



# Mechanism of sonochemical reduction of permanganate to manganese dioxide in aqueous alcohol solutions: Reactivities of reducing species formed by alcohol sonolysis



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## ABSTRACT

The sonochemical reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  in aqueous solutions was investigated as a function of alcohol concentration under Ar. The rate of  $\text{MnO}_4^-$  reduction initially decreased with increasing alcohol concentration, and then increased when the alcohol concentration was increased further. The concentrations at which the reduction rates were minimum depended on the hydrophobic properties of the added alcohols under ultrasonic irradiation. At low concentrations, the alcohols acted as OH radical scavengers; at high concentrations, they acted as reductant precursors:  $\cdot\text{R}_{\text{ab}}$ , formed by abstraction reactions of the alcohols with sonochemically formed OH radicals or H atoms, and  $\cdot\text{R}_{\text{py}}$ , formed by alcohol pyrolysis under ultrasonic irradiation. The results suggest that the reactivity order of the sonochemically formed reducing species with  $\text{MnO}_4^-$  at pH 7–9 is the sum of  $\text{H}_2\text{O}_2$  and  $\cdot\text{H} > \cdot\text{R}_{\text{py}} > \cdot\text{R}_{\text{ab}}$ . The peak wavelengths of  $\text{MnO}_2$  colloidal solutions formed at high 1-butanol concentrations shifted to shorter wavelengths, suggesting the formation of small particles at high 1-butanol concentrations. The rates of sonochemical reduction of  $\text{MnO}_2$  to  $\text{Mn}^{2+}$  in the presence of 1-butanol were slower than that in the absence of 1-butanol, because the sonochemical formation of  $\text{H}_2\text{O}_2$  and  $\cdot\text{H}$ , which act as reductants, was suppressed by 1-butanol in aqueous solutions.

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## 1. Introduction

Manganese oxides are widely used as electrochemical capacitors [1–5], catalysts [6–8], sensors [9–11], and adsorbents [12,13]. The size and shape of the  $\text{MnO}_2$  nanoparticles and their crystal structures strongly influence their physicochemical properties. Various synthetic methods such as controlled chemical reactions [13,14], hydrothermal reactions [6,8], and  $\gamma$ -ray irradiation [15,16] have been developed for controlling the properties of  $\text{MnO}_2$ . Recently, sonochemical reduction and ultrasound-assisted techniques have been used to synthesize shape- and structure-controlled  $\text{MnO}_2$  nanoparticles for use as catalytic electrodes in electrochemical capacitors [1,2,17,18].

Control of the rate of reduction of metal ions is an important subject, because the rate of reduction affects nucleation and growth during the formation of metal nanoparticles [19–21]. Previous studies have shown that the rates of sonochemical reduction of  $\text{Ag(I)}$ ,  $\text{Pd(II)}$ ,  $\text{Au(III)}$ ,  $\text{Pt(II)}$ , and  $\text{Pt(IV)}$  are strongly dependent on the

types and concentrations of organic additives such as alcohols, surfactants, and water-soluble polymers, because such organic additives act as the precursors of reducing radicals under the extremely high temperature and pressure conditions produced during cavitation bubble collapse [19–33]. There are three reduction pathways via three types of reducing radical under sonication in the absence and presence of organic additives: reduction pathway 1 is reduction by primary reducing radicals, i.e., H atoms, formed from water sonolysis; reduction pathway 2 is reduction by secondary reducing radicals,  $\cdot\text{R}_{\text{ab}}$ , which are formed by H abstraction from organic additives by OH radicals and H atoms formed by water sonolysis; and reduction pathway 3 is reduction by reducing radicals,  $\cdot\text{R}_{\text{py}}$ , which are formed by pyrolysis of organic additives. It has been suggested that in the presence of organic additives, the sonochemical reductions of  $\text{Ag(I)}$  to  $\text{Ag(0)}$  and  $\text{Pt(II)}$  to  $\text{Pt(0)}$  mainly proceed via reduction by  $\cdot\text{R}_{\text{ab}}$ , and the sonochemical reductions of  $\text{Au(III)}$  to  $\text{Au(0)}$ ,  $\text{Pd(II)}$  to  $\text{Pd(0)}$ , and  $\text{Pt(IV)}$  to  $\text{Pt(II)}$  mainly proceed via reduction by  $\cdot\text{R}_{\text{py}}$  [22,24–26,31]. Recently, Dharmarathne et al. reported the reaction of ferricyanide and methyl viologen with organic radicals formed in the sonolysis of alcohols in aqueous solutions [32]. They suggested that  $\cdot\text{R}_{\text{py}}$  is more

