**CO₂ Activation and Hydrogenation by PtHₙ⁻ Cluster Anions**

**Xinxing Zhang, Gaoxiang Liu, Karl-Heinz Meiwes-Broer, Gerd Ganteför, and Kit Bowen*\)**

**Abstract:** Gas phase reactions between PtHₙ⁻ cluster anions and CO₂ were investigated by mass spectrometry, anion photoelectron spectroscopy, and computations. Two major products, PtCO₂H⁻ and PtCO₂H₂⁻, were observed. The atomic connectivity in PtCO₂H⁻ can be depicted as H₂Pt(HCO₂)⁻, where the platinum atom is bound to a bent CO₂ moiety on one side and a hydrogen atom on the other. The atomic connectivity of PtCO₂H₂⁻ can be described as H₂Pt(HCO₂)₂⁻, where the platinum atom is bound to a formate moiety on one side and two hydrogen atoms on the other. Computational studies of the reaction pathway revealed that the hydrogenation of CO₂ by PtHₙ⁻ is highly energetically favorable.

The transformation of carbon dioxide into reduced, higher value molecules, such as methanol and formic acid, is of great interest for both environmental and economic reasons. In solution, ligand-protected transition metal hydride complexes, LₙMH, often play important roles in these processes.[1–19] The critical reduction step involves the insertion of the C=O group of carbon dioxide into the M–H bond to produce a formate–metal adduct, LₙM-OC(O)H, from which the formate product can be generated. There are, on the other hand, fewer reports of CO₂ reduction by ligandless metal hydrides. Those studies that have been conducted include the methanation of CO₂ on Mg,NiH surfaces,[20] and similar reactions on hydrogen-loaded LaNi₅ and LaNi₅Cr surfaces, where their hydrides play critical roles.[21] Gas phase work is even rarer. While naked (ligandless) transition metal hydrides have been generated in the gas phase as both positive and negative ions (for example, FeD⁺, CoD⁺, NiD⁺, CrH⁻, NiH⁻, CoH⁻, CuH⁻, and FeH⁻⁻)[22–25] we are not aware of them being utilized in CO₂ reactivity studies. However, a recent report details the gas phase, ligand-protected, activation of CO₂ by a Cp₅TiH⁺ metal hydride cation.[19]

The present work focuses on the hydrogenation of CO₂ via reactions with platinum hydride cluster anions, PtHₙ⁻. Platinum hydride cluster anions were chosen because platinum is an excellent hydrogenation catalyst, their hydrides are good sources of hydrogen, and their excess negative charges promote the activation of CO₂. The two products of these reactions, PtCO₂H⁻ and PtCO₂H₂⁻, were identified by mass spectrometry and characterized by anion photoelectron spectroscopy. Ab initio computational studies of the mechanistic pathway revealed that the hydrogenation of CO₂ by PtHₙ⁻ is strongly favorable energetically.

The details of experimental and computational methods are provided in the Supporting Information. The mass spectra with or without CO₂ pulsed into the reaction cell are shown in Figure 1. With no CO₂ in the cell, only PtHₙ⁻ cluster anions were observed in the mass spectrum (Figure 1A; Supporting Information, Figure S1). Individual PtHₙ⁻ species were identified by recording anion photoelectron spectra at every mass peak in the series. These spectra are shown in Figure S1 (Supporting Information), beginning at 194 amu and continuing in single amu steps up to 203 amu. (Mass 202 is missing in the mass spectrum, indicating that PtH₄⁻ is not present.) The photoelectron spectrum at mass 194 was identified as the well-known photoelectron spectrum of Pt⁺. As well as Pt⁺ peaks from another Pt⁺ isotope, new peaks in the photoelectron spectrum at mass 195 are due to PtH⁻. New peaks on top of those in the photoelectron spectrum at mass 196 are due to PtH₂⁻, and so on, up to PtH₅⁻. No PtH₆⁻ was present.

