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The impact of univalent impurities on the efficiency of peroxynitrite formation under photolysis of crystalline alkali nitrates

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Abstract

The introduction of the thallium ions (I) into potassium nitrate crystals has been stated to result in the decrease of the quantum yield of peroxynitrite under photolysis (253.7 nm), which is due to lesser efficiency of its formation from the triplet excited state of the nitrate ion symmetry $^3E'$ than from the singlet one. The introduction of the nitrite ions into alkali nitrate crystals by means of co-crystallization is found out to result in the increase of the quantum yield of peroxynitrite, which is brought about by the increase of free volume in the neighborhood of impurity centers.

Keywords: Peroxynitrite; Photolysis; Alkali nitrate crystals; Nitrite; Thallium

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1. Introduction

The photo-decomposition of crystalline nitrates has been studied for more than 70 years. However, there are no systematic studies on the impact of any factors on the efficiency of photoproducts formation so far. Recently, it has been found out that it is peroxynitrite–oxoperoxonitrate (1-) that is the main product of transformation of the nitrate ion in solids under photolysis (253.7 nm) [1]. The decomposition of peroxynitrite under photolysis results in nitrite and oxygen [1,2]. It is evident that to find out the mechanism of the impact of any factors on photolysis of crystalline nitrates, it is necessary to study their influence on the efficiency of the peroxynitrite formation.

The goal of the present paper is to determine the effect of impurities on the quantum yield of peroxynitrite in UV-irradiated (253.7 nm) alkali nitrate crystals at varying their concentrations. The nitrite ions and the thallium (I) ions were chosen as impurities.

2. Experimental

Alkali nitrate crystals, both pure and doped, were grown by slow evaporation of saturated aqueous solutions. The nitrates and the nitrites used were a.r. grade (three times crystallized from redistilled water before use). NO_2^- was introduced into the alkali nitrate solutions in the form of corresponding nitrite salts. Tl^+ was introduced into the potassium nitrate solutions in the form of the nitrate salt. We failed to grow the crystals of other alkali nitrates doped with Tl^+. The shapes of both doped alkali nitrate crystals and pure crystals were the same. Alkali nitrate crystals containing impurities were washed with a saturated solution of the appropriate nitrate.

The concentration of impurities in the samples was calculated on the basis of the data on their concentration in the solution obtained after the dissolving of non-irradiated crystals. The procedure for the chemical analysis of nitrite was described earlier [3]. The concentration of the nitrite ions was 0.136–0.70, 0.029–0.627, 0.336–1.874 and 0.030–0.658 mol% in $NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$ crystals, respectively. The Tl^+ concentration in the doped KNO_3 crystals was determined by the iodinometrical method [4] and it was 0.058–1.20 mol%.

In every instance the plates (1 cm × 0.5 cm and thicknesses l varying from 0.0050 to 0.5000 cm), both pure and doped, were polished parallel to growth sides of $RbNO_3$ and $CsNO_3$ crystals, to the cleavage fracture of $NaNO_3$ crystals and to the crystallographic c-axis of KNO_3 crystals. It would be more convenient to prepare the plates suitable for optical measurements when the doped KNO_3 crystals are polished perpendicularly to the c-axis because in this case the absorption of non-polarized light by the

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plates is of isotropic character [5]. However, we failed to grow such crystals.

An analyzing and photolyzing non-polarized light beam was directed perpendicularly to the surface of the plates. The spectra were registered by means of a "SPECORD UV–VIS" spectrophotometer at room temperature. To increase the reliability of the data three to five crystals of each alkali nitrate were studied.

The samples were irradiated at room temperature with a low-pressure mercury lamp. After the irradiation, the samples could be stored in the dark at room temperature for 0.5–2 h (during this period of time the optical spectra of irradiated crystals remain unchanged) and analyzed within this period of time.

The incident light (253.7 nm) flux $I_0 = (1.6 \pm 0.1) \times 10^{15}$ photons $\mathrm{cm^{-2}\,s^{-1}}$ was measured by the method described elsewhere [6]. For the samples, partially absorbing the photolyzing light, the absorbed light flux I was determined as

$$I = I_0(1 - 10^{-A_{253.7}}) \quad (1)$$

where $A_{253.7}$ is the optical density of the crystal at 253.7 nm.

