



Ion-exchange chromatographic analysis of peroxyntic acid



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ARTICLE INFO

Article history:

Received 16 September 2015

Received in revised form

17 December 2015

Accepted 18 December 2015

Available online 22 December 2015

Keywords:

Peroxyntic acid

Ion-exchange chromatography

Low pH

Low temperature

Decomposition behavior

Molar extinction coefficients

ABSTRACT

Ion-exchange chromatographic analysis of peroxyntic acid (O_2NOOH) was performed by combining an acidic eluate with an UV-vis detector and immersing the separation column in an ice-water bath. The decomposition behavior of peroxyntic acid in the solution was also studied using this system. The fraction for the peroxyntic acid peak was collected. Ion-exchange chromatographic analysis of this fraction, after standing at room temperature for 24 h, showed that the decomposition products were mainly nitrate ions with a very small amount of nitrous acid. The peroxyntic acid peak area correlated perfectly with the total amount of decomposition products. The ion-exchange chromatographic isolation allowed us to evaluate the molar extinction coefficient of peroxyntic acid precisely in a wider wavelength range than previous reports. The value decreases monotonically from $1729 \pm 26 M^{-1} cm^{-1}$ at 200 nm to $12.0 \pm 0.5 M^{-1} cm^{-1}$ at 290 nm.

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1. Introduction

Peroxyntic acid (O_2NOOH), a type of peracid containing a hydroperoxide group, is of interest in environmental chemistry because of its photosynthetic formation in the Earth's atmosphere [1]. Peroxyntic acid has been synthesized in aqueous phase by reacting nitrite with hydrogen peroxide under cold and low pH conditions [2,3]. Despite many studies of peroxyntic acid in aqueous solutions [2–12], different molar extinction coefficients (ϵ_{O_2NOOH}), which are fundamental physical constants, have been suggested; for example, $256 M^{-1} cm^{-1}$ at 240 nm for synthetic peroxyntic acid under acidic solutions by Appelman and Gosztola [2] and $400 M^{-1} cm^{-1}$ at the same wavelength in a pulse radiolysis study by Løgager and Sehested [4]. These large differences may be caused by the contamination of peroxyntic acid with other compounds such as nitrous and nitric acids in solution. This suggests that purification of peroxyntic acid is necessary for a further investigation of its physical and chemical properties. However, peroxyntic acid is yet to be isolated owing to its instability.

According to the literature [4,5], peroxyntic acid dissociates to nitrous acid and oxygen via a first-order reaction. Its lifetime follows Arrhenius behavior, becoming longer at lower temperatures.

For example, the half-life (τ) is reported as 27 s in acidic solution (pH 3.0) at 25.0 °C, compared with 636 s at 5.0 °C [5]. Another important factor in peroxyntic acid stability is pH. Kenley et al. [6] reported that $\tau = 18$ s in a pH 4.90 acetate buffer at 10.0 °C, while in a pH 1.36 hydrochloric acid solution at the same temperature, it was 441 s. This stability at lower temperatures and low pH represented an opportunity to isolate peroxyntic acid in solution.

In the last 40 years, high-performance liquid chromatography (HPLC) has become a powerful tool in the analysis of mixtures. HPLC, particularly ion-exchange chromatography (IEC), has been widely used for the analysis of ionic species [13,14]. HPLC analysis at low temperatures has been studied since the 1980s [15–17]. As an example, Moriyasu et al., studied the rotamers of formanilide, a zwitterion, using a thermally controlled HPLC system at -30 to 0 °C [17]. Considering the dependence of peroxyntic acid's stability on solution pH, acidic eluents are required to analyze peroxyntic acid using IEC. To perform IEC under acidic conditions, we studied the separation behavior of anions at pH 2–4 at room temperature. The results showed that IEC analysis of nitrite, bromide, and nitrate ions was possible even at low pH values such as pH 2, with a quaternary ammonium salt-based column and a UV detector. Based on these results, we studied the IEC analysis and purification of peroxyntic acid at low temperatures and low pH. The decomposition behavior of peroxyntic acid in solution has also been studied using this system. The molar extinction coefficient of peroxyntic acid was determined from the relationship between the