When CO₂ was added to the cell, the ion intensity of the PtHₙ⁻ series decreased, and a new series of PtCO₂Hₙ⁻ cluster anions appeared (Figure 1B). No other products were observed in the entire mass spectrum. The lowest mass peak at 239 amu is due to PtCO₂H⁻, while the highest mass peak at 245 amu is due to PtCO₂H₂⁻; hence, PtCO₂H⁻ and PtCO₂H₂⁻ coexist in the ion beam. Since there is essentially no mass peak at 244 amu, we are confident that PtCO₂H₃⁻ is not present in the beam. The intensity of PtCO₂H₄⁻ is calculated...
to be 29% of that of PtCOH (Supporting Information, Figure S2). More detailed mass spectral and photoelectron spectral analysis of the PtCOH− and PtCOH2− cluster anions are presented in Figure S2 and S3 (Supporting Information). Note that both PtCOH− and PtCOH2− have closed-shell electron configurations.

The photoelectron spectrum of PtCOH2− is presented in Figure 2, and was measured with the third harmonic output of a Nd:YAG laser (3.496 eV). It was recorded at mass 245 amu to ensure that the resulting photoelectron signal was primarily due to PtCOH2−. This spectrum is dominated by a band that ranges from electron binding energy (EBE) = 3.0 to 3.5 eV, with a maximal spectral intensity at EBE = 3.24 eV. Thus, 3.24 eV is the vertical detachment energy (VDE) value for PtCOH2−, that is, the transition energy at which the Franck-Condon overlap is at its maximum between the anion’s wave function and that of its neutral counterpart. The electron affinity (EA) is the energy difference between the relaxed ground state of the anion, and the relaxed ground state of its neutral counterpart. The EA value for PtCOH2− is estimated to be 3.1 eV by extrapolating the lower EBE side of the band to zero photoelectron intensity. The small peak at EBE = 3.08 eV and other very weak features at the low EBE side of the main band are due to the much less abundant isotopomer of PtCOH− at mass = 245 (Supporting Information, Figure S2).

The photoelectron spectrum of PtCOH− is shown in Figure 3C. With five spectral bands in evidence, it is more complicated than that of PtCOH2−. Its features are due, not only to the photodetachment of PtCOH2−, but also to the photodissociation of PtCOH− into PtH+ and CO2, followed by photodetachment of the resultant anion, PtH−. The latter is a two-photon process, where one photon is absorbed, inducing fragmentation, while another photon photodetaches the anionic product of dissociation. This can be seen by comparing the photoelectron spectrum of PtCOH− with that of PtH+. Unfortunately, we did not observe the photoelectron spectrum of PtH+ itself in these experiments. This was because every isotopic mass peak of PtH+ overlapped with at least one of the following anions: Pt+, PtH+, or PtH2+. Nevertheless, we were still able to identify the photoelectron spectral transitions in PtH+ by comparing the photoelectron spectra at mass = 194 (Pt+; Figures 3A) with that at mass = 195 (a combination of Pt+ and PtH+; 3B).

The photoelectron spectrum for mass 195 (Figure 3B), Pt+ peaks at EBE = 2.1, 2.2, 2.9, and 3.4 eV (green dots) share the spectrum with three additional peaks at EBE = 1.60, 1.85, and 3.08 eV (red dots); these are due to PtH+. Significantly, the latter peaks reappear in the photoelectron spectrum of PtCOH− in Figure 3C, not only at the same EBE positions, but also with nearly identical relative intensities. It is clear that the peaks denoted by red dots in the photoelectron spectrum of PtCOH− are due to PtH+. PtCOH− has undergone both photodetachment and photodissociation.

As an aside, the embedded photoelectron spectrum of PtH+ has allowed us to determine, for the first time, that the VDE value of PtH+ is 1.60 eV and the EA value of PtH is 1.5 eV. While the photoelectron study of PtH2− was not an explicit goal of this work, it does add to the mosaic of accumulated data on transition metal hydrides.