3. Results

Recently, it has been stated that the use of the potentiometric titration to determine the peroxynitrite in the nitrate crystals under short UV-exposition cannot be relied upon [7]. In addition, the chemical analysis to determine the concentration of peroxynitrite in the solution containing Tl^+ is impossible because of their redox properties. Therefore, the content of peroxynitrite in the samples has been determined in terms of its own optical absorption in irradiated crystals.

The evolution of the absorption spectrum of the starting pure $NaNO_3$ crystal with thickness 0.01 cm to the intermediate photoproducts is shown in Fig. 1. As seen, there appears a new band with its maximum at 339 nm, overlapping the 292 nm band of the non-irradiated $NaNO_3$ crystal. Because the nitrite ions, absorbing light in the optical region (320–400 nm) can be formed under photolysis of crystalline nitrates [1,2], then, to determine the nature of the photo-induced optical band, the $NaNO_3$ crystals doped with the nitrite ions were studied. The spectra of the non-irradiated doped $NaNO_3$ crystals (the concentration of the nitrite ions equal to 0.31 mol%) with dissimilar thicknesses are shown in Fig. 2.

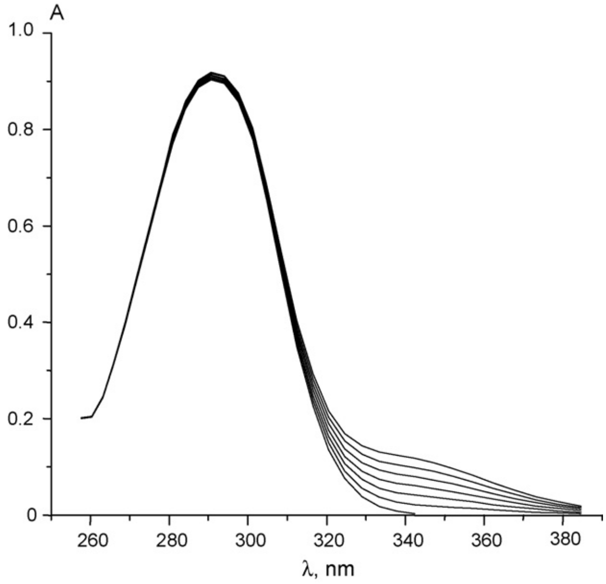

Fig. 1. Absorption spectra of the UV-irradiated $NaNO_3$ crystal with thickness 0.01 cm. Exposure time in the order of optical density increase—0, 10, 20, 30, 40, 50, 60 min.

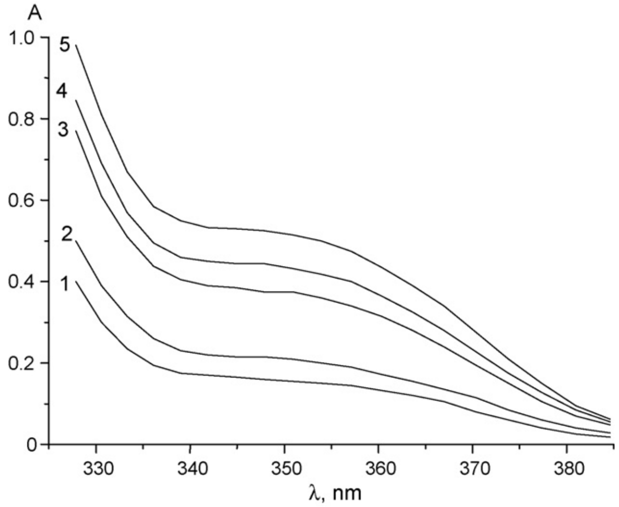

Fig. 2. Absorption spectra of $NaNO_3$ crystals doped with the nitrite ion (0.31 mol%). l = 0.082 (1), 0.092 (2), 0.122 (3), 0.131 (4) and 0.140 cm (5). An analyzing non-polarized light beam directed perpendicularly to the cleavage fracture of the crystals.

