

974. *The Thermal Explosion of Ammonium Perchlorate.*

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New measurements of the induction period for the thermal explosion of ammonium perchlorate are reported and discussed in terms of the theory of self-heating.

THE thermal decomposition of ammonium perchlorate is probably unique in the extremely wide temperature range over which the reaction can be studied. Pressure-time measurements have been used to follow the isothermal reaction over the considerable temperature interval of 200—440° C.¹⁻³ The reason for this is that the salt decomposes by two distinct mechanisms. At low temperatures, the kinetics may be interpreted in terms of an intergranular reaction³ which leaves blocks of loosely attached residue. At high temperatures these blocks decompose according to the contracting cube law. The mechanisms of these two reactions have been ascribed to electron-transfer^{3,4} and proton-transfer² respectively, and the activation energies associated with these two processes found to be 32 and 40 kcal./mole respectively.

Above 440° the reaction is too fast to be followed manometrically, but after an induction period (τ) there is a sudden large pressure change which is often accompanied by a flash of light. This induction period was measured as a function of temperature with the object of determining which of the two chemical processes referred to above is responsible for the explosion and of adding generally to our knowledge of the perchlorate decomposition. The only previous published measurements of τ appear to be from a few runs by Glasner and Makovsky⁵ in the course of a study of the decomposition of guanidine perchlorate.

Induction periods were measured by dropping 50 mg. fragments of pellets of ammonium perchlorate into a glass reaction vessel embedded in a heavy copper block surrounded by a furnace. Pellets were outgassed before decomposition, but the reaction was carried out under 1 atm. of air to suppress sublimation. The reaction has been shown previously² not to be affected by gaseous oxygen up to at least 400°. The results are depicted in Fig. 1 in the form of a plot of $\log \tau$ against $1/T$ (°K). The points appear to lie on two straight lines. However, at 490° (the point of inflection) the induction period is reduced to about 30 sec., so that the time required to heat the sample to the temperature of the reaction vessel must be exerting a considerable effect on the results. It being assumed that heat is transferred to the pellet by conduction through the glass, a rough calculation shows that the heat-up time (τ_0) will be of the order of 10 sec. The value of τ_0 required to linearise the plot of $\log (\tau - \tau_0)$ against $1/T$ (°K) was found empirically to be 15 sec., and this was therefore taken as the heat-up time. The slope of this plot (line *b*) corresponds to an energy of activation of 41.5 kcal./mole.

Logarithmic plots of the rate-constants for the low-temperature and high-temperature

¹ Bircumshaw and Newman, *Proc. Roy. Soc.*, 1954, *A*, **227**, 115; 1955, *A*, **227**, 228.

² Galwey and Jacobs, *J.*, 1959, 837.

³ Galwey and Jacobs, *Proc. Roy. Soc.*, 1960, *A*, **254**, 455.

⁴ Galwey and Jacobs, *Trans. Faraday Soc.*, 1959, **55**, 1165.

⁵ Glasner and Makovsky, *J.*, 1954, 1606.

reactions are shown in Fig. 2 on a scale sufficient to permit extrapolation into the explosion region. It is evident that the low-temperature process (despite its lower activation energy) still occurs more rapidly than the high-temperature process. Calculation shows that the intergranular reaction is 99% complete in times of 0.2—3.5 sec. in the explosion range, so that this reaction is clearly not responsible for the explosion, which requires much longer times. In contrast, calculations based on the explosion times and the kinetic equation² for the high-temperature process, $1 - (1 - \alpha)^3 = kt$, yield values for the fractional decomposition α at the instant of explosion of 0.33 and 0.30 respectively at the lower and the upper limit of the temperature range over which induction periods were measured. This shows that explosion occurs when the residue from the intergranular reaction is about one-third decomposed. The activation energy found from Fig. 1 (41.5 kcal./mole) is in agreement with this conclusion.

The calculation of induction periods to explosion is a rather intractable task unless approximations are made. With the assumptions of uniform temperature and

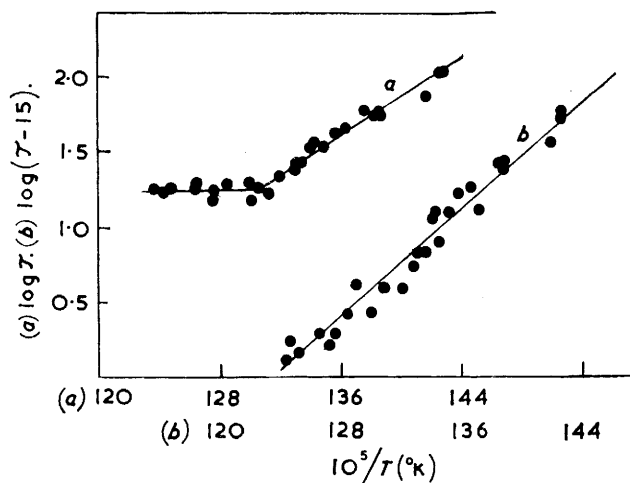


FIG. 1. Plots of the logarithm of the induction period to explosion of pellets of ammonium perchlorate against the reciprocal of the absolute temperature. (a) $\log \tau$; (b) $\log (\tau - 15)$. (τ is in seconds.)

