325. *The Acceleration of the Decomposition of Solids by the Emission from Radium.*

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The rate of decomposition of solids is a function of the rates (1) of nuclear formation and (2) of the propagation of the reaction outwards from the nuclei. Both of these components might be expected to be influenced by external stimuli. The formation of nuclei by bombardment of the solid with α-particles, β- and γ-radiation, etc., should be possible in favourable circumstances, and by the same agencies the rate of propagation might be accelerated by the removal of obstructions in the path of the reaction.

It is well known that both rates are dependent on temperature, so in searching for the effects produced by external stimuli the temperature of the solid cannot be ignored. Roginski (*Physikal. Z. Sowjet Union*, 1932, **1**, 656) records experiments with nitroglycerine [probably at room temperature] in which the explosive was subjected to the action of fast electrons. Four to ten molecules were decomposed for each electron, but no marked acceleration of the reaction occurred. The nuclei formed did not increase in size at the temperature of the experiment, although at higher temperatures the reaction was shown to be autocatalytic. In the work now to be described, the effects produced by the emission from radium on crystals of barium azide were found to be very dependent on temperature. At room temperature, it was not possible to produce nuclei which would grow at higher temperatures. No action of the stimulus could be observed unless the temperature of the solid was sufficiently high for thermal decomposition to occur. Contrary to expectation,

it was found that the main influence of the emission lies not in nuclear formation but in an acceleration of the rate of propagation of the reaction through the solid.*

Barium Azide.—The technique described by Garner and Hailes (*Proc. Roy. Soc.*, 1933, *A*, **139**, 576) was used. The barium azide was prepared by Harvey (*Trans. Faraday Soc.*, 1933, **29**, 653) and consisted of dehydrated crystals, 1—2 mg. in weight. The decomposition commences to be appreciable in the neighbourhood of 100°, at which temperatures there is a long induction period which is followed by an acceleration of the reaction (Harvey, *loc. cit.*). The acceleration obeys the equation $\log_{10}dp/dt = k_1t/2{\cdot}303 + \text{const.}$, in which k_1 is an acceleration constant which increases rapidly with temperature. When 1 mg. of radium, enclosed in a thin glass tube, is placed in close proximity to a crystal of barium azide, the acceleration of the rate of decomposition is very marked at 110°, the induction period is reduced from 120 to 60 minutes, and k_1 is increased fourfold.

The nuclei of metallic barium which are formed are very similar in character both for the thermal and the accelerated reaction, but in the latter the nuclei present on that face of the crystal nearest to the radioactive source are much larger than those on the other faces of the crystal. This is an indication that the rate of growth of the nuclei is accelerated by the radium.

The rate curves were analysed on the basis of the theory put forward previously (Garner and Hailes, *loc. cit.*; see also preceding paper). In these papers, the equation $\log_{10}dp/dt = k_1t/2{\cdot}303 + K\log_{10}(N_0/k_1)$ was derived, in which k_1 is a branching coefficient and N_0 is the number of nuclei formed per minute. The intercepts given by plotting $\log_{10}dp/dt$ against t should be proportional to $\log_{10}N_0/k_1$, and from the intercept, by adding $\log_{10}k_1$, a value proportional to $\log_{10}N_0$ should be obtained (see Table I).

TABLE I.

No. of expt.	Temp.	Induction period, mins.	$k_1/2{\cdot}303$.	$K\log_{10}(N_0/k_1)$.	$K\log_{10}N_0$.
Thermal					
1	110·5°	120	0·0246	—	—
2	111·0	120	0·0287	$\bar{1}\bar{0}$·96	$\bar{1}\bar{1}$·41
5	111·5	120	0·0265	$\bar{9}$·02	$\bar{1}\bar{1}$·44
11	109	145	0·0218	—	—
12	118	90	0·0404	$\bar{1}\bar{0}$·81	$\bar{1}\bar{1}$·42
Average at 110—110°				$\bar{1}\bar{0}$·98	$\bar{1}\bar{1}$·42
Accelerated					
3	110·5	60	—	—	—
4	110·5	55	0·118	$\bar{1}\bar{0}$·57	$\bar{1}\bar{1}$·64
6	109·5	65	—	—	—
7	111·0	60	0·123	$\bar{1}\bar{1}$·99	$\bar{1}\bar{1}$·08
10	110·0	68	0·091	$\bar{1}\bar{1}$·98	$\bar{1}\bar{2}$·94
Average at 110—111°				$\bar{1}\bar{0}$·18	$\bar{1}\bar{1}$·22

The experimental values for the thermal reaction agree fairly well with those of Harvey (*loc. cit.*), who finds at 110° an acceleration constant of 0·0262. Under the action of radium this is increased four times. The number of nuclei formed per minute, N_0, is shown by the figures in the last column to be little affected. In fact, a slightly higher average value is found for the thermal reaction. This is, however, within the error of experiment, which is quite large on account of the length of extrapolation which is necessary in deriving the intercept.

In the preceding paper, it has been shown that the nuclei formed in exothermic changes do not spread uniformly throughout the solid, especially in the early stages of their growth. It was suggested that this is due to a lack of homogeneity of the crystals; a nucleus starting in one crystal grain spreads uniformly throughout the grain, but its progress is hindered at the boundary of the grain. It was suggested that the reaction spreads from grain to grain across suitable bridges between the grains. The branching coefficient, k_1,

* (*Note added in proof*) Kallmann and Schränkler (*Naturwiss.*, 1933, **21**—**23**, 379) have succeeded in detonating explosives with positive ions, and Muraour (*Chim. et Ind.*, 1933, **30**, 39) has caused crystals of silver acetylide to detonate by bombardment with electrons.

is a measure of the frequency with which the reaction passes from one grain to another. So the effect of the emission from radium on k_1 is either that associated with the removal of the hindrance to the passage of the chemical reaction across the boundaries of the grains, or is due to a speeding up of the rate within the individual grains. Since pre-insulation at a lower temperature has no effect on the reaction, it would appear that the activation of the reaction is ephemeral in character, and to be effective, must occur simultaneously with the spread of the reaction through the solid.

Mercury Fulminate.—Similar experiments were carried out with crystals of mercury fulminate, but it was found that the reactions constants were unaffected by the presence of radium (Table II).

TABLE II.

No. of expt.	Temp.	Induction period, hrs.	$k_1/2{\cdot}303$.	No. of expt.	Temp.	Induction period, hrs.	$k_1/2{\cdot}303$.
Thermal				*In presence of radium*			
1	112°	8·75	0·0134	2	112°	8·75	—
4	113	8·5	0·0119	3	112	8·5	0·0138
6	113·5	7·75	0·0180	5	113	7·25	0·0190
8	113·5	8·0	0·0180	7	113·5	8·0	0·0203

The fulminate crystals were prepared more than two years ago and had been kept in a desiccator in the dark. The length of the induction period is greater and k_1 smaller than would be expected from the results of Hailes. Possibly the crystals have undergone some slight deterioration in the interval. The table shows that neither the induction period nor k_1 is appreciably affected by the presence of 1 mg. of radium within several mm. of the crystal. There is no appreciable effect on either the number or the rate of growth of the nuclei.

SUMMARY.

The thermal decomposition of crystals of barium azide is accelerated by the emission from radium. It is concluded that the effect is due to an acceleration of the growth of the nuclei and not to an increase in their number.

The thermal decomposition of mercury fulminate is unaffected by the presence of radium.

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