259. *Solid-phase Reactions in Silver Fulminate.*

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The thermal decomposition of silver fulminate at 190, 195, 200, 205, and 210° has been studied. There is an initial rapid decomposition which follows a first-order decay with an activation energy of 0·28 ev. This is followed by an acceleratory period, which obeys the relationship $(P - P_0)^{\frac{1}{2}} = k_2(t - t_0)$. The activation energy for this stage is 1·24 ev.

It is suggested that the initial and rate-determining step is the transfer of an electron from the top of the fulminate band to the top of the Fermi level of the metallic nuclei. The " hole " formed in this way reacts with an adjoining fulminate group with liberation of gases.

WHEN heated, solid silver fulminate decomposes to a gas and silver. In this Paper the results of a study of the thermal decomposition in the solid phase, and of the thermal and impact sensitivities of this compound, are presented. Data on ultraviolet absorption spectra, dielectric constant, refractive indices, and X-ray diffraction have been used in an interpretation of these results.

EXPERIMENTAL

Preparation of the Compound.—The compound was prepared by adding absolute alcohol (30 c.c.) to a 21·5% solution (19 c.c.) of silver nitrate in nitric acid at 60—80°. The freshly precipitated product was dissolved in a 20% solution of ammonium acetate at 50° and cooled very slowly to room temperature, glistening needle-shaped crystals being obtained (Found: Ag, 71·9; calc. 71·9%). The thermal decomposition was studied after storage of the sample in a dessicator covered with dark cloth for 3—4 weeks. The apparatus was similar to one described earlier.

Impact sensitivity and induction periods to explosion at various temperatures were studied as described in an earlier Paper.[1] Ultraviolet absorption spectra of transparent single crystals were measured on a Beckmann model DK_2 spectrophotometer. The low-frequency dielectric constant of a pelleted sample, prepared by the consolidation of small crystals, was studied on a capacitance bridge (716C, General Radio Company, Massachusetts). Rotation X-ray-diffraction photographs were taken after heating the crystals for 1—3 hr.

RESULTS

Thermal decomposition was studied at 190, 195, 200, 205, and 210° (see Fig. 1). Three stages can be discerned: (i) an initial rapid change which slows down progressively; (ii) an acceleratory stage; and (iii) final decay. In Fig. 2 are given curves showing the variation of $\log [P_0/(P_0 - P)]$ with t, where P_0 is the pressure at the end of the first stage, and P the pressure at any time, t. The curves being linear, the initial decay is probably first-order, *i.e.*,

$$\log [P_0/(P_0 - P)] = k_1 t \qquad (1)$$

where k_1 is the rate constant. Values of P_0 and t_0 have been selected somewhat arbitrarily to indicate the slope of the curve.

In Fig. 3 are shown plots of $\log k_1$ against the reciprocal of the absolute temperature, T. From the slope of this curve the activation energy for the first-order reaction is found to be 6·45 kcal. mole^{-1} or 0·28 ev. Data for the acceleratory stage have also been analysed. In Fig. 4 are shown plots of $(P - P_0)^{\frac{1}{2}}$ against $(t - t_0)$, where t_0 is the time when the pressure is P_0. Since these curves are linear, the acceleratory stage appears to obey the relationship

$$(P - P_0)^{\frac{1}{2}} = k_2(t - t_0) \qquad (2)$$

where k_2 is the rate constant. The curves showing the variation of $\log k_2$ with (I/T) are shown in Fig. 5. The activation energy for the acceleratory stage is found to be 28·62 kcal. mole^{-1} or 1·24 ev.

¹ Singh, *Trans. Faraday Soc.*, 1959, **55**, 124.

A spectrophotometric trace showing % transmission at room temperature through a transparent crystal of silver fulminate in the region 2000—3500 Å is shown in Fig. 6. The absorption edge at 3180 Å corresponds to a probable width of the forbidden-energy gap as 3·88 ev.

The low-frequency dielectric constant (K_s) of the pelleted sample is 11·80 $\pm$ 0·50, and the refractive [2] indices of the crystal are 2·50 and 2·70 for sodium light polarised along the needle-axis and perpendicular to the needle-axis, respectively. The mean of these gives the dielectric constant (K_h) at very high frequency as 7·96.

Results of the determination of the impact sensitivity are given in Fig. 7. The variation of % explosions with heights of fall of the ball follows a steep curve. The critical heights for 50% explosions are found to be 15 and 20 in. for silver and mercury fulminates, respectively. The impact sensitivity of silver fulminate is higher than that of mercury fulminate.

