Conformer of the peroxynitrite ion formed under photolysis of crystalline alkali nitrates – cis or trans?

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Abstract. The optical and infrared reflectance spectra of the crystalline powders prepared by co-crystallization of caesium nitrate, nitrite, and peroxynitrite from alkali solution have been studied. We find that the trans conformer forms under photolysis of crystalline pure caesium nitrate. Under its dissolution the trans conformer transforms to the cis conformer.

1. Introduction

The peroxynitrite ion ($ONOO^-$) plays an important role in a variety of physiological processes [1-4] and in photochemistry of the nitrate ion [5-7]. It can exist in two geometric forms, as cis and trans conformer, due to the partial double bond between the nitrogen atom and the first peroxide oxygen atom [1]. On the basis of quantum chemical calculations it was concluded that in gas phase cis conformer is more stable than trans conformer [1,8]. In tetramethylammonium peroxynitrite crystal the peroxynitrite ion was observed in cis form [9]. Pfeiffer and Mayer suggested that in vivo peroxynitrite is formed in trans form [10]. Both forms were produced under UV irradiation (193 nm) of potassium nitrate in an argon matrix [11]. In some cases the geometric form of the peroxynitrite ion is not established [6,7]. So, the geometric form of the peroxynitrite ion in condense phase depends on the synthesis method. To describe the reactions involving the peroxynitrite ion need to know its geometric structure because it may play a major role in peroxynitrite reactivity [12].

The maximum position of the optical absorption band due to cis conformer of the peroxynitrite ion in aqueous solution should be observed at 310.4 nm while for the trans conformer at 338.8 nm based on Krauss' calculations [13]. Other calculations indicate that the maximum position should be observed at 303 and 374 nm for the cis and the trans conformer, respectively [14]. The absorption band due to peroxynitrite, synthesized from nitrite and hydrogen peroxide, observed in alkali solution has maximum position at ~302 nm [15]. The absorption maxima for KOONO, formed by photolysis of KNO_3 in solid argon matrix, were observed at 325 and 375 nm. These bands were attributed to absorption of cis and trans conformer, respectively [11]. Photolysis of crystalline potassium and caesium nitrates results in optical band at 350 and 355 nm, respectively, due to peroxynitrite [6,16]. It has been suggested that this band corresponds to absorption of trans conformer [17].

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For various quantum chemical methods calculated harmonic fundamentals for cis and for trans conformer of the peroxynitrite ion are dissimilar up to 250 cm^{-1} [18]. Moreover maxima of bands observed in IR spectra of the peroxynitrite ion in solids differ from the calculated data for cis and for trans conformer [11,18,19]. At the same time maxima of bands observed in laser Raman spectrum of the peroxynitrite ion synthesized from nitrite and hydrogen peroxide in alkali solution are close to the calculated data for cis conformer [1].

The goal of present work is to study optical and IR reflectance spectra of peroxynitrite, synthesized by different methods in alkali solution, introduced into caesium nitrate crystals by co-crystallization. Comparison of these spectra with corresponding spectra of peroxynitrite, obtained by photolysis of pure nitrate salt, will determine geometric form of it for the latter case.

2. Experimental

All chemicals used were analytical reagent grade or better. Saturated alkaline solutions of caesium nitrate (pH 13) were prepared by dissolution of appropriative amount of solid NaOH and solid

i) untreated salt;
ii) untreated salt and a small amount of caesium nitrite salt;
iii) photolyzed salt

(solutions 1-3, respectively). All the solutions were placed in Petri dishes. In addition, solution 4 was prepared by photolysis of Petri dish with solution 1. Caesium nitrate crystalline powders were grown by slow evaporation of the solutions during 24 h at room temperature. The powders before using were washed with saturated alkali solution of caesium nitrate and then they were stored at room temperature for 1 h.

Photolysis was carried out with a low-pressure mercury lamp with uviol glass at room temperature. Further in the text we denote used samples as follows:

- powder obtained from solution 1 is sample 1;
- powder obtained by photolysis of sample 1 during 1 h is sample 2;
- powders obtained from solutions 2-4 are samples 3-5, respectively.

The procedures for the chemical analysis of peroxynitrite and nitrite were described earlier [20]. Concentration of peroxynitrite in sample 2 and nitrite in sample 3 was ~10^{-5} mol/g and ~5×10^{-3} mol/g, respectively. Concentration of peroxynitrite in samples 4,5 was approximately 50 and 100 times smaller than in sample 2, respectively. Concentration of nitrite in samples 4, 5 was approximately a two hundred times smaller than in sample 3.

The optical and infrared reflectance spectra of the samples were recorded at room temperature by means of a "Shimadzu UV-2450" and Tenzor 27 spectrophotometers, respectively. To achieve good signal-to-noise ratio for IR reflectance spectra the results of 250 scans were accumulated and averaged.

