Articles

Theoretical Study on the Thermodynamics of the Elimination of Formic Acid in the Last Step of the Hydrogenation of CO$_2$ Catalyzed by Rhodium Complexes in the Gas Phase and Supercritical CO$_2$

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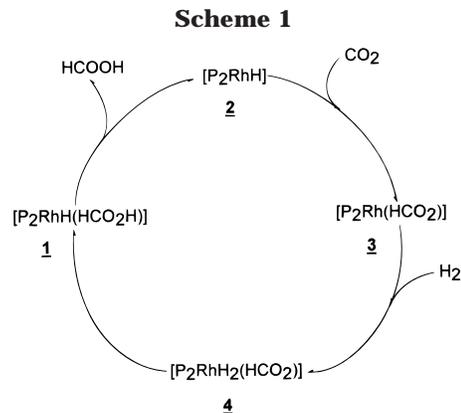
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How coordination of a CO$_2$ molecule can assist in the release of HCOOH from the [P$_2$Rh-(HCOOH)] complex in the last step of the hydrogenation of CO$_2$ catalyzed by rhodium complexes has been investigated by density functional methods. The effect of a supercritical CO$_2$ solution has been included using the polarizable continuum method. It has been found that the presence of a CO$_2$ molecule in the model of the active site favors the thermodynamics of the HCOOH dissociation from the [P$_2$Rh(HCOOH)] species.

Introduction

The homogeneous catalytic hydrogenation of CO$_2$ to formic acid catalyzed by transition-metal complexes, usually rhodium diphosphine complexes, is a promising approach to the use of CO$_2$ as a raw material in chemical synthesis.[1−16] The most widely accepted catalytic cycle for this hydrogenation catalyzed by rhodium complexes involves four steps, as shown in Scheme 1:[1,5−11] (1) insertion of the incoming CO$_2$ molecule into the Rh−H

Scheme 1

bond of the unsaturated T-shaped neutral 14-valence-electron (VE) active species[1,4,9−12,15,17] [P$_2$RhH] complex **2** to yield complex **3**, (2) oxidative addition of H$_2$ to the vacant site of complex **3**, (3) reductive elimination to yield complex **1**, and (4) release of HCOOH from complex **1** to recover the catalytic species complex **2**. In a series of recent works, Dedieu *et al.*[18−20] have explored theoretically the possibility that a single step consisting

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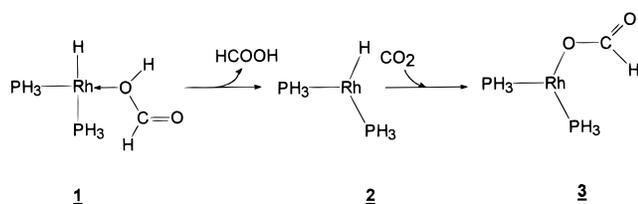
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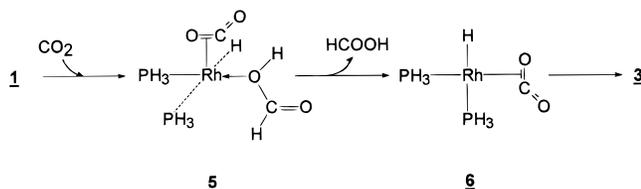(18) Hutschka, F.; Dedieu, A.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1742.
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Scheme 2

1   **2**   **3**

Scheme 3

5   **6**

of a σ-bond metathesis instead of the two-step oxidative-addition/reductive-elimination process (steps 2 and 3) can occur during the transformation from complex **3** to complex **1**, by taking the [(PH$_3$)$_2$RhH] species as a model for the catalytically active site. From these investigations the authors conclude that the σ-bond metathesis process, despite being more often associated with early-transition-metal complexes than with d^8 complexes,[21] is kinetically more favorable than the two-step oxidative-addition/reductive-elimination process by about 4 kcal mol^{-1}. Interestingly, they have also shown that an external base can assist the heterolytic cleavage of H$_2$ on the way from **3** to **1**, by reducing the energy requirements by about 10 kcal mol^{-1}.[20]

