

Three procedures of reversible dissolution/deposition of gold using halogen-containing organic systems

Yukimichi Nakao

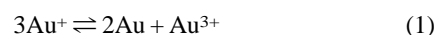
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Gold is reversibly and repeatedly dissolved and deposited under restricted conditions in a solution consisting of an elemental halogen, a halide and acetonitrile by a procedure involving one of three physical operations: addition of methanol, cooling, or evaporation to dryness.

Most organic and inorganic substances are 'physically' dissolved in aqueous or organic media, and hence are often recovered from solution by means of physical operations such as (i) addition of non-solvent, (ii) cooling, or (iii) evaporation (to concentrated solutions or dryness), which results in deposition.^{1,2} On the other hand, metals are 'chemically' dissolved as metal ions. Therefore, it has been believed that an appropriate reductive treatment is necessarily required to recover them in the metallic state.

We reported new organic solvent systems consisting of an elemental halogen (X₂), a halide (X⁻), and an organic solvent (organic-X systems, X = Cl, Br, I), which dissolve a number of

metals including noble metals.³ It is found that metallic gold is deposited in solutions of some organic-X systems, which are previously saturated with gold, not by chemical treatment but by each of the physical operations (i)–(iii), and that gold is dissolved in solutions obtained from the resulting supernatants or residues. UV-VIS spectroscopy confirmed that such reversible dissolution/deposition of gold is, in most cases, a chemical process based on the following disproportionation equilibrium.⁴



Shifts to right and left in this equilibrium correspond to the deposition and dissolution of gold, respectively.

Three typical procedures of repeated dissolution/deposition of gold involving each of the operations were carried out in selected organic-X systems containing acetonitrile (AN). Dissolution of gold was performed using an excess amount of gold wire of 0.2 mm diameter under refluxing, and deposition of

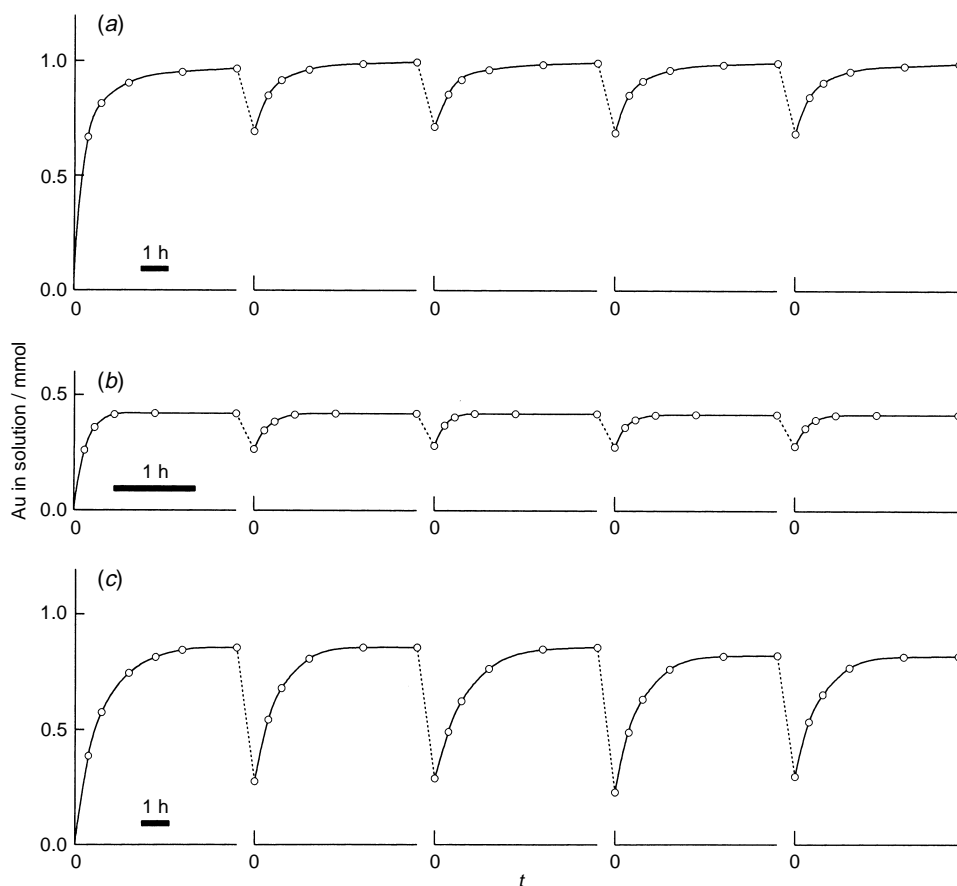


Fig. 1 Time-course of gold content in the solutions during repeated dissolution/deposition of gold using (a) Br₂ (0.5 mmol)–[NEt₄]Br (1 mmol)–AN (2 g), (b) I₂ (1 mmol)–[NEt₄]I (1 mmol)–AN (10 g) and (c) I₂ (0.5 mmol)–NaI (1 mmol)–AN (2 g): dissolution of gold was carried out under refluxing at 82 °C. Each of the gold-saturated solutions was treated by (a) adding methanol (8 g), heating at 60 °C for 2 h, the supernatant was evaporated to dryness, and the residue was redissolved in An (2 g), (b) cooling to 20 °C and allowing to stand overnight or (c) evaporating to dryness, and the residue was redissolved in AN (2 g). The broken lines correspond to reduction in gold content in the solutions upon deposition of gold.

