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Platinum Complex Catalyzed Decomposition of Formic Acid

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Dedicated to Professor Dr. Hans-Herbert Brintzinger on the occasion of his 75th birthday

Keywords: Platinum / Hydride ligands / Hydrogen storage / C–H activation / Ab initio calculations / Homogeneous catalysis / Formic acid decomposition

The decomposition of formic acid catalyzed by a cationic hydridoplatinum tetradentate phosphane complex was studied by NMR spectroscopy, isotope labeling and DFT calculations. In the initial step dihydrogen is formed by the reaction of the formic acid with the hydrido ligand yielding a platinum formate cation. The formato ligand is then transformed to CO_2 by a β-H transfer of the formate C–H bond to the Pt center revealing the initial cationic Pt–H complex. The reaction sequence was illuminated by deuterium and C-13 isotope labeling revealing the cationic Pt–D complex as only Pt complex product if a deuterated formate ligand was used. The transfer of the hydrido ligand to an ensuing coordination site at the Pt center is assisted by the labile bonding character of the phosphane ligand. The activation energy was calculated to be +110 kJ/mol above the initial formate complex. The decomposition reaction was observed to be completely reversible yielding formic acid from CO_2 and H_2 at a pressure of around 40 bar. Thus, this reaction provides an excellent example for dihydrogen storage and release on demand using a Pt complex as catalyst.

Introduction

The storage and on-demand generation of dihydrogen is in the focus of interest among other options for future energy concepts.[1,2] While physical storage of hydrogen gas is still difficult the use of a chemical storage technique bears the possibility to store total mass amounts of 4–13% of hydrogen in a liquid transportable medium at 298 K. The challenge is to develop a fast release as well as a reversible storage concept. Due to the high mass amount of H_2 in organic molecules, i.e. methanol and formic acid, these materials are feasible storage media. Storage of H_2 in formic acid has the advantage of a low reaction enthalpy ($\Delta H^{298\,\mathrm{K}} = 14.7\ \mathrm{kJ\,mol^{-1}}$)[3] for the hydrogenation/dehydrogenation of CO_2. In contrast to storage of dihydrogen as hydrides or liquid dihydrogen the storage of H_2 in formic acid does not account for a significant additional contribution in the energy balance of storage and release of H_2. In addition a fast release-on-demand of H_2 can be achieved. The thermal release of dihydrogen from formic acid has been known in organic chemistry for a long time employing dispersed Pt and Pd metal as catalyst.[4]

However, the release of H_2 from metal particles has its caveat; a part of the released dihydrogen gas is dispersed into the metal lattice or adsorbed on the surface which affords additional energy for an activated release.[5] If dihydrogen is released employing a Pt electrode, the formation of CO as further product retards the catalytic reaction by formation of a CO adduct to the Pt catalyst. Therefore a CO-tolerant catalyst is required.[1a,5] Thus, mechanistic investigations have to be performed to understand the influencing factors, and to develop new catalysts with regard to new found structure–property relationships. Besides metallic also molecular based catalyst systems containing platinum-group metals have been reported for the decomposition reaction of formic acid.[6–11] Many research efforts have been made to optimize the catalyst systems with regard to reaction parameters and cocatalysts.[10] However, despite these efforts little is known experimentally about intermediates and reaction steps of the catalytic decomposition of formic acid and the structure of the actual catalytically active species. A number of reaction intermediates and single steps have been postulated that are in accord with experimental observations. However, an experimental proof has not been provided.[6]

From technical perspective the observed activity of the Pt- and Pd-metal based catalyst systems is a good starting point for investigations on the reaction path and possible intermediates. To study the reaction path in detail by means of spectroscopic techniques, we synthesized a defined Pt hydrido complex as entry point for the catalysis and investigated its reaction with formic acid.

