as a benchmark to compare with our own calculations on the catalytic sequestration of CO_2 and its conversion into the carbonate form.

In a recent study we demonstrated that by using a cluster model of the $\{Mo_{132}\}$ nanocapsule, the reaction pathway of the reversible cleavage of methyl-*tert*-butyl ether[22] was successfully unravelled. The model assembly was defined to mimic the nature of the active sites of the Keplerate and it was formulated as $[\{(Mo^{VI})Mo^{VI}_5O_{13}(OH)_8\}_2\{Mo^{V}_2O_4\}]^{6+}$ containing two pentagonal $\{(Mo^{VI})Mo^{VI}_5\}$-units and one linker unit of the type $\{Mo^{V}_2O_4\}$. It fully retained the essential characteristics of the $\{Mo_{132}\}$ reactive sites and therefore we have selected that model for the present study. Since the formation of the carbonate anion takes place in aqueous media, the presence of water molecules inside the Keplerate sphere must play an essential role in the reaction and therefore it is essential that the cluster model should incorporate a sufficiently large number of water molecules. Thus we included 13 additional water molecules explicitly in this study, so the model used is formulated as $[\{(Mo^{VI})Mo^{VI}_5O_{13}(H_2O)_6(OH)_8\}_2\{Mo^{V}_2O_4(H_2O)\}]^{6+}$, which leaves one vacant coordination site reserved for the incoming CO_2 molecule at one of the two Mo^{V} sites, while the second one bears a water molecule which is supposed to undergo nucleophilic addition.

As expected the CO_2 molecule, being nonpolar, does not coordinate in the initial stage to an Mo^{V} centre either in an η^1 or η^2 fashion. Notwithstanding, we could characterize a weakly bound stationary point structure in which CO_2 is hydrogen-bonded to the water molecule in one Mo^{V} centre and to a water molecule on Mo^{VI}, thus located in the vicinity of the reactive centre. This will be our starting point (named Reactants) for the reaction path studies defining the zero of energies.

The highest energy reaction path explored **TS1** (Fig. 2) is perhaps the most intuitive pathway involving a concerted nucleophilic addition of an aqua ligand to CO_2 followed by the subsequent proton rejection and formation of a local Zundel cation

