

**646.** *The Decomposition of Mercury Fulminate.*

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The thermal decomposition of mercury fulminate has been investigated with particular attention to the effects of ageing, pre-irradiation, and crushing on the kinetics. Two forms, (i) freshly prepared, exponential, or white, and (ii) aged, brown, or cubic are distinguished. The method of conversion of one into the other, and the resultant changes of physical structure, have been studied. These results have proved useful in formulating mechanisms of decomposition in terms of the grosser imperfections (sub-grain boundaries) which separate the sub-grains of the crystal.

WHEN mercury fulminate is heated to about 100°, it evolves mainly carbon dioxide and nitrogen, leaving a solid residue of uncertain composition. The conclusions of various workers concerning the kinetics and mechanism of decomposition differ in many respects. Farmer<sup>1</sup> distinguished two forms, the white and the brown, which behaved differently on decomposition, but did not analyse his results in any detail. The white and the brown

<sup>1</sup> Farmer, *J.*, 1922, 174.

variety undoubtedly correspond to our fresh and aged material respectively. Garner and Hailes<sup>2</sup> found that the acceleratory process of the decomposition was preceded by a period during which gas was slowly evolved at a constant rate. Grinding eliminated the initial process and enhanced the rate during the acceleratory period which was fitted, up to 20% decomposition, by the equation

$$\log \left\{ \frac{dp}{dt} - \left( \frac{dp}{dt} \right)_0 \right\} = k_1 t + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $(dp/dt)_0$  represents the constant initial rate and  $k_1$  is a velocity constant. The activation energy was 30.4—32.2 kcal./mole, compared with the value of 27.7 kcal./mole which Garner and Hailes had calculated from Farmer's results. Equation (1) was shown to be consistent with a chain mechanism in which the branching coefficient was a constant. It was suggested that reaction was initiated in the non-crystalline material which cements the grains of the crystal together. Only a few CNO ions in these cracks occupy sufficiently open positions for decomposition to occur; and occasionally the decomposition of one CNO ion uncovers two or more others so that a chain is set up. Grinding eliminates the linear process by increasing the number of reaction centres.

These conclusions were somewhat modified in a later paper,<sup>3</sup> the  $p$ - $t$  plots being described by the expression

$$dp/dt = k_2 t^m \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $m$  for whole crystals varied from 11.2 to 22.8. The dependence (2) was described in terms of the non-uniform growth of reaction centres by transference of reaction from grain to grain at a few singular points on their mutual boundaries.

Vaughan and Phillips,<sup>4</sup> using Service material, considered the Prout-Tompkins equation<sup>5</sup>

$$\log p/(p_f - p) = kt + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

( $p_f$  = final pressure corresponding to complete decomposition), which describes a branching chain mechanism with interference of branches, to be valid throughout the decomposition and obtained an activation energy of 26 kcal./mole for the acceleratory process. However, in a re-analysis of these results, Garner and Haycock<sup>6</sup> fitted the first 10% of decomposition after the linear process with the cubic equation (4)

$$p - p_0 = k_3(t - t_0)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $p_0$  and  $t_0$  are approximately the co-ordinates corresponding to the end of the linear process. From this dependence they concluded that spherical nuclei are formed at the point  $(p_0, t_0)$  and thereafter grow at a constant rate.

The present investigation was undertaken to extend these results and to correlate the different viewpoints into a coherent theory consistent with our present and more detailed knowledge of the structure of ionic crystals.

#### EXPERIMENTAL

*Materials.*—"Fresh" fulminate was prepared by precipitation from a solution of the salt in equal volumes of water, ethyl alcohol, and ammonia solution ( $d$  0.880) by dropwise addition of acetic acid with stirring at room temperature. This procedure gave crystals which, after filtration and drying, passed through a 400-mesh B.S.S. sieve. "Aged" fulminate results from the storage of fresh material for about 2 years.

The apparatus used and experimental procedures followed were similar to those outlined by Thomas and Tompkins.<sup>7</sup>

<sup>2</sup> Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576.

<sup>3</sup> *Idem*, *J.*, 1933, 1393.

<sup>4</sup> Vaughan and Phillips, *J.*, 1949, 2741.

<sup>5</sup> Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.

