CCLXXXIX.—*The Thermal Decomposition and Detonation of Lead Azide Crystals.*

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THE majority of investigations on the decomposition of solid bodies have shown that reaction commences by the formation of nuclei on the surface, which increase in size as the decomposition proceeds. A good example of nucleus formation is seen in the case of the decomposition of silver oxalate (MacDonald and Hinshelwood, J., 1925, **127**, 2764). Here silver nuclei are produced which can be destroyed by oxygen and the reaction thereby inhibited.

For this type of solid decomposition, the rate of reaction at any time is dependent upon the rates of (a) nucleus formation, and (b) growth of the interface formed between the reactant and its products (compare Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2263). If the nuclei be produced at a rapid rate on the surface, then a stage is soon reached when the interface becomes a series of plane surfaces parallel to the surfaces of the crystal (compare Garner and Tanner,

J., 1930, 47). The rate of growth of the interface has been discussed for various types of case by Topley and his collaborators (Topley and Hume, *Proc. Roy. Soc.*, 1928, **120**, 211 ; Topley and Spencer, J., 1929, 2633) and by Roginski and Schulz (*Z. physikal. Chem.*, 1928, **138**, 21).

In general, there will be two kinds of critical increment governing the rate of thermal decomposition of solids, *viz.*, those of (1) the rate of nucleus formation and (2) the rate of penetration into the solid of the interface at which reaction proceeds. Likewise, for the process of detonation, it is possible that there are two critical increments, *viz.*, that of the rate of formation of centres of detonation and that of the rate of detonation. The nature of the mechanism whereby thermal decomposition passes into detonation is not understood ; in fact, there is little experimental work bearing on this question. Thus, although the assumption that there is a critical increment of detonation may perhaps not be justifiable, yet it provides a reasonable line of approach to the study of detonation. The average time of heating before detonation occurs can be measured, and the reciprocal of this can be defined as the probability of detonation. From the temperature coefficient of this probability, a value for the detonation increment can be obtained in the usual manner.

It has been found that lead azide exists in two distinct crystalline forms, the ordinary or α-, and a less usual or β-form. The first is orthorhombic, the second monoclinic ; the β-variety is more easily detonated by shock or friction than the other. This information, hitherto unpublished, was supplied to us by Messrs. Nobel's, who also undertook the preparation of the crystals necessary for our experiments.

In the present investigation, the critical increments of the rate of thermal decomposition of α- and β-azides have been determined, and an approximate value for the critical increment of the rate of formation of centres of detonation for α-azide obtained. The critical increments found are : thermal decomposition (1) α-azide = 47,600 cals., (2) β-azide = 38,800 cals., and (3) detonation = 200,000 cals. An attempt has also been made to account for the differences which exist between the explosive properties of α- and β-azide. The present work has shown that for crystals of the same area, at 260°, the β-form decomposes about 20 times more rapidly than the α-form.

The rate of decomposition of a substance in the solid state is given by the equation

$$- dx/dt = \nu n A e^{-E/RT} \quad . \quad . \quad . \quad . \quad (1)$$

where ν is the frequency of molecular decomposition, n the number

of molecules per sq. cm. of surface, A the area of interface, and E the critical increment. Thus, variations in ν, n, or E of the two forms could account for their difference in stability. The difference between the critical increments is, however, more than sufficient to account for the difference between the rates of thermal decomposition. Thus, the greater instability of the β-form may be tentatively ascribed to the lower value of its critical increment.

There is a marked difference between the appearances of partially decomposed crystals of the α- and the β-azide. The former rapidly darkens over the whole surface, and a broken crystal shows a white fracture with a black edge. The decomposition is obviously of the normal type, and the rate of formation of nuclei on the surface of the α-form must be very large. The β-form decomposes irregularly in patches, but since the crystals of the azide are very thin, it is difficult to determine whether or not these patches originate in nuclei begun on the surface or in the interior of the crystal. The rate of formation of nuclei appears to be smaller for the β- than for the α-form.

