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Theoretical investigation of catalytic HCO_3^- hydrogenation in aqueous solutions

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Abstract

Density functional theory along with a dielectric continuum solvation model has been applied to identify possible reaction intermediates for the catalytic hydrogenation of HCO_3^- anion into HCO_2^- that occurs in aqueous solutions in the presence of water-soluble ruthenium complexes. Bicarbonate ion is shown to coordinate to a Ru-dihydride species, which then undergoes a protonation process that yields a CO_2 complex. The C–H bond formation is found to take place via CO_2 insertion into a Ru–H bond and the direct elimination of the formate product is shown to be an energetically favored step, which is assisted by the water medium. We find that water is directly involved in the reaction as a protonating/deprotonating agent and also acts as a coordinating ligand.

Keywords: Aqueous; Hydrogenation; Carbon dioxide; Bicarbonate; DFT

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1. Introduction

Homogeneous catalytic hydrogenation of carbon dioxide belongs to the most thoroughly investigated reactions aiming at utilizing CO_2 as a C1 building block for organic syntheses [1–3]. In many respects, the use of water as a reaction medium in these reactions seems to be advantageous. For instance, the standard free enthalpy of the formation of formic acid from CO_2 and H_2 (Eq. (1)) is a positive value ($\Delta G^\circ_{298} = 7.9\,\text{kcal/mol}$), whereas the hydration of the components turns the reaction slightly exergonic ($\Delta G^\circ_{298} = -1.0\,\text{kcal/mol}$) [3].

$$H_2 + CO_2 \rightleftharpoons HCOOH \qquad (1)$$

In contrast with the reduction of CO_2 in organic solvents, where the reactants and the products have only one possible form, in water, the protonation equilibria must also be considered (Eqs. (2) and (3)). These equilibria suggest that the reactive species and the products vary with changes in the pH, temperature and CO_2 pressure.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+ \qquad (2)$$

$$HCOOH \rightleftharpoons HCOO^- + H^+ \qquad (3)$$

Several experimental findings indicate that water can notably influence the catalytic process not only as a bulk solvent, but as a participant in the reaction. The so-called "water effect" was observed in the course of these reactions in organic solvents, which means that a small amount of water increased the catalytic activity as a result of the interaction between CO_2 and H_2O molecules or between water and the catalyst [1,4].

Some of the most common metal-complexes used for the hydrogenation of carbon dioxide in aqueous solutions involve rhodium and ruthenium centers, and sulfonated triphenylphosphines and phosphine analogues of adamantane as ligands [4]. The rhodium complex of *m*tppts (*meta*-trisulfonato-triphenylphosphine) was used by Leitner's group for the hydrogenation of carbon dioxide in aqueous solutions of amines [5,6]. Based on kinetic and spectroscopic results, the insertion of carbon dioxide into the Rh–H bond of the catalytically active $[RhHL(mtppts)_3]$ ($L{=}H_2O$ or $HNMe_2$) species, the oxidative addition of H_2 to the metal center, and

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the reductive elimination of formic acid were thought to be the key steps of the reaction mechanism.

The reduction of carbon dioxide in amine-free aqueous solutions catalyzed by the ruthenium complexes of *m*tppms (meta-sulfonatophenyl-diphenylphosphine) and pta (1,3,5-triaza-7-phosphaadamantane) were investigated extensively by Joó and his co-workers [7–10]. The reactions were very slow, when unbuffered solutions of CO_2 were used. Nevertheless, high catalytic activity was found in slightly basic solutions, which suggests that HCO_3^- is likely a more reactive form than CO_2 in aqueous reaction media. Experimental results showed that in the absence of H_2 gas, $\{[RuCl_2(m\text{tppms})_2]_2\}$ and HCO_3^- formed a complex with the stoichiometry of $\{[Ru(HCO_3^-)_2(m\text{tppms})_2]_2\}$ [9] and when all substrate molecules reacted, *cis*-$[RuH_2(m\text{tppms})_4]$ remained in the reaction mixture. Since spectroscopic and kinetic results did not provide further information about the reaction intermediates, theoretical mechanistic calculations were thought to be important to reveal the mechanistic steps of HCO_3^- reduction in aqueous solutions (Eq. (4)).

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \tag{4}$$

The reduction of CO_2 has been extensively investigated by means of theoretical methods as well [11–15]. Sakaki and his co-workers have recently presented a thorough DFT study to describe the reduction of CO_2 catalyzed by *cis*-$[RuH_2(PMe_3)_4]$ [15]. According to the suggested mechanism, the reaction takes place via the coordination of CO_2 to the *cis*-$[RuH_2(PMe_3)_3]$ species and a subsequent insertion into the Ru(II)–H bond. The next step was found to be the isomerization of the ruthenium(II) η^1-formate intermediate followed by metathesis of this intermediate with a H_2 molecule leading to formic acid. Previous calculations carried out for this reaction used PH_3 as model ligand [13,14], however the latest work by Sakaki revealed that the application of the real PMe_3 ligands and the inclusion of solvent effects were both necessary to provide reasonable energetics for the reactions.

