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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

Christian Silvio Pomelli
Scuola Normale Superiore, Piazza dei Cavalieri, 7 56126 Pisa, Italy
Jacopo Tomasi*
Dipartimento di Chimica e di Chimica Industriale, Universitá degli studi di Pisa, Via Risorgimento, 35 56124 Pisa, Italy
Miquel Solà*
Institut de Química Computacional and Department de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain

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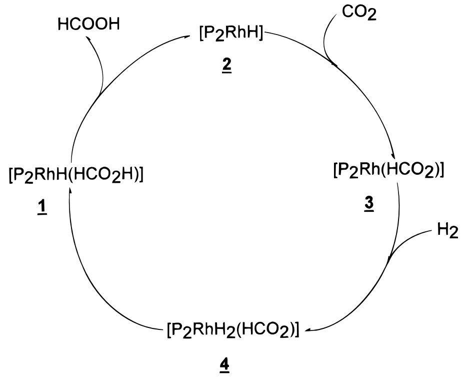
How coordination of a CO_2 molecule can assist in the release of HCOOH from the [P_2Rh(HCOOH)] complex in the last step of the hydrogenation of CO_2 catalyzed by rhodium complexes has been investigated by density functional methods. The effect of a supercritical CO_2 solution has been included using 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_2Rh(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 bond of the unsaturated T-shaped neutral 14-valence-electron (VE) active species[1,4,9−12,15,17] [P_2RhH] 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

Scheme 1



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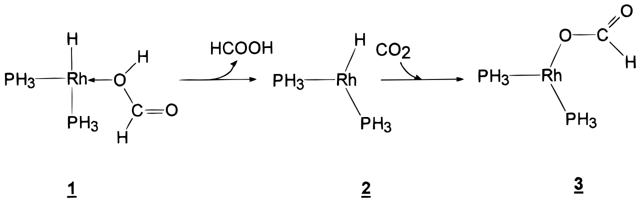
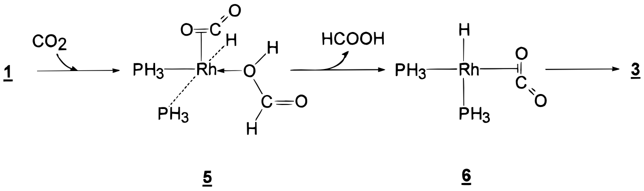
Scheme 2



Scheme 3

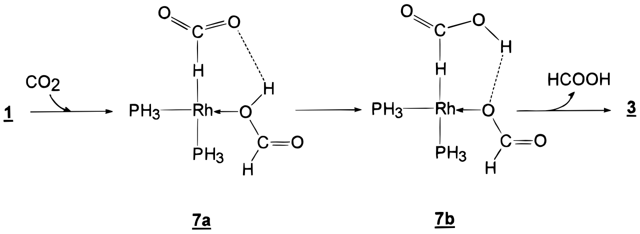


of a σ-bond metathesis instead of the two-step oxidative-addition/reductive-elimination process (steps 2 and 3) can occur during the transformation from complex **3** to complex **1**, by taking the $[(PH_3)_2RhH]$ species as a model for the catalytically active site. From these investigations the authors 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 $[P_2RhH(HCO_2H)]$ 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 4, which in turn can rearrange to complex **7b**, which after release of HCOOH may form complex **3**, closing the catalytic cycle.

Scheme 4



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 $R_2P(CH_2)_nPR_2$ 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 ($\epsilon = 1.49$) has been obtained by linear interpolation between tabulated values,[43] while the density ($\rho = 0.817$ 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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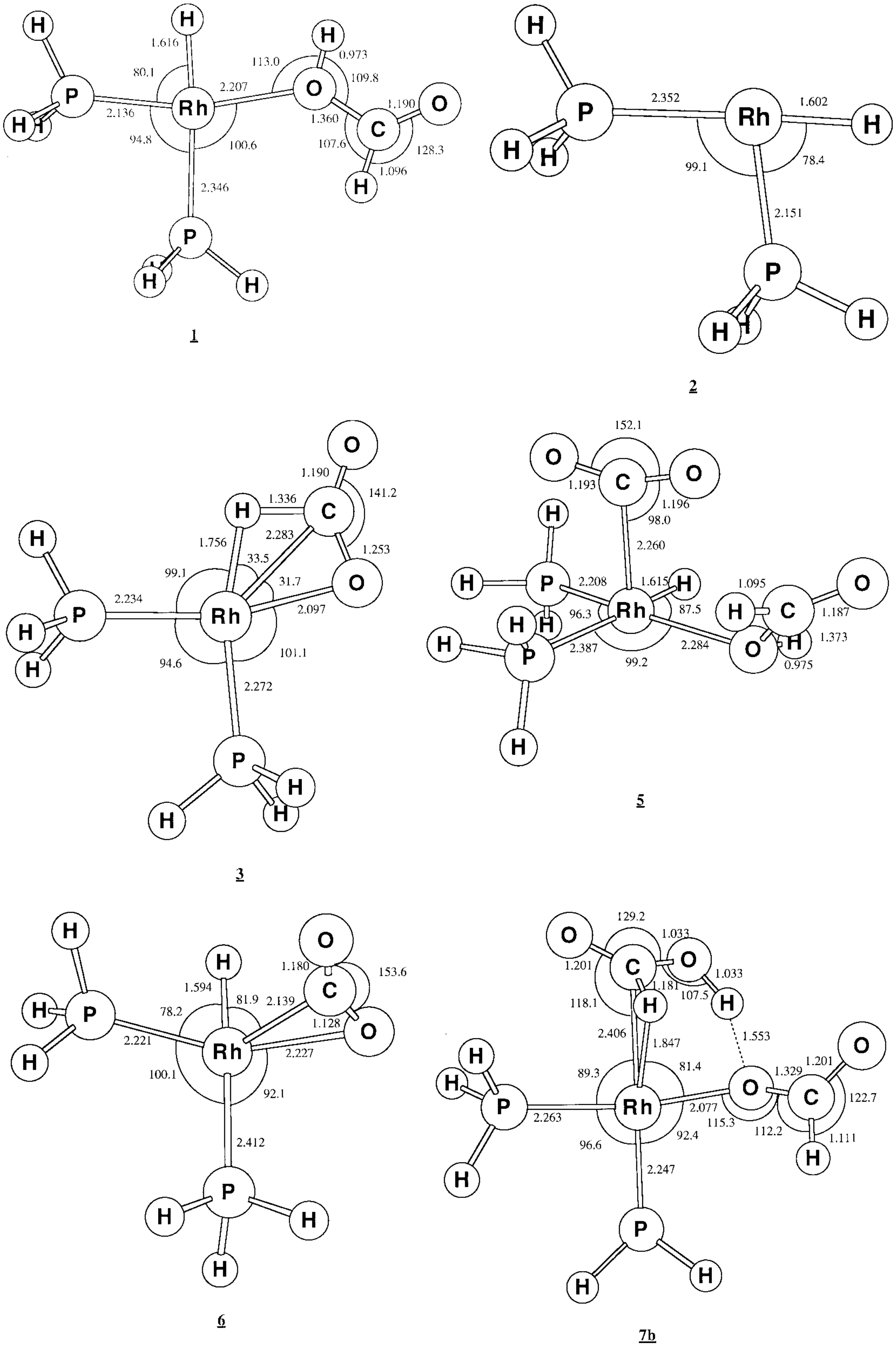

1

2

3

5

6

7b

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.

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