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Abstract

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On the Radiation Stability of Alkali-Metal Azides under γ-Irradiation

(Presented by Academician V. N. Kondrat’ ev, June 19, 1964)

In studying the radiation stability of nitrates of alkali and alkaline-earth metals (1–5) and bromates of alkali metals (6), it was shown that, in a series of salts of the same type, the radiation yield depends on the magnitude of the free volume of the crystal unit cell, represented by the difference between the volume of the unit cell in the crystal lattice and the volume of the ions forming it. The radiation-chemical yield of salts of the same type is the greater, the greater the free volume of the crystal; and their radiation stability, decreasing from lithium to cesium, proves to be the reverse of the series of thermal stability. An analogous dependence was also obtained for permanganates of alkali metals (7). The discrepancy between the series of radiation and thermal stability is explained by the fact that thermal stability depends on the strength of the polarizing action exerted on the anion by the cation, whereas radiation stability is determined mainly by the magnitude of the free volume of the crystal unit cell. These regularities were obtained for salts belonging to the first group of thermal decomposition reactions according to the classification (8) (decomposition occurs through rupture of bonds within the anionic component of the lattice), and radiolysis and thermal decomposition of them lead to the formation of different products. In this connection it is of interest to determine what factors will govern the radiation stability of compounds whose thermal decomposition proceeds through rupture of the bond between the anionic and cationic components of the lattice (the second group of decomposition reactions according to (8)). Such compounds may include alkali-metal azides, which decompose on heating with formation of the metal and nitrogen. A similar composition of products is also formed in their radiolysis; see, for example, (9–10). However, there are no data allowing these substances to be arranged in a series according to radiation stability as a function of the characteristics of the crystal lattice and the parameters of the ions forming the lattice azides, which is very important for elucidating the mechanism of radiolysis in general and of azides in particular.

In the present work, the order of stability of solid alkali-metal azides under γ-irradiation and the factors determining this stability are considered.

Fig. 1. Radiolysis of alkali-metal azides under the action of Co^{60} γ-irradiation. Solid lines—decomposition of the azide ion; dashed lines—appearance of free metal

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Experimental Part

Recrystallized Na azide was used for the work. The K, Rb, and Cs azides were prepared by the exchange reaction between barium azide and the sulfate of the corresponding metal. The azides washed with alcohol and ether were dried, ground, analyzed for the azide ion, and stored over P_2O_5. Samples of the azides, sealed in a glass ampoule 3 cm in diameter and 10 cm high, were irradiated in the central channel of a cobalt unit* at a dose rate of $2.9 \cdot 10^{16}$ eV/ml · sec. The irradiation temperature was 35–40°. The total the dose was determined by multiplying the dose rate by the irradiation time. The absorbed dose for each salt (eV/g) was found by multiplying the total dose by the ratio of the electron density of the salt to the electron density of the dosimetric solution.

Proceeding from the assumption that the radiolysis of azides proceeds with complete destruction of the anion and formation of the metal, the irradiated samples were analyzed after dissolution in water for metal and for the remaining undecomposed azide ion. The amount of metal was determined by neutralizing the resulting solution with 0.1 N HNO_3; the azide ion was determined by the Mayrikh method ([11]), by titration with silver nitrate. The large percentages of decomposition and the accuracy of the method gave reproducible results for the azide ion.

Fig. 1. Radiolysis of alkali-metal azides under the action of Co^{60} γ-irradiation. Solid lines—decomposition of the azide ion; dashed lines—appearance of free metal.

Figure 1 shows the dependences of the degree of decomposition of the azides on the absorbed dose; the solid lines correspond to decomposition of the azides according to the loss of azide ion, and the dashed curves were calculated from the amount of free metal formed in the irradiated azide. It is evident from the figure that, in the dose interval studied, deep radiation decomposition of the azides occurs and no appreciable saturation effect is observed. The resistance of the azides to irradiation decreases from Na to Cs; however, there is no agreement

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* Irradiation was carried out on the cobalt γ-unit of the Institute of Nuclear Physics, Academy of Sciences of the Uzbek SSR, by S. G. Pashinskii, to whom the authors express their gratitude.

between the curves obtained from the azide ion and from free metal. This discrepancy, especially large for the Rb and Cs azides, may be connected with the following causes:

