



Short Communication

Chemical and spectral behavior of nitric acid in aqueous sulfuric acid solutions: Absorption spectrum and molar absorption coefficient of nitronium ion



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ABSTRACT

The chemical species formed from nitric acid in aqueous solutions of sulfuric acid (up to 18.0 mol L⁻¹) were studied by optical spectroscopy method. The concentration region of nitronium ion formation was identified and NO₂⁺ ion absorption spectrum was measured ($\lambda_{\max} \leq 190$ nm and $\epsilon_{190} = 1040 \pm 50$ mol⁻¹ L cm⁻¹).

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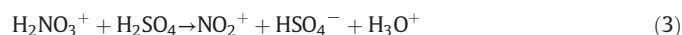
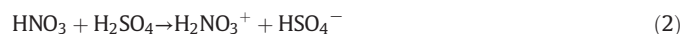
1. Introduction

Nitronium ion (NO₂⁺) is a chemically reactive species present in concentrated nitric acid and its solutions containing strong inorganic acids. The extensive use of nitric acid for a variety of practical purposes, first of all, for nitration of organic compounds [1,2] and used nuclear fuel processing [3], provokes considerable interest in the formation and properties of this ion. Note also that heterogeneous reactions of dinitrogen pentoxide (N₂O₅) on aerosol particles play a critical role in regulating the tropospheric reactive nitrogen availability. In these reactions, the nitronium ion is also formed in intermediate stages of N₂O₅ hydrolysis [4–6].

Nitronium ion is the product of the chemical transformation of nitric acid in aqueous solutions or nitrogen oxides in aerosols. Its formation has been studied by a variety of physicochemical methods (cryoscopy, electrical conductivity, thermography, and so on) [1,2]. Using Raman spectroscopy, it has been found that the content of dissociated nitrate (NO₃⁻) in aqueous solutions decreases as the nitric acid concentration increases, and in the pure anhydrous acid, nitronium ions NO₂⁺ are formed via the following dissociation reaction [7–9]:



Nitric acid is completely converted to nitronium ions in concentrated sulfuric acid. According to Raman spectroscopy data, the addition of water up to 10% mass fraction does not affect the concentration of nitronium ions [10]. Further dilution reduces the concentration of these ions, and in solutions containing <85 mass % sulfuric acid, they are no longer detectable. A systematic study of the Raman spectra of ternary solutions, HNO₃–H₂SO₄–H₂O, has revealed the effect of the acid and water concentrations on the chemical species derived from nitric acid [11–15]. Optical spectroscopy has been used as suitable means to identify molecular and ionic species present in the solutions [16–19]. It was also noted that the optical band of the NO₃⁻ ion ($\lambda_{\max} = 302$ nm) gradually shifts to shorter wavelengths (down to 265 nm) as the H₂SO₄ concentration increases up to 100 mass %. This shift is attributable to the formation of undissociated acid species, various hydrates, protonated species, and nitronium ion. However, the exceptionally high short-wavelength absorption of concentrated nitric acid solutions ($\lambda < 250$ nm) restricts the applicability of UV spectroscopy for systematic investigation of HNO₃ solutions in this optical range. Presumably, NO₂⁺ is formed in sulfuric acid according to the reactions



Since nitronium ion plays a critical role in many processes, its precise detection by optical method is essential for the understanding of its

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specific functions. We have set ourselves the task to record the absorption spectrum of the NO_2^+ ion. For this purpose, we have chosen conditions that provided, as fully as possible, the possibility to perform measurements in the short-wavelength range ($\lambda < 250$ nm) up to 190 nm. These conditions include the use of sulfuric acid as an optically transparent medium for dilute solutions of nitric acid and the use of thin quartz cuvettes (the path length of the cell is 0.1–0.2 cm). This simple approach proved to be successful and allowed us to measure the absorption spectrum of the NO_2^+ ion and to elucidate the influence of acidity on the nitric acid transformations.

