Ultrasonics - Sonochemistry 41 (2018) 397–403

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Sonochemistry of aqueous $NaAuCl_4$ solutions with C3–C6 alcohols under a noble gas atmosphere

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ARTICLE INFO

Keywords:
Ultrasonic cavitation
Au(III) reduction
Alcohol degradation
Gaseous product
Noble gas
Bubble interface region

ABSTRACT

The effect of the type of C3–C6 alcohol, solution temperature, and dissolved gas on the rate of Au(III) reduction was investigated in $NaAuCl_4$ aqueous alcohol solution with a 200-kHz ultrasound irradiation system. It was confirmed in the presence of C3–C6 alcohol that more highly hydrophobic alcohols more effectively accumulated at the argon bubble interface region, and the reducing radicals formed here. To avoid changes in the bubble temperature during collapsing bubble, the effects of the solution temperature on the rate of Au(III) reduction and on the rate of formation of the gaseous compounds (CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6) were investigated in the presence of low concentration (1.0-mM) of 1-hexanol. Both of the rates showed a good relationship with the gas solubility: the amount of dissolved gas at different solution temperatures affected the number of high-temperature bubbles formed. The changes in the concentrations of the gaseous compounds formed from 1-hexanol degradation suggested that CO and the pyrolysis radicals acted as reductants. Finally, the effect of the type of dissolved gas was investigated in the presence of 1.0-mM Au(III) and 1.0-mM 1-hexanol. The rates of 1-hexanol degradation, Au(III) reduction, and gaseous compound formation increased in the order He < Ne < Ar < Kr < Xe, and this order was related to the amount of noble gas dissolved in the aqueous solution.

1. Introduction

Sonochemistry is a possible approach to the efficient production of reducing radicals, which can be used to reduce metal ions and form size- and shape-controlled metal nanoparticles [1–11]. It has been proposed that the sonochemical reduction of Au(III) in aqueous alcohol solution under a noble gas atmosphere proceeds as follows [1–4]:

$$H_2O \rightarrow {}^{\cdot}H + {}^{\cdot}OH \tag{1}$$

$$RHOH + {}^{\cdot}OH({}^{\cdot}H) \rightarrow {}^{\cdot}R_{ab} + H_2O(H_2) \tag{2}$$

$$RHOH \rightarrow {}^{\cdot}R_{py} \tag{3}$$

$$Au(III) + 3\,{}^{\cdot}R \rightarrow Au(0) + 3H^+ \tag{4}$$

where RHOH is the alcohol, ${}^{\cdot}R_{ab}$ are secondary radicals, ${}^{\cdot}R_{py}$ are pyrolysis radicals, and ${}^{\cdot}R$ is an abbreviation for unspecified radicals. The primary radicals, ${}^{\cdot}H$ and ${}^{\cdot}OH$, are formed by sonolysis of water [reaction (1)]. These primary radicals can abstract a H atom from RHOH to produce secondary radicals, ${}^{\cdot}R_{ab}$, as seen in reaction (2). Pyrolysis radicals, ${}^{\cdot}R_{py}$, are formed by pyrolysis of RHOH inside and at the interface region of high temperature bubbles [reaction (3)]. These radicals, abbreviated as ${}^{\cdot}R$, then reduce Au(III) to Au(0) as seen in reaction (4). Yeung et al. [1] and Nagata et al. [2] reported that the sonochemical reduction of Au(III) in aqueous alcohol solution occurred under Ar and that the Au(III) reduction rate was enhanced by the addition of alcohols with higher hydrophobicity. A suggested reason for this rate increase was because the amounts of ${}^{\cdot}R_{ab}$ and ${}^{\cdot}R_{py}$ formed were larger than the amount of ${}^{\cdot}H$ formed in the sonolysis of water. Later, Caruso et al. reported that the surface excess of an alcohol additive could be correlated with the Au(III) reduction rate during sonication because the surface excess was related to the number of alcohol molecules at the bubble interface [4]. It has also been reported that various types of ${}^{\cdot}R_{ab}$ and ${}^{\cdot}R_{py}$ are formed during sonolysis of organic compounds, such as surfactants, and that the reactivity of ${}^{\cdot}R_{ab}$ and ${}^{\cdot}R_{py}$ depends on the type of metal ion of Pt(IV), Pt(II), Au(III), Pd(II), Ag(I), and MnO_4^- [5–8]. Okitsu et al. reported that the sonochemical reduction of MnO_4^- in aqueous alcohol solution proceeded more effectively through reactions with ${}^{\cdot}R_{py}$ than those with ${}^{\cdot}R_{ab}$, although these radicals could not reduce MnO_2 [8].

