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Mechanistic Insights into Hydride Transfer for Catalytic Hydrogenation of CO₂ with Cobalt Complexes

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The catalytic hydrogenation of CO₂ to formate by Co(dmpe)₂H can proceed via direct hydride transfer or via CO₂ coordination to Co followed by reductive elimination of formate. The different nature of the rate-determining step in the two mechanisms may provide new insights into designing catalysts with improved performance.

Increasing the use of carbon-neutral energy sources, such as solar and wind, will be facilitated by the ability to design catalysts for the interconversion of electrical and chemical energy. Such catalysts could be used to convert carbon-neutral electricity to fuels, or transform gaseous fuels, such as H₂, into carbon-based liquid fuels through the hydrogenation of CO₂. The development of a synthetic carbon cycle based on carbon-neutral energy would have the potential for large-scale expansion in the use of renewable energy for transportation. However, the rational design of stable, highly active, and energy efficient catalysts for this transformation has remained elusive.

The catalytic hydrogenation of CO₂ to formate by Co(dmpe)₂H can proceed via direct hydride transfer or via CO₂ coordination to Co followed by reductive elimination of formate. The different nature of the rate-determining step in the two mechanisms may provide new insights into designing catalysts with improved performance.

Two possible routes are investigated for the transfer of a hydride from Co(dmpe)₂H to CO₂, as shown in Figure 2: (I) a direct hydride transfer that involves transfer of the hydride directly from the metal complex to an encountered CO₂, and (II) an associative pathway, which involves binding of CO₂ through its carbon to the metal (resulting in a formal oxidation to Co(III)) followed by reductive elimination to generate formate and the Co(I) complex. The possibility of the associative pathway was considered because the Co(dmpe)₂H complex is five-coordinate, and we hypothesized that the Co center could participate in the CO₂ activation.

To characterize the key species involved in these two pathways, quantum mechanical calculations were carried out using the hybrid B3P86 exchange and correlation functional and 6-31G** basis set for all the non-metal atoms and the Stuttgart-Dresden relativistic
effective core potential and its associated basis set (SDD)\(^3\) for Co. This level of theory has been shown to provide good accuracy for the prediction of the thermodynamics properties (hydricities, acidities, and reduction potentials) and reactivity of cobalt and nickel hydride complexes.\(^4\) For HCo(dmppe), the thermodynamic data were determined in acetonitrile (MeCN) solution,\(^5\) 9b, 10 whereas catalysis for the hydrogenation of CO\(_2\) was investigated in tetrahydrofuran (THF).\(^6\) Accordingly, calculations were performed in both solvents (For more details, see ESI).

Figure 3. Free energy profile of direct hydride transfer pathway relative to the total energy of Co(dmppe)\(_2\)H and CO\(_2\).

The free energy profile for the direct transfer of the hydridic hydrogen to CO\(_2\) without binding of the CO\(_2\) to the metal center is displayed in Figure 3 (optimized structures of relevant stationary points are illustrated in Figure S1 and Figure S2). The reaction involves a weakly bound intermediate RC\(_0\) resulting from electrostatic interactions between the electrophilic carbon of CO\(_2\) and the Co-H moiety. However, the weak electrostatic interactions and the loss of entropy make the formation of RC\(_0\) endergonic (+7.1 kcal/mol in THF, and +5.0 in MeCN). RC\(_0\) is considered to be the initial catalytic state in the activation of CO\(_2\), and it shows an OCO bond angle of (178.8\(^\circ\)) that is close to free CO\(_2\). The free energy of activation for the hydride transfer TS\(_1\) (relative to unbound Co(dmpe)\(_2\)H and CO\(_2\)) is calculated to be a 17.2 kcal/mol in THF. The TS\(_1\) possesses an imaginary vibrational frequency of 4111 cm\(^{-1}\) corresponding to the movement of the hydride along the axis containing carbon of the CO\(_2\) and cobalt metal. The key entities (carbon, hydride and Co atoms) are strictly confined to a linear conformation and both bonds (Co-H = 1.56 Å and C-H = 1.70 Å in THF) are stretched along the reaction coordinates whereas the OCO bond angle is reduced significantly to 153\(^\circ\) (see Figures S1). The nucleophilic attack of the hydride to CO\(_2\) leads to the formation of a H-bound formate Int\(_1\) complex (OCO angle of 129.5\(^\circ\), consistent with a formate ion), strongly hydrogen bonded to the metal center (See Natural Bond Orbital analysis in ESI and Figure S3). The hydride transfer reaction is slightly endergonic in THF (+1.1 kcal/mol) and exergonic in MeCN (-4.7 kcal/mol) relative to the energy of CO\(_2\) and Co(dmpe)\(_2\)H.