The photoelectron spectrum of PtCOH− resides on the high EBE side of Figure 3C as two peaks (blue dots), a small peak at EBE = 3.30 eV and a broader band that reaches its maximum photoelectron intensity at EBE = 3.46 eV. Thus, 3.46 eV is the VDE value for PtCOH−. We further assign its EA value as 3.30 eV. The spacing between these two peaks is 0.16 eV, which is very close to the 1280 cm−1 C−O stretching frequency that we calculated for PtCOH. This value is consistent with a weakening of the C−O bond caused by the activation of the CO moiety. Based on photodissociation products of PtCOH− (PtH+ and CO2 inferred), we speculate that the structure of PtCOH− consists of a CO2 moiety and a PtH+ moiety. As seen below, our computations bear that expectation out.

Figure 4 presents the optimized structures of PtCOH− and PtCOH2−. The calculated 3D coordinates of these two products are provided in the Supporting Information. For PtCOH−, the global minimum is found to have D2v symmetry. It can be viewed as a formate anion/PtH adduct, namely H2Pt(HCO2)−, where the platinum atom is planar tetra-coordinated (PTC) by two hydrogen atoms and the two oxygen atoms of the formate anion moiety. A PTC structure is stable and commonly seen in platinum-containing molecules.
CO₂ insertion and hydrogen atom migration, charge is also transferred from the platinum hydride anion to CO₂, making the formate anion moiety negatively charged by −0.77 e⁻.

In the optimized structure of PtCO₂H⁻, the only hydrogen atom is bonded to platinum. The platinum atom also bonds to the carbon atom of the CO₂ moiety, which is bent from its original linear structure, indicating that CO₂ has been activated by PtH⁻. This structure is consistent with photo-dissociation evidence observed in the photoelectron spectrum. NPA shows that the negative charge is also partially transferred from PtH⁻ to CO₂, resulting in a total charge of −0.66e on the CO₂ moiety. The O-C-O bond angle is determined to be 139.5°, close to the 134° bond angle of the free CO₂ anion at its global minimum. This indicates that, even though hydrogenation of the CO₂ moiety does not occur, CO₂ nevertheless becomes activated by its interaction with PtH⁻. The behavior of PtH⁻ is analogous to that of Au⁺, its isoelectronic analogue, which is known to activate CO₂ by charge transfer.[29,30]

Table 1 presents the EA and VDE values of PtCO₂H⁻/PtCO₂H⁺ and PtCO₂H⁻/PtCO₂H₂⁺ calculated at different theory levels. Agreement among different levels of theory is very good, and is also excellent between the calculated and experimental values.

<table>
<thead>
<tr>
<th>VDE/EA values [eV]</th>
<th>PtCO₂H⁻/PtCO₂H⁺</th>
<th>PtCO₂H⁻/PtCO₂H₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>3.24/3.10</td>
<td>3.46/3.30</td>
</tr>
<tr>
<td>UPB0</td>
<td>3.37/3.21</td>
<td>3.55/3.23</td>
</tr>
<tr>
<td>CCSD</td>
<td>3.10/2.94</td>
<td>3.38/3.28</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>3.19/2.94</td>
<td>3.46/3.44</td>
</tr>
</tbody>
</table>

