



Comparison of the oxidation of two porphyrin complexes by bromate with respect to wave propagation

Krisztina Rácz, Maria Burger, Zsuzsanna Ungvarai-Nagy*

Department of Inorganic and Analytical Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest 112, Hungary

ARTICLE INFO

Article history:

Available online 6 August 2009

Keywords:

Autocatalysis
Porphyrin complex
Silica gel
BZ reaction

ABSTRACT

The kinetics and mechanism of the oxidation of iron(III) protoporphyrin IX (hemin) and iron(III) meso-tetra(4-sulfonatophenyl)porphine (TPPSFe) were compared. Both reactions exhibit sigmoid-shaped time dependence of the absorbance of the porphyrin complexes during the course of the reaction. The oxidation of hemin was proved to be an autocatalytic reaction resembling very much the autocatalytic subset reaction of the BZ oscillators. The oxidation of TPPSFe was proved not to be autocatalytic. It consists of consecutive reaction steps without any feedback. One of the intermediates absorbing in the same region as TPPSFe could be identified as an iron(V)-oxo complex of TPPS. According to the kinetic differences, single autocatalytic wave fronts could be observed in the autocatalytic hemin–bromate reaction if hemin was fixed and stabilized in silica gels, while no wave formation appeared in the TPPSFe–bromate system. The kinetic differences are in agreement with the different structures of the two porphyrin complexes.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Porphyrin containing iron complexes play an important role both in biochemistry and chemistry [1]. For example hemin, the iron(III) complex of protoporphyrin IX is the prosthetic group in the active centres of many enzymes [2,3]. As another example, the water soluble iron(III) complex of meso-tetra(4-sulfonatophenyl)porphine (TPPSFe) acts as an effective catalyst for the transfer of oxygen atoms and is therefore used in the oxidative degradation of chlorophenols which are highly toxic environmental pollutants [4,5]. Porphyrin complexes have found application in nonlinear dynamics, too. Hemin has been applied in the minimal pH oscillator containing hydrogen sulfite, hydrogen peroxide and hemin [6,7] and also in the autocatalytic subset of the oscillating Belousov–Zhabotinsky (BZ) reaction [8].

Based on this latter finding, the reaction of hemin with acidic bromate can be regarded as a new candidate for autocatalytic wave propagation. Under appropriate conditions, we have been able to observe single autocatalytic wave fronts in the hemin–bromate–sulfuric acid system. However, experimental study of the oxidation of hemin by bromate is complicated because of the poor solubility of hemin in aqueous media and also because of its sensitivity to acids [8]. To overcome these problems, we tried to replace hemin by the above mentioned sulfonated phenyl derivative of hemin, TPPSFe which is both a water soluble and an acid-resistant compound. Similarly to hemin, TPPSFe

is also oxidized by bromate and the oxidation is represented by a sigmoid-shaped kinetic curve as characteristic for autocatalytic reactions [9]. However, in the reaction mixture of the new porphyrin complex and acidic bromate, no waves could be observed. We have compared the kinetics and mechanism of the two reactions and we have found substantial differences between them. In this paper we describe the results of our studies on the comparison of the oxidation of hemin and TPPSFe by bromate from the point of view of nonlinear behaviour. Despite the similar structure of the two porphyrin complexes and the similar form of their kinetic curves, they react with acidic bromate in a completely different way which explains the support or lack of wave propagation. The kinetic differences are in agreement with the geometric characteristics of the structure of the two complexes.

2. Experimental details

Solutions were prepared from analytical reagent grade chemicals. Hemin was purchased from Fluka and also prepared from defibrinated fresh bovine blood treated with NaCl-containing glacial acetic acid according to the method of Fischer [10]. TPPSFe was prepared in a four-step process using the Gonsales method as described by Srivastava and Tsutsui [11]. In aqueous media, hemin is only stable above pH 7. Below this pH value, it decomposes accompanied by a slow precipitate formation. Therefore, solutions of hemin were prepared in 0.2 M NaOH or 15% sodium silicate (water glass). TPPSFe could be easily dissolved in water.