The intermediate Int\(_1\) complex can undergo a facile intramolecular rearrangement via a transition state TS\(_{20}\) (activation barrier of only 3.0 kcal/mol relative to Int\(_1\) in THF) to form an O-bound (Co-(\(\eta^1\)-OCOH)) formate complex (Figure S1 and S2). The relative free energies of both intermediates (Int\(_{10}\) and Int\(_{20}\)) are similar, +1.1 and +1.1 kcal/mol in THF. Due to the similarities in energies as well as the low barrier for their interconversion, formate could be released from either of these intermediates.

Similar pathways with distinct elementary steps for hydride transfer and the subsequent rearrangement from an H-bound to O-bound formate have been suggested previously for the L\(_0\)\(^8\), \(^9\) and Ru\(_6\) metal complexes. In particular, the formation of O-bound formate intermediate with trans-[Ru(dmpe)\(_2\)H\(_2\)] complex was also reported in previous studies.\(^6\) However, in these cases, the hydride transfer step was not the rate determining step.\(^6c, 12\) In contrast, in the present work, the direct hydride transfer pathway is clearly limited by the hydride transfer step, and not by the subsequent rearrangement.

The calculated overall free energy required for the hydrogenation of CO\(_2\) to formate is -6.2 kcal/mol (Figure 3) in MeCN, which compares favorably with previous estimated values of -8 kcal/mol.\(^5\) \(^9b, 10\) Instead, the reaction in THF was calculated to be uphill by 5.9 kcal/mol. This difference in overall free energy indicates a large solvent effect, consistent with the different dielectric constants of the two solvents and consequently their different ability to solvate the formate anion.

For further comparison, we explored an associative pathway in which CO\(_2\) binds to the metal center rather than interacting directly with the hydridic hydrogen as in the direct hydride transfer pathway. The reaction free energy profile is shown in Figure 4 (optimized structures are given in Figures S4 and S5). The initial step in the associative pathway is the binding of CO\(_2\) to the Co metal center with the endergonic formation of the encounter complex RC\(_A\), which has an association free energy of +7.3 kcal/mol and a Co...CO\(_2\) distance of 5.56 Å in THF solution. In spite of the notable structural difference between RC\(_A\) (from the direct hydride transfer pathway) and RC\(_A\), there is only a small energetic difference (0.2 kcal/mol in THF) between the two structures. The association of CO\(_2\) proceeds by binding CO\(_2\) to the Co to form a six coordinated Co(dmpe)\(_2\)(H)(CO\(_2\)) precursor complex Int\(_1A\) via the transition state TS\(_{1A}\) (with activation barrier of +15.8 kcal/mol and +13.6 kcal/mol in THF and MeCN, respectively). This coordination results in a change of formal oxidation state of the metal center from Co(I) to Co(III). TS\(_{1A}\) is characterized by an OCO bond angle of 158°, a Co-C distance of 3.08 Å, and an imaginary frequency of 154i cm\(^{-1}\) (Figure S4).