first-order kinetics and the neglect of self-cooling,⁶ the relative excess temperature $\theta = (E/RT_0^2)(T - T_0)$ obeys the equation

$$d\theta/dt = (1/\tau_\infty)f(\theta) \quad \dots \quad (1)$$

where $1/\tau_\infty = (QAE/C_p RT_0^2) \exp(-E/RT_0)$ and $f(\theta) = \exp \theta$, the exponential approximation, or $f(\theta) = 1 + (e - 2)\theta + \theta^2$, the quadratic approximation. Here T_0 is the (constant) temperature of the surroundings, Q the heat of reaction, $A \exp(-E/RT_0)$ the rate constant of the reaction, and C_p the heat capacity of the reactant. In the adiabatic approximation, where self-cooling is neglected, the results of the exponential and the quadratic approximation are in good agreement with the solution obtained without approximating the term $\exp(-E/RT)$.⁶ The time (t_n) taken for θ to reach a specified value n is obtained by integrating (1) to yield

$$t_n = \tau_\infty g(n) \quad \dots \quad (2)$$

where $g(n) = 1 - e^{-n}$ for the exponential approximation, or

$$g(n) = 1.112 \left[\tan^{-1} \left(\frac{2n + 0.72}{1.807} \right) \right] - 0.4163$$

for the quadratic approximation. In either case, t_n increases relatively slowly with n for

⁶ Gray and Harper, *Trans. Faraday Soc.*, 1959, **55**, 581.

$n > 1$, so it is convenient to calculate approximate induction periods from the simple relation

$$t_n = \tau_\infty \dots \dots \dots (3)$$

Actually, for $n = 1.5$ (the right order for the experimental value) $g(n) = 0.777$ for the exponential and 0.904 for the quadratic approximation.

The results of the calculation of induction periods from equation (3) are compared with the experimental results in Fig. 3. The value of 312 cal. g.⁻¹ was used for Q and 40 cal. deg.⁻¹ mole⁻¹ for C_p . The results are rather sensitive to the value of E . The value obtained from the isothermal kinetics (Fig. 2) is 40.1 kcal. mole⁻¹, and that from the plot of the experimental data in the form $\log(\tau/T_0^2)$ versus $1/T_0$ is 41.1 kcal. mole⁻¹. (The slight difference between this value and that obtained from Fig. 1 is due to the T_0^2 term.)

FIG. 2. Arrhenius plots for the isothermal decomposition of ammonium perchlorate extrapolated into the temperature region (shown bounded by two vertical dotted lines) in which the thermal explosion was studied. (a) Intergranular reaction. (b) Complete decomposition.

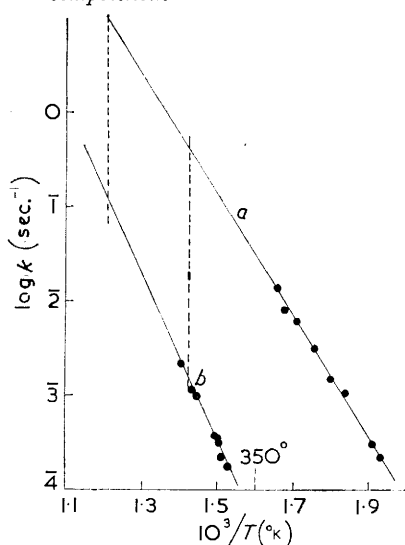
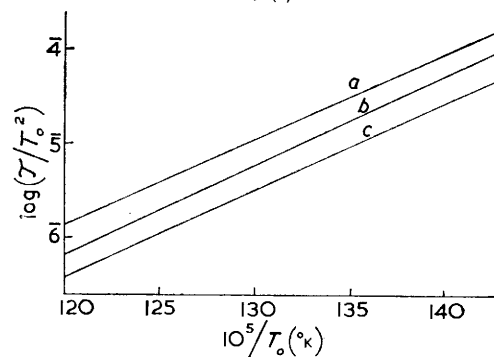


FIG. 3. Comparison between Arrhenius plots for the experimental induction periods and those calculated from the theory given in the text (equation 3). (a) Experimental results; (b) $E = 41.1$ cal. mole⁻¹; (c) $E = 40.1$ cal. mole⁻¹.



Both values have been used for the calculation. It is evident that the results of this calculation are much shorter than the experimental values for induction periods, the value of τ/t_n being about 2. This discrepancy is unlikely to be made good by corrections for self-cooling (which are readily applied with the quadratic approximation⁶) nor is it due to the use of the exponential or quadratic approximations which are good for the required range of θ . The assumption of first-order kinetics may cause serious errors in some solid-state reactions, but with ammonium perchlorate, the time required for the first process is short (although not negligible) and after this, a deceleratory process obeying the equation: $1 - (1 - \alpha)^{\frac{1}{2}} = kt$, sets in. The first 25% of the process is virtually linear, as is also true for the first-order law.

The major difficulty in calculating induction periods for thermal explosions from isothermal kinetic data is thus probably the rather large errors normally inherent in the determination of E and A .