

Composition of a Silver(I) Carbonyl Complex in Aqueous Solution. An Investigation Using Equilibrium Measurements, ^{13}C NMR and Infrared Spectroscopy

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The equilibrium reaction between carbon monoxide and monovalent silver in acidic silver/sodium perchlorate solutions has been studied by manometrical methods. The dissolved carbonyl complex that was formed appeared to contain one CO and one Ag^+ . By NMR spectroscopy the ^{13}C -resonance was detected both in samples containing the silver(I) carbonyl complex and in samples with physically dissolved CO alone. The shift of the complex was determined. By infrared spectroscopy the CO-stretching frequency of the complex was detected.

Most of the work on the complex formation between monovalent silver and carbon monoxide reported up to now involves solutions with very low water activity. Earlier investigators¹ suggested that a complex where two Ag^+ were bound per CO was formed when CO was absorbed in concentrated H_2SO_4 containing Ag^+ . From later absorption measurements on this and other similar systems it has, however, been concluded² that a complex of the composition $\text{Ag}(\text{CO})_2^+$ is formed. The existence of a 1/1-silver carbonyl complex in liquid anhydrous HF has been demonstrated³ potentiometrically.

Unlike the situation in anhydrous solutions, the absorption of carbon monoxide in aqueous media containing a silver(I) salt is very low. This might be the reason why complex formation between aqueous Ag^+ and CO has not been observed until recently.⁴

The present work deals with the absorption of carbon monoxide in aqueous solutions containing dissolved silver perchlorate and, in certain cases,

even sodium perchlorate to keep the ionic strength constant. Perchloric acid was added to all solutions in order to keep the pH low. This was necessary to prevent the reduction of Ag^+ by CO which otherwise would have disturbed the measurements. It has, however, been shown⁴ that the rapid reversible absorption of CO noted in such acidic silver perchlorate solutions occurs due to the formation of an addition complex between Ag^+ and CO and does not depend on CO-reactions that involve reduction of Ag^+ or any protolytic reaction. The equilibrium measurements were performed at 25.0 °C, other measurements at room temperature. Concentrations are given in molal (*m*) i.e. mol/1000 g solvent (H_2O). Pressures are given in Torr.

RESULTS AND DISCUSSION

Equilibrium measurements. After every addition of carbon monoxide the equilibrium values of the partial pressure (P_{CO}) and the total concentration of dissolved carbon monoxide (CO_t) were determined. As is evident from Table 1, the reproducibility in the quotient $\text{CO}_t/P_{\text{CO}}$ was good for each set of experimental conditions. The concentration of carbon monoxide complexed with Ag^+ , (CO_{Ag}), is calculated as a difference between CO_t in the solution containing Ag^+ and CO_t in a corresponding solution where Ag^+ has been completely replaced by Na^+ , which is equivalent to the physical solubility, CO_{phys} . It follows that

$$\text{CO}_{\text{Ag}} = C'P_{\text{CO}} \quad (1)$$

Table 1. CO-absorption in aqueous perchlorate solutions at 25.0 °C. In every experiment the absorption quotients were calculated at CO-pressures varying from ca 100 to 900 Torr, cf. Fig. 1.

[Ag ⁺] (m)	[Na ⁺] (m)	[H ⁺] (m)	(CO _i /P _{CO}) × 10 ⁶ (m Torr ⁻¹)	(CO _{Ag} /P _{CO} Ag _t) × 10 ⁶ (Torr ⁻¹)
0	4.00	0.10	0.532 ± 0.029	—
1.00	3.00	0.10	3.550 ± 0.018	3.018 ± 0.047
2.00	2.00	0.10	6.572 ± 0.058	3.020 ± 0.044
3.00	1.00	0.10	9.780 ± 0.169	3.083 ± 0.066
4.00	0	0.10	12.682 ± 0.075	3.038 ± 0.026

with $C' = \text{const.}$ if $\text{Ag}_t = \text{const.}$

In different experiments different amounts of monovalent silver were used but, throughout the whole series of equilibrium measurements, the sum of the concentrations of Ag^+ and Na^+ was kept constant. Under these conditions C' appears to be proportional to Ag_t (cf. Table 1) and therefore:

$$\text{CO}_{\text{Ag}} = C'' P_{\text{CO}} \text{Ag}_t \quad (2)$$

with $C'' = \text{const.}$ (cf. Fig. 1). Thus the equilibrium constant K for the reaction $\text{Ag}^+(\text{aq}) + \text{CO} = \text{AgCO}^+(\text{aq})$ is identical with C'' , and $K = (3.040 \pm 0.030) \times 10^{-6} \text{ Torr}^{-1}$ is obtained from Table 1.