3. Experimental results

Fig. 1 displays optical reflectance spectra of samples 1-5. The single band due to nitrate with maximum position at 306 nm for sample 1 was observed. As seen, spectra 2-5 differ from spectrum 1. Fig. 2 displays difference spectra calculated as the difference between spectra 2-5 and spectrum 1 (hereinafter, spectra 2'-5').

The broad band with maximum position at 359 nm and the narrow band with maximum position at 370 nm are observed in the spectra 2' and 3', respectively. The parameters of the former band are similar to the one for optical absorption band due to peroxynitrite in photolyzed caesium nitrate crystal [16], while the parameters of the latter band and its vibrational structure (indicated by arrows) are similar to the one of the optical absorption band due to nitrite introduce into caesium nitrate crystal by co-crystallization [21]. Based on these facts and the composition of samples 2 and 3 we can conclude that the band at 359 nm is due to peroxynitrite, and the band at 370 nm is due to nitrite.

The single weakly band with maximum position at ~310 nm is observed in spectrum 4'. Because sample 4 contains both nitrite and peroxynitrite, we can conclude that this band is due to the latter.

The spectra of samples 1-3 are identical. So, both nitrite, introduced into the powder by co-crystallization, and peroxynitrite, introduced into the powders by UV irradiation, has not band in this region of the infrared reflectance spectra. As seen, in the infrared reflectance spectra of samples 4 and 5 two bands at 630 and 640 cm^{-1} were observed. These bands unstable and they are not registered in the infrared reflectance spectra after storage for 24 hours at room temperature. Simultaneously peroxynitrite completely decay, based on the data of chemical analysis. So, it can be concluding that bands at 630 and 640 cm^{-1} are due to peroxynitrite.

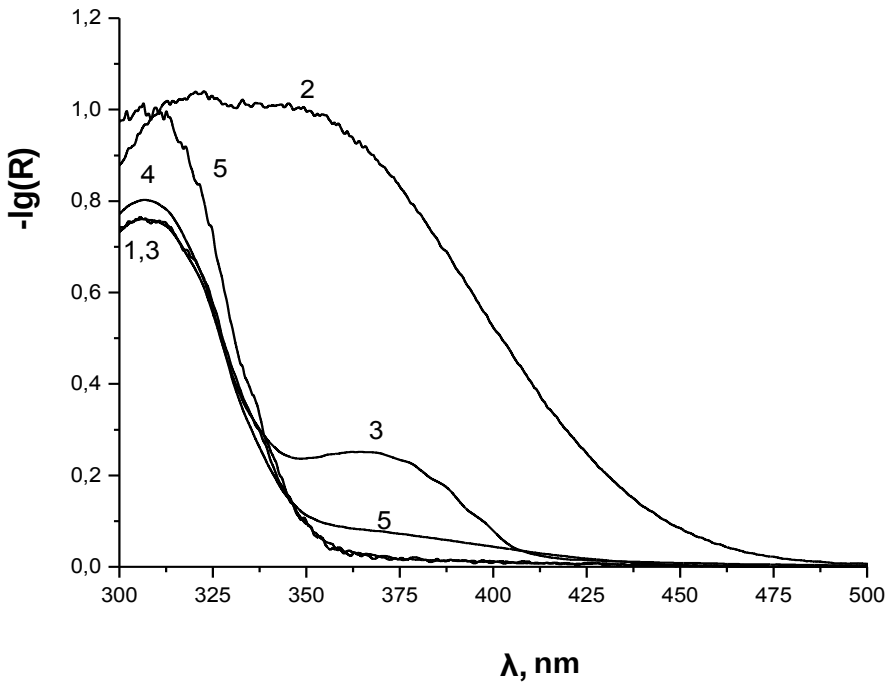


Figure 1. Optical reflectance spectra of the samples 1-5 (1-5, respectively).

The spectrum 5’ consists of two bands. The band in the long-wavelength region with maximum position at ~370 nm can be represented as a superposition of the bands in the spectra 2’ and 3’. The shape of the band in the short-wavelength region with maximum position at ~310 nm is similar to the shape of the band in the spectrum 4’. So, spectrum 5’ can be described as superposition of spectra 2’-4’, and it is due to nitrite and peroxynitrite.