<sup>6</sup> Garner and Haycock, *Proc. Roy. Soc.*, 1952, *A*, **211**, 335.

<sup>7</sup> Thomas and Tompkins, *ibid.*, 1951, *A*, **210**, 111.

RESULTS

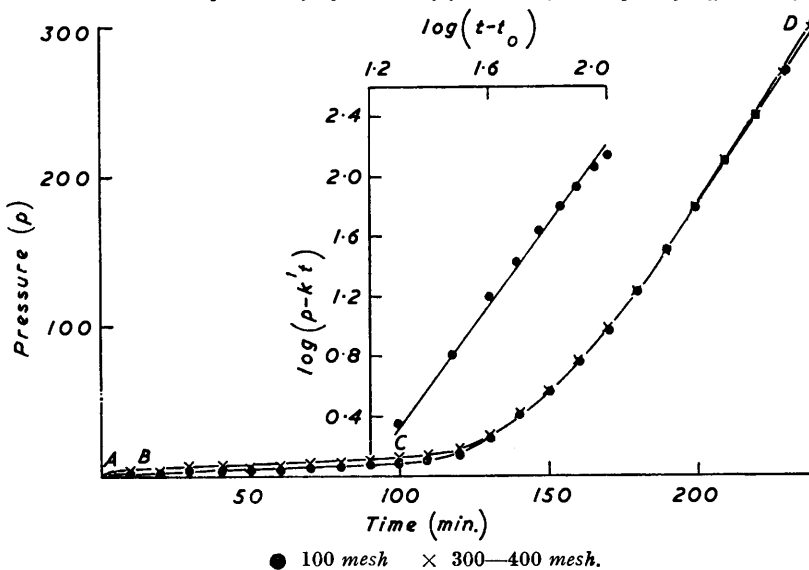
*Aged Material.*—Typical  $p-t$  plots for the decomposition of the two samples of crystal size (i) 300—400 mesh, (ii) 100 mesh are given in Fig. 1, which show that there is little effect of particle size on the rate. For ease of discussion, the plot has been divided into four sections: (i) the initial decay  $AB$ , (ii) the linear process  $BC$ , (iii) the acceleratory process  $CD$ , and (iv) the final decay process after  $D$ . The fourth section is not illustrated in Fig. 1 because we are only interested in (i), (ii), and (iii).

The initial decay follows a first-order law

$$\log \left\{ \frac{p_D}{(p_D - p)} \right\} = k_D t \quad . . . . . (5)$$

where  $p_D$  is the pressure at the completion of the process and corresponds to *ca.* 0.4% decomposition. Preliminary measurements indicate that the activation energy is around 5 kcal./mole.

FIG. 1. The thermal decomposition of aged mercury fulminate for samples of different crystal size.



The acceleratory period can be fitted with Garner's expression (4) up to 10% decomposition but a better fit, extending both to higher and to slightly lower percentage decomposition, is given by

$$p - p_D = k_3(t - t_0)^3 + k^1 t \quad . . . . . (6)$$

where  $k^1$  is the rate constant of process (ii), and  $t_0$  refers to the co-ordinate at the end of the linear process. The activation energy obtained from the temperature coefficient of  $k_3^{\frac{1}{3}}$  is 27 kcal./mole.

*Effect of Pre-irradiation.*—Illumination with mercury resonance radiation ( $\lambda$  2537 Å) causes evolution of gas at a constant rate for 120 minutes, after which the rate slowly decreases. The rate of gas evolution, which corresponds on average to about 2.5% decomposition per hour, is proportional to the square of the intensity of illumination at constant temperature, suggesting that the two molecules of fulminate (or two fulminate anions) are engaged in the act of decomposition. A considerable amount of gas is given off after cessation of irradiation and this "dark" rate, as with potassium azide and barium styphnate monohydrate, follows a first-order decay law consistent with desorption of gaseous product that had accumulated on internal and external surfaces during photolysis.

