Identification of a Silver(I)carbonyl Complex in Aqueous Solution

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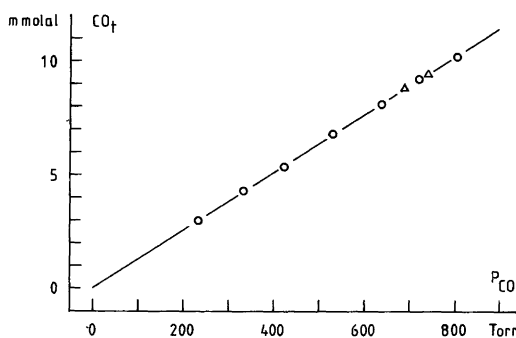*Fig. 1.* Carbon monoxide absorption in a 4 molal silver perchlorate solution at 25.0 °C. ○ denote values after synthesis of the complex. △ denote values after splitting of the complex.

To date the reported work with silver(I)carbonyl complexes has involved solutions that are essentially anhydrous. For the absorption of carbon monoxide in concentrated H_2SO_4 containing Ag^+, Manchot[1] suggested that a complex with a molar ratio, Ag^+/CO, equal to 2 was formed. Later investigators[2] have studied similar systems with very low water activity containing Ag(I) and CO and suggest that the complex formed had a molar ratio, Ag^+/CO, equal to 1/2. In contrast to the case of anhydrous media, the absorption of carbon monoxide in aqueous solutions containing a silver(I) salt is quite low. However, we were able to create suitable conditions to make accurate measurements by manometrical methods,[3] and our results demonstrate the existence of a monocarbonyl complex containing silver(I) that is stable under CO-atmosphere. To prevent the reduction of Ag^+ by CO the pH was kept low, and to avoid photoinduced formation of silver light was kept away from the reaction vessel.

In the equilibrium measurements the total concentration of dissolved carbon monoxide (CO_t) was calculated as a function of the partial pressure (P_{CO}). After each addition of carbon monoxide equilibrium was quickly reached upon shaking the reaction vessel, and the equilibrium pressure could be determined accurately less than one minute after the addition. The results from such measurements in acidic silver perchlorate solution (4.00 m Ag^+ and 0.10 m H^+) are presented in Fig. 1. It is evident that equilibrium is easily attained as CO_t/P_{CO} is the same after formation and after splitting of the complex. From the measurements in the silver solution $CO_t/P_{CO} = (1.268 \pm 0.008) \times 10^{-5}$ molal Torr^{-1}) was obtained, and from a corresponding experiment in sodium perchlorate solution (4.00 m Na^+ and 0.10 m H^+) the physical solubility was determined. In this case the value of the quotient was $(0.053 \pm 0.003) \times 10^{-5}$. Therefore the concentration of complex-bound carbon monoxide is given by eqn. (1).

$$CO_{Ag} = (1.215 \pm 0.011) \times 10^{-5} P_{CO} \qquad (1)$$

As CO_{Ag} is linear in P_{CO} exactly one molecule of CO is bound in the complex and (1) therefore expresses the concentration of this complex.

It is well known that Ag^+ can be reduced by CO according to eqn. (2).

$$2Ag^+ + CO + H_2O = 2Ag(s) + CO_2 + 2H^+ \qquad (2)$$
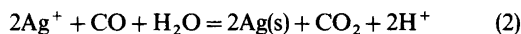
The kinetics for this reaction has been thoroughly studied by McAndrew et al.[4] These authors suggest that the reduction of Ag^+ occurs *via* a silver compound formed in the equilibrium reaction (3).

$$Ag^+ + CO + H_2O = AgCOOH + H^+ \qquad (3)$$

It was thus important to judge whether the rapid reversible CO absorption was a protolytic reaction or not. The potential between a glass electrode and a silver electrode, which gives a direct measure of $\{Ag^+\}/\{H^+\}$, was therefore measured. The silver perchlorate solution used had the concentrations 4.00 m Ag^+ and 0.01 m H^+, and was thus less acidic than the solutions used in the equilibrium measurements. The reason for this was to gain sufficient accuracy in the determination of the potential. The solution was saturated with CO by bubbling the gas through a fritted disk during 10 min, whereby the potential decreased from 290 to 289 mV. In view of the rapid attainment of equilibrium mentioned above, 10 min are doubtlessly sufficient to obtain a concentration of the complex corresponding to atmospheric pressure. If the measured CO_{Ag} was caused by reaction (3), the concentration of H^+ would increase in the same way as the concentration of the complex. Therefore a calibration curve was obtained by titrating the silver solution (4.00 m Ag^+ and 0.01 m H^+) with a solution of the same total concentration, but with $[H^+]$ raised to 0.20 m. In constructing the calibra-

tion curve the potential (E) was plotted against the change in $[H^+]$. Using least squares a linear fit was then made. In equation (4) where "i" stands for

$$E = s + r(RT/F)\ln(([Ag^+]_i - \Delta[H^+])/([H^+]_i + \Delta[H^+])) \qquad (4)$$

initial, s and r were found to be 122.9 ± 2.3 and 1.088 ± 0.024, respectively. The mean deviation for the potential was calculated to be 0.26 mV. The propagation of this error leads to an E-dependent error in $\Delta[H^+]$, and for the potential after 10 min of CO bubbling (289.0 mV) one gets $\Delta[H^+] = 0.50 \pm 0.10$ mmolal.

This change in $[H^+]$ thus corresponds to only a low percent of the observed concentration of the complex (9.234 ± 0.084). In the potentiometric measurements slow reduction of Ag^+ took place due to the relatively low acidity. The slight increase in $[H^+]$ during CO bubbling should therefore be caused by reaction (2) rather than primary formation of the silver complex. This monocarbonyl is therefore of addition type and probably a 1/1 metal carbonyl complex analogous to those formed between Cu(I) and CO in aqueous media.

1. Manchot, W., König, J. and Gall, H. *Ber. Dtsch. Chem. Ges. 57* (1924) 1157; Manchot, W. and König, J. *Ibid. 60* (1927) 2183.
2. Souma, Y. and Sano, H. *Chem. Lett.* (1973) 1059; Souma, Y., Iyoda, J. and Sano, H. *Inorg. Chem. 15(4)* (1976) 968.
3. Vestin, R. *Acta Chem. Scand. 8* (1954) 533.
4. McAndrew, R. T. and Peters, E. *Can. Metall. Q. 3(2)* (1964) 153.