Decomposition of Solid Potassium Nitrate by Incident 100 keV Ions†

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Synopsis. Potassium nitrate was bombarded at 100 keV energy with ion beams extracted from a discharge of D_2, He, N_2, and O_2, and the yield for the formation of nitrite ion was determined: $G(NO_2^-)$=1.8, 1.8, 0.5, and 0.5, respectively. The results suggest that the reaction takes place *via* electronic excitations.

Whereas a lot is known about chemical reaction induced by ionizing radiations, very little information exists about chemical reaction induced by energetic particles having energies of 1 to 100 keV. Ions at keV energies have been used to initiate chemical reactions in gaseous methanol,[2,3] crystalline nitrate,[4] and condensed simple gases (H_2O, CH_4, CO).[5,6] The results in these low energy ion-impact experiments were interpreted as due to elastic collisions of incident ion with atoms leading to atomic displacements in the target molecules. Ions at higher energies lose energy more and more in inelastic collisions leading to electronic excitations of the molecule. Puglisi *et al.*, thus, studied chemical effects of elastic and inelastic collisions of 15—100 keV ions with benzene.[7]

In the present work, 100 keV ions were used to initiate the decomposition of potassium nitrate. Potassium nitrate was chosen because its radiolytic behavior toward ionizing radiations was well known: The only radiolytic products reported are nitrite ions and oxygen. The objectives of this work were to obtain the nitrite ion yields for 100 keV ions and to see the effect of the nature of bombarding ions on the decomposition yield.

Experimental

The sample to be irradiated was about 80 mg of polycrystalline potassium nitrate (Koso Chemical Co., Inc, Analytical Grade), pressed into a disk of the diameter of 10 mm, and mounted onto the sample holder by means of clamps. It was irradiated at ambient temperature in vacuum (*ca.* 10^{-5} Pa) with energetic ions. Ions were produced by discharge of D_2, He, N_2, and O_2 in a radio-frequency source,[8] extracted and accelerated at desired energies and were focussed through an aperture of 8 mmϕ onto the sample. The current density of the ion beam was measured by a Faraday cage and was 10 $\mu A\,cm^{-2}$ throughout this work. Composition of the ionic species from each gas was analyzed magnetically; *i.e.*, D_2:D^+ (47%), D_2^+ (19%), and D_3^+ (34%); He: He^+ (99%); N_2: N^++N_2^{2+} (6%), N_2^+ (94%); and O_2: O^+ (17%), O_2^+ (82%), and O_3^+ (1%).

After irradiations, the samples were dissolved in water and the concentration of nitrite ions produced was determined spectrophotometrically[9] by adding 1-naphthylamine and sulfanilic acid. The molar absorption coefficient used was 35000 $mol^{-1}\,dm^3\,cm^{-1}$ at 520 nm.

†Chemical Reactions Induced by Energetic Particles. II.[1]

Results and Discussion

The yields of nitrite ion as a function of incident ion dose are shown in Fig. 1 for the bombardment with 100 keV ions. The rapid initial decomposition is followed by a decline in rate. At lower bombarding energies, *e.g.* 20, 50, and 80 keV, somewhat lower values for the initial yield were obtained, though the shape of the yield-dose curves remained unchanged.

From the initial slope of the curves in Fig. 1, the G-value for the formation of nitrite ions per 100 eV of the energy absorbed may be calculated. The results are included in Table 1, together with the $G(NO_2^-)$'s reported in the literature for other radiation sources.

On the other hand, we have calculated the electronic (S_e) and nuclear (S_n) stopping power of KNO_3 for these 100 keV ions according to the method of Lindhard *et al.*[10—12] The ratio S_e/S_n gives a relative amount of electronic and nuclear (elastic) energy deposition. Some relevant values of $S_e/(S_e+S_n)$ are included in Table 2. There may be seen a correlation between $G(NO_2^-)$ value and $S_e/(S_e+S_n)$ value. It should be remembered that ionizing radiations, *e.g.* α, β,

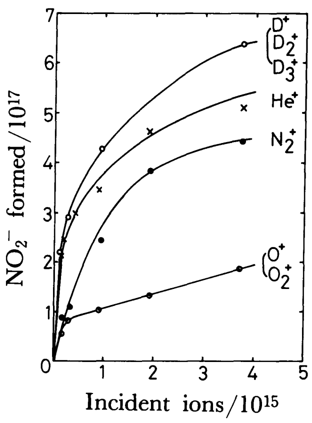

Fig. 1. Yield-dose curves for various 100 keV ions incident on potassium nitrate. Current density: 5 $\mu A/0.5\,cm^2$.

TABLE 1. COMPARISON OF $G(NO_2^-)$ FROM KNO_3 OBTAINED BY VARIOUS RADIATIONS.

i) This work (100 keV)

D^+,D_2^+,D_3^+	He^+	N_2^+	O^+,O_2^+
1.8±0.2	1.8±0.2	0.5±0.1	0.5±0.2

ii) Literature values

10 keV He^+	3.4 MeV α	1.5 MeV e^-	^{60}Co γ
1.54[4]	2.2[13]	1.48[14]	1.46[15]

TABLE 2. SOME VALUES OF $S_e/(S_e+S_n)$ FOR THE IONS TRAVERSING KNO_3.

Energy/keV	Ion			
	D^+	He^+	N^+	O^+
100	1.0	0.99	—	—
50	0.99	0.97	0.67	0.58
20	0.98	0.91	0.42	0.39

*) It is assumed that a molecular ion traversing a solid decomposes into atomic fragments. Thus, in the calculation of stopping power, a 100 keV-N_2^+ ion, for example, is regarded as two 50 keV-N^+ ions.

and γ rays and protons, lose most of their energy by electronic excitations. Thus, it may be concluded that the energetic ion-induced decomposition of nitrate leading to the formation of nitrite is mainly through electronic excitations.

Moreover, it is interesting to compare the yield-dose curve for oxygen-ion bombardment with that for nitrogen-ion bombardment. As the concentration of oxygen increases due to implantation, the yield for nitrite ion diminishes. This fact suggests that a nitrate ion-reforming reaction from nitrite ion and oxygen-containing species take place:[13]

$$NO_2^- + 1/2\,O_2(O, O^+, O^-, O_2^-, \text{or } O_3) \longrightarrow NO_3^- \qquad (1)$$

The yield-dose curve for deuterium ion should be compared to that for helium ion. The difference in yield at higher doses (shown in Fig. 1) may be ascribed to the elimination of the oxygen-containing species (Reaction 1) by the implanted deuterium ion.

In conclusion, it was found that electronic excitations play an important role in ion-induced decomposition of potassium nitrate and that the effect of different bombarding ion is to accelerate or decelerate the nitrate reforming thermal reaction.

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