Dissolution of Noble Metals in Halogen–Halide–Polar Organic Solvent Systems

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Noble metals (Pd, Ag and Au) can be dissolved in a variety of halogen–halide–polar organic solvent systems.

Since the era of alchemy, *aqua regia* has been used to dissolve noble metals such as gold. In the past decade some organic metal-dissolving systems have been developed,[1–3] but are not greatly superior to the conventional aqueous systems in practical use. Recently, we have succeeded in dissolving many metals in organic systems which consisted of an elemental halogen, a long-chain quaternary ammonium halide (cationic surfactant), and benzene.[4] Since then a variety of organic systems using polar organic solvents have been tested. One of them using chlorine dissolves gold faster than *aqua regia*.

Table 1 Rates of dissolution of noble metals in organic systems

	Organic systems[a]				Rate of dissolution/μm h^{-1}			Residual halogen
No.	Halogen	Halide	Solvent	T/°C	Pd	Ag	Au	(%); t/h
1	Cl_2	Et_4NCl	MeCN	30	170[c]	190	170	92; 6
2	Cl_2	Me_3NHCl	MeCN	30	110[c,d]	23[d]	230	88; 6
3	Br_2	Et_4NBr	MeCN	80[b]	170	470	58	94; 24
4	Br_2	KBr	MeOH	30	85	0	29	90; 24
5	I_2	KI	MeOH	65[b]	10	0	20	100; 24
6	I_2	NaI	Me_2CO	56[b]	15	38	0.5	100; 24

[a] Halogen, 0.5 mmol; halide, 1 mmol; solvent, 10 g. [b] Reflux temperature. [c] A precipitate was formed. [d] Dissolution stopped before completion.

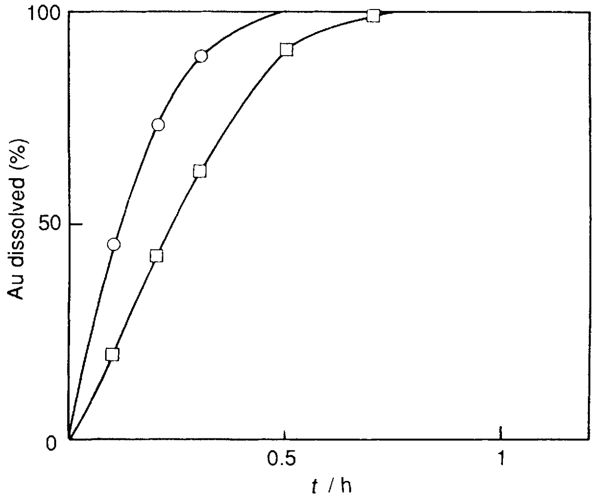

Fig. 1 Dissolution of 0.2 mm diameter Au wire at 30 °C: ○, in Cl_2 (0.5 mmol)–Me_3NHCl (1 mmol)–MeCN (10 g); □, in *aqua regia* (10 g)

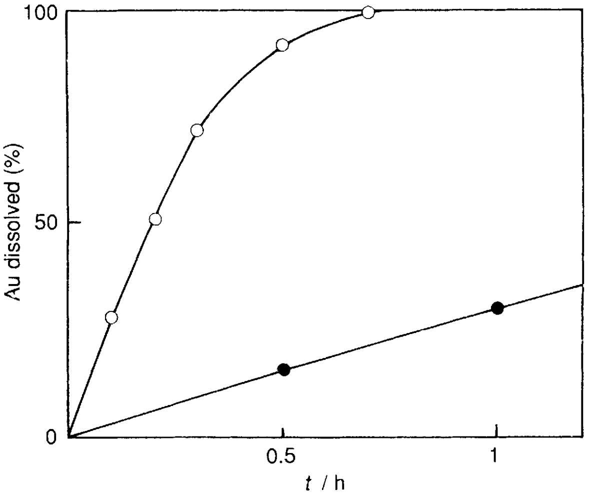

Fig. 2 Dissolution of 0.2 mm diameter Au wire in tincture of iodine (10 g) containing 1.2 mmol of I_2, 1.2 mmol of KI and 7.8 ml of ethanol: ●, at 30 °C; ○, at 81 °C (under reflux)

Tincture of iodine for medical use is another such system which dissolves gold smoothly. In this report we describe the features of such dissolution systems for noble metals.

The systems were prepared by dissolving 0.5 mmol of an elemental halogen (Cl_2, Br_2 or I_2) and 1 mmol of a halide salt in 10 g of a polar organic solvent. The rates of dissolution of noble metals (Pd, Ag or Au) were measured in the manner previously reported[4] using 0.2 mg atom of the noble metal in the form of 0.2 mm diameter wire. The stabilities of the halogens in the organic systems in the absence of metals were evaluated by measuring the residual halogen by iodometry.

In general, chlorine reacts more easily with most polar organic sovlents than it does with metals. However, acetonitrile is exceptionally resistant to chlorine at low temperatures and can be employed in metal-dissolving systems. In such chlorine-acetonitrile systems, quaternary ammonium chlorides and amine hydrogen chlorides can be used as the halide component (Table 1, Nos. 1 and 2). Among these systems, one that contains Me_3NHCl was sufficiently stable and dissolved gold most effectively. As shown in Fig. 1, this system dissolved gold more rapidly than *aqua regia* at 30 °C, in spite of the relevant concentrations being much lower.

Bromine is less reactive than chlorine with either organic solvents or metals. Thus, a system consisting of bromine, Et_4NBr, and acetonitrile (Table 1, No. 3) could be used even under reflux. As well as three noble metals (Pd, Ag and Au), three base metals (Fe, Ni and Zn) could be dissolved. Products were separated from in each case and purified by recrystallization in a similar manner to that previously reported.[4] These products were identified by elemental analysis as being the ionic systems $[TEA]^+{}_2[PdBr_4]^{2-}$, $[TEA]^+[AgBr_2]^-$, $[TEA]^+[AuBr_4]^-$, $[TEA]^+[FeBr_4]^-$, $[TEA]^+{}_2[NiBr_4]^{2-}$ and $[TEA]^+{}_2[ZnBr_4]^{2-}$ ($[TEA]^+$ = $[Et_4N]^+$). Some of these compounds have been prepared by other methods.[5–7]

Potassium bromide was applied only in methanol systems at low temperatures because bromine tends to react with methanol (Table 1, No. 4). On the other hand, the I_2–KI–methanol system was stable even under reflux (Table 1, No. 5). Both methanol systems were characteristically ineffective in dissolving Ag, because of the formation of a protecting layer of silver halide on the Ag surface. Tincture of iodine, a solution of I_2 and KI in ethanol, was expected to dissolve metals and indeed it dissolved gold rapidly (Fig. 2). In medical use, it is therefore important not to allow tincture of iodine to come into contact with metals.

The system I_2–NaI–acetone dissolved both Au and Ag (Table 1, No. 6), and was successfully applied to extraction of these metals from ore containing 13.1 ppm of Au and 389.2 ppm of Ag in a similar way to the benzene system already reported.[4] The extraction efficiencies for Au and Ag were 99.3 and 93.5%, respectively.

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