

Chloro Complexes of Gold in Dimethyl Sulfoxide

T.E. Suarez, R.T. Iwamoto, and J. Kleinberg

Received November 30 1972

The chloro complexes of gold(I) in dimethyl sulfoxide have been investigated electrochemically. Potentiometric studies yielded the following values for K_{AuCl} and $K_{AuCl_2^-}$: $10^{10.9}$ and $10^{5.7}$. Conventional and cyclic voltammetric experiments with $AuCl_4^-$ are also reported.

Introduction

Because of its pronounced tendency to disproportionate in aqueous medium, relatively little work has been carried out on the solution chemistry of gold(I). The two studies^{1,2} which have been reported on the behavior of this unstable species in acetonitrile indicate that non-aqueous media can be extremely valuable in establishing the chemistry of gold(I) in solution. To develop a more complete picture of the behavior of gold(I) in solution, potentiometric and voltammetric examination of its chloro complexes in dimethyl sulfoxide was undertaken. As our work neared completion, a report on the redox chemistry of gold(I) species in dimethyl sulfoxide appeared in the literature.³ In view of a substantial difference observed in the stability of one of the chloro complexes and our inability to determine the reason for this discrepancy, we think it important to report our findings on gold(I). In addition, some interesting voltammetric observations on gold(III)-chloro complexes are described.

Experimental Section

The solvent, dimethyl sulfoxide, and the salts, tetraethylammonium perchlorate and tetraethylammonium chloride, were purified as reported in a previous communication.⁴ Stock solutions of gold(I) perchlorate in acetonitrile were prepared by dissolving bis(acetonitrile)gold(I) perchlorate² in the solvent. Dimethyl sulfoxide solutions of gold(I) perchlorate were made by adding 0.20 to 2.00 ml of the stock gold(I) solution in acetonitrile and 0.574 g of tetraethylammonium perchlorate (0.10 F) to a darkened 25-ml volumetric flask and diluting to the mark with deaerated solvent. These solutions were stable for 10-12

hr. when kept in the dark. Appropriate dilutions of the solutions were made for electrochemical measurements. The gold(I) content of the diluted solutions was determined by potentiometric titration with chloride ion. The varying amounts of acetonitrile in the diluted solutions had no effect on the electrochemical results.

Tetraethylammonium tetrachloroaurate(III) was precipitated by adding an aqueous solution of tetraethylammonium perchlorate to a similar solution of tetrachloroauric acid. The precipitate was washed five times with cold water and dried in vacuo at 50° for 4 hr.²

p-Toluenesulfonic acid (reagent grade) was recrystallized twice from warm water and dried under vacuum for 48 hr; m.p., 102-104°; lit., 104-105° for the monohydrate.

The basic equipment for the potentiometric and voltammetric measurements has been described.⁴ For the potentiometric work the titration cell was protected from light to prevent photochemical reduction of the gold(I), and a gold wire was used as the indicator electrode.

Coulometric data on gold(III) solutions were obtained with equipment described earlier.⁵

Results and Discussion

A typical potentiometric titration curve for the gold(I)-chloride system in dimethyl sulfoxide is shown in Figure 1. From such curves, the stepwise formation constants K_{AuCl} and $K_{AuCl_2^-}$ were calculated by a method described earlier for the analysis of gold(I)-chloride complexes in acetonitrile.² Values of $10^{10.9+0.1}$ and $10^{5.7+0.1}$ were obtained for the 1:1 and 2:1 species. (Corrections for ion-pair formations between $Et_4N^+ Cl^-$ and ClO_4^- have been made.) A formal potential of 1.358 v. vs. the "DMSO" reference electrode⁴ was found for the gold(I)-gold metal system, which was shown to follow Nernstian behavior (0.059 ± 0.004 for the coefficient of the log term in the Nernst expression). The value for $K_{AuCl_2^-}$ agrees very well with that reported from another laboratory,³ but there is substantial difference in the K_{AuCl} constant ($10^{10.9}$ vs. $10^{12.6}$). Because our electrolytic medium was 0.10 F tetraethylammonium perchlorate and that of the other investigators 0.10 F *p*-toluenesulfonic acid, we

(5) D.W. Du Bois, R.T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, **8**, 815 (1969).