For kinetic experiments, the reactions were followed spectrophotometrically by monitoring the absorption of hemin and

* Corresponding author. Tel.: +36 1 209 0555; fax: +36 1 372 2608.

E-mail address: ungvarai@chem.elte.hu (Z. Ungvarai-Nagy).

TPPSFe using a Milton Roy Spectronic 3000 Array spectrometer. The solutions in its 1 cm cuvette were thermostatted and during kinetic measurements stirred with a magnetic stirrer. The whole spectra were taken from 200 to 700 nm at different times during the course of the reaction or continuous absorbance versus time plots were recorded at the maximum of the Soret band of the porphyrin complexes at 365 and 394 nm for hemin and TPPSFe, respectively. The absorbance at these wavelengths was a linear function of the concentration and yielded absorption coefficients which were in good agreement with the literature data [8,9]. The hemin–bromate reaction was started by adding sulfuric acid as the last component to the slightly basic mixture of hemin and bromate. In the case of the oxidation of TPPSFe by bromate, the reaction was started by adding bromate to the TPPSFe solution at the given pH. If necessary, the pH of the solutions was maintained at a constant value using a Britton–Robinson buffer prepared by mixing an acidic solution of 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid and a basic solution of 0.2 M sodium hydroxide in different ratios.

For wave propagation experiments, gels were prepared as described earlier [12,13]. 10 cm³ of 15% water glass solution containing 1–5 μmol hemin or TPPSFe was mixed with 5 cm³ 0.5 M sulfuric acid solution. The mixture was poured into 3 Petri dishes of a diameter of 5 cm to gelate. After the gelation process, the solidified gels were washed twice with 5 cm³ 0.1 M sulfuric acid solution and then with freshly boiled and cooled distilled water. Gels were used immediately after preparation by bringing them into contact with 5 cm³ acidic bromate solution of appropriate concentrations. Autocatalytic reaction fronts started spontaneously from the wall of the Petri dish. The velocity of fronts was determined from selective pictures taken by a digital camera. All experiments were carried out at 20.0 °C.

3. Results

3.1. Kinetic measurements

In a concentration range of 5×10^{-6} – 5×10^{-4} M hemin, 0.08–0.8 M bromate and 0.06–0.6 M sulfuric acid, hemin has been proved to be oxidized by acidic bromate when the $[\text{H}_2\text{SO}_4]/[\text{BrO}_3^-]$ ratio is between 5–20. This concentration range represents an optimum in which the acidity of the system is low enough to avoid decomposition of hemin by the acid and on the other hand, high enough for the oxidation of hemin by bromate which proceeds only in acidic medium. In the given concentration range, the decomposition of hemin by sulfuric acid is suppressed by the much faster oxidation by bromate. An example for the reaction of hemin with acidic bromate is presented in Fig. 1 in a series of time resolved spectra. The kinetic curve of the same reaction is drawn in Fig. 2. The absorbance versus time kinetic curves taken at the intense Soret band of the porphyrin complex show an S-shaped time dependence which is characteristic for autocatalytic reactions. The reaction has been studied in detail but the experimental realization of the hemin–bromate reaction is a complicated task mainly because of the above mentioned coincidence with the acidic decomposition and the mixed kinetic behaviour resulting from it.