To our knowledge, no theoretical investigation has been carried out for the reduction of HCO_3^- into HCO_2^- in water. Aqueous solutions present an essentially different environment compared to organic solvents, since water does not only provide a dielectric medium to stabilize polar intermediates, but also participates as a possible ligand to coordinate to the metal center, or as a reactant in proton transfer reactions between the complex and the solution. This enables new reaction paths compared with the ones in organic solvents. The main objective of our present work was to provide a theoretical description for the aqueous reduction of bicarbonate ion catalyzed by $\{[RuCl_2(m\text{tppms})]_2\}$ and identify the role of water as a solvent and reactant in this process.

1.1. Computational details

Cis-$[RuH_2(PMe_3)_4]$ [16] was adopted as a model for the spectroscopically detected *cis*-$[RuH_2(m\text{tppms})_4]$ species, which means that we employed PMe_3 ligands to represent the aromatic phosphines. The drawbacks of phosphine truncation in modeling reactions of metal–phosphine complexes [17] are well known, however, based on the similarity of the donor/acceptor properties of PMe_3 and PAr_3 type phosphines [18] and assuming that the bulky substituents on the phosphine ligands are not involved directly in the catalytic process, nor that they represent steric hindrance, we do not expect that the applied phosphine simplification would introduce significant errors in the obtained relative energies. The only step for which this simplification may cause notable effects is the dissociation of a phosphine molecule from the metal center, because the energy of such phosphine dissociation might be altered by steric effects. In order to assess the steric effects for this step, calculations have been carried out for *cis*-$[RuH_2(PPh_3)_4]$ and *cis*-$[RuH_2(PPh_3)_3]$ complexes.

We first carried out density functional theory calculations to identify the structures of the reaction intermediates of the catalytic process. In some cases, we also located the transition states corresponding to different steps of the reaction. Normal coordinate analysis has been used to verify the nature of these stationary points, and for each transition structure we calculated the intrinsic reaction coordinate (IRC) routes towards the corresponding minima. If the IRC calculations failed to reach the energy minima on the potential energy surface, we performed geometry optimizations from the initial phase of the IRC path.

Most of the calculations have been performed at the B3LYP/SDDP level of density functional theory using the Gaussian 03 program [19], where B3LYP is the applied hybrid functional [20–22] and SDDP refers to a basis set including the Stuttgart–Dresden relativistic small core ECP basis set for ruthenium and the Dunning/Huzinaga DZ + polarization all electron basis set for the lighter atoms [23–26]. For the obtained structures, we estimated the effect of the bulk aqueous medium ($\varepsilon = 78.4$) by the application of the polarizable continuum model (PCM) [27] as implemented in Gaussian 03. We have calculated the standard free energy change for every reaction step including the solvent effects by the application of PCM/UA0 methodology [27b]. These values will be referred to as ΔG°_{aq} throughout the paper.

The calculations for the two model complexes involving the bulky PPh_3 ligands (*cis*-$[RuH_2(PPh_3)_4]$ and *cis*-$[RuH_2(PPh_3)_3]$) have been carried out with the ADF 2004.01 program package [28] by applying the BLYP [29,21] density functional along with the ZORA triple-ξ polarization Slater-type orbital (STO) basis set. The frozen core approximation was applied for the Ru(1s-3d) and P(1s–2p) inner shells and also for the 1s shells of the C and O atoms. The relativistic effects were taken into account by the zero-order regular approximation (ZORA) [30–32].

2. Results and discussion

Before the detailed description of the reaction mechanism it is relevant to compare the overall energetics of the hydrogenation reactions of CO_2 and HCO_3^- (reactions 1 and 4). As Table 1 indicates, the inclusion of solvent effects is clearly required to predict accurate thermodynamic data for these reactions, and also it is seen that the calculated ΔG°_{aq} values for the two reactions are rather similar.

Table 1
Calculated thermodynamic data for the reduction of CO_2 or HCO_3^-[a]

Reaction	ΔG°_{gas} (kcal/mol)	ΔG°_{aq} (kcal/mol)
$H_2 + CO_2 \leftrightharpoons HCOOH$	6.1 [7.9]	−1.9 [−1.0]
$H_2 + HCO_3^- \leftrightharpoons HCO_2^- + H_2O$	8.1	−2.3

[a] ΔG°_{gas} denotes the free energy change for the gas phase reaction, while ΔG°_{aq} includes the solvation energies of the components as estimated by the PCM/UA0 methodology. The experimental values for the first reaction are shown in brackets.