(1) A.D. Goolsby and D.T. Sawyer, *Anal. Chem.*, **40**, 1978 (1968).
(2) O. Bravo and R.T. Iwamoto, *Inorg. Chim. Acta*, **3**, 663 (1969).
(3) A. Foll, M. Le Demez, and J. Courtot-Coupez, *Bull. Soc. Chim. France*, 1972, p. 408.
(4) T.E. Suarez, R.T. Iwamoto, and J. Kleinberg, *Inorg. Chim. Acta*, **7**, 292 (1973).

redetermined both constants in the latter medium. The constants (K_{AuCl} , $10^{10.7}$ and $K_{\text{AuCl}_2^-}$, $10^{5.5}$) were in good agreement with our previously determined values; thus, interesting, there is no electrolyte effect. In addition, it should be pointed out that the *p*-toluenesulfonic acid we used (m.p. 104°) was the monohydrate and therefore the electrolytic medium was 0.1 molar in water; from the source (Eastman Kodak) of the acid employed by the other investigators we presume that it too was the monohydrate. Of further interest is the fact that the formal potentials in the two media were in close agreement and differed from that reported by the others after adjustment of our value to their reference electrode [1.407 v. (ours); 1.492 (theirs) vs normal hydrogen electrode].

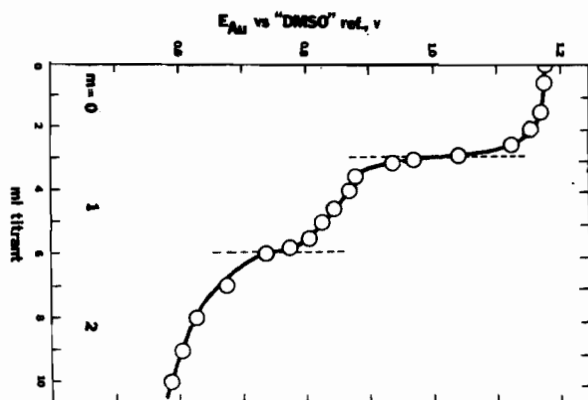


Figure 1. Titration curve for 10 ml of $5.87 \times 10^{-4} F$ gold(I) in dimethyl sulfoxide (0.10F in tetraethylammonium perchlorate) with $2.01 \times 10^{-3} F$ tetraethylammonium chloride.

Voltammetric reduction of gold(I) perchlorate solution ($ca. 1 \times 10^{-4} F$) at the rotating platinum electrode gave a one-step irreversible ($E_{1/4} - E_{3/4}$, 0.100 v.) reduction wave at 0.77 v. vs S.C.E. in 0.10 F tetraethylammonium perchlorate medium. At a stationary platinum electrode, a single reduction step with a peak potential of 0.73 v. vs S.C.E. was obtained at a scan rate of 1.5 v. per min. No oxidation of gold(I) or of gold to gold(I) was observed within the anodic limit of the medium, 1.2 v. It was noted in a cyclic voltammetric experiment that the reduction step on the second sweep occurred at a slightly more positive potential than 0.73 v., suggesting an overvoltage effect due to the plating out of gold.

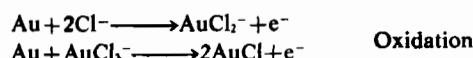
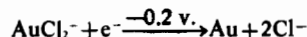
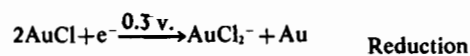
A gold(I) chloride solution ($ca. 1 \times 10^{-4} F$), prepared by mixing stoichiometric quantities of tetraethylammonium chloride and gold(I) perchlorate solutions, was reduced voltammetrically at the rotating platinum electrode. A long drawn-out wave beginning at 0.4 v. and leveling out at -0.2 v. vs S.C.E. was obtained. At a stationary platinum electrode and a scan rate of 1.5 v. per min., the reduction wave resolved itself into two steps, the first at 0.3 and the second at -0.2 v.; the heights of the two steps were identical. Two oxidation steps were observed on the anodic return sweep, the first at 0.46 and the second at 0.75 v.

