

# Gas-Phase Spectroscopic Studies on Energetics and Reactions of Transition-Metal Complexes

Summary of Ph.D. dissertation

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# 1 Introduction and Aims of the Work

The chemistry of transition-metal complexes nowadays still undergoes development at an incredible pace. One of the reasons for this is the wide range of applications these compounds have found, ranging from catalysts in industrial processes or precursors in chemical vapor deposition to nonlinear optical materials and antitumor drugs. Several key biochemical transformations are also mediated by metalloenzymes. The stability, catalytic activity and selectivity of transition-metal compounds depend on various factors. In this respect, basic information concerning their thermochemistry, dissociation kinetics and energetics is of significant importance. The observed trends can often be explained in terms of the varying electronic structure or coordination sphere; investigation of adequately chosen model compounds can therefore also deepen our understanding of structure–property relationships.

Gas-phase investigations offer several advantages that make them capable of complementing condensed-phase techniques. For example, the studied systems can often be more well-defined, and the effects of the ligand sphere can be studied in a detailed way. Moreover, somewhat paradoxically, properties of active centers of metalloenzymatic systems can often be understood better on the basis of trends determined in the absence of an averaged interaction with a solvent.

In my thesis, I present results from gas-phase experimental studies of four transition-metal systems. Although the methods and the obtainable accuracy varies, one of the main goals in each case was to determine experimental dissociation energies, from which we could derive conclusions about bonding preferences, ligand–ligand interactions, the effect of electronic structure and oxidation state, or a reaction mechanism.

## 1.1 Carbonyl–Chalcocarbonyl Exchange

Carbon monoxide can be considered as the prototype of  $\sigma$ -donor,  $\pi$ -acceptor ligands. Nevertheless, its compounds, showing various coordination modes, are not only interesting from a theoretical point of view; transition-metal carbonyls are widely used as catalysts in

industrial transformations. The usual starting step for the formation of the catalytically active, coordinatively unsaturated species is the metal–carbonyl bond cleavage. Therefore, the metal–carbonyl bond energies are of great importance. In the last few years, several carbonyl complexes (e.g.,  $\text{CpMn(CO)}_3$ ,  $\text{Cp} = \text{cyclopentadienyl}$ ) were investigated in our laboratory by the threshold photoelectron photoion coincidence (TPEPICO) technique, which was shown to be appropriate for determining accurate metal–carbonyl bond energies.

Heavier chalcogene analogues of CO, namely, CS and CSe, are unstable molecules when isolated, but can be stabilized in the coordination sphere of transition metals. Only a little is known about their thermochemistry; they form stronger bond to the metal center as compared to CO, which is explained by their enhanced  $\sigma$ -donor and  $\pi$ -acceptor character, but accurate bond dissociation energies cannot be found in the literature. Their effect in transition-metal complexes on the bonding of the other ligands is unknown, either.

- Thus, we aimed in the present work to study the chalcocarbonyl analogues of the earlier investigated  $\text{CpMn(CO)}_3$  by the TPEPICO method, in order to determine the metal–chalcocarbonyl bond energies and to obtain insight into the effect of chalcocarbonyl substitution on the bonding of the other carbonyls to the metal center.

## 1.2 Bond Dissociation Energies in Metallocenes

Metallocenes and their derivatives form another important class of organometallic compounds; Cp itself is one of the most studied ligand among the  $\pi$ -donor systems. The numerous applications of its transition-metal complexes include chemical vapor deposition and catalysis in polymerization reactions, for which a crucial aspect is the stability of the metal–Cp bond. Although there are several electron ionization studies on the  $3d$  metallocene complexes in the literature, the reliability of the given bond dissociation energies is questionable because of the lack of careful analysis of the kinetic shift and the thermal energy distribution. For nickelocene, there is also a time-resolved photodissociation study along with extrapolation using

the Rice–Ramsperger–Kassel–Marcus (RRKM) theory, however, it uses only two rate points. Motivated by this fact, a TPEPICO study was carried out on manganocene earlier in our laboratory.