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effective than  $R_{ab}$  for the reduction of ferricyanide at high alcohol concentrations. Although some researchers have investigated the sonochemical reduction mechanism, the characteristics of the reducing radicals formed in the sonolysis of organic additives in aqueous solutions are still unclear.

Recently, Okitsu et al. and Abulizi et al. reported the sonochemical reduction of  $MnO_4^-$  in water. They found that the sonochemically formed  $H_2O_2$  affected the rates of reduction of  $MnO_4^-$  to  $MnO_2$  and  $MnO_2$  to  $Mn^{2+}$ , because  $H_2O_2$  acted as a reductant for both  $MnO_4^-$  and  $MnO_2$  [34,35]. Abulizi et al. found that nanostructured  $\delta$ - $MnO_2$  was formed in water and the  $\delta$ - $MnO_2$  morphology changed from aggregated sheet-like or needle-like structures to spherical, cubic, or polyhedral nanoparticles when the solution pH was increased from 2.2 to 9.3 [35]. These papers focus on the discussion for the reaction of the sonochemically formed  $H_2O_2$  with  $MnO_4^-$  or  $MnO_2$ . In this study, we investigated the sonochemical reduction of  $MnO_4^-$  or  $MnO_2$  as a function of alcohol concentration and investigated the characteristics of the sonochemically formed  $\cdot R_{py}$ ,  $\cdot R_{ab}$  and  $\cdot H$ . UV/visible spectroscopy was used to examine the properties of the formed  $MnO_2$  particles. We identified an unusual phenomenon that helps to explain the roles and characteristics of reducing radicals formed in the sonolysis of aqueous alcohol solutions.

## 2. Experimental section

Reagent-grade  $KMnO_4$ , ethanol, 1-propanol, 1-butanol, 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 $\phi$  oscillator (Kaijo; Lot. No. 19p29, Japan) and a 200 kHz ultrasonic generator (Kaijo 4021 type, 200 W; Lot. No. 1033, Japan). Details of the irradiation set-up and the characteristics of the reaction vessel are given elsewhere [20]. An Ar-saturated aqueous solution (60 mL) containing 0.10 mM  $KMnO_4$  was irradiated in a water bath, which was maintained at 20 °C 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. The effects of alcohol on the sonochemical reactions were investigated by injecting pure alcohol or aqueous alcohol solution into the sample solution through a silicone rubber septum using a microsyringe, after Ar bubbling. After irradiation, the solution was sampled through the septum using a syringe, and then placed in a vial.

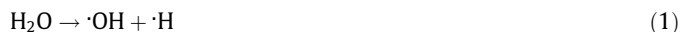
The absorption spectra of the irradiated solutions were recorded using UV–visible spectrophotometers (Shimadzu UV-2550 or UV-2100, Japan), and the apparent rates of  $MnO_4^-$  reduction during ultrasonic irradiation were determined. The apparent concentrations of  $H_2O_2$  formed during the sonolysis of pure water and aqueous alcohol solutions were determined using the KI colorimetric method [36]. The apparent rate of  $H_2O_2$  formation during ultrasonic irradiation was determined from the slope that was obtained from the change in  $H_2O_2$  concentration as a function of irradiation time. The pH of the sample solution was measured using a pH meter (Horiba B-112, Japan). The formed  $MnO_2$  colloidal solutions were characterized using UV–visible spectroscopy.

