580. *Thermal Decomposition of Explosives in the Solid Phase. Part III. The Kinetics of Thermal Decomposition of Mercury Fulminate in a Vacuum.*

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The kinetics of thermal decomposition, in a vacuum, of bulk mercury fulminate have been studied between 70° and 100°. Advances have been made in the interpretation of the decomposition curves; the course of breakdown has been almost completely described by mathematical equations. The results are in accord with the general theory of solid-phase decomposition put forward by Prout and Tompkins (*Trans. Faraday Soc.*, 1944, **40**, 488). It is shown that certain anomalous results previously obtained can be explained on the basis of self-heating of the fulminate.

WHEN heated slowly, mercury fulminate can be made to decompose without explosion. The first attempt at a comprehensive study of the decomposition was made by Farmer (*J.*, 1922, **121**, 174), who caused mercury fulminate to decompose initially in a vacuum using the vacuum stability apparatus which had been developed by him (*J.*, 1920, **117**, 1432, 1603) for use in assessing the thermal stability of certain high explosives. His experiments were carried out mainly at 80°. Sigmoid gas-evolution–time curves were obtained after an initial quiescent period, and the gas evolved was mainly carbon dioxide. Farmer concluded that the acceleration of decomposition, noted after the initial quiescent period, was due to a solid autocatalyst. Although he provided valuable data, he did not attempt complete mathematical interpretation of his gas-volume–time curves. The most complete investigation published on the decomposition of mercury fulminate is that of Garner and Hailes (*Proc. Roy. Soc.*, 1933, *A*, **139**, 576) and a summary of much of this work, with additional remarks on the breakdown, is included in a paper by Garner, Gomm, and Hailes (*J.*, 1933, 1393). Garner and Hailes worked with single crystals of known surface area. Experiments were conducted within the temperature range 100—120°, and decomposition took place in a platinum bucket under high vacuum. Many of Farmer's results were confirmed and a number of important advances were made in the interpretation of the decomposition.

One of the characteristics of this thermal decomposition is that it takes place without the incidence of partial melting. Work carried out on the kinetics and mechanisms of this type of solid-phase decomposition has been briefly mentioned in Part I (*J.*, 1947, 1562). Prout and Tompkins (*loc. cit.*) have proposed a theory of solid-phase decomposition which appears more complete than Garner's, and they derived mathematical relationships which should describe the decomposition curve almost completely. The salient features of the theory seemed applicable to the decomposition of mercury fulminate, and these authors noted that two of their derived equations appeared to hold for one of Garner's pressure–time curves for fulminate. The present paper covers work on the thermal breakdown of masses of small crystals, covering a temperature range of 70—100°. A more complete interpretation of the reaction curves has been obtained in the light of the theory of Prout and Tompkins, and the data on self-heating, obtained in Part II, have aided the interpretation of the results of kinetic work.

EXPERIMENTAL.

The apparatus used for following the thermal decomposition was essentially that of Farmer (*J.*, 1920, **117**, 1432). Analyses of the gaseous products were carried out by the methods described in Part I (*loc. cit.*). It was found that by using 0·2 g. of fulminate the complete decomposition could be followed without re-evacuation of the apparatus; for studying the early stages of the breakdown 0·8 g. could be used without the necessity for re-evacuation. In all experiments at any one temperature the results were found to be quite reproducible. No indication of incipient melting was observed during the decomposition, and although no change in crystal form was detected after complete breakdown the average size of the residual brown particles indicated that disintegration had taken place. Typical gas-volume–time curves are given in Figs. 1 and 2. They confirm the presence of an initial quiescent period which is followed by a sigmoid volume–time curve. The total volume of gas evolved on complete decomposition was about 49 ml. per g. of fulminate. 20% Additions of the solid residue shortened the induction period considerably, but re-evacuation of a reaction tube at different stages to remove gaseous breakdown products, followed by continuation of the experiment, did not affect the progress of the reaction.

	Composition, %, of gaseous products at 100°.	
Gas.	*ca.* 40% Decomposition.	" Total " decomposition.
CO	1·0	0·7
N_2	5·4	4·4
CO_2	92·2	93·7
N_2O	1·4	1·2

Analysis of the gaseous products obtained revealed no considerable variation in their composition. Typical analyses are given in the table at the bottom of the previous page.