The effect of pre-irradiation at constant intensity for varying times on the subsequent thermal decomposition at 108° was also studied. It was found that (i) the initial decay process is eliminated, (ii) the value of  $p_0$  is substantially unaffected, though  $t_0$  is decreased, (iii) the applicability of the cube law is extended to 20% decomposition though the point of inflection of

the  $p-t$  plot is lowered from 65 to 50% decomposition, and (iv) the velocity parameters are related by

$$k_3 \text{ (irradiated)} - k_3 \text{ (unirradiated)} \propto k^1 \text{ (irradiated)} - k^1 \text{ (unirradiated)}$$

With increasing periods of pre-irradiation,  $k_3$  and  $k^1$  approach saturation values about three times greater than those found for unirradiated aged material, and  $t_0$  decreases linearly.

*Effect of Crushing.*—Crushing (*i.e.*, rolling the rounded end of a glass rod over crystals spread thinly on a glass plate) has similar effects on the subsequent thermal decomposition to pre-irradiation. The initial decay process is removed,  $t_0$  is decreased, and the linear and the cubic rate are increased proportionally (Fig. 2). Pre-irradiation of such crushed crystals, however, does not further increase the rates although  $t_0$  continues to decrease. The values of  $k_3$  obtained

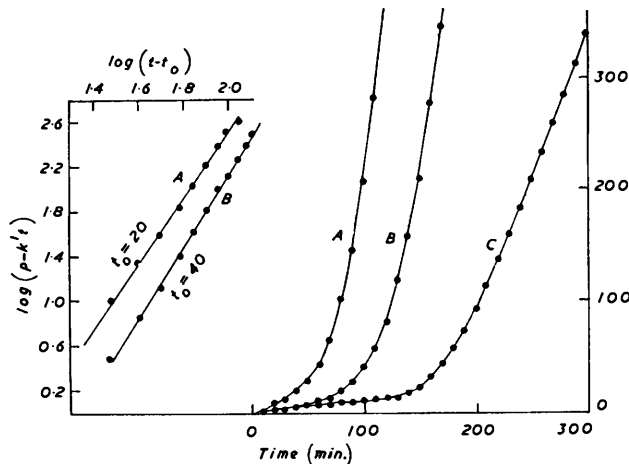
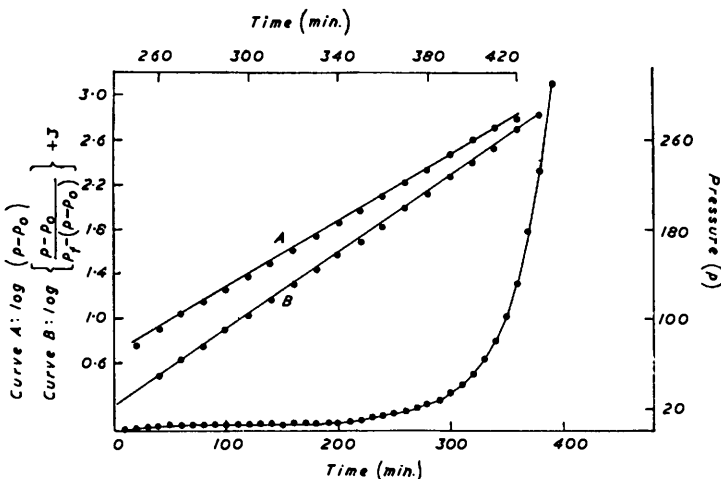


FIG. 2. The effects of crushing and pre-irradiation on the thermal decomposition of aged mercury fulminate.

A, Pre-irradiated.  
B, Crushed.  
C, Aged.

FIG. 3. The analysis of the decomposition plot for fresh mercury fulminate.

A,  $\log p$  against  $t$ .  
B, Prout-Tompkins equation.