As described above, both the alcohol additive and the organic

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http://dx.doi.org/10.1016/j.ultsonch.2017.09.040
Received 17 August 2017; Received in revised form 22 September 2017; Accepted 22 September 2017
Available online 23 September 2017
1350-4177/

additive act as precursors for the sonochemical formation of reductants in aqueous solution, and the concentration and the type of the additives thus determine the rate of reduction of the metal ions and the characteristics of the metal nanoparticles formed. Although there are a number of reports on the sonochemical reduction of metal ions and the sonochemical formation of metal nanoparticles, the rate of degradation of the organic additive and the rate of formation of its degradation products have not been investigated in detail. In this study, we therefore investigated the sonochemical reactions of aqueous $NaAuCl_4$ solutions that contain C3–C6 alcohols under a noble gas atmosphere. The rate of degradation of the alcohol additive and the rate of formation of the gaseous compounds were analyzed in comparison with the rate of reduction of Au(III). On the basis of our results, we discuss the alcohol degradation and Au(III) reduction mechanisms in detail. In addition, the temperature at the interface region of the collapsing bubbles was estimated from the sonolysis of a dilute aqueous 1-hexanol solution and the chemical reactions at the interface region of the collapsing bubbles are discussed.

2. Experimental section

Reagent-grade $NaAuCl_4$, 1-propanol, *t*-butanol, 1-butanol, 1-pentanol and 1-hexanol, potassium iodide, sodium hydroxide, ammonium molybdate tetrahydrate, and potassium hydrogen phthalate were supplied by Wako Pure Chemical Industries, Ltd. (Japan) and used as received. All solutions were prepared with water purified using a Millipore Milli-Q system.

Ultrasonic irradiation was performed using a 65-mm-diameter oscillator (Kaijo, Lot. No. 19G9, Japan) and a 200-kHz ultrasonic generator (4021-type, 200 W; Kaijo, Lot. No. 37G4, Japan). The chemical efficiency of acoustic cavitation depended on the conditions of the ultrasound irradiation system so that the chemical efficiency was the indicator to understand the real conditions of the used ultrasound irradiation system. A gas-saturated 1.0-mM Au(III) aqueous solution (60 mL) was irradiated in a water bath, which was maintained at constant temperature using a cold water circulation system (Taitec CL-150R, Japan). The vessel was mounted at a fixed position (4.0 mm from the oscillator). The reaction vessel was closed during irradiation to exclude air. To investigate the effect of alcohol on the sonochemical reactions, pure alcohol or aqueous alcohol solution was injected into the sample solution through a silicone rubber septum using a microsyringe after gas bubbling and then the sample solution was irradiated.

After irradiation, the solution was sampled through the septum using a syringe and then analyzed. The concentrations of Au(III) and H_2O_2 were measured by the appropriate colorimetric methods [3,12], where the absorption spectra of the sample solutions were recorded using a UV–visible spectrophotometer (Hitachi U-3300, Japan). The initial Au(III) reduction rate was measured to analyze the Au(III) reduction rate. To analyze the gaseous products, namely, CH_4, C_2H_6, C_2H_4, C_2H_2, CO, and CO_2, the reaction vessel was maintained at room temperature (approximately 20 °C) for about 1.5 h after 15 min of sonication to allow the gaseous products to reach equilibrium. After equilibrium was attained, the gaseous products were sampled and analyzed by gas chromatography (GC-FID and GC-TCD). For comparison, similar experiments were performed for aqueous alcohol solutions that did not contain Au(III). The temperature at the interface region of the collapsing bubbles was analyzed by a modified methyl radical recombination method with 1-hexanol, although methane [13] and *t*-butanol [14–16] have been used as precursors for methyl radicals. The concentration of 1-hexanol was measured by gas chromatography (GC-FID), for which 1-heptanol was used as an internal standard. The concentration of the gaseous products in gas phase was converted to a concentration of the irradiated solution.