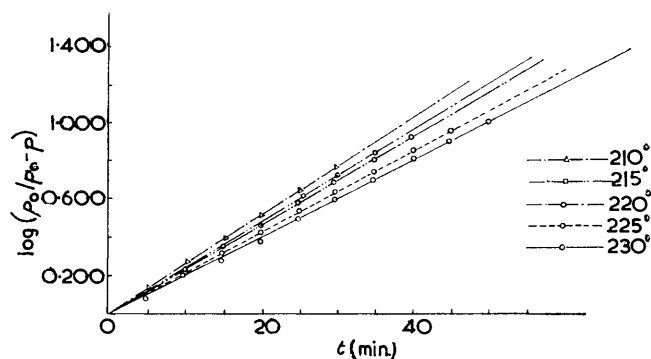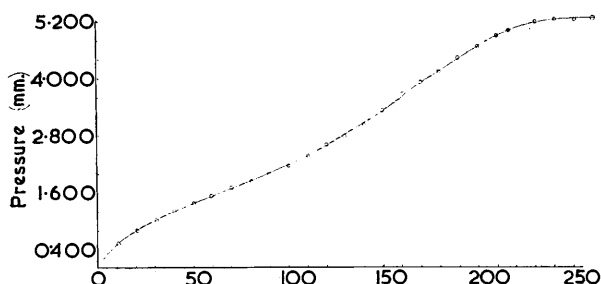
FIG. 1. Thermal decomposition of silver fulminate.

FIG. 2. First stage of the decomposition.

The induction period (τ) for the build-up of an explosion decreases with increase in temperature. The variation of log (induction period) with $1/T$ is given in Fig. 8. From the slope of this linear curve the energy of activation is calculated to be 14·2 kcal. mole^{-1}. The compound's low activation energy is responsible for its fairly high thermal sensitivity. The temperature of explosion for an induction period of 5 sec. is 238°. This is higher than that for mercury fulminate (225°).

X-Ray diffraction photographs of single crystals heated for 1 and 3 hr. are given in Figs. 9 and 10. It is observed that the partially decomposed sample gives a new pattern of rings superimposed upon the original diffraction spots due to mercury fulminate. Measurements show that the rings arise from the formation of randomly-oriented FCC crystallites of silver.

DISCUSSION

Beyond 190—210° self-heating becomes appreciable, and the reaction tends to build up explosively. At 190—210°, during the initial stage (Fig. 1) there is a rapid evolution of gas which slows down according to first-order kinetics. Unlike mercury fulminate,[3] silver fulminate evolves a large volume of gas during the initial stage The first-order decay lasts for an appreciable time. The linear stage, which is prominent in mercury fulminate,

[2] Bowden and Yoffe, " Fast Reactions in Solids," Butterworth, London, 1958, p. 51.
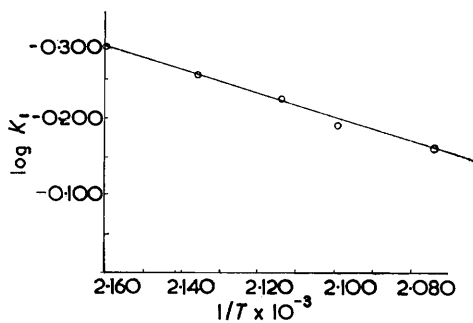[3] Bartlett, Tompkins, and Young, *J.*, 1956, 3323.

FIG. 3. Variation of rate of decomposition with the reciprocal of the temperature (first stage).
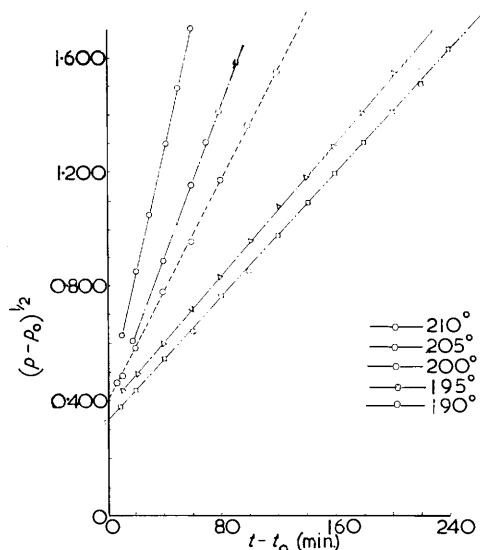

