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Fig. 1.

Figure 1: Fig. 1.

Abstract

Full Text

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The Effect of Preliminary Proton Irradiation on the Rate of Thermal Decomposition of Potassium Permanganate

(Presented by Academician M. M. Dubinin, 18 XII 1962)

In connection with the results of studies ([1−8]), in which it was shown that preliminary irradiation with X-rays and γ-radiation increases the rate of subsequent thermal decomposition of permanganates, it seemed of interest to determine how the rate of thermal decomposition changes as a result of preliminary irradiation of permanganates with protons. In contrast to γ-radiation and X-rays, which belong to lightly ionizing radiation and are characterized by a low linear density of energy transfer to the surrounding medium, protons belong to heavy ionizing radiation with a high linear density of energy transfer. It could therefore be expected that, upon preliminary irradiation of permanganates with protons, specific features would appear that are not observed upon irradiation with X-rays and γ-radiation. Taking this into account, and also the fact that the effect of preliminary proton irradiation on the rate of thermal decomposition reactions has in general been little studied, we carried out an investigation of the effect of proton irradiation on the rate of subsequent thermal decomposition of potassium permanganate.

Fig. 1. Effect of preliminary irradiation with protons (4.5 MeV) on the rate of thermal decomposition of $KMnO_4$ at 218°. 1 −unirradiated sample; 2 −absorbed dose 0.06 Mrad; 3 −1.2 Mrad; 4 −4.8 Mrad; 5 −9.6 Mrad

For carrying out the irradiation, a beam of protons with an energy of 4.5 MeV extracted from a cyclotron was used. The beam intensity was determined by the usual method in such cases ([9]), by measuring the ionic current with a copper grid mounted in the vacuum system in the path of the beam before the sample. Since the range of the protons in our experiments was no greater than the thickness of the sample layer, the absorbed dose was calculated from the formula

$$D = \frac{I \cdot S_0 \cdot E \cdot \tau}{q \cdot S_p \cdot m} \text{ eV/g},$$

Fig. 2. Influence of preliminary irradiation with X-rays (200 keV) on the rate of thermal decomposition of $KMnO_4$ at 218°. 1—unirradiated specimen; 2—absorbed dose 0.42 Mrad; 3—0.84 Mrad; 4—1.68 Mrad

Figure 2: Fig. 2. Influence of preliminary irradiation with X-rays (200 keV) on the rate of thermal decomposition of $KMnO_4$ at 218°. 1—unirradiated specimen; 2—absorbed dose 0.42 Mrad; 3—0.84 Mrad; 4—1.68 Mrad

where I is the ionic current, q is the proton charge, S_0 is the surface area of the sample, S_p is the area of the grid, E is the energy of the protons incident on the sample, τ is the irradiation time, and m is the mass quantity of the sample. Special-

but it was shown by special experiments that macroscopic heating of the specimen under the irradiation conditions used by us in the present work (ion-current value 0.01-0.02 μA, irradiation time from 1 to 60 min) could not exert a substantial influence on the rate of thermal decomposition of permanganate.

The results of experiments studying the influence of preliminary proton irradiation on the rate of thermal decomposition of potassium permanganate in the coordinates α (fraction of substance that has reacted) and τ (decomposition time) are shown in Fig. 1. It follows from them that preliminary irradiation with protons exerts a strong influence on the rate of thermal decomposition of permanganate. The results obtained for proton irradiation may be compared with the acceleration of the thermal decomposition of potassium permanganate activated by X-rays ([8]) with an energy of 200 keV (Fig. 2*).

Fig. 2. Influence of preliminary irradiation with X-rays (200 keV) on the rate of thermal decomposition of $KMnO_4$ at 218°. 1—unirradiated specimen; 2—absorbed dose 0.42 Mrad; 3—0.84 Mrad; 4—1.68 Mrad

In Fig. 3 is shown the dependence of the relative change in the reaction-rate constant, calculated from the equation

$$\lg \frac{\alpha}{1-\alpha} = kt + \text{const},$$

on the dose absorbed during preliminary irradiation of permanganate with protons and X-rays. Comparison of these curves shows that preliminary irradiation with protons, at the same absorbed dose, exerts a greater influence on the rate of decomposition of permanganate than irradiation with X-rays. The reason for this is apparently connected with the difference in the radiation-chemical transformation during irradiation of permanganates with protons and with X-rays, which leads to the accumulation in permanganate crystals of radiolysis products in the form of impurities of a new phase and other lattice defects that accelerate thermal decomposition. This difference follows above all from the fact that, under proton irradiation, the linear energy-transfer density is much greater than

Figure 3 graph: relative increase in the rate constant versus absorbed dose

Figure 3: Figure 3 graph: relative increase in the rate constant versus absorbed dose

under X-ray irradiation. Under proton irradiation one must take into account the appearance of thermal spikes, which are not formed under X-ray irradiation.

As a consequence of the appearance of thermal spikes in the track region, an increase in the rate of radiolysis may occur owing to a local rise in temperature, similar to what occurred under the action of α-particles formed in the decay of Po^{210}, on alkali-metal nitrates ([10]), and also, possibly, a radiation-chemical decomposition supplementing the thermal decomposition of permanganates. This should increase the amount of substance decomposed as a result of irradiation and ultimately lead to a greater influence of irradiation on thermal decomposition. Among other possible reasons for a change in the character of radiolysis associated with a high energy-transfer density, one should also note the high concentration of free ele-

* The calculation of α was carried out according to the total transformation found from experiment, and not from the stoichiometric reaction equation, as in work ([8]). Therefore the absolute values of α for the X-ray experiments are somewhat different.

electrons, ions, and radicals along the particle track upon proton irradiation. However, in our case this factor apparently does not play a significant role because of the high mobility, in an ionic crystal, of electrons, positive holes, and excitons, since if their accumulation in the track did occur, their effect on the amount of substance transformed and the kinetic effect would be the opposite of what was observed in our experiments.

In addition to factors associated with the high linear density of energy transfer under proton irradiation, it is also necessary to take into account the possibility of displacement of atoms or ions in the permanganate lattice; the role of this may be neglected if irradiation is carried out with X-rays ([7,8]). The accumulation of lattice defects as a result of displacement phenomena may also be one of the reasons why proton irradiation has a greater effect on the rate than X-ray irradiation. The effect on thermal decomposition of displacement phenomena caused both by direct collisions and by those associated with the Szilard–Chalmers effect has been shown in work ([11]) for the dehydration of manganese oxalate dihydrate irradiated with neutrons. However, unlike this reaction, on which ionizing radiation has no effect and the role of displacement processes is therefore evident, the process of thermal decomposition of permanganates is very sensitive to the ionizing action of radiation.

Fig. 3. Relative change in the rate constant of thermal decomposition of potassium permanganate as a function of the absorbed dose: *1*—irradiation with X-rays; *2*—irradiation with protons

Moreover, whereas the dehydration of manganese dihydrate in work ([11]) was carried out at 75-95°, the thermal decomposition of potassium permanganate in our experiments was carried out at 218°, and therefore the probability of annealing of displacements upon heating the substance to the decomposition temperature is greater in our case. Taking all this into account, it may be assumed that the principal reason for the increase in the kinetic effect under proton irradiation lies in the occurrence of thermal spikes; in addition, displacement phenomena may possibly play a definite role. Final conclusions concerning the role of each of these factors can be drawn only after additional studies have been carried out.

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Note: Figure translations are in progress. See original paper for figures.