In a subsequent series of experiments, we tried to replace hemin by TPPSFe which differs from hemin practically only in the four sulfonatophenyl groups and is therefore well soluble in water and also stable against acids. TPPSFe reacts with bromate in a broader concentration range than hemin does because the reaction is not disturbed by the presence of the acid. The reaction occurs in the whole acidic pH range from pH 0 to 7 at very different ratios of the reagents. At the same concentrations, the reaction is considerably faster than the corresponding oxidation of hemin. In a concentration range of 5×10^{-6} – 5×10^{-4} M TPPSFe, 0.008–0.08 M

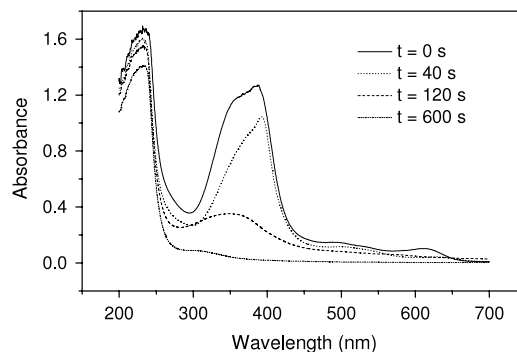


Fig. 1. Time resolved spectra recorded during the oxidation of hemin by bromate at different times after starting the reaction. Initial concentrations: $[\text{hemin}]_0 = 2.21 \times 10^{-5}$ M, $[\text{BrO}_3^-]_0 = 0.033$ M, $[\text{H}_2\text{SO}_4]_0 = 0.21$ M.

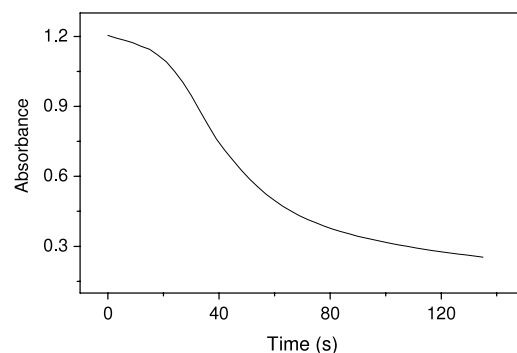


Fig. 2. Absorbance versus time curves recorded at 365 nm in the hemin–bromate reaction at the same initial concentrations as in Fig. 1.

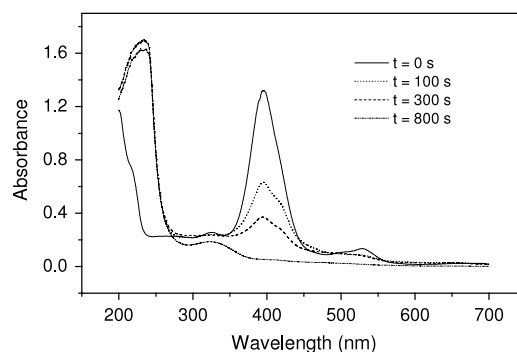


Fig. 3. Time resolved spectra recorded during the oxidation of TPPSFe by bromate at different times after starting the reaction. Initial concentrations: $[\text{TPPSFe}]_0 = 1.22 \times 10^{-5}$ M, $[\text{BrO}_3^-]_0 = 0.05$ M at pH 5.02.

bromate and at pH 4–7, the reaction was slow enough to follow it by a simple spectrophotometric method. Fig. 3 demonstrates the process recorded over the whole spectrum in different times. The respective kinetic curve of the reaction taken at the Soret band of TPPSFe is depicted in Fig. 4. Also in this case, several different concentration combinations were recorded to make a picture from the kinetics of the reaction.

3.2. Comparison of the two reactions

The oxidation of TPPSFe starts with a well separated fast absorbance decrease but after that, the sigmoid part of the kinetic curve in Fig. 4 is very similar to the behaviour of hemin shown in Fig. 2. At first sight, it is not surprising and seems to be in agreement with the analogous structure of the two compounds, hemin and TPPSFe.

However, comparing the conditions of the two reactions and the two series of spectra presented in Figs. 1 and 3, several differences can be observed. First of all, hemin is oxidized by bromate

Download English Version:

<https://daneshyari.com/en/article/1899770>

Download Persian Version:

<https://daneshyari.com/article/1899770>

[Daneshyari.com](https://daneshyari.com)