DFT calculations were carried out to investigate the mechanism of CO₂ activation and hydrogenation. The reaction pathways were calculated for the reactions of PtH⁻ and PtH⁻ with CO₂, respectively. The pathway of CO₂ hydrogenation by PtH⁻ is presented in Figure 5. Before reaction, PtH⁻ exhibits C₃v symmetry. The first step in the reaction is CO₂ activation by charge transfer from PtH⁻. As soon as CO₂ approaches the platinum atom, it bends, and the energy drops by 0.61 eV (structure 1a). The highest occupied molecular orbital (HOMO) of structure 1a (Figure 5) indicates that the excess electron density is delocalized over the entire cluster. Furthermore, according to NPA, the net charge on the CO₂ moiety is −0.39 e⁻, showing that it has been significantly activated. After activation, the CO₂ moiety is ready to accept a hydrogen atom from PtH⁻. The insertion of CO₂ into the Pt–H bond passes through the first transition state (structure TS1), with an energy barrier of 0.42 eV. Once the hydrogen atom has transferred to CO₂, hydrogenation is complete, yielding structure 1b (a local minima). Structure 1b must overcome a small rotational barrier (0.09 eV, TS2) so that PtCO₂H⁻ may reach the global minimum structure shown in Figure 4A (that is, structure 1c in Figure 5). This permits the other oxygen atom to coordinate with the platinum atom, further stabilizing the entire cluster.

The potential energy pathway for the reaction between CO₂ and PtH⁻ is presented in Figure 6. As in the first step in the reaction between CO₂ and PtH⁻, CO₂ is also activated in this case by charge transfer with the platinum atom, forming a bond between the platinum and carbon atoms (structure 2a). The HOMO of this structure also shows substantial delocalization. The activation of CO₂ provides 1.70 eV of stabilization energy to structure 2a of PtCO₂H⁻. (Interestingly, this is much larger than the analogous stabilization energy for CO₂ activation in PtCO₂H⁻, which is...
0.61 eV.) Nevertheless, even though CO$_2$ activation has been achieved at this point in the CO$_2$ and PH$_3$ pathway (via structure 2a), the reaction cannot proceed further to CO$_2$ hydrogenation. The reason that the reaction stops at this juncture is because of 2.84 eV energy barrier, against which hydrogen atom transfer from structure 2a to TS3 would have to occur. (Again, this energy is much higher than the analogous 0.42 eV barrier in the CO$_2$ and PtH$_3$ -reaction.) The reaction cannot proceed to structure 2b. Our photoelectron spectrum of PtCO$_2$H$^-$ and accompanying calculations imply that we have made and photodetached structure 2a, rather than structure 2b. Figure 6 also shows the energy needed to photodissociate structure 2a into PH$_3$ + CO$_2$ (that is, 1.70 eV + 1.68 eV = 3.38 eV). We irradiated PtCO$_2$H$^-$ with 3.496 eV photons when measuring the photoelectron spectrum, which is only slightly more energy than what is required to dissociate PtCO$_2$H$^-$. Everything that we deduced from Figure 3C is consistent with the energetics presented in Figure 6, in terms of the photodetachment and the photodissociation of PtCO$_2$H$^-$. 

Lastly, while there is some evidence that PtH$_2^-$ existed in the ion beam (Supporting Information, Figure S1), there is no evidence that it reacted with CO$_2$; no PtCO$_2$H$_2^-$ was observed in the mass spectrum. The reasons for the inertness of PtH$_2^-$ toward CO$_2$ may be both structural and electronic. PtH$_2^-$ exhibits $D_{h}$ symmetry. Thus, since the platinum atom is surrounded by hydrogen atoms, it is difficult for CO$_2$ to gain access to the platinum atom. Furthermore, PtH$_2^-$ is a very stable species because of $\sigma$-aromatic bonding. Both geometric and electronic features of PtH$_2^-$ are highlighted in Figure S4 (Supporting Information). Our calculations also show that PtH$_2^-$ and CO$_2$ do not react.

### Acknowledgements

This material is based upon work supported by the National Science Foundation (NSF) under Grant No. CHE-1360692 and by the Air Force Office of Scientific Research (AFOSR), under Grant No. FA9550-15-1-0259.

### Keywords:

ab initio calculations - anion photodetachment - carbon dioxide fixation - metal hydrides

### How to cite:

Angew. Chem. 2016, 128, 9796–9799


Received: May 3, 2016
Revised: June 7, 2016
Published online: July 1, 2016