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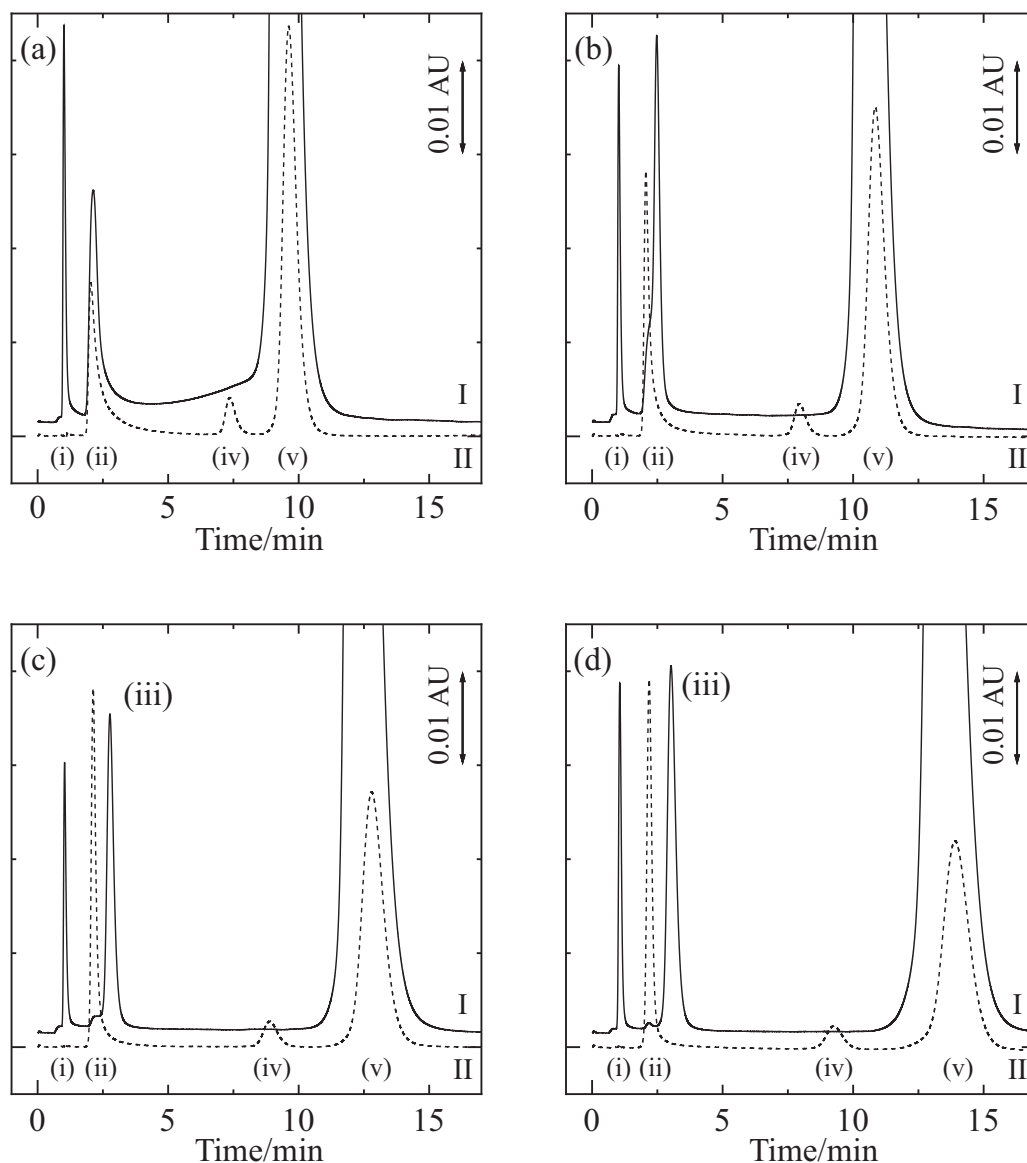


Fig. 1. Ion-exchange chromatograms for peroxyntitric acid solution under optimized condition. Column bath temperature: (a) 40 °C, (b) 25 °C, (c) 10 °C, (d) 0 °C (ice-water temperature). (I) Peroxyntitric acid solution (dilution ratio: 1/100, injection volume: 5 μ L). (II) Standard solution containing 20 mgL⁻¹ of nitrite, bromide and nitrate each (injection volume: 50 μ L). Eluent: 10 mM hydrochloric acid; flow rate: 1.5 mL min⁻¹. Wavelength: 220 nm. (i) Hydrogen peroxide, (ii) nitrous acid, (iii) peroxyntitric acid, (iv) bromide, and (v) nitrate.

concentration of decomposition products and the peak area of peroxyntitric acid.

2. Materials and methods

2.1. Apparatus and reagents

IEC measurements were performed on HPLC equipment (Agilent 1100 System) with a UV–vis photodiode array detector (DAD-3000 RS, Thermo Scientific). The path length of the detector was 7.0 mm. In this system, polyetheretherketone (PEEK) tubing was used to avoid the influence of the metal corrosion. The separation column, PCI-201S (i.d. 4.6 mm, length 100 mm, TOA DKK), was polymeric quaternary ammonium salt-based. The flow rate of the eluate was fixed at 1.5 mL min⁻¹. In order to prevent the degradation of peroxyntitric acid, the column was immersed in an ice-water bath. For experiments changing the temperature of the column bath, a liquid

circulation cooling unit (CL-150R, TAITEC) was used. The PEEK tubing (i.d. 0.75 mm, length 5 m) between the pump and the injector was immersed in the column bath to precool the eluent.

All chemicals were of analytical grade and used without further purification. Water was purified using a Milli-Q system.

2.2. Preparation of the peroxyntitric acid solution

The following synthetic method was employed for the preparation of peroxyntitric acid solutions [2,3]. Hydrogen peroxide (30%, 1.2 mL) was mixed with nitric acid (3 M, 0.8 mL). Separately, sodium nitrite (6.0 g) was dissolved in water (10 mL). Both solutions were cooled in an ice-water bath. The nitrite solution (0.8 mL) was added dropwise to the stirred hydrogen peroxide solution, which was then stored in an ice-water bath. The resulting solution was diluted 100-fold with ice-cold water and immediately analyzed.

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