The mechanism of radiolysis of alkaline-earth nitrates

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Abstract. The formation of peroxynitrite and nitrite in crystalline alkaline-earth nitrates under \( \gamma \)-irradiation at 310 K by optical reflectance spectroscopy has been studied. The radiolysis of \( \text{Sr(NO}_3\text{)}_2 \) and \( \text{Ba(NO}_3\text{)}_2 \) results in nitrite and peroxynitrite, \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) and \( \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) – nitrite. The mechanism for nitrite and peroxynitrite formation under \( \gamma \)-irradiation of crystalline alkaline-earth nitrates has been discussed.

1. Introduction
The radiolysis of solid inorganic nitrates has brought forth numerous experimental studies [1-6]. Gamma radiolytic decomposition of nitrates is known to produce nitrite – \( \text{NO}_2^- \). Recently, it has been found out that it is peroxynitrite – \( \text{ONOO}^- \) that is one of the radiolysis products of crystalline alkali nitrates [6-8]. The analysis of literature data shows that peroxynitrite is formed from high-energy excited state of the nitrate ion – \( \text{NO}_3^-*(>4.8 \text{ eV}) \) both in water solution [9] and in solids [6]. Since \( \text{NO}_3^-* \) can be formed under radiolysis of alkaline-earth nitrates it can be assumed that peroxynitrite can be formed too.

In this paper, the formation of peroxynitrite and nitrite under \( \gamma \)-irradiation of crystalline alkaline-earth nitrates by optical reflectance spectroscopy was studied to develop the mechanism of solid nitrates radiolysis.

2. Experimental
All nitrates used were analytical reagent grade. All solutions were prepared in doubly distilled water. The powders of barium, strontium, calcium, and magnesium nitrates were grown by slowly evaporating from the solutions. The presence of crystallization water in calcium and magnesium nitrate crystals was indicated by absorption in the ranges 3200-3900 and 1400-1800 cm\(^{-1}\) of the IR reflectance spectra. The formulas \( \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) and \( \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) were determined based on the water content in crystalline hydrates.

The samples were irradiated with \(^{60}\text{Co} \) \( \gamma \)-rays at \( \sim 310 \text{ K} \). The dose rate 0.16 Gy/s was measured with a Fricke dosimeter, assuming the radiation chemical yield of \( \text{Fe}^{3+} \) to be equal to 15.6 \( \text{(100 eV)} \)\(^{-1}\). The dose absorbed by the sample was calculated using the mass energy absorption coefficients.

The optical reflectance spectra of both untreated and irradiated crystalline samples were recorded by means of a “Shimadzu UV-2450” spectrophotometer at room temperature. Figure 1 displays the optical reflectance spectra of untreated alkaline-earth nitrates. The band with maximum position at
293, 282, 271, and 275 nm for Mg(NO$_3$)$_2$·6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Sr(NO$_3$)$_2$, and Ba(NO$_3$)$_2$, respectively, was observed.

The infrared reflectance spectra of untreated samples were recorded at room temperature by means of a FSM 1201 spectrophotometer.

3. Results

Irradiation of the samples up to ~70 kGy results in new band in the optical reflectance spectra (Figures 2 and 3), whose maximum position at 344, 348, 335, and 338 nm for crystalline Mg(NO$_3$)$_2$·6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, Sr(NO$_3$)$_2$, and Ba(NO$_3$)$_2$, respectively, is observed. The spectra of irradiated alkaline-earth nitrates are stable at room temperature. The maximum position of the broad band in γ-irradiated Sr(NO$_3$)$_2$ and Ba(NO$_3$)$_2$ are similar to the one of the optical absorption band due to peroxynitrite in these photolyzed crystals (333 and 340 nm, respectively) [10]. Based on this fact and the shape of the band it can be assumed that γ-induced band in the optical reflectance spectra due to peroxynitrite.

