



Pure gold dissolution in dilute chloric, bromic or iodic acid solution containing abundant halide ions



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ARTICLE INFO

Article history:

Received 1 July 2016

Received in revised form 15 November 2016

Accepted 2 December 2016

Available online 08 December 2016

Keywords:

Gold dissolution rate constant

chlorate

bromate

bulk water structure

ionic strength

ABSTRACT

The pure gold dissolution has been explored in (dilute) chloric, bromic, or iodic acid (HXO_3 , $X = \text{Cl}, \text{Br}, \text{I}$) aqueous solution containing abundant halide ions at 60 °C. It has been found that mixtures between sodium chlorate and HCl ($\text{NaClO}_3 + \text{HCl} \rightleftharpoons \text{HClO}_3 + \text{NaCl}$) in 20 mL are effective media for the dissolution of pure gold-wire (99.95 %, ca. 20 mg, 0.25 mm diameter). The gold-wire dissolution is much more enhanced by HBr than HCl in NaClO_3 solution. At 0.50 mol dm^{-3} NaClO_3 , for instance, $\log(k/\text{s}^{-1})$ values are -5.11 and -3.40 (ca. 50-fold increase) for 1.0 mol dm^{-3} HCl and HBr, respectively, where “pseudo” first-order dissolution rate constants (k/s^{-1}) have been evaluated by the changes in the mass of gold-wire. In HClO_3 solution containing abundant halide ions ($X^- = \text{Cl}^-, \text{Br}^-$), the Au metal should be oxidized mainly by X_2 to be AuX_4 , where X_2 is produced by the oxidizing power from HClO_3 , just as dilute HNO_3 (< 2 mol dm^{-3}) containing abundant NaCl. In NaBrO_3 solution, however, HBr does not acquire any superiority to HCl in the gold dissolution. In NaIO_3 solution, the effect of HX at the lower concentrations (< 0.03 mol dm^{-3}) of NaIO_3 increases in the order of $\text{HCl} < \text{HBr} < \text{HI}$. The gold dissolution in hypochlorous acid (HClO) containing halide ions has been also examined as the reference. A new diagram has been proposed in order to verify that even the conjugate anion (ClO_3^- or NO_3^-) from a strong acid (HClO_3 or HNO_3) is subject to be protonated in the “aqueous solution” modified by electrolytes of very high concentrations ($> \sim 5$ mol dm^{-3}).

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1. Introduction

Gold is very stable, as indicated by its lack of reactivity in air and in the majority of aqueous solutions, including strong acids. Gold only dissolves in oxidizing solutions containing certain complexing ligands, for example, cyanide, halides, thiosulfate, thiourea, and thiocyanate [1]. The mixture of concentrated HNO_3 with HCl, *aqua regia* [2], is a well-known medium of dissolving gold and other precious metals, such as platinum and palladium. For a long time, many people have believed vaguely that gold dissolution in *aqua regia* is based on the evolution of NOCl and Cl_2 , i.e., $\text{HNO}_3 + 3 \text{HCl} \rightleftharpoons \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$. However, one has to recognize properly that the cue of gold dissolution in *aqua regia* is not only the strong oxidizing power from concentrated HNO_3 but also the complexing ability of Cl^- toward Au^{3+} to produce the AuCl_4^- species.

Cotton and Wilkinson [3] have noted that 0.1 mol dm^{-3} aqueous nitric acid is dissociated by about 93% and that the oxidizing power of nitric acid is very dependent on concentration, and below about 2 mol

dm^{-3} the acid has virtually no oxidizing power. The formation of NO_2^+ (the nitronium or nityl ion) is well established in 100% HNO_3 or $\text{HNO}_3\text{-H}_2\text{SO}_4$ [4,5]. However, we have managed to discover that even dilute HNO_3 (< 2 mol dm^{-3}) as well as concentrated HNO_3 can exhibit strong oxidizing power in bulk solution [6] and reversed micellar systems [6,7], providing concentrated salts are present. The origin of the strong oxidizing power from the dilute HNO_3 (< 2 mol dm^{-3}) has been demonstrated to be also NO_2^+ , which should be generated from un-dissociated HNO_3 molecules in such “modified” media [6,7].

Once observing the strong oxidizing power from dilute nitric acid containing abundant foreign salts, it is an easy task for us to apply such media for dissolving gold instead of *aqua regia*. Gold and platinum have been dissolved successfully in dilute HNO_3 (< 2 mol dm^{-3}) containing halide salts and even in seawater [8,9].