Experimental[5] and more precisely theoretical[18,19] studies have shown that the HCOOH elimination from the [P$_2$RhH(HCO$_2$H)] complex **1** is the rate-limiting step of the process. In particular, Dedieu *et al.*[18,19] have found that the energy needed for surpassing this last step is 24.6 kcal mol^{-1}. Such a relatively high energy requirement for the release of HCOOH does not meet the expected standards for a process that occurs rapidly at moderate temperatures and that is fully reversible.[9] It has been suggested that the presence of a base may facilitate the release of HCOOH,[2,10,20,22] although no conclusive data on this point have been reported to date. On the other hand, it has been also pointed out[18] that substitution of HCOOH by CO$_2$ may follow an associative mechanism that should be less energy demanding than the dissociative one depicted in Scheme 2.

Two possible associative mechanisms can be conceived. First, the incoming CO$_2$ molecule may occupy a vacant coordination site of the 16-VE complex **1**. It is expected that the presence of this new ligand may facilitate the liberation of formic acid in the last step of the hydrogenation process (Scheme 3). Second, the CO$_2$ molecule may bind the hydride ligand through a donor–acceptor interaction[23] to yield the complex **7a** in Scheme

Scheme 4

7a   **7b**
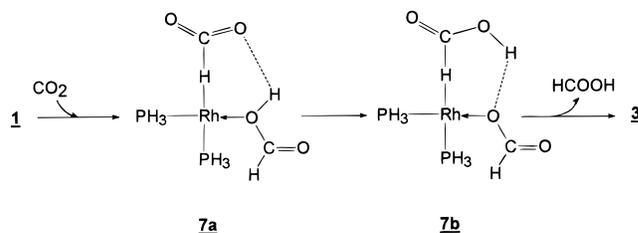
4, which in turn can rearrange to complex **7b**, which after release of HCOOH may form complex **3**, closing the catalytic cycle.

In this work, we have undertaken the study and analysis of the dissociative and the two proposed associative mechanisms for the release of HCOOH from complex **1**. Our aim is to discuss the mechanism that operates in the last and rate-limiting step of the hydrogenation of CO$_2$ by rhodium complexes. The results obtained show how the coordination of a CO$_2$ molecule to complex **1** prior to the liberation of formic acid facilitates its release by reducing the energy requirements.

Usually the hydrogenation of CO$_2$ by rhodium complexes is carried out in organic solvents or aqueous solutions at moderate temperatures (50–160 °C). This notwithstanding, in the quest for improving the efficiency of this catalytic process, the use of supercritical fluids, especially supercritical carbon dioxide (scCO$_2$), as solvents has been explored recently.[1,2,22,24,25] The favorable effects of the scCO$_2$ solution on the catalysis, as compared to common organic solvents, have been attributed to, among other factors, the higher solubility of H$_2$, the higher concentration of CO$_2$, the rapid diffusion of the reactants, and the weakening of solvation around reacting species.[22,24–27] To discuss other possible effects of the scCO$_2$ solution, our study has been performed both in the gas phase and (taking into account the effects of a scCO$_2$ solution) by means of the polarizable continuum model (PCM) method.[28–31]

Computational Details

All computations have been performed at the B3LYP level[32,33] through use of the GAUSSIAN 94 package.[34] The geometries of all molecular systems studied in this work have been fully optimized without symmetry constraints with the

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Table 1. Relative Energies of the Different Complexes Analyzed, Calculated with Respect to the Total Energy of 1 + CO$_2$^{a}

species	$\Delta E_{\text{gas phase}}$, kcal mol^{-1}	ΔE_{scCO_2}, kcal mol^{-1}
1 + CO$_2$	0	0
2 + HCOOH^b + CO$_2$	21.9	20.1
3 + HCOOH^b	8.1	6.2
5	−13.9	−14.1
6 + HCOOH^b	−0.9	−1.3
7b	−7.4	−10.9

^{a} Total energies for **1** + CO$_2$ are −5 726.193 375 and −5 726.198 065 au in the gas phase and in scCO$_2$, respectively. Zero-point energies are not taken into account. All values have been computed on the singlet potential energy surface.[18] ^{b} *trans*-HCOOH.

