

Mössbauer investigation of the reaction of ferrate(VI) with sulfamethoxazole and aniline in alkaline medium

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Abstract Mechanisms on the oxidation of sulfamethoxazole (SMX) and aniline by ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe(VI)) in alkaline medium suggested the formation of Fe(VI)-SMX or Fe(VI)-aniline intermediates, respectively. Fe(V) and Fe(IV) as other intermediate iron species have also been proposed in the mechanism. In this paper, rapid freeze Mössbauer spectroscopy was applied in rapidly frozen samples to explore intermediate iron species in the reactions of SMX and aniline with Fe(VI) . In both reactions, Fe(VI)-SMX and Fe(VI)-aniline intermediates were not seen in second-minute time scale. Fe(V) and Fe(IV) were also not observed. Fe(III) was the only final species of the reactions.

Keywords Ferrate · High-valent iron species · Fe(II) · Fe(III) · Antibiotics · Electron-transfer · Rapid-freeze technique · Mössbauer spectroscopy

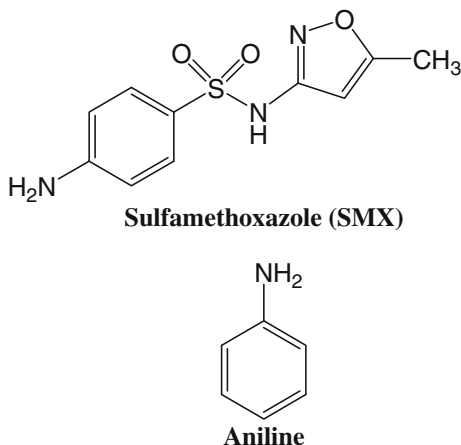
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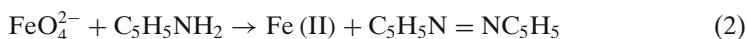
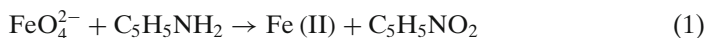
Fig. 1 Structures of sulfamethoxazole (SMX) and aniline



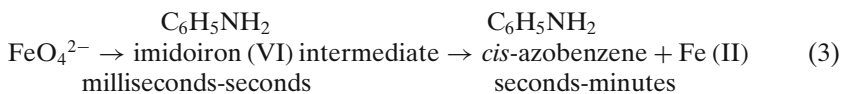
1 Introduction

The application of potassium ferrate(VI) (K_2FeO_4 , Fe(VI)) in water and wastewater treatment is attracting increasing interest [1–8]. Fe(VI) is a strong oxidizing agent with a standard reduction potential of 2.20 V under acidic conditions, however it is relatively mild oxidant in the basic conditions with a standard reduction potential of 0.72 V [9]. Like ozone, Fe(VI) does not produce carcinogenic bromate ion in treatment of Br^- containing water [7]. Because of growing concern of chlorine disinfection by-products (DBPs), Fe(VI) shows promise as an alternative disinfectant [10]. Fe(VI) can also be an effective oxidant for removal of organic micropollutants such as estrogens and certain pharmaceuticals [11–17]. No antibacterial activity against *E. coli* after complete removal of antibiotic, trimethoprim by Fe(VI) was observed [14].

The understanding of the mechanisms of oxidation reactions carried out by Fe(VI) is in progress [18, 19]. In our laboratory, we are attempting to advance knowledge on the mechanism of oxidation of antibiotics by Fe(VI) [14, 20]. The present paper deals with antibiotic, sulfamethoxazole (SMX), which consists of two moieties, an aniline ring and a five-membered heterocyclic aromatic group, connected to both sides of the sulfonamide linkage ($-NH-SO_2-$) (Fig. 1). In the proposed mechanism of Fe(VI) with SMX, intermediate iron in +4 oxidation state has been suggested [20]. However, no direct evidence was provided to confirm this intermediate iron species. Furthermore, a recent study proposed Fe(VI)-SMX intermediate species and analyzed their kinetics results based on this assumption [15]. Moreover, studies on aniline, a substructure molecule of SMX (see Fig. 1) have also been performed [21–23]. Under condition of using excess molar amounts of Fe(VI) to aniline, nitrobenzene was the product of the reaction (1) while azobenzene was formed when excess aniline was used (2).



