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COBALT(II)-CHLORIDE SYSTEM IN ACETONE: DETERMINATION OF SOME HEATS OF FORMATION BY FLOW CALORIMETRY *

U. BIADER CEIPIDOR, V. CARUNCHIO, G.D'ASCENZO and M. TOMASSETTI

Istituto di Chimica Analitica, Università di Roma, Rome (Italy)

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ABSTRACT

The possibility of determining the heats of complex formation in solvents other than water using flow microcalorimetry is discussed. The results obtained for the cobalt(II)-chloride system are discussed in terms of the donor properties of the solvent. In particular it was found that ΔH_3 = —7.8 kcal mole^{-1} and ΔH_4 = —2.2 kcal mole^{-1}, in acetone, while the reactions are known to be endothermic when the solvent is water.

INTRODUCTION

The configurational changes occurring in the cobalt(II)-chloride system have been previously studied in various solvents [1—4]. A connection between these changes and the donating power of the solvent [5] was suggested on the basis of NMR or visible spectra. However, little thermodynamic data exists to support and/or explain the configurational equilibrium was reported previously [1,2].

$$\underset{\text{(oct.)}}{CoCl_2D_4} \rightleftharpoons \underset{\text{(tetr.)}}{CoCl_2D_2} + 2\ D$$

Any shift in this equilibrium is dependent on factors such as the temperature or solvent properties. Consequently, the first tetrahedral species, encountered in the sequence CoD_6^{2+} (oct.), $CoClD_5^+$ (oct.), $CoCl_2D_4$ (oct.) or $CoCl_2D_2$ (tetr.), $CoCl_3D^-$ (tetr.), $CoCl_4^{2-}$ (tetr.) may be $CoCl_2$ (equilibrium shifted to the right) or $CoCl_3^-$ (equilibrium shifted to the left). Flow microcalorimetry was used to determine heats of formation for the system described above.

Peristaltic pumps are usually employed in this technique, but represent a serious limitation when the solvents employed interact with rubber or silicon tubes. The use of organic solvents such as acetone has been made possible by exchanging the peristaltic pumps for syringes; this means that the materials in contact with organic solutions are glass (syringes), stainless steel (connections), teflon (calorimeter tubes), and gold (calorimetric cell).

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The cobalt(II)-chloride system was studied by adding variable amounts of LiCl to $CoCl_2$ solutions in acetone. Cobalt(II) perchlorate was not employed owing to difficulties in obtaining this salt free of water. Chloride/cobalt ratios lower than 2 could not be examined, thus species such as $CoCl^+$ and $CoCl_2$ were not included [1].

EXPERIMENTAL

All the solutions were prepared using previously dried analytical grade products. Acetone and $CoCl_2$ were dehydrated as described previously [1]. The water content of the solutions, measured as before [1], was found to be less than 0.05%. The use of freshly-prepared solutions meant that dry-box operations were not necessary, since the water content of solutions stored in ground-glass stoppered flasks remained invariant for at least 2 days.

Calorimetric measurements were performed with an LKB 10700-1 flow microcalorimeter, at 25 ± 0.1°C. The pumps used were Braun model UNITA I equipped with 50-ml syringes, allowing flow rates ranging from 1.25 μl min^{-1} up to 5.00 ml min^{-1}. A flow rate of 0.50 ml min^{-1} was used in all measurements.

RESULTS AND DISCUSSION

A step-wise formation reaction

$$CoCl_{n-1}D_{m-n+1}^{(3-n)+} + Cl^- \rightleftharpoons CoCl_nD_{m-n}^{(2-n)+} + D$$

was taken as a model. However, a dissociation constant $K_{LiCl} = 2.8 \times 10^{-6}$ has been reported [6] for LiCl in acetone, thus suggesting a reaction in which LiCl and not Cl^- is involved. Other literature data [7] do not agree ($K_{LiCl} = 10^{-3}$) with this result. Under our experimental conditions, i.e. total LiCl concentration around 10^{-2} M, the value $K_{LiCl} \simeq 5.6 \times 10^{-2}$ was obtained from the heat of dilution of the pure salt in acetone. This means that about 90% of the LiCl present is ionized, and that the description of the step-wise formation reaction reported above, i.e. involving Cl^-, is correct.

Heats of reaction were determined for solutions containing a fixed amount of anhydrous $CoCl_2$ in acetone and a variable concentration of LiCl. The results obtained for $CoCl_2$ (5.00×10^{-3} M and 1.00×10^{-3} M), corrected for the heats of dilution of the reagents, are shown in Fig. 1. More concentrated solutions were not examined owing to the difficulty of dissolving the required amount of dried LiCl in acetone, while more dilute solutions were subject to problems caused by the loss of sensitivity in the calorimetric measurements. No change in the heat evolved per mole of reactants was observed on increasing the flow rates of the solutions from 0.50 up to 2.00 ml min^{-1}. It was therefore assumed that the formation reactions examined were completed during the time spent in the calorimetric cell.

It can be seen from Fig. 1 that the two curves representing different initial concentrations of $CoCl_2$ intersect where C_L/C_M (Ligand/Metal) is about 5.

