579. *Thermal Decomposition of Explosives in the Solid Phase. Part II. The Delayed Explosion of Mercury Fulminate.*

By J. Vaughan and L. Phillips.

The influence of various factors on the length of the induction period preceding explosion of mercury fulminate has been investigated within the temperature range 100—140°. Self-heating of the fulminate has been shown to be of major importance in the transition from thermal decomposition to explosion. The theoretical implications of the results are discussed.

When heated, mercury fulminate can undergo a delayed explosion. Lafitte and Patry (*Compt. rend.*, 1931, **193**, 173) noted this and carried out experiments in which small quantities of fulminate were dropped on the surface of mercury kept at a steady temperature. Within the temperature range 135—280° the induction period preceding explosion was found to decrease with increase in temperature; below 135° no explosion occurred. Those authors gave no details as to actual weights of fulminate taken and did not attempt an analysis of their results. Garner and Hailes (*Proc. Roy. Soc.*, 1933, *A*, **139**, 576) carried out more precise work on this phenomenon, using mainly single crystals contained in a platinum bucket under high vacuum, and their results were in general agreement with those of the earlier workers. Semenoff has pointed out (" Chemical Kinetics and Chain Reactions," O.U.P., 1935, p. 428) that the phenomenon of delayed explosion occurs when the velocity of decomposition reaches a sufficiently high value during the period of self-acceleration. The effect has been observed for many explosives and in the cases of " nitroglycerine " and tetryl, for example, has been studied systematically by

Roginsky (*Physikal. Z. Sowjetunion,* 1932, **1**, 640). Garner and Hailes's results for mercury fulminate led to a fairly straight line when the logarithm of the induction period was plotted against the reciprocal of the absolute temperature. These authors used their results to determine the energy term and temperature-independent factor of the Arrhenius equation (cf. Roginsky, *loc. cit.*); they stated that explosion occurred at the beginning of the reaction acceleration, and that the minimum temperature for explosion, under their conditions, was 105—115°. Also, they quoted durations of induction periods obtained in atmospheres of hydrogen and of helium; helium caused a slight increase, as compared with the time *in vacuo*, and a longer delay in the case of hydrogen was assumed to be caused by the smoothing out, by the hydrogen, of any local temperature differences within the crystal. The form of mercury fulminate in general industrial and military use is a mass of small crystals (loose or pressed into pellets) and the present paper describes an extension of the work on delayed explosion, to cover such material. More light has thereby been thrown on the rôle of self-heating in the passing of thermal breakdown into explosion. Furthermore, it had been appreciated by Garner and Hailes that the value of the so-called " ignition temperature " of fulminate would vary with the experimental conditions; the work described has yielded further information on the factors influencing this value for a mass of small fulminate crystals.

EXPERIMENTAL.

The mercury fulminate used was approved British Service material in the form of small crystals with a purity greater than 99·0%, and was dried *in vacuo* for a week before use. Induction periods preceding explosion were determined by two methods.

(*a*) Sealed or open Pyrex-glass tubes (volume 1·2 ml., internal diameter $\frac{3}{16}$'', external diameter $\frac{1}{4}$'', length 1·5''), containing loose fulminate, were placed in holes (diameter $\frac{5}{16}$'', depth 3'') drilled concentrically from the upper face of an electrically-heated, cyclindrical, steel block. The temperature of the block was controlled by a variable resistance and recorded by a thermocouple placed in one of the holes. The temperatures of the holes were checked for consistency, and the reading of the thermocouple was checked with a standardised thermometer before the start of each experiment. Even for an experiment lasting 5 hours the temperature could be maintained to within 0·2°. The glass tubes fitted loosely into the holes so that the apparatus approximated to an air-bath. For some experiments, however, Wood's metal was used, as indicated, in the holes to constitute a metal-bath for the glass tubes. In all experiments the holes were lightly plugged with cotton wool.

