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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 fulfil 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 WCl_6 or OsO_4
- many of the metal complexes used in gravimetry such as [Ni(dimethylglyoxime)$_2$] or [Al(oxychinolinate)$_3$], and
- source materials for chemical vapour deposition such as [M^{n+}(acetylycetonate)$_n$] or Na[Nb(O(CH$_2$)$_2$OCH$_3$)$_6$] [1].

Simple salts are not volatile, because the anions have to be shared between cations in order to fulfil 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'X$_3$ or Pyridine

$M'X_3$ (M' = Fe, Al, Ga, In; X = Cl, Br, I) and pyridine are molecular ligands which have been studied in some detail. $M'X_3$ and MX_2 form two chelating $M'X_4$-tetrahedra which may coordinate to M with an edge or with a face. As an example, the formation of $Co(AlCl_4)_2$ assuming tetrahedral coordination of Co [2] is shown in the *Scheme*. Complexes of this type have been reviewed by *Schäfer* [3] and *Papatheodorou* [4]. Gaseous complexes of Co halides with pyridine have recently been characterized [5][6].

Reactions 1 and *2* illustrate how Al_2Cl_6 or pyridine volatilize $CoCl_2$. The temperature range, where a particular equilibrium dominates at 1 bar of Al_2Cl_6 or 1 bar of pyridine, is indicated.

Table 1 shows that it is appropriate to say that Al_2Cl_6 and pyridine carry $CoCl_2$ into the gasphase.

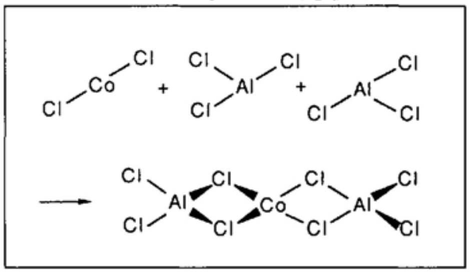
To investigate the formation of gaseous metal complexes vapor pressure measurements have to be performed. The most frequently used method is high-temperature UV/VIS spectroscopy but entrainment, evaporation from a *Knudsen* cell, chemical transport *etc.* have also been used [3][4].

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].

$$CoCl_2(s) + Al_2Cl_6(g) \xrightleftharpoons{250\text{–}450°} Co(AlCl_4)_2(g) \xrightleftharpoons{> 600°} ClCo(AlCl_4)(g) + AlCl_3(g) \qquad (1)$$

$$CoCl_2(s) + 2\ py(g) \xrightleftharpoons{280\text{–}380°} CoCl_2py_2(g) \xrightleftharpoons{> 400°} CoCl_2py(g) + py(g) \qquad (2)$$

Scheme. *Formation of $M(AlCl_4)_2(g)$*



3. Solvation Effects in Complex Formation

$M(AlX_4)_2$ and [$CoX_2(py)_2$] are molecular species and, therefore, their formation can also be studied in weakly coordinating solvents [9][10].

Table 2 shows that the formation constants of $M(AlX_4)_2$ are larger in solution

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

Species	$CoCl_2$	$Co(AlCl_4)_2 = CoCl_2$ in 1 bar of Al_2Cl_6	[$CoCl_2(py)_2$]= $CoCl_2$ in 1 bar of pyridine
Pressure	$2.3 \cdot 10^{-9}$ bar [7]	$4.3 \cdot 10^{-2}$ bar [2]	$1.4 \cdot 10^{-3}$ bar [6]

Table 2. *Formation Constants of $M(AlX_4)_2$ in the Gas Phase and in Solution at 298 K*

$$\begin{tikzcd}
Al_2X_6(g) + MX_2(s) \arrow[r, "K_{gas}"] \arrow[d, "\text{Solvatation}" , "Al_2X_6"'] & M[AlX_4]_2(g) \arrow[d, "\text{Solvatation}", "M[AlX_4]_2"'] \\
Al_2X_6(sln) + MX_2(s) \arrow[r, "K_{sln}"] & M[AlX_4]_2(sln)
\end{tikzcd}$$