The formation of the pseudo octahedral intermediate Int\(_{1A}\)
is mildly endergonic in THF (±1.4 kcal/mol relative to Co(dmpe)H and CO₂) and appreciably exergonic in MeCN (±3.8 kcal/mol). From the NBO analysis (Table S2), the total charge on the CO₂ group in CO₂-bound six-coordinate intermediate Int₁₃ is calculated to be -0.64, indicating that the CO₂ is activated. Subsequently, the intermediate Int₁₃ undergoes an intramolecular hydride transfer from the Co center to the electrophilic carbon of CO₂. This step generates the H-bound intermediate formate complex Int₂₄ via a triangle-shaped transition state TS₂₄ (+12.2 kcal/mol and +7.7 kcal/mol in THF and MeCN, respectively, with an imaginary frequency of 271i cm⁻¹). In TS₂₄, the Co-H and Co-C bonds are elongated to 1.55 Å and 2.17 Å respectively, whereas C-H distance is reduced to 1.38 Å (See Figure S4). This reductive elimination step yields Int₂₄, which has a molecular structure and relative energy similar to the intermediate Int₁₃ that is formed in the direct hydride transfer pathway. Therefore, the H-bound formate complex is generated in either pathway and can rearrange to the O-bound formate complex and dissociate.

Binding of CO₂ to form the six-coordinate Int₁₃ complex has the highest activation barrier in the associative pathway. In contrast, the highest barrier found in the direct hydride transfer mechanism comes from the hydride transfer (confirmed with frontier molecular orbitals diagram in Figure S6). The barrier for the associative pathway is slightly lower (~1.4 kcal/mol) than for the direct hydride transfer pathway in both THF and MeCN (Table S1). Note that different DFT exchange and correlation functionals and basis sets (See discussion in ESI) give similar results. Therefore, the present calculations favor the reduction of CO₂ by Co(dmpe)H as occurring by an associative pathway with CO₂ binding to the metal center, followed by a reductive elimination. However, because the barriers for the two calculated pathways are very close in energy, the direct hydride transfer mechanism is also possible. In addition, the calculated barriers for both mechanisms (17.2 kcal/mol and 15.9 kcal/mol) are consistent with the experimentally observed rate (turnover frequency of 3400 h⁻¹ at 21 °C in THF) that corresponds to an overall barrier of 17.5 kcal/mol through transition state theory.

As a possible approach to distinguishing between the direct hydride transfer and associative mechanisms, we calculated the kinetic isotope effects (KIE). The KIE values were determined from the vibrational frequency calculations that include the zero point energy (ZPE) terms by labeling hydride with deuterium. Due to the very different nature of the rate determining steps, the two mechanisms displayed distinct KIE values (Table S1). The direct hydride transfer pathway shows a normal KIE (KS/KD=1.33) consistent with the hydride transfer being the rate-limiting step. In contrast, the associative pathway is characterized by a small inverse isotope effect (KD/KS=0.92), which is consistent with the fact that the hydride transfer is not the rate-determining step in the associative pathway. The two pathways may be experimentally distinguishable based on the difference in the KIEs.

In summary, the present computational study suggests two possible pathways for the catalytic hydrogenation of CO₂ using Co(dmpe)H complex. The associative pathway, in which CO₂ binds to the metal center first, is favored by approximately 1.4 kcal/mol over the direct hydride transfer pathway in which the hydride is directly transferred from the cobalt complex to CO₂. To the best of our knowledge, the pre-coordination of CO₂ to Co as a rate-determining step in the associative pathway has not been reported before for M-H complexes. The accessibility of this new pathway may provide valuable insight for the rational design of catalysts.

Notes and references

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† Electronic Supplementary Information (ESI) available: Details of the computational methods, NBO analysis, optimized geometries (in THF and MeCN) and XYZ coordinates of all the species. See DOI: 10.1039/c000000x/


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[Diagram showing chemical reactions involving phosphorus compounds and carbon dioxide.]