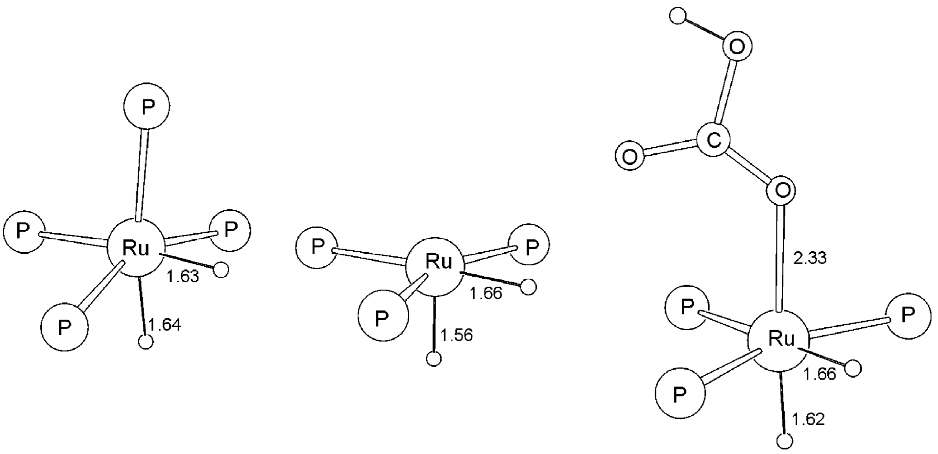
According to the experimental findings, the hydrogenation of bicarbonate ion takes place with very high efficiency around pH 8, where the dominant Ru-containing species detected by ^1H and ^{31}P-NMR-spectroscopy is *cis*-$[RuH_2$(*m*tppms)$_4]$ [33]. This complex, which contains a Ru(II) metal center and two equivalent hydride ligands was considered as the starting point for the reaction mechanism.

Since all our attempts to describe the direct migration of the hydrido ligand to an incoming HCO_3^- gave extremely high energy barriers for the C–H bond formation, we assumed that the hydrogenation reaction involves the coordination of HCO_3^- to the metal center. The coordination may occur via the replacement of a phosphine ligand by HCO_3^- leading to the anionic *cis*-$[RuH_2$(*m*tppms)$_3(HCO_3)]^-$ complex, or alternatively via the formation of the [RuH(*m*tppms)$_4(HCO_3)]$ monohydride species. In our present study, we focus on the first route because the optimized structure of *cis*-$[RuH_2(PPh_3)_4]$ suggests that the hydrido ligands are very much hindered by the bulky phosphines in this complex, thus interaction with other reactants seems to be sterically unfavorable.

It is fairly difficult, if not impossible to provide accurate energetics for the phosphine–bicarbonate exchange with the present simplified model (i.e. $PR_3 = PMe_3$), which neglects the steric repulsion between the bulky aromatic phosphines. Indeed, the calculated ΔG°_{aq} for this process is +22.1 kcal/mol, which is clearly a significant overestimation. In order to quantify this effect, we considered a more realistic model for the dissociation of the phosphine ligand from the coordinatively saturated tetraphosphine complex and carried out DFT calculations at the BLYP/TZP level using the ADF package. The extended model involves PPh_3 as a model ligand for *m*tppms and the calculations indicate that the phosphine dissociation in *cis*-$[RuH_2(PPh_3)_4]$ can easily take place since the calculated dissociation energy is only 4.5 kcal/mol, which is much smaller than the value obtained for the *cis*-$[RuH_2(PMe_3)_4]$ model (28.8 kcal/mol). Taking these results into account we can conclude that the replacement of a phosphine ligand by HCO_3^-, which is present in reasonable concentration in the solution under the typical reaction condition of pH 8, is a thermodynamically feasible process, therefore we considered *cis*-$[RuH_2(PMe_3)_3(HCO_3)]^-$ complex for the further steps (see Fig. 1). We note that the remaining part of the investigated mechanism does not involve phosphine dissociation or coordination processes, therefore we found the simplified PMe_3 ligands satisfactory for subsequent calculations.