Nitrous acid (HNO_2) solutions containing halide ions ($X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) have been found to be also good media for gold dissolution [9]. We have discussed that gold is oxidized mainly by the halogens (X_2) and, at the same time, the stable AuX_4^- complexes are formed in not only dilute HNO_3 but also HNO_2 solutions containing abundant halide ions. The halogens (X_2) are evolved from the halide ions through the strong oxidation power of NO_2^+ ($E^\circ = +1.51$ V) or NO^+ (the nitronium ion, $E^\circ = +1.45$ V) species in dilute HNO_3 or HNO_2 , respectively [4,9,10]. The oxidizing intermediate of NO_2^+ or NO^+

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should be generated from the molecules of HNO₃ or HNO₂ and not from the conjugate anion, NO₃⁻ or NO₂⁻, cf., Eqs. (1) and (2).



Even though dilute HNO₃ is a strong acid ($pK_a = -1.34$) [11], we have insisted that the complete dissociation of HNO₃ should be suppressed and the molecules of HNO₃ are present [6–9] in “aqueous solution” modified by the added electrolytes of high concentrations [12], in common words, at very high ionic strength.

Incidentally, we have proposed a new mechanism for S_N1 (R-X) solvolysis reactions in binary mixed solvents between water and organic solvents containing alkali metal (M⁺) and alkaline earth metal (M²⁺) perchlorates [13–18]. In such media, promoted formation of carbocations takes place through direct chemical interaction between M⁺ or M²⁺ and the leaving anion (X⁻) from the substrate. We would like to discuss of the relation between “modified” aqueous solution and high ionic strength in the final section (3–7) of the present paper.

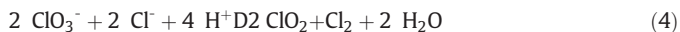
As for oxyacids of chlorine, the acid strength increases in the order of HClO < HClO₂ < HClO₃ < HClO₄, however, oxidizing power decreases in the order of HClO > HClO₂ > HClO₃ > HClO₄ [19]. The pK_a values of the acids are reported to be 7.53, 1.95, -2.7, and -7.3 for HClO, HClO₂, HClO₃, and HClO₄, respectively [11]. Pascal and Favier [20] have mentioned that very weak basicity of ClO₄⁻ is correlated to the very strong acidity of HClO₄ ($pK_a = -18$) (J. Potier, private communication). Perchloric acid may be too strong to evaluate its accurate dissociation constant, and actually exhibits no oxidizing power in aqueous solution under ambient conditions. Moeller [19] has mentioned about the oxidizing powers more generally “if reduction to the free halogen is considered, oxidizing power decreases with increase in oxidation number of the halogen for chlorine, bromine, or iodine.” Douglas et al. [21] have noted of the oxidation ability of HClO₄ as follows: “Hot concentrated perchloric acid is an extremely explosive oxidizing agent. Cold dilute HClO₄ does not even oxidize I⁻. The E°_{cell} is very favorable, but the reaction is slow. Reactions involving atom transfer, commonly involved for oxoanions, are often slow.”

In order to acquire the spontaneous and strong oxidation ability, in our opinion, protonation is essential for an oxoanion (oxyanion), such as ClO⁻ or ClO₄⁻ (even the conjugate base anion from a strong acid). This is a very simple theory and independent from the formal oxidation state of the central element from +1 to +7 (ClO⁻ to ClO₄⁻). Hypochlorous acid ($pK_a = 7.53$) [11] is so weak that the conjugate ClO⁻ ion is easily protonated, then, the molecule of HO-Cl may catch another proton to release a H₂O molecule [cf. Eq. (3)] at low pH. The intermediate species of Cl⁺ can take two electrons of other species.



Alternatively, the combination of two molecules of HClO can produce Cl⁺ and ClO⁻, releasing H₂O. On the other hand, the protonation of ClO₄⁻ is quite difficult or almost impossible in dilute aqueous solution. In order to force the ClO₄⁻ ion to accept a proton, more or less, the alternation of bulk water conditions to “dihydrogen ether” [12,13,15] conditions, in our term, should be essential.

Chloric acid is a strong or fairly strong acid ($pK_a = -2.7$) [11]. It is well known that concentrated HClO₃ possesses strong oxidizing power, as the concentrate HNO₃ does. The mixture between concentrated HClO₃ and HCl evolves ClO₂ and Cl₂ [cf. Eq. (4)] although dilute HClO₃ solution is mere a strong acid and should exhibit no oxidizing power.