(*b*) In a cylindrical sand-bath five steel tubes, 5½'' long by 1½'' internal diameter, were arranged concentrically. The tubes were open at their upper ends and the bath was surrounded by a jacket containing a suitable constant-boiling mixture of glycerol and water. The open end of each steel tube was plugged with cotton-wool and a pad of cotton-wool covered the bottom. Temperatures in the holes were consistent with each other and were constant to 0·2° for the duration of the longest experiment. Pressed fulminate pellets wrapped in cotton-wool, or loose fulminate in sealed Pyrex-glass tubes similarly wrapped, were placed in the tubes. The cotton-wool plugs were replaced and the temperature was checked throughout the experiment by means of a thermometer in one of the steel tubes, kept free for that purpose.

Initial experiments, designed to determine the induction periods preceding explosion, were divided into two series, concerned with fulminate in loose and in pellet form. In one series 0·2-g. lots of loose fulminate were heated in sealed glass tubes as in method (*a*). Four simultaneous determinations were carried out at each temperature. It was expected that the individual times to explosion would vary and that a larger number of determinations than four would be required to obtain a reliable estimate of the true time to explosion at a given temperature. The results in the range 116—140° were, however, consistent and the mean values should therefore be reliable. Results are given in Table I. Fig. 1 shows that there is a linear relationship between the logarithm of the induction period and the reciprocal of the absolute temperature. The activation energy E, obtained from the equation $\log_{10}t = E/4{\cdot}57T + \log_{10}B$ or from the slope of the graph, is 37·8 kcals.

TABLE I.

Temp.	Time to explosion (mins.).	Mean.	Temp.	Time to explosion (mins.).	Mean.
116°	235·5, 236, 236·5, 236·5	236	130°	37·08, 37·8, 39·2	38·03
117·5	180·5, 183, 184, 185	183	135	22·0, 22·3, 22·67, 23·55	22·6
120	131, 133, 133, 135	133	140	12·75, 12·77, 13·17, 13·17	12·95
125	68·5, 70, 73, 78	72			

TABLE II.

Temp.	Time to explosion (mins.).	Mean.	Temp.	Time to explosion (mins.).	Mean.
100°	415, 420, 425	420	107°	185, 189, 195	190
103	296, 300, 305	300	110	120, 123, 126	123
105	233, 235, 241	236	115	74, 75, 76	75

In the second series of experiments, pellets, each made by pressing 10 grains (0·648 g.) of mercury fulminate into a thin copper sheath under a load of 400 lb./sq. in., were wrapped in cotton-wool and heated as in method (*b*). Three simultaneous determinations were carried out at each temperature, the range covered being 100—115°. Results are collected in Table II, and the linear relationship between

$\log_{10}t$ (where t is the induction period) and $1/T$ where T = absolute temperature) is shown in Fig. 1. From the graph the energy of activation is 32·9 kcals.

It was desired to detect, if possible, any actual self-heating before explosion and this was accomplished by means of a thin, calibrated thermocouple of copper–contra with junctions spot-welded. The " hot " junction was placed in the centre of 0·2 g. of loose fulminate in a standard open Pyrex-glass tube, the junction being held in place by a plug of cotton-wool. The heating-bath was that of method (*a*). Readings were taken at one-minute intervals until the self-heating effect became marked, when more frequent readings were taken. In these experiments the bath temperature was taken to be that registered by the thermocouple in the fulminate during the early stages of the experiment. Temperature–time curves for two runs are given in graphs *A* and *B*, Fig. 2, both graphs showing a preliminary period during which the temperature of the fulminate remained at that of the heating bath. Then, as self-heating set in, the temperature began to rise, and the rise accelerated until the decomposition culminated in an explosion. The total recorded rise with 0·2 g. and a steady bath-temperature of about 129° was usually about 8°. In one experiment (graph *A*) with a slightly shorter induction period, explosion coincided with a flick of the galvanometer needle indicating a rise in temperature of 33°. Graph *C*, Fig. 2, shows the effect of removing the fulminate sample after 35·5 minutes, allowing it to cool for 7·5 minutes, and then replacing it in the heating block. Explosion occurred 6·5 minutes after replacement and the

FIG. 1.