2. Experimental

Solutions of nitric acid in sulfuric acid were prepared by diluting concentrated high purity grade chemicals (H_2SO_4 , Acros Organics, extra pure, 96 mass % and HNO_3 , Rotipuran 65 mass %). The concentration of H_2SO_4 was determined by titration with alkali solutions and by measuring the specific density. The solutions were prepared at 20 °C using triply distilled water. The resistivity of used water at 25 °C was equal to 18.2 M Ω at 25 °C. The NaNO_3 salt was also used as the source of nitrate ions in the preparation of concentrated sulfuric acid solutions. The use of the salt ruled out dilution of H_2SO_4 with water. The results obtained with either HNO_3 or NaNO_3 as the sources of nitrates were shown to be identical in the study. The optical spectra were recorded on a Cary 50 spectrophotometer. The absorption spectrum of HNO_3 in the solution with H_2SO_4 was calculated by subtracting of H_2SO_4 absorption.

3. Results and Discussion

The optical absorption spectra of HNO_3 (0.1 mol L $^{-1}$) in sulfuric acid in the optical region of ≥ 250 nm are shown in Fig. 1. At H_2SO_4 concentration below 2.0 mol L $^{-1}$, the spectrum exhibits an absorption band for the dissociated nitrate species, NO_3^- ion, with a maximum at 303 nm and the molar absorption coefficient (ϵ) of 7.1 mol $^{-1}$ L cm $^{-1}$. As the H_2SO_4 concentration increases, the band gradually shifts toward shorter wavelengths to reach 264 nm when the acid content exceeds 11.8 mol L $^{-1}$ (Fig. 1a). In the H_2SO_4 concentration range from 15.4 to 16.0 mol L $^{-1}$, the 264 nm band disappears and a new band, smoothly increasing toward the UV region, appears instead (Fig. 1b).

The optical absorption spectra of HNO_3 in sulfuric acid at ≤ 250 nm wavelengths (down to 190 nm) are shown in Fig. 2. Dilute nitrate solutions (1 · 10 $^{-3}$ mol L $^{-1}$) were used. The absorption band of the NO_3^- ion ($\lambda_{\text{max}} = 202$ nm and $\epsilon_{202} = 1.04 \cdot 10^4$ mol $^{-1}$ L cm $^{-1}$) in this optical

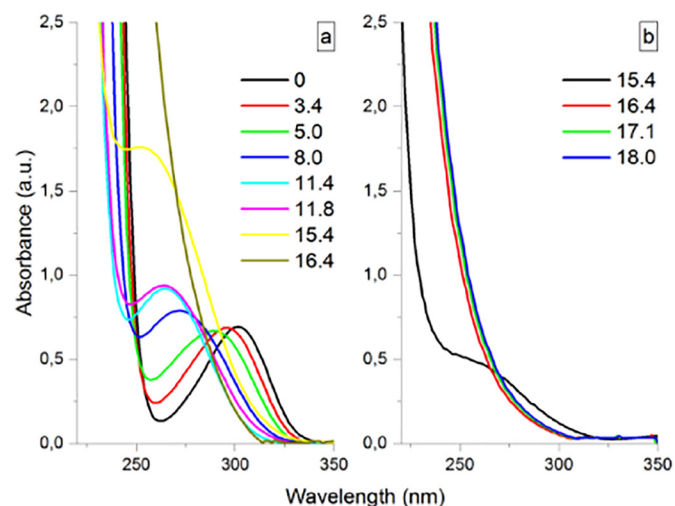


Fig. 1. Evolution of the absorption spectra of HNO_3 (0.1 mol L $^{-1}$) depending on the H_2SO_4 concentration (mol L $^{-1}$). The path length of the cell (l) is 1 cm (a) and 0.2 cm (b).