As the concentration of the complex is low (at atmospheric pressure only ca. 2‰ of the total concentration of Ag^+), Ag_t is equal to the concentration of free Ag^+ to a good approximation. With the assumption that the activities of the carbonyl

complex and the free silver ion are proportional to their concentrations, one therefore concludes that in the dissolved silver(I) carbonyl complex one CO is bound to one Ag^+ .

¹³C NMR measurements. The samples used in the NMR measurements were made up of the same components as in the equilibrium measurements, and filled into an inner NMR sample tube. The shift standard—dioxane (δ 66.5 ppm)—was kept in an outer sample tube. The use of double tubes did, however, not affect the shift as was demonstrated in a special calibration experiment (See Experimental). Shift measurements were made in solutions of four different ionic strengths: 0.30, 1.10, 4.10 and ca. 25 m perchlorate solutions.

The physical solubility (CO_{phys}) is strongly influenced by the ionic strength. Thus we have found that in a 1.10 m perchlorate solution $\text{CO}_{\text{phys}}/P_{\text{CO}} = (1.068 \pm 0.025) \times 10^{-6} \text{ m Torr}^{-1}$, while in a 4.10 m

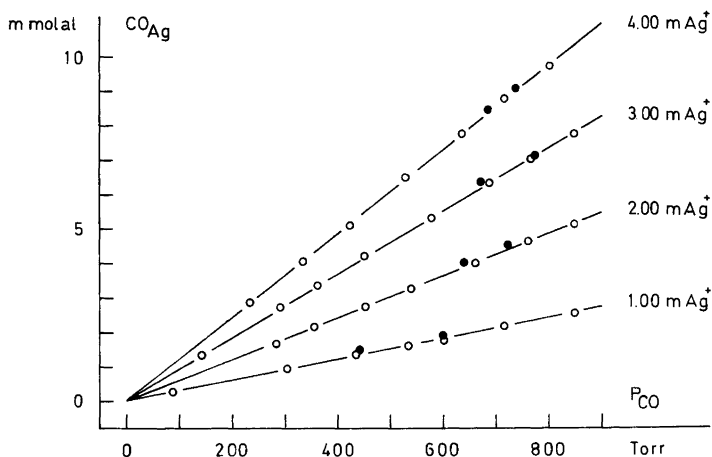


Fig. 1. CO-absorption in aqueous silver/sodium perchlorate solutions. $[\text{Na}^+] + [\text{Ag}^+] = 4.00 \text{ m}$ and $[\text{H}^+] = 0.10 \text{ m}$. Ag^+ -concentrations are marked on the diagram. \circ denotes values after synthesis of the complex, \bullet denotes values after splitting of the complex.

Table 2. ^{13}C -shift determinations of dissolved carbon monoxide in silver/sodium perchlorate solutions.

$[\text{Ag}^+]$ (<i>m</i>)	$[\text{Na}^+]$ (<i>m</i>)	P_{CO} (Torr)	$\text{CO}_{\text{phys}}/\text{CO}_{\text{Ag}}$	δ_{obs} (Hz)	δ^a (Hz)
0	0.20	1183	—	2960.16	—
0	1.00	777	—	2960.55	—
0	1.00	1400	—	2960.49	—
0	4.00	1.489	—	2962.04	—
1.00	0	409	0.3512	2774.63	2709.35 ± 2.09
1.00	0	993	0.3512	2774.66	2709.39 ± 2.09
1.00	0	1440	0.3512	2773.87	2708.32 ± 2.11
1.00	3.00	1041	0.1749	2752.53	2715.88 ± 2.31
2.00	2.00	1043	0.08747	2736.05	2716.28 ± 1.25
3.00	1.00	1031	0.05831	2730.29	2716.28 ± 0.85
4.00	0	1033	0.04374	2727.92	2717.68 ± 0.65
25	0	1151	—	2725.45	—

^a Calculated from eqn. (3).

