



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photolysis of crystalline alkali nitrates via excitation of NO_3^- to the state of symmetry $2^1E_1^1$

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ARTICLE INFO

Article history:

Received 27 August 2015

Accepted 9 September 2015

Available online 8 October 2015

Keywords:

Photo excitation

Photolysis

Nitrate

Nitrite

Peroxynitrite

Radicals

ABSTRACT

Photolysis of crystalline alkali nitrates has been studied using optical, IR, and EPR spectroscopy and chemical analysis of the aqueous solutions of the exposed samples. Excitation of the nitrate ion to $2^1E_1^1$ ($a_1^1 \leftarrow e^1$) state by exposure to light with wavelength of 172 nm at 300 K leads to formation of nitrite and peroxynitrite ions. The photolysis at 77 K results in formation of fragment NO_2 , O^- , and O_3^- radicals. The quantum yields of the nitrite and peroxynitrite ions were calculated. The nitrite ions and peroxynitrite ions are formed in deep layers of the samples. The mechanism of radical formation is connected with photochemical transformations of the nitrate ion in the surface layer of the crystal.

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1. Introduction

Photochemical transformations in inorganic crystals are typically studied with regard to either the electron excitation to the conduction band, or to generation of one type of excitons. In rare cases only, several types of excitons differing in energy, symmetry or multiplicity can be excited in a single matrix in the available spectral range. This allows selective study of the subsequent transformations of these excitons. Among these compounds, crystals of inorganic nitrates are the most appropriate object to investigate.

Optical spectra of crystalline alkali nitrates are sufficiently well studied [1–3], and they are shown to weakly depend on the matrix cation [4–6]. Low-energy excited states of the nitrate ion have the symmetry (within the point group D_{3h}): $^1A_1^1$, $^3E_1^1$, $1^1E_1^1$ and $2^1E_1^1$, and they occur as a result of the transitions: $a_2^1 \leftarrow a_2^1$ ($\lambda_{\text{max}} \sim 300$ nm), $a_2^1 \leftarrow e^1$ ($\lambda_{\text{max}} \sim 250$ nm), $a_2^1 \leftarrow e^1$ ($\lambda_{\text{max}} \sim 200$ nm) and $a_1^1 \leftarrow e^1$ ($\lambda_{\text{max}} \sim 185$ nm), respectively [7].

The photolysis of crystalline alkali nitrates under excitation of the nitrate ion to $1E_1^1$ state [8–12] has been previously investigated using spectroscopy in the UV and IR ranges and chemical analysis of the exposed sample solutions. Generation of $1E_1^1$ states causes formation of nitrite and peroxynitrite ions.

Under the action of low pressure mercury lamp light with a quartz bulb ($\lambda = 254 + 185$ nm), i.e., under simultaneous excitation of $1E_1^1$ and $2E_1^1$ states [13,14] at 300 K, on the potassium nitrate using the EPR method, three paramagnetic centers (PC) were found to be formed. At low exposure doses, O^- and O_3^- oxygen radicals were observed, and at high doses, NO_2 nitrogen dioxide was detected additionally. Irradiation at 77 K does not result in the formation of NO_3 or NO_3^{2-} radicals.

Crystalline orbitals corresponding to the $2^1E_1^1$ nitrate ion state are split into the band, and consist mainly of nitrate ion orbitals with an insignificant contribution of the cation [15]. This suggests that the excited state $2^1E_1^1$ may result in separation of the charges with their subsequent localization on anions and formation of NO_3 and NO_3^{2-} radicals. Other possible mechanisms of chemical degradation of the excitation energy are related to isomerization and dissociation of the nitrate ion with the formation of peroxynitrite, nitrite and oxygen, and radical NO_2 , NO , O^- and O_2^- products.

In this research, we have studied the formation of paramagnetic and diamagnetic products of photochemical transformations in alkali metal nitrates under the action of UV light with a wavelength of 172 nm.

2. Experimental

Alkali nitrate crystals were grown by slow evaporation of saturated aqueous solutions of the salts. Optical spectra were recorded with the spectrophotometer Shimadzu 2450 at 300 K. IR

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spectra were recorded using the Fourier transform spectrometer Tensor 27 (Bruker) with a diffuse reflectance attachment at 300 K. The EPR spectra were recorded with the X-band spectrometer Bruker EMX Micro 6/1 at 77 K or 300 K. The photolysis was carried out by means of the xenon (172 nm) excimer lamp [16]. The quantum yields were calculated using the data on radiation intensity provided by the lamp manufacturer. Nitrite and peroxyxynitrite were detected in the solutions of the photolyzed samples. The analysis was performed according to the technique described in Ref. [17].

3. Experimental results

Photolysis of crystalline nitrates exposed to 172 nm light at 300 K results in the formation of nitrite and peroxyxynitrite ions detected in UV (Fig. 1) and IR spectra (Fig. 2) and also by chemical analysis. The nitrite and peroxyxynitrite spectroscopic parameters coincide with the parameters obtained for similar spectra of the nitrates exposed to 253.7 nm light [8,9,18,19]. The concentration of peroxyxynitrite ions achieves its stationary value within 2–3 min (Fig. 3). The nitrite ions, after the initial phase of rapid accumulation (10–15 s) continue to accumulate at a lower rate with the kinetics close to the linear one (Fig. 4). In NaNO_3 , we have not found ONOO^- in the solutions of the irradiated samples although in the IR spectrum of the exposed crystals, its bands can be observed at 766 and 1492 cm^{-1} . The ONOO^- band might be observed in the Raman spectrum at 1425 cm^{-1} [12].

