Reversible dissolution/deposition of gold in iodine–iodide–acetonitrile systems

Yukimichi Nakao*[a] **and Kozo Sone**[b]

[a] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan*
[b] *Department of Chemistry, Faculty of Science, Josai University, 1-1 Keyakidai, Sakado, Saiyama 350-02, Japan*

Gold can be dissolved on heating in iodine–iodide–acetonitrile solvent systems, where the ratio I_2/I^- is > 0.5, as $[AuI_2]^-$, and deposited from the resulting solution on cooling *via* the formation of $[AuI_4]^-$.

We have reported that halogen–halide–organic solvent systems, such as the well known 'tincture of iodine', can serve as good solvents for metals, in particular noble metals such as silver, gold and palladium.[1,2] Now we find that, in some of these systems, gold can be dissolved on heating and deposited on cooling quite reversibly. The observed phenomenon is thus just like simple recrystallization, although chemical reactions (shifts of redox equilibria) are certainly underlying it.

A small piece of gold wire (*ca.* 1.2 mmol, 0.2 mm in diameter) was added to a solvent system composed of I_2 (1.5 mmol), $[NEt_4]I$ (1 mmol) and acetonitrile (10 g) and the mixture was refluxed at 82 °C with stirring. After 2 hours, the solution dissolved 0.30 mmol of the gold. Upon removal of the undissolved gold wire and cooling to 20 °C and standing for *ca.* 1 day, 43% of the dissolved gold deposited as a fine powder.[†][‡] When the resulting solution was refluxed again with a new piece of gold wire, an amount of gold equal to that deposited before is dissolved again, and deposited once more on cooling; this process can be repeated indefinitely.[§]

The amount of dissolved gold (Au_{diss}), which saturates this solvent system under reflux, depends strongly on the amount of I_2 (a_{I_2}) in it. The solid-line curve in Fig. 1 shows that the degree of dissolution of gold shows two distinct regions, *i.e.* an initial linear increase, leading to a maximum of *ca.* 1 mmol Au_{diss} at a_{I_2} = 0.5 mmol (region A), and then a gradual decrease (region B). Reversible dissolution/deposition of gold occurs only in region B; the dissolution in region A is irreversible, with no gold deposit forming on cooling. The vertical arrows in region B (Fig. 1) indicate the amount of gold deposited from the solutions at 20 °C, the dotted-line curve thus indicates the amount of gold saturating the solutions at 20 °C.[¶]

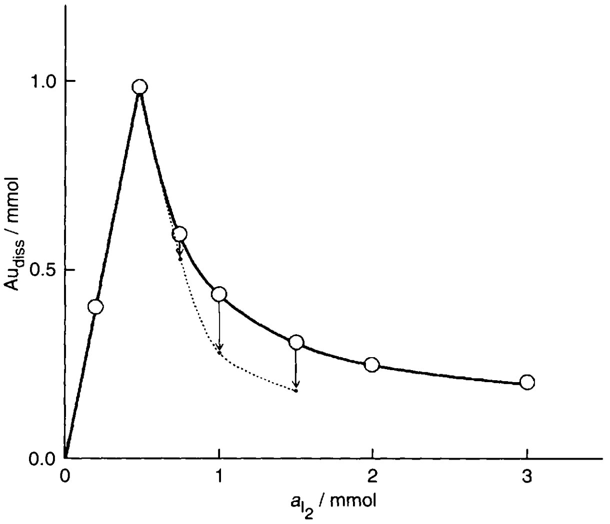

Fig. 1 Dependence of the amount of gold saturating the I_2 (a_{I_2} mmol)–$[NEt_4]I$ (1 mmol)–acetonitrile (10 g) system (Au_{diss}) on the value of a_{I_2}; (—) under reflux (82 °C) and (---) under cooling (20 °C). When a_{I_2} > 2 mmol, a black precipitate of approximate composition $[NEt_4]I_7$ containing 2–5% gold is formed on cooling the refluxed solution, and disturbs the study (in the system with $[NBu_4]I$ this does not occur, so that the reversible dissolution/deposition of gold can be followed up to a_{I_2} = 3 mmol).

Now it is well known that I_2 readily reacts with I^- in organic solvents forming the stable I_3^- ion [eqn. (1)].[3]

$$I_2 + I^- \rightleftharpoons I_3^- \quad (1)$$

The formation of this ion is nearly quantitative (p*K* ≈ 7) in acetonitrile; the I_3^- ion formed is an effective oxidant toward noble metals,[1,2] and, in the presence of I^-, reacts with gold to form the very stable $[AuI_2]^-$ complex [eqn. (2)].

$$2Au + I_3^- + I^- \rightleftharpoons 2[AuI_2]^- \quad (2)$$

Dissolution of gold in region A occurs in this way, and effective dissolution of gold occurs, therefore, when comparable amounts of I_3^- and I^- are present. However, if one of the components is deficient less gold dissolves, hence the presence of a maximum value of Au_{diss} for the stoichiometric solution (0.5 mmol) of I_3^- and I^-, which dissolves *ca.* 1 mmol of gold under reflux. The brown colour of the solvent system, which is due to the presence of I_3^-, is thereby lost, and the system turns into a light yellow acetonitrile solution of the complex $[NEt_4][AuI_2]$.[||]

