The mechanism of CO₂ hydration: a porous metal oxide nanocapsule catalyst can mimic the biological carbonic anhydrase role†‡

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The mechanism for the hydration of CO₂ 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 CO₂ as a chemical starting material.2–5 Living organisms having the carbonic anhydrase enzyme carry out the simplest CO₂ transformation, i.e. hydration to carbonic acid, in an easy manner. The presence of an electrophilic Zn center together with a network of water layers in the first metal coordination sphere facilitates the reaction possible, which is rather slow in the absence of a catalyst. The exploration of carbonic anhydrase6–9 and related analogues10 has afforded major bio-inspired catalytic routes for CO₂ fixation over the past few decades. On the other hand, synthetic chemistry afforded new transition metal based catalysts that can convert CO₂ into other chemical entities, for instance CO₂ reduction to methanol,11 coupling with oxiranes to produce cyclic carbonates,12–14 or other value added chemicals.15,16

Some of us reported recently17 a novel way to sequestrate and transform CO₂ 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 \([[[\text{Mo}^{VI}]\text{Mo}^{VI}O_2\{(\text{H}_2\text{O})_6\}]_{12}\{\text{Mo}^{VI}X_2[\mu^2-Y]\}]_{30}]^{2-}\) (M = Mo, W; M0 = Mo; X = O, S; Y = bridging ligand, e.g. RCOO−, SO₄²⁻).18 This sort of capsule contains 12 pentagonal \(\{\text{Mo}^{VI}\}\) units placed at the vertices of an icosahedron and linked by 30 binuclear \(\{\text{Mo}^0\}\) units. This arrangement leads to the formation of capsules (Fig. 1) with twenty \(\{\text{Mo}_2\text{O}_3\}\)-type pores and a cavity where a large quantity of water molecules, anions or other species can be confined.19,20 By bubbling CO₂ in an aqueous solution of \([\text{NH}_4]_{42}\square\square[[\{\text{Mo}^{VI}\}\text{Mo}^{VI}O_2\{(\text{H}_2\text{O})_6\}]_{12}\{\text{Mo}^{VI}O_2[\mu^2-\text{CH}_3\text{COO}]\}]_{30}]\) ca. 10 \(\text{CH}_3\text{COONH}_4\) ca. 300 \(\text{H}_2\text{O} \equiv [\text{NH}_4]_{42}\) Anion 1a ca. 10 \(\text{CH}_3\text{COONH}_4\) ca. 300 \(\text{H}_2\text{O} \equiv \text{Compound 1}\) at pH 7 the carbonate derivative \([\text{NH}_4]_{72}\square\square\square\square[[\{\text{Mo}^{VI}\}\text{Mo}^{VI}O_2\{(\text{H}_2\text{O})_6\}]_{12}\{\text{Mo}^{VI}O_2[\mu^2-\text{CH}_3\text{COO}]\}]_{30}]\) ca. 260 \(\text{H}_2\text{O} \equiv \text{Compound 2}\) was obtained.21 The pictorial representation of the \(\{\text{Mo}_{132}\}\) 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 diffussion into the inner cavity or, more interestingly, whether the carbonate anion formation took place in situ inside the capsule, either at the Mo⁷ or Mo⁹ coordination sites, by a metal catalysed nucleophilic addition of water to a solubilised CO₂ molecule, likewise the accepted mechanism of carbonic anhydrase.

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Fig. 1 The pictorial representation of the \(\{\text{Mo}_{132}\}\) Keplerate capsule.
The CO₂ transformation is also reversible via acidification of the aqueous solution of Compound 2. The results of the theoretical study presented herein suggest that this transformation of CO₂ to carbonate is actually the third example known to date of a catalytic process occurring inside the \{Mo₁₃₂\} capsule, where the Mo⁵ and also the Mo⁶ sites play a role.

The mechanism of the hydration of CO₂ to form the carbonic acid has been a subject of theoretical studies over the past few decades. 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. The uppermost energy barrier of carbon dioxide hydration is always the initial step of water addition. The arrangement of this initial transition state 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 CO₂ and its conversion into the carbonate form.

In a recent study we demonstrated that by using a cluster model of the \{Mo₁₃₂\} nanocapsule, the reaction pathway of the reversible cleavage of methyl-tert-butyl ether was successfully unravelled. The model assembly was defined to mimic the nature of the active sites of the Keplerate and it was formulated as \[\text{\{Mo}^6\text{Mo}^6\text{O}^{13}(\text{OH})^8\text{\}₂\{\text{Mo}^5\text{O}_4}\}^{6+}\] containing two pentagonal \{\text{Mo}^6\text{Mo}^6\text{\}₂\}-units and one linker unit of the type \{\text{Mo}^5\text{O}_4\}.