solution the quotient is only one half of this value (*cf.* Table 1). However, the resonance of physically dissolved CO alone was detected at the three lower ionic strengths. Due to rapid exchange between physically dissolved and complex bound carbon monoxide, solutions that contain Ag^+ also show a single resonance. In these equilibrium mixtures the following relation holds for the observed shift, δ_{obs} ,

$$\delta_{\text{obs}} = \frac{\text{CO}_{\text{phys}}\delta_0 + \text{CO}_{\text{Ag}}\delta}{\text{CO}_t} \quad (3)$$

where δ_0 and δ denote the shifts of physically dissolved and complex bound carbon monoxide, respectively. Ag^+ -containing solutions of three different ionic strengths were used. Both P_{CO} and $[\text{Ag}^+]$ were varied and the shift of complex bound CO was calculated according to (3). The results from the shift determinations are presented in Table 2.

From the solutions not containing Ag^+ but varying in ionic strength an almost constant shift (184.0 ppm) was observed. However, the shift of complex bound carbon monoxide shows a certain dependence on the ionic strength. The observed increase in shift of the physically dissolved CO when the ionic strength is increased from $I=0.30$ to $I=4.10$ may therefore, although small, be significant. The accepted values at $I=1.10$ and $I=4.10$ were 2960.52 and 2962.04 Hz respectively.

The partial pressure of carbon monoxide was varied in the solution with $[\text{Ag}^+]=1.00$ and $[\text{Na}^+]=0$. The variation in shift is found to be nonsystematic and amounts to no more than 0.8 Hz

as a maximum. This discrepancy is of an order that can be expected as a consequence of the choice of experimental parameters, and the shift is therefore considered to be independent of P_{CO} .

In measurements where $[\text{Ag}^+] + [\text{Na}^+] = 4.00$ *m*, the partial pressure was held practically constant while $[\text{Ag}^+]$ was varied from 1.00 to 4.00 *m*. The calculated shift of the complex increased by about 2 Hz. However, a certain uncertainty in the calculation of the shift of the complex will be made due to concentration errors. By solving (3) for δ and differentiating with respect to CO_{phys} and CO_{Ag} one gets an estimation of the maximum shift error caused by the concentration errors. The calculated shift errors are presented in Table 2. It is evident that the small systematic change in the calculated shift of the complex when $[\text{Ag}^+]$ is varied at constant ionic strength can be explained by these errors. It is also clear that the uncertainty will be minimal at maximal $[\text{Ag}^+]$. We therefore conclude that the shift of the complex is independent of $[\text{Ag}^+]$ and accept 2717.7 ± 1.0 Hz as its value in a 4.10 *m* perchlorate solution. In spite of the fact that the estimation of the shift errors is maximized, these errors do not explain the relatively large shift difference between calculations from measurements in 1.10 and 4.10 *m* perchlorate solutions.

If the shift of the complex was the same in all solutions — say 2713 Hz — the observed shift in the solution with $[\text{Ag}^+]=25$ *m* would lead to a physical solubility of CO more than 7 times as high as that in a 4.10 *m* perchlorate solution. As mentioned, the physical solubility decreases with increasing ionic strength. It therefore follows

that the shift of the complex depends on the ionic strength. This dependence, here measured from an outer standard, would probably be very similar if measured from an inner standard. This follows from the calibration experiment, and the fact that the influence of the ionic strength on the shifts of physically dissolved and complex bound CO, respectively, is of different magnitude.

The fact that the calculated shift of the complex is independent both of P_{CO} and $[Ag^+]$ strongly supports the conclusion from the equilibrium measurements that the silver(I) carbonyl complex is of 1/1-composition. It should be noted however that the observed shift alone is independent of the partial pressure provided that $[Ag^+]$ and the ionic strength are kept constant. With the concentrations used in our experiments a pressure dependent shift would have resulted if other complexes than monocarbonyl were present. Of special interest is the circumstance that this pressure dependence would occur even if silver carbonyl complexes with different CO-content had the same shift. In fact, if one assumes a polycarbonyl complex with nCO in equilibrium with the monocarbonyl and physically dissolved CO, formula (3) would take the form

$$\delta_{obs} = \frac{\delta_0 k_0 + \delta k_1 + \delta \frac{p}{100-p} \left(\frac{P_{CO}}{760} \right)^{n-1}}{1 + \frac{p}{100-p} \left(\frac{P_{CO}}{760} \right)^{n-1}} \quad (4)$$

where $k_0 = CO_{phys}/P_{CO}$ and $k_1 = [\text{monocarbonyl}]/P_{CO}$. δ stands for the shift of the silver(I) carbonyl complexes – supposed to be the same – and p is the assumed percent of CO_t present in the polycarbonyl at 760 Torr.