A free radical mechanism for the reaction, based on EPR measurements was proposed when excess amounts of aniline to Fe(VI) was used [21]. In this free radical mechanism, FeO_4^{3-} (Fe(V)) was also the intermediate high-valent iron species. However, a study under similar experimental conditions contradicted the free radical based mechanism, and the imidoiron(VI) intermediate as the intermediate was suggested before the formation of final product, *cis*-azobenzene (3) [21].



In the last few years, we are attempting to explore mechanism of the oxidation reactions of Fe(VI) using the Mössbauer spectroscopy in order to establish any intermediate iron(VI)-substrate species or to distinguish one-electron steps ($\text{Fe(VI)} \rightarrow \text{Fe(IV)} \rightarrow \text{Fe(III)}$) and two-electron steps ($\text{Fe(VI)} \rightarrow \text{Fe(IV)} \rightarrow \text{Fe(II)}$) [5, 24, 25]. The oxidation states of iron can be determined unequivocally by the Mössbauer technique [26] and therefore, any intermediate iron species of the reaction may be known. In the current paper, we have applied Mössbauer technique to the reactions of Fe(VI) with SMX and aniline to learn about the mechanism of the reactions.

2 Experimental methods

The samples for Mössbauer spectroscopy were prepared by mixing solutions of 0.2 M Fe(VI) with either SMX or aniline in 10 M NaOH and in 0.01 M phosphate buffer (pH 11.0). The experiments at pH 9.0 for the reaction of Fe(VI) with aniline were performed under anaerobic solutions in which 0.2 M Fe(VI) (a ferrate(VI) sample enriched in ^{57}Fe isotope) and 0.2 M aniline were mixed to achieve the molar ratio 1:1. Anaerobic conditions were obtained by degassing with a stream of nitrogen to remove oxygen prior to mixing them together and the volume used for each solution was 100 μL . The mixing of solutions was performed in a Mössbauer sample holder (i.e., in a tiny bowl) within second time scale. The sample holder was then immersed into liquid nitrogen (78 K). The cooling rate provided by this method preserves the original structure of the solution and iron species in the liquid state [25].

The transmission ^{57}Fe Mössbauer spectra were recorded at $T = 100$ K using a Mössbauer spectrometer in a constant acceleration mode with a $^{57}\text{Co(Rh)}$ source and velocity range from -5 to 5 mm/s. The isomer shift values are given relative to metallic alpha iron at room temperature. The Mössbauer spectra were evaluated assuming Lorentzian line shapes using the least squares method with the help of the MossWinn^R code. It was expected that the effects of non-ideal absorber thickness and variable recoil-free fractions for iron atoms in non-equivalent structural sites are all within experimental error.

3 Results and discussion

Initially, solid SMX was added into 0.1 M Fe(VI) solution in 10 M NaOH solution. It was expected that such high concentration of hydroxide would stabilize any intermediate Fe(V)/Fe(IV) species [27]. As shown in Fig. 2, the Mössbauer

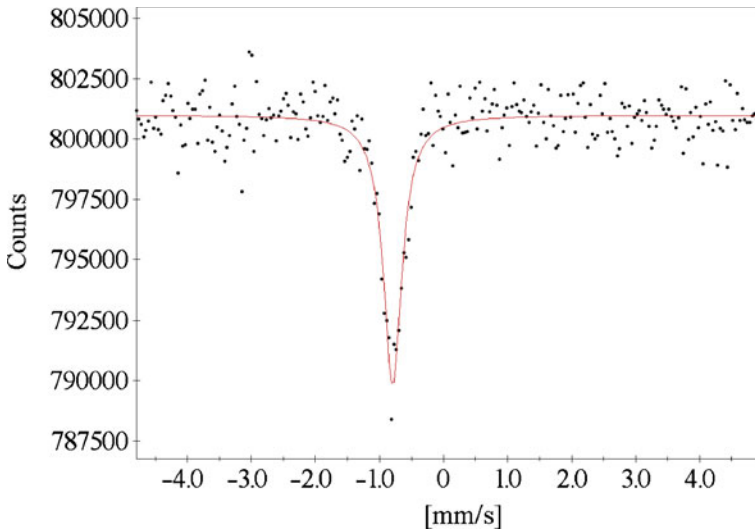


Fig. 2 Mössbauer spectrum of the frozen solution of the mixture of 0.1 M Fe(VI) and solid SMX