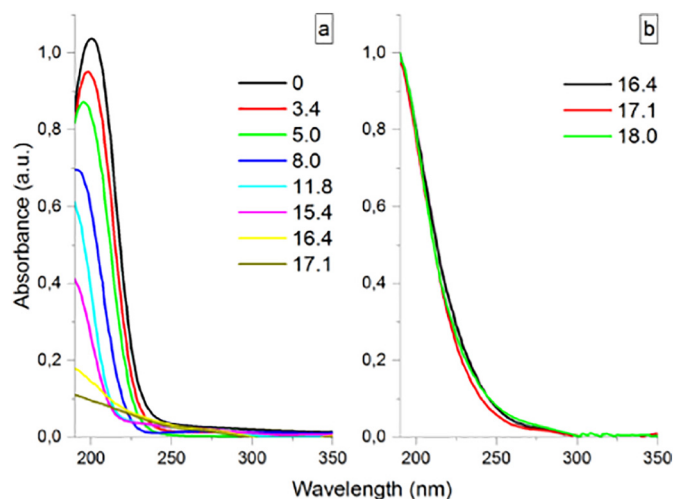


Fig. 2. (a) Evolution of the absorption spectra of HNO_3 (1 · 10 $^{-3}$ mol L $^{-1}$) depending on the H_2SO_4 (mol L $^{-1}$) concentration ($l = 0.1$ cm). (b) Normalized absorption spectra of HNO_3 depending on the H_2SO_4 concentration (mol L $^{-1}$).

region also remains almost invariable up to H_2SO_4 concentration of approximately 2 mol L $^{-1}$. At higher concentration, the absorbance decreases and the band shifts toward shorter wavelengths (Fig. 2a). When the H_2SO_4 concentration is above 16.5 mol L $^{-1}$, the spectrum exhibits absorption the intensity of which smoothly increases toward shorter wavelengths. This absorption does not have a clear-cut maximum and remains virtually the same for HNO_3 in 17–18 mol L $^{-1}$ solutions of sulfuric acid (Fig. 2b). Obtained results are in a relatively good agreement with photoabsorption cross sections in UV-region for potassium nitrate dissolved in 96.0 mass % (18.0 mol L $^{-1}$) sulfuric acid [6].

The whole set of spectrophotometric data for nitric acid solutions in sulfuric acid is in good qualitative and quantitative agreement with the results of Raman spectroscopic studies. According to a number of publications [10–15], nitric acid is completely converted to nitronium ions in concentrated sulfuric acid, and down to 90 mass % H_2SO_4 , the concentration of nitronium ions is not changed. Further dilution reduces the concentration of this species, which is not detectable in solutions containing <85 mass % sulfuric acid. The changes in the UV spectra observed in Figs. 1 and 2 are associated with gradual protonation of free NO_3^- ions with increasing H_2SO_4 concentration and formation of HNO_3 molecules, protonated H_2NO_3^+ species, and possibly other species. Finally, when the sulfuric acid content is above 16.5 mol L $^{-1}$, the solution contains only NO_2^+ ions. Nitric acid is noticeably weaker than sulfuric acid. Hence, as compared with sulfuric acid it can be treated as a weak base. The formation of the nitronium ion from nitric acid in aqueous sulfuric acid can be conventionally regarded as the reaction of a weak base with a strong acid (reactions 2 and 3).

In the gas phase, the formation of NO_2^+ is caused by proton transfer in the reaction of H_3O^+ with HNO_3 and also in ion-catalyzed reaction which converts N_2O_5 to HNO_3 [4–6]. The larger clusters $\text{NO}_2^+(\text{H}_2\text{O})_n$ are then formed in subsequent association reactions with H_2O . Mass spectrometric studies demonstrated a considerable influence of the degree of hydration of the $\text{NO}_2^+(\text{H}_2\text{O})_n$ cluster on its decomposition [20]. The $\text{NO}_2^+(\text{H}_2\text{O})_n$ cluster with $n \leq 3$ was shown to dissociate with elimination of a water molecule. At $n \geq 4$, it undergoes internal hydration to give an HNO_3 molecule and H_3O^+ ion. Here, one can trace a certain analogy with the processes that take place in sulfuric acid solutions where the stability range of the nitronium ion is also restricted by the presence of a minor amount of water (~10 mass%).

Fig. 3a shows the dependence of the absorption spectra of HNO_3 on its concentration in 18.0 mol L $^{-1}$ H_2SO_4 . The formation of chemically identical species (NO_2^+ ions) is confirmed by identity of the spectra (Fig. 3b) and by strict linear dependence of absorbance on the nitrate concentration (Fig. 3c).

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