It can be assumed that the photo-induced optical spectra in the long-wavelength region for $NaNO_3$ crystal consist of a single band with its maximum at 339 nm due to peroxynitrite. This assumption can be supported by the following:

(i) the half-width of the photo-induced band ($H_{1/2}$ = 5500 $\mathrm{cm^{-1}}$) is similar to the half-width of the low-energy peroxynitrite absorption band in other alkali nitrate crystals [2,8];
(ii) the parameters of the low-energy absorption band ($\lambda_{max} \approx 351$ nm, $H_{1/2} \approx 2700\ \mathrm{cm^{-1}}$) due to the nitrite ions introduced into $NaNO_3$ crystals by co-crystallization (Fig. 2) differ from those of the photo-induced absorption band (Fig. 1);
(iii) the accumulation of optical density at 339 nm under irradiation of $NaNO_3$ crystals (Fig. 1) corresponds to the accumulation of peroxynitrite under long UV-exposition determined by potentiometric titration after the dissolving of irradiated samples [7].

On the basis of the data represented in Fig. 1 and in [7] it can be stated that the absorption of non-polarized light by peroxynitrite in the $NaNO_3$ crystals is isotropic and the value of molar absorptivity of peroxynitrite is equal to 1000 $\mathrm{M^{-1}\,cm^{-1}}$ (339 nm).

On the basis of the data represented in [2,7], the values of molar absorptivity of peroxynitrite in $RbNO_3$ and $CsNO_3$

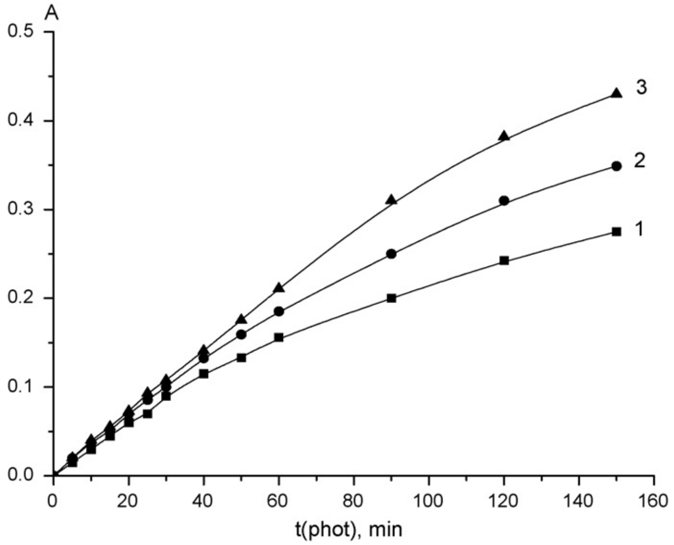

Fig. 3. The curves of optical density (339 nm) accumulation vs. photolysis time for doped $NaNO_3$ crystals with thicknesses 0.018 cm. The concentration of the nitrite ions equal to 0 mol% (1), 0.136 mol% (2) and 0.34 mol% (3).

crystals were calculated. They are equal to $3800\,M^{-1}\,cm^{-1}$ (343 nm) and $7100\,M^{-1}\,cm^{-1}$ (349 nm), respectively.

The accumulation curve of optical density at 339 nm under photolysis of $NaNO_3$ crystals containing $NaNO_2$ as an impurity is represented in Fig. 3. The accumulation curves of optical density (in the maximum of photo-induced optical band) for three other alkali nitrates crystals doped with the nitrite ions are similar.

The content of peroxynitrite N (mol/cm^2) in the UV-irradiated $NaNO_3$, $RbNO_3$ and $CsNO_3$ doped crystals was calculated in terms of Beer's law. In the KNO_3 doped crystals the content of peroxynitrite was calculated by the equation [9]:

$$N = A_{\max}(\alpha'\varepsilon^{\perp})^{-1} \tag{2}$$

where $A_{\max}$ is the optical density in the maximum of photo-induced absorption band; $\alpha' = [\alpha(m-1)+1]/m$; $m = \varepsilon^{\perp}/\varepsilon^{\parallel}$; $\alpha = (\cos^2\theta + 1)/2$; $\theta = 90°$ is the angle between the direction of light beam and the crystallographic c-axis of crystal, therefore α is equal to 0.5 [11]. The values $\varepsilon^{\perp}$ and $\varepsilon^{\parallel}$ when light beam is directed perpendicular to (i.e. an electrical field intensity vector $\boldsymbol{E}$ parallel to) and parallel to (i.e. an electrical field intensity vector $\boldsymbol{E}$ perpendicular to) the c-axis of crystal are equal to 3600 and $300\,M^{-1}\,cm^{-1}$, respectively [3]. Eq. (2) holds true if $A_{\max} < 0.15$ [9].