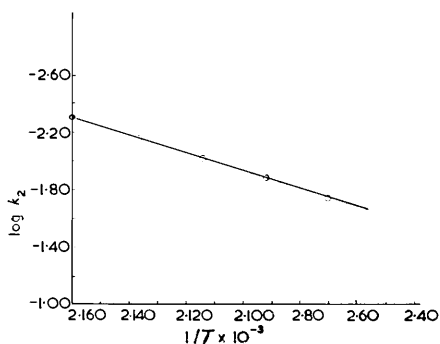FIG. 4. Second stage of the decomposition.

FIG. 5. Variation of rate of decomposition with the reciprocal of the temperature (second stage).
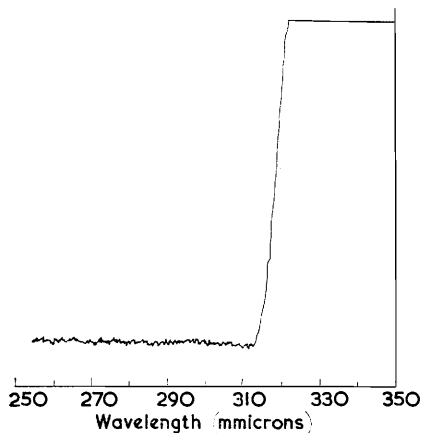

FIG. 6. Variation of percentage transmission with wavelength for a crystal.
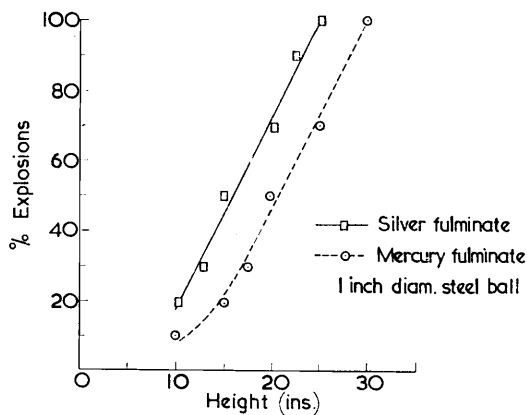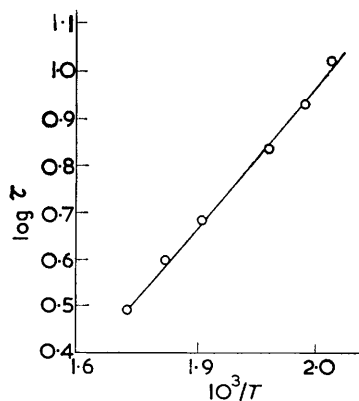

FIG. 7. Impact sensitivity.

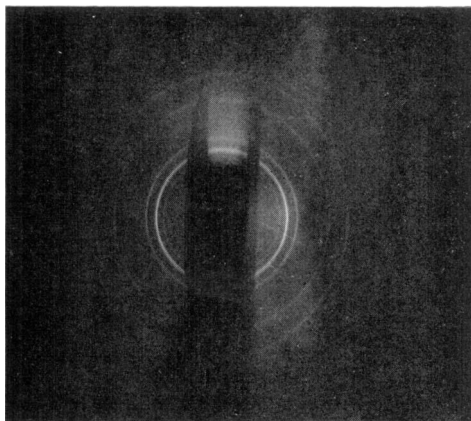FIG. 8. Variation of log (induction period τ) with the reciprocal of the absolute temperature.

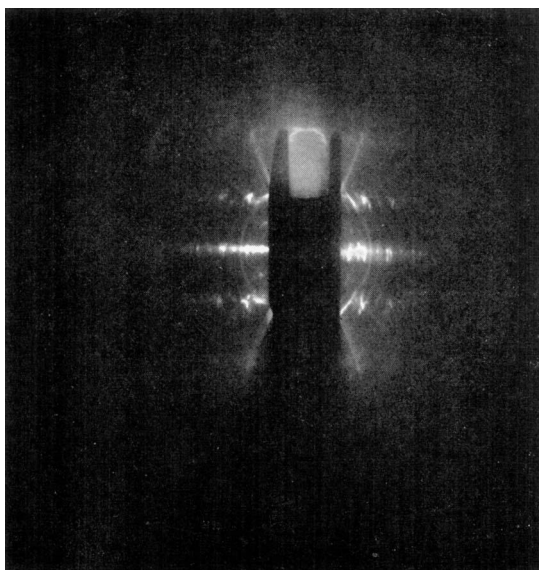FIG. 9. Rotation X-ray photographs of silver fulminate heated for 1 hr. at 190°.