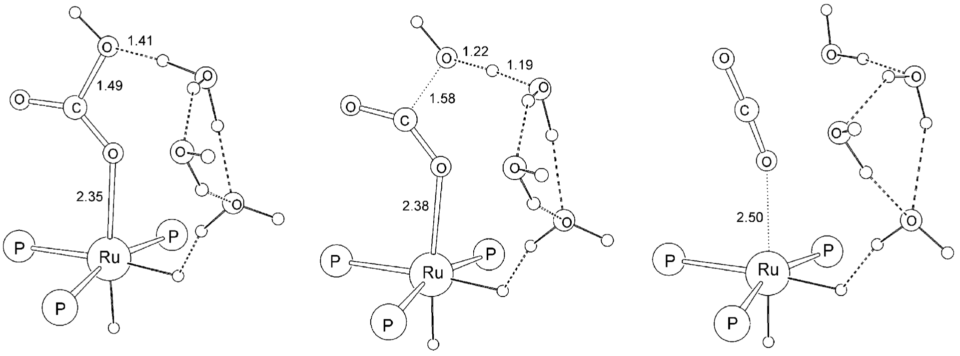
The interaction between the hydrido ligands and HCO_3^- in **3** is found to be unfavored. Since the partially positive carbon atom of HCO_3^-, to which the hydride should be transferred, is hindered by the negatively charged oxygen atoms, the interaction between the hydrido ligands and bicarbonate is quite unlikely. One can therefore assume that the elimination of OH^- from the coordinated bicarbonate ion as a result of the interaction with a hydronium ion is a possible reaction path. This reaction may proceed via the protonation of HCO_3^- on the oxygen already bearing a proton, which simultaneously induces the cleavage of the C–O bond to form a coordinated CO_2 and a water molecule. Experimental findings also showed that the rate of reaction increased when CO_2 pressure was applied over the bicarbonate solutions. The explanation for this finding was that acidic solutions have a positive effect on the catalytic activity [3].

We mention here that the description of proton transfer reactions by means of theoretical methods is not straightforward. Application of reduced models such as H_3O^+, for instance, gives unrealistic results due to the unnaturally high acidity of H_3O^+, which does not exist in real aqueous solutions. Application of the explicit solvent environment of the complex



1 **2** **3**

Fig. 1. Optimized structures for *cis*-$[RuH2(PMe_3)_4]$ (**1**), *cis*-$[RuH_2(PMe_3)_3]$ (**2**) and *cis*-$[RuH_2(PMe_3)_3(HCO_3)]^-$ (**3**) complexes.



4 $\mathbf{TS_{4\text{-}5}}$ **5**

Fig. 2. Optimized structures representing the OH^- elimination from the coordinated HCO_3^- anion.

is computationally demanding, hence small clusters of water molecules were used as in our previous work on H/D exchange processes catalyzed by water-soluble Rh(I) hydrides [34].

A cluster of $[H_3O(H_2O)_2]^+$ was chosen as a model for the protonating agent in aqueous solution. As shown in Fig. 2, structure **4** is characterized by a strong hydrogen-bond formed between the protonating hydrogen and the O–H oxygen of bicarbonate. Structure $\mathbf{TS_{4-5}}$ represents the transition state, which corresponds to the OH^- elimination from the coordinated bicarbonate ion. This transition state lies very close in energy to the corresponding minimum (structure **4**) (within less than 1 kcal/mol), which suggests a rather low barrier for the protonation reaction. The IRC calculations from $\mathbf{TS_{4-5}}$ towards the product side indicated the cleavage of the C–O bond and resulted in a species (**5**) with a weakly coordinated CO_2 and a water molecule. The calculated $\Delta G^{\circ}_{\mathrm{aq}}$ for the dehydration reaction is −4.8 kcal/mol. We note that our attempts to describe the protonation of bicarbonate by a neutral $(H_2O)_3$ cluster gave rather unfavorable energetics, which suggests that the presence of the acidic hydronium is required for the OH^- elimination.

