

communication have found that it disappears completely in mixtures of $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_4 at a constant molarity of one. In this medium the rotation of D-Co en₃³⁺ at 546 and 578 m μ shows no anomaly and changes linearly with the mole fraction from 1 M Na_2SO_4 to 1 M $\text{Na}_2\text{S}_2\text{O}_3$ (see Fig. 3).

Experimental. A preparation of the double salt (+)_D-[Co en₃]Cl₃, $\frac{1}{2}$ NaCl, 3 H₂O prepared by a modified method¹¹ was used. (Found: C 16.70; N 19.86; Cl 29.18. Calc.: C 16.80; N 19.60; Cl 28.93). All other chemicals were commercial products of AnalaR grade.

The absorption measurements were made with a Cary 14 spectrophotometer. The reference cells contained a cobaltfree solution of the same saltmedia.

The polarimetric measurements were made with a Perkin-Elmer polarimeter, model 141, in a 1 dm cell at 20°C.

1. Larsson, R. and Johansson, L. *Proc. Symp. Coord. Chem., Tihany 1964*, Akadémiai, Budapest 1965, p. 31.
2. Larsson, R. and Norman, B. J. *J. Inorg. Nucl. Chem.* **28** (1966) 1291.
3. Larsson, R., Mason, S. F. and Norman, B. J. *J. Chem. Soc.* **1966** 301.
4. Posey, F. A. and Taube, H. *J. Am. Chem. Soc.* **78** (1956) 15.
5. Kiss, A. v. and Czeplédy, D. v. *Z. anorg. Chem.* **239** (1938) 27.
6. Gimblett, F. G. R. and Monk, C. B. *Trans. Faraday Soc.* **51** (1955) 793.
7. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **11** (1932) No. 10.
8. Larsson, R. *Acta Chem. Scand.* **16** (1962) 2267.
9. Bjerrum, J. *Advances in Chemistry Series* **62** (1967) 178, *Alfred Werner Centennial Volume*.
10. Corey, E. J. and Bailar, J. C., Jr. *J. Am. Chem. Soc.* **81** (1959) 2620.
11. Galsbøl, F. *To be published*.

Received April 13, 1967.

Heats of Reaction of Antimony Pentachloride with Propionyl Chloride and Ethyl Chlorocarbonate

GERD OLOFSSON

Thermochemistry Laboratory, University of Lund, Lund, Sweden*

In previous communications values have been reported of the enthalpy of formation of adducts between antimony pentachloride and compounds having the general formula $\text{R}_1\text{R}_2\text{C}=\text{O}$.¹⁻³ The experiments reported in this paper conclude the study of the effects of systematic variations in R_1 and R_2 such that the two atoms attached to the carbonyl group are any two of the elements carbon, nitrogen, oxygen, and chlorine. It includes the cases where R_1 is a chlorine atom and R_2 an ethyl or an ethoxy group.**

Experimental. Materials. Ethylene chloride was treated as given in Ref. 1 and antimony pentachloride as given in Ref. 3. Propionyl chloride (Fluka) was fractionally distilled and purity checked by potentiometric titration after hydrolysis and also by NMR measurements. NMR spectra were run on the pure sample and on a sample to which 0.7 % (mole) water had been added. The purity was judged to be better than 99.5 %. d_4^{25} 1.0505. Ethyl chlorocarbonate (Fluka) was distilled in an all-glass apparatus and transferred to break-off ampoules. Titration after alkaline hydrolysis indicated purity of 99 ± 1 %.

Apparatus. Calorimetric and infrared equipment see Ref. 4. The NMR spectra were recorded on a Varian A 60 spectrometer.

Calibration and corrections to standard states, see Ref. 1.

Calorimetric procedure, see relevant parts of Ref. 4.

Units of measurements. The results of the calorimetric experiments are expressed in terms

* Sponsored by The Swedish Natural Science Research Council and The Swedish Technical Research Council.