3-21G basis set[35−38] supplemented with polarization functions (of exponents 0.8, 0.8, 0.55, and 1.1 for O, C, P, and H, respectively). An additional *f*-type polarization function on Rh has not been included because, for similar rhodium complexes, it has been reported that it has little effect on energetic values.[39] Owing to computational limitations, two PH$_3$ groups have been used to simulate the two phosphine ligands in complexes **1**−**7** instead of the experimentally more common methyl- or phenyl-phosphine or R$_2$P(CH$_2$)$_n$PR$_2$ bidentate diphosphane ligands.[1−5,14,17] Since most reactions studied here involve ligand addition or dissociation processes, only the thermodynamics of the processes has been analyzed.

To introduce solvent effects, the PCM model due to Tomasi *et al.*[28−31] has been applied on the gas-phase optimized geometries of complexes **1**−**7**. In this model the solvent is represented by a continuous polarizable dielectric with permittivity ϵ and density ρ, and the solute is placed inside a cavity accurately defined by its own geometry.[40] Dielectric polarization due to the solute is simulated by the creation of a system of virtual charges on the cavity surface. The charge distribution on the surface polarizes in turn the charge distribution of the solute. This process is iterated until self-consistency in the solute electron density is obtained. The free energy of solvation is then evaluated as a sum of four terms of different physical origin, namely, the electrostatic, the dispersion, the repulsion, and the cavitation free energies.[31,41] A GEPOL cavity with an average area of the tesserae of 0.4 Å^2 has been used in all calculations.[42] The value of the dielectric constant of the scCO$_2$ solution (ϵ = 1.49) has been obtained by linear interpolation between tabulated values,[43] while the density (ρ = 0.817 g cm^{-3}) has been inferred from the empirical graphical correlation found between ρ and ϵ, $\rho = (\epsilon - 1.0)/0.6$.[43]

Results and Discussion

Figure 1 shows the optimized structures for the six complexes that could be involved in the release of HCOOH from complex **1**, while Table 1 gathers the

relative energies of these complexes with respect to **1** + CO$_2$.[44] From the values of this table it is found that direct release from complex **1** to yield **2** + HCOOH requires 21.9 kcal mol^{-1} in the gas phase at the level of theory employed in this work. Dedieu *et al.*[18,19] have reported a similar value of 24.6 kcal mol^{-1} computed at the MP2 level. In scCO$_2$ the energy required for the dissociation is reduced by 1.8 kcal mol^{-1}, which is not surprising if one considers the increase in the value of the dipole moments when going from complex **1** and CO$_2$ to complex **2** and HCOOH.[45] Interestingly, the insertion of CO$_2$ on the Rh−H bond of complex **2** to yield the η^3-(O,C,H) trihapto complex **3** is an exothermic process by −13.8 kcal mol^{-1} (−13.9 kcal mol^{-1} in scCO$_2$). The energy barrier for this insertion reported by Dedieu *et al.*[19] was only 4.2 kcal mol^{-1} in the gas phase, and therefore the insertion process appears to be too fast to account for the rate-limiting step of the full catalytic cycle. Indeed, both experimental[12] and theoretical[39,46] studies indicated that insertion of CO$_2$ into a Rh−H bond is an exothermic process with a low energy barrier. For this reason, the insertion process will not be the subject of further research here.

Despite the fact that the dissociation process is favored in scCO$_2$, the energy required is still too high for a catalytic process. For this reason, we have analyzed the two possible associative mechanisms depicted in Schemes 3 and 4 corresponding to two HCOOH dissociation processes assisted by a CO$_2$ molecule. Obviously, the high concentration of CO$_2$ in scCO$_2$ should favor the efficiency of these two associative mechanisms.