M	K_{gas} X = Cl [3]	X = Br [9]	$K_{soln.}$, X = Br Cyclohexane [9]	Toluene [10]	p_{MCl2} bar at 673 K [7]
Cr	$5.4 \cdot 10^{-5}$	$1.3 \cdot 10^{-6}$	0.06	2.2	$2.1 \cdot 10^{-11}$
Mn	$2.7 \cdot 10^{-7}$	-	0.05	2.1	$6.9 \cdot 10^{-8}$
Co	$4.4 \cdot 10^{-6}$	$6.5 \cdot 10^{-6}$	0.006	0.54	$9.3 \cdot 10^{-9}$
Ni	$1.2 \cdot 10^{-7}$	-	0.006	0.017	$4.8 \cdot 10^{-9}$
Zn	$6.7 \cdot 10^{-4}$	-	-	1.5	$8.2 \cdot 10^{-4}$
Cd	$8.4 \cdot 10^{-7}$	-	0.02	7	$6.9 \cdot 10^{-6}$
Pd	$8.3 \cdot 10^{-4}$	$4.7 \cdot 10^{-5}$	1.1	–	–

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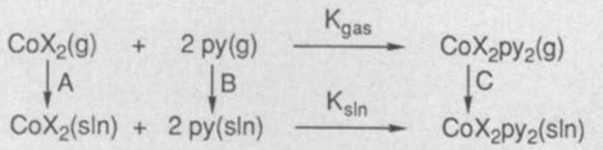
Table 3. *Formation of [$CoX_2(py)_2$] in the Gas Phase and in Solution at 298 K*



	K_{gas}		$K_{soln.}$(acetone)	
	Cl	Br	Cl	Br
ΔH [kJmol^{-1}]	–232	–320	–44.8	–41.0
ΔS [Jmol^{-1}K^{-1}]	–197	–326	–47.7	–35.2
ΔG [kJmol^{-1}]	–173	–222	–30.6	–30.5

A,B,C: solvation energies. $\Delta H_B = -36.5$ kJmol^{-1} [13].

Table 4. *Bond Energy* [kJmol^{-1}] *of Pyridine to CoX_2*

Medium	gas [5][6]		acetone [11]	
	first py	second py	first py	two py
$CoCl_2$	–159	–80	–21.3	–44.8
$CoBr_2$	–245	–82	–	–41.0

than in the gas, indicating that the free energy of solvation of $M(AlCl_4)_2(g)$ is more negative than the free energy of solvation of Al_2X_6 making the complexes more stable in solution than in the gas.

At a Al_2X_6 pressure of 1 bar K_{gas} equals the pressure of $M(AlX_4)_2(g)$ while at [Al_2X_6] = 1 M $K_{soln.}$ equals the concentration of $M(AlX_4)_2$(soln.). Within the series of metals in *Table 2*, the similarity of the various K_{gas} and $K_{soln.}$ in spite of the very different vapor pressures of the corresponding MCl_2 is striking. This has been interpreted in the following way [3][10]: when MX_2 evaporates, the coordination of M is reduced (in many cases) from six in the lattice to two in the gas. On the other hand, if $MX_2(s)$ forms $M(AlX_4)_2(g)$ or $M(AlX_4)_2$(soln.) the coordination number of M^{2+} remains six, if the AlX_4^--tetrahedra coordinate to M^{2+} by their face, or it is four if the AlX_4^--tetrahedra coordinate to M^{2+} by their edge. Thus, if MX_2 forms a gaseous complex its coordinative environment changes much less than if it evaporates, and this levels out the differences between various M^{2+}.

The complexes of CoX_2 with pyridine are much more stable in the gas phase than in solution (*Table 3*). For comparison, acetone has been chosen as a solvent [11]. The solvation energies of CoX_2 and [$CoX_2(py)_2$] have not yet been determined, but the small enthalpy of solvation of pyridine suggests that the solvation energy of CoX_2 dominates the reaction in solution. As the free energy of formation of the complexes is much more negative in the gas phase than in solution, the solvation energy of CoX_2 must be much more negative than the one of [$CoX_2(py)_2$]. This is opposite to what is observed in the system CoX_2/Al_2X_6 where the complexes are much more stable in solution than in the gas phase.

We may note that substituted pyridines (*e.g.* 2- and 3-Cl-pyridine, picolines *etc.*) do not form gaseous complexes with CoX_2. Sublimation enthalpies of such complexes have been reported [12], but the data were obtained by vapor-pressure measurements, and they most probably reflect the decomposition according to *Reaction 3* rather than sublimation.

$$CoX_2L_2(s) \rightarrow CoX_2(s) + 2\,L(g) \quad (3)$$

From the temperature dependence of *Reaction 4*, we obtain the bond energy of pyridine to $CoCl_2$ and to $CoBr_2$ (*Table 4*).

$$\begin{aligned} &CoX_2(g) + 2\,py(g) = CoX_2py(g) \\ &+ py(g) = CoX_2py_2(g) \qquad (4) \end{aligned}$$

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.

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