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OXIDATION OF A WATER-SOLUBLE PORPHYRIN COMPLEX BY BROMATE

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Abstract

The water-soluble iron(III) complex of meso-tetra(4-sulfonatophenyl)porphine is oxidized by bromate in nearly neutral aqueous solutions in an overall six-electron three-step consecutive reaction. Kinetics and mechanism of the reaction are described.

Keywords: Porphyrin, bromate, oxidation, TPPS

INTRODUCTION

Porphyrin complexes have found a lot of applications in chemical and biochemical research [1]. Iron(III) porphyrin complexes are used as catalysts for the oxidative degradation of chlorophenols which is an effective treatment of these highly toxic pollutants [2,3]. Some porphyrin complexes can be used as enzyme model compounds like hemin which is known to be the part of the active centres of many enzymes that contain heme as a prosthetic group [4,5]. Hemin has been applied also in the minimal pH oscillator that involves hydrogen sulfite and hydrogen peroxide [6,7].

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Hemin can even replace ferroin in the autocatalytic subset of the oscillating Belousov-Zhabotinsky reaction [8]. In a recent publication we have shown how the acidic decomposition of hemin can be suppressed in the presence of bromate, and instead of decomposing, hemin can be oxidized by bromate in acidic medium in an autocatalytic manner. The main problem in studying this reaction arises from the solubility of hemin in water and its sensitivity against acids. To overcome this problem, we prepared the water-soluble and acid-resistent iron(III) complex of a porphyrin derivative, iron(III) meso-tetra(4-sulfonato-phenyl)porphine chloride (TPPSFe), and studied its oxidation by bromate. TPPSFe was shown to be oxidized by bromate but the reaction appeared to be completely different from the oxidation of hemin. Despite of the similar chemical structure of the two compounds, they react with bromate under different conditions in a different way. We studied the kinetics and mechanism of the oxidation of TPPSFe by bromate. Here we present the first results of our investigations.

EXPERIMENTAL

Solutions were prepared from analytical reagent grade chemicals with doubly distilled water. The iron complex of TPPS was prepared as described previously [9]. HOBr was prepared by the method of Noszticzius [10]. All experiments were carried out at $20.0^{\circ}C$. The reagent solutions were mixed to give initial concentrations of 0.0083 - 0.083 mol/L BrO_3^- and 4.2×10^{-6} - 4.7×10^{-5} mol/L TPPSFe at a pH of 4 -7. For setting the pH of the solutions, Britton-Robinson buffers were used. The reaction was started by adding bromate to the TPPSFe solution at the given pH.

The reaction was followed spectrophotometrically by monitoring the absorption of TPPSFe using a Milton Roy Spectronic 3000 Array spectrometer. The solutions in its 1 cm cuvette were thermostated and during kinetic measurements stirred with a magnetic stirrer. The bromide ion concentration and the pH of the solutions were measured using a Radelkis Br^- sensitive electrode, a calomel reference electrode and a Radelkis combination glass electrode, respectively, connected to a Radelkis OP-104 pH meter.

Numerical simulations and parameter estimations were carried out on a PC using CVODE integration package [11,12].

RESULTS AND DISCUSSION

Sodium bromate and potassium bromate are commercially available very stable oxidizing agents reacting at a measurable rate only in acidic solutions below pH 5 to give bromide ions in an overall six-electron oxidation process.