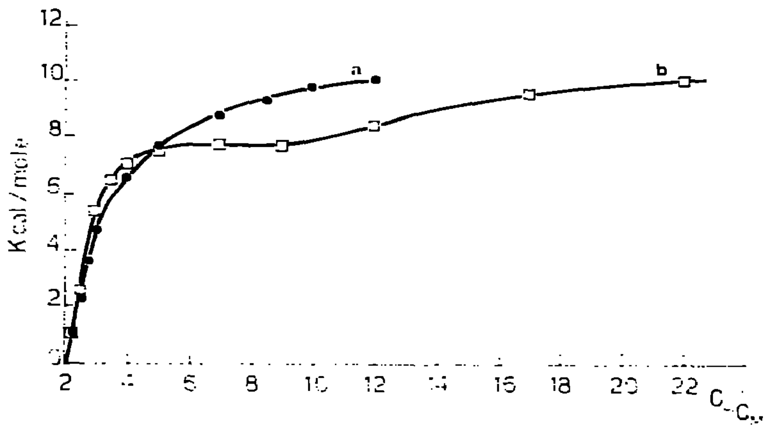

Fig. 1. Heat evolved on mixing solutions of $CoCl_2$ and LiCl in acetone at various total chloride/total cobalt ratios (C_L/C_M). (a) $C_M = 5.00 \times 10^{-3}$ M; (b) $C_M = 1.00 \times 10^{-3}$ M.

This does not allow the determination of stability constants by the method of corresponding solutions [8], suggesting that the equilibrium constants vary with concentration. (It was not possible to maintain a constant ionic strength in acetone owing to the low solubility of the salt and the difficulties involved in drying it.) On the other hand, the curve corresponding to an initial concentration of 1.00×10^{-3} M $CoCl_2$ suggests the formation of a $CoCl_3^-$ species when examined by the "mole ratio" method [9] extended to calorimetric data. This species prevails for C_L/C_M ratios up to 8, while another species is formed on increasing this ratio still further. On the basis of the results obtained previously [1], this latter species was assigned as $CoCl_4^{2-}$ and prevails when $C_L/C_M \geqslant 20$. The value of ΔH_3 was determined from the constant value of the curve for 1.00×10^{-3} M $CoCl_2$ in the range C_L/C_M = 4—8, assuming that $CoCl_2$ is the dominant species when $C_L/C_M = 2$; ΔH_4 was determined from the upper limit value of the curve, as above. The values obtained, with confidence limits from graphical interpolation, are $\Delta H_3 = -7.8 \pm 0.2$ kcal mole^{-1} and $\Delta H_4 = -2.2 \pm 0.4$ kcal mole^{-1}.

The ΔH_n values obtained have been used in conjunction with previously determined [1] log K_n values to obtain ΔS_n. This procedure is not rigorous owing to the fact that the log K_n values were concentration constants measured in more dilute solutions (about 10^{-4} M). However, considering the limitations imposed by operating in non-aqueous solutions, the results obtained can be regarded as close approximations to the true values. The results obtained for this system in both acetone and water are given in Table 1.

It can be observed that the formation constants for the step-wise reaction are higher in acetone than in water and that this is due to an enthalpic effect, at least for the formation of $CoCl_3^-$ and $CoCl_4^{2-}$ species. This observation agrees with the bulk donation properties [5] of water (DN = 33) which are greater than those of acetone (DN = 17). The exchange of a solvent molecule in the coordination sphere of cobalt(II) for a Cl^- ion therefore requires an increase in the enthalpy of the system when the solvent is water, and the reverse when the solvent is acetone. Consideration of these results shows that the correct DN value for water is related to its "bulk" donor properties (even

TABLE 1

Thermodynamic quantities obtained for the cobalt(II)-chloride system in both water and acetone solution

n	$\ln K_n$		ΔH_n (kcal mole^{-1})		ΔS_n (e.u.)	
	Water [4]	Acetone [1]	Water [4]	Acetone	Water [4]	Acetone
1	−1.77	—	2.9	—	6.1	—
2	−6.38	—	2.1	—	−5.6	—
3	−5.78	17.62	11.3	−7.8	26.2	8.7
4	−4.73	6.41	0.8	−2.2	−6.7	5.3

if in 6 M HCl [4]), rather than its "free" donor properties (DN = 18) as previously reported [1]. This misunderstanding was due to the assignment of a tetrahedral configuration to the $CoCl_2$ species by Zeltmann et al. [4]. The entropy values reported for water in Table 1 seem to indicate octahedral $CoCl_2$. The greatest change in entropy would be expected when a configurational change occurs [10], and Zeltmann himself reports the greatest value to be ΔS_3. This is consistent with a reaction which can be described as

$$\underset{\text{(oct.)}}{CoCl_2(H_2O)_4} + Cl^- \rightleftharpoons \underset{\text{(tetr.)}}{CoCl_3H_2O^-} + 3\ H_2O$$

with both $Co(H_2O)_6^{2+}$ and $CoCl(H_2O)_5^+$ octahedral and $CoCl_4^{2-}$ tetrahedral. In acetone the ΔS_3 and ΔS_4 values are positive and similar, which suggests that no configurational change occurs on formation of $CoCl_3^-$.

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