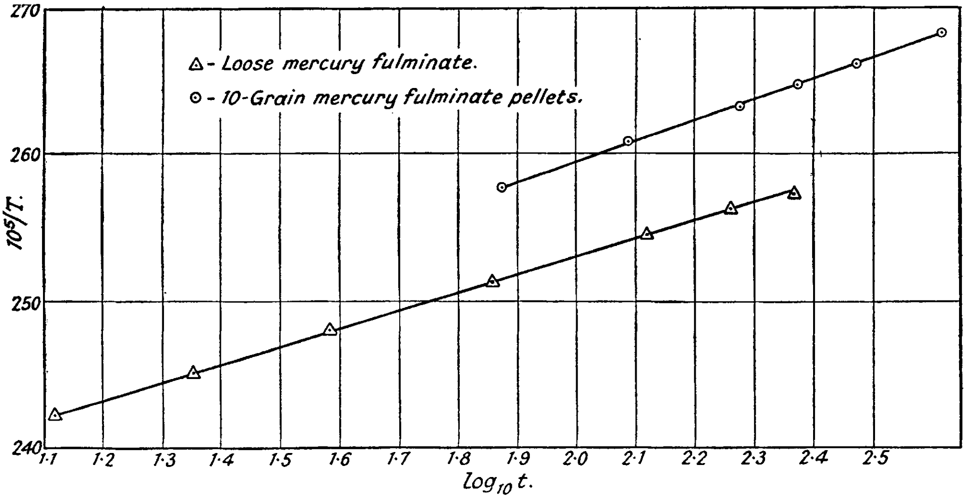
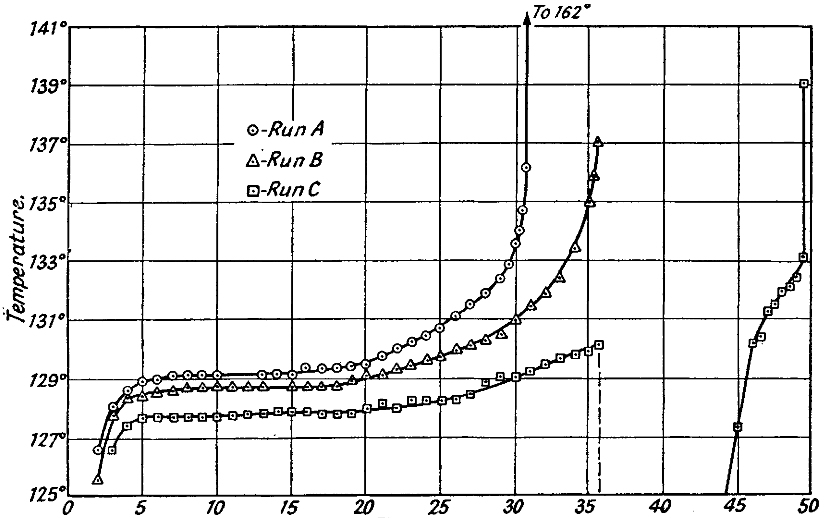


FIG. 2.



temperature–time curve shows no preliminary steady-temperature period. This indicates that Farmer's assumption (*J.*, 1922, **121**, 174) of the production of a non-volatile catalyst is correct.

Experiments were then carried out to determine the effect on the induction period of diluting the fulminate with materials not classed as detonants. Considerations of practical usefulness led to experiments being conducted on fulminate diluted with potassium chlorate and antimony trisulphide, in the mass ratios fulminate : potassium chlorate : antimony trisulphide = 3 : 3 : 2. The liquid-heated bath of method (*b*) was employed, and comparative experiments were carried out on fulminate and the mixture. The weight of each fulminate sample was 0·2 g. and the weight of mixture was 0·533 g., corresponding to 0·2 g. of fulminate. The samples were contained in standard, sealed Pyrex-glass tubes which were wrapped in cotton-wool, and the experiments were conducted in the apparatus of method (*b*). Results given in Table III show that the induction period is considerably lengthened by dilution.

