# 156. *The Initiation of the Detonation Wave in Solid Explosives.*

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Muraour (*Chem. Ind.*, 1933, **30**, 39) has suggested that the initiation of a detonation wave in an explosive requires the simultaneous decomposition in the same region of a *large* number of molecules. This theory of the origin of the detonation wave serves the very useful purpose of correlating many of the facts concerning explosives and explains detonation by shock, by fast electrons (*idem, ibid.*), as well as by heat. It is therefore of interest to examine the theory further and to attempt to form an idea as to the magnitude of a detonation centre. Gomm and the author (J., 1931, 2123) put forward the above hypothesis for the special case of lead azide and deduced from the temperature coefficient of the time lag before detonation that four molecules were required to form a centre of detonation. Later, Sutton (*Nature*, 1934, **133**, 463) showed that the unit cell of the lead azide crystal contains eight groups of three molecules and suggested that the unit of detonation is one group of three molecules. The experimental data already available on the decomposition of lead azide make it possible to decide the maximum size of detonation centres.

A possible line of investigation into the origin of the detonation wave is to search for events which possess a probability which is the same as, or greater than, that of detonation. It is obvious that events which possess smaller probabilities cannot be the cause of the inception of the wave. In the case of lead azide, it can be shown that the simultaneous decomposition of more than two adjacent molecules has a smaller probability than that of detonation.

Crystals of lead azide decompose on the surface and soon become coated with a coherent film of lead. The interface between lead azide and lead, which is the surface on which the reaction occurs, is parallel to the faces of the crystals, and no very large error will be made if we assume that in the early stages of the decomposition its area is equal to that of the exterior of the crystal. On this basis, at 290°, the number of molecules of azide decomposing per sec. in one sq. cm. of interface is $1{\cdot}1 \times 10^{16}$; the number of molecules in the interface is approximately $3 \times 10^{14}$, so that about 30 molecular layers are decomposed per sec. The detonation wave passes through lead azide with a speed of 5300 m./sec. and hence each molecular layer hands on activation energy to the next in $10^{-13}$ sec. This will be taken to be the time within which adjacent molecules must decompose in order that the energy liberated may be available as activation energy. This time may be too long, but its order is all that is required. The probability of the simultaneous decomposition of two adjacent molecules within the time interval $10^{-13}$ sec. will be $1{\cdot}1^2 \times 10^6/3 \times 10^{14} = 4 \times 10^{-9}$; for three molecules this will be $1{\cdot}5 \times 10^{-20}$, and for four, $5 \times 10^{-32}$ (leaving out of account that there are several adjacent positions open). The chance of the binary event at 290° is $2{\cdot}5 \times 10^3$ per sec.; this is greater than that of detonation, which, on the basis of 1 sq. cm. of interface, is once in 25 secs. Errors in estimating the area of the interface or the time taken in handing on activation energy may partly account for the discrepancy. On the other hand, the chances of the ternary and the quaternary events will be once in $10^7$ secs., and once in $10^{18}$ secs. respectively. These chances are much smaller than that of detonation, so they are ruled out as a possible cause of detonation. This should be true, not only of lead azide, but of explosives generally, for in order that the ternary and the quaternary decompositions should occur sufficiently frequently it would be necessary that the explosive decomposes at $10^6$ or $10^{17}$ times faster than the rate found for lead azide at 290°. Such rates of reaction would themselves be accounted rates of explosion. Hence, it may be concluded that the detonation centre formed during the thermal reaction in explosives cannot be greater than two molecules. It should be borne in mind, however, that this may not apply to detonation by shock or fast electrons at room temperature.

On heating an explosive, detonation occurs after a time lag, $\tau$, which decreases with increase in temperature, and the normal relation between $\tau$ and $T$ is that given by an equation of the Arrhenius type, $\log (1/\tau) = A/RT +$ const., where $A$ (detonation) may be called the critical increment of detonation (cf. Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576; Andréew, *Physikal. Z. Soviet Union*, 1934, **5**, 174). A similar equation also holds below the detonating temperature for the length of the induction period of the thermal decomposition, or, more generally, for the time for half-decomposition of solid explosives, and in this case, $A$ (thermal) is the critical increment of the thermal decomposition which can be checked by other methods. For mercury fulminate, $A$ (thermal) $=$ 30·4 kg.-cals., whereas $A$ (detonation) varies from 27 to 31 kg.-cals. according to the shape and purity of the crystals. Thus the critical increment for detonation is the same as that of the thermal decomposition within experimental error, so it must be concluded that the time lag in the case of fulminate is mainly controlled by the rate of the thermal decomposition and that the manner in which the time lag changes with temperature has little bearing on the phenomena of detonation. Andréew (*loc. cit.*) has determined $A$ for a number of explosives (some liquid and some solid) and except for lead azide the values range between 10 and 40 kg.-cals., and are so low that one suspects that in the majority of these cases the critical increments have little connexion with the detonation process.

There is an additional reason why $A$ (detonation) must be influenced by the thermal process. In solids, decomposition occurs at an interface which does not exist at the beginning of the decomposition, and a time interval must elapse before this interface reaches its maximum extent. Detonation arises in this interface and the probability of detonation will depend on its area. Consequently, the time to detonation will include time taken in manufacturing the interface at which detonation occurs. The surface of lead azide becomes rapidly coated with a film of lead and the maximum area of the interface is soon attained, hence in this case the time required to form the interface is not the controlling factor in the length of the detonation time. This accounts for the fact that differences are found between $A$ (detonation) [*i.e.*, 200 (Garner and Gomm, *loc. cit.*), 78·7 (Andréew, *loc. cit.*)] and $A$ (thermal), *i.e.*, 48 kg.-cals. The errors involved in the determination of $A$ (detonation) due to self-heating and changes in the area of the interface are, however, very great, and little reliance can be placed on the actual numerical values given above. All that can be said is that the critical increment of detonation is considerably larger than that of the thermal reaction. On the hypothesis that detonation is caused by the simultaneous decomposition of two molecules, the critical increment of detonation should be 96 kg.-cals.