1) the radiolysis of azides partly proceeds with the formation of nitrides;
2) the metal formed during radiolysis combines with oxygen or carbon dioxide from the air, with formation of carbonate, nitrate, and nitrite;
3) decomposition by hydrogen of the azide ion, liberated during dissolution of the salt, is possible:

$$NaN_3 + 2H + H_2O \rightarrow NaOH + NH_3 + N_2.$$

Of all the reasons listed above, the first and third are eliminated, since they should lead to an even greater alkalinity of the solution than in the case of stoichiometric agreement of the data for decomposition of the azides into nitrogen and metal. Possible formation of carbonate ([12]) is also excluded, since replacement of the azide ion by carbonate in the analytical procedure used by us could only lead to underestimated results for radiolysis. Formation of nitrite and nitrate is more probable. This is also indicated by the available data on formation of calcium nitrate during irradiation of calcium fluorite ([13]), as well as results on formation of sodium nitrite and nitrate during oxidation of sodium azide by oxygen ([14]). We did not succeed in detecting nitrate ion in the irradiated azides. Nitrite ion was detected by reaction with α-naphthylamine and sulfanilic acid after binding the azide ion, which interferes with the determination. It should be noted that most clearly

reaction took place in the case of irradiated azides of Rb and Cs. As possible reasons for the formation of the nitrite ion, one may point to a chemical reaction with NO_2, formed in the process of ionization of air, and to a possible increase in the rate of oxidation of the azide by oxygen under the action of irradiation. Final conclusions on this question can be drawn only after additional studies have been carried out.

Table 1

Cation	Cation radius, Å	Ionization potential, eV	Free volume of the crystal unit cell, Å*	Decomposition temperature, °C ([15])	Initial radiation-chemical yield, molecules/100 eV
Na^+	0.98	5.138	26.1	240–275	2.4
K^+	1.33	4.339	28.4	222–255	3.95
Rb^+	1.48	4.176	34.1	–355	6.05

Cation	Cation radius, Å	Ionization potential, eV	Free volume of the crystal unit cell, Å*	Decomposition temperature, °C (15)	Initial radiation-chemical yield, molecules/100 eV
Cs^+	1.69	3.893	40.7	–395	10.0

* The free volume of the unit cell was calculated by us from X-ray data on the dimensions of the azide unit cell (16, 17), generally accepted crystallographic cation radii, and the radii of N^{-3} and N^{+5} (18).

From the initial slope of the curves for the decrease of the azide ion with dose, the radiation-chemical yield of azide decomposition was calculated. The linear dependence of the initial radiation-chemical yield of azide decomposition on the free volume of the crystal unit cell (Fig. 2 and Table 1) indicates an influence of the packing density of the crystals on the radiolysis of azides. The difference in free volumes probably determines, as in the radiolysis of nitrates (3), the conditions for diffusion of the products of radiolysis from the place of their formation. This stage in radiolysis, in contrast to the thermal decomposition of these salts, is the principal one and ultimately determines the magnitude of the radiation yield. This peculiarity of the radiation-chemical decomposition of alkali-metal azides, which distinguishes it from the thermal decomposition of these salts, despite the fact that the composition of the products formed in the reaction and, apparently, the chemistry of the reaction are the same (in both cases the reaction products are metal and nitrogen), may be a consequence of differences in the conditions under which the radiation and thermal decomposition reactions of azides proceed. The thermal decomposition of these salts, beginning at active sites on the external surface and on the internal surface formed by defects of the crystal, is then localized at the interface between the reaction product and the initial substance (19, 20). It is determined mainly by the detachment of an electron from the azide ion and by the conditions of subsequent decomposition of the azide radical on the surface of the crystal. In contrast, radiolysis proceeds in the bulk of the crystal lattice under conditions in which, owing to the cage effect (the degree of manifestation of which (2, 6) depends on the magnitude of the free volume), the role of processes connected with recombination of the radicals formed during radiolysis and with their diffusion in the lattice from the place of formation to the yield of the final product sharply increases. This may be the reason for the discrepancy established in the present work between the series of thermal and radiation stability of alkali-metal azides (see Table 1).

Fig. 2. Dependence of the initial radiation-chemical yield of azides on the magnitude of the free volume.

It has been shown that, for alkali-metal azides, radiation stability and thermal stability do not coincide.

Fig. 2. Dependence of the initial radiation-chemical yield of azides on the magnitude of the free volume

Figure 2: Fig. 2. Dependence of the initial radiation-chemical yield of azides on the magnitude of the free volume

The magnitude of the initial radiation-chemical yield of decomposition of alkali azides increases linearly with increasing free volume of the unit cell of the crystalline azide.

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