The values of initial peroxynitrite quantum yield in the samples with varying concentrations of nitrite impurity were calculated from the initial linear part of the accumulation curves. Fig. 4 displays the dependence of the quantum yield of peroxynitrite $\varphi_{\exp}$ from the nitrite impurity concentration in alkali nitrate crystals. As seen from Fig. 4, the peroxynitrite quantum yield increases with the impurity concentration.

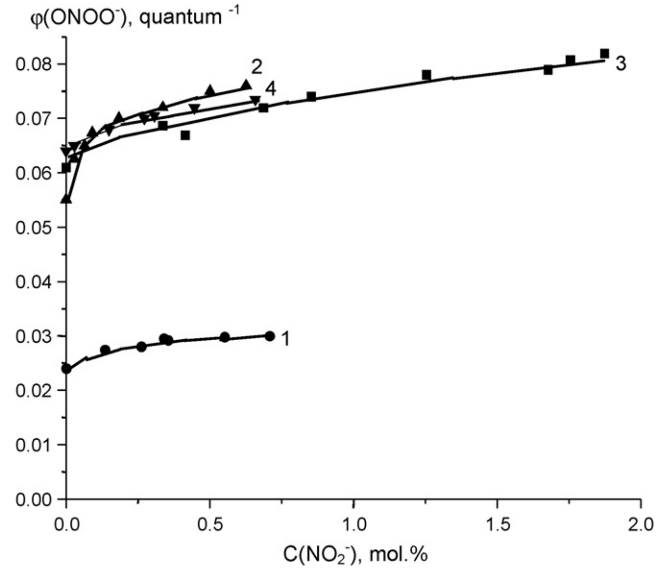

Fig. 4. The dependence of the peroxynitrite quantum yield value from nitrite impurity concentration under UV-photolysis of the crystalline alkali nitrates ($NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$—1, 2, 3 and 4, respectively).

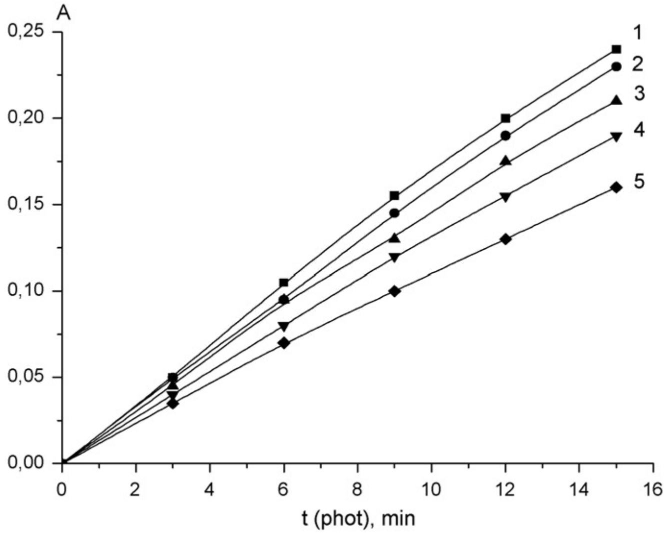

Fig. 5. The curves of optical density (349 nm) accumulation vs. photolysis time for the doped KNO_3 crystals with thicknesses 0.18 cm. The concentration of the thallium (I) ions equal to 0 mol% (1), 0.058 mol% (2), 0.076 mol% (3), 0.20 mol% (4) and 1.20 mol% (5).

The accumulation of optical density at 349 nm under photolysis of the KNO_3 crystals containing $TlNO_3$ as an impurity is represented in Fig. 5. The accumulation of peroxynitrite in the crystals was calculated by means of the method described above. The values of the peroxynitrite initial quantum yield in the KNO_3 crystals with different Tl^+ concentrations are represented in Table 1. As seen, increase in the impurity concentration results in the decrease of the quantum yield of peroxynitrite.

