676. *The Thermal Decomposition of Thallous Bromate.*

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Thermal decomposition of thallous bromate *in vacuo* has been investigated at 120—165°, and the overall reaction found to be essentially $4TlBrO_3 \longrightarrow 2Tl_2O_3 + 2Br_2 + 3O_2$. In addition, a very small amount of thallous bromide was formed, and infrared absorption data for partially decomposed crystals suggested the formation of an intermediate product (of unknown constitution). The kinetics of the reaction, determined by oxygen pressure–time measurements, showed that the rapid evolution of a small quantity of gas by a first-order decay process, followed by a slow linear-rate reaction, preceded the main autocatalytic stage. The respective activation energies were determined. Intense ultraviolet irradiation *in vacuo* at room temperature changed the crystals from colourless to light brown, caused slight decomposition, and had a small effect on the kinetics of subsequent thermal decomposition. The mechanism and the effects of ageing and ultraviolet pre-irradiation are discussed.

THE kinetics of the thermal decomposition of thallous bromate have been found to resemble those of mercury fulminate [1] and lithium aluminium hydride [2] in that rapid evolution of a small quantity of gas followed by a slow linear-rate reaction precedes the main autocatalytic stage. Further, although the effects were much less pronounced than with fulminate, intense irradiation with ultraviolet light at room temperature caused slight decomposition and influenced the early stages of subsequent thermal decomposition. It was of interest therefore to see how far the mechanism could be interpreted in terms of reactions initiated at imperfections between the sub-grains of the crystals, a theoretical approach applied successfully by Bartlett, Tompkins, and Young to the fulminate decomposition [1,3] and by some of the present authors [4] to certain aspects of the

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[1] Bartlett, Tompkins, and Young, *J.*, 1956, 3323.
[2] Garner and Haycock, *Proc. Roy. Soc.*, 1952, *A*, **211**, 335.
[3] Tompkins and Young, *Discuss. Faraday Soc.*, 1957, **23**, 202.
[4] Simpson, Taylor, and Anderson, *J.*, 1958, 2378.

decomposition of ammonium dichromate. As in the latter investigation, kinetic experiments have been supplemented by infrared absorption measurements and microscopical observations.

EXPERIMENTAL

Thallous bromate was prepared by slow addition of potassium bromate (0·05 mole) in water (125 c.c.) to thallous nitrate (0·05 mole) in water (400 c.c.) at 70—80°, the precipitate being then brought completely into solution by heating almost to the b. p. The solid obtained by cooling overnight was recrystallised from water (400 c.c.) with slow cooling. The crystals, although small (0·1—0·3 mm.) and compact, showed numerous striæ and occasional dendritic growths, and unfortunately the habit was not improved by further crystallisations. Of two preparations, the first (referred to below as "aged") was stored in air in the dark in a closed weighing bottle for *ca.* 2 years before use; the second ("fresh") was used within a few weeks of its preparation.

The apparatus and experimental procedures were very similar to those previously described,[4, 5] except that a thermostat-controlled Pirani gauge protected by liquid-nitrogen traps was added to the system. The gauge was calibrated with oxygen against the Macleod gauge. For experiments at 140—165°, the volume of the system (4350—6700 c.c.) was such that decomposition of 7—10 mg. of thallous bromate gave a final oxygen pressure not exceeding 0·1 mm., any bromine evolved being condensed in a liquid-nitrogen trap placed immediately after the reaction vessel. To study the initial stages of the reaction at 120—142°, 28—32 mg. were used in a volume of 936 c.c.; measurements were then terminated at oxygen pressures not greater than 0·08 mm. The reaction vessel's thermocouple, against which the platinum bucket containing the sample rested during the reaction, gave no indication of self-heating in any of the experiments. During ultraviolet irradiation (10 hr.) at a distance of 15 cm. from a 300 w Hanovia mercury lamp, crystals were spread in a thin layer in a vitreous silica tube. The tube was continuously evacuated with an oil-pump and occasionally shaken to expose fresh surfaces.

RESULTS

Microscopical Observations.—When crystals were heated (2—3°/min.) in air on a hot-stage microscope, a number of irregularly shaped black nuclei appeared at 120—130°, and then increased in number and size in an indefinite manner with rising temperature until at 170—180° the crystals were completely black and showed numerous cracks and pits on the surfaces. Independently of the black nuclei, and separated from them, a number of red-brown patches also developed (140—150°) and these appeared to be within the crystals rather than on the surfaces. Black nuclei were often seen to grow through, but not to be initiated in, the brown areas. The same phenomena occurred when crystals were heated *in vacuo*, and both the brown and the black areas remained unchanged over several days if partially decomposed crystals were cooled to room temperature. It seems unlikely therefore that the brown areas were due solely to occluded bromine. In general, crystals appeared completely black after only 10—15% decomposition.

