

**ACTION OF
\$\gamma\$-RADIATION
FROM
\$\mathrm{Co}^{60}\$ ON
\$\mathrm{Ca}(\mathrm{NO}_3)_2 \cdot
4\mathrm{H}_2\mathrm{O}\$**

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Abstract

Full Text

PHYSICAL CHEMISTRY

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**ACTION OF γ -RADIATION FROM Co^{60} ON
 $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$**

(Presented by Academician V. A. Kargin, 21 III 1958)

The formation of compounds of the type $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ may be regarded as a special case of the formation of complex compounds. Owing to the neutrality of water molecules, the complex ions formed in this case retain the same charge as that possessed by the complex-forming species. The ion acting as the complex-forming species may be either the cation or the anion of the salt.

The absence of data on the internal structure of the overwhelming majority of crystalline hydrates and on their properties makes it impossible to outline any regularities in their stability. It has only been established that an increase in the charge and a decrease in the volume of the cation usually promotes an increase both in the number of molecules of water of crystallization and in the strength of their bond.

The radiation stability of crystalline hydrates has scarcely been studied at all. Only the works of Doigen and Davis ⁽¹⁾ on the photochemical decomposition of lanthanum nitrate crystalline hydrate and of Hohanadel and Davis ⁽²⁾ on the action of γ -radiation on aqueous lanthanum nitrate are known. In these works it is merely noted that aqueous lanthanum nitrate decomposes at a higher rate than the anhydrous salt.

In order to elucidate the principal features of the behavior of crystalline hydrates of inorganic salts under the action of radiation, as compared with anhydrous salts and concentrated solutions, several series of experiments were carried out with solid calcium nitrate— $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Salt of chemically pure grade was irradiated in vacuum at a temperature of 25°. A number of experiments were carried out with melts of calcium nitrate. The melts were prepared by melting the salt in vacuum and were supercooled solutions (supercooling temperature 30°), which remained for a long time without separation of crystals. Co^{60} with a dose rate of $6.2 \cdot 10^{19}$ eV/g · h was used as the radiation source.

Qualitative and quantitative determination of the gaseous products of decomposition of the salt was carried out in a microburet for gas analysis. The accuracy of measurement was 2-3%. Nitrite was determined colorimetrically by the method developed by Mikhalchuk and Osherovich ⁽³⁾. The measurement error

Fig. 1. Dependence of the amount of nitrite formed on the irradiation dose: 1—solid $\text{Ca}(\text{NO}_3)_2$, 2—solid $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 4—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with addition of glucose.

Figure 1: Fig. 1. Dependence of the amount of nitrite formed on the irradiation dose: 1—solid $\text{Ca}(\text{NO}_3)_2$, 2—solid $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 4—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with addition of glucose.

was $5 \cdot 10^{-7}$ mole of nitrite ion per gram of salt. As a result of the experiments carried out, it was established that aqueous calcium nitrate is destroyed under the action of γ -radiation with formation of nitrite and oxygen. Similarly

Table 1

Object irradiated	$G_{\text{NO}_2^-}$, mol/100 eV	Electrons for the dose of NO_3^-	$G_{\text{NO}_2^-}^a$, mol/100 eV	G_{O_2} , mol/100 eV
Solid $\text{Ca}(\text{NO}_3)_2$	0.2 ± 0.01	0.78	0.25	—
Solid $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.77 ± 0.02	0.52	1.5	0.37 ± 0.02
Melt $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.07 ± 0.01	0.52	0.13	0.02 ± 0.01
Melt $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with addition of glucose	0.26 ± 0.01	0.52	0.5	0.02

in the case of irradiation of solid anhydrous nitrate salts, the oxygen formed in the course of irradiation remains predominantly inside the crystals. After melting the irradiated salt, it is possible to obtain an amount of oxygen equivalent to the nitrite formed.

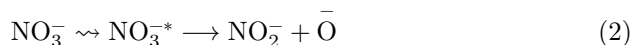
Figure 1 gives the dependences of the amount of nitrite formed on the irradiation dose. In the left part of the figure the curves are given for the solid crystalline hydrate and the solid anhydrous salt, and in the right part—for the melt and for the melt with addition of glucose.

Fig. 1. Dependence of the amount of nitrite formed on the irradiation dose: 1—solid $\text{Ca}(\text{NO}_3)_2$, 2—solid $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 4—melt of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with addition of glucose.