spectrum of the frozen solution showed a single component having isomer shift of -0.82 mm/s and this represents non reacted Fe(VI). The Fe(V) and Fe(IV) species as intermediates of the reaction between Fe(VI) and SMX were not seen. Furthermore, no reaction between Fe(VI) and SMX was observed because no Mössbauer spectra of Fe(III)/Fe(III) as the final product of Fe(VI) reduction were found.

Next, the experiments between Fe(VI) and SMX were extended to pH 11 in phosphate buffer to increase the rate of the reaction. Lowering the pH generally increases the rate of the reactions in the alkaline medium [13, 28, 29]. In this set-up, two solutions were mixed at pH 11 and were frozen in ~ 10 s to 180 s time intervals. Mössbauer spectra of these frozen solutions, shown in Fig. 3, had one singlet and a doublet, which represent Fe(VI) and ferrihydrite, respectively. The identification of ferrihydrite is based on Mössbauer parameters of the doublet. The doublet component increase with the reaction time (see Fig. 3a and b). The final Fe(III) species is consistent with the earlier study on the reaction of Fe(VI) with SMX [20]. The intermediate high-valent iron species were again elusive even at pH 11. It is possible that the intermediate iron species, Fe(V) and Fe(IV), formed during the reaction, were either reacting with SMX or self-decomposing to give Fe(II)/Fe(III) within the time scale (~ 10 s) of the freezing of the mixed sample.

Similarly, the study of Fe(VI) with aniline was carried out in 10 M NaOH and at pH 11. In 10 M NaOH solution, no reaction of Fe(VI) with aniline was observed and Mössbauer spectrum had a single component of Fe(VI). Lowering the reaction solution to pH 11 showed the decay of Fe(VI) with the concomitant growth of the doublet component. Again, no intermediate iron species could be observed. It seems that if Fe(VI)-aniline intermediate formed during the reaction, it must have a life of less than 10 s i.e. time needed to mix the solution, followed by freezing. The doublet component corresponds to Fe(III). This contradicts with the earlier work in which Fe(II) was the final product [22]. It is very likely that Fe(II) produced from the

Fig. 3 Mössbauer spectra of the frozen solutions of the mixture of 0.1 M Fe(VI) and 0.01 M SMX in phosphate buffer at pH 11.0. **a** 10 s; **b** 180 s