Surprisingly, bromate reacts with TPPSFe even at pH 5-7 in a multistep reaction. Below pH 5, the reaction gets very fast. Above pH 7, TPPSFe is reported to form an oxo-bridged dimer [13], and is not oxidized by bromate. Our studies cover the pH region 4-7 where the reaction proceeds at a moderate rate. Figure 1 presents the process in a series of time resolved spectra. The UV region of the spectrum of TPPSFe is covered by the large absorption band of bromate used in excess but in the visible range, remarkable changes indicate the conversion of the porphyrin complex. The intense Soret band of the porphyrin ring at $\lambda = 394$ nm disappears showing that the complex is finally oxidized to a product that does not contain a porphyrin ring. While decreasing, the Soret band widens and a well expressed shoulder of the peak appears at higher wavelengths.
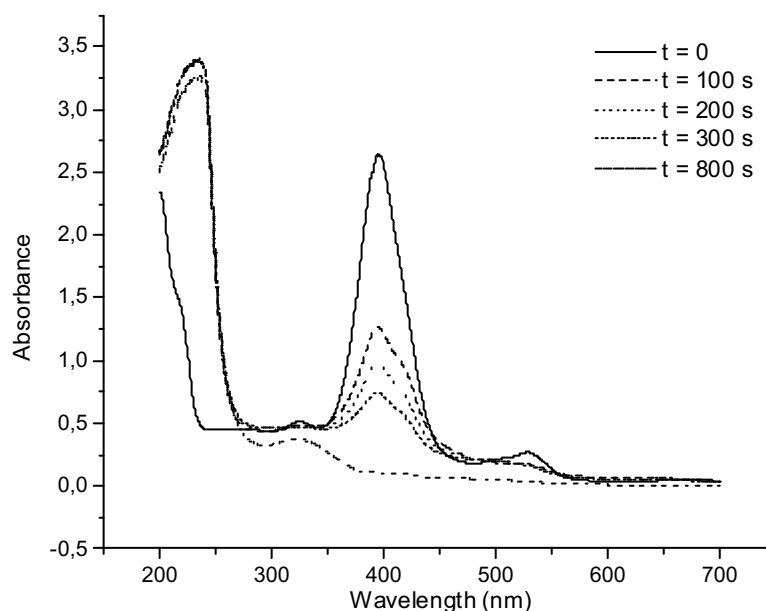

Fig. 1. Time-resolved spectra recorded during the oxidation of TPPSFe by bromate at 0, 100, 200, 300 and 800 s after starting the reation. Initial concentrations: $[TPPSFe]_0 = 2.44 \times 10^{-5}$ mol/L, $[BrO_3^-]_0 = 0.05$ mol/L at pH 5

Kinetic curves depicting the time dependence of the Soret band at 394 nm show a multiple redox process occurring (Fig. 2). There is a fast, well separated first part of the reaction followed by a very slow change at almost constant absorbance and finally an S-shaped decrease again.
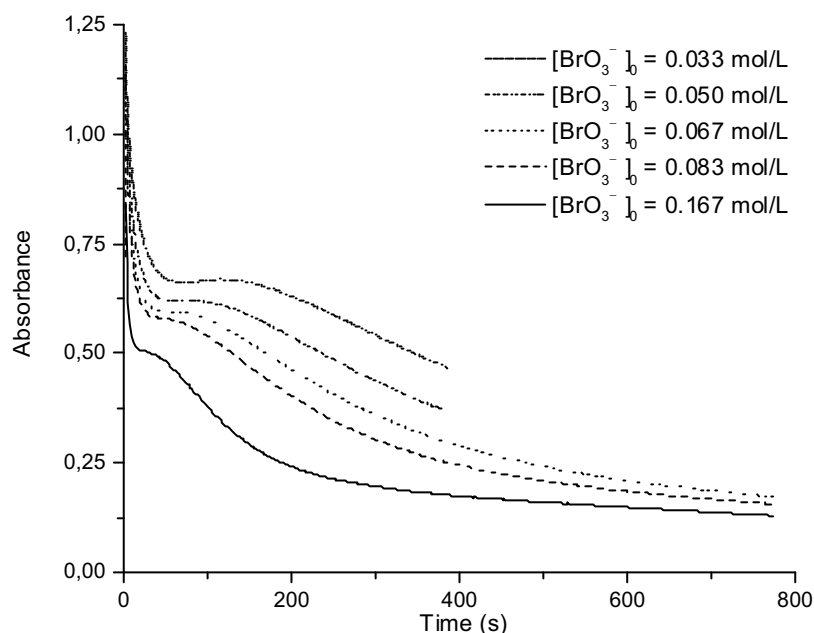
Fig. 2. Absorbance *vs*. time curves of the TPPSFe - bromate reaction measured at pH 5 at different initial bromate concentrations. $[TPPSFe]_0 = 2.44 \times 10^{-5}$ mol/L