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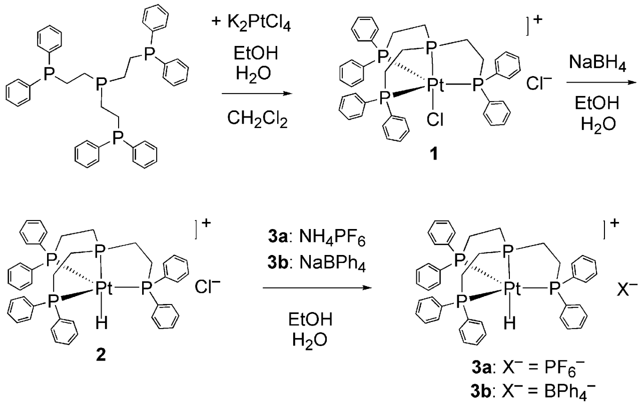
Results and Discussion

For synthesis of a defined mononuclear Pt^{II} hydrido complex we chose the PP$_3$ ligand {PP$_3$: tris[2-(diphenylphosphanyl)ethyl]phosphane}, which has been successfully employed in the chemistry of platinum group metals.[12] Reaction of the Pt^{II} chlorido precursor **1**[13] with sodium tetrahydroborate resulted in formation of complex **2** and after anion exchange complexes **3** were obtained (Scheme 1) in excellent yields. All complexes where fully characterized by NMR spectroscopy and in addition, the geometries of complexes **1**, **2**, **3a** and **3b** were investigated by X-ray structure analysis (Figure 1).



Scheme 1. Synthesis of hydrido complexes.

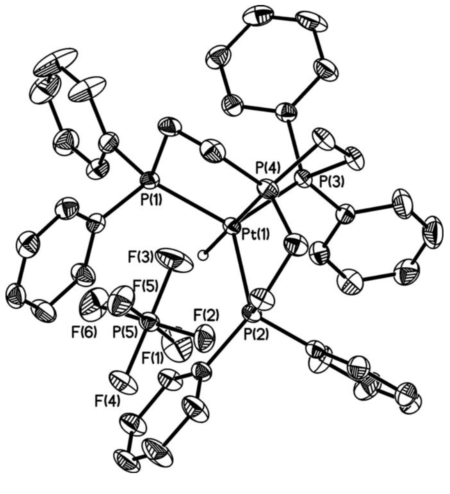


Figure 1. Molecular structure representation of complex **3a** (hydrogen atom shown as sphere of arbitrary radius, and thermal displacement set at 50% probability).

The cationic Pt complex fragment exhibits a distorted pseudo trigonal-bipyramidal coordination environment with the hydrido ligand occupying an axial coordination site (Figure 1).

The temperature invariant vt-^{1}H NMR spectroscopic hydrido resonance (193 K to 298 K) of **3a** at δ = –8.26 ppm (doublet of quartet) and coupling constants [^2J(H,P) and ^1J(P,Pt)], indicate a trigonal bipyramidal structure in [D$_2$]-dichloromethane solution. Additional coupling of the hydrido ligand to the ^{195}Pt atom can be observed, which indicates a Pt-bound hydride atom in solution (Figure 2).

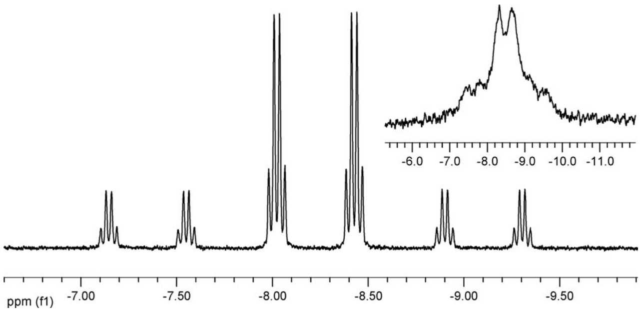


Figure 2. ^{1}H NMR spectrum of cation **3** (only hydride region shown) [^2J (H,P$_{eq}$) = 11.4 Hz, ^2J (H,P$_{ax}$) = 161.8 Hz, ^1J (H,Pt) = 702.1 Hz] (inset: ^{2}H NMR spectrum of **5** in the depicted region).