After ultraviolet irradiation, crystals were of a uniform light brown colour but otherwise unchanged in appearance under the microscope. The colour was stable both in dry air and *in vacuo*, but in moist air, over a period of several days, the colour gradually blackened and appreciable quantities of bromine were evolved. When heated, pre-irradiated crystals behaved in a manner very similar to that described above.

Chemistry of the Reaction.—The gaseous products of the reaction were shown to be oxygen and bromine and the black solid product to be mainly thallic oxide. Although a small amount of thallous bromide could be extracted from the solid product with hot water, the *X*-ray powder photograph showed only the spacings of Tl_2O_3. As calculated from the final pressure of non-condensable gas in the kinetics experiments at 140—165°, the quantity of oxygen evolved was 0·76 ± 0·04 mole per mole of thallous bromate and was independent of the temperature of decomposition or the age or pre-irradiation of the crystals. Decomposition of 0·25 g. samples at 150—155° in an evacuated tube attached to a liquid-nitrogen trap yielded 0·4 ± 0·05 mole

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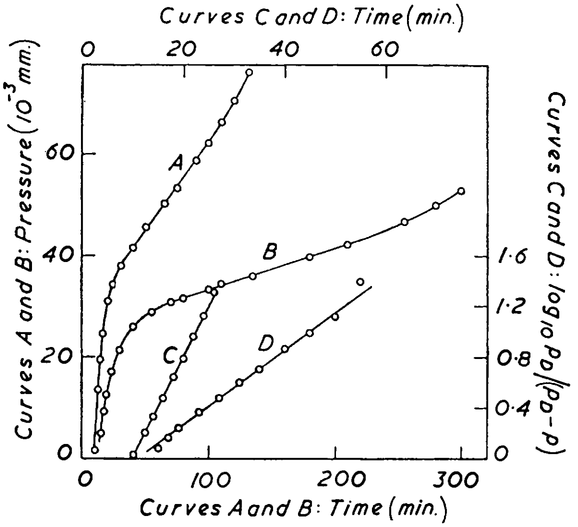
[5] Taylor, *J.*, 1955, 1033.

of bromine per mole. (Attempts to carry out bromine determinations with 0·45 g. samples at 170° were vitiated by minor explosions.) The overall reaction is thus essentially $4TlBrO_3 \longrightarrow 2Tl_2O_3 + 2Br_2 + 3O_2$, but with a further process occurring only to a small extent in which some of the bromine is retained in the solid product as thallous bromide. The loss in weight of samples in the kinetics experiments was 28 ± 3% compared with 31·3% required by the above equation.

Intense irradiation of crystals at room temperature in a quartz vessel attached to the thermal decomposition apparatus caused less than 0·3% of decomposition in 10 hr., as judged from the pressure of evolved oxygen. Traces of bromine were also evolved. When freshly irradiated crystals were crushed under a few drops of distilled water, the liquid gave a slight blue colour with starch–potassium iodide paper, indicating free bromine or some other oxidising agent.

FIG. 1. *First-order decay and linear-rate processes for aged crystals.*
A and C: 135·5°, pre-irradiated.
B and D: 135·3°, un-irradiated.



It is significant that the same blue colour was obtained even after the irradiated crystals had been stored in a corked tube in air for three months.

In a search for intermediate products, infrared absorption measurements (KBr disc technique, Hilger H 800 spectrophotometer) were carried out on fresh thallous bromate and on samples which had been severally 11, 50, 81, and 100% decomposed at 160°. The relative intensities of the bromate ion peak[6] at 770 cm.$^{-1}$ showed that about 90% of the ions had disappeared by the time that only 60% of the possible oxygen had been evolved. Although the formation of an intermediate is thus indicated, and one from which oxygen is released on heating, the absence of new absorption peaks precluded its identification.

Kinetics of Oxygen Evolution.—The decomposition can be divided conveniently into three parts: (1) the two initial reactions terminating at between 3 and 7% decomposition, (2) the acceleration stage, which at 35—50% decomposition gives way to (3) the decay stage.