The solvent system in region B is more complex; in addition to I^- (which nearly disappears at a_{I_2} = 1 mmol) and I_3^-, small amounts of unstable higher polyiodide ions, I_5^- and I_7^- (p*K* ≈ 2–3),[5] as well as some free I_2, are expected to appear with an increase of a_{I_2}. Some insights into the reaction of gold with such a complicated medium can now be obtained from a study of UV–VIS spectra.[**]

The spectra of the solvent system with a_{I_2} = 1.5 mmol were measured at four stages of dissolution/deposition of gold, *i.e.* before the dissolution of gold (*a*), when under reflux (*b*), when the refluxed solution is cooled to 20 °C, and the deposition of gold is imminent (*c*), and after completion of deposition (*d*). All the spectra show strong bands at 291 and 372 nm, which nearly coincide with the values (291 and 360 nm) reported for I_3^- in acetonitrile;[6] the slight shift of the latter band is probably due to the presence of higher polyiodide ions (I_n^-). Their intensities indicate that the concentration of I_3^- (and accompanying I_n^- ions) in the solvent system decrease markedly from (*a*) to (*b*); however, a part of the decrease is restored at (*c*), and still more at (*d*).

On the other hand, two groups of weaker bands are found in the spectra of gold-containing solutions: (*i*) a band near 200 nm with a shoulder at *ca.* 217 nm, which is most evident at stage (*b*) and gets progressively weaker stepwise in going to stages (*c*) and (*d*), and (*ii*) two bands at 510 and 665 nm, for which the intensity decreases in the order (*c*) > (*d*) > (*b*). These latter bands considerably darken the solvent system. Bands (*i*) are ascribed to I_2 and $[AuI_2]^-$; both of these absorb at *ca.* 200 nm, and the latter shows a band at 217 nm in acetonitrile. Bands (*ii*), on the other hand, are thought to be due to the unstable complex

$[AuI_4]^-$, which is formed by the reaction of $[AuI_2]^-$ and I_2 [eqn. (3)].

$$[AuI_2]^- + I_2 \rightleftharpoons [AuI_4]^- \tag{3}$$

Recently we obtained a visible spectrum of the complex $[NEt_4][AuI_4]$ prepared according to the method of Ryan[7] in acetone solution at −78 °C; it is composed of two bands at *ca.* 510 and 670 nm, and their shapes and relative intensities are very similar to those of the bands (*ii*).

All these spectral results lead to us to the following conclusion: with an increase of a_{I_2} [region B], an increasing portion of gold dissolved as $[AuI_2]^-$ [eqn. (2)] is oxidized to $[AuI_4]^-$ by I_2 [eqn. (3)], so that an equilibrium mixture of the two complexes (and undissolved gold) is formed in the solution under reflux. While the equilibrium of eqn. (2) shifts to the right on heating, that of eqn. (3) shifts to the right on cooling.[8,9] Thus when the refluxed solution is quickly cooled, the amount of $[AuI_4]^-$ increases and that of $[AuI_2]^-$ decreases at first, but over time both complexes decompose, with the deposition of gold, until a new equilibrium state is attained. The overall change may thus be expressed as a disproportionation equilibrium:[10]

$$3[AuI_2]^- + 2I_2 \rightleftharpoons 2Au + [AuI_4]^- + 2I_3^- \tag{4}$$

which can be derived from eqns. (1)–(3).

Footnotes

† These data were obtained by weighing the gold wire after dissolution or the gold powder after deposition, after washing with methanol and drying. The purity of the deposited gold was checked by atomic absorption spectrometry.

‡ The deposit of gold begins to form within several minutes after cooling to 20 °C if the solution is in contact with a ground-glass surface; however, it takes several hours if the solution is kept in a smooth quartz vessel. It seems likely that the first deposit of gold catalyses further deposition.

§ A similar dissolution/deposition of gold takes place in I_2–$[NBu_4]I$–acetonitrile solvent systems. Comparable amounts of gold are dissolved and deposited, although the rate of dissolution is much slower. More or less similar changes are also observed in other iodine–iodide–organic solvent systems, *e.g.* I_2–KI–methanol, I_2–$[NBu_4]I$–nitromethane, and I_2–cetylpyridinium iodide–benzene. However, such a reversible dissolution/deposition could not be observed with any other metals, nor in Cl_2–Cl^-– and Br_2–Br^-–organic solvent systems, in which gold dissolves exclusively in the form of very stable $[AuX_4]^-$ (*cf.* refs. 1 and 2).

¶ These amounts are in accord with the values obtained by keeping gold, with stirring, in these solvent systems at 20 °C for a few days.

‖ Crystals of this complex of the same colour can be obtained on evaporating the solution to dryness, and, after recrystallization from ethanol, identified by mp (103 °C), IR (*cf.* ref. 4), and elemental analysis (C, 16.53; H, 2.98; N, 2.56; I, 43.68; Au, 33.6. Calc. C, 16.54; H, 3.47; N, 2.41; I, 43.68; Au, 33.90%).

** Since the solutions are all deeply coloured owing to the strong absorption of I_3^-, the spectra were measured using thin films with spacers of 8 and 200 μm thicknesses. To obtain a spectrum at stage (*b*), use was made of such a film of a 'just refluxed' solution kept at *ca.* 80 °C, *i.e.* just below the reflux temperature of the solvent system.

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