FIG. 10. As Fig. 9, but specimen heated for 3 hr.

is masked in silver fulminate by the prolonged initial decay. The decomposition of silver fulminate may thus be assumed to take place in three stages: (i) initial decay; (ii) acceleratory stage; and (iii) final decay.

Evolution of gases in the first stage, which is quite common in solid-phase thermal decomposition, may be attributed to either desorption of trapped or adsorbed gases or to reactions at energetically favourable positions. The activation energy for the initial first-order decay in silver fulminate (0·28 ev per molecule) is low for any chemical reaction. The initial decay may, therefore, be attributed to the evolution of gases that are adsorbed at interfaces within the grain boundaries. The desorption of these gases follows first-order kinetics. A slow process involving the formation of metallic nuclei at energetically favourable sites may also be occurring towards the end of this stage. Its kinetics are masked by the relatively faster reaction involving prolonged desorption of gases.

During the accelerating stage, the reaction follows a power law with an index $n = 2$. Presumably, the reaction is propagated in two dimensions, starting at metallic nuclei at the edges of blocks, which are formed slowly during storage. The reaction proceeds from nuclei at the edges towards the centre by the advance of a two-dimensional reaction interface moving along crystallographic planes.
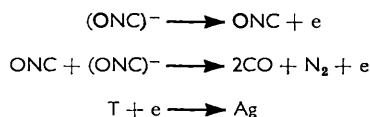
The initial and rate-determining step in solid-phase reactions at the interfaces may be the transfer of an electron from the top of the fulminate band to either the bottom of the conduction band or the top of the Fermi level of the metallic nuclei. To decide this point it is necessary to know the energy gap between the top of the fulminate band and the bottom of the conduction band. The absorption spectrum of silver fulminate is shown in Fig. 6. There is a sharp fall in absorption at 3180 Å; additional data at low temperature and on photoconductivity are essential to establish the mechanism of light absorption. The energy corresponding to the absorption edge may represent the energy of formation of an exciton which dissociates by further absorption of thermal energy into a free electron and hole. In materials of high dielectric constant, such as silver fulminate, the optical energy gap in question is given by the photon energy at the absorption edge. The position of the absorption edge in silver fulminate gives an optical energy gap, ε, of 3·88 ev. The ratio of high frequency to low frequency dielectric constant (K_h/K_s) is 0·675; hence the thermal-energy gap, ε_T, is 2·62 ev per molecule much higher than the activation energy (1·24 ev per molecule) for the acceleratory stage.

The activation energy involved in transfer of an electron by means of thermal motion from the top of the fulminate band to the top of the Fermi level of metallic nuclei of silver is given by the expression:

$$E = \varepsilon_T + \chi - \phi \qquad (3)$$

where χ is the crystal affinity and ϕ is the work function of silver. The crystal affinity of silver fulminate is not known, but it may be assumed to be the same as for silver bromide. This gives $E = 3·60$ ev. Substitution of values of various parameters in expression (3) yields $E = 1·53$ ev, which is sufficiently close to the experimental value (1·24 ev per molecule). The small difference may be due to a poor value of χ.

On transfer of an electron from the fulminate band a hole is formed, which may react with an adjoining fulminate ion according to the equations:

$$(ONC)^- \longrightarrow ONC + e$$

$$ONC + (ONC)^- \longrightarrow 2CO + N_2 + e$$

$$T + e \longrightarrow Ag$$

The trap (T) which is a silver ion may capture an electron (e), the silver atom adding on to the growing nucleus.

Another interpretation is that the initial rate-determining step may be rupture of the

Ag–O link (bond energy [4] 1·4 ± 0·4 ev). This may be followed by reaction between an ONC free radical and an adjoining fulminate group.

The mechanism involving metallic nuclei outlined earlier is more general and is applicable to various solids.[5] It is probable that decomposition of silver fulminate follows this mechanism rather than the one involving rupture of the Ag–O link.

[4] Gaydon, " Dissociation Energies," Chapman & Hall Ltd., London, 1953, p. 219.
[5] Jach, *Trans. Faraday Soc.,* 1963, **4**, 947.