- The aim of the present work was to continue this investigation with the  $\text{Cp}_2\text{M}^+$  ( $\text{M} = \text{Cr}, \text{Co}, \text{Ni}$ ) systems, in order to map the dissociation processes and to determine accurate  $[\text{CpM}-\text{Cp}]^+$  bond dissociation energies. The availability of all these data raises the question how one can explain the trends along the first transition-metal row, which we also try to answer.

### 1.3 Copper–Pyridine Interaction in Oxidation State +2

Copper, like transition metals in general, forms compounds in several oxidation states. Metal–ligand interactions play an important role here, since the stability of the various redox states is influenced by the ligand environment, and vice versa, the preferred structure of the coordination sphere depends on the oxidation state of the metal. Knowledge of this interplay contributes to the understanding of systems as complicated as metalloenzymes, where an extremely fine tuning of the redox reactivity is achieved by the ligand environment.

One very basic model of biochemically relevant copper coordination is provided by its complexes with pyridine, a simple *N*-heterocyclic ligand preferring  $\sigma$ -type coordination to the metal via its lone pair. The chemistry of  $\text{Cu}^{\text{I}}$  with pyridine in the gas phase has been investigated in several studies, and in particular, detailed data about the copper–pyridine bond dissociation energies is available.

- We therefore wanted to extend these investigations, and to study how changing the oxidation state influences pyridine binding. While highly accurate techniques such as TPEPICO could have been used for these systems as well, part of our aims here was to investigate the possibility of using commercially available ion-trap mass spectrometers to obtain approximate bond dissociation energies.

## 1.4 Copper–Disulfide Interaction

Due to the availability of several oxidation states, copper can be, and indeed is widely, applied as a redox catalyst. Following biological examples, disulfide as a potential oxidant in copper-catalyzed reactions has recently enjoyed growing attention. It was found that by appropriately choosing the ligand environment, interconversion between disulfide-bridged dicopper(I) and bis( $\mu$ -thiolato)dicopper(II) is feasible, providing an analogy with  $\text{Cu}_2\text{O}_2$  systems. On the other hand, oxidative addition of sulfur–sulfur bond is well known for several transition metals; the availability of the copper(III) oxidation state and its occurrence in various coupling reactions suggest this to be a viable mode of copper–disulfide interaction as well. Finally, copper catalysis of disulfide cleavage by merely acting as a Lewis acid can also be envisaged, as it was found in an organic hydroxysulfenylation reaction.

- To learn more about these ways of interaction, we decided to investigate a copper-catalyzed intramolecular redox reaction of imines and disulfides, leading to benzothiazoles. Our aim was to get some insight into the reactive intermediates formed in this reaction, and to try to distinguish among the above discussed possibilities for disulfide activation using ion-trap mass spectrometry.

## 2 Experimental Methods

One of the techniques that allows determination of bond dissociation energies with high accuracy is the threshold photoelectron photoion coincidence spectroscopy (TPEPICO), which was used in the first two projects of the present thesis. TPEPICO can be described as a combination of photoelectron spectroscopy and photoionization mass spectrometry. In the TPEPICO experiment, the sample undergoes photoionization, and both the resulting photoelectrons and the corresponding molecular ions are detected in coincidence. Because monochromatic light is used, and only the zero kinetic energy electrons are detected, the resulting ions have well-defined energy

distribution. It is determined by the photon energy, the ionization energy, and the thermal energy of the neutral molecule. The resulting ion internal energy is distributed among its vibrational degrees of freedom; if it exceeds the lowest bond dissociation energy, the ion eventually dissociates. The parent and daughter ions are identified by using a time-of-flight (TOF) mass spectrometer setup. The ions that dissociate in the acceleration region of the spectrometer yield asymmetric, quasi-exponential peaks in the TOF spectra, which allows the kinetics of the corresponding unimolecular dissociation to be studied.