The major portion of the sigmoid decomposition curve was satisfied by two equations of the form

$$\log v/(v_f - v) = kt + c \qquad (1)$$

where v = volume of gaseous products at time t, v_f = final volume of gas evolved, and k and c are constants. As would be expected if Prout and Tompkins's theory were applicable, obedience to this type of equation is peculiar in that a plot of $\log v/(v_f - v)$ against time resulted in two straight lines inclined at an angle (Figs. 1 and 2), *i.e.*, different values of k and c applied in the two cases. This general equation applied throughout the temperature range studied and held, with some variation from test to test, from about 10% decomposition until the final stages of the decay period. Letting k_3 represent the velocity constant applicable up to the inflexion point, and k_4 the corresponding constant for the decay portion of the curve, it was found that for k_3 excellent agreement could be obtained for all temperatures within the range studied. For k_4, results were usually in agreement, but at the higher temperatures it was not unusual to find that values obtained in two tests at the same temperature were quite different; these occasional large variations in the values of k_4 are not considered to be due to experimental error and are discussed later. Values of k_3 and k_4 are collected in the accompanying table:

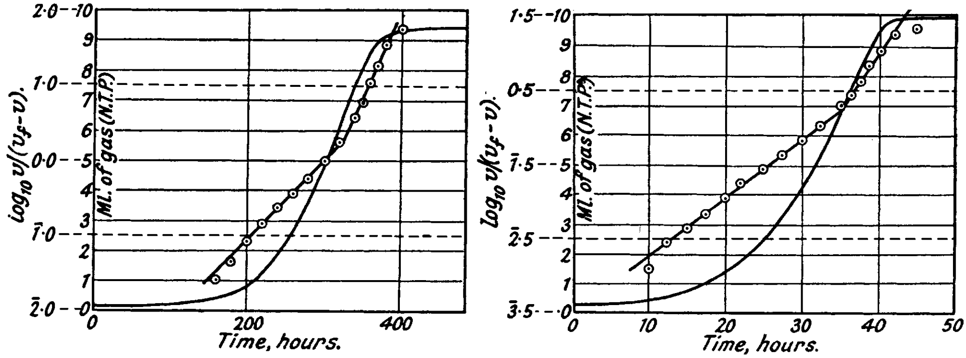


FIG. 1, at 74·9°.

FIG. 2, at 94·3°.

Thermal decomposition of 0·2 *g. of mercury fulminate.*

Temp.	10^6k_3 (sec.$^{-1}$).	10^6k_4 (sec.$^{-1}$).
70·0°	4·15, 3·86, 3·90, 3·95	8·71, 9·69, 9·31, 9·55
74·9	6·74, 6·59, 6·40, 7·05	15·8, 16·3, 14·5, 16·5
79·5	11·2, 12·6, 10·4, 12·6	33·2, 32·4, 36·6, 39·1
85·5	19·4, 20·8, 19·6	58·4, 58·4, 97·0
89·5°	32·7, 34·7	86·2, 105
95·2	53·4, 54·1	116, 106
100·1	88·7, 89·1	198, 289

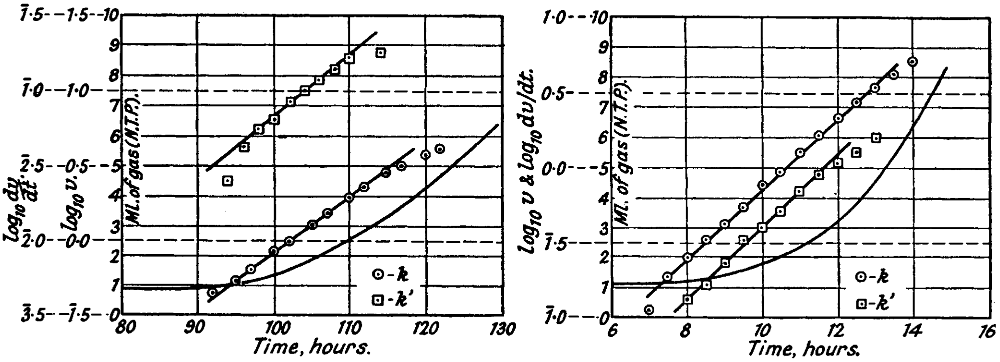


FIG. 3, at 79·9°.

FIG. 4, at 98·5°.

Thermal decomposition of 0·8 *g. of mercury fulminate.*

During the early stages of the reaction, up to 10—20% decomposition, the breakdown was found to obey an equation essentially the same as one derived by Prout and Tompkins (*loc. cit.*), *i.e.*

$$\log v = kt + c \qquad (2)$$

and Figs. 3 and 4 show this concordance. This equation was found to hold from shortly after the end of the induction period and, within the range covered by this equation, the relation

$$\log \mathrm{d}v/\mathrm{d}t = k^1t + c^1 \qquad (3)$$

similar to that derived by Garner and Hailes (*loc. cit.*) was found to apply (Figs. **3** and 4). Values of k and k^1 are given in the table below, and are mainly for tests at temperatures of 90° or below, because the use of 0·8-g. samples for their determinations introduced a danger of explosion at higher temperatures.

