

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} .

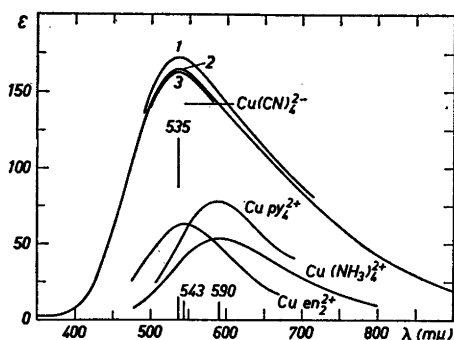


Fig. 1. Spectra of the tetracyanocuprate(II) ion, and of some copper(II) tetra-amine complexes.³⁻⁵ The tetracyanocuprate solutions were prepared by mixing methanol solutions of copper(II) *p*-toluenesulphonate and sodium cyanide at -70°C .

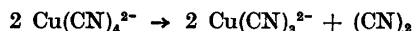
Curve	wt % CH_3OH	$[\text{Cu}(\text{CN})_4^{2-}]$ (20°C)	$[\text{CN}^-]$ (20°C)
1	80	0.00457 M	0.0729 M
2	100	0.00897 M	0.738 M
3	100	0.00897 M	0.0100 M

For calculation of ϵ at -70°C the complex concentrations given for 20°C were multiplied by 1.072 for 80 wt %, and by 1.105 for 100 wt % CH_3OH .

Considering the position of the cyanide ion in the spectrochemical series, this fact would seem to indicate that the cyanide complex, instead of being planar, most probably has a deformed tetrahedral configuration. It has been shown recently

by other methods that the tetrahalogenocuprate(II) complexes not only in the solid state,⁶ but also in solution^{7,8} have a similar deformed configuration.

The autoreduction. If as found previously,¹ the redox reaction



is second order in the concentration of the copper(II) complex

$$d[\text{Cu}(\text{II})]/dt = -k[\text{Cu}(\text{II})]^2$$

the integrated expression can be written

$$k = A(1/[\text{Cu}(\text{II})])/\Delta t$$

Now introducing $1/[\text{Cu}(\text{II})] = \epsilon/A$ where A is the absorbance per cm cell length, the following simple expression is obtained

$$k = \epsilon \cdot A(1/A)/\Delta t$$

The spectrophotometric measurements were made at the wavelength of the maximum of absorption 535 $m\mu$, and the value of ϵ was taken as $172 \text{ l}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ in all the experiments.

Some results are given in Table 1, and Fig. 2 shows for solutions 1-3 how well the linear relationship between the reciprocal absorbance and time is fulfilled. The temperature dependence of the rate constant was examined for solutions 1 and 4, and the activation energies E_A from straight line Arrhenius plots was determined to be 14.0 kcal/mole in 80 wt % and 11.9 kcal/mole in 50 wt % methanol. By means of these activation energies the rate constants in Table 1 were adjusted to exactly -20°C and -28°C , respectively. In the solutions the concentration of free cyanide is varied about threefold at an approximately constant ionic strength,

Table 1. Values of the rate constant k determined at -20.0°C for 80 wt %, and at -28.0°C for 50 wt % methanol solutions prepared from copper(II) *p*-toluenesulphonate, sodium cyanide and sodium *p*-toluenesulphonate.

Soln. No.	$[\text{Cu}(\text{CN})_4^{2-}]$ mole/l(20°C)	$[\text{CN}^-]$ mole/l(20°C)	$[\text{C}_7\text{H}_7\text{SO}_3^-]$ mole/l(20°C)	k $\text{l}\cdot\text{mole}^{-1}\cdot\text{min}^{-1}$
Initial concentrations in 80 wt % methanol				
1	0.00457	0.0273	0.0546	41.0
2	0.00457	0.0501	0.0319	29.2
3	0.00457	0.0729	0.0091	25.4
Initial concentrations in 50 wt % methanol				
4	0.00440	0.0280	0.0543	100.5
5	0.00440	0.0508	0.0316	85.0
6	0.00440	0.0736	0.0088	74.8