As far as the **1** → **5** → **6** → **3** associative dissociation process is concerned, we have found that the interaction of the unsaturated 16-VE complex **1** with CO$_2$ to yield the 18-VE complex **5** is exothermic by −13.9 kcal mol^{-1} in the gas phase and by −14.1 kcal mol^{-1} in scCO$_2$, in line with earlier experimental[12,47,48] and theoretical[18,19,39,46,49] studies of coordination of CO$_2$ in rhodium complexes. Dissociation of HCOOH from complex **5** to yield complex **6** is endothermic by only 13.0 kcal mol^{-1} in the gas phase. Therefore, release of HCOOH from complex **5** is 8.9 kcal mol^{-1} less endothermic than dissociation from complex **1**. Dissociation of HCOOH from complex **5** is even slightly more favored in scCO$_2$, where the energy requirement for the dissociation of HCOOH is only 12.8 kcal mol^{-1}. Efforts to locate a transition state (TS) in the reaction path from **5** to **6** + HCOOH have been made by means of linear transit calculations. These calculations have shown that there is a continuous increase in energy during this process,

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(40) The sphere radii used for atoms were from the UATM model set of radii[50] (OH, 1.59 Å; PH$_3$, 2.37 Å; O, 1.59 Å; CH, 1.86 Å), except for rhodium, for which a value of 1.63 Å was taken. The calculations were carried out at 210 atm and 323 K, simulating earlier published experimental conditions for the hydrogenation of CO$_2$ in scCO$_2$.[2,22]

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(44) Total energies for complexes **1**−**3**, **5**, **6**, and **7b** are −5 538.574 280, −5 349.755 963, −5 537.397 095, −5 726.215 792, −5 537.411 436, and −5 726.211 035 6 au in the gas phase and −5 538.581 512, −5 349.765 013, −5 537.404 889, −5 726.220 544, −5 537.416 749, and −5 726.215 439 au in scCO$_2$, respectively. Zero-point energies are not included.

(45) The gas-phase dipole moment for *trans*-HCOOH is 1.37 D, and for complexes **1**−**3**, **5**, **6**, and **7b** the gas-phase dipole moments are 1.74, 2.23, 5.83, 3.99, 4.35, and 7.66 D, respectively.

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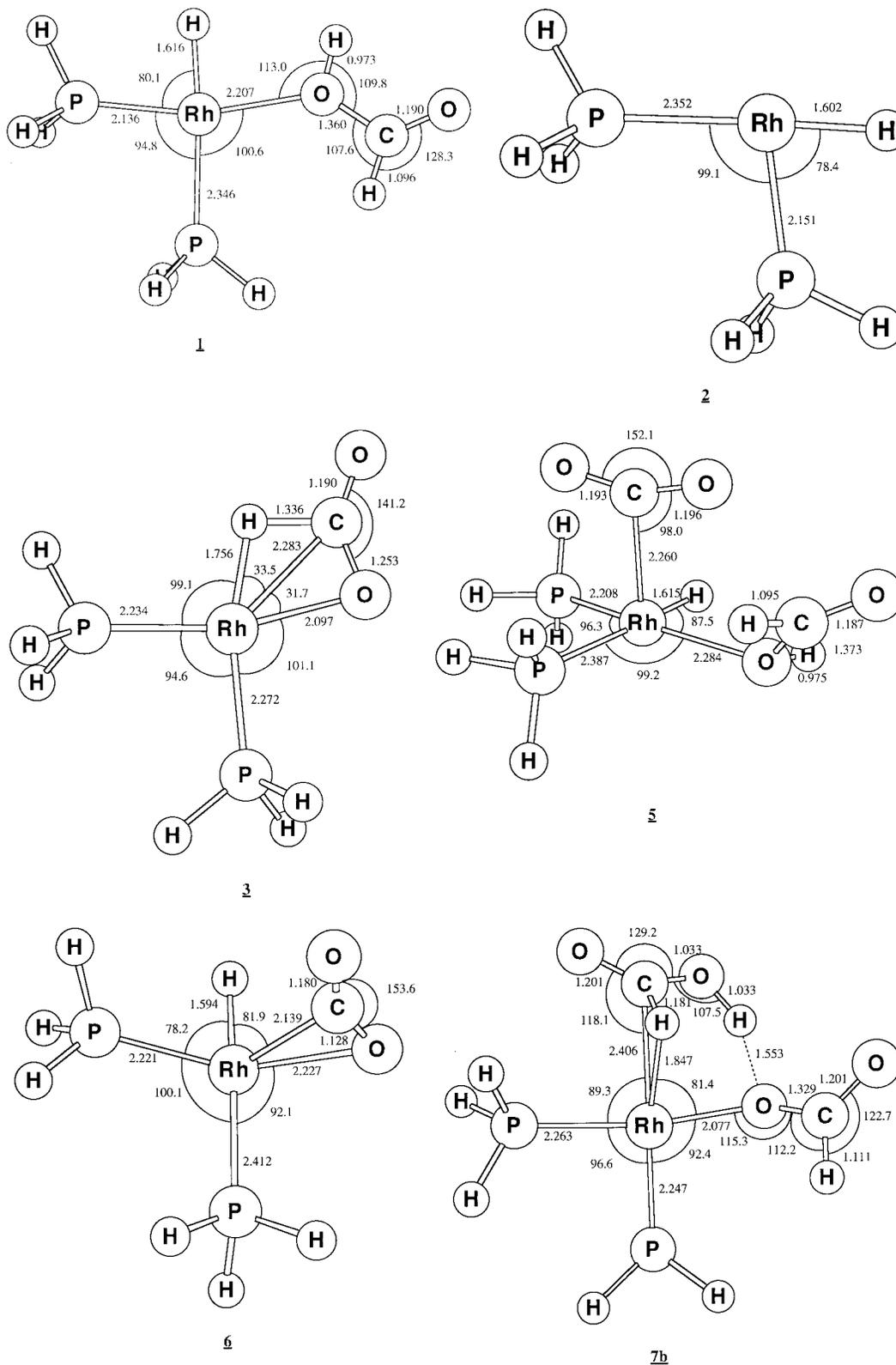(50) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.