gold was carried out by adding methanol to the solution, cooling it, or evaporation to dryness. Amounts of gold in the solutions were determined by weighing the residual gold wire and the deposited gold. The contents of Au species in the solutions were evaluated by UV–VIS spectra which were measured using thin liquid films (8 or 200 μm thickness) on the basis of the characteristic bands of each species: $[\text{AuBr}_2]^-$ (192, 200, 212 nm), $[\text{AuBr}_4]^-$ (256, 395 nm), $[\text{AuI}_2]^-$ (217 nm) and $[\text{AuI}_4]^-$ (510, 670 nm).

First, deposition of gold was caused by adding methanol to gold-saturated solutions from organic–X systems in which the ratio X_2/X^- was near to 0.5. The supernatant was then evaporated to dryness to give a residue, which was redissolved in AN, and the resulting solution, after separation from the deposited gold, was used for the next dissolution of gold. Fig. 1(a) shows a procedure of repeated dissolution/deposition of gold involving addition of methanol using an organic–Br system consisting of Br_2 (0.5 mmol), $[\text{NEt}_4]\text{Br}$ (1 mmol), and AN (2 g). The following equilibrium is proposed on the basis of UV–VIS spectra of the solutions before and after dissolution of gold.

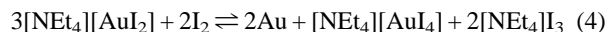


A similar dissolution/deposition of gold occurred in gold saturated solutions of either organic–Cl systems or organic–I systems. In the latter, another equilibrium as given below seems to be involved, since the Au^{3+} species was not detected.



Although the methanol is apparently likely to act as non-solvent, it would actually shift the disproportionation equilibrium to the right as well as water.⁴

Second, as recently reported,⁵ gold is deposited by cooling gold-saturated solutions of organic–I systems in which the I_2/I^- ratio was >0.5 . Such deposition of gold was not observed in the solutions of either organic–Cl or organic–Br systems. The supernatants could be used for further dissolution of gold at elevated temperatures. Fig. 1(b) illustrates a procedure of repeated dissolution/deposition of gold using a system consisting of I_2 (1 mmol), $[\text{NEt}_4]\text{I}$ (1 mmol), and AN (10 g), which involves alternating heating and cooling. The following equilibrium has already been proposed for this process.⁵



Third, gold was deposited in solutions from certain organic–I systems by concentrating the solution. It was reported that, when the ratio I_2/I^- is 0.5 and the cation of the iodide is $[\text{NEt}_4]^+$, evaporation of the gold-saturated solution gives an Au^+ complex, $[\text{NEt}_4][\text{AuI}_2]$.⁵ On the contrary, when the cation was an alkali-metal ion or an alkaline-earth metal ion, gold was deposited as the solution was concentrated by evaporation. After AN was completely removed, the resulting tarry residue was redissolved in AN, and the solution to be used again for dissolution of gold was separated from the deposited gold as quickly as possible. Fig. 1(c) shows a procedure using a system consisting of I_2 (0.5 mmol), NaI (1 mmol), and AN (2 g), involving deposition of gold by evaporation. In this case, the Au^{3+} species, $[\text{AuI}_4]^-$, was confirmed to be formed with deposition of gold. Thus, the equilibrium for this process would be as follows.



Dissolution/deposition of gold in the procedures stated above were all reversible and the efficiency of dissolution of gold was maintained constant throughout although a definite amount of gold still remained dissolved in the solution after deposition of gold. These procedures can be expected to be applied to a completely closed gold-recovering process which is very useful for the extraction of gold from ores and wastes of electronics industries. The gold thus recovered should also be of higher purity.

References

- 1 *Polymer Fractionation*, ed. M. J. R. Cantow, Academic Press, New York, 1967, pp. 43–66.
- 2 *An Introduction to Separation Science*, ed. B. L. Karger, L. R. Snyder and C. Horvath, Wiley, New York, 1973, pp. 303–336.
- 3 Y. Nakao, *J. Chem. Soc., Chem. Commun.*, 1992, 426.
- 4 R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978, pp. 22; 65.
- 5 Y. Nakao and K. Sone, *Chem. Commun.*, 1996, 897.

Received in Cambridge, UK, 16th June 1997; 7/04171C