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Note

Formation of iron(VI) in ozonalysis of iron(III) in alkaline solution

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Abstract

Here we report the formation of iron in hexavalent state, $Fe^{VI}O_4^{2-}$ in ozonalysis of iron(III) in alkaline medium. The formation of tetrahedral $Fe^{VI}O_4^{2-}$ ion is confirmed by UV–Visible and Mössbauer spectroscopic techniques. The value of isomer shift, δ, of the tetraoxy anion is consistent with known δ values for various salts of iron(VI) ion.

Keywords: Iron(VI); Iron(III); Ozone; Mössbauer spectroscopy

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1. Introduction

Iron is the most abundant transition element on Earth and commonly exists in compounds of its +2 and +3 oxidation states. Iron ions in these two oxidation states are generally used in biological electron transfer processes [1]. Iron in higher oxidation states such as +4, +5, and +6 are involved in iron enzymes, organic synthesis, and Fenton chemistry [2–4]. Examples include capability of Fe(IV) and Fe(V) at enzymatic sites to abstract H and/or to break C–C bond [2,5], participation of high-valent nonheme iron-oxo species in biometric oxidations [6,7], and involvement of aqua oxoiron(IV) in environmental and catalytic chemistry [8,9].

Under strong oxidizing environment, higher oxidation states of iron have been obtained [10,11]. In recent years, iron(VI) $Fe^{VI}O_4^{2-}$ has received much attention because of its potential use in high energy density rechargeable batteries, in cleaner (‘‘greener’’) technology for organic synthesis, and in wastewater treatment [3,12–18]. Iron(VI) is generally produced by oxidizing a basic solution of Fe(III) salt by hypochlorite [19]. For the last few years, there is emphasis of green chemistry and alternates to use of chlorine are being sought. In keeping with this goal, in this paper, we attempted ozone as an oxidant to form iron(VI). Ozonation is considered relatively environmentally-friendly process and does not produce chlorinated by-products.

Ozone has strong oxidizing properties: the redox potentials in acid, neutral, and alkaline solutions are as follows [20]:

$$O_3 + 2H^+ + 2e^- = O_2 + H_2O \quad E^0 = +2.075\ V \tag{1}$$

$$O_3 + H_2O + 2e^- = O_2 + 2OH^- \quad E^0 = +1.246\ V \tag{2}$$

Ozone has the great advantage over other oxidants because of its strong oxidizing property. Ozonation is commonly used to prepare transition-metal complexes in which the central atom has a high oxidation state [21]. For example, iron(IV) in acidic solution can be formed by oxidation of iron(II) with ozone Eq. (3) [22,23]. The iron(IV) species in aqueous solution has a half life of about 10 s, thus allowed to measure reaction kinetics of this species with inorganic and organic compounds.

$$Fe_{aq}^{2+} + O_3 \rightarrow Fe^{IV}O^{2+} + O_2 \tag{3}$$

The reduction potentials of iron(VI)/iron(III) couples in acid and alkaline solutions are presented by

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$$FeO_4^{2-} + 8H^+ + 3e^- = Fe^{3+} + 4H_2O \quad E^0 = +2.20\ V \qquad (4)$$

$$FeO_4^{2-} + 4H_2O + 3e^- = Fe(OH)_3 + 5OH^- \quad E^0 = +0.72\ V \qquad (5)$$

In alkaline solution, the redox potential of the ozone/oxygen couple is higher than that of $FeO_4^{2-}/Fe(OH)_3$ couple, which suggests that ozone can oxidize iron(III) in alkaline solution to give iron(VI). In the present work, formation of Fe(VI) by ozonolysis of Fe(III) is demonstrated for the first time.

2. Experimental

Initially, $Fe(NO_3)_3$ was added to 10 M KOH solution, heated and boiled for 2–3 h. After cooling to room temperature, the $Fe(OH)_3$ residues were separated by filtration. The concentration of Fe(III) in solutions obtained was about 10^{-4} M. Ozonation was carried out in a bubble contactor at room temperature. Oxygen-fed laboratory glass ozonizer (Medozon/03, Russia) was used for ozone production. An initial ozone concentration of 10^{-3} M, volume flow velocity at 5–10 l/h of the gas mixture containing ozone and oxygen, and the volume of the reaction mixture 5–20 ml were used. Ozone concentration in the gas phase was recorded by ozone spectrophotometer analyzer, Medozon 254/5. The contact time between Fe(III) and ozone to observe the formation of Fe(VI) was 30 min. There was approximately 70% conversion of Fe(III) to Fe(VI), which gave an estimated formation rate of Fe(VI) as 1.4×10^{-4} M/h.

The UV–Vis measurements were carried out on Cary 3E Varian spectrometer. Mössbauer absorption spectra were measured on a Perseus spectrometer working at constant velocities. The control and the adjustment of the spectrometer-vibrator rate were performed by a laser interferometer. A standard γ-source of ^{57}Co in metallic chromium matrix with the activity of 0.5 GBq (a product of Cyclotron, Co., Ltd., Obninsk, Russia) was employed. Isomer shifts in this paper are presented relative to α-Fe at 25 °C.