To test the reactivity of the Pt^{II} hydrido complex **3a** towards decomposition of HCOOH, a solution of **3a** in [D$_2$]dichloromethane ($1.47 \cdot 10^{-2}$ mol L^{-1}) and 1.50 mmol formic acid was stirred at 35 °C. Upon addition of the acid immediate gas formation can be observed. ^{1}H NMR spectroscopic data of the reaction mixture revealed a signal at δ = 4.60 ppm which is indicative for the formation of dihydrogen and after rapid cooling of the mixture a small signal at δ = 8.46 ppm [d, ^4J(H,P$_{ax}$) = 10.8 Hz] indicative for a formato ligand. In order to determine the fate of the carbon dioxide fragment in the formato ligand we repeated the reaction employing ^{13}C labeled formic acid, which revealed the expected ^{13}C NMR shift for $^{13}CO_2$ (at δ = 124.8 ppm). Chemical shifts of H$_2$, the formato ligand and CO$_2$ are in accord with previously published data on related complexes.[7,14] The time-dependent decomposition of formic acid was monitored by NMR spectroscopic and volumetric measurements (Figure 3).

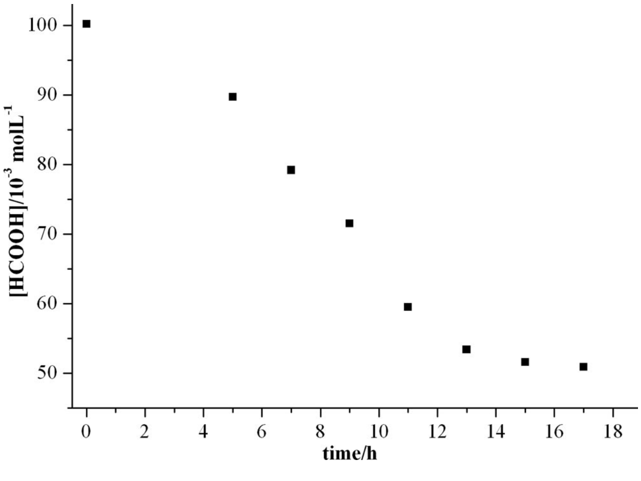
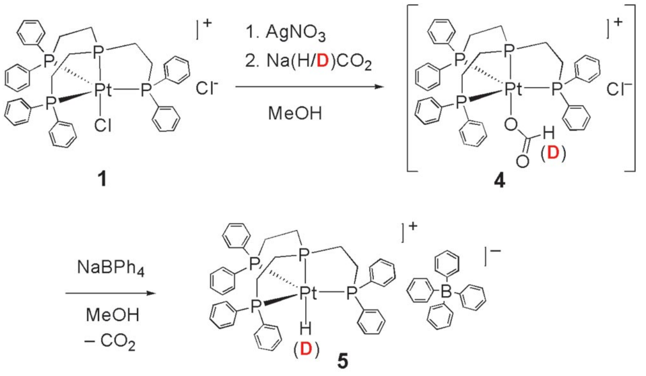


Figure 3. Decomposition of formic acid at 35 °C in CD$_2$Cl$_2$ monitored by ^{1}H NMR spectroscopy.

Upon initial rapid evolution of H_2 and CO_2, the catalysis saturated after 13 h using 7 equiv. of formic acid. When the reaction was performed in neat formic acid at 70 °C, it continues at nearly constant rate for more than 60 h.

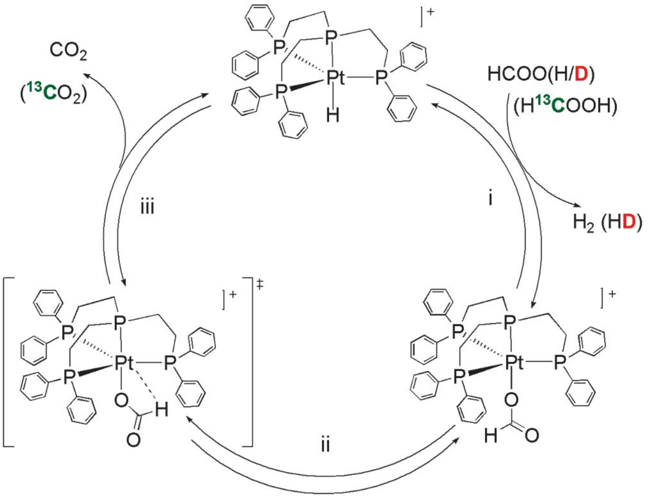
Previous reports on related decomposition reactions postulated a formato complex as key intermediate which transforms into a hydrido complex by β-H transfer to the metal center. However, no experimental indication for this reaction has been given.[7]