In a preliminary experiment, the rates of  $MnO_4^-$  reduction in 0.10 mM  $MnO_4^-$  in the absence of ultrasound were investigated in 10 mM ethanol, 1-propanol, and 1-butanol aqueous solutions at 20 °C. In the absence of ultrasound, the rates of  $MnO_4^-$  reduction were too slow to determine within a reaction time of several hours.

## 3. Results and discussion

### 3.1. Sonochemical reduction of $MnO_4^-$ in absence and presence of alcohols

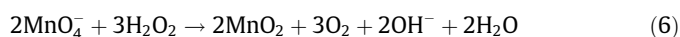
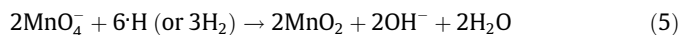
It has been suggested that the following reaction occurs [36] when an aqueous solution is irradiated under Ar:



The formation of OH radicals and H atoms occurs via pyrolysis of water molecules, because the temperature in acoustic cavitation bubbles reaches extremely high temperatures during bubble collapse. In pure water, OH radicals and H atoms recombine to form  $H_2O_2$ ,  $H_2$ , and  $H_2O$  [37–40]:



Okitsu et al. reported that the sonochemical reduction of  $MnO_4^-$  to  $MnO_2$  in pure water consists of reactions (5) and (6) [34]:



As a result, the pH of the solution increases as reduction of  $MnO_4^-$  to  $MnO_2$  proceeds [34]. Abulizi et al. recently reported that the rate of  $MnO_4^-$  reduction with  $H_2$  is negligibly slow at room temperature [35]; therefore, H atoms and  $H_2O_2$  are considered to be the main reductants for  $MnO_4^-$ .

In this study, we investigated the sonochemical reductions of  $MnO_4^-$  to  $MnO_2$  and  $MnO_2$  to  $Mn^{2+}$  in the presence of alcohols. Fig. 1 shows the changes in the absorption spectrum of a 0.10 mM  $MnO_4^-$  aqueous solution in the presence of 1.0 mM 1-butanol during ultrasonic irradiation under Ar. The color of the sample solution gradually changed from purple to pale yellow under ultrasonic irradiation. Fig. 1a shows that the absorption peaks of  $MnO_4^-$  located at around 480–580 nm gradually disappeared during ultrasonic irradiation, and a new broad peak at 364 nm emerged at 25 min of irradiation. However, the intensity of the new peak decreased after further irradiation, as shown in Fig. 1b. This phenomenon will be discussed in Section 3.4. Previous reports [14,34,35,41–43] suggest that this new peak can be attributed to the absorption of colloidal  $MnO_2$  particles. In Fig. 1a, two isosbestic points are present at 519 and 576 nm. In general, an isosbestic point is observed when one compound is converted to the other compound. If complex reactions occurred simultaneously, an isosbestic point could not be observed clearly. Therefore, the presence of two isosbestic points indicates that the reduction of  $MnO_4^-$  to  $MnO_2$  proceeds under ultrasonic irradiation.

The effect of 1-butanol on the sonochemical reduction of  $MnO_4^-$  to  $MnO_2$  was investigated based on the apparent rates of  $MnO_4^-$  reduction at various concentrations of 1-butanol. Fig. 2a shows that the rate of  $MnO_4^-$  reduction changes significantly with changing 1-butanol concentration, and the minimum rate of  $MnO_4^-$  reduction is observed at 0.50 mM 1-butanol. We were surprised that a valley concentration ( $C_{valley}$ ) was observed for the rate of reduction in Fig. 2a, because it has been reported that the rates of sonochemical reduction of noble metal ions increase simply with increasing concentration of organic additives [25,26], and there has been no report of  $C_{valley}$  in plots of sonochemical reduction rate of metal ions vs concentration of organic additives. To identify the reason for the existence of  $C_{valley}$ , the rates of  $MnO_4^-$  reduction were investigated in the presence of various concentrations of 1-propanol or ethanol, which have shorter alkyl chains

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