** The interaction between antimony pentachloride and COCl_2 is certainly very weak. No attempts have therefore been made to measure the enthalpy of adduct formation with phosgene as donor.

of the defined calorie equal to 4.1840 abs. joules, and refer to the isothermal process at 25°C and to the true mass. The molecular weights were computed from the 1961 table of atomic weights.⁵

Results. The enthalpy of formation and the stability constant for the adduct formation reaction between antimony pentachloride and propionyl chloride have been determined calorimetrically. The following equation has been derived for the relation between the enthalpy of formation ΔH , and the stability constant, K , for formation of 1:1 adducts:⁴

$$(-\Delta H)^2 + \Delta H \cdot h \left(1 + \frac{d}{a} + \frac{V}{a \cdot K} \right) + \frac{h^2 \cdot d}{a} = 0 \quad (1)$$

d and a are the amounts of donor and acceptor, respectively, V the total amount of solution, and h the heat evolved per mmole of donor in an experiment where an unknown amount of adduct is formed. The water content of the ethylene chloride was determined by measuring the amount of $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ adduct formed in the calorimeter charged with solvent.⁶ It was estimated to be 0.4 ± 0.1 mmole per charge.

Ethyl chlorocarbonate gave a much higher heat of reaction value, -21.4 kcal.mole⁻¹, which, together with the fact that the solution was discoloured, indicated that a chemical reaction had taken place. The reaction was, however, instantaneous. Test tube experiments indicated decomposition to CO_2 and, mainly, $\text{C}_2\text{H}_5\text{Cl}$. Only a small amount of HCl was found (*cf.* Ref. 7). At the concentrations used in the calorimetric experiments the reaction products dissolved readily in the ethylene chloride.

The results of the calorimetric experiments are summarized in Tables 1–3. In Table 1 the first and second columns give the amounts of $\text{C}_2\text{H}_5\text{COCl}$ and SbCl_5 , respectively. Column 3 shows the total amount of heat evolved in an experiment and the last column the heat evolved, corrected for heat of solution, per mmole of donor. In Table 2, columns 1 and 2 give the amounts of $\text{C}_2\text{H}_5\text{OCOCl}$ and SbCl_5 , the third column the heat evolved, and the last column the molar enthalpy change. The first two heat of solution experiments with propionyl chloride (Table 3) were performed in pure ethylene chloride and the third and fourth

Table 1. Measurements of the heat of reaction between SbCl_5 and $\text{C}_2\text{H}_5\text{COCl}$ in ethylene chloride solution.

mmole donor	mmole SbCl_5	q cal	h cal/mmole
1.900	3.38	1.68	0.96
1.373	3.92	1.40	1.09
3.301	31.4	8.50	2.65
2.461	32.6	6.22	2.60
2.357	33.0	5.96	2.60

Table 2. Measurements of the heat of reaction between SbCl_5 and $\text{C}_2\text{H}_5\text{OCOCl}$.

mmole	g SbCl_5	q cal	$-\Delta H$ kcal/mole
1.056	1.29	22.74	21.53
1.703	1.40	36.18	21.25
			21.4 ± 0.2

Table 3. Heat of solution measurements.

Donor	mmole	q cal	ΔH kcal/mole
Propionyl chloride	2.451	-0.18	0.07
	2.574	-0.19	0.07
	2.211	-0.18	0.08
	3.016	-0.20	0.07
			0.07 ± 0.00
Ethyl chlorocarbonate	2.131	-0.12	0.06
	2.857	-0.16	0.06
			0.06 ± 0.00

in a 0.025 M solution of propionyl chloride. No difference could be detected between the two sets of experiments. The heat of solution of ethyl chlorocarbonate was determined in pure ethylene chloride.

The calculated enthalpy and stability constant values for the addition of antimony pentachloride to propionyl chloride, with both reactants and reaction product in ethylene chloride solution, are: $-\Delta H = 3.3 \pm 0.2$ kcal/mole and $K = 14 \pm 1$ l.mole⁻¹, respectively. The ΔH - and K -values were derived by inserting the experimental data in eqn. (1) and solving the equation systems obtained. ΔG for the

reaction is found to be $+0.33 \pm 0.04$ kcal/mole (computed from K expressed in atm^{-1}) and the ΔS value -12 ± 1 e.u. is derived for the adduct formation reaction.