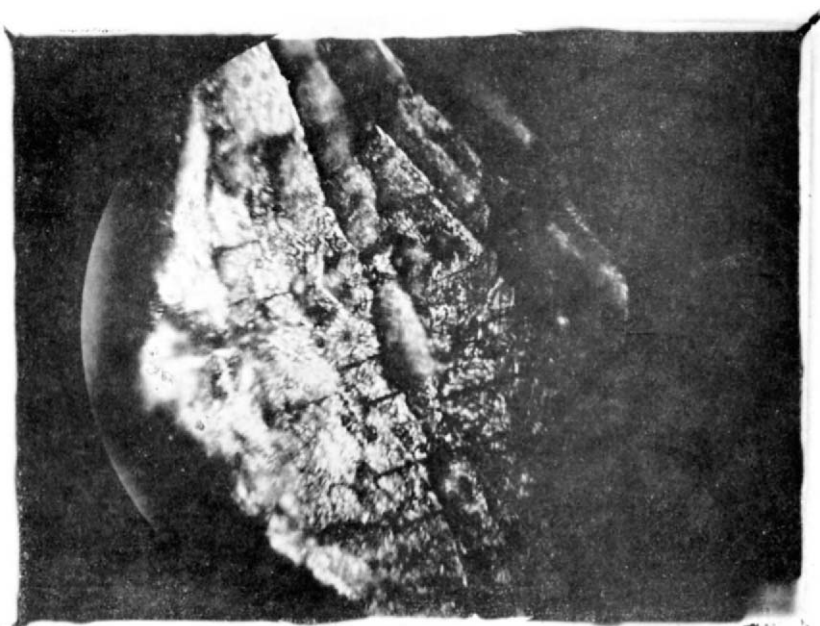
with crushed crystals are within 10% of those obtained from uncrushed, aged crystals which had been pre-irradiated for a time sufficient to attain the maximum value of  $k_3$  (*ca.* 1 hr.).

*Freshly Prepared Material.*—A typical decomposition curve is shown in Fig. 3. The principal differences from the decomposition of aged material are (i) the linear process extends over twice the time found for aged fulminate, although  $p_0$  is less ( $\frac{1}{4}$ — $\frac{1}{3}$ ), and (ii) the acceleratory process below *ca.* 35% decomposition can be fitted by the exponential relation

$$\log(p - p_0) = k_0 t + \text{constant} \quad \dots \quad (7)$$

The suitability of equation (7) below 2% decomposition is greater for samples precipitated by dilute acetic acid from ammoniacal solution than for those obtained simply by dilution with

*Cracks, roughly parallel and about 10  $\mu$  apart, produced in fresh mercury fulminate crystals by exposure to ultraviolet light.*



[To face p. 3326.]

water. The maximum rate of decomposition occurs at about 50% decomposition. Freshly prepared material obeys the cube law up to 50% decomposition after crushing and up to 20% decomposition after pre-irradiation (Fig. 4).

Since both ammonia and water are used in the preparation of mercury fulminate, layers of these reagents adsorbed at the surface of freshly prepared material might contribute to the ageing process. Consequently, fresh material was stored for 48 hours in presence of (i) 10 mm. pressure of water vapour, and (ii) moist ammonia vapour, but it was found that the subsequent thermal decomposition was unaffected in both cases. With aged crystals, treatment with water vapour had no effect except slightly to reduce the value of  $p_D$ , though after exposure to moist ammonia vapour the subsequent thermal decomposition was found to proceed according to an exponential law [equation (7); see Fig. 5].

*Microscopical Observations.*—When aged crystals (60–100 mesh) were irradiated with ultraviolet light of wavelength 2537 Å, cracks were produced at the surface (see Plate), the first of these appearing after five minutes' irradiation. The number increased to a maximum in the same manner as  $k^1$  and  $k_3$  over the same period. No additional cracks were seen to form during the subsequent thermal decomposition and no discrete nuclei were apparent at any stage, the

FIG. 4. The decomposition of fresh crystals of mercury fulminate after (A) crushing and (B) pre-irradiation.

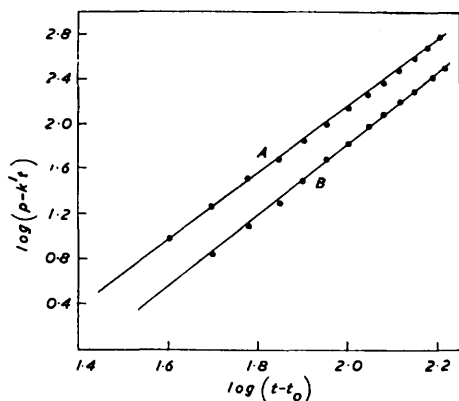
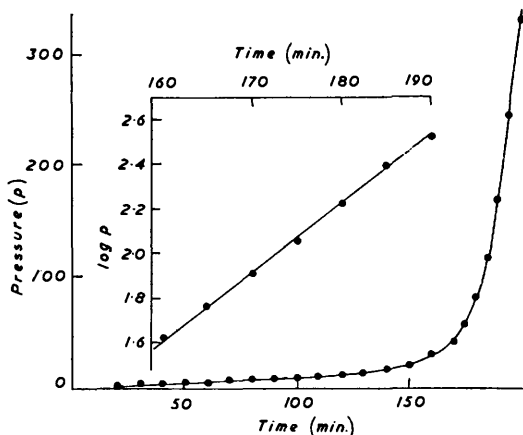
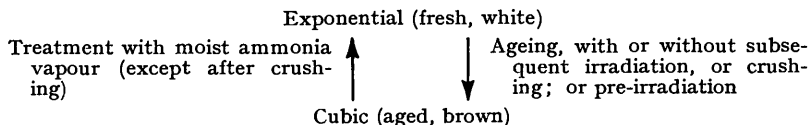