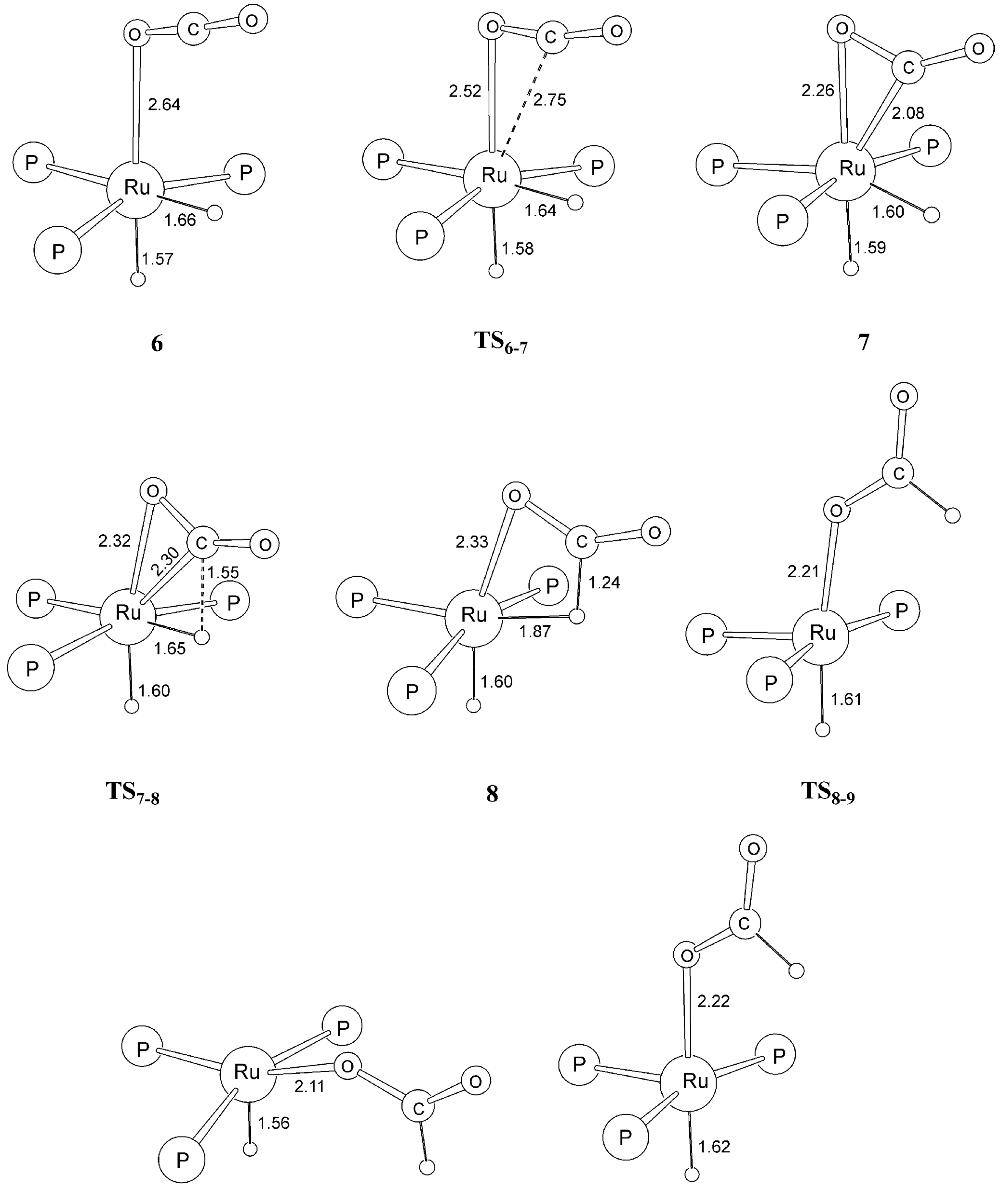
The complex formed after the OH^- elimination was optimized in the absence of the water cluster (**6**), as shown in Fig. 3. The next step of the reaction is the insertion of CO_2 into the Ru–H bond, which was extensively studied by Sakaki and his co-workers [13–15]. Our mechanism is very similar to the one discussed in their latest work [15], therefore we only briefly summarize the identified elementary steps.

In complex **6**, the CO_2 molecule is weakly bound to the ruthenium center as indicated by the OCO angle of carbon dioxide, which is almost linear in this complex. The binding energy of CO_2 in complex **6** is only 3.7 kcal/mol, however, considering the entropy contribution for a possible dissociation process, the elimination of CO_2 is predicted to be thermodynamically allowed ($\Delta G^{\circ}_{\mathrm{aq}} = -6.1\,\mathrm{kcal/mol}$). The dissociation of CO_2 from complex **6** leads to the formation of complex **2**, which can coordinate another bicarbonate ion and re-enter the catalytic cycle. An alternative reaction channel from complex **6** is the formation of **7** containing an $\eta^2_{\mathrm{C,O}}$-coordinated CO_2 (Fig. 3) via $\mathbf{TS_{6-7}}$, which represents only a very small energy barrier. The coordination process is clearly more favored than CO_2 dissociation, because the calculated $\Delta G^{\circ}_{\mathrm{aq}}$ value for the $\mathbf{6} \rightarrow \mathbf{7}$ step is −17.5 kcal/mol.