Dichlorogold(I) anion solutions of $ca. 1 \times 10^{-4} F$

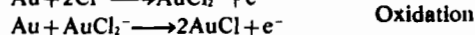
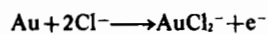
concentration were made by stoichiometric combination of tetraethylammonium chloride and gold(I) perchlorate solutions and were voltammetrically reduced at the rotating platinum electrode. A single irreversible step was found at -0.3 v. Cyclic voltammetry at the stationary platinum electrode gave a single reduction step with a peak potential of -0.37 v. at a scan rate of 1.5 v. per min. On the return sweep, two oxidation steps were observed at 0.5 and 0.8 v., values very close to those found in the gold(I) chloride experiments.

From the voltammetric studies on the gold(I) chloride and dichlorogold(I) solutions it appears that reduction of these species is followed by the same oxidation steps. The following sequences of reactions could very well account for the electrochemical observations noted above.

AuCl



AuCl_2^-



The voltammogram for a $10^{-3} F$ solution of tetraethylammonium tetrachloroaurate(III) in dimethyl sulfoxide at the rotating platinum electrode showed two reduction steps and an oxidation step. The first reduction step occurred at 0.13 v. and its height was twice that of the second step which was at -0.35 v. vs S.C.E. Coulometric reduction of a solution $5.8 \times 10^{-4} F$ in AuCl_4^- at 0.10 v. with a platinum electrode showed the first reduction to be a two-electron process (1.8 moles of electrons per mole of AuCl_4^-). The oxidation wave occurred at 0.95 v. Oxidation of $3.5 \times 10^{-4} F$ solution of tetraethylammonium chloride at the rotating platinum electrode gave a wave at 1.0 v. This observation suggests that the anodic step observed for the AuCl_4^- solution can be attributed to oxidation of chloride ion. From the magnitude of the currents of the anodic steps in the two solutions and from additional experiments on AuCl_4^- solutions containing added chloride ion, it is concluded that a small proportion ($ca. 10\%$) of the gold(III) complex is dissociated in dimethyl sulfoxide.

At the stationary platinum electrode and a scan rate of 1.5 v. per min., reduction of a $5 \times 10^{-4} F$ solution of AuCl_4^- showed two steps, the first at 0.12 and the second at -0.45 v., with a peak height ratio of 2:1. On the return anodic sweep, three oxidation steps, one at 0.5, another at 0.8, and the third at 1.0 v., were found. The first two steps are identical to those observed in cyclic voltammograms of AuCl and AuCl_2^- solutions. When the initial cathodic sweep with the AuCl_4^- solution was reversed before the reduction of gold(I) takes place, no oxidation

steps at 0.5 and 0.8 v. were observed. It is clear then that reduction of gold(I) to the metal must take place before the 0.5 and 0.8 v. oxidation steps appear in the return sweep. When the reduction step at 0.12 v. for solutions of AuCl_4^- was scanned (1.5 v. per min.) repeatedly without going out to the oxidation step at 1.0 v., the peak current decreased rapidly with increasing number of scans. If the cyclic experiment is carried out by scanning beyond 1.0 volt, the peak height for the reduction step decreases only slightly with increasing number of scans. Even when the last experiment is performed at the very high scan rate of 1200 v. per min., no change occurs in the cyclic voltammograms.

The cyclic voltammetric experiments show clearly that the gold(I) species formed on reduction of AuCl_4^- is essentially quantitatively reconverted to AuCl_4^- only on scanning beyond 1.0 v. This raises the interesting question of the nature of the gold(I) spe-

cies formed on reduction of AuCl_4^- at 0.12 v. which cannot be reversibly oxidized. Two possibilities come to mind: (1) A tetrachlorogold(I) species, AuCl_4^{3-} , is formed but its geometry differs from that of AuCl_4^- (square planar). (2) Reduction gives a species containing fewer than four coordinated chloride ligands. The regeneration of AuCl_4^- on scanning beyond 1.0 v. may possibly, occur from an electrochemical oxidation of gold(I) or by chemical oxidation by elemental chlorine which is generated electrochemically from chloride ion at about 1.0 v., each type of oxidation being followed by appropriate chemical change. Studies are currently underway to gain insight on the cyclic voltammetric processes.

Acknowledgment. The research described herein was supported in part by the National Science Foundation (GP-11313 and GP-28332). This support is gratefully acknowledged.