4. Discussion

4.1. Effect of the thallium (I) ions

Let us assume that the quantum yield of peroxynitrite in doped alkali nitrates depends on the available free space volume. It was stated that the quantum yields of peroxynitrite under UV-irradiation of pure $RbNO_3$ and $CsNO_3$ crystals with the same

Table 1
The value of peroxynitrite quantum yield in UV-irradiated KNO_3 crystals doped with Tl^+

$C(Tl^+) \times 10^{-6}$ (mol/g)	φ_{exp} (10^{-2} quantum^{-1})	I_{singl}/I_0 (%)
0	5.5 ± 0.1	90
5.8	5.3 ± 0.1	52
7.6	4.9 ± 0.2	47
20	4.3 ± 0.2	28
120	3.7 ± 0.2	6

type of the crystalline lattice were, in fact, the same (taking into account the experimental error) [7], i.e. they depend neither on the available free space volume (51.1 and 52.5 Å^3 for $RbNO_3$ and $CsNO_3$, respectively [10]) nor the nature of the cation. However, as is shown in the present paper, the introduction of Tl^+ into the crystalline lattice of KNO_3 (the ionic radius of Tl^+–1.48 Å is larger than the ionic radius of K^+—1.33 Å) results in decrease of the quantum yield of peroxynitrite by ~33%.

If the concentration of Tl^+ in the doped KNO_3 crystal is equal to 1.2 mol%, the available free space volume is equal to 54.96 Å^3, i.e. it reduces by 0.1% compared with the available free space volume of the pure KNO_3 crystal (55.0 Å^3 [10]). On the other hand, the available free space volume in the pure $RbNO_3$ crystal is ~3% less than in the pure $CsNO_3$ crystal. Hence, it is impossible to explain the decrease in the quantum yield of peroxynitrite under photolysis of KNO_3 crystals doped with Tl^+ by means of the available free space volume decrease.

Let us consider an alternative approach. In a pure KNO_3 crystal the optical absorption at 253.7 nm is due to two transitions into singlet and triplet high-energy excited states of the nitrate ion symmetry E′, with the ratio of their intensities ~10:1 [11]. The optical absorption at 240–260 nm increases when the thallium ions (I) are introduced into the KNO_3 crystal, though, thallium (I) ions do not absorb photolyzing light [11]. This can be explained by the increase of the oscillator strength of the transition into the high-energy excited state symmetry $^3E'$ of the nitrate ion in the doped crystals.

Based on the eigenvalues of the absorptivity tensor of a pure KNO_3 crystal at 253.7 nm [11] and the eigenvalues of the molar absorptivity tensor connected with the thallium (I) ions (2300 ($\boldsymbol{E} \perp \boldsymbol{c}$) and 280 ($\boldsymbol{E} \parallel \boldsymbol{c}$) $M^{-1}\,cm^{-1}$ [12]), the energy of photolyzing light responsible for exciting the $^1E'$ state of the nitrate ion was calculated for crystals with different impurity concentrations. These values are represented in Table 1. When peroxynitrite is formed only from singlet high-energy excited states of the nitrate ion $^1E'$, decrease in its quantum yield must be proportional to decrease in the energy of photolyzing light responsible for exciting the $^1E'$ state of the nitrate ion. From Table 1 it can be seen that the energy of photolyzing light responsible for exciting the singlet state $^1E'$ for the maximum impurity concentration is 15 times as less as for a pure sample and the value of the quantum yield is 1.5 times as less. Thus, peroxynitrite can be formed from high-energy excited states of the nitrate ion symmetry E', both singlet and triplet.

It is evident that the quantum yields of peroxynitrite from the singlet (φ_1) and the triplet (φ_3) states of the nitrate ion symmetry E' can be calculated from the experimentally observed quantum yield of peroxynitrite φ_{exp} in the KNO_3 crystal doped with Tl^+:

$$\varphi_{exp} = \frac{\varphi_1 I_{singl}}{I_0} + \frac{\varphi_3 I_{tripl}}{I_0} \tag{3}$$

where I_{singl}/I_0 and I_{tripl}/I_0 are the portions of irradiation energy responsible for exciting the nitrate ion in the singlet and the triplet states of symmetry E', respectively.

The experimental data (Table 1) can be described by a set of the equations, viz. Eq. (3), if the φ_3 and φ_1 values are equal to 0.034 ± 0.005 quantum^{-1} and 0.057 ± 0.005 quantum^{-1}, respectively.

Thus, the possibility of the peroxynitrite ions formation from the high-energy excited triplet states of the nitrate ions symmetry $^3E'$ in pure alkali nitrate crystals can be neglected.