The frequency ν [equation (1)] might correspond with some vibration frequency of the N_3 group, in which case it was of interest to measure the infra-red absorption spectra of the two forms. Measurements between 10 and 1μ, however, indicate that they possess the same absorption spectra. Calculations made with the aid of equation (1) lead to a frequency of decomposition 10^7 times greater than that corresponding to a near infra-red frequency.* Topley and Hume (loc. cit.) were the first to make calculations of this nature, and they found for calcium carbonate hexahydrate a still bigger discrepancy. In the case of the azides, since the decomposition is exothermic, the discrepancy might be due to the occurrence of a chain mechanism, and the chain length required is 10^7. Such speculations as to the cause of the discrepancy are, however, of doubtful value without further evidence, for it would appear that exothermic change is possible even when the activation energy of a molecule is less than its critical increment (compare Roginski and Rosenkewitsch, Z. physikal. Chem., 1930, B, 10, 47).

Detonation.—The normal detonating temperature of lead azide in air is 350° (Wöhler, Ber., 1913, 46, 2050). In vacuum, this may be lowered to 290° or even 280° after long evacuation. The effect of the air is no doubt partly due to its action in preventing the heating of the crystals during the reaction : in a vacuum, loss of energy occurs only by radiation, whereas in air there is an additional

* The value of ν used is that calculated previously from the rate of detonation of azide, viz., $\nu = 1\cdot25 \times 10^{13}$ (Garner, Trans. Faraday Soc., 1930, 26, 1).

loss due to bombardment by gas molecules. Thus, when a crystal is surrounded by gas, it will undoubtedly be kept cooler than when in a vacuum. This, however, does not entirely account for the depression of the detonating temperature on removal of the air. The temperatures of single crystals immediately preceding their detonation have been calculated, and these show that at most the temperatures were only 2° or 3° above that of the bath. Thus, the principal effect of the air or water vapour must be ascribed to some other cause. The action is probably more local in character, *i.e.*, the cause lies in the interface itself. Molecules of gas which are adsorbed in the interface will collide with newly formed nitrogen molecules and may remove their energy before they have time to activate undecomposed molecules of lead azide. The effect of a few adsorbed molecules would be large, if the reaction followed a chain mechanism. This phenomenon is being quantitatively studied in the case of mercury fulminate.

The probability of detonation increases very rapidly with temperature. Below 290°, the crystal may or may not detonate within the period of thermal decomposition, but at 295° detonation occurs on an average within 3 minutes. The probability of detonation thus possesses a very high temperature coefficient and critical increment. The critical increment of the formation of detonation nuclei is approximately 4 times that of the rate of thermal decomposition. It may be that four molecules of azide are concerned in the formation of centres of detonation. This high critical increment of the detonation process explains the stability of azide crystals at room temperature. The probability of detonation calculated from the equation $P = Be^{-E/RT}$ is negligibly small at room temperatures if the value of E chosen is that of the detonation process, but not if the critical increment corresponding to the thermal decomposition be taken.

For the temperature range 290—295°, the rate of thermal decomposition immediately preceding detonation has been measured. This depends on the pressure of the gas above the crystal, as well as upon the temperature of the crystal. For pressures of 3—10 $\times$ 10^{-4} cm., the rate is 4.6×10^{14} molecules per minute for α-azide crystals 0·04 cm.^{2} in area. At higher pressures, 7×10^{-3} cm., the rate is 2.6×10^{15} molecules per minute.

Lead azide crystals are not very suitable for accurate investigation of these phenomena, mainly because they break up into several fragments on heating. It is best, therefore, to delay detailed consideration of the above phenomena until a more ideal detonant has been found. β-Azide is unsuitable because the crystals decompose in patches. Mercury fulminate crystals give a

very great degree of reproducibility, and perhaps this substance will prove to be an ideal case.

Experimental.

The weights of the largest crystals available ranged from 0·002 to 0·005 g.   Their rates of decomposition were measured by suspending them in a platinum bucket in a Pyrex vessel surrounded by a furnace which was kept at temperatures ranging between 200° and 300°.   The exploratory work was carried out with the α-azide, and several facts were observed, which determined the final design of the apparatus.   The crystals often broke up into several fragments on heating, and the fracture was accompanied by the