FIG. 5. The decomposition of aged mercury fulminate after exposure to moist ammonia vapour.



whole crystal gradually becoming brown as the reaction proceeded. The cracks created by pre-irradiation could be removed by treatment with moist ammonia vapour but not with water vapour alone, and the exponential law was then obeyed.

Summarising the conversion processes diagrammatically we have :



## DISCUSSION

*The Reactant Matrices.*—It is becoming increasingly evident from published work on silver oxalate,<sup>8</sup> from current work on azides, and from the present results on mercury fulminate, that changes occurring in the solid after preparation (termed ageing) are largely responsible for lack of agreement amongst the results of various workers. As with silver oxalate, the kinetic expressions applicable to the acceleratory process of the decomposition of fresh and aged mercury fulminate are different, although the activation energies are the same. These differences are therefore associated with changes of structure of the material and not with alternative reaction mechanisms.

All solids contain imperfections, and apart from the external surface itself, the most

<sup>8</sup> Tompkins, *Trans. Faraday Soc.*, 1948, **44**, 206; Finch, Jacobs, and Tompkins, *J.*, 1954, 2053.

extensive are low-angle or sub-grain boundaries which divide the crystals into blocks or sub-grains of linear dimensions 1—10  $\mu$ . These boundaries often comprise arrays of parallel edge dislocations in the principal lattice planes of the crystal (tilt boundaries), as, for example, in polygonised sodium chloride crystals,<sup>9</sup> but more generally consist of two-dimensional arrays of dislocations with mixed character, *e.g.*, screw and edge dislocations. These disordered regions generally arise from the presence of impurities and are known to have enhanced reactivity. We believe that they play an important role in the decomposition of ionic crystals generally. In contrast, we have little evidence which suggests that vacancies or other isolated defects are effective in contributing to the kinetics of decomposition of this material.

*Effects of Crushing, Grinding, and Pre-irradiation.*—During crushing, the crystals fracture along the original sub-grain boundaries,<sup>10</sup> individual blocks being formed in a cold-worked condition. These blocks are probably covered with a superficial layer of decomposed fulminate due to the frictional heat generated during crushing. Pre-irradiation has a similar effect in causing separation into blocks since cracks which are visible at a magnification of 500 are produced by the light at intervals of 10—15  $\mu$ . Even though actual fragmentation, such as occurs in crushing, does not take place, the result is nevertheless the division of the crystal into largely independent blocks. These cracks are created preferentially at points of weakness and high reactivity, *i.e.*, at points of emergence at the surface of sub-grain boundaries, and it is at such sites that photolysis preferentially takes place.

Ageing also effects the separation of the crystal into largely independent blocks. The gas evolved with low activation energy during the initial decay period probably comprises the gaseous products of a slow, prolonged decomposition at room temperature during storage, since in the ageing process the fulminate becomes brown throughout the crystal. The most probable sites of decomposition are the highly reactive sub-grain boundaries which extend throughout the crystal. The initial decay process is thus conceived to be desorption of these trapped gaseous products, the amount of this desorption being diminished by exposure to water vapour and reduced almost to zero by treatment with moist ammonia vapour. Both these highly polar vapours displace the non-polar carbon dioxide formed in the crystalline interstices during ageing. Similarly, crushing and pre-irradiation eliminate the initial desorption by rupturing the crystal at the sub-grain boundaries.