Spectrophotometric measurements were carried out at different initial concentrations of the reagents. Kinetic curves recorded in different buffer solutions from pH 4-7 indicate a clear pH dependence of all but the 1st phase of the reaction which is pH independent. Varying the concentration of bromate and TPPSFe affects all three phases of the reaction (cf. Fig. 2).

The first phase of the reaction was separate from the other parts and therefore, it could be analyzed independently. First, initial rates were calculated from the absorbance changes measured at different initial concentrations of the reagents using van't Hoff's method. The net rate equation was determined to be

$v = k_1[TPPSFe][BrO_3^-]$

The initial rate is independent of the pH of the solution. The value of the rate constant is
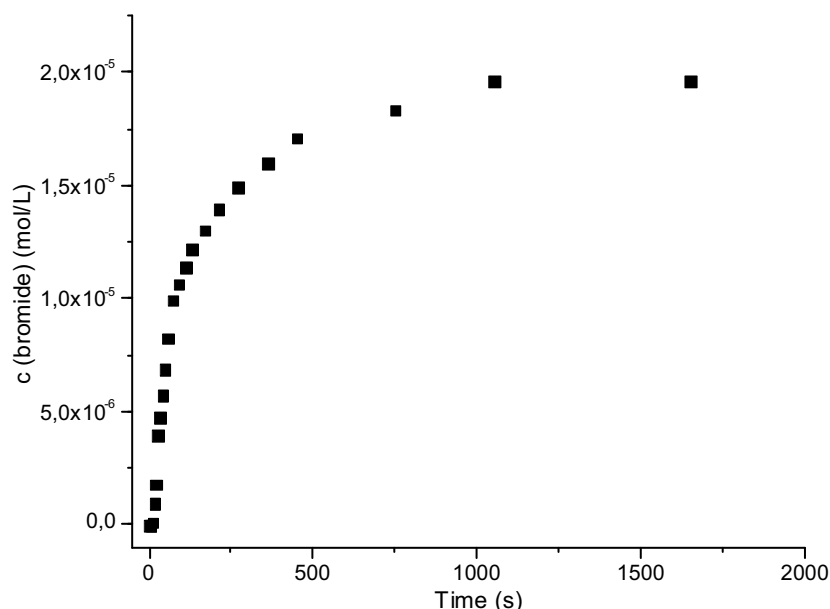
$k_1 = 0.15$ mol^{-1} Ls^{-1}.

Fig. 3. Bromide ion concentration *vs.* time curve recorded in the TPPSFe - bromate reaction. Initial concentrations: $[\text{TPPSFe}]_0 = 2.37 \times 10^{-5}$ mol/L, $[\text{BrO}_3^-]_0 = 0.042$ mol/L at pH 6

The rate constant of the fast first part of the reaction was determined in an other way, too. In independent experiments, potentiometric curves were recorded using a bromide ion selective electrode as presented in Fig. 3. The time dependence of the Br^- concentration shows a monotonic increase. The total conversion in bromide ion concentration reaches in every case a saturation value which is increasing with increasing initial TPPSFe concentration. At initial [TPPSFe] below 2.5×10^{-5} mol/L, the ratio of $[\text{Br}^-]_\infty/[\text{TPPSFe}]_0 = 1$. At higher initial TPPSFe concentrations, the final bromide ion concentration is increasing less than linearly and in these cases, the ratio $[\text{Br}^-]_\infty/[\text{TPPSFe}]_0$ is smaller than 1. In every case when this ratio equals 1 in the net reaction, 1 mol bromide is produced during the conversion of 1 mol TPPSFe. Bromate was used in a large excess, hence, the $[\text{Br}^-]$ *vs.* time curves could be treated as pseudo first order ones. Substituting $[\text{TPPSFe}] = [\text{TPPSFe}]_0 - [\text{Br}^-]$ and $[\text{TPPSFe}]_0 = [\text{Br}^-]_\infty$ yields