Infrared fluorescence and the time frame of the TPEPICO experiments set a lower limit on the rate constant, for which the dissociation can be detected in practice. Reactions will therefore only be observed for ions having excess energy above the dissociation limit; this excess is called kinetic shift. For a proper treatment of this effect, a precise statistical analysis of the processes occurring in the TPEPICO apparatus is necessary. This protocol involves calculation of the energy distribution of the parent ions, determination of energy-dependent rate constants using an unimolecular rate theory like the Rice–Ramsperger–Kassel–Marcus theory, and modeling the experimental TOF spectra and relative ion abundances at various photon energies. The bond dissociation energy is treated as a parameter in this procedure, and together with other parameters it is adjusted iteratively until the best fit to the experimental information is achieved.

The accuracy of the TPEPICO technique comes at the price of custom-built instrumentation and time-consuming modeling procedure. A less precise but still quantitative solution is to use instead collision-induced dissociation experiments, which can be carried out on commercially available ion-trap mass spectrometers (IT-MS). This method was used for the third and fourth projects, in connection with electrospray ionization (ESI), which provides a direct link from the investigated solution to the gas phase.

The key component of this experimental setup is the quadrupole ion trap, a versatile mass analyzer, in which the ions can be trapped and stored by an oscillating quadrupole electric field for several hundreds of milliseconds. Changing the field parameters or increasing

the kinetic energy of ions by excitation with auxiliary electric fields can lead to the selective ejection of ions with a given  $m/z$  ratio. Excitation can also cause an increase in ion internal energy due to repeated collisions with the low pressure buffer gas present in the ion trap; sufficient energy for fragmentation can easily be transferred. Unfortunately, the conversion of the experimental data from these collision-induced dissociation measurements into absolute binding energies is not straightforward because of the complexity of processes in the ion traps. Instead of a detailed modeling protocol, empirical procedures and calibration can be used here for the analysis.

### 3 Results

The main results and conclusions drawn from the work can be summarized as follows.

1. From TPEPICO experimental results along with the rigid activated complex (RAC) RRKM analysis of the dissociation rates, we determined Mn–CO bond dissociation energies in  $\text{CpMn}(\text{CO})_n\text{CX}^+$  ( $n = 2, 1$ ;  $\text{X} = \text{S}, \text{Se}$ ) ions and Mn–CX bond energies in  $\text{CpMnCX}^+$  species. By the use of the results of previous  $\text{CpMn}(\text{CO})_3$  measurements, the Mn–CX bond energies in  $\text{CpMn}(\text{CO})_n\text{CX}^+$  ( $n = 2, 1$ ;  $\text{X} = \text{S}, \text{Se}$ ) complexes were also obtained [1].
2. Using earlier data on  $\text{CpMn}^+$ , it was possible to determine the heats of formation of the neutral  $\text{CpMn}(\text{CO})_2\text{CX}$  ( $\text{X} = \text{S}, \text{Se}$ ) sample molecules, the molecular ions and the various fragment ions. The enthalpies of the carbonyl replacement with CS and CSe ligands in the neutral complexes were also obtained [1].
3. The results show that CS is always more strongly bound to the transition-metal center than CO, by  $\sim 1$  eV in average, and CSe forms even stronger bonds than CS by  $\sim 0.6$  eV. This is in accordance with the better  $\sigma$ -donor,  $\pi$ -donor and  $\pi$ -acceptor properties of CX. On the other hand, the CX substitution hardly affects the other Mn–CO bond dissociation energies [1].