Fig. 1.
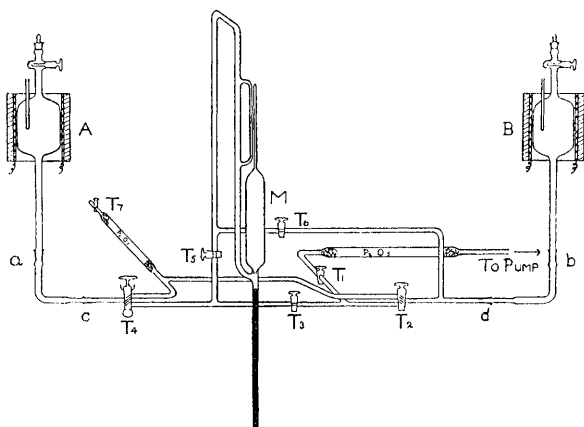
evolution of small volumes of gas.   The fracture was very probably due to droplets of water entrapped in the crystals during crystallisation.   Reproducible results could not be obtained until the crystal had been heated to a temperature higher than that at which it was desired to make measurements.   It was also observed that the detonation temperature varied with the pressure of gas in the apparatus.   It was thus necessary to bake out the apparatus thoroughly before an experiment.

Apparatus.—Two Pyrex reaction vessels were used (A and B, Fig. 1), which were connected to a McLeod gauge M and through a phosphoric oxide tube to the pumps.   These were surrounded by lagged furnaces, worked on constant voltage and capable of being raised and lowered.   The furnaces and McLeod gauge were surrounded by wooden jackets to protect them from draughts. The temperature was measured by means of a copper–constantan thermocouple, which was inserted into a vertical tube in the reaction vessel.   The platinum bucket containing a crystal was suspended

by thin platinum wire in a cold part of the apparatus below the furnace. It could be raised into position by coiling the platinum wire round the extended barrel of the tap at the top of the apparatus.

Procedure.—A single crystal was weighed, and its surface area determined under the microscope. It was introduced into a platinum bucket which had been previously baked out at red heat. The bucket was lowered into the reaction vessel until it was well below the furnace. The furnace was then heated to the required temperature and the apparatus evacuated over-night. (This was after the empty vessel had been previously baked out for several days.) In the morning, the furnace was lowered, and after the reaction vessel had cooled to 50°, the crystal was raised into position.

Fig. 2.

Time, minutes.
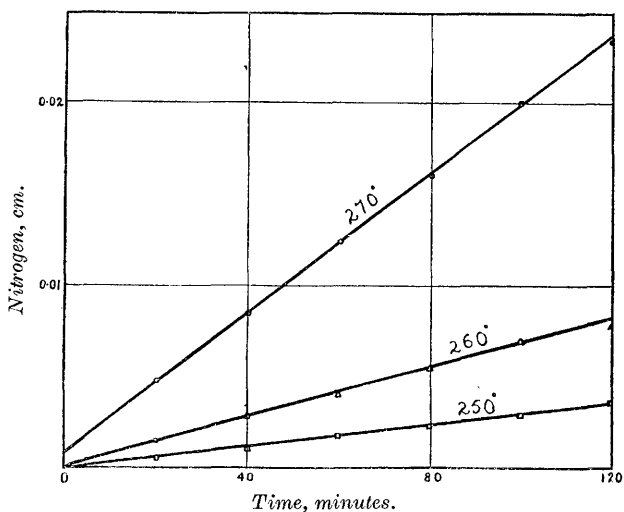
Finally, the furnace was pulled up round the reaction vessel. By this method the crystal was not subjected to too rapid heating. The pumps were kept on until the temperature had reached 120°.

The crystal was heated for a short time at the highest temperature of an experiment (say 280°), and then the rate of reaction was measured at that temperature until a constant rate was obtained. Subsequently, the rates were measured for lower temperatures on the same crystal. The total change in the area of interface of the crystal during a series was small, but occasionally a correction was necessary for the area of the interface.

The rate of evolution of nitrogen was linear with respect to time (Fig. 2). In Table I are given the temperature coefficients for α-lead azide.

TABLE I.

α-Lead azide.

| Expt. No. | Temperature coefficient over range | | | | | |
	220—230°	230—240°	240—250°	250—260°	260—270°	270—280°
15	2·04	1·67	1·94	2·33	—	—
16	—	—	—	—	3·00	2·06
18	2·05	2·37	2·25	1·93	2·31	2·93
20	2·37	2·22	2·06	1·66	2·36	4·68

The temperature coefficient is constant over the range 220—280°, and its average value is 2·43. The critical increment calculated from this is 47,600 cals., and the wave-length of the quantum corresponding with the increment is 0·5939 μ.