$d[\text{Br}^-]/dt = k'([\text{Br}^-]_\infty - [\text{Br}^-])/[\text{Br}^-]_\infty$ and after integration

$\ln[([\text{Br}^-]_\infty - [\text{Br}^-])/[\text{Br}^-]_\infty] = -k't$ where $k' = k_1 [\text{BrO}_3^-]$.

From the linear time dependence of the expression $\ln[([\text{Br}^-]_\infty - [\text{Br}^-])/[\text{Br}^-]_\infty]$, the rate constant k_1 can be determined. Its value is within the experimental error the same as the rate constant determined from the initial rates.
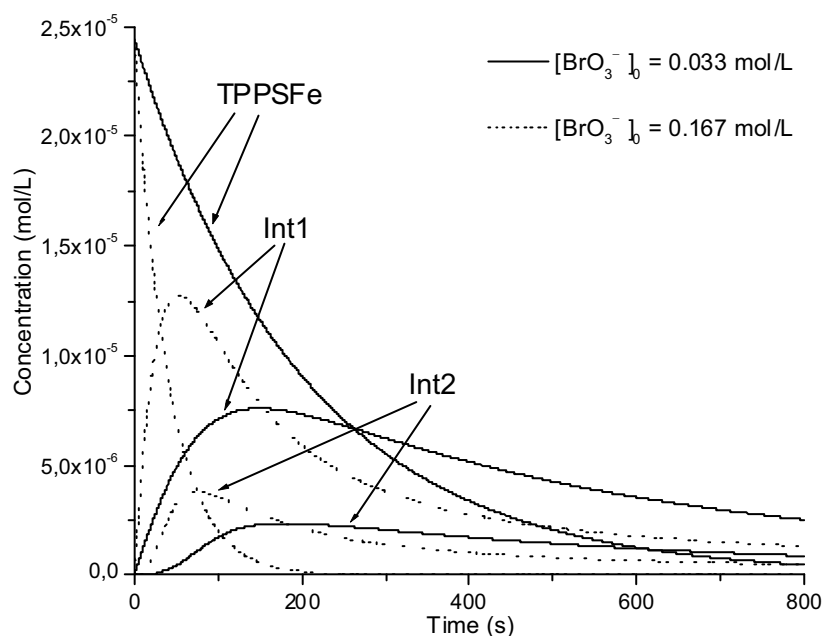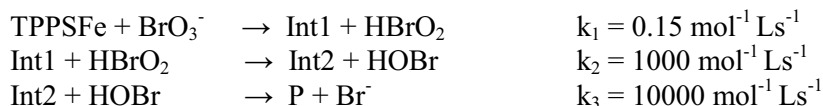
Fig. 4. Calculated concentrations of the species TPPSFe, Int1 and Int2 at an initial concentration of $[\text{TPPSFe}]_0 = 2.44 \times 10^{-5}$ mol/L

On the absorbance curves, the fast first step of the oxidation is followed by an S-shaped decrease in which at several concentration combinations, both a minimum and a maximum can be observed. This means that at least three consecutive steps, and at least 2 intermediates must be involved in the reaction mechanism. On the other hand, Br^- measurements proved that 1 mol Br^- is formed from BrO_3^- during the complete oxidation of 1 mol TPPSFe corresponding to an overall six-electron process. These two experimental observations are in good agreement with literature data on the oxidation of TPPSFe by different oxidizing agents [3], and also with the known biochemical pathway of porphyrin degradation yielding biliverdin and carbon monoxide in three consecutive oxygen-transfer steps in an overall six-electron process [14].