Treatments leading to a cubic law in the subsequent thermal decomposition (ageing, crushing, and pre-irradiation) therefore cause decomposition at the sub-grain boundaries such that the sub-grains of the reactant phase become predominately non-contiguous, *i.e.*, they become separated from each other by barriers of reaction product. The cubic relation describes the kinetics of processes which occur within the individual blocks themselves.

Moist ammonia vapour, which reconverts cubic material produced by ageing or pre-irradiation into the exponential (fresh) form, does so by healing the barriers or cracks produced by the previous treatment. Capillary condensation of water vapour followed by dissolution of ammonia provides a good solvent for mercury fulminate, so that the surface mobility of the constituent ions is enhanced. During removal of the solvent, unchanged fulminate is deposited in the sub-grain boundaries or cracks which then consist of reaction product, formed during ageing or photolysis, and freshly deposited fulminate. The essential condition for obedience to the cubic equation, the non-contiguity of the sub-grains, is no longer maintained and the exponential law is then valid (see below). These results suggest that the exponential relationship is associated with the propagation of the decomposition from block to block.

*The Linear Process.*—The constant rate, with an activation energy of 19 kcal./mole, is readily conceived as an interfacial reaction proceeding into each block from surfaces which have been sufficiently well nucleated (the first stages of the contracting-envelope concept). Both crushing and pre-irradiation, which cause a three- to four-fold increase in the rate of

<sup>9</sup> (a) Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford, 1953; (b) Dekeyser, Bristol Conference of the Physical Society, July, 1954; (c) Amelinckx, Van der Vorst, Gevers, and Dekeyser, *Phil. Mag.*, 1955, **46**, 450.

<sup>10</sup> Relation of Properties to Microstructure, Amer. Soc. Metals, 1954, p. 163.

this process but do not affect the activation energy, produce cracks, thereby increasing the area of the nucleated surface and therefore the rate of decomposition. Although the period over which the process extends and the extent of decomposition, as measured by  $p_0$ , differ for the aged and the fresh material, the identical kinetics and activation energies are evidence that the same mechanism is operative for both.

*The Acceleratory Process.*—With material which obeys a cube law, (i) the acceleratory process starts at the same  $p_0$  value (same extent of decomposition) for all temperatures even though the preceding linear process may have been accelerated by preliminary crushing or pre-irradiation; (ii) the ratio of  $k_3$  (the cube rate constant) to  $k^1$  (the linear rate constant) remains constant at constant temperature when both  $k_3$  and  $k^1$  are increased to their maximum values by pre-irradiation; (iii) the linear process continues independently after point  $C$  ( $p_0, t_0$ ); and (iv) at some point along  $CD$ , the rates of decomposition of the linear and the acceleratory process are equal, but since the activation energies are different (19, 27 kcal./mole), the respective pre-exponential factors have different orders of magnitude ( $10^{4-5} : 1$ ; acceleratory : linear).

Conclusions (iii) and (iv) are also valid for the decomposition of material which obeys the exponential law.

Since the linear process is probably an interface reaction at the surface of the blocks, the constancy of  $p_0$  for cubic material requires that the thickness of the superficial layer of reaction product round each block shall attain a critical value before the acceleratory process is initiated. At this point, the strain induced by the misfit at the reactant-product interface causes secondary cracking in directions predominantly perpendicular to the interface. The cusps of the cracks are probably propagated stepwise and discontinuities (cleavage steps) appear at approximately regular intervals down the cracks.<sup>10</sup> The decomposition spreads simultaneously over the faces of the secondary cracks, thereby increasing the volume strain energy until this is relieved, at least in part, by slip at the cleavage steps when isolated sub-blocks, identified with the classical mosaics of the original crystal, are formed within the sub-grains of the parent crystal. The high value of the ratio of the pre-exponential factors of the acceleratory and the linear process ( $10^{4-5} : 1$ ) suggests that when reaction is initiated in a sub-block it is completely decomposed by a co-operative process propagated rapidly.<sup>11</sup> The sub-block, now wholly decomposed, detaches itself from the reactant matrix and triggers off the decomposition of an adjacent sub-block,<sup>12</sup> the process being statistically independent of direction and requiring a thermal activation energy of 27 kcal./mole. The product matrix thus comprises a conglomerate of sub-blocks, approximately hemispherical in shape and bounded by the original sub-grain boundaries. The whole process therefore corresponds to three-dimensional growth of reaction centres, all of which are created at approximately the same time  $t_0$ , the appropriate rate expression being  $p = k_3(t - t_0)^3$ , where the parameter  $k_3$  contains a term denoting the total number of blocks in the crystal.