TABLE III.

	Time to explosion (mins.).	
Temp.	$Hg(CNO)_2$.	Mixture.
123°	80·0, 100·0	109·5, 127·5
113	280·0, 298·0	348·0, 384·0

The next step was to determine the effect of direct variation of thermal insulation on the induction period of undiluted mercury fulminate. 0·2-G. samples of loose fulminate in standard, sealed Pyrex tubes were heated at 113° under two contrasting conditions of thermal insulation. In the first place the liquid-heated air-bath of method (*b*) was used. With two samples of fulminate the times to explosion were 280 and 298 minutes. Secondly, when the steel heating block was used at 113°, with the glass tubes immersed in Wood's metal, the fulminate had not exploded after 7·5 hours, and explosion could not be produced by raising the temperature of the heating block to 200°. When the second experiment was repeated, and the temperature raised to 120° after 6·5 hours' heating, the samples gave audible evidence of final decomposition at 6 hours 40 minutes from commencement of experiment. In this repeat experiment none of the three samples underwent a true explosion. In two cases the final " puffs " were just sufficient to break the glass tubes, but in the third case the tube was unbroken, being covered internally by a mirror of what appeared to be mercury.

If self-heating exerted a major influence on the explosion of fulminate, it would be expected that for the same weight of pressed fulminate the shape of the pellet would affect the length of induction period. Thus, fulminate pressed into a sphere would be expected to give a shorter induction period than the same weight pressed under the same load into a narrow cylinder since dissipation of heat would be more rapid from the cylinder, a sphere having the lowest area : volume ratio. Experimental difficulties in shaping suitable pellets were too great to allow work to be carried out in this direction at the time. On the same theoretical basis, however, increasing the weight of fulminate and retaining essentially the same shape of pellet should lead to a reduction of the induction period owing to increased thermal protection of the fulminate in the interior. Experiments were carried out on fulminate pellets conforming roughly to the above conditions. 4-, 6-, 8-, and 10-Grain pellets were made under a load of 400 lb./sq. in. and the pellets' containers, made of thin copper, were in the form of right cylinders of equal base area. Table IV summarises the experimental results, and shows that there is a marked decrease in induction period with increase in weight of fulminate.

TABLE IV.

	Time to explosion (mins.).			
Temp.	4-Grain.	6-Grain.	8-Grain.	10-Grain.
115°	145	120	—	75
110°	204	—	157	123

DISCUSSION.

From the experimental results given above it is clear that self-heating is a major factor influencing the transition of thermal decomposition to explosion in bulk mercury fulminate. Direct evidence has been obtained for this self-heating, and when conditions are chosen such that this heat is dissipated by dilution of the fulminate or by immersing the sample in a good conductor of heat the induction period can be markedly increased and in some circumstances explosion can be prevented. Further evidence for the important influence of self-heating has been obtained from experiments on similar fulminate pellets of different weight, increase in weight being accompanied by decrease in induction period.

When the induction periods are measured at different temperatures, the same weights of fulminate being used, there is a linear relationship between the logarithm of the induction period and the reciprocal of the absolute temperature for both loose fulminate and pressed pellets. This relationship has been demonstrated by Garner and Hailes for single fulminate crystals and by other workers for initiating substances generally (*e.g.*, Garner and Marke, *J.*, 1936, 663; Garner and Gomm, *J.*, 1931, 2123; Andreew, *Physikal. Z. Sowjetunion*, 1934, 5, 174). The energy of activation found for loose fulminate was 37·8 kcals. and for 10-grain fulminate pellets it was 32·9 kcals. For single crystals of fulminate *in vacuo* Garner and Hailes obtained a value of 32·2 kcals.

