

The peroxyxynitrite formation under photolysis of alkali nitrates

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Abstract

The kinetics of peroxyxynitrite accumulation in UV-irradiated (253.7 nm) alkali nitrates has been studied. The quantum yield of peroxyxynitrite and its stationary concentration which can be created in a thin layer of the sample within a lengthy exposure have been calculated. The distance of the transfer of a low-energy excited state of the nitrate ion annealing peroxyxynitrite was stated to be $1.2 \text{ nm} < R_0 > 1.5 \text{ nm}$.

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1. Introduction

The peroxyxynitrite anion – oxoperoxynitrate (1–) (ONOO^-) – has attracted increasing interest in both the physiological process [1,2] and the photochemistry of an aqueous solution [3]. The decay of peroxyxynitrite was examined as the function of concentration, temperature, and pH [4]. During last 15–20 years there was a growth in interpreting the photolysis processes of crystalline nitrates. Peroxyxynitrite was stated to contribute much to the formation of final products of photodecomposition – nitrite and oxygen [5]. Based on the experimental data and the energy of excited states of the nitrate ion, the mechanism for the photolysis of solid nitrates qualitatively describing all the available experimental results was suggested [6]. However, the kinetic values characterizing the mechanism of peroxyxynitrite accumulation have not been determined so far.

First of all, it is due to a low sensitivity of the potentiometric method for the determination of peroxyxynitrite resulting in a large error in calculating the content of peroxyxynitrite in the sample after a short exposure for unrepresentative sampling [7].

Then, the inverse kinetics problem of the photolysis of solids in the absence of the diffusion of reaction products in the sample has been solved only for simple kinetic schemes. The attempt to experimentally overcome the difficulties arising when quantitatively analyzing the experimental results obtained for photolyzed potassium nitrate (by intensive mixing a fine powder under irradiation) turned out to be a failure because the present authors did not succeed in carrying out actinometry [5].

The goal of the present paper is to determine the kinetics of peroxyxynitrite accumulation under the photolysis of alkali nitrates followed by its analysis, which enables us to calculate kinetic parameters of the formation and the decay of peroxyxynitrite when the diffusion of photoproducts out of “cage” can be neglected as well as their reaction with water.

2. Experimental

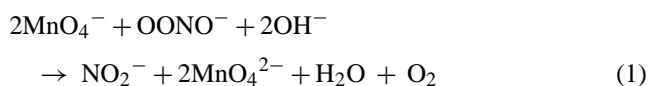
Alkali nitrate crystals were grown by slow evaporation of saturated aqueous solutions. The nitrates used were a.r. grade (three times crystallized from redistilled water before use). The samples were prepared by pressing the respective nitrates into tablets (2 cm^2 , $\sim 0.5 \text{ g}$). The samples were irradiated with a low-pressure mercury lamp at room temperature. After the

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irradiation the samples were stored at room temperature for at least 2 h and then analyzed.

The incident light flux, $I_0 = 1.6 \pm 0.1 \times 10^{15}$ photons $\text{cm}^{-2} \text{s}^{-1}$, was measured with potassium ferrioxalate as an actinometer [8].

The solution prepared by dissolving an irradiated nitrate tablet in 15 ml of 1 M solution KOH (pH ~ 13) was taken. The permanganate alkaline solution was made by adding 1 ml of 1 M KOH to 100 ml of $\sim 10^{-3}$ M solution of permanganate. The silver chloride electrode was used as the reference electrode and the platinum electrode as an indicator. It took 2 min for the potential to become constant after adding every other portion of the titrant. Peroxynitrite and potassium permanganate in alkali solution reacted with each other according to [9]



3. Results

The accumulation of peroxynitrite under the photolysis of crystalline alkali nitrates is represented in Fig. 1. The irradiation of the samples by the low-pressure mercury lamp light passed through the glass filter (>300 nm) does not result in the photo bleaching of peroxynitrite.