Temp.	10^6k (sec.$^{-1}$).	10^6k^1 (sec.$^{-1}$).	Temp.	10^6k (sec.$^{-1}$).	10^6k^1 (sec.$^{-1}$).
70·0°	9·80, 9·70	8·89	84·5°	32·3, 36·2	29·7, 44·4
75·3	16·0, 12·3	17·3, 13·3	89·9	51·8, 67·0	70·5, 57·1
79·9	23·2, 24·3	29·1, 26·9	98·5	152, 155	157, 148

It was found that, in general, equation (3) held for a smaller portion of the curve than did equation (2).

The Arrhenius equation connecting velocity constant with temperature

$$k = Be^{-E/RT} \quad \text{or} \quad \log_{10}k = -E/4{\cdot}57T + \log_{10}B$$

(where k = velocity constant, R = gas constant, T = absolute temperature, and E and B are constants) was then applied for values of k, k_3, k_4, and k^1. In the case of k_4 it is assumed (see p. 2744) that the higher values at 85° and 100° were the results of self-heating and only the low values of k_4 at these temperatures were used. The four straight lines obtained are shown in Figs. 5 and 6, and the slopes of these lines gave values of E which were in good agreement:

Velocity constant	k	k_3	k_4	k^1
E (kcals. per mole)	24·9	26·0	25·3	25·2

When values of k, k_3, k_4, and k^1 were substituted in the Arrhenius equation, values for $\log_{10}B$ of 10·8, 11·2, 11·1, and 11·0, respectively, were obtained. The dependence of each k on temperature was very similar, and from Figs. 5 and 6, the decomposition of mercury fulminate between 70° and 100° is subject to a temperature coefficient of 2·8 per 10°.

FIG. 5.

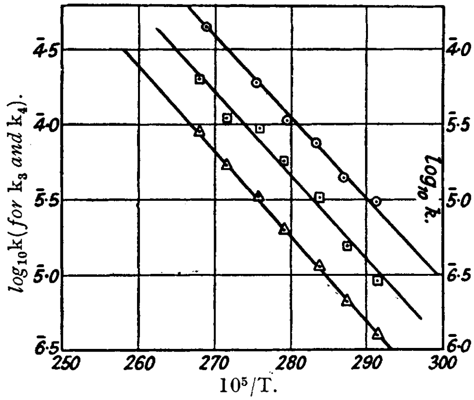
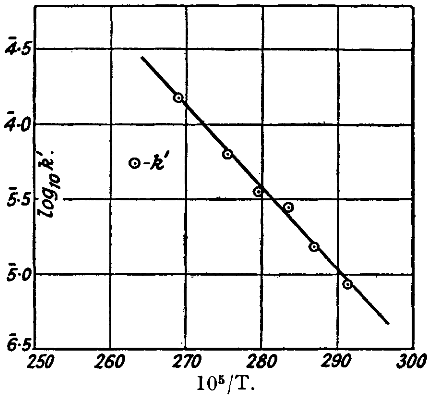


FIG. 6.



Thermal decomposition of mercury fulminate: dependence of k, k^1, k_3, k_4, *upon absolute temperature.*
⊙ = k. △ = k_3. ⊡ = k_4.

DISCUSSION.

The results of the work described above confirm that (*a*) the decomposition curves are S-shaped preceded by a pronounced quiescent period, (*b*) the solid end-products exert some catalytic influence on the breakdown but the normal rate of decomposition is not affected by the gaseous products of reaction.

The value of 49 ml. of gas evolved per g. of fulminate found compares with values of 45 ml. obtained by Farmer (1922, *loc. cit.*), *ca.* 54 ml. by Garner and Hailes, and 52 ml. by Narayana (*Current Sci.*, 1944, **13**, 313). The temperature coefficient for the reaction of 1·11 per degree is in agreement with Farmer's value of 1·12—1·13. Analyses of the evolved gases showed that approximately 93% was carbon dioxide and of the remainder *ca.* 5% was nitrogen. Narayana (*loc. cit.*) stated that the evolved gases consisted entirely of carbon dioxide and monoxide in the ratio 3 : 1. This is not in agreement with present results or with Farmer's qualitative findings. The oxygen content of the gases was 62—63% of the available oxygen in mercury fulminate; this agrees with the observations by Garner and Hailes. Comparison of the gases evolved at 40% and 100% decomposition shows no appreciable variation in composition. This indicates that the nature of the decomposition remains essentially the same throughout, and this finds confirmation in the fact that the values of the activation energy E, determined by application of the Arrhenius equation to values of k, k_3, k_4, and k^1, are in good agreement.