The next elementary step on this route is the insertion of carbon dioxide into the Ru–H bond, which proceeds through transition state $\mathbf{TS_{7-8}}$ and leads to the Ru(II)-formate complex **8**. The energy barrier for this step is 11.8 kcal/mol and intermediate **8**, which is 5.0 kcal/mol less stable than the η^2-CO_2 complex, can be characterized by an agostic type C−H...Ru interaction. The final product in the CO_2 insertion process is complex **9**, which is formed by the shift of the formate ligand to the former position of the hydride ligand. The calculated $\Delta G^{\circ}_{\mathrm{aq}}$ for this rearrangement is −2.3 kcal/mol and the corresponding transition state ($\mathbf{TS_{8-9}}$) represents only a very small energy barrier. We note that another possible formate complex can be formed in the insertion process (structure **9’** in Fig. 3), however, this structure has the formate in *trans* position to the hydride ligand and lies 4.7 kcal/mol higher in energy than complex **9**.

The product of the CO_2-insertion (**9)** has an empty coordination site in trans position to the remaining hydride ligand. Since hydride ligands have very strong trans destabilizing effect, this is not a favorable coordination site for molecules such as H_2 to be activated, and it is more likely that one of the surrounding water molecules occupies this vacancy and saturates the complex again. The coordination of a water molecule leads to complex **10** (Fig. 4) and the free enthalpy change for this step is $\Delta G^{\circ}_{\mathrm{aq}} = 1.2\,\mathrm{kcal/mol}$. From this point, the reaction mechanism is completed by the dissociation of the product and the regeneration of the catalytically active hydride species.

The dissociation of the formate ion from **10** can be envisaged as a next step of the reaction, which leads to the formation of a cationic species **11**. This step is quite different from the one proposed by Sakaki and his co-workers for the reduction of CO_2 in organic solvents [15]. Their suggestion for the elimination of formic acid involves the coordination of an H_2 molecule and metathesis to get formic-acid, which can dissociate from the complex. However, the dissociation of formate ion is facilitated by the polar nature of the water medium, that can solvate ions, such as formate and $[RuH(H_2O)(PMe_3)_3]^+$. The $\Delta G^{\circ}_{\mathrm{aq}}$ for the elimination of HCO_2^- is predicted to be 5.3 kcal/mol in

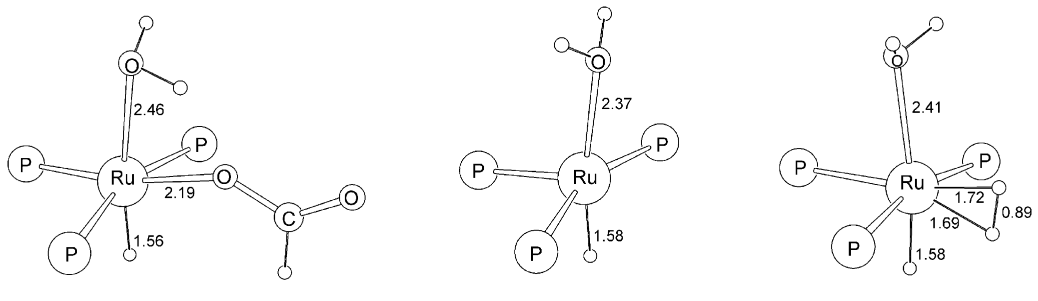


6 **TS_{6-7}** **7**

TS_{7-8} **8** **TS_{8-9}**

9 **9'**

Fig. 3. Optimized structures representing the insertion of carbon dioxide into the Ru–H bond.



10 **11** **12**

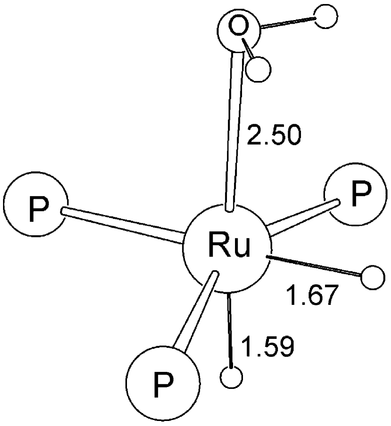
Fig. 4. Optimized structures for $[RuH(H_2O)(HCO_2)(PMe_3)_3]$ (**10**), $[RuH(H_2O)(PMe_3)_3]^+$ (**11**) and $[RuH(H_2)(H_2O)(PMe_3)_3]^+$ (**12**) complexes.

aqueous solution, hence decoordination of the formate ion seems to be energetically possible in water.

To complete the catalytic cycle, the catalytically active dihydride species must be regenerated. The most obvious way for this to occur is the coordination of a H_2 molecule to the empty coordination site in **11** and the immediate deprotonation of the coordinated hydrogen molecule. The ΔG°_{aq} for the H_2-coordination process is −7.1 kcal/mol and the optimized structure of the product formed (**12**) is shown in Fig. 4. The H–H distance of the coordinated H_2 is 0.89 Å, which shows that the coordinated H_2 molecule is in an activated state and can possibly be deprotonated to regenerate the starting Ru-hydride of the catalytic cycle.