To estimate the uncertainty of the experimental procedure, the function of error distribution was determined. For this purpose, the bar graph of the variation range of calculated errors as the differences (D) between average values and replicate experimental values of the peroxynitrite content in UV-irradiated KNO_3 samples was plotted. The bar graph of the variation range is shown in Fig. 2. The number of observations in every experimental point amounted

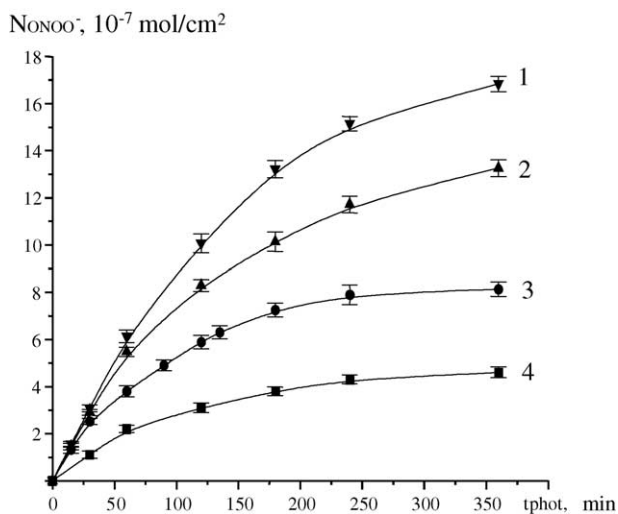


Fig. 1. The curves of peroxynitrite accumulation vs. photolysis time for alkali nitrates (1, 2, 3 and 4 – CsNO_3 , RbNO_3 , KNO_3 and NaNO_3 respectively).

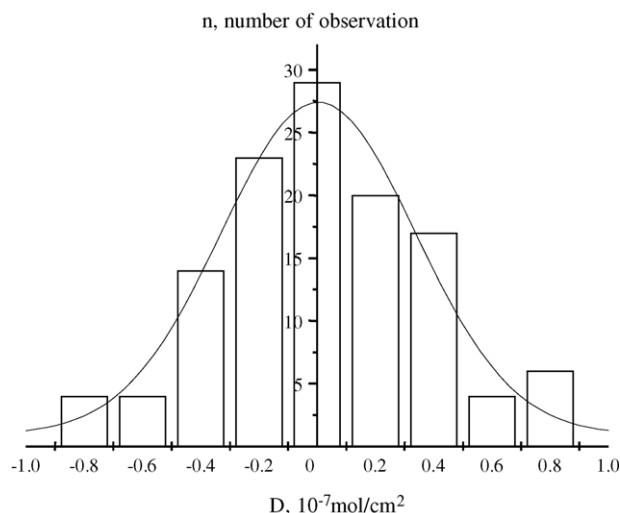


Fig. 2. The bar graph of the variation range of sampling of calculated errors of the peroxynitrite values in UV-irradiated KNO_3 samples (D – the differences between theoretical values and replicate values, N – the sampling frequencies) and the fitting curve of normal distribution.

from ~ 20 to ~ 30 . The analysis of the data represented in Fig. 2 in terms of the χ^2 -criterion confirms that the error distribution was described by the normal distribution. Thus, all the D differences could be attributed to the only one parent population and therefore, the pooled standard deviation was 4.5×10^{-8} mol/cm 2 for all the grouped data. The value of the pooled standard deviation for all alkali nitrates was also 4.5×10^{-8} mol/cm 2 .

Taking into account the peroxynitrite content in photolyzed crystalline alkali nitrates under short UV-exposition (see Fig. 1), it becomes evident that the value of uncertainty of the experimental procedure is close to the estimated values. For the confidence level 0.05 it can be calculated that a required number of n observations must be 9–12 with the accuracy $C \leq 10\%$ if peroxynitrite content in the sample is $\sim (1.5\text{--}2.0) \times 10^{-7}$ mol/cm 2 .

The values of peroxynitrite quantum yield were calculated on an initial linear part of the accumulation curves. The quantum yields are given in Table 1 and, as seen, they are less than those in [10]. This can be easily accounted for by an insufficient number (2–3) of observations, which, as shown above, leads to a large error in the determination of peroxynitrite at short exposures.