It fully retained the essential characteristics of the \{Mo₁₃₂\} 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 \[\text{\{Mo}^6\text{Mo}^6\text{O}^{13}[(\text{H}_2\text{O})_6(\text{OH})_2\text{\}₂\{\text{Mo}^5\text{O}_4(\text{H}_2\text{O})\}]^{6+}\], which leaves one vacant coordination site reserved for the incoming CO₂ molecule at one of the two Mo⁵ sites, while the second one bears a water molecule which is supposed to undergo nucleophilic addition.

As expected the CO₂ molecule, being nonpolar, does not coordinate in the initial stage to an Mo⁵ centre either in an \(\eta^1\) or \(\eta^2\) fashion. Notwithstanding, we could characterize a weakly bound stationary point structure in which CO₂ is hydrogen-bonded to the water molecule in one Mo⁵ centre and to a water molecule on Mo⁶, 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 CO₂ followed by the subsequent proton rejection and formation of a local Zundel cation.
The higher acidity of the Mo VI centre prompted us to explore a bicarbonate coordinated intermediate resulting from the nucleophilic addition of a hydroxo group to CO2. Given that the Mo VI centres are more Lewis acidic than Mo V (e.g. on average 0.1 pKa units lower in Mo VI for the Keggin structure29) the likely candidate for a good reactant would be 2b bearing the \{MoV(OH)–O–MoVI(OH)\} unit rather than 2a (\{MoV(OH)–O–MoVI(OH)\}). 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 rel ay from the aqua-ligand in the Mo V centre nucleophile with the nucleophilic addition of the hydroxo group to CO2. The \(\Delta G\) estimate for the 2a \(\rightarrow\) 2b conversion is further widened to 17 kJ mol\(^{-1}\) in favour of 2b. The reason for this will be discussed below.

In an \emph{in vacuo} fragment analysis shows that the interaction energy in 2b between the CO2 molecule and the metolate 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, \emph{i.e.} the 4d orbital contribution in the HOMO rests mostly in the 4d\(_{xy}\)–4d\(_{yz}\) 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 \(\text{TS}_2\text{d}, 2\) 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 \emph{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 CO2 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 \{MoV\}-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 \(\text{TS}_3\) has a similar energy value to \(\text{TS}_w\) (the uncatalysed transition state) but intermediate 3a is not sufficiently stable to be considered a viable route (see ESI,3 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 orders10 (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 \(\text{TS}_w\) and \(\text{TS}_2\text{b}\) is that the latter is a slightly “lesser bound” transition state with a reaction coordinate \((\text{C–O})\) bond order 0.377 whereas in \(\text{TS}_w\) it is 0.557 in line with Hammond’s postulate. The \(\angle (\text{O–C–O})\) angles are also considerably different between \(\text{TS}_w\) (139°) and \(\text{TS}_2\text{b}\) (152°) consistent with a larger electron cloud of the incoming O(–C) and consequently a lower angular distortion of CO2. The leaving proton is also more bound to the oxygen atom in \(\text{TS}_w\) (MBO = 0.430) than in \(\text{TS}_2\text{b}\) (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 MoV–OH bond in 2a (v-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.

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 characterised14 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 MoVI mofeties, the relative thermodynamic stability of 2a and 2b species was determined. The calculated \(\Delta E(2\text{a} \rightarrow 2\text{b})\) 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 WV centres are less (Lewis) acidic with respect to Mo VI in relation to Mo VI.
The \textit{in situ} bicarbonate formation, promoted by the Mo\textsuperscript{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\textsubscript{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\textsuperscript{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\textsuperscript{VI} centre will act as a proton acceptor in tandem with the nucleophilic addition to CO\textsubscript{2} which is the protolysis of the aqua ligand in (His)$_3$Zn–OH\textsubscript{2}$^-$.

Carbonic anhydrase enzyme is remarkable. The subtle differences in the mechanism with that operating in the carbonic anhydrase enzymes is 28 kJ mol$^{-1}$ with respect to a comparable micro-solvated CO\textsubscript{2} hydrate.

These results pave the way for defining a new application of Keplarate anionic species CO\textsubscript{2} as CO\textsubscript{2} storage nanodevices.

While the Mo\textsuperscript{V} sites still remain the active catalytic host in Keplarate catalysis there is a clear involvement of the adjacent Mo\textsuperscript{VI} centres as promoters of Bronsted acidity and proton relay. This work was funded by the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2014-52824-R, by the Generalitat de Catalunya project 2014SGR409, and by the ICIQ Foundation. The Severo Ochoa Excellence Accreditation (SEV-2013-0319) and the COST Action CM1203 “Polyoxometalate Chemistry for Molecular Nanoscience (PoCheMoN)” are gratefully acknowledged. NAGB gratefully acknowledges COFUND/Marie Curie action 291787-ICIQ-IPMP for funding. A.M. acknowledges continuous financial support by the Deutsche Forschungsgemeinschaft and the ERC (Brussels) for an Advanced Grant.

Notes and references