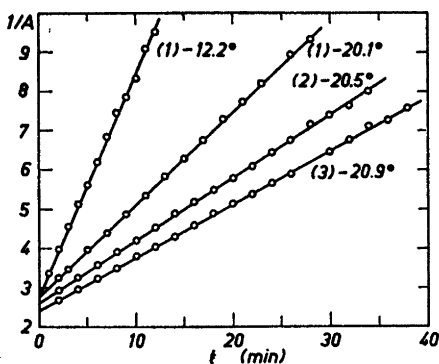


Fig. 2. Plots of $1/A$ versus time for solutions 1–3 in Table 1.

and as it will be seen, without having a very great influence on the rate constant. The decrease in the constant with increasing cyanide concentration is highest in the 80 wt % methanol solutions which have the smallest dielectric constant. This is consistent with a medium effect, but it is also possible that the tricyano complex which might exist in minute concentrations preferably at the lowest cyanide concentrations has a higher decomposition rate than the tetracyano complex.

Table 2. Dependence of the rate constant k on the composition and dielectric constant D of the solvent. Initial concentrations $[\text{Cu}(\text{CN})_4^{2-}] = 0.00466 \text{ M}$, $[\text{CN}^-] = 0.0142 \text{ M}$ (20°C).

CH_3OH wt %	k (-20°C) $\text{l.mole}^{-1}.\text{min}^{-1}$	D^a	$\log k/D$
100	25.3	40.0	0.0351
88.5	44.2	46.9	0.0351
76	58.6	53.4	0.0331
65	75.9	59.3	0.0318
54.5	186	65.4	0.0348
44	391	70.9	0.0366
34	1110	76.2	0.0399

^a Estimated values for D (-20°C) from data in the literature.⁹

Table 2 shows how the composition of the methanol-water solvent influences the rate constant. As should be expected for a bimolecular reaction between doubly charged ions of the same sign, the rate of decomposition increases strongly with increasing water content of the solvent. The table shows that there is some correlation between $\log k$ and D , but that the theoretically predicted linear relationship between $\log k$ and $1/D$ is only badly fulfilled.

Experimental. The spectra were measured with a slightly modified Cary 14 spectrophotometer equipped with a vacuum-isolated 1 cm cell (with quartz windows) which was kept at the desired temperature by circulation of cooled methanol from a Lauda Ultra-Kryostat, Type UK 80 DW. The temperature of the solution in the cell was measured with a copper-constantan thermo couple and with an accuracy of about 0.1°C . The purple complex solutions were prepared by mixing solutions of the components precooled in the cryostat. Solutions with less than 4 moles NaCN per mole copper(II)-*p*-toluenesulphonate were not examined as they gave a green precipitate. The chemicals were the same as those used in the previous paper. The methanol stock solutions were analyzed at 20°C . For calculation of concentrations at other temperatures data from the literature¹⁰ were used.

1. Paterson, R. and Bjerrum, J. *Acta Chem. Scand.* **19** (1965) 729.
2. Baxendale, J. H. and Westcott, D. T. *J. Chem. Soc.* **1959** 2347.
3. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* **2** (1948) 297.
4. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. K. *Acta Chem. Scand.* **8** (1954) 1275.
5. Bjerrum, J. *Acta Chem. Scand.* **18** (1964) 843.
6. Morosin, B. and Lingafelter, E. C. *J. Phys. Chem.* **65** (1961) 50.
7. Smith, G. P. and Griffiths, T. R. *J. Am. Chem. Soc.* **85** (1963) 4051.
8. Forster, D. *Chem. Commun.* **1967** 113.
9. Harned, H. S. and Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York 1958, p. 161.
10. Tommila, E. *Suomen Kemistilehti* **B 15** (1942) 9.

Received April 18, 1967.