(1) *Initial reactions.* To avoid inconveniently high rates, the initial reactions had to be studied at 120—142° compared with 140—165° for the other two parts, but it is known qualitatively that the same essential features occur in both temperature ranges. For aged crystals, with or without pre-irradiation, Fig. 1 shows the two initial reactions to consist of (*a*) a rapid first-order decay process[7] given by the equation $\log_{10}[p_D/(p_D - p)] = kt$, where p_D is the pressure (mm.) at the conclusion of the process, followed by (*b*) a slow constant-area interface reaction terminating at pressure p_0 which corresponded to 3—4% decomposition. The values of p_D and p_0 were increased by pre-irradiation (cf. Fig. 1) but not appreciably by increase in decomposition temperature. The value of k at a given temperature was approximately doubled by pre-irradiation, while the linear rate increased about five-fold. The temperature coefficients of k and of the linear rate gave activation energies respectively of 35 ± 1·5 and

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[6] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[7] For review of kinetic equations see Garner, " Chemistry of Solid State," Butterworths, London, 1955, p. 184.

36 ± 4 kcal./mole, and neither value was changed by pre-irradiation. With fresh crystals, the initial reactions were very similar, except that the value of p_0 was higher than for aged crystals (corresponding to 5—7% decomposition), and tended to increase with increasing temperature.

(2) *Acceleration stage.* Irrespective of the age of crystals or the temperature (140—165°), the acceleration stage terminated at *ca.* 35% decomposition, and at *ca.* 50% after pre-irradiation. Figs. 2 and 3 show that the stage can be represented [7] by the Prout–Tompkins equation $\log_{10} [\alpha/(1 - \alpha)] = k_1t + \text{const.}$, where α is the fraction decomposed at time t, or by $p - p_0 = k_2(t - t_0)^3$ where p is the pressure (mm.) at time t and where p_0 and t_0 were found by trial and error. There was, however, a tendency, particularly at the higher temperatures, for the fit of the cubic equation to be improved by pre-irradiation, and then to be slightly better than that of the Prout–Tompkins equation. At a given temperature with fresh crystals, values of k_1 and $k_2^{\frac{1}{3}}$ were increased by about 25% by pre-irradiation, but with aged crystals the values were either unchanged or tended to decrease. In the absence of pre-irradiation, the velocity constants for aged crystals tended to be slightly greater than those for fresh crystals. Crushing of the crystals did not affect the kinetics significantly. The temperature coefficient of k_1 or of $k_2^{\frac{1}{3}}$ always gave the same activation energy, 50 ± 2 kcal./mole.

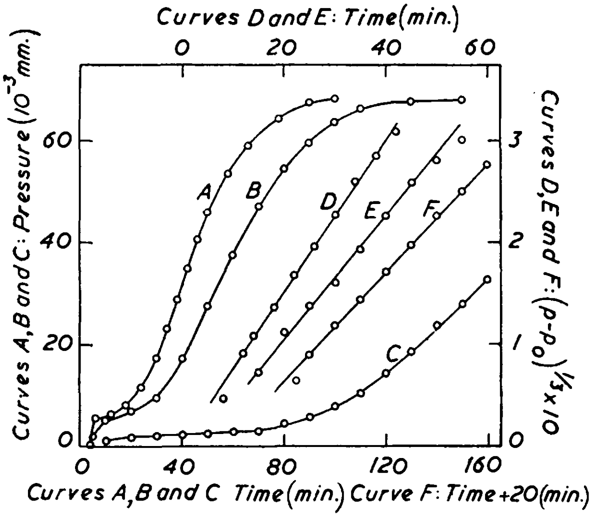

FIG. 2.

A and B: pressure–time plots for fresh crystals, with and without pre-irradiation respectively, A 160·5°, *B* 160·1°.

C: pressure–time plot for un-irradiated aged crystals, 151·6°.

D, E, and F: cube-law plots for curves A, B, and C respectively.

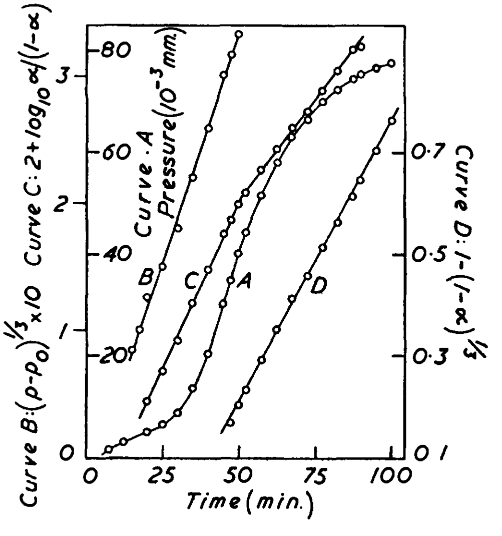

FIG. 3.

A: pressure–time plot for aged pre-irradiated crystals, 160°.

B, C, and D: cube-law, Prout–Tompkins, and contracting-sphere equation plots respectively for curve A.