Comparison of the activation energies for loose and pressed fulminate demonstrates further the importance of self-heating. For instance, E for loose fulminate was larger than that for pressed fulminate, owing, it is considered, to greater heat dissipation from the former. It would appear, therefore, that ideal conditions for the maximum effect of self-heating would be in a single crystal. (In this connection, Garner and Hailes, *loc. cit.*, have shown, in experiments on loose fulminate *in vacuo*, that ignition occurring in one crystal is not necessarily communicated to the whole mass.) Garner and Hailes have shown that self-heating of the crystal *as a whole* is improbable under their conditions, and Garner (*Trans. Faraday Soc.*, 1938, **34**, 986) is of the opinion that localised self-heating, over a few molecules *only*, is a pre-requisite of explosion. This is the basis of the theories proposed by Garner and Gomm (*loc. cit.*) and by Muraour (*Compt. rend.*, 1932, **194**, 280) as the most probable mechanism of explosion in initiating explosives generally. This theory stipulates localised self-heating over a few adjacent molecules, followed immediately by the explosive self-propagation of the reaction by chains. If such limited self-heating is alone sufficient to cause explosion, it is difficult to explain Garner and Hailes's failure to bring crushed or ground fulminate to explosion *in vacuo* at 120°, and the failure in the present work to obtain explosion of loose fulminate heated in a Wood's metal bath at 113°. In both series of experiments self-heating of the fulminate as a whole could be regarded as non-existent but, on the other hand, it is probable that marked localised self-heating does occur. Furthermore, although the lengthening of the induction period for single crystals obtained in hydrogen and in helium by Garner and Hailes could readily be explained by dissipation of heat from comparatively large areas in the crystal, yet the possibility of the dissipation of heat from self-heated areas the size of a few molecules inside the crystal is doubtful. (This argument applies to Garner and Hailes's experiment in which the induction periods of single crystals were increased by covering them with an additional piece of platinum.) In this connection it is noteworthy that the ratio (1 : 1·13) of the induction periods obtained by Garner and Hailes in helium to those in hydrogen is approximately the same as the ratio (1 : 1·14) of the thermal conductivities of these gases.

It therefore appears reasonable to conclude that theories of the explosion process in which the controlling factor is "self-heating" extending only over a few molecules of mercury fulminate are incorrect. The mechanism of the process can be envisaged as a decomposition initiated at surface nuclei, which spreads down crevices formed in the crystals as a result of strains set up by product molecules, until accumulation of the latter at the surface of these cracks sets up lateral strains and cracks when branching occurs (Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488; Vaughan and Phillips, following paper); this branching will be enhanced by the formation of autocatalytic decomposition products, and above a critical temperature it becomes so rapid that heat is produced faster that it can be dissipated, *i.e.*, "self-heating" is set up over a relatively large area, whereupon the consequent acceleration of the reactions causes explosion. This view is comparable with that of Andreew (*Physikal. Z. Sowjetunion*, 1933, **4**, 120), in which explosion is thought to occur when, at a critical temperature, the length of the "macro-chains" causing decomposition becomes infinite, and is also in agreement with Semenoff's theory of degenerate explosions (*loc. cit.*) whereby, in the absence of extensive self-heating, the velocity of decomposition reaches a peak and then falls off without attaining explosive speed.

Finally, Roginsky (*loc. cit.*, p. 687) has pointed out that, unless it is determined under standard conditions, the value of the "ignition temperature," for explosives generally, loses its meaning because variable conditions may lead to variation in factors influencing this value. In the case of bulk mercury fulminate it is clear that the ignition temperature will depend on the amount of fulminate taken and on the conditions for thermal insulation and heat transfer. This helps to explain the great variation in some published values for the minimum temperature of explosion for a mass of small fulminate crystals, *e.g.*, 190° (Wohler and Metter, *Z. Schiess. Sprengst.*, 1907, **2**, 204), 130° (Hoitsema, *Z. physikal. Chem.*, 1896, **21**, 147). Garner has shown that the value for a single crystal of fulminate depends upon the purity, size, and crystal form. These factors would be expected to hold in the case of bulk fulminate.

University College, Swansea.
Explosives Research and Development Establishment,
Waltham Abbey.

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