Figure 1. The most relevant geometrical parameters of complexes **1**–**7**.

and therefore, it has not been possible to find a TS for this pathway. The insertion of CO_2 into the Rh–H bond of complex **6** to yield complex **3** is a slightly endothermic process by 9.0 kcal mol^{-1} in the gas phase and 7.5 kcal mol^{-1} in scCO$_2$. As before, from the calculations by Dedieu et al.,[19] one can expect that the insertion of CO_2 into the Rh–H bond that forms complex **3** from complex

6 will possess an small energy barrier (only slightly larger than 9 kcal mol^{-1}).

With respect to the **1** → **7a** → **7b** → **3** associative mechanism, it must be noted that the charge-transfer complex **7a** is not a true minimum on the potential energy surface and that, starting from a geometry close to this hypothetical structure **7a**, the optimization led

directly to the formation of complex **7b**. Complex **7b** is stabilized by the presence of the agostic interaction between rhodium and the H attached to the C atom of the HCOOH ligand and also by the intramolecular hydrogen bond between HCOOH and $HCOO^-$ ligands. Dissociation of HCOOH from **7b** to yield complex **3** is endothermic by 15.5 kcal mol^{-1} in the gas phase and 17.1 kcal mol^{-1} in scCO$_2$. Attempts to find a TS for the **7b** → **3** path by means of linear transit calculations have been also unproductive, and a continuous rise in energy has been found for the dissociation of HCOOH from **7b**.

Both associative processes favor release of HCOOH. The lowest energy requirement for the dissociation corresponds to the **1** → **5** → **6** associative process. The energy needed for the dissociation of HCOOH is still high enough, as compared to the barriers reported by Dedieu *et al.*[19] for the full catalytic cycle, to indicate that release of HCOOH is the rate-limiting step in the hydrogenation of CO$_2$ by rhodium complexes, as found experimentally.[5] In this **1** → **5** → **6** associative process,

the scCO$_2$ solution has a minor effect on the release of HCOOH, reducing the energy required for dissociation by 0.2 kcal mol^{-1}. Therefore, the dielectric properties of the scCO$_2$ solution do not seem to play a relevant role on the thermodynamics of this process, and as a consequence, the high rate of reaction in scCO$_2$[2,22,24] must be attributed to other factors such as the rapid diffusion, the weak catalyst solvation, the high miscibility of H$_2$ in scCO$_2$, and especially the high concentration of CO$_2$ molecules, since they can assist the dissociation of HCOOH from complex **1** through the **1** → **5** → **6** associative mechanism.