4. In the TPEPICO experiments for chromocene, cobaltocene, and nickelocene, the dissociation of the  $\text{Cp}_2\text{M}^+$  ions was found to proceed by the parallel loss of neutral cyclopentadienyl ligand, CH, and  $\text{C}_2\text{H}_2$  groups. In addition, isomerization of nickelocene occurs, yielding a complex with pentafulvalene ( $\text{C}_{10}\text{H}_8$ ) and  $\text{H}_2$  ligands, subsequently undergoing  $\text{H}_2$  loss [2].
5. The modeling of the measured TOF distributions and breakdown diagrams using simplified statistical adiabatic channel model (SSACM) provided reliable 0 K appearance energies of  $\text{CpM}^+$  ions and by combining them with the adiabatic ionization energies, the following  $[\text{CpM-Cp}]^+$  bond dissociation energies were obtained:  $(5.04 \pm 0.16)$  eV for  $\text{Cp}_2\text{Cr}^+$ ,  $(5.77 \pm 0.15)$  eV for  $\text{Cp}_2\text{Co}^+$ , and  $(3.96 \pm 0.15)$  eV for  $\text{Cp}_2\text{Ni}^+$  [2].
6. Using a simple molecular orbital picture of the electronic structure of the  $\text{Cp}_2\text{M}^+$  and  $\text{CpM}^+$  ions, we explained the trend in the experimental  $[\text{M-Cp}]^+$  bond dissociation energies including earlier TPEPICO data on  $\text{Cp}_2\text{Mn}^+$  but with the notable exception of  $\text{Cp}_2\text{Fe}^+$ , for which there is no TPEPICO result available [2].
7. In accordance with earlier studies, a comparison of the RAC-RRKM model with SSACM indicates that both theories are capable of fitting the rates over a broad range, but RAC-RRKM predicts notably lower bond dissociation energies [2].
8. From IT-MS collision-induced dissociation experiments in copper-pyridine complexes, it was found that  $(\text{py})_2\text{Cu}^+$  loses a pyridine ligand, whereas the major fragmentation of  $(\text{py})_2\text{CuCl}^+$  corresponds to a loss of chlorine atom, with a less favorable accompanying pyridine loss. For these two latter pathways, we determined a bond dissociation energy of  $[(\text{py})_2\text{Cu-Cl}]^+ = (1.73 \pm 0.16)$  eV and a rough estimate for  $[(\text{py})\text{CuCl-py}]^+ = (2.61 \pm 0.27)$  eV. The preference for chlorine loss is supposedly the consequence of the decreased stability of the resulting low-coordinated  $\text{Cu}^{\text{II}}$  species  $(\text{py})\text{CuCl}^+$ , in comparison with the other product  $(\text{py})_2\text{Cu}^+$  [3].

9. Our experiments on the copper–pyridine system furthermore indicate that IT-MS can be used for estimation of bond dissociation energies, however, in order to get more justification, more systems, ions of different mass ranges as well as sizes need to be included in the test of the calibration process [3].
10. ESI-IT-MS studies on the intramolecular redox reaction of imine disulfides revealed that a single  $\text{Cu}^{\text{I}}$  is sufficient for the catalytic process. On the basis of the experimental results, the involvement of oxidative addition to form intermediate  $\text{Cu}^{\text{III}}$  species seems plausible [4].

## 4 Papers Forming the Basis of the Dissertation

- [1] Á. Révész, C. I. Pongor, A. Bodi, B. Sztáray, T. Baer, “Manganese–Chalco-carbonyl Bond Strengths from Threshold Photoelectron Photoion Coincidence Spectroscopy”, *Organometallics* **2006**, *25*, 6061.
- [2] Á. Révész, L. Szepes, T. Baer, B. Sztáray, “Binding Energies and Isomerization in Metallocene Ions from Threshold Photoelectron Photoion Coincidence Spectroscopy”, *J. Am. Chem. Soc.* **2010**, *132*, 17795.
- [3] Á. Révész, P. Milko, J. Žabka, D. Schröder, J. Roithová, “Reduction from Copper(II) to Copper(I) upon Collisional Activation of  $(\text{pyridine})_2\text{CuCl}^+$ ”, *J. Mass Spectrom.* **2010**, *45*, 1246.
- [4] J. Srogl, J. Hývl, Á. Révész, D. Schröder, “Mechanistic Insights into a Copper–Disulfide Interaction in Oxidation of Imines by Disulfides”, *Chem. Commun.* **2009**, 3463.