3. Results and discussion

The various forms of Fe(III) hydroxide/oxide are very insoluble (except in acid solution), however, $Fe(OH)_3$ is converted into $Fe(OH)_4^-$ complex under strong alkali condition [24]. Formation of complex can be obtained at pH value as low as 10.7, but due to rapid formation of precipitates at this pH, it is advantageous to use pH values higher than 12. In the experimental set up, the $Fe(OH)_4^-$ complex was prepared in 10 M OH^- solution. The ozonation of the solution resulted in a dark purple color; the spectrum of which is shown in Fig. 1.

The absorption spectrum in Fig. 1 has a peak at 510 nm, a characteristics of iron(VI) in alkaline solution [25]. The formation of iron(VI) can be represented by:

$$2Fe(OH)_4^- + 3O_3 + 2OH^- \rightarrow 2FeO_4^{2-} + 3O_2 + 5H_2O \qquad (6)$$

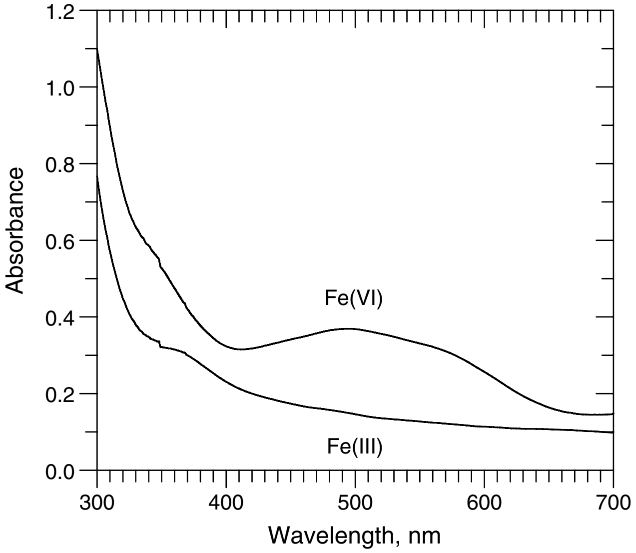

Fig. 1. Electron spectra of Fe(III) solution in 10 M KOH: before (1) and after (2) completion of the ozonation (room temperature).

The spectrum in Fig. 1 appears compatible with a tetrahedral geometry of other high-valent metal oxoanions such as CrO_4^{3-} and MnO_4^-, which also absorb at long wavelengths. The band of iron(VI) at 510 nm corresponds to ligand-to-metal charge transfer [26].

Next, Mössbauer spectroscopic investigation of the iron(VI) solution prepared by ozonation was carried out in order to further confirm the oxidation state of iron. A value of isomer shift, δ, of Mössbauer spectrum is sensitive to the oxidation state of iron [27]. The measurements of the iron(VI) solution were unsuccessful due to low concentration of FeO_4^{2-} ions and strong absorption of low-energy

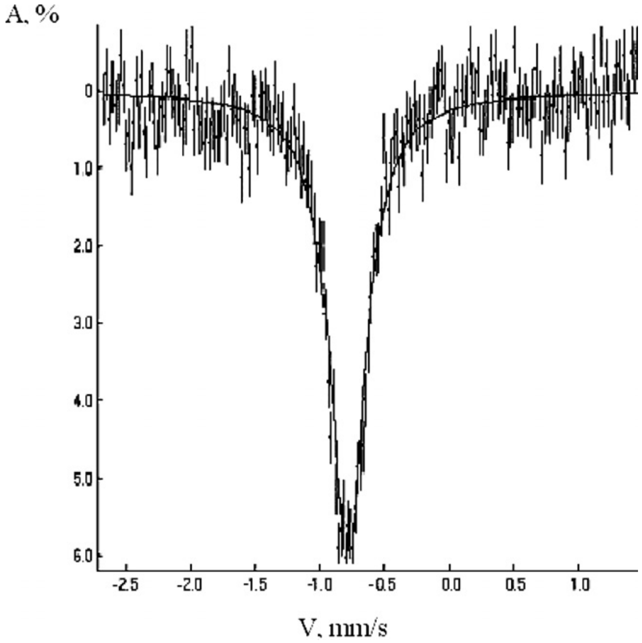

Fig. 2. Mössbauer spectrum of Fe(VI) frozen solution in 5 M NaOH (77 K).

Mössbauer radiation by the solvent. To solve this problem, $Fe(NO)_3$ enriched with ^{57}Fe (95%) was used as iron(III) source. Iron(VI) ions were prepared by ozonalysis of iron(III) in 5 M NaOH. The resulted solution was frozen in liquid nitrogen for Mössbauer measurements. Mössbauer spectrum of the frozen solution (77 K) is presented in Fig. 2. The spectrum contains one single-line with the isomer shift $-0.80(1)\ \mathrm{mm\ s^{-1}}$ and full width at half-height $0.32(5)\ \mathrm{mm\ s^{-1}}$. The δ in Fig. 2 is similar to values of δ for various salts of iron(VI) ion, which vary from -0.79 to $-0.85\ \mathrm{mm\ s^{-1}}$ [28]. Thus, the iron(VI) species synthesized in the present study is the same as has been prepared chemically using hypochlorite ion and by other techniques [15,29–31].

4. Conclusions

The high-valent iron(VI) was obtained in oxidation of iron(III) by ozone in alkaline medium. This procedure can be used as a simple and environmentally-friendly method to produce FeO_4^{2-} ion. The UV–Visible and Mössbauer spectra were found consistent with the hexavalent iron state of the ion.

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