Temperature Coefficient of β-Azide.—Since the β-form did not break up on heating, the temperature coefficients could be determined by comparing the rates of decomposition of different crystals, as was done with copper sulphate pentahydrate (Garner and Tanner, *loc. cit.*). The rate of reaction was found to be unimolecular (see Table III). The ranges 250—260° and 260—270° were determined in this way. For the lower temperatures, the same method was adopted as for α-azide; above 220°, the crystals decomposed too quickly to allow this method to be used. The average value, *viz.*, 2·06, gives a critical increment of 38,800 cals.

TABLE II.

β-Lead azide.

| Temperature range	200—210°	210—220°	250—260°	260—270°
Temp. coeff.	1·89	2·04	2·44	1·87

Mode of Decomposition of the Crystals.—*α-Azide.* This form of crystal becomes coated with metallic lead very rapidly on heating. No visible nuclei can be seen, but a partially decomposed crystal on being broken always shows a white interior surrounded by a black edge. Thus, it is clear that the reaction begins on the surface and passes inwards. The rate of decomposition of a given weight of α-azide is greater the smaller the size of the crystals, which confirms the above deduction. At the end of the reaction, only five-sixths of the available nitrogen had been evolved as gas.

β-Azide. This form of crystal does not become completely coated with metallic lead until a later stage in the decomposition, which occurs irregularly throughout the mass of the crystal. This probably accounts for the different form of its pressure–time curve when the crystal is heated at constant temperature until decomposition is complete (Fig. 3). It undergoes complete decomposition into a pseudomorph of metallic lead, the arrangement of the crystal-

lites of metal being quite at random.   We are indebted to Messrs.
Nobel's for the *X*-ray examination of these pseudomorphs.

Decomposition   at   Constant   Temperature.—α-*Azide.*   A   typical
curve for the decomposition of a single crystal of α-azide at 270°
is given in Fig. 3 : it is very nearly linear, showing scarcely any
induction period, and is similar in type to that of copper sulphate
pentahydrate, in that it shows an abrupt change of slope near the

Fig. 3.

α Azide at 270

β Azide at 270°

Nitrogen, cm.

Time, hours.
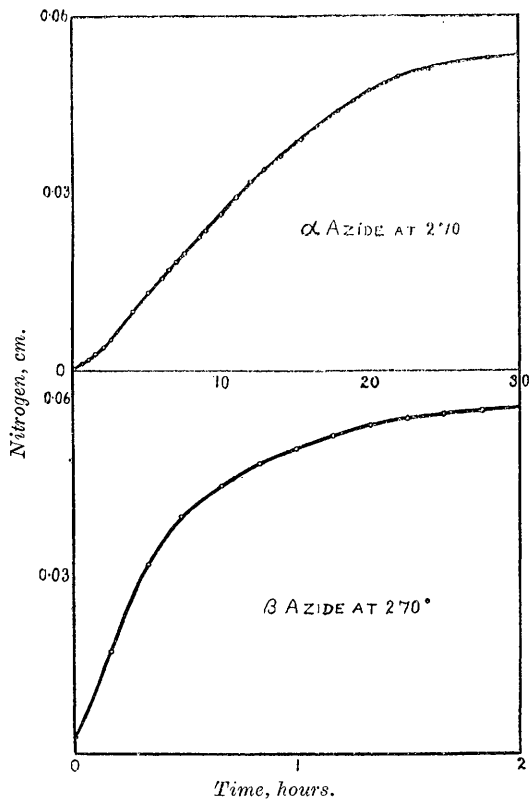
end of the decomposition.   It is of the form expected for a reaction
involving the production of large numbers of nuclei on the surface.
The equations of Roginski and Schulz (*loc. cit.*) fitted the results
fairly well.

β-*Azide.*   The curves for this substance are different from those
of the α-form in that they change more gradually from the beginning
to the end (Fig. 3).   After the effects of the induction period are
over, the decomposition is very nearly unimolecular (Table III).