Now, if say 5 % of CO_t is contained in a dicarbonyl complex at atmospheric pressure, formula (4) leads to a difference in the observed shift of 4.5 Hz at the pressures 409 and 1440 Torr. This should be compared with the measured difference of less than 1 Hz. From this pressure independence it therefore follows that no more than 1 % of the total concentration of dissolved carbon monoxide can be bound in a dicarbonyl complex. Of course higher carbonyls can be present to a still lesser extent. Our shift values (174.0–174.6 ppm) thus refer to the monocarbonyl complex. It is interesting to note that these values are in the same region as those obtained for the dicarbonyl complex in nonaqueous media.²

Infrared measurements. Because of the low concentration of the Ag(I) carbonyl complex and the low transmittance of a film of water, only the most concentrated equilibrium solution could be used for detection of the CO stretching frequency. A single absorption was noted at 2172 cm^{-1} . The physical solubility of carbon monoxide in our highly concentrated silver perchlorate solution is less than one percent of the concentration of the complex. The observed IR-absorption therefore doubtlessly occurs due to the CO-stretching in the monocarbonyl complex. It should also be pointed out that this frequency is in the region where the CO-stretching frequency of the silver(I) dicarbonyl complex in nonaqueous systems has been observed.^{2,5}

EXPERIMENTAL

Equilibrium measurements. The manometrical equilibrium measurements were performed in an apparatus consisting of a water-jacketed gas burette, an open mercury manometer with a glass scale and a temperature-regulated reaction flask. The flask was allowed to sway by rubber tubing and during the absorption it was mechanically shaken. The apparatus has been described by Vestin in more detail⁶

At the beginning of each experiment the reaction flask contained a weighed amount of an acidic silver/sodium perchlorate solution of known composition. The temperature was maintained at 25.0°C . The volume of the gas phase was determined in each experiment by calibration with nitrogen. After evacuation to vapour pressure, measured quantities of carbon monoxide were added whilst the reaction flask was shaken vigorously. Constant pressure readings were obtained after less than 1 min shaking indicating that equilibrium was attained. Thereafter the equilibrium pressure and concentration of dissolved carbon monoxide were determined.

¹³C NMR measurements. A 10 mm NMR sample tube equipped with two stopcocks was used. This could be connected either to the reaction vessel or directly to the manometrical apparatus *via* its shaking device. The former technique was used in experiments where the equilibrium pressure was regarded to be the critical parameter. It was possible to first establish equilibrium in the reaction flask at a desired pressure, and then to connect the sample tube to the vessel and adjust the CO-pressure in the tube to the same value as inside the flask. The filling of the tube did then not disturb the established equilibrium. In all NMR experiments ¹³C-enriched CO was used.

The shift standard – 40 % dioxane in D₂O – was kept in an outer 12 mm tube. The use of double tubes did not affect the shift determinations which the following calibration experiment shows:

(1) As in all measurements 40 % dioxane in D₂O was kept in the outer tube. In the inner tube 3 % dioxane and 10 % acetone in H₂O was kept. The shift between dioxane and acetone (methyl carbon) was 913.58 Hz.

(2) The content in the inner tube from (1) was transferred to a 12 mm tube, and a shift of 914.05 Hz was measured.

The noted difference of less than 0.50 Hz is not significant, and therefore the use of double tubes in the shift determinations is justified. All spectra were run on a Varian XL-100 spectrometer, operating at a ¹³C-frequency of 25.2 MHz, using an external proton lock.

Infrared measurements. A transmittance spectrum was obtained mathematically from single beam recordings from the test solution and the reference. The spectra were run on a Digilab FTS 14 interferometer. The cell was equipped with BaF₂-windows and a teflon spacer (0.025 mm).

The test solution was prepared in the reaction flask and an equilibrium pressure of about 760 Torr was chosen. The IR-cell was connected to the flask via teflon connections and CO was streamed through the cell before it was filled with the equilibrium mixture.

Chemicals. Carbon monoxide of two qualities was used: for the equilibrium and IR measurements, AGA 4.1, with minimum purity 99.997 % by vol.; for NMR measurements, ¹³C enriched CO (90 %) from Prochem. Other chemicals were of reagent grade.

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