The four equations fitting various portions of the breakdown curve cover almost the whole of the decomposition, with the exception of the early quiescent period which, in accordance with the theory of Prout and Tompkins, should at first approximate to a linear reaction. It has been found that, within the acceleration period governed by equation (2), equation (3), essentially the same as one derived by Garner, holds and gives values of k^1 similar to that of k. The conformity to these two equations and the similarity between the values of the two constants were noted by Garner, Gomm, and Hailes (*loc. cit.*), who found that equation (3) was more reliable between 100° and 115°. Inspection of the two equations shows that equation (3) is a differentiated form of (2), and agreement between the constants is, therefore, to be expected, but in the present work it has been noted that, at temperatures below 100°, equation (2) generally holds for a longer period than equation (3).

Since Prout and Tompkins's mathematical equations have, in the present investigation, been shown to apply to the breakdown of fulminate, it is feasible that the mechanism of decomposition envisaged by these authors should also hold. Thus, although the shape of the crystals appears to be retained during breakdown, the unit cell of the product molecules is probably different from that of the fulminate, thereby fulfilling a condition productive of planes of strain. Furthermore, the catalytic effect of the end-products will tend to enhance the strains created in the crystal, with consequent cracking and disintegration of it. It has been noted in the present work that considerable disintegration of the crystals occurs during decomposition.

At any one temperature the values of k and k_3, holding until the approach of the inflexion point, are consistent throughout the temperature range studied and show obedience to the Arrhenius law. In the case of k_4, applicable during the decay period, it has been pointed out that some variation was obtained at higher temperatures and, in extreme cases, it was only when the lower values of k_4 were taken that the Arrhenius equation was obeyed satisfactorily. There seems to be a ready explanation of this effect. As was shown in Part II (*loc. cit.*), the thermal decomposition of mercury fulminate is accompanied by self-heating, but this would not be expected to become extensive during the earlier stages of the breakdown; hence, values of k and k_3 would not be appreciably influenced by this effect at lower temperatures. With the approach of the inflexion point the extent to which self-heating develops should influence the kinetics of the final decay period. As an extreme example it has been demonstrated (Part II) that at 113°, with good thermal insulation, 0·2 g. of fulminate in a sealed glass tube will explode, but if the heat developed is dissipated, by surrounding the tube with Wood's metal, explosion can be prevented. High values of k_4 obtained at the higher of the temperatures involved in the present experiments can be accounted for by the presence of the self-heating effect and, since this effect should diminish with decrease in temperature of experiment, consistent values of k_4 at low temperatures can be expected. Such consistent values were in fact obtained when the temperature was below 80°.

These considerations of the self-heating effect seem to have a bearing on certain other results obtained by Garner and Hailes. These investigators found that the period of decay was fairly well accounted for by an equation for unimolecular breakdown. Whilst the present work was being carried out it was observed that Garner and Hailes's decay constants showed an appreciable deviation from the Arrhenius equation. Furthermore, those authors had noted that the temperature coefficient was appreciably greater for their decay constants than for their acceleration constants; this would seem to indicate that the apparent activation energy was greater for the "decay" than for the "acceleration" portion of the decomposition curve. Now this difference can be accounted for either on the basis of self-heating during the decay period or by the onset of a different reaction. It has been shown in the present investigation that in the temperature range 70—100° the reactions in the thermal decomposition of fulminate are essentially the same throughout the breakdown. It appears, therefore, that the high temperature coefficient of the decay constant observed by Garner and Hailes must be ascribed to self-heating. This self-heating would become progressively greater with increasing temperature and cause localised increases in temperature. The values of the velocity constant would, therefore, show corresponding increases, resulting in a greater temperature coefficient. In addition, any variations in the self-heating effect might explain the fact that Garner's decay constants show deviation from the Arrhenius equation, a deviation noted occasionally in the present experiments, when carried out at temperatures approaching the range covered by the experiments of Garner and Hailes.

Finally, it may also be pointed out that, with increase in temperature, self-heating should begin to be effective at progressively earlier stages in the decomposition; this is in line with the observation, made by Garner and Hailes in reporting their results on the delayed explosion of fulminate at temperatures well above 100°, that explosion seemed to occur in the early part of the acceleration period.

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