The values in Table III have been used in calculating the critical increment.
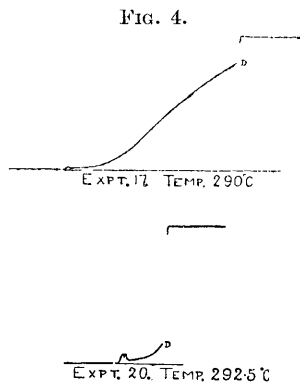
TABLE III.

t.	k_{270}.	t.	k_{270}.	t.	k_{260}.	t.	k_{250}.
7	0·0426	17	0·0377	20	0·0170	60	0·00698
27	0·0315	37	0·0330	60	0·0163	120	0·00689
47	0·0286	57	0·0309	80	0·0165	·180	0·00683
77	0·0268	77	0·0297	105	0·0165	240	0·00681
101	0·0255	97	0·0286	150	0·0169	300	0·00657

The rate of reaction at any time is proportional to the volume of the unchanged material. It is difficult to explain this behaviour, and the thinness of the plates makes it difficult to observe what is happening in the crystal itself.

Detonation Experiments on α-*Azide.*—The pressure changes at detonating temperatures, 290° and upwards, occurred too rapidly to be measured on a McLeod gauge, so that a Pirani gauge was fused on to one of the reaction vessels below the ground joint *b* of vessel B (Fig. 1). This gauge, which was kept in ice during a measurement, was connected to a Moll galvanometer and a photographic recording apparatus. The electrical circuit was so balanced that there was no deflexion when there was a hard vacuum in the apparatus. The gauge was calibrated with the gaseous product of the reaction.

The platinum bucket containing the crystal was kept at about 100° in the side tube *a* or *b* during the

FIG. 4.

EXPT. 17. TEMP. 290°C

EXPT. 20. TEMP. 292·5°C

evacuation of the reaction vessel. On introducing it into the reaction vessel, there was a small rapid evolution of gas. This showed itself as a flick on the photographic curves. It was very largely eliminated by immersing a side tube in liquid air. The bucket was watched by means of a mirror below the vessel; a bright flash occurred on detonation, and the bucket was blown to fragments. The pressures at the beginning and end of each experiment were measured on a McLeod gauge.

Tracings of typical photographic records are given in Fig. 4. These records were time-marked. At D, the movement of the beam of light reflected from the galvanometer mirror is so rapid as to leave no trace on the photographic paper. Thus, the thermal change passes abruptly into detonation. The results are summarised in Table IV, which gives the time that elapsed before detonation

occurred.   Four experiments were done at each temperature, and the series was carried out under strictly standardised conditions.

TABLE IV.

Temp.	Time to detonation (mins.).	Average time (mins.).	Rate (cm./min. $\times$ 10^4).	Number of molecules decomposed per min.
295°	2·9, 3·0, 2·9, 2·5	2·8	4·4, 3·6, 5·6, 23·2	4·6 $\times$ 10^{14}
292·5	4·3, 6·0, 9·7, 4·9	6·2	4·2, 3·1, 5·6, 4·7	4·7 $\times$ 10^{14}
290·0	16·6, ∞, ∞, 17·3	17·0	28·7, 20·7	2·6 $\times$ 10^{15}
285·0	No detonation			
280·0	No detonation			

In one experiment at 280°, where the crystal and vessel were evacuated for 3 days (the normal time was over-night), detonation occurred in 8·1 minutes.   This is an illustration of the effect of gas on the detonation temperature.

The curves for those experiments where the crystal did not detonate were similar to Fig. 3.   They were not reproducible from crystal to crystal because of the fracture of the crystal during heating, as mentioned before.

The rates of reaction immediately preceding detonation are given in Table IV.   In col. 4 is given the rate of change of pressure for a constant area of 0·04 sq. cm., and in the last column, the mean value for the number of molecules decomposing per minute per 0·04 cm.² initial surface.   These rates are sufficiently high to affect appreciably the temperature of the crystal.   Since the crystals become coated with a layer of finely divided lead, they will behave as a black body, as far as the emission of radiation is concerned.   Assuming the emissivity of the crystal to be that of a black body, the temperature of the crystal before detonation has been calculated :

Bath temp...............................	295°	292·5°	290·0°
Corrected temp..........................	296·95°	294·5°	298·9°
Gas pressure (cm. $\times$ 10^4)	4	8	70

