

Theoretical studies on the chemical activation of carbon dioxide

Ph. D. theses

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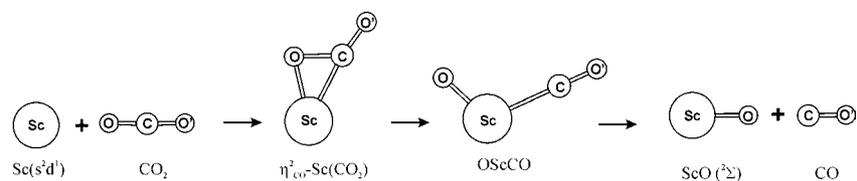
2004

My Ph. D. thesis is based on the work carried out in the Chemical Research Center of the Hungarian Academy of Sciences under the supervision of Dr. Imre Pápai. I studied the reactions of transition metal centers with carbon dioxide, as well as the structure of metal complexes having significance in CO₂ activation.

The electronic structure of the investigated systems was described mainly by means of Density Functional Theory (DFT). The results were verified in some cases by higher-level ab initio methods. While modeling reactions in solutions, solvent effect was also taken into account.

The new results included in my dissertation can be summarized as follows.

[1] I gave a detailed description of the mechanism of the reaction $\text{Sc} + \text{CO}_2 \rightarrow \text{ScO} + \text{CO}$ on the potential energy surfaces belonging to the electronic configurations $^2A'$ and $^2A''$. On both surfaces, the initial step of the reaction is the coordination of the CO₂. The metal atom is then inserted into the coordinated carbon dioxide almost spontaneously (through a rather small energy barrier), followed by a rearrangement of the structure of the resulting complex and its dissociation into ScO + CO fragments.



With the calculations I successfully interpreted the matrix isolation experiments concerning to this reaction, I provided reasonable estimates for the activation energies of the gas phase reaction. I demonstrated with

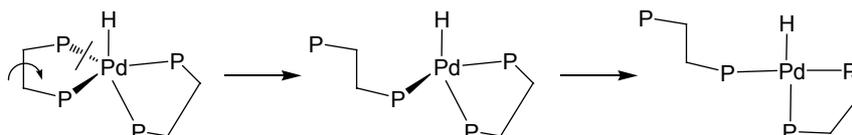
the theoretical study that this apparently simple reaction can actually proceed on more than one potential energy surfaces, and on either surface a series of complex steps leads to the product. On the basis of the results, it can be concluded that in case of the theoretical study of gas phase reactions of the type $M + CO_2$, the experimental results should be interpreted with particular care.

[2] I studied the presumed active $[RhH_2Cl(P^iPr_3)]_2$ form of the complex $[RhCl(P^iPr_3)(C_2H_4)]_2$ enhancing the catalytic '2+2' coupling reaction of allenes and carbon dioxide with PH_3 model ligands, and gave an estimate for the dimerization energy. In this case the theoretical determination of the structure was necessitated by the lack of unambiguous experimental data about the structure of the hydride complex acting as clue intermediate in the reaction.

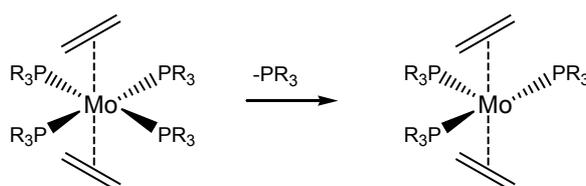
[3] I determined the structure of the newly prepared $[PdH(dppe)_2]^+$ complex using the QM/MM method. The complex prepared experimentally could not be crystallized, therefore, no X-ray diffraction data were available. The crystal structure of the analogous Ni- and Pt-complexes were determined, but the X-ray method gives no information about the position of the hydrogen connected to the metal atom. Using theoretical calculations, I succeeded in unambiguously identifying the structure of the pentacoordinated complex.

[4] According to the experiments, the complex $[PdH(dppe)_2]^+$ is unstable in solution, and can easily be transformed in the disproportionation reaction $2[PdH(dppe)_2]^+X^- \rightarrow [Pd(dppe)_2] + [Pd(dppe)_2]^{2-}X^{2+} + H_2$. This suggests a dual (hydride and proton donor) character of palladium. According to NMR measurements, one of the metal–phosphorous bonds

of the pentacoordinated palladium-hydride complex may break in solution yielding an unsaturated, tetracoordinated hydrido complex. With my calculations, the existence of the unsaturated complex could be supported, and also a low-barrier transition state corresponding to the break of the metal–phosphorous bond could be identified.



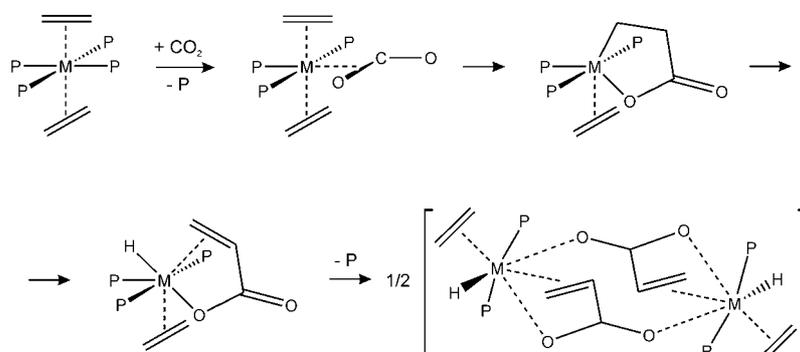
[5] I determined the structure of the $[M(C_2H_4)_2(PR_3)_n]$ ($M = Mo, W$; $R = H, CH_3, n = 3, 4$) complexes, and investigated the metal–ligand interaction by decomposition of the metal–phosphine binding energy. In earlier experiments one of the phosphine ligands was found to get easily separated, and the resulting unsaturated complex can participate in various reactions. According to the calculations, the dissociation energy belonging to the PH_3 model ligand, frequently used in theoretical studies, is much higher than that of the PMe_3 ligand used in the experiments.



