Efficient photochemical recovery of rhenium from aqueous solutions

Hisao Hori [a,*], Yuta Yoshimura [a], Takafumi Otsu [a], Kotomi Kume [a], Yuki Mitsumori [a], Shuzo Kutsuna [b], Kazuhide Koike [b]

[a] Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan
[b] National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan

A B S T R A C T

Recovery of rhenium from aqueous solutions by photoinduced-electron transfer from an electron donor to excited-state ReO_4^- is reported for the first time. Specifically, irradiation of aqueous ReO_4^- in the presence of 2-propanol as the electron donor efficiently decreased the ReO_4^- concentration in the solution and resulted in formation of a precipitate consisting of amorphous ReO_2 and ReO_3 and formation of acetone by oxidation of 2-propanol. After 19 h of irradiation, ReO_4^- had completely disappeared, and 89.1% of the initial rhenium content was recovered in the collected precipitate. Although an induction period prior to the decrease in the ReO_4^- concentration was observed, the induction period could be eliminated by introduction of acetone to the reaction system, which afforded 94.7% recovery of rhenium within 6 h of irradiation. The acceleration of the reaction induced by acetone could be explained by an increase in the light absorption of ReO_4^- via precomplexation with acetone, which resulted in an increase in the emission intensity from the excited rhenium species.

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1. Introduction

Rhenium, which is a minor metal in the Earth's crust and has a high melting point (3180 °C, second only to that of tungsten), has vital applications in industry. Rhenium used in superalloys for turbine blades for aircraft and thermal power plants accounts for 70% of total rhenium consumption, and rhenium in petroleum reforming catalysts for the production of lead-free high-octane gasoline accounts for 20% [1]. The rest is used in electronic parts such as electrical contacts, electron targets, and heating elements. The utility of rhenium for these applications arises from its high heat resistance, high corrosion resistance, and high hardness [2]. In addition, some rhenium compounds have unique catalytic activities: for example, rhenium oxides catalyze the selective oxidation of methanol to methylal (dimethoxymethane) [3], and rhenium diimine complexes catalyze CO_2 reduction to CO under visible-light irradiation [4]. Increases in aircraft production (approximately 36,770 new airplanes will be built from 2014 to 2033, owing to mainly the rapid growth of low-cost carriers [5]) and new applications of rhenium can be expected to increase the global demand for this metal.

Molybdenum and copper ores are the sole economically viable mineral sources of rhenium, which is obtained as a by-product of the metallurgical processing of these ores; specifically, the rhenium component is oxidized to volatile Re_2O_7 in the flue dusts and then collected in aqueous solution in the form of perrhenate ion (ReO_4^-) [6–10]. In addition, during processing of secondary raw materials (spent catalysts and alloys), the rhenium content is also transformed into ReO_4^- in aqueous solutions [7,11–13]. The recovery of ReO_4^- from aqueous solutions is difficult because of its low concentration and high solubility at all pH values. Reported techniques for effectively recovering rhenium (present as ReO_4^-) from aqueous solutions include adsorption on ion exchange resins [7,9,13,14], solvent extraction with amines [15–17], precipitation through the formation of a less-water-soluble zinc complex [12], adsorption on activated carbon [18], and adsorption on biomaterials such as algae [19]. Among these techniques, ion exchange and solvent extraction have been extensively studied and have been introduced in real-world industrial processes [10,16]. However, these techniques require additional steps to separate the collected ReO_4^- from resins or solvent, as well as recrystallization to precipitate a salt (typically NH_4ReO_4, generated by addition of NH_4OH), and the mother liquor generally contains a non-negligible amount of ReO_4^- (4–35 g/L as NH_4ReO_4) [12]. Finally, the collected precipitate is heated at 700–800 °C in the presence of hydrogen gas to produce metallic rhenium.
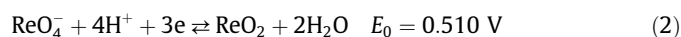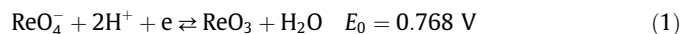
The emission of light from the excited state of ReO_4^- has never been reported, although the anion is known to have an absorption maximum around 249 nm in water [20], and emissions from

* Corresponding author.
E-mail address: h-hori@kanagawa-u.ac.jp (H. Hori).

tetravalent $ReCl_6^{2-}$ and $ReBr_6^{2-}$ have been reported [21]. We speculated that if aqueous ReO_4^- could emit with a lifetime at least on the order of nanoseconds, photoinduced electron transfer from an electron donor to the excited state of the anion might result in the formation and precipitate of an insoluble reduced rhenium species (such as ReO_3), which could easily be separated from the aqueous solution (Scheme 1).

Such a reaction scheme would eliminate the need for further separation and recrystallization steps. With this idea in mind, we investigated the photochemical reactions of ReO_4^- in the presence of several electron donors. The overall reduction reactions of ReO_4^- may be represented by Eqs. (1) and (2) (E_0: standard reduction potentials) [22], if the products are ReO_3 and ReO_2.

$$ReO_4^- + 2H^+ + e \rightleftarrows ReO_3 + H_2O \quad E_0 = 0.768 \text{ V} \quad (1)$$

$$ReO_4^- + 4H^+ + 3e \rightleftarrows ReO_2 + 2H_2O \quad E_0 = 0.510 \text{ V} \quad (2)$$

Herein, we report an effective method for photochemical recovery of rhenium from aqueous solutions of ReO_4^-, although the optimum scheme ended up being somewhat different from the scheme that we initially envisioned.