(3) *Decay stage.* Fig. 3 is typical of the results obtained at 140—165° and showed that the stage is well represented [7] by the Prout–Tompkins equation, or by the contracting-sphere equation, $1 - (1 - \alpha)^{\frac{1}{3}} = k_3 t$. At a given temperature, the respective velocity constants were not changed significantly by ageing or pre-irradiation of the crystals, and their temperature coefficients gave the same activation energy, 35 ± 2 kcal./mole.

DISCUSSION

Thallous bromate on ageing at room temperature does not change in appearance or undergo the slow decomposition which occurs with mercury fulminate, and it is therefore unlikely that the initial reactions involve merely desorption of gaseous products. The relatively high activation energy, *ca.* 35 kcal./mole, shows that the first-order decay and linear-rate processes both involve actual decomposition of the bromate. The processes (cf. mercury fulminate [1]) are consistent with (*a*) rapid decomposition at the sub-grain boundaries, the rate being determined at any given time by the fraction $(p_D - p)/p_D$ of available material, followed by (*b*) progression, for a short distance into the sub-grains, of a constant-area interface created during (*a*). Process (*b*) would correspond to the beginning of a contracting-envelope mechanism. Since pre-irradiation caused only slight decomposition of the solid, but increased the rates of (*a*) and (*b*) and also the value of p_0, its effect seems to be at least in part one of nucleation at and near sub-grain boundaries. Reaction (*a*) would then proceed from a larger number of centres and reaction (*b*) progress more rapidly and further into the body of the sub-grains. The higher values of p_0 for fresh than for aged crystals suggest that in the former a larger amount of disordered material is available at the boundaries so that decomposition occurs to a greater depth. Ageing would then be regarded as a type of annealing in which strain and disorder at the boundaries were relieved. It must be remembered, however, that the fresh and the aged crystals came from separate (but otherwise identical) preparations, and this may have caused part of the observed differences. Further, after aged crystals were recrystallised, an increase in p_0 occurred, but not quite up to the fresh-crystal value.

It is reasonable to assume that the above concept of the initial reactions is applicable in the higher temperature range where the main autocatalytic stage of the reaction was studied. Accordingly, it might be expected that crystals for which p_0 is relatively high would contain at the beginning of the acceleration a large number of non-contiguous crystal blocks, which may decompose in a manner analogous to the spherical growth of nuclei and have p–t^3 kinetics (cf. mercury fulminate [1]). However, as Fig. 3 shows for aged irradiated crystals, a clear decision between Prout–Tompkins and cubic-equation kinetics could not be made, and the same applied to fresh crystals. It was found, at most, that after pre-irradiation the cubic equation was in general slightly the more satisfactory, and then applied up to the maximum rate at *ca.* 50% decomposition as against *ca.* 35% for un-irradiated crystals. With fresh crystals after irradiation there was also a small increase in the acceleration velocity constants. At the conclusion of the initial reactions therefore the crystals may in fact consist of largely non-contiguous blocks whether pre-irradiated or not.

In the acceleration and decay stages, the activation energies, 50 and 35 kcal./mole respectively, both refer to linear growth, and since over a considerable fraction of the decomposition the corresponding rates do not differ by a factor of more than ten, the pre-exponential factor for the acceleration process must be 10^{6-7} greater than that for the decay process. This indicates that during the acceleration a single act of decomposition can trigger off the decomposition of a further considerable number of molecules, and/or that the reaction proceeds from a much greater number of reaction centres than the decay process. The occurrence of an intermediate, suggested by the infrared data, may be related to the above in that its formation may involve the higher activation energy and pre-exponential factor, and its decomposition the lower values.

A different interpretation of the decomposition mechanism (suggested to us by a referee) may be derived on the assumption that the solid consists initially of a fixed number of isolated microcrystals, already nucleated, together with a number of larger, more perfect crystals. Random decomposition of the microcrystals by a linear-growth mechanism could then account for the initial reactions, the activation energy for linear growth being 35 kcal./mole, leading to an activation energy with respect to the extent of volume decomposition, α, of 3×35 kcal./mole. In the acceleration stage involving the more perfect crystals, one would expect that up to 10—15% of decomposition nuclei are being created and grow, and therefore that the kinetics in the simplest case would depend on t^4 and not t^3. By experiment, the p–t^3 relation is preferred, although in some of the runs a p–t^4 relation is almost as satisfactory. Nevertheless, the growth activation energy will now be 3×35 kcal./mole, so that the activation energy for nucleation would be about $(3 \times 50 - 3 \times 35) = 45$ kcal./mole. Nucleation on the more perfect crystals as a result of the initial reactions may not therefore be possible. The decay-stage activation energy, also 35 kcal./mole, again relates to a linear-growth process, so that consistency of activation energy values for the latter process is observed throughout the decomposition.

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