Volatile Metal Complexes

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Abstract. The thermodynamics of the formation of gaseous metal complexes and their solvation in nonaqueous solvents is briefly reviewed.

1. Introduction

For a metal complex to be volatile, it has to be of adequate thermal stability and it must be molecular, i.e., the ligands have to fulfill the coordination requirements of the metal and they must — at the same time — compensate its (positive) charge. Examples are:

- the halides and oxides of metals in high oxidation states such as WCl₆ or OsO₄
- many of the metal complexes used in gravimetry such as [Ni(dimethylglyoxime)₆] or [Al(oxychinolinate)₄], and
- source materials for chemical vapour deposition such as [M⁺(acetylacetonate)₄] or Na[Nb(O(CH₃)₂OCH₃)₂]

Simple salts are not volatile, because the anions have to be shared between cations in order to fulfill the coordination requirements of the cations, thus an infinite lattice is formed. Such a lattice may be broken down into molecular units by reaction with molecular ligands replacing some of the bridge- and lattice-forming ligands in the coordination sphere of the metal.

2. Gaseous Complexes with M'X₃ or Pyridine

M'X₃ (M' = Fe, Al, Ga, In; X = Cl, Br, I) and pyridine are molecular ligands which have been studied in some detail. M'X₃ and MX₂ form two chelating M'X₄-tetrahedra which may coordinate to M with an edge or with a face. As an example, the formation of Co(AlCl₄)₂ assuming tetrahedral coordination of Co [2] is shown in the Scheme. Complexes of this type have been reviewed by Schäfer [3] and Papathanodorou [4]. Gaseous complexes of Co halides with pyridine have recently been characterized [5][6].

Table 1 shows that it is appropriate to say that Al₂Cl₆ and pyridine carry CoCl₂ into the gasephase.

To investigate the formation of gaseous metal complexes vapor pressure measurements have to be performed. The most frequently used method is high-temperature UV/VIS spectroscopy but entrainment, evaporation from a Knudsen cell, chemical transport etc. have also been used [3][4].

When theoreticians interpret the spectra of metal complexes, they usually consider the complex as an isolated species, not as a solvated one. Spectra of gaseous complexes offer, therefore, a unique opportunity to compare theory and observation [6][8].

Table 1. Partial Pressure of Cobalt-Containing Species at 350°C

| Species | CoCl₂ | Co(AlCl₄)₂/CoCl₃ in 1 bar of AlCl₃ | Co(AlCl₄)₂/CoCl₃ in 1 bar of pyridine |
|---------|-------|----------------------------------|-------------------------------------|
| Pressure| 2.3·10⁻⁸ bar | 4.3·10⁻² bar | 1.4·10⁻³ bar |

Table 2. Formation Constants of M(AlX₄)₂ in the Gas Phase and in Solution at 298 K

| M   | Kgas | Ksolv | pM(AlX₄)₂ | X = Cl [3] | X = Br [9] | pM(AlX₄)₂ | X = Br [9] | pM(AlX₄)₂ | X = Br [9] |
|-----|------|-------|-----------|------------|-----------|-----------|------------|-----------|------------|
| Cr  | 5.4·10⁻⁶ | 1.3·10⁻⁹ | 0.06       | 2.2        | 2.1       | 6.9·10⁻⁸  | 9.3·10⁻⁹   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Mn  | 2.7·10⁻⁶ | -      | 0.05       | 1.5        | 1.5       | 6.9·10⁻⁸  | 8.2·10⁻⁸   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Co  | 4.4·10⁻⁶ | 6.5·10⁻⁶ | 0.006      | 0.54       | 0.54      | 9.3·10⁻⁹  | 9.3·10⁻⁹   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Ni  | 1.2·10⁻⁶ | -      | 0.017      | 1.5        | 1.5       | 4.8·10⁻⁸  | 8.2·10⁻⁸   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Zn  | 6.7·10⁻⁶ | -      | -          | 7          | 7         | 6.9·10⁻⁸  | 8.2·10⁻⁸   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Cd  | 8.4·10⁻⁶ | -      | -          | 7          | 7         | 6.9·10⁻⁸  | 8.2·10⁻⁸   | 4.8·10⁻⁸  | 8.2·10⁻⁸   |
| Pd  | 8.3·10⁻⁶ | 4.7·10⁻⁶ | 1.1       | -          | -         | -         | -          | -         | -          |
Table 3. Formation of \([\text{CoX}_2(\text{py})_2]\) in the Gas Phase and in Solution at 298 K

|            | \(\Delta H\) [kJmol\(^{-1}\)] | \(\Delta S\) [Jmol\(^{-1}\)K\(^{-1}\)] | \(\Delta G\) [kJmol\(^{-1}\)] |
|------------|---------------------------------|---------------------------------|--------------------------|
| Cl         | –232                            | –320                            | –44.8                    |
| Br         | –197                            | –326                            | –47.7                    |
| acetone    | –173                            | –222                            | –30.6                    |

\(\Delta H \) and \(\Delta G\) are the changes in enthalpy and free energy, respectively, with respect to the reaction 3 rather than sublimation.

Table 4. Bond Energy [kJmol\(^{-1}\)] of Pyridine to \(\text{CoX}_2\)

| Medium      | Bond Energy [kJmol\(^{-1}\)] |
|-------------|-----------------------------|
| for first py |                             |
| CoCl\(_2\)  | –159                        |
| CoBr\(_2\)  | –245                        |
| for second py |                           |
| CoCl\(_2\)  | –80                         |
| CoBr\(_2\)  | –82                         |
| acetone     |                             |
| for first py |                             |
| CoCl\(_2\)  | –21.3                       |
| CoBr\(_2\)  | –44.8                       |
| for two py  |                             |
| CoCl\(_2\)  | –44.8                       |
| CoBr\(_2\)  | –44.8                       |

The average bond energy of pyridine to cobalt is more negative for CoBr\(_2\) than for CoCl\(_2\), and it is much more negative in the gas phase than in solution. In solution, the pyridine replaces solvent molecules, and we observe the energy of this substitution, while, in the gas phase, we observe the formation of the Co-pyridine bond. This very important difference should always be kept in mind, when energetics of reactions in solution are discussed or interpreted.

3. Conclusion

The study of complex formation in the gas phase and in solution is the only means to separate solvation effects from individual metal-ligand interactions. Therefore, it yields true metal-ligand bond energies, and the spectra of gaseous complexes are particularly well suited to compare chemical-bond calculations with experimental observations.

In addition, gaseous complexes are useful to prepare materials by chemical vapor deposition (CVD) [1] and to perform metal analysis by gas chromatography [14]. The role of gaseous complexes in many fields such as catalysis or corrosion has not yet been investigated.