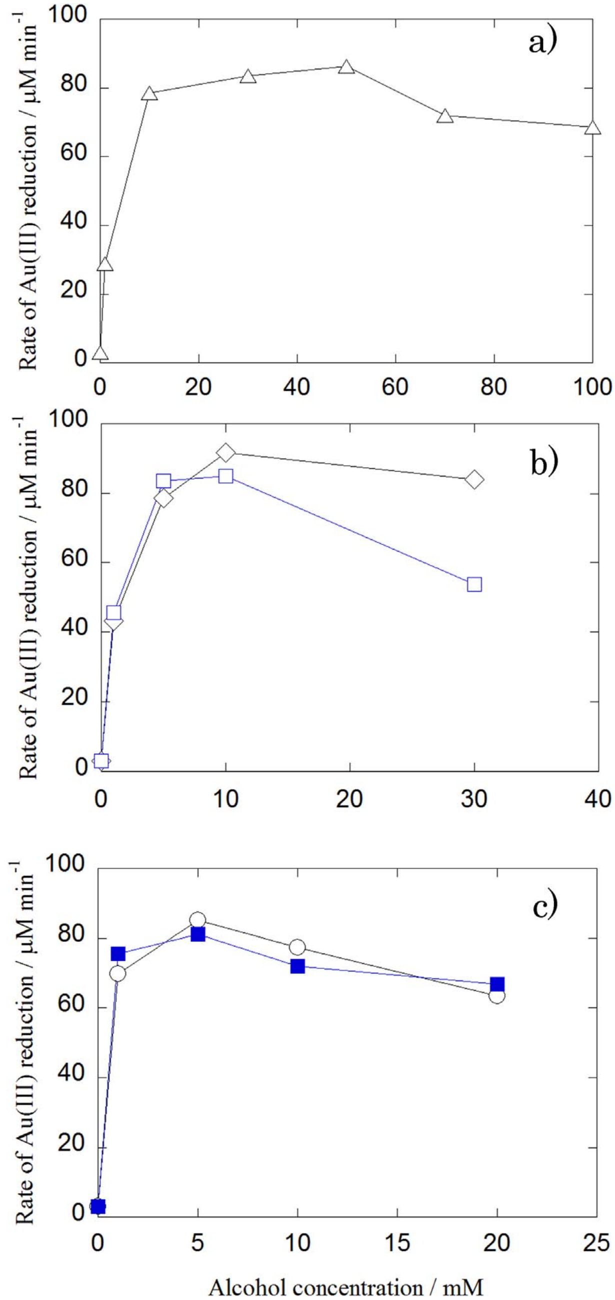

Fig. 1. Rates of Au(III) reduction as a function of alcohol concentration. (a) (△); 1-propanol, (b) (□); 1-butanol, (◇); *t*-butanol, (c) (○): 1-pentanol, (■): 1-hexanol. Condition: 1.0-mM $NaAuCl_4$, Ar atmosphere, 20 °C.

3. Results and discussion

3.1. Effect of the type and concentration of alcohol on the Au(III) reduction rate

A 1.0-mM Au(III) solution was irradiated under Ar at 20 °C. Fig. S1 shows the typical result for the changes in Au(III) concentration with sonication time in the absence and presence of *t*-butanol (10 mM). Fig. 1a–c shows the effect of the type and concentration of alcohol on the Au(III) reduction rate. For all aqueous alcohol solutions, the Au(III) reduction rate first increased with increasing alcohol concentration to a maximum value, and then decreased at higher alcohol concentrations. On the basis of reactions (1)–(4), the results shown in Fig. 1 can be explained as follows: the rate of reduction increases with increasing alcohol concentration because of the increasing amounts of $^{\cdot}R_{ab}$ and