On the absorption curves, the second and third steps are overlapped and therefore, their rate constants were determined by model calculations. The main steps of the proposed simple mechanism are the following:

$$\text{TPPSFe} + \text{BrO}_3^- \rightarrow \text{Int1} + \text{HBrO}_2 \qquad k_1 = 0.15 \text{ mol}^{-1}\text{Ls}^{-1}$$
$$\text{Int1} + \text{HBrO}_2 \rightarrow \text{Int2} + \text{HOBr} \qquad k_2 = 1000 \text{ mol}^{-1}\text{Ls}^{-1}$$
$$\text{Int2} + \text{HOBr} \rightarrow \text{P} + \text{Br}^- \qquad k_3 = 10000 \text{ mol}^{-1}\text{Ls}^{-1}$$

Among the inorganic intermediates, $HBrO_2$ and $HOBr$ reflect the electron-change of one oxygen-transfer process. The effect of $HOBr$ on the reaction was also proven experimentally. It appeared to accelerate the oxidation corresponding to the mechanism. The ordinary differential equations resulting from this model were solved numerically using the CVODE integration package [12,13] applying the Backward Differentiation Formulas with Newton iteration with the following initial conditions: $[Int1]_0 = 0.0$ mol/L, $[Int2]_0 = 0.0$ mol/L,
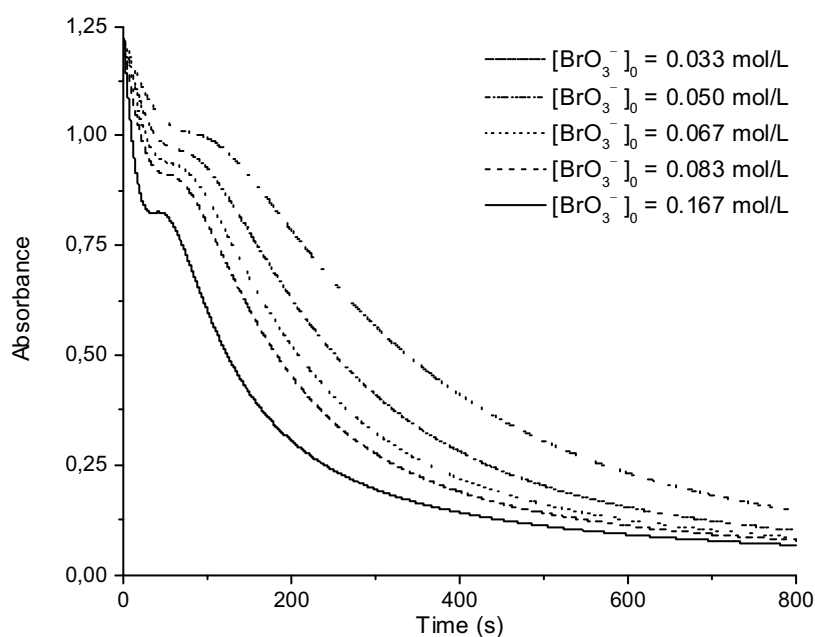

Fig. 5. Calculated variation of absorbance *vs.* time curves using different initial concentrations of bromate at an initial concentration of $[TPPSFe]_0 = 2.44 \times 10^{-5}$ mol/L. The absorbance is scaled on the following relation $A = 50000([TPPSFe] + 0.3[Int1] + 2.5[Int2])$

$[TPPSFe]_0$ and $[BrO_3^-]_0$ as in the experiments. The value of k_1 was taken from the experiments, k_2 and k_3 were determined by calculations to get the best fit of the experimentally measured kinetic curves. The calculated concentrations of the organic species for two selected cases are depicted in Fig. 4. With appropriate absorption coefficients, these concentrations can reproduce the absorbance curves experimentally measured and the main features of the concentration dependences very well (Fig.5). More detailed description of the mechanism and identification of the intermediates will be presented in a forthcoming paper.

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