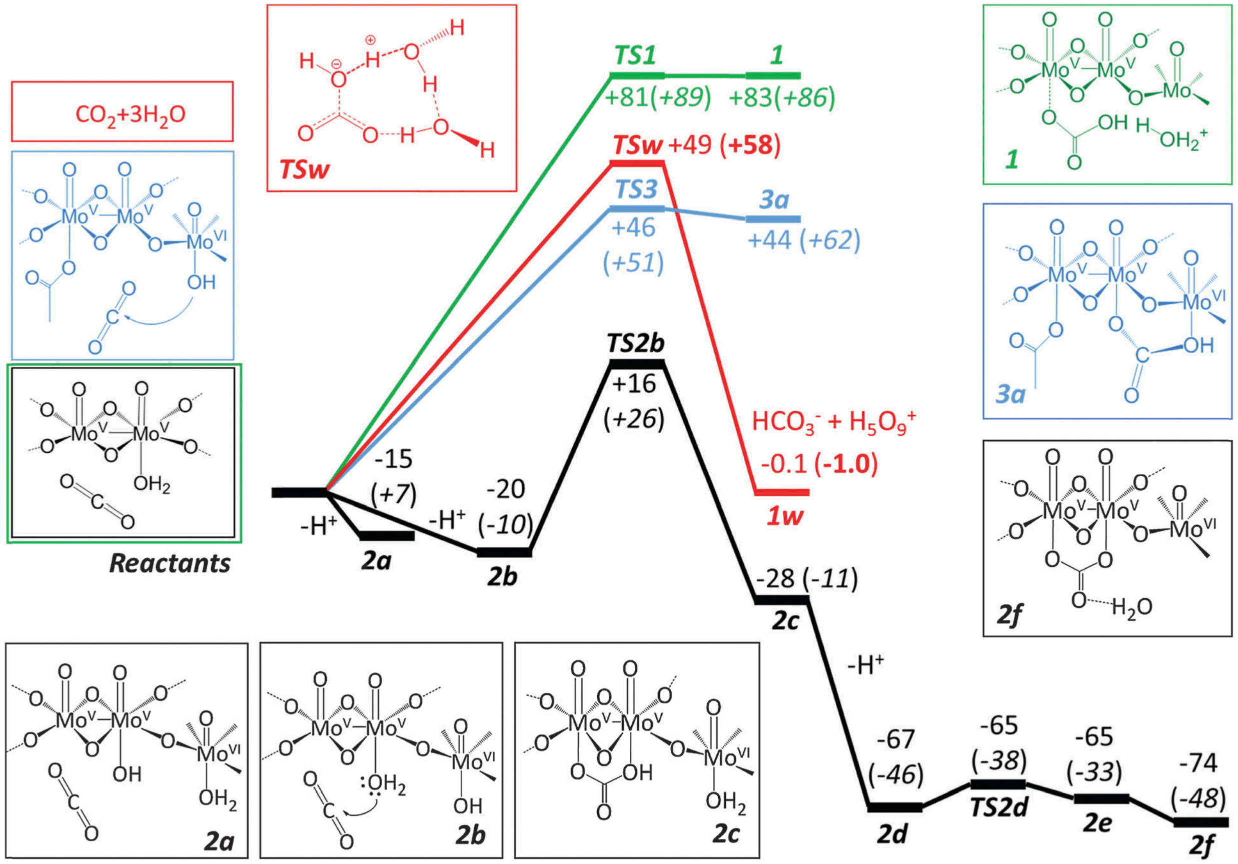

Fig. 2 Several mechanistic pathways for CO_2 hydration: in red the uncatalysed reaction is presented; in green the iso-charge pathway leading to the formation of a local H_3O^+ cation; in blue is the route with direct Mo^{VI} intervention in the formation of bicarbonate; in black the proposed catalytic pathway. Electronic energies and Gibbs free energies in parentheses are evaluated using a partial Hessian. All energies in kJ mol^{-1}.

($H_5O_2^+$) sponsored by the hydrogen bonding of the neighbouring aqua ligands. Note that the neighbouring water ligands coordinated to Mo^{VI} centres contribute to stabilizing the rejected proton and the concomitant formation of bicarbonate. Although we explored multiple conformational possibilities, a coordinated adduct of the type $\{O_2C–OH_2\}$ could not be obtained.

Owing to the accumulation of positive charge closer to the metal centres, **TS1** transition state is shown to be too excessively high in energy (+89 kJ mol^{-1}) to become a competitive pathway vis-à-vis the unassisted **TSw** transition state for hydration of CO_2.

In light of these results we explored a different route that yielded a bicarbonate coordinated intermediate resulting from the nucleophilic addition of a hydroxo group to CO_2. Given that the Mo^{VI} centres are more Lewis acidic than Mo^V (*e.g.* on average 0.1 pK_a units lower in Mo^{VI} for the Keggin structure[29]) the likely candidate for a good reactant would be **2b** bearing the $\{Mo^V(OH_2)–O–Mo^{VI}(OH)\}$ unit rather than **2a** ($\{Mo^V(OH)–O–Mo^{VI}(OH_2)\}$). This is borne out by the relative energetics of the two isomers, which favour **2b** by some 5 kJ mol^{-1}. The mechanism should expectedly involve a proton relay from the aqua-ligand in the Mo^V centre concerted with the nucleophilic addition of the hydroxo group to CO_2. The ΔG estimate for the **2a** → **2b** conversion is further widened to 17 kJ mol^{-1} in favour of **2b**. The reason for this will be discussed below.

An *in vacuo* fragment analysis shows that the interaction energy in **2b** between the CO_2 molecule and the metalate cluster is −39.3 kJ mol^{-1} showing a weak interaction between them.

It should be mentioned that throughout the process the local Mo^V character of the linker units is retained throughout the process, *i.e.* the 4d orbital contribution in the HOMO rests mostly in the $4d_\sigma$–$4d_\sigma$ interaction localised on the linker unit.

The bicarbonate intermediate undergoes further deprotonation resulting in **2d**. The release of a proton from **2d** to **2e** has a negligible energy barrier (for **TS2d**, 2 kJ mol^{-1} in electronic or + 8 kJ mol^{-1} in free energy). The carbonate intermediate **2e** is approximately iso-energetic with its parent bicarbonate **2d** but can be easily converted to **2f** with lower free energy. The intermediate **2f** has one non-coordinated water molecule which stabilises the carbonate ligand *via* hydrogen bonding. The Mo–carbonate bond lengths in **2e** are 2.392 and 2.329 Å, which are within the error limits of the experimentally determined values.[12]

The higher acidity of the Mo^{VI} centre prompted us to explore another possible mechanistic route in which the direct nucleophilic addition to the CO_2 molecule takes place directly by the hydroxo group coordinated to the Mo^{VI} sites while the vacant coordination site of Mo^V is utilized to stabilize the transition state. A subsequent backflip of bicarbonate or carbonate to the $\{Mo^V_2\}$-linker would be necessary to be consistent with the final carbonate adduct. The initial steps of this pathway are sketched in blue as shown in Fig. 2. The transition state **TS3** has a similar energy value to **TSw** (the uncatalysed transition state) but intermediate **3a** is not sufficiently stable to be considered a viable route (see ESI,‡ for these additional structures).