Table 1 gives data on the yield of nitrite and oxygen per 100 eV. Here the G' -values are G -values, referred to the ratio of the number of electrons in the nitrate ion to their total number in the salt.

At present, the radiation stability of a fairly large number of solid nitrates has been studied (⁴⁻⁶). The primary process of interaction of an ionizing particle with a substance consists in the transfer of part of the energy to one of the electrons of the molecule. It is assumed that approximately half the energy of the ionizing particle is spent on ionization, and the other half on excitation of molecules. The subsequent behavior of ionized and excited molecules depends strongly on the state of aggregation and on the physicochemical properties of the medium.

In anhydrous nitrates the principal transformation processes may be considered to be:



The share of the transformation due to each of these processes is unknown. The oxygen split off in reaction (2) apparently remains in the immediate vicinity of the NO_2^- ion, and the reverse reaction of formation of nitrate from nitrite and oxygen plays an essential role. The possibility of the reverse reaction was shown by us using potassium nitrate as an example (⁷).

In the case of crystalline hydrates, water molecules may be regarded as an impurity which can also undergo ionization and capture electrons. It is obvious that the two transformation processes of the nitrate ion under the action of radiation cited above will also take place in the crystalline hydrate. Further, if a water molecule is capable of capturing an electron, then



The hydrogen atom formed may interact with a nearby NO_3^- ion, giving a nitrite ion.

As noted above, in anhydrous salts the reverse reaction of oxidation of nitrite by oxygen takes place. In the case of crystalline hydrates, the rate of the reverse reaction apparently drops sharply owing to the structural features of the crystalline hydrate, and the oxygen atom formed by reaction (2) may react with a nearby NO_3^- ion, giving NO_2^- and O_2 .

Apparently, the combination of these two factors can explain the increase in the yield of nitrite in the crystalline hydrate as compared with the anhydrous

Fig. 2. Dependence of the nitrite yield on the concentration of calcium nitrate

Figure 2: Fig. 2. Dependence of the nitrite yield on the concentration of calcium nitrate

salt. The structure of very concentrated solutions of inorganic salts has been studied by a number of authors^(8,9). The general conclusion that may be drawn from these works is that, with increasing concentration of the solution, the distribution of ions in the solution tends toward the distribution characteristic of crystalline hydrates. In our case, if the concentration of nitrate in the melt is recalculated to the water of crystallization, we obtain approximately a 26M solution of $\text{Ca}(\text{NO}_3)_2$, and the distribution of ions in it will apparently differ little from their distribution in the crystalline hydrate. Obviously, all three transformation processes—ionization, excitation, and the influence of water molecules—will also apply to this system. However, the share of each of these processes in the total yield of nitrate conversion into nitrite will differ from their share in the solid crystalline hydrate.

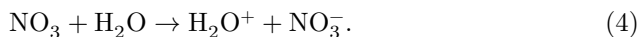
Fig. 2. Dependence of the nitrite yield on the concentration of calcium nitrate

Most authors who have studied concentrated nitrate solutions observed a sharp increase in the nitrite yield (up to 4.5 mol/100 eV) in the concentration region from 0.1 to 2 M. The explanation of this effect was associated with the possibility of a direct action of radiation on the NO_3^- ion.

The effect we observed—a sharp decrease in the nitrite yield in the melt as compared with the solid crystalline hydrate—led us to investigate the radiation-chemical stability of calcium nitrate over a wide concentration range, from 0.1M to 26M.

The dependence of the nitrite yield on the concentration of calcium nitrate is shown in Fig. 2. Indeed, in the concentration region up to 2M a sharp increase in the nitrite yield is observed (up to 5.4 mol/100 eV). At higher concentrations the curve falls sharply, which argues against the assumption of the effectiveness of direct action of radiation on the nitrate ion.

In our opinion, the reason for the decrease in the nitrite yield in strongly concentrated solutions may be the reaction



The NO_3 radical formed in this case may prove stable, surviving until the reaction $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$ or a similar reaction that lowers the effectiveness of the process. Upon solidification of the melt and ordering of the ion arrangement in the crystal lattice, the minimum distances between the H_2O^+ ion formed during radiolysis and the nearest NO_3^- ion increase, and the formation of the NO_3 radical becomes difficult. The nitrite yield observed in the melt should apparently be attributed to the direct action of radiation on the nitrate anion. This

type of assumption does not exclude the possibility of partial conversion at the expense of products of water radiolysis, as is confirmed by introducing into the melt an acceptor of OH radicals—glucose.

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