Sant’Anna et al. [22] have noted that chlorine dioxide (ClO₂) is still widely used as an oxidizing species such as pulp and textile bleaching,

and because of its disinfectant properties in water purification and treatment of industrial wastes. Indeed, the chlorate chemistry is much less understood than the chlorite and chlorine dioxide chemistry.

The oxidation of halide ions by halates (XO₃) in acidic solutions has been studied for a long time [23–25]. Hong et al. [26] have studied the kinetics and mechanism of the chloride-ClO₃ reaction in H₂SO₄ of higher concentrations and proposed a mechanism involved HClO₂ and HClO.

Recently, Sant’Anna et al. [22] have proposed a mechanism for chlorate-chloride system containing strong acids, in which, chlorate and chloride form the intermediate Cl₂O₃²⁻ and, then, protonation of the species follows. Similar intermediate species (BrOClO₂⁻) and its protonation have been proposed for the chlorate and bromide system in strong acid and high ionic strength media [27]. As the reaction intermediate, however, Villata et al. [28,29] have proposed not only the formation of chloric acid (HClO₃) but also the protonated chloric acid (H₂ClO₃⁺) in chlorate-bromide or iodide in ionic strength of 3.0 mol dm⁻³ solution containing Mo^v as the catalyst. Galajda et al. [30] have reported photochemically induced autocatalysis in the chlorate ion-I₂ system. Kinetic studies of the bromate-bromide [31–33] and iodate-iodide reactions [34,35] have been reported.

In the present paper, the pure gold dissolution is explored in (dilute) haloic acid (HXO₃, X = Cl, Br, I) media containing halide ions. The gold dissolution in hypochlorous acid (HClO) containing halide ions is also examined as a reference. The alternation of bulk water properties with the addition of abundant electrolytes is discussed in order to verify that even the conjugate anion (NO₃⁻ or ClO₃⁻) from a strong acid (HNO₃ or HClO₃) is somehow protonated in the “aqueous media” modified by electrolytes of very high concentrations.

2. Experimental section

The sample of pure gold was commercially available: gold wire (Nilaco, 99.95%, 0.25 mm diameter). Commercially available salts were used as received: LiClO₄ (> 98%), NaClO₃ (> 98%), NaBrO₃ (> 99.5%), NaIO₃ (> 99.5%), KClO₃ (> 99.5%), NaI (> 99.5%), and Na(ClO) 5H₂O (available chlorine > 39%) from Wako Pure Chemical Industries; Ca(ClO)₂ (available chlorine 65%) and Mg(ClO₄)₂ (ACS reagent) from Aldrich. Nitric acid (60% JIS S), HCl (5.0 mol dm⁻³), HBr, and HClO₄ (60–62% JIS S grade), were purchased from Wako. The HI solutions were prepared by mixing HClO₄ and NaI solutions. Ethanol, 1-propanol, 2-propanol, *t*-butyl alcohol, and acetone of GR grades were also purchased from Wako. Pure water purified by a MilliQ System was used (< 0.1 μS cm⁻¹).

Chloric or bromic acid solutions containing halide ions were prepared by mixing NaClO₃ or NaBrO₃, respectively, with HX (X = Cl, Br) solutions. Iodic acid solutions containing halide ions were also prepared from NaIO₃, mixing with HX (X = Cl, Br, and I) solutions. A gold sample of 19.7 ± 0.5 mg (i.e. 5.0 × 10⁻³ mol dm⁻¹) in a 20 mL volumetric flask was kept at the constant temperature of 60 (± 0.1) °C in a Yamato shaking incubator, model BT100, being shaken 60 times in a minute. The changes in mass of a piece of gold-wire (ca. 20 mg) were measured by a Mettler Toledo electronic analytical scale, model AB204-S. Before the dissolution, the pieces of gold-wire were rinsed with acetone and were air-dried on dried sheets of the KimWipes paper. After the partial dissolution, the pieces were washed with pure water and rinsed with acetone. The “pseudo” first-order dissolution rate constants (k/s^{-1}) were evaluated from the slope of ln [S] vs. *t*, with the correlation coefficients of more than 0.98, where [S] represents the relative mass (m_t/m_0) of gold remains at a certain time.

3. Results and Discussion

3.1. Gold-wire dissolution in HClO₃ containing chloride and bromide ions

Fig. 1(a) shows the effective dissolution of gold-wire in mixtures of various ratios between sodium chlorate and hydrochloric acid, which

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