With fresh material, the value of  $p_0$  is smaller ( $\frac{1}{4}$ — $\frac{1}{3}$ ) than that obtained with aged material, indicating that the total amount of decomposed inter-subgranular material is less at  $t_0$ . It is suggested therefore that the critical thickness of the superficial layer of product is attained only over patches of the surfaces of the sub-grains. At these areas, as with cubic material, secondary cracks are locally produced, but instead of ultimately terminating, as in cubic material, at fully decomposed sub-grain boundaries, some will meet undecomposed boundary material. The sub-grains of fresh material are not largely independent non-contiguous domains, but are linked to each other by bridges of the undecomposed reactant. The sub-block formation does not spread uniformly throughout the individual sub-grains as in cubic material, but extends tree-like through the whole crystal *via* the bridges in a branching manner, because cracking can only originate in each sub-grain from that part of the surface which is covered with a product layer of the critical thickness. The mechanism of the sub-block decomposition and the "triggering off" of adjacent sub-blocks is the same as in cubic material, and hence the activation energy is unchanged.

<sup>11</sup> (a) Acock, Garner, Milsted, and Willavoys, *Proc. Roy. Soc.*, 1947, *A*, **189**, 308; (b) Hartshorne and Roberts, *J.*, 1951, 1097.

<sup>12</sup> Burgers, *Proc. k. ned. Akad. Wetenschap.*, 1947, **50**, 595.



The initial reaction centres present at  $t_0$  are largely concentrated at the external surfaces, since only here is the product layer of critical thickness complete; however, many of the initial centres of reaction do not continue to propagate the decomposition in every direction since this is only possible where adjacent sub-blocks are already present. Further, in transference of reaction from block to block more than one bridge is normally available so that branching takes place. An exponential rate law can thus be expected.<sup>2</sup> It must be emphasised that although the acceleratory process is associated with the higher activation energy (27 kcal./mole) this energy requirement is sufficient to initiate the decomposition of a chain of  $10^{4-5}$  molecules of fulminate, whereas, in the linear process the low energy of 19 kcal./mole has to be gained for each molecule (or pair of molecules) decomposing. Consequently, the linear process, still apparent at low percentage decomposition, is quickly swamped by the acceleratory process, the speed of travel of which is so much greater through the crystal. Further, the ageing process which extends over months is so slow that relaxation processes have ample time to occur whereas in the rapid process of "bridging" the sub-grains during decomposition, these processes cannot take place; indeed, this is one of the main factors in block-to-block infection.

Finally one would expect that in the initial stages the rate of the exponential process would be slower than that of the cubic process since the number of reaction centres is smaller. The experimental results are in accord with this. Similarly, depending on the number of initial centres of reaction which continue to grow, interference to the branching would be expected. Consequently, for fresh material, the Prout-Tompkins equation should be valid over a greater range than the simple exponential expression, as is illustrated in Fig. 3. It is considered that the service material used by Vaughan and Phillips probably corresponds to our aged material.

The activation energy of 27 kcal./mole obtained here is in good agreement with that recorded by Vaughan and Phillips (26 kcal./mole) and that calculated from Farmer's results (27.7 kcal./mole), but is appreciably less than the value given by Garner and Hailes for single crystals. Their higher values may be due to self-heating, which cannot be entirely eliminated by use of a hydrogen atmosphere since reaction proceeds throughout the crystal and is not confined to those surfaces of the crystal in contact with cooling gases.

In conclusion, it is clear from the present work, from that previously reported on the silver oxalate decomposition, and from unpublished results with azides, that ageing brings about changes in the physical structure of freshly prepared material which determine to varying degrees the kinetics of the decomposition. The marked similarity in the behaviour of mercury fulminate and silver oxalate also suggests that the present theoretical approach in terms of the grosser imperfections—a theory which may be regarded as an extension and generalisation of that previously suggested on the basis of results obtained on silver oxalate—may have a much wider applicability to other solid decompositions.

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