Certain conclusions can be drawn as to the probable mechanism of the decomposition of lead azide in the solid state. The reaction, $\text{PbN}_6 \longrightarrow \text{Pb} + 3\text{N}_2$, is exothermic to the extent of 106 kg.-cals. It is conceivable that the process occurs in two stages, (1) $\frac{1}{2}\text{Pb}^{\cdot\cdot} + \text{N}_3' \longrightarrow \frac{1}{2}\text{Pb} + \text{N}_2 + \text{N} - 51$ kg.-cals., which should be just possible with the experimental critical increment of 48 kg.-cals., and (2*a*) $\frac{1}{2}\text{Pb}^{\cdot\cdot} + \text{N}_3' + \text{N} \longrightarrow \frac{1}{2}\text{Pb} + 2\text{N}_2 + 157$ kg.-cals. It is unlikely that the second stage is (2*b*) $\frac{1}{2}\text{Pb}^{\cdot\cdot} + \text{N}_3' + \text{N} \longrightarrow \frac{1}{2}\text{Pb} + \text{N}_2 + 2\text{N} - 51$ kg.-cals., since this would require considerable activation energy. Since the $\text{N}_3$ groups in azides are in contact in the solid state (cf. Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904), it is probable that (1) and (2) occur as one process with the liberation of 154 kg.-cals. of energy, and that the real unit of the reaction is a molecule of lead azide or two $\text{N}_3'$ ions. It is uncertain in what manner the energy of the reaction is distributed among the products, especially as the reaction occurs in contact with the solid lattice. There is, however, sufficient energy available, should the molecules be suitably orientated in the lattice, for a reaction chain to be formed. Below the detonating temperature, if a reaction chain exists, it must be of finite length. Calculations made by means of the Polanyi–Wigner equation indicate a chain length of $10^6$ for lead azide. The chain length is probably affected by the lattice energy since at room temperature, it is very difficult to start chains in explosive substances by α-particles, fast electrons, etc. (Roginski, *Physikal. Z. Soviet Union*, 1932, **1**, 640; Muraour, *loc. cit.*; Kalbmann and Schränkler, *Naturwiss.*, 1933, **21**—**23**, 379). The tracks of reaction chains in the solid state may be either two- or three-dimensional, and normally they will begin and end on molecules of decomposition product. In lead azide, the chains arising during the thermal decomposition must be mainly two-dimensional, for the interface at which reaction occurs is quite sharp, but in mercury fulminate they are probably three-dimensional, for the decomposition products are distributed in a finely divided condition throughout the crystal. This difference between the character of the reaction interfaces of these two detonating substances must play an important part in determining their specific explosive properties. Lead azide is very brisant, and this is to be expected since it possesses a sharp interface of reaction. Mercury fulminate is much less sensitive and is very slow in attaining its maximum speed of detonation, and this is in agreement with the fact that the thermal reaction progresses in a diffuse manner throughout the crystal.

On account of the diffuseness of the decomposition of fulminate, it would be expected that the chain length will diminish as the reaction proceeds. The tracks of the chains will pass to an increasing extent through partially decomposed material and will therefore end sooner. The presence of decomposition products and deterioration on ageing exert very marked effects on the detonating properties of fulminate. A crystal decomposed to the extent of one-tenth to one-fifth will not explode at the usual temperatures and, in experiments in the detonation range, it is always found that detonation either occurs before the crystal is one-fifth decomposed or it does not occur at all. In this case, *the chance of detonation is not primarily a function of the rate of thermal decomposition,* for the rate of reaction continues to increase all through the detonating range up to the time of half-decomposition. This leads one to the conclusion that the detonation centre is not formed by the simultaneous decomposition of two adjacent molecules, the probability of which should increase up to the time of half-decomposition, but is a result of the intersection of two reaction chains. A large amount of energy will be liberated at the point of intersection, which will be greater than that set free by the simultaneous decomposition of two molecules independently. The probability of two chains meeting in a two-dimensional system would be of the same order as that of two adjacent molecules decomposing independently, so it is an event which might very well be responsible for detonation in the case of lead azide. Since in the case of fulminate the chain length decreases as the crystal decomposes, the chance of intersection of the chains will also diminish. Thus the inertness of partially decomposed fulminate can be satisfactorily explained.

In corroboration of the chain theory, it is found that the rate of reaction towards the end of the decomposition follows the unimolecular equation. This is true for mercury fulminate, lead styphnate, and barium azide. If the crystals are decomposing by reaction chains which follow irregular tracks there must be residues of isolated molecules which can only decompose one at a time. These will be activated independently and must therefore decompose according to the unimolecular law. The activation energy of the isolated molecules is 27 kg.-cals. in the case of barium azide, which is somewhat greater than the activation energy in the beginning of the reaction, *viz.*, 21 kg.-cals. (Harvey, *Trans. Faraday Soc.*, 1933, **29**, 144, 653).

## SUMMARY.

It is shown that the number of molecules forming a detonation centre in solid explosives cannot exceed two. Arguments have been advanced in support of a chain theory of solid decomposition, and on this basis it is possible to account for the variations in the sensitivity of explosives. It is suggested that the initiation of the detonation wave is due to the intersection of two reaction chains.

THE UNIVERSITY, BRISTOL. [*Received, April 11th,* 1934.]