There are structural differences between the catalysed and uncatalysed systems namely with regard to each transition state which are summarised in Fig. 3. The Mayer–Mulliken bond orders[30] (MBOs) were also analysed in the present case which reflect the bond strength between the different atoms in any given system. The most striking difference between **TSw** and **TS2b** is that the latter is a slightly ''lesser bound'' transition state with a reaction coordinate (C–O) bond order 0.377 whereas in **TSw** it is 0.557 in line with Hammond's postulate. The ∠(O–C–O) angles are also considerably different between **TSw** (139°) and **TS2b** (152°) consistent with a larger electron cloud of the incoming O(–C) and consequently a lower angular distortion of CO_2. The leaving proton is also more bound to the oxygen atom in **TSw** (MBO = 0.430) than in **TS2b** (MBO = 0.250). In the latter case the outgoing proton from the aqua ligand is already at a large distance (1.535 Å, see Fig. 3). Interestingly the Mo^V–OH bond in **2a** (α-hydroxo isomer) is stronger (MBO = 0.450) than the Mo^{VI}–OH bond in **2b** (MBO = 0.219). This causes a vibrational stiffness in the **2a** isomer decreasing its entropy and increasing the free energy difference with respect to **2b**.

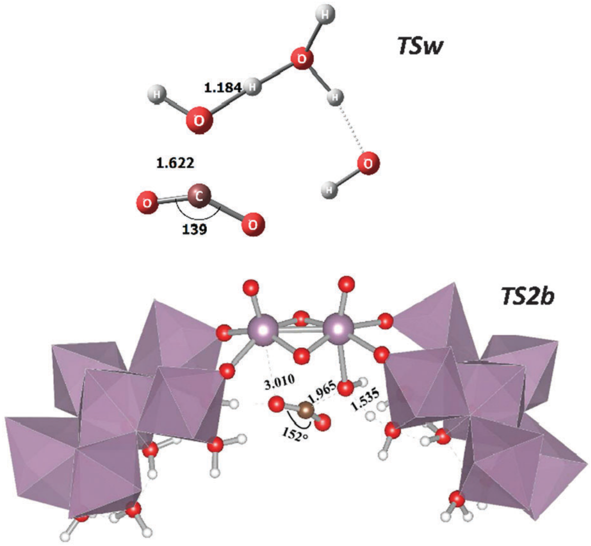

Fig. 3 Transition state structures for the uncatalysed $CO_2 + 3H_2O$ (**TSw**) and for the catalysed reaction (**TS2b**). Selected distances in Å and angles in degrees.

Finally to predict the potential reactivity of related systems, additional calculations were carried out on model analogues of the $\{W_{72}Mo_{60}\}$ and $\{W_{132}\}$ nanocapsules. The former nanocapsule has been characterised[31] experimentally although the latter is still unknown. Since the key point in the mechanism is the generation of the nucleophilic hydroxo species coordinated to the star-shaped M^{VI} moieties, the relative thermodynamic stability of **2a** and **2b** species was determined. The calculated ΔE(**2a** → **2b**) is −65 kJ mol^{-1} for the mixed W/Mo oxo-cluster model and −85 kJ mol^{-1} for the hypothetical full W system. This points to a likely enhanced reactivity of the heavier metal Keplerates in the order $\{Mo_{132}\} < \{W_{72}Mo_{60}\} < \{W_{132}\}$. These results also indicate that W^V centres are less (Lewis) acidic with respect to W^{VI} than Mo^V in relation to Mo^{VI}.

DFT based calculations enabled unravelling the CO_2 hydration reaction pathway as evidenced involving Compound **1** by considering the known mechanism in the aqueous solution.

The *in situ* bicarbonate formation, promoted by the Mo^V centres, inside the capsule is kinetically more favourable than direct carbonate uptake from aqueous solution. Three trials were performed in the present work, which can be summarised as follows:

(i) A neutral charge pathway with aqua ligand nucleophilic addition to CO_2 results in a high kinetic barrier $\Delta E^{\ddagger} = +81$ kJ mol^{-1} and a product of exceedingly high energy.

(ii) A hydroxo ligand pathway in which the nucleophilic attack takes place on a Mo^{VI} site. This is a high energy process requiring +44 kJ mol^{-1} at the calculation level to form a product.

(iii) A hydroxo ligand pathway where the hydroxo group in an Mo^{VI} centre will act as a proton acceptor in tandem with the nucleophilic addition of CO_2 to an aqua ligand at the Mo^V sites. The activation energy $\Delta E^{\ddagger} = +36$ kJ mol^{-1} is the lowest of all the trials, even lower than the uncatalysed hydration reaction, and the ensuing product assembly is 28 kJ mol^{-1} more stable than the reactant assembly.

Therefore the most plausible mechanism for the formation of Compound **2** will be the latter based on comparison of computed energies with respect to a comparable micro-solvated CO_2 hydration. The resemblance of the mechanism with that operating in the carbonic anhydrase enzyme is remarkable. The subtle differences lie in the first steps of the latter mechanism: the rate-limiting step is the protolysis of the aqua ligand in $(His)_3Zn–OH_2$[3b,4] which is then followed by a lower energy nucleophilic addition to CO_2 whereas the Keplerate acts in a concerted single step for both. These results pave the way for defining a new application of Keplerate anionic capsules as CO_2 storage nanodevices.

While the Mo^V sites still remain the active catalytic host in Keplerate catalysis there is a clear involvement of the adjacent Mo^{VI} centres as promoters of Brønsted acidity and proton relay.

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