The comparison of the initial quantum yields of nitrite and peroxyxynitrite obtained by photolysis at 172 nm and 254 nm (Table 1) demonstrated a significant increase in the nitrite yield and insignificant increase in the peroxyxynitrite yield. For cesium nitrate, the total quantum yield of the photolysis products is seen to almost achieve the theoretically possible value.

The formation of paramagnetic products in the photolysis of crystalline nitrates exposed to light with a wavelength of 172 nm at 300 K is not found. This may be the result of significant heating of the irradiated layer due to high density of the absorbed energy which leads to annealing of the radicals. The absorption coefficient of light with a wavelength of 172 nm in alkali nitrates is estimated as $\sim 10^5\text{ cm}^{-1}$ [21]. The lack of NO_3 and NO_3^{2-} radicals may be also attributed to insufficient spatial separation of the charges formed under photoexcitation, which leads to subsequent rapid recombination.

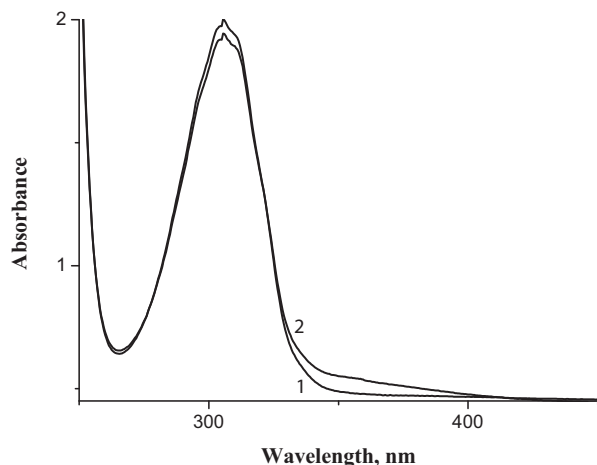


Fig. 1. Optical spectra of the CsNO_3 single crystal exposed to light with a wavelength of 172 nm at 300 K: before photolysis (1), after photolysis (2).

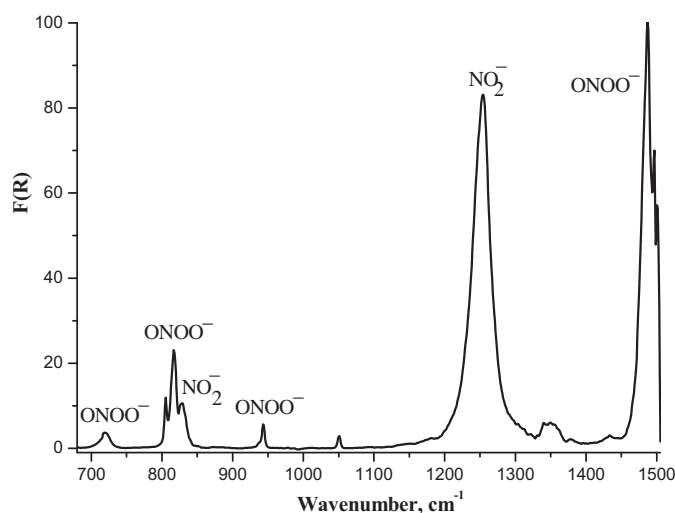


Fig. 2. IR spectrum induced by irradiation of KNO_3 at 172 nm.

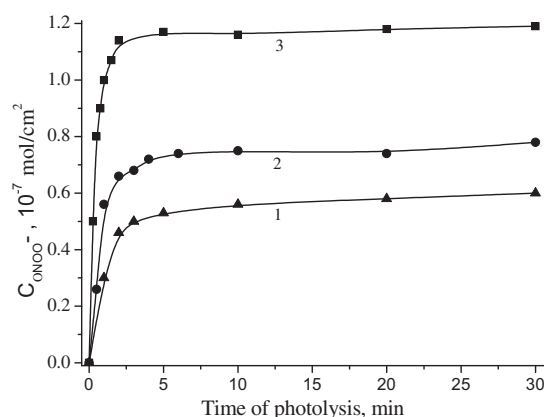


Fig. 3. Accumulation of peroxyxynitrite under photolysis of potassium (1), rubidium (2) and caesium (3) nitrates by light with a wavelength of 172 nm at 300 K. Chemical analysis.

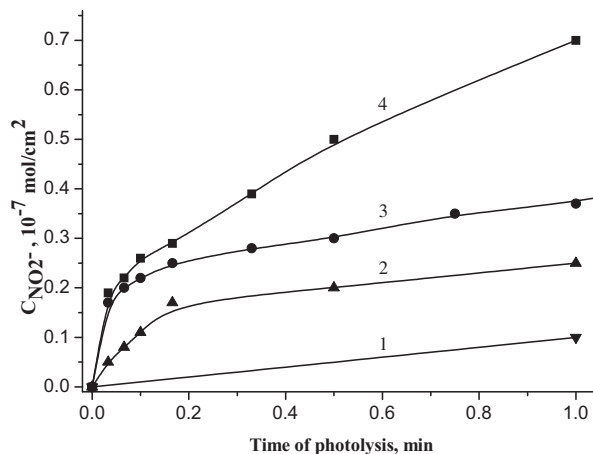


Fig. 4. Accumulation of nitrite under photolysis of sodium (1), potassium (2), rubidium (3) and cesium (4) nitrates by light with a wavelength of 172 nm at 300 K. Chemical analysis.

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