These corrected temperatures will be too high, because the detonation occurred at appreciable gas pressures.   This will be particularly the case with the experiments at 290°, where the pressure was 7×10^{-3} cm.   It is not possible to make an accurate allowance for the effect of gas pressure on the above temperatures, for the heat interchange will be between the crystal and the platinum bucket in which it is lying.   It is clear, however, that the experiments at 290° must be left out of account in determining the probability of detonation.   From the results at 295° and 292·5° the temperature coefficient is 2·2 for 2·5°, which gives a critical increment of 200,000 cals.   This result, while showing that the critical increment of detonation is much bigger than that of the thermal decomposition, is only known very approximately.

Near Infra-red Absorption Spectra.—Azide crystals decompose when heated by means of an infra-red beam, becoming white owing to reaction with the air. It was thus not possible to place the crystal between the source of radiation and the slit of an infra-red spectrometer; it was possible, however, after making small modifications to a Hilger rock-salt spectrometer, to obtain measurements

Fig. 5.
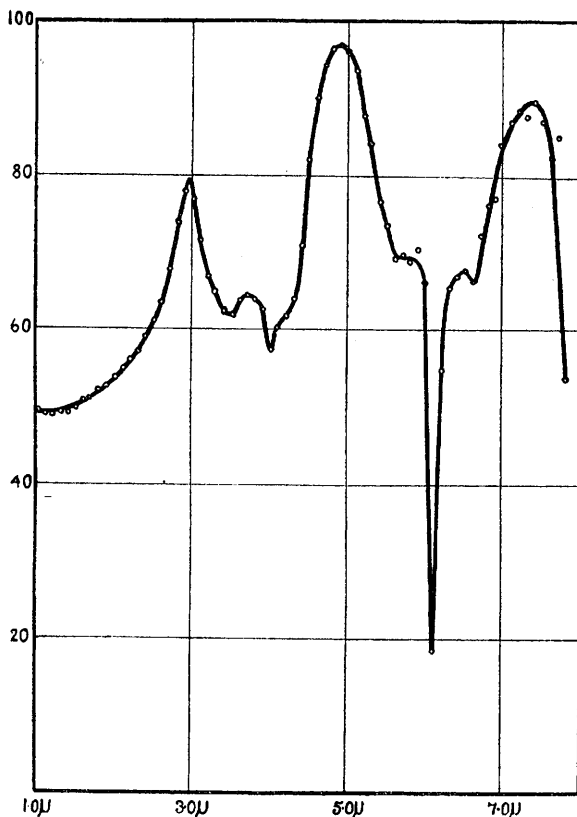
of absorption spectra by placing the crystal on the slit in the dispersed beam. The β-crystals were found to be the most suitable, for almost perfect crystals were available, 5 mm. long, and were sufficiently thin for measurement. A typical absorption curve is given in Fig. 5, and the band maxima are shown in Table V, together with the frequency differences.

The α-crystals were less suitable for measurement since they were too thick, were often hollow, and were much more irregular than

4 A

TABLE V.

β-Azide. Wave-length, μ.	Frequency × 10⁻¹³.	Δν.	α-Azide. Wave-length, μ.
2·94	10·21	——	·2·92
3·70	8·11	2·10	3·70
4·90	6·12	1·99	Flat max. at
7·40	4·05	2·07	4·6—5·0

the β-form. With the best crystal available, the figures given above were obtained. No differences could be detected between the spectra for the two short axes of the crystals.

Action of Ultra-violet Radiation.—It was not found possible to detonate azide crystals with the ultra-violet light from a mercury vapour lamp. The crystals, however, became black, and in this state were more sensitive to heat.

Summary.

The rates of decomposition of the α- and the β-form of lead azide have been measured between 210° and 295°. The β-form decomposes much more rapidly than the α-form. The critical increments found were : α-form, 47,600 cals.; β-form, 38,800 cals. The difference between the critical increments accounts for the greater instability of the β-form.

The infra-red absorption spectra of these crystals have been measured, and are very similar in the two cases. The bands observed are probably those of the N_3 group.

The critical increment of detonation has been shown to be 200,000 cals. The rates of decomposition immediately preceding detonation have been measured. The detonating temperature is lower in vacuum than in air.

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