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THE THERMAL DECOMPOSITION OF CRYSTALS OF BARIUM AZIDE.

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Crystals of barium azide, BaN_6 . H_2O , lose their water of crystallisation when kept at room temperature, giving a white pseudomorph. These dehydrated crystals decompose at a measurable rate at temperatures above 95° C., liberating nitrogen and metallic barium. The pressure-time curves obtained for the reaction are similar in character to those of mercury fulminate.¹ There is an induction period the length of which decreases with increasing temperature and a period of acceleration of the reaction which obeys the law

$$\log (dp/dt - dp_0/dt) = k_1 t + const.$$
, . (1)

previously found to hold for the decomposition of fulminate.

¹ Farmer, J.C.S., 121, 174, 1922; Garner and Hailes, Proc. Roy. Soc., 139A, 576, 1933.

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Experimental.

The experimental technique has been described in previous papers, and since very few modifications have been made in the methods employed, it is unnecessary to describe it in detail.

Barium azide obtained from the General Electric Company was crystallised from water and crystals of good shape, 1-4 mg. in weight, selected. A single crystal of known weight was suspended in a platinum bucket in the apparatus outlined in Fig. 2,² and a small platinum disc was placed over the crystal at the bottom of the bucket. The bucket was suspended in a cold part of the apparatus while the reaction vessel was being evacuated. After evacuation for 24 hours, the crystal was lowered into the reaction vessel and periodical pressure measurements taken on a McLeod gauge. The volume of the apparatus, calibrated with dry air from a small mercury weight pipette fused in the side of the apparatus, was approximately 3000 c.c. At 128° C., the volume calculated from the equation $v = p_1/p_2$, where p_2 is the pressure in the apparatus and p_1 the pressure of the same amount of gas when occupying I c.c., ranged from 3110 to 3140 c.c. between 2.7×10^{-3} . The drift in the values between these pressures was probably due partly to thermal diffusion and partly to adsorption.

The amount of nitrogen liberated from a single crystal I-2 mg. in weight was found to be 98.5 per cent. of that calculated from the weight of azide taken (the mean of six experiments).

Results.

Typical pressure-time curves are given in Fig. 1 (I and A). These show an induction period over which there was an approximately linear rate of evolution of gas, $2-5 \times 10^{-7}$ cm. per min., which includes gas liberated from the walls of the reaction vessel. This gives dp_0/dt in equation I. At the end of the induction period the acceleration of the reaction occurs according to equation I (see Fig. I (II.)). The exponential law only holds for about I/10 of the total decomposition. This period is shorter than for fulminate crystals, and much shorter than for ground fulminate and lead styphnate. In the last two cases the law holds up to the time of half decomposition. The acceleration is sometimes terminated by a change of slope (at A), after which for a brief period the rate is approximately constant. For the last 20 per cent. of the decomposition the unimolecular law is obeyed.

The experiments were carried out over the range of temperature $100-130^{\circ}$ C., over which range a black crystalline residue was obtained. Some work was done at higher temperatures with a Pirani gauge which showed that it was difficult to cause the crystals to detonate. Above 140° C., the reaction was sometimes sufficiently violent to blow the disc out of the bucket and on these occasions no pseudomorph was left behind. Thus the process which occurred may correspond to the first stages of detonation.

Centres of Decomposition.—If partially decomposed crystals be removed from the apparatus during the period of acceleration of the reaction, and examined under the microscope, it is seen that centres of decomposition have been formed consisting of metallic barium (Fig. 2). These, which occur both on the surface and throughout the mass, have





an irregular shape, and in a few cases a ring structure. On standing in the air the barium oxidises, and towards the end of the oxidation is present as a ring corresponding with the external boundary of the original centre.



The distribution of the centres over the surface is unusual. They are grouped in clusters on the surface in a manner not determined by a probability law. This indicates either that the surface does not possess

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uniform properties all over, or that the centres are formed from one another. The number of the centres in unit volume is not so high within the crystal as on the external surface. Nor are those inside the crystal as large as those formed on the external surface. In consequence of this, the centres on the surface begin to touch one another long before the reaction is complete. This possibly accounts for the change of slope at A.