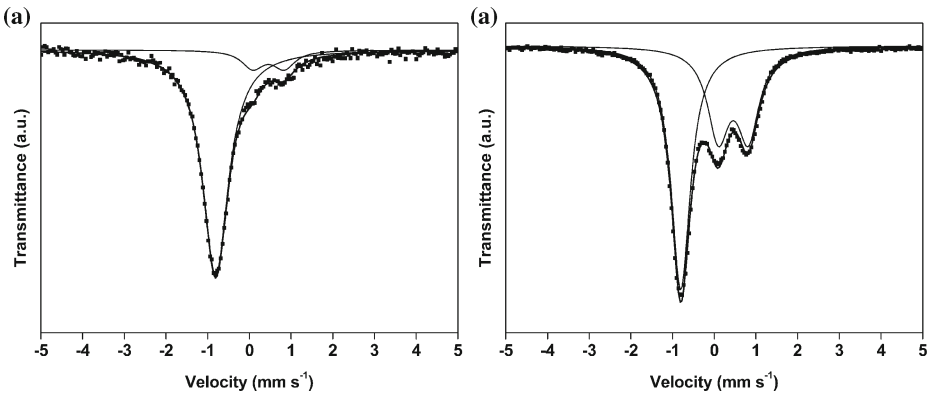
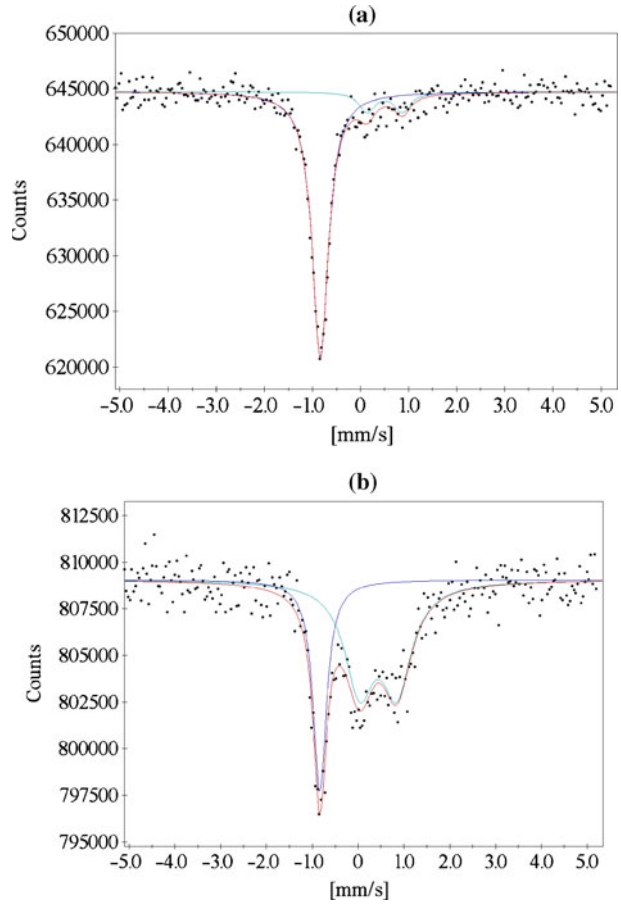


Fig. 4 Mössbauer spectra of the frozen solutions of the mixture of 0.2 M Fe(VI) and 0.2 M aniline in phosphate buffer at pH 9.0. **a** ~ 3 s; **b** 60 s

reaction might have been oxidized by inherent oxygen in the reaction solution. It is known that the oxidation of Fe(II) at such high pH is rapid [30].

Finally, the reaction of Fe(VI) with aniline was studied at pH 9.0, but under anaerobic conditions to make sure no oxygen present in the solution. The reaction was studied at a molar ratio of 1:1 ([Fe(VI)];[aniline]). The Mössbauer spectra, collected after immediate freezing of the solution (~3 s) and 60 s, are presented in Fig. 4. The results were not different from the reaction conducted at pH 11. Besides not observing any of high-valent iron species, expected Fe(II) was also not seen. Because of anaerobic condition, the oxygenation of Fe(II) to form Fe(III) could be ruled out. This suggest the possibility of the reaction between Fe(VI) and Fe(II) under studied conditions, which is fast ($k \geq 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and yielded Fe(III) [31].

It is noteworthy that the Mössbauer parameters of the resultant Fe(III) species are the same in every experiment within experimental error, and are close to that of ferrihydrite. This shows that even at not too high pH (i.e., pH 9.0) the phosphate buffer could not compete with OH⁻ ions in coordinating to iron and the formation of hydroxides/oxyhydroxides were preferred. This process can also stabilize Fe(III) and therefore accelerates decomposition of intermediate oxidation states of iron.

4 Conclusions

Mössbauer spectroscopy approach was shown as an experimental technique to study the mechanism of oxidation of sulfamethoxazole and aniline by Fe(VI). However, freezing of samples of the reaction within three seconds was not sufficient in identifying any of the possible intermediate iron species, Fe(VI)-SMX/Fe(VI)-aniline, Fe(V) and Fe(IV), during the reaction. Further improvement in freezing of reaction samples on the time scale of milliseconds is needed to establish the intermediate iron species, which will allow better understanding of role of high-valent iron, Fe(V) and Fe(IV) species in oxidation reactions of Fe(VI).

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