2. Experimental

2.1. Materials

Potassium perrhenate (99.99%) and rhenium (IV) oxide (ReO_2, 99.7%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Other reagents were obtained from Wako Pure Chemical Industries (Osaka, Japan). Argon (99.99%) was purchased from Taiyo Nippon Sanso (Tokyo, Japan).

2.2. Photochemical procedures

A cylindrical Pyrex photochemical cell (22-mL volume) equipped with a quartz window and a rubber septum was used for the photochemical reactions. The ionic strength of the reaction solution was maintained by the addition of $NaClO_4$. In a typical run with 2-propanol as the electron donor, the cell was charged with an aqueous solution (10 mL) containing ReO_4^- (103.7 μmol; 10.37 mM, as the potassium salt), 2-propanol (0.50 M), $NaClO_4$ (0.10 M) and a poly(tetrafluoroethylene) stir bar. The pH of the solution was 5.2. The solution was saturated with argon gas, and the cell was sealed with a rubber septum, placed in a water bath, and irradiated with UV–visible light (220–460 nm) from a 200 W xenon–mercury lamp (L2001-01L; San-Ei Electric, Osaka, Japan) while stirring. The light from the lamp was introduced into an optical-quartz glass fiber, passed to a quartz cell containing pure water to cut the infrared light, and then introduced into the cell.
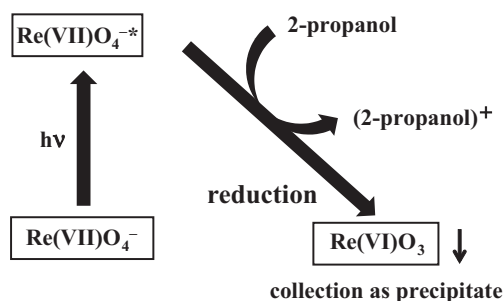
The irradiance at the center of the light spot on the sample was 98 mW cm^{-2}, as measured with a UV detector (UVD-S254, Ushio, Tokyo, Japan; sensitive wavelength, 220–310 nm). The reaction temperature was kept constant at 20 °C. After a specified time passed, the cell was placed in an argon-filled globe bag and opened, and the reaction mixture was centrifuged to separate the reaction solution and the precipitate. The supernatant was subjected to ion chromatography, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and headspace gas chromatography–mass spectrometry (GC/MS). The collected precipitate was washed with pure (Milli-Q) water under an argon atmosphere, dried under vacuum overnight, and subjected to X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy, and ICP-AES. The XRD, XPS, and transmission electron microscopy measurements were performed in the absence of air whenever possible.

2.3. Analysis

The ReO_4^- concentrations in the reaction solutions were quantified with an ion-chromatography system (IC-2001, Tosoh, Tokyo, Japan) consisting of an automatic sample injector (30-μL injection volume), a degasser, a pump, a separation column (TSKgel IC-Anion-PW$_{XL}$, 4.6 mm i.d., 3.5-cm length, Tosoh), a column oven (40 °C), and a conductivity detector equipped with a suppressor device. The mobile phase was an aqueous solution containing $NaHCO_3$ (1.7 mM), Na_2CO_3 (1.8 mM), and acetonitrile (20 vol.%); and the flow rate was 0.8 mL min^{-1}. The detection limit for ReO_4^- was 78 μg L^{-1}, calculated from a signal-to-noise ratio of 3. The total rhenium concentrations in the reaction solutions were quantified by ICP-AES (SPS-3500, SII Nanotechnology, Tokyo, Japan).

To elucidate the fate of 2-propanol, we analyzed the reaction solutions with a headspace GC/MS system consisting of an automatic headspace sampler (HP7694, Agilent Technologies, Palo Alto, CA, USA) and a GC/MS instrument (GC6890N, Agilent) equipped with a fused-silica capillary column (PoraBOND-Q, Agilent). The carrier gas was helium, and the flow rate was 1.0 mL min^{-1}. The sample solution was heated at 80 °C for 1 h in the headspace sampler, and an aliquot of the gas phase (1.0 mL) was introduced into the GC/MS system in split mode (ratio, 30/1). The oven temperature was kept at 50 °C for 2 min, raised to 200 °C at a rate of 10 °C min^{-1}, and held at that temperature for 5 min. Analyses were conducted in full-scan mode (m/z 10–100).

Scheme 1. Postulated reaction scheme for photochemical recovery of rhenium from aqueous solution.
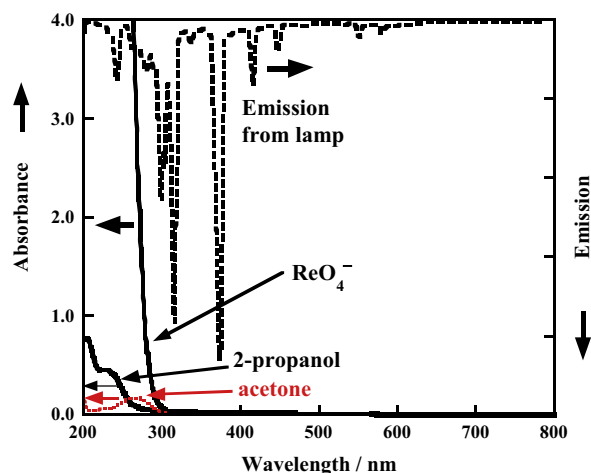

Fig. 1. Wavelength distribution for the absorptions of ReO_4^- (10.37 mM in water), 2-propanol (0.50 M in water) and acetone (9.0 mM in water) and the emission from the xenon–mercury lamp. The path length for the measurement of the absorption spectra was 1.0 cm. Effect of acetone on the reaction is discussed in Section 3.5.