The number of centres and their size increases with time. Attempts were made to count these centres and to determine the manner in which their number increased throughout the reaction, but it was found that for crystals of the same batch, heated at the same temperature for the same length of time, the numbers obtained were not reproducible. This is very probably the cause of the variations observed in the velocity of the reaction in the crystal (see later). In one experiment at 100.5° C., a crystal of about 2 mg., when removed from the apparatus after heating for 330 minutes, gave approximately 1000 centres visible on the surface. This is in marked contrast with the behaviour of crystals of mercury fulminate which on heating become browned throughout, without showing any marked structure under the microscope.

The matrix in which the centres are embedded does not undergo any visible change of colour or appearance on heating, so that it is probable that the formation of centres is the only chemical change that occurs, although the lack of reproducibility in the number of centres makes it impossible to ascertain this with any certainty.

Velocity Constants of the Reaction.

The early stages of the reaction after the induction period are governed by the equation

$$dp/dt = kp, \quad \dots \quad \dots \quad \dots \quad (2)$$

which on integration, gives

$$\log_{10} p = kt/2 \cdot 303 + \log_{10} p_0. \qquad . \qquad . \qquad (3)$$

Here $\log_{10} p_0$ is a constant independent of temperature within experimental error, and has the average value 9.87 (log. cm. Hg). From equations (2) and (3) it follows that

$$\log_{10} dp/dt = kt/2 \cdot 303 + \log_{10} k + \log_{10} p_0. \qquad (4)$$

This equation is also in agreement with the facts, and the experimental values of $\log_{10} (kp_0)$ given in the table agree with those calculated from equations (2) and (3) within experimental error.

Consequently, there are several ways in which the experimental results may be tabulated. Equation (4) has been employed as a basis for calculations, since this was the equation used in the earlier paper on fulminate,¹ and also since it appeared to be the most important equation of the three. In the following table is given the temperature of the experiment, the weight of the crystal in mg., the length of the induction period in minutes, the time when $\log_{10} dp/dt = 10^{-5}$ cm./min., $k/2 \cdot 303$ from equation (4), $k/2 \cdot 303$ from the equation dp/dt = kp, the constant from equation (1) and the velocity constant of the unimolecular reaction calculated from equation

$$k_2 = \frac{1}{t} \log_{10} \frac{p_f}{p_f - p_t}$$
 . . . (5)

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T° C.	Wt. in mg. w.	Induction Period. min.	Time log rate = 5 min.	$\begin{array}{c} \frac{k_{1}}{2^{\prime}303} \\ \text{Equation} \\ (4). \end{array}$	$\underbrace{\begin{smallmatrix} \frac{k_1}{2,303}\\ \text{Equation}\\ (5). \end{smallmatrix}}_{}$	Const. Equation (1).	k ₂ .
98.9 100.2 103.1 106.6 107.0 109.0 109.8 110 113.5 114.6 116.5 118.8 119.0 123.2 125.0 128.1 120.1	1.521 2.128 0.930 2.187 1.83 2.032 1.461 1.716 1.003 1.72 0.76 2.705 1.425 2.095 4.125 1.28 1.574	340 270 245 150 130 115 120 90 60 60 55 40 30 25 20	520 399 287 2125 178 166 147 173 113 1095 84 655 70 47 35 285 265	0.0108 0.0151 0.0246 0.0281 0.0266 0.0320. 0.0262 0.0361 0.0390 0.0457 0.0584 0.0462 0.0848 0.0962 0.0949	0.0091 0.0107 0.027 0.0229 0.0229 0.0240 0.0302 0.0263 0.0263 0.0407 0.0339 0.0447 0.0537 0.0589 0.080 0.110 0.105	$\begin{array}{c} \overline{11} \cdot 500 \\ \overline{11} \cdot 000 \\ \overline{10} \cdot 60 \\ \overline{10} \cdot 60 \\ \overline{11} \cdot 72 \\ \overline{10} \cdot 15 \\ \overline{10} \cdot 62 \\ \overline{10} \cdot 20 \\ \overline{10} \cdot 20 \\ \overline{10} \cdot 92 \\ \overline{10} \cdot 94 \\ \overline{9} \cdot 26 \\ \overline{9} \cdot 36 \\ \overline{9} \cdot 50 \\ \overline{8} \cdot 48 \end{array}$	0.0253 0.0253 0.0253 0.0253 0.0253 0.0253 0.0253 0.0594 0.0678 0.1080 0.133 0.133
131.7	o·86	20	22.5	0.1219	0.003	8.26	0.132

All rates have been calculated in cm./min. With the aid of these data, it is possible to reproduce the experimental curves.