With the help of the energy decomposition, I showed that the difference between the bond energies of the two ligands is caused mainly by steric interactions.

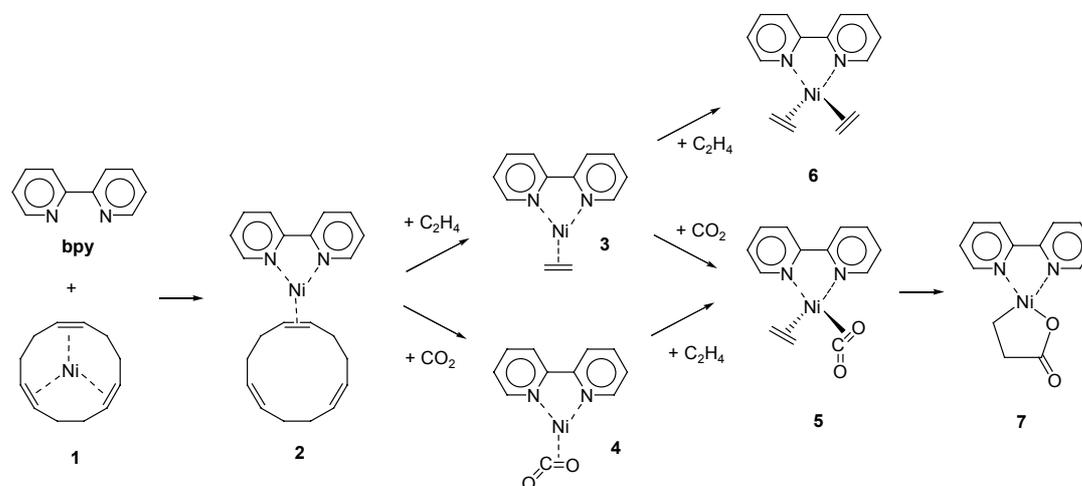
[6] I studied in details the elementary steps of the mechanism of the reaction $2 Mo(C_2H_4)_2(PMe_3)_4 + 2 CO_2 \rightarrow [MoH(CH_2CHCOO)(PMe_3)_2]_2$

+ 2 PMe₃. The hypothetical mechanism of the reaction based on experimental data could be supported by theoretical calculations, as well.



I studied the effects of the PMe₃ → PH₃ simplification, and I found that using the smaller model ligand has significant influences not only in the steps with phosphine dissociation, but also in other steps of the reaction. Taking solvent effect into account made further correction of the calculated reaction energetics. By revealing the details of the reaction mechanism, prediction of the energetics of similar reactions may become possible.

[7] I identified the elementary steps of the reaction [Ni(cdt)] + L₂ + CO₂ + C₂H₄ → [Ni(L₂)(CH₂CH₂COO)] + cdt (L₂ = bpy, dcpe, mbpy, nbpy).



I showed that in this case the coordination of the carbon dioxide to the metallic center is not a precondition of the reaction, and the reaction cannot proceed further because of the great stability of the metallacycle formed. I demonstrated that, by altering the ligands, the barrier of the carbon–carbon coupling step – which is considered the rate determining step of the reaction – can be controlled. The accuracy of the DFT method was verified by higher-level CCSD(T) calculations. An estimation of the solvent effect was also given.

In summary, it can be established that there are several areas where the quantum chemical calculations may successfully contribute to the research dealing with the application of carbon dioxide in synthetic chemistry:

By identifying the elementary steps of the reactions, the details of the hypothetical reaction mechanism based on experimental results can be revealed.

The rate-determining steps of the reactions and the factors influencing the reaction barriers (supplementary ligands, solvent effect) can be identified.

The structure of newly prepared compounds, potential catalysts, reaction intermediates can be determined, even if this would meet serious difficulties by experimental techniques.

Publications related to these theses

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[9] Megyes, T.; Schubert, G.; Kovács, M.; Radnai, T.; Grósz, T.; Bakó, I.; Pápai, I.; Horváth, A. "Structure and Properties of the $[\text{Ru}(\text{bpy})(\text{CN})_4]^{2-}$ Complex and Its Solvent Environment: X-ray Diffraction and Density Functional Study" *J. Phys. Chem. A* **2003**, *107*, 9903.

[10] Bakó, I.; Schubert, G.; Nemes, L. "Quantum Chemical Calculation of the Ground State Geometry and Vibrational Frequencies for the C_{60}^+ Ion" *Internet Electron. J. Mol. Des.* **2003**, *2*, 690.

[11] Bakó, I.; Schubert, G.; Megyes, T.; Pálinkás, G.; Swan, G. I.; Dore, J.; Bellisent-Funel, M.-C. "Structural investigation of liquid formic acid by neutron diffraction. II: Isotopic substitution for $\text{DCOO}[\text{H}/\text{D}]$ " *Chem. Phys* **2004**, *306*, 241.