4.2. Effect of the nitrite ions

It is experimentally stated that the absorption of photolyzing light by the nitrite ions introduced into the nitrate matrix by co-crystallization at the concentrations mentioned above can be neglected. Therefore, the mechanism for peroxynitrite formation under the photolysis of crystalline alkali nitrates can be presented by the scheme [2]. When crystalline alkali nitrates are irradiated by 253.7 nm light, the high-energy excited state of the nitrate ion $NO_3{}^{-*}$ (E') is formed:

$$NO_3{}^- + h\nu \rightarrow NO_3{}^{-*}(E') \tag{4}$$

with the quantum yield $\varphi(E')$ equal to 1. The nitrate ion in this excited state can be either transformed into the peroxynitrite ion:

$$NO_3{}^{-*}(E') \xrightarrow{k_1} ONOO^- \tag{5}$$

or relaxed into the low-energy excited state $NO_3{}^{-*}$ (A_1'') or into the ground state:

$$NO_3{}^{-*}(E') \xrightarrow{k_2} NO_3{}^-({}^1A_1') \quad \text{or} \quad NO_3{}^{-*}(A_1'') \tag{6}$$

The formation of additional peroxynitrite in the neighborhood of the nitrite ion impurity $(NO_2{}^-)_{doped}$ is described by

$$NO_3{}^{-*}(E') + (NO_2{}^-)_{doped} \xrightarrow{k_3} [ONO_2{}^- \cdots (NO_2{}^-)_{doped}] \tag{7}$$

As the excited state of the nitrite ion symmetry B_2 is close to the high-energy excited state of the nitrate ion symmetry E' [13], the latter may be deactivated by the nitrite ion impurity:

$$NO_3{}^{-*}(E') + (NO_2{}^-)_{doped} \xrightarrow{k_4} [Pr \cdots (NO_2{}^-)_{doped}] \tag{8}$$

The nitrate ion and/or the complex $[NO_2{}^- \cdots O]$ products (Pr) can be formed by the reaction (8).

Based on the steady-state concentrations of intermediate products which are the high-energy excited states of the nitrate ion $NO_3{}^{-*}$ (E'), the experimentally observed quantum yield of peroxynitrite can be described as

$$\varphi_{exp} = \frac{1 + k'[NO_2{}^-]}{(1/\varphi_0) + ((k' + k'')[NO_2{}^-]/\varphi(E'))} \tag{9}$$

Table 2
Kinetics parameters of the mechanism for the peroxynitrite accumulation under the photolysis of alkali nitrates doped with nitrite

Matrix	k' (10^{-19} cm^3)	k'' (10^{-19} cm^3)
$NaNO_3$	0.5	14.5
KNO_3	1.5	17.6
$RbNO_3$	1.0	9.4
$CsNO_3$	0.3	2.8

where $k' = k_3/k_1$; $k'' = k_4/k_1$; $\varphi_0 = \varphi(E')(k_1/(k_1 + k_2))$ is the quantum yield of peroxynitrite in a pure alkali nitrate crystal.

The values of k' and k'' constants were calculated from the data represented in Fig. 2 and summarized in Table 2.

Let us consider the factors accounting for increase in the quantum yield of peroxynitrite under photolysis of alkali nitrate crystals doped with the nitrite ion. When introduced into the nitrate matrix by co-crystallization, the nitrite ion displaces the nitrate ion in a regular lattice site. While the site that was occupied by one of the oxygen atoms in the displaced nitrate ion, becomes vacant, resulting in local free volume increase. Hence, to form the peroxynitrite ion from the high-energy excited state of the nitrate ion $NO_3{}^{-*}$ (E'), a reactionary volume oriented in a certain way in the crystalline lattice is needed.

5. Conclusion

The quantum yield of peroxynitrite increases at small concentrations of impurity nitrite ions. This can be accounted for by the fact that high-energy excitation states of the nitrate ion symmetry E', formed under photolysis of crystalline alkali nitrates, are transferred to another ions. These states can be transformed to form the peroxynitrite ion after having localized in the neighborhood of the impurity ions. A transfer of the excitation states of the nitrate ions can be realized under photolysis of water solutions of nitrates as well. If this is the case, the presence of impurities, which are deactivators of the excitation states of the nitrate ions, in a water solution can result in peroxynitrite quantum yield decrease under photolysis.

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