Temperature Coefficient of the Reaction.

The velocity constants of the reaction, k_1 and k_2 , are dependent on the temperature and the graphs of $\log_{10} constant$ against 1/T give straight lines (Fig. 3) from which the critical increments of the reaction may be calculated. Those for k_1 and k_2 are of the same order, being 21·1 and 27 K. cal. respectively. The constant, equation (1), is also dependent on the temperature and its critical increment is larger than either of the above. The errors which occur in the determination of the constant are too large to make it worth while quoting the actual figure.

Discussion.

The decomposition of barium azide is associated with the formation of a relatively small number of centres visible under the microscope. An attempt was therefore made to explain the acceleration of the reaction in terms of the growth of the interface between the barium nuclei and the azide. The growth of the nuclei can be considered in terms of two hypotheses: (I) the number of the nuclei is constant from the beginning to the end of the reaction,* that is, they are all formed on introduction of the crystal into the reaction vessel; and (2) the nuclei are the result of thermal activation and are formed at an approximately constant rate, viz., N_0 per minute. According to the first hypothesis, since the nuclei all start at the same time, their external areas will be equal in magnitude, so that the total area of the interface will be proportional to $m^{2/3}$, where m is the mass decomposed, or $dp/dt = kp^{2/3}$. Since in solid reactions the rate of penetration of the interface into the solid is usually found to be

* This is actually in disagreement with observation, for the number of centres definitely increases with time.

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constant, it is possible that the rate of reaction would be found proportional to t^2 . The second hypothesis leads to the equation,

$$dp/dt = k(1 + 2^2 + 3^2 + 4^2 \dots t^2) = k(2t^3 + t^2 + 2t + 1),$$

or for long times such as are found in the present experiments, $dp/dt=kt^3$. Actually, the experiments show that dp/dt = kp, and that the rate increases approximately as the tenth power of the time * instead of the square or the cube of the time as expected from hypotheses (I) and (2), so that neither hypothesis is in agreement with the experimental facts. The difficulties of applying the usual conceptions of the rate of growth of centres to the decomposition of barium azide seem to be insuperable.

A branching mechanism of some kind is indicated. This could be of the type postulated in an earlier paper,² according to which the reaction spreads throughout the mass of the solid by means of branching chains which possess a *spatial* character. These chains were assumed to branch according to the expression, $dN = (N_0 + kN)dt$, where N_0 is the number of chains started per minute, and N the number of branches in existence at any time, k being a branching coefficient. This leads to the expression found, $\log (dp/dt - a) = k_1t + const$. The objection to this view lies in the fact that very substantial nuclei of metallic barium are formed instead of the metallic cloud predicted by the above mechanism. If this hypothesis were correct, then the crystal should darken gradually throughout the mass, as was observed for fulminate.

It is hoped that further work on the action of β and γ radiation on barium azide crystals ³ will lead to the elucidation of some of the above difficulties in the interpretation of the experimental results.

Summary.

The thermal decomposition of single crystals of dehydrated barium azide has been studied between the temperatures 100-130° C. An induction period is observed which is similar to that found for mercury fulminate. The reaction accelerates at a rate which increases as the tenth power of the time and the acceleration obeys the law, $\log (dp/dt - a) = k_1 t + const$. previously found to hold for fulminate and lead styphnate. Towards the end of the reaction, the unimolecular law is obeyed.

Nuclei of metallic barium are produced both on the surface and in the interior of the crystal.

I wish to express my thanks for a grant from Imperial Chemical Industries, Ltd., which has defrayed the cost of the apparatus employed in the research.

* The plot of log dp/dt against log t for the period of acceleration gives a slightly curved line of which the slope is approximately 10. ³ Cf. Nature, 1933, 131, 513.

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