To study the decomposition of a Pt–formato complex we attempted the synthesis of the appropriate PP_3Pt–formato complex (Scheme 2). However, from the reaction of the chlorido complex **1** with one equivalent of sodium formate in the presence of silver nitrate only the hydrido complex **3b** could be obtained.[15] To gain deeper insights into the atomic rearrangements and the source of the hydrido ligand we repeated the reaction with $[D_1]$sodium formate. From this reaction only the deuterido complex **5** could be detected by ^1H and ^2H NMR spectroscopic measurements. The NMR spectra of the hydrido and the deuterido complex **5** are depicted in Figure 2. The exclusive formation of a Pt–D bond from the Pt–OC(D)O complex is indicative for β-H(D) transfer from the formato C–H(D) group to a Pt center.



Scheme 2. Proposed formate decomposition path by β-H(D) transfer to the Pt atom.

The observation of a fast release of CO_2 from a formato ligand compared to the overall rate of formic acid decomposition implies that the β-H transfer to the metal center is not the rate-determining step. On the other hand this suggests that formation of H_2 from the hydrido complex and HCOOH is rate determining. If HCOOD is used as formic acid component the formation of a mixture of HD/H_2 has been detected which is indicative of an equilibrium step (i) depicted in Scheme 3. To investigate the reversibility of the decomposition reaction, we studied the reactivity of complex **3a** towards CO_2/H_2. At a pressure of about 40 bar (H_2:CO_2 in a ratio of 1:1) in a stainless steel autoclave at room temperature rapid formation of formic acid can be observed together with the formato ligand and the Pt–H species after transfer of the reaction mixture to a NMR tube. The former appears to be one resting state during formic acid formation under the reaction conditions of high pressure. From our studies the reaction cycle represented in Scheme 3 can be deduced.



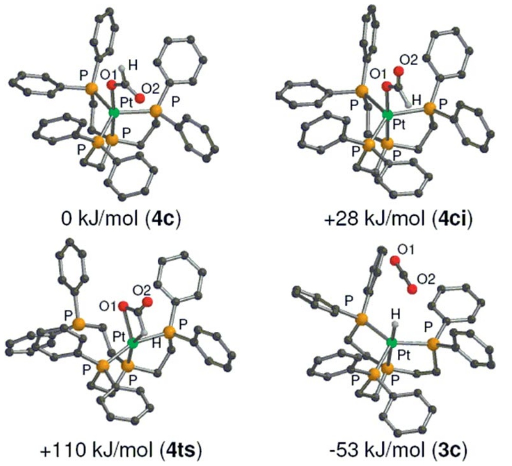
Scheme 3. Proposed catalytic cycle for the decomposition and formation of formic acid.

In order to gain deeper insights into the observed instability of the formate complex towards loss of CO_2 we performed calculations by the density functional theory method which has been successfully employed on related complexes.[16,17]

Optimization of the formate cation **4c** and final cation **3c** (Figure 4) of the decomposition sequence revealed bond parameters in agreement with experimental values. For complex **4c** distances $Pt–P_{eq}$ of 240.9 to 247.9 pm for the equatorial coordinated P-atoms and a distance $Pt–P_{ax}$ of 222.6 pm and angles P–Pt–P of 86° and 112–122° and P_{ax}–Pt–O1 of 172° indicate a nearly pseudo trigonal bipyramidal coordination environment around the Pt center. The distances Pt–O1 of 212.7 pm and Pt–O2 of 326.5 pm indicate a η^1-coordinated formato ligand. The energy of the final state complex **3c** after CO_2 loss is calculated to be $-53\ kJ\,mol^{-1}$ below initial complex **4c**. Thus, the decomposition of the cation **4c** is calculated to be exothermal. The exothermicity of the decomposition reaction surprises because a reaction enthalpy estimated from bond strength data would clearly favour a Pt–O ($391 \pm 42\ kJ\,mol^{-1}$) bond over a Pt–H bond ($330\ kJ\,mol^{-1}$).[18]

The transfer of a hydrogen atom from the formato ligand to the Pt center would require a close Pt–H contact. We therefore rotated the formato ligand around the C–O1 bond around 180° yielding cation **4ci** with a calculated energy of $+28\ kJ\,mol^{-1}$ above cation **4c**.