4. Discussion

The qualitative kinetic curve of the change of content of an initial substance and the products of its photolysis in the bulk of a solid sample differs from the qualitative kinetic curve of the change of its concentration in any thin layer of this sample. If diffusion does not occur and the transfer of matter into or out of the system has no effect on the chemistry, the concentration profile of the product formed during a one-step

Table 1
Kinetics parameters of the mechanism for peroxyxynitrite accumulation under the photolysis of alkali nitrates

Substances	C_∞ ($\times 10^{-2}$ mol/l)	$\varphi(\text{ONOO}^-)$ (quantum $^{-1}$)	k_3/k_5 ($\times 10^{19}$ cm $^{-3}$)	R_0 (nm)
NaNO $_3$	0.6	0.024 ± 0.006	7.0	1.5
KNO $_3$	2.4	0.055 ± 0.005	11.0	1.3
RbNO $_3$	2.3	0.061 ± 0.006	9.3	1.4
CsNO $_3$	2.5	0.064 ± 0.002	9.5	1.4

photochemical reaction under lengthy photolysis of the sample with a large optical density can be described by means of three areas. In the first area the concentration of the product is constant; in the second (the reaction area), the concentration of the product decreases from its value in the first area up to ~ 0 and in the third, the concentration is ~ 0 [11]. Thus, the accumulation of the photoproduct in solids is described by means of two stages. In the first stage the reaction area is formed, in the second it shifts into the depth of the sample parallel to the photolyzed surface without changing its shape.

Let us consider the mechanism described by a photochemical reaction of the product formation and fast (not limited) reactions of its decay. The product (peroxyxynitrite) does not absorb photolyzed light (253.7 nm [6]) and the amount of the initial substance decomposed can be neglected. Hence, based on formal kinetics (the surface illuminated by a uniform parallel beam of monochromatic radiation with the intensity I_0 , the exposure time being t), the stationary concentration of the product C_∞ is observed in the first area with thickness d . The continuation of irradiation results in the reaction area moving to a thin layer with thickness Δl within Δt_0 . The rate of light absorption in this layer is

$$\Delta I = e^{-Kd}(1 - e^{-K \cdot \Delta l})I_0 \cdot \Delta t_0 \quad (2)$$

where K is the host matrix absorptivity.

Further irradiation results in the reaction area moving to Δl within Δt_1 . Then, the rate of light absorption in the layer located at the distance $d + \Delta l$ from the illuminated surface is equal to the one calculated from Eq. (2):

$$\Delta I = e^{-K(d+\Delta l)}(1 - e^{-K \cdot \Delta l})I_0 \cdot \Delta t_1 \quad (3)$$

The product content in the sample increases by the ΔN value at the exposure time Δt_1 , hence $\Delta l = \Delta N/C_\infty$. From Eqs. (2) and (3) it follows that

$$\frac{\Delta t_1}{\Delta t_0} = \exp\left(-K \frac{\Delta N}{C_\infty}\right) \quad (4)$$

and

$$C_\infty = \frac{K \cdot \Delta N}{\ln(\Delta t_1/\Delta t_0)} \quad (5)$$

From Eq. (5) it follows that after the reaction area is formed, every other n -fold increase of exposure time results in ΔN increase of the product content in the sample. Also, if the mechanism of photolysis is described by a photochemical reaction of the product formation and by its first-order kinetics decay, the inverse kinetics problem can be solved in the analytical form.

The mechanism for peroxyxynitrite accumulation under the photolysis (253.7 nm) of crystalline alkali nitrates can be presented by the following simplified scheme [6] (Fig. 3), where NO_3^{*-} (E') is the high-energy excited state, NO_3^{*-} (A_1') is the low-energy excited state and NO_3^- ($^1A_1'$) is the ground state of the nitrate ion.