In contrast, the maximum position of the narrow band in γ-irradiated crystalline Mg(NO$_3$)$_2$·6H$_2$O and Ca(NO$_3$)$_2$·4H$_2$O are dissimilar to the broad band due to peroxynitrite in these photolyzed crystals (maximum position at 322 and 319 nm, respectively) [10]. Taking into account

i) the parameters of optical absorption band due to nitrite in alkali nitrates crystals doped with nitrite [8, 11];

ii) the parameters of optical absorption band due to nitrite in γ-irradiated RbNO$_3$ and CsNO$_3$ crystals [8];

iii) the details of the radiation-induced absorbance 320-380 nm with fine structure of at least nine peaks (see Table). They are similar to the fine structure of radiation-induced absorbance 320-380 nm, as detectable in irradiated NaNO$_3$ and KNO$_3$ crystals with absorbed doses 160 kGy [12] (see Table) due to species contains the O-N=O grouping,

we can conclude that radiation-induced band in γ-irradiated crystalline Mg(NO$_3$)$_2$·6H$_2$O and Ca(NO$_3$)$_2$·4H$_2$O is due to nitrite. It can be assumed that the observed band is a superposition of three individual bands which maximum position shifted relative to each other by 5-7 nm, because in the NaNO$_2$ crystal the vibration frequencies for the nitrite ion $v'_1$ and $v''_2$ in the B$_1$ state are equal to 1020 and 630 cm$^{-1}$, respectively [13].

Taking into account the fact that radiolysis of alkaline-earth nitrates results in nitrite, and based on our experimental results we can conclude that radiolysis of crystalline Sr(NO$_3$)$_2$ and Ba(NO$_3$)$_2$ results in nitrite and peroxynitrite, and crystalline Mg(NO$_3$)$_2$·6H$_2$O and Ca(NO$_3$)$_2$·4H$_2$O – nitrite.
4. Discussion
Since peroxynitrite, formed under photolysis of crystalline hydrated alkaline-earth nitrates, is stable [10], and it does not register in the optical reflectance spectra of γ-irradiated crystalline Mg(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O, we can conclude that the high-energy excited state of the nitrate ion, resulting in peroxynitrite formation, is not formed. A mechanism of the water effect on the radiolysis of crystalline hydrated alkaline-earth nitrates can be discussed based on the pathways of degradation of electronic excitations formed under irradiation.

Table. Fine-structure peak positions (nm) of optical absorption in γ-irradiated NaNO₃ and KNO₃ [12], optical reflectance absorption in irradiated Mg(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O.

|        | NaNO₃ | KNO₃ | Mg(NO₃)₂·6H₂O | Ca(NO₃)₂·4H₂O |
|--------|-------|------|---------------|--------------|
| 343    |       | 342  | 358           |              |
| 349    |       | 349  | 358           | 362          |
| 355    |       | 356  | 358           | 356          |
| 360    |       | 362  |               | 362          |
| 370    | 372   | 372  | 375           | 374          |
| 378    | 380   | 381  | 378           |              |
| 388    |       | 386  | 387           |              |

Theoretical or experimental study of the energy bands structure of crystalline hydrated alkaline-earth nitrates is not available in the literature; therefore we consider the one for crystalline alkali nitrates. The structure of energy bands for them is characterized by the discontinuity of the spectrum of the vacant state [8] to result the first narrow conductivity band. The maxima in electron state densities corresponding to the first and the second conductivity bands are in the ~4 and ~10 eV regions, respectively, if the energy of the last occupied state is assumed to be zero. For alkaline-earth nitrate crystals the location of bands can be shifted as much as ~1 eV.