The error limits, expressed as standard deviations of the means, include estimates of errors due to uncertainties in the water content of the calorimetric liquid and in the purity of the donor sample.

In the solid state $\text{SbCl}_5 \cdot \text{C}_2\text{H}_5\text{COCl}$ exists as a molecular adduct with only a small amount of the oxocarbenium salt present.⁹ Infrared measurements on ethylene chloride solutions (0.44 M in SbCl_5 , 0.015 M in propionyl chloride; ethylene chloride in the reference cell) exhibit a sharp peak at 1585 ± 5 cm^{-1} . This is assigned to the carbonyl stretching frequency of bounded propionyl chloride. No peaks were observed in the region 2000–2600 cm^{-1} , where absorption by the ethyl oxocarbenium group would be expected to be found.⁹ This shows that in solution the complex $\text{SbCl}_5 \cdot \text{C}_2\text{H}_5\text{COCl}$ exists predominantly in the form of a molecular addition compound. The carbonyl stretching frequency of the free propionyl chloride (a 0.015 M ethylene chloride solution) was found to be 1782 ± 3 cm^{-1} . This reveals a shift in frequency caused by adduct formation of 197 cm^{-1} , which is an astonishingly large value.* It can be compared with the shift of 162 cm^{-1} given when ethyl propionate acts as donor. The ΔH - and K -values for the formation of the ethyl propionate adduct are -16.82 kcal.mole⁻¹ and 3.0×10^6 l.mole⁻¹, respectively.⁴ The comparison shows that the shifts in the carbonyl stretching frequencies caused by adduct formation with antimony pentachloride cannot be used to settle the relative-donor strength of these donors.

1. Olofsson, G., Lindqvist, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 259.
2. Olofsson, G. *Acta Chem. Scand.* **18** (1964) 11.
3. Olofsson, G. *Acta Chem. Scand.* **21** (1967) 93.
4. Olofsson, G. *Acta Chem. Scand.* **21** (1967). *In press.*
5. Cameron, A. E. and Wichers, E. *J. Am. Chem. Soc.* **84** (1962) 4175.
6. Olofsson, G. *Acta Chem. Scand.* **21** (1967). *In press.*
7. Underwood, H. W., Jr. and Baril, O. L. *J. Am. Chem. Soc.* **53** (1931) 2201.

* A carbonyl shift of the same magnitude (186 cm^{-1}) was noticed for the adduct $\text{GaCl}_3 \cdot \text{CH}_3\text{COCl}$ (measured as a liquid film).⁹

8. Olah, G. A., Kuhn, S. J., Tolgyesi, W. S. and Baker, E. B. *J. Am. Chem. Soc.* **84** (1962) 2733.

9. Cook, D. *Can. J. Chem.* **40** (1962) 480.

Received April 15, 1967.

Spectrophotometric and Reaction Kinetic Studies of the Tetracyanocuprate(II) Complex in Methanol-Water Mixtures at Low Temperatures

OLE MØNSTED and JANNIK BJERRUM

Chemistry Department I, Inorganic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

In a previous paper¹ the stability and autoreduction of the tetracyanocuprate(II) complex was studied by means of emf measurements in 60 wt % methanol. The stability constant β_4 was determined to be $10^{10.7}$ at -45°C , and it was confirmed that the autoreduction of the complex is second order in the copper(II) concentration in agreement with the results of Baxendale and Westcott.² In this communication the spectrum of the tetracyano complex is determined at low temperature, and the autoreduction of the complex more closely examined.

The spectrum of the tetracyanocuprate(II) complex at -70°C in methanol solutions with varying excess of cyanide is shown in Fig. 1. It will be seen that the spectrum of the complex is only slightly different in 80 wt % and 100 wt % methanol, and the lack of dependence of the spectrum on the concentration of free cyanide shows clearly that the tendency of the complex to form a pentacyanocuprate ion is negligible. The figure, for comparison, also includes the spectra of some copper(II) tetra-amine complexes,³⁻⁵ and it will be seen that the hypsochromic shift of the band of the cyanide complex relative to the bis-(ethylenediamine)copper(II) complex is remarkably low only at about 300 cm^{-1} .