The reaction path from cation **4ci** to cation **3c** was evaluated by a linear transit technique which located the transition state at a Pt–H distance of 208.6 pm and a C–H distance of 123.3 pm. The energy of this transition state **4ts** was calculated to be $110\ kJ\,mol^{-1}$ above complex **4ci** and 82 kJ/mol above cation **4ci**. In the transition state one equatorial Pt–P bond was significantly elongated with a distance Pt–P of 372 pm and angles P–Pt–P of nearly 86° and 160°



0 kJ/mol (**4c**) +28 kJ/mol (**4ci**)

+110 kJ/mol (**4ts**) -53 kJ/mol (**3c**)

Figure 4. Optimized structures of stationary points depicted along the reaction path of formate decomposition (all but one hydrogen atoms were omitted for clarity).

around the Pt center which indicate a more square-planar coordination environment (Figure 4). An η^2-coordinated formato ligand was not observed in the optimized initial state which was proposed to be a stable side product retarding catalysts activity.[19] The absence of a stable η^2-coordinated formato ligand is attributed to the steric congestion around the pentacoordinate Pt center. Close contacts of phenyl ring C-atoms and O1 in **4c** are calculated to be 348 and 350 pm and for O2 318 pm and 330 pm which are close to the sum of the Van-der-Waals radii (325 pm). The pentacoordinate ligand increases the energy of the initial cation **4c** and thus, decreases the activation energy. On the other hand one of the Pt–P bonds is released along the reaction path which suggests that the ligand is flexible enough to support a fast H-transfer to the Pt center but preventing formation of a stable η^2-bonded formato complex. Thus, the PP_3 ligand acts as a hemilabile ligand facilitating the transition state by thermodynamically destabilizing the initial complex **4c** and lowers the energy of the transition state **4ts** by decoordination of one phosphane arm. In addition the exothermy of the reaction is increased by the recoordination of the phosphane arm which stabilizes the final product complex **3c**. This can be explained by a weakening of the Pt–O bond by nonbonding repulsions. In summary we presented the catalytic decomposition of formic acid to dihydrogen in diluted solution at low temperature following a sequence $[Pt–H]^+$, $[Pt–OCHO]^+ + H_2$, $Pt–H + CO_2$.

Together with the evidence from calculations this is the first direct evidence for the commonly proposed β-H transfer from a formato ligand to a metal center.[7]

Pt-catalyzed formation and decomposition of formic acid provides an ideal reversible and low energy cost storage method for hydrogen even if a diluted Pt complex solution is employed. The decomposition starting from a $(PP_3)Pt–H$ species follows formation of dihydrogen and the appropriate Pt–formato complex which regenerates the initial complex and CO_2. The decomposition reaction studied here is reversible; upon increase of the CO_2/H_2 pressure an increase of the formic acid concentration was observed at room temperature. The Pt catalyst system presented here does not provide a free coordination site at the Pt center in the initial state of the decomposition reaction which prevents poisoning of the catalyst by Lewis bases. On the other hand, a free coordination site can be created in situ to allow a fast decomposition reaction via β-H transfer from the formato ligand to the Pt atom. This concept would aid the development of new catalysts based on mechanistic studies. Further mechanistic investigations and syntheses of improved catalysts are currently performed.

Experimental Section

Decomposition of Formic Acid: 3a (225 mg, 0.22 mmol) was dissolved in 15 mL CD_2Cl_2 and 56.7 µL HCOOH (69.2 mg, 1.50 mmol) was added. The reaction mixture was stirred at 35 °C. NMR samples were prepared in 2 h intervals.

Supporting Information (see also the footnote on the first page of this article): Detailed experimental procedures; analytical and structural data.

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