Application of the steady-state assumption for excited states of the nitrate ion gives

$$\frac{dx}{dt} = \varphi I_0 k' \left(1 - \frac{k''x}{x + k'''}\right) \quad (6)$$

which on integration gives

$$x + \frac{k''k'''}{k'' - 1} \ln\left(1 - \frac{k'' - 1}{k'''}x\right) = -(k'' - 1)k'\varphi_0 I_0 t \quad (7)$$

where $k' = \frac{k_1}{k_1 + k_2 + k_4}$, $k'' = \frac{k_2}{k_1}$, $k''' = \frac{k_3}{k_5}$, x is the concentration of peroxyxynitrite.

From Eq. (7) it follows that the quantum yield of peroxyxynitrite $\varphi(\text{ONOO}^-)$ is equal to $\varphi_0 k'$ and $k''' = C_\infty(k'' - 1)$. The quantum yield φ_0 of high-energy excited states of the nitrate ion NO_3^{*-} (E') is equal to 1.

To quantitatively determine C_∞ , the above procedure and the data on peroxyxynitrite accumulation were used. For the calculations, the host matrix absorptivities of single crystals of rubidium and cesium nitrates at 253.7 nm (36 and 34 cm $^{-1}$, respectively [12]) were taken instead of required absorptivity for polycrystalline samples.

Absorptivities (K_{calc}) for polycrystalline samples of sodium and potassium nitrates at 253.7 nm were calculated in terms of

$$K_{\text{calc}} = 2K_\perp + K_\parallel \quad (8)$$

where K_\perp and K_\parallel are eigenvalues of absorptivity tensor [13]. The obtained values were 36 ± 1 and 43 ± 1 cm $^{-1}$ for sodium and potassium nitrates, respectively.

The C_∞ values are given in Table 1. To compare these values for potassium nitrate with those in [5], the density of

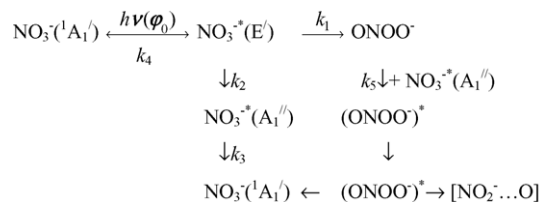


Fig. 3. Primary photoprocesses and subsequent reactions during crystalline alkali nitrates photolysis.

its fine powder was estimated. The density of a single crystal (2.11 g/cm^3) turned out to be 2–3 times more than for a fine powder. Thus, experimental and theoretical values are in a good agreement.

To estimate the k_3/k_5 ratio, two extreme cases should be considered. It is clear that k_2 cannot be less than k_4 . Let us consider the case when $k_2 \approx k_4$. Then the kinetic parameters are $\varphi(\text{ONOO}^-)(1+2k'')=1$ and $k''' = C_\infty(k'' - 1)$.

Thus, the final equation for k_3/k_5 is

$$\frac{k_3}{k_5} = \frac{C_\infty}{2} \left[\frac{1}{\varphi(\text{ONOO}^-)} - 3 \right] \quad (9)$$

The k_3/k_5 values are represented in Table 1.

When $k_2 \gg k_4$:

$$\frac{k_3}{k_5} = C_\infty \left[\frac{1}{\varphi(\text{ONOO}^-)} - 2 \right] \quad (10)$$

and k_3/k_5 is approximately twice as large as the one in Table 1.

The k_3/k_5 ratio is equal to the critical concentration of peroxyxynitrite $[\text{ONOO}^-]_0$:

$$[\text{ONOO}^-]_0 = \left(\frac{4}{3} \pi R_0^3 \right)^{-1} \quad (11)$$

where R_0 is the critical distance of energy transfer corresponding to the distance between the donor and the acceptor when the rate of energy transfer is equal to the rate of the deactivation of the donor in the absence of the acceptor. The values of the critical distance of energy transfer for alkali nitrates are shown in Table 1 ($k_2 \approx k_4$). When $k_2 \gg k_4$, R_0 is $\sqrt[3]{2}$ as less. Therefore, $1.2 \text{ nm} < R_0 < 1.5 \text{ nm}$ and the distance

of the transfer of a low-energy excited state of the nitrate ion annealing peroxyxynitrite is 1–2 constants of the lattice.

Acknowledgements

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