On the basis of our previous work [34], it is reasonable to assume that the deprotonation takes place by proton transfer from the dihydrogen ligand to the surrounding water molecules. In order to describe this step, we carried out calculations for a model that involves complex **12** interacting with a water trimer and also for the corresponding dihydride species where the proton is transferred to the water cluster (see structures **13** and **14** in Fig. 5). The transition state for the deprotonation reaction could not be identified in these calculations because of the flat nature of the potential energy surface corresponding to structure **14**. In fact, the geometry optimization procedure initiated from the dihydride...$(H_3O^+)(H_2O)_2$ species converged to **13** after leaving the flat part of the surface, however, the thermodynamic gap estimated from the energy difference between **13** and **14** is reasonably low (11 kcal/mol) and it is expected to be even smaller if larger water clusters were used to represent the bulk water medium since the proton affinity of a water cluster increases with its size [35]. Certainly, estimation of reliable energetics would require a full coordination sphere of water molecules around the ruthenium, however such calculations are computationally prohibited by the applied method.

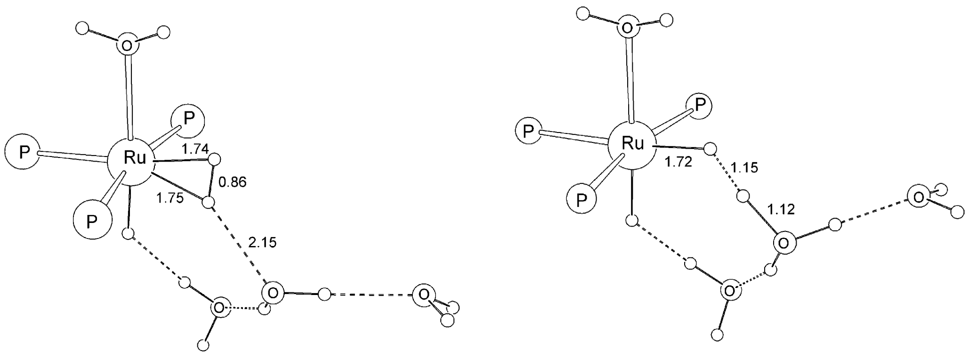
The resulting product of the deprotonation (**15**) was optimized without the water cluster and its structure is shown in Fig. 6. The dissociation of a water molecule gives **2**, which can coordinate another HCO_3^- to repeat the catalytic cycle. The ΔG°_{aq} for the water dissociation is found to be 0.9 kcal/mol for this model.



15

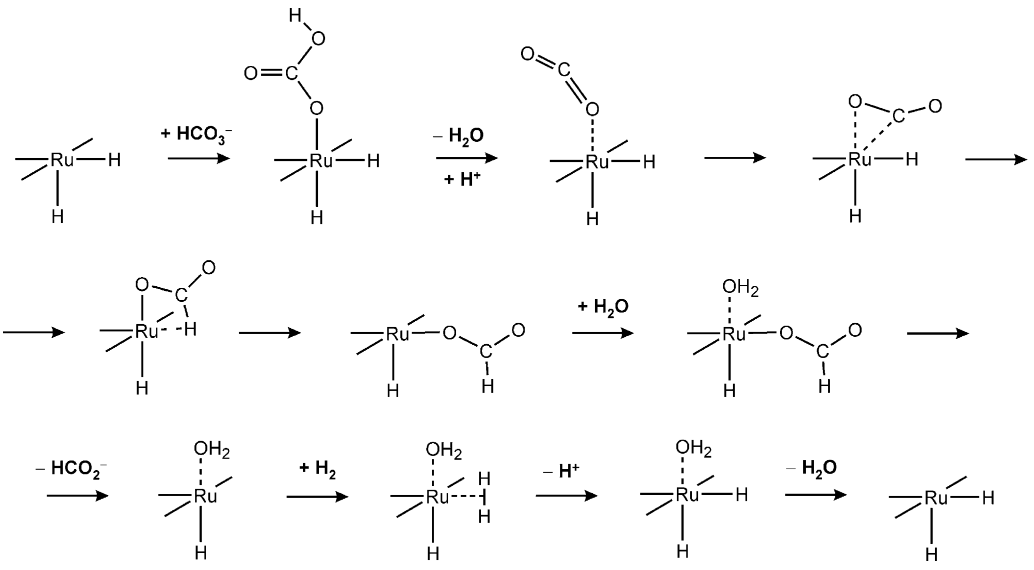
Fig. 6. Optimized structure for $[RuH_2(H_2O)(PMe_3)_3]$ (**15**).