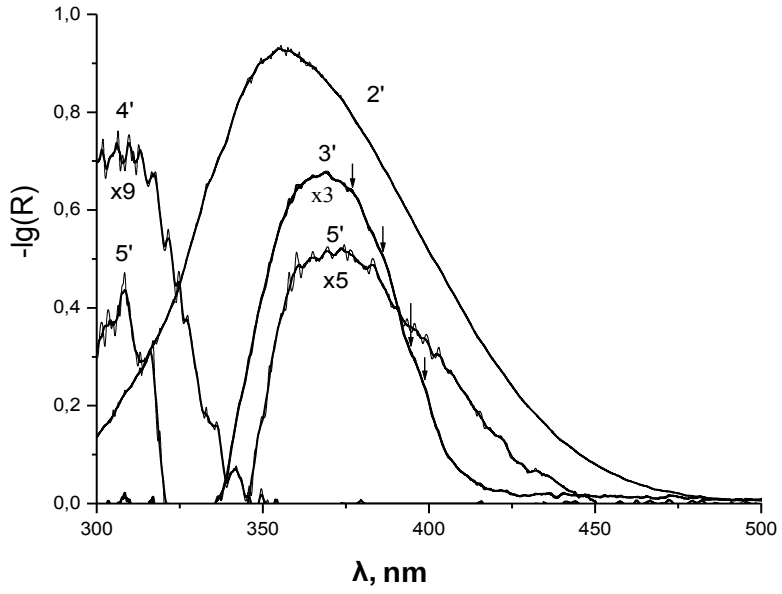


Figure 2. Difference spectra of the samples 2-5 (2'-5', respectively).

Fig. 3 displays the infrared reflectance spectra of samples 1-5.

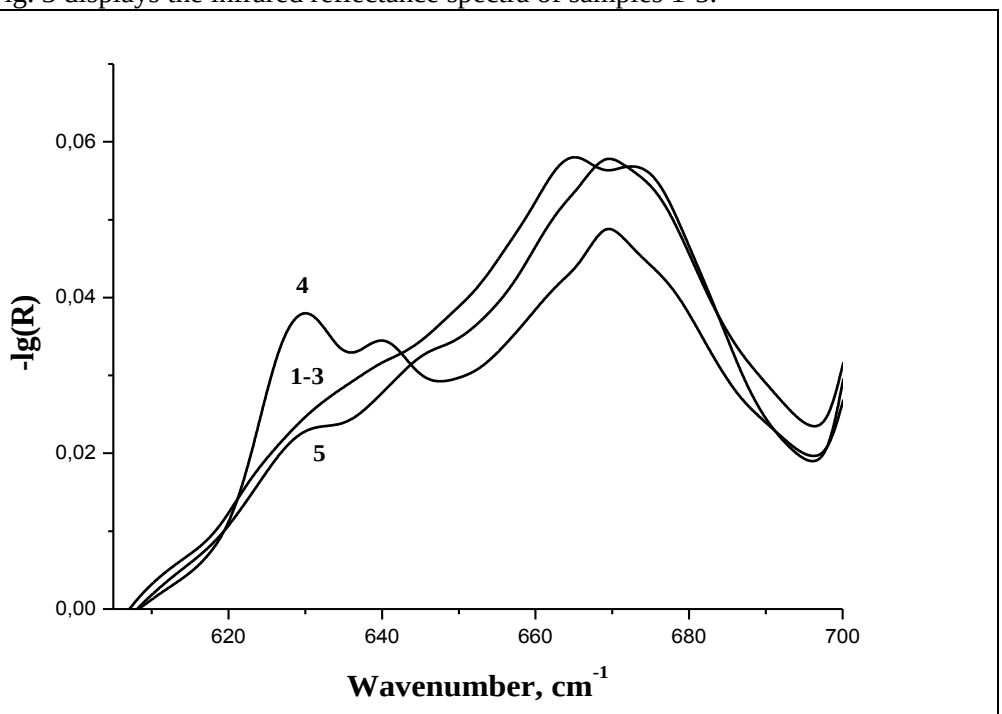


Figure 3. IR spectra of the samples 1-5 (1-5, respectively).

4. Discussion

Comparison of the optical and infrared reflectance spectra of UV irradiated samples 2 with the spectra of the sample 4, contained peroxynitrte introduced by co-crystallization, data of chemical analysis on

peroxynitrite, and stability of it in the corresponding samples allow us to suggest that spectroscopic parameters of peroxynitrite in sample 2 differ from the one in the sample 4. Since, peroxynitrite in aqueous alkali solution is in cis form [14,15] then in sample 4 it should be in this form. So, peroxynitrite in sample 2 must be in trans form and its formation under photolysis can be represented as follows

$$NO_3^-(solid) \xrightarrow{h\nu(253.7nm)} trans-ONOO^-(solid).$$

Trans conformer transform to more stable in aqueous alkali solution cis conformer under dissolution

$$trans-ONOO^-(solid) \rightarrow cis-ONOO^-(aq)$$

and this conformer introduce to crystal lattice under co-crystallization

$$cis-ONOO^-(aq) \rightarrow cis-ONOO^-(solid).$$

From our experimental data it follows that peroxynitrite in sample 5 is in cis and trans forms. Because peroxynitrite in aqueous alkali solution is stable as cis conformer then trans conformer in sample 5 can be form under photolysis of powder which lies at the bottom of a Petri dish. It could be argued that in crystalline caesium nitrate cis conformer in contrast with trans conformer is unstable and it isomerizes into the nitrate ion during storage.

5. Conclusion

Dissolving of UV irradiated samples generate in a solution trans conformer of the peroxynitrite ion. So, it allows us to study its chemical reactions and it would be useful to explain a variety of physiological processes involving the trans conformer of the peroxynitrite ion.

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