The initial stage of the radiolysis of crystalline alkali nitrates results in the charges with holes in valence band and electrons in the second conductivity band. Anan’ev and Seliverstov [8] suggested...
that an electron from this band can relax to the first conductivity band to generate ~ 6 eV with subsequent formation of a high-energy excited state of the nitrate ion. Triplet high-energy excited state of the nitrate ion can be dissociated to form the nitrite ion and singlet ones can be transformed to form the peroxynitrite ion. Electrons from the first conductivity band and the holes from the valence band can be recombined without dissociation. It can be assumed that this mechanism is suitable for anhydrous alkaline-earth nitrates based on the fact that under \( \gamma \)-irradiation nitrite and peroxynitrite are formed.

We assume, that in hydrated alkaline-earth nitrates, when an electron from the second conductivity band relax to the first conductivity band it generate energy sufficient for the ionisation of the water molecule to produce the complex \([e^-, H_2O^+]\). At the same time a high-energy excited state of the nitrate ion does not form.

The mechanism of formation of radiolysis product, taking into account the fact that reactions occur in "cage", is following. Electron, formed under the ionisation of the water molecule, reacts either with the nitrate ion \((k < 1\cdot10^{10} \text{ M}^{-1}\text{c}^{-1})\) to produce excited radical \((\text{NO}_3^2^-)^*\)

\[
\text{NO}_3^- + e \rightarrow (\text{NO}_3^2^-)^*
\]

or with water molecule (hereinafter all rate constants are determined for water solution [14, 15])

\[
e^- + H_2O \rightarrow e^- + OH^* + H^+
\]

Electron fast react with \(H^+ (k = 2.2\times10^{10} \text{ M}^{-1}\text{s}^{-1})\)

\[
e^- + H^+ \rightarrow H^*
\]

OH• react with the nitrate ion \((k < 1\cdot10^5 \text{ M}^{-1}\text{c}^{-1})\) rather than \(H^* (k = 2.4 \text{ M}^{-1}\text{c}^{-1})\)

\[
\text{NO}_3^- + OH^* \rightarrow \text{NO}_3^- + OH
\]

Formed under former reaction \(H^* \) react with \(\text{NO}_3^- (k = 2.4\times10^7 \text{ M}^{-1}\text{s}^{-1})\)

\[
\text{NO}_3^- + H^* \rightarrow \text{HNO}_3^-
\]

Excited radical \((\text{NO}_3^2^-)^*\) either relax to ground state

\[
(\text{NO}_3^2^-)^* \rightarrow \text{NO}_3^2^-
\]

or dissociate to produce the nitrite ion

\[
(\text{NO}_3^2^-)^* + H_2O \rightarrow \text{NO}_2^- + OH^- + OH
\]

Reaction of water molecule with \(\text{NO}_3^2^- (k = 5.5\times10^4 \text{ s}^{-1})\) results in the radical \(\text{NO}_2^-\)

\[
\text{NO}_3^- + H_2O \rightarrow \text{NO}_2^- + 2OH
\]

\(\text{HNO}_3^*\) may dissociated to produce the radical \(\text{NO}_2^-\) too

\[
\text{HNO}_3^* \rightarrow \text{NO}_2^- + OH
\]

The reaction of both \(\text{NO}_2^-\) and \(\text{NO}_3^-\) with water results in the nitrite ion under dissolving of irradiated samples.

Thus, it is possible to consider the radiolysis of hydrated alkaline-earth nitrates as the one of water solution of the nitrate salts.

5. Conclusion

The mechanism of the radiolysis products formation in hydrated and anhydrous alkaline-earth nitrates can be accounted for by the peculiarities of degradation of electronic excitation. This mechanism allows us to explain the fact why radiation-chemical yield of nitrite in hydrated alkaline-earth nitrates is higher than that for anhydrous nitrates [16, 17]. This is due to
i) energy of irradiation is mainly spent on the formation of the complex \([e^-, H_2O^+]\), but not on the formation of high-energy excited state of the nitrate ion;
ii) the value of rate constant for reaction of the nitrate ion with electron resulting in excited \((\text{NO}_3^2^-)^*\) formation is very fast.

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