The elementary steps identified in the present study are summarized in Scheme 1. The mechanism that emerges from our current work for the catalytic hydrogenation reaction of HCO_3^- to HCO_2^- in aqueous medium involves the following steps. Replacement of a phosphine ligand by a bicarbonate ion can take place as an initial step of the reaction. Proton transfer from an incoming solvated hydronium ion to the coordinated bicarbonate leads to OH^- elimination from the coordinated bicarbonate resulting in a CO_2 molecule that is weakly bound to the metal center. The possibility of this step, which involves hydronium ions as reactants, was supported by the experimental finding, that applying CO_2 pressure over HCO_3^- solutions increased the reaction rate by lowering the pH of the solution. The formation of the $\eta^2_{C,O}$–coordinated CO_2 complex was shown to be favored energetically with respect to CO_2 decoordination allowing for a CO_2 insertion process into the Ru–H bond. Our results indicate that the reduction of the C atom of the substrate cannot take place directly in the HCO_3^- ion, but the substrate is first transformed into CO_2 and it is activated by its coordination to the metal atom. We also found that the formate ion formed in the reduction process can easily



13 **14**

Fig. 5. Structures representing the deprotonation of the coordinated H_2 in $[RuH(H_2)(H_2O)(PMe_3)_3]^+$. Structure **13** corresponds to an energy minimum, whereas **14** represent a structure from the flat part of the potential energy surface.



Scheme 1. Summary of the proposed reaction mechanism.

dissociate from the metal center because the solvation of the ionic species is energetically favored. We showed that the water molecules do not only act as protonating and deprotonating agents in the reaction, but they may directly coordinate to the metal center if empty coordination sites are available. Our calculations indicate that the active catalyst can be regenerated by the coordination of H_2 to a monohydride species and a subsequent deprotonation of the dihydrogen moiety.

It should be noted here that the proposed mechanism raises the following question. All experiments show that CO_2 is unreactive in this catalytic system, whereas application of CO_2–pressure over bicarbonate solutions can increase the reaction rate. Nevertheless, according to the supposed mechanism, CO_2 is formed in the vicinity of the complex and can be inserted into the Ru–H bond. Neither experimental, nor theoretical results can provide a satisfying explanation for this behaviour, although the results provide some hints for this issue. First, when CO_2 and HCO_3^- are both present in the solution in reasonable concentration, the negatively charged anion coordinates more favorably to the metal center (see calculated ΔG°_{aq} values), while the addition of CO_2 over the solution lowers the pH and can facilitate the proton assisted OH^- elimination from the coordinated bicarbonate. Moreover, at the pH of unbuffered CO_2 solutions the catalyst is present as [RuHCl(*m*tppms)$_3$], which is likely to be less reactive than the dihydride being present under neutral and basic conditions. Finally, the low reaction rates with CO_2 can also be explained by its slow dehydration in aqueous solutions.

We would like to point out clearly that we do not mean to provide the full mechanistic description of the title reaction in the present work. Certainly, other reaction routes have to be examined in future studies, and approximations introduced in the applied methodology have to be systematically assessed. The main approximations include the simplification of the phosphine ligands, the application of a continuum model to describe the solvent effects, and the utilization of approximate exchange–correlation energy functionals in the electronic structure calculations. It is also expected that the explicit treatment of a large number of solvent molecules, the incorporation of nuclear quantum effects (tunneling and zero-point energy vibrations) for the proton transfer processes, and a dynamic mechanistic approach is needed to obtain more insight into the mechanism of hydrogenation reactions in aqueous media. Our work, however, may serve as a starting point for forthcoming investigations.

3. Summary

In the theoretical study presented above, a possible reaction mechanism for the reduction of bicarbonate anion in aqueous solutions was proposed. We demonstrated that the hydrogenation of bicarbonate and carbon dioxide have different mechanistic possibilities in water compared with their analogous reactions in non-polar organic solvents. These differences are related to the facts that water can act as a proton-donor or proton-acceptor in the reaction steps, and water can facilitate the formation of charged compounds more than non-polar organic solvents.

The reaction mechanism was revealed by the application of PMe_3 ligands instead of the real sulfonated aromatic phosphine ligands. The energetics of the reaction mechanism was characterized in terms of ΔG°_{aq} free enthalpy values that were obtained from density functional calculations in conjunction with the use of dielectric continuum methods. This approach is thought to be relevant since several steps of the reaction mechanism include dissociation and coordination processes, in which the entropy contributions are usually significant, and also the majority of the steps include charged species, which can be described in a realistic manner only by calculations including solvent effects.

We can conclude from our results that none of the reaction steps of the proposed reaction mechanism occur with high energy barriers, which is in accordance with the experimental findings that HCO_3^- is effectively reduced under mild conditions with *cis*-[RuH$_2$(*m*tppms)$_4$] as catalyst.

Acknowledgements

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