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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

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*-trisulfonatotriphenylphosphine) 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)).

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \qquad (4)$$

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.