

### 910. *Kinetics of the Thermal Decomposition of Sodium Azide.*

By P. W. M. JACOBS and A. R. TARIQ KUREISHY.

Reproducible results for the thermal decomposition of sodium azide have been obtained by (i) precipitating the salt as a fine powder from aqueous solutions acidified with hydrazoic acid and (ii) decomposing it in the form of small pellets, preferably under argon. When these precautions are observed the kinetics obey the Avrami-Erofeev equation with  $n = 2$ . An alternative method of finding the activation energy of the reaction without fitting the results to a kinetic equation is introduced. Both methods yield a value of 38 kcal./mole for the activation energy for the thermal decomposition of sodium azide.  $\text{OH}^-$  and  $\text{Cl}^-$  ions retard the reaction but  $\text{Fe}^{3+}$  ions catalyse it. A mechanism for the reaction is postulated which explains these and previously observed facts.

THE thermal decomposition of sodium azide has been studied previously by Garner and Marke<sup>1</sup> and, more recently, by Secco.<sup>2</sup> Initially, the pressure was found<sup>1</sup> to increase linearly with time, the activation energy associated with this linear process being 34 kcal./mole. Secco<sup>2</sup> observed an initial decay reaction, similar to that observed in potassium azide.<sup>3</sup> Below 300° the rate gradually falls to a constant value.<sup>2</sup> At temperatures below 350° a white residue remains, and is chemically identical with the original salt but, above this temperature, there is no residue and the rate of decomposition rises rapidly after the initial decay period. The activation energy associated with the linear process is reported to be  $50 \pm 5$  kcal./mole, whereas the third accelerative stage of the reaction is said to be temperature-independent. Photography of partially decomposed crystals shows the decomposition to be an interfacial reaction.<sup>2</sup>

The thermal decomposition of sodium azide is thus seen to be a rather complicated process despite the overall chemical simplicity of the reaction



Undoubtedly, this is due in part to the volatility of sodium. Usually, the course of the decomposition of solids may be separated into "nucleation" and "growth" stages but, if the metallic product is volatile, the growth of the first-formed nuclei may well be impeded. This paper describes the results of work in which we have attempted to obtain more detailed information about the nucleation process by (i) carrying out the reaction

<sup>1</sup> Garner and Marke, *J.*, 1936, 657.

<sup>2</sup> Secco, *J. Phys. and Chem. Solids*, 1962, 24, 469.

<sup>3</sup> Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, A, 215, 265.

under a pressure of an inert gas, argon, to retard the evaporation of sodium, and (ii) altering the number of potential nucleus-forming sites by suitable variations in the method of preparation of the sodium azide.

#### EXPERIMENTAL

The vacuum line was conventional, except for the pressure gauge, which consisted of a mercury manometer with a vertical platinum wire sealed into one limb. The platinum wire formed one arm of a Wheatstone bridge circuit, which was energized from a stabilized d.c. power supply, the out-of-balance voltage from the bridge being fed to a recorder (10 mV. full scale). Variations in the mercury level in the manometer caused a change in the resistance of the wire and hence in the out-of-balance bridge voltage. Pressure changes of  $10^{-4}$  mm. could be detected, and the gauge provided a very convenient method of following either very short or very long runs; also, its sensitivity is the same at all ambient pressures. The empty manometer must, however, be scrupulously clean, and the mercury must be distilled into it under vacuum to prevent sticking. Careful thermostating of the gauge is essential.

*Materials.*—Seven different samples of sodium azide were used. These were:

(1) Hopkin and Williams' sodium azide (I) used as received without further purification.

(2) "Alkaline" sodium azide. (I) was dissolved in distilled water giving a solution of pH 9. This was filtered and sodium azide was precipitated by the addition of absolute alcohol, filtered, washed with absolute alcohol and reprecipitated as before, the product (II) being dried *in vacuo* over silica gel.

(3) "Acid" sodium azide (III) was prepared as under (2) except that the solution was made acid (pH 6.5) by the addition of hydrazoic acid solution before each precipitation.

(4) "Acid (HCl)" sodium azide (IV) was prepared as under (3) except that hydrochloric acid was used instead of hydrazoic acid.

(5) "FeCl<sub>3</sub> doped sodium azide" (V) was obtained by adding to an aqueous solution of (I) sufficient ferric chloride solution to give the required molar ratio, either 0.05% (Va) or 1% (Vb) and reprecipitating the product as before. The solution containing 1 M % ferric chloride was deep red in colour, indicating the presence of free hydrazoic acid, but the solution containing 0.05 M % ferric chloride was acidified with just sufficient hydrochloric acid to give the red coloration before the azide was precipitated.

(6) "1 M % Fe<sub>2</sub>O<sub>3</sub> mixture" (VI). This was prepared by shaking together ferric oxide and (III) in the mole ratio 1 : 100 until a uniform mixture was obtained.

The azide was decomposed in the form of small pellets 8–35 mg. in mass. If the reaction is carried out in a Pyrex vessel, the sodium attacks the glass and this exerts a catalytic effect in subsequent runs; this difficulty was avoided by carrying out the reaction in a small nickel crucible, which was enclosed by the decomposition chamber.

#### RESULTS AND DISCUSSION

Plots of the fractional decomposition  $\alpha$  against time ( $t$ ) for (I) *in vacuo* were fitted reasonably well (see Fig. 1) by the Avrami-Erofeev equation<sup>4</sup> with  $n = 2$ ,

$$[-\log(1 - \alpha)]^{1/n} = k(t - t_0) \quad (1)$$

The range of  $\alpha$  over which the equation fits the results and the induction period  $t_0$  in equation (1) both depend on the initial mass ( $m$ ) of the reactant but  $k$  is independent of  $m$  in the range 7.9 – 34.3 mg. For  $m = 7.9$  mg., the equation holds for  $0.27 < \alpha < 0.97$ , but for  $m = 17.5$  mg. it holds in the range  $0.01 < \alpha < 0.67$ . This was typically the range for  $m > 12$  mg., but in one experiment with  $m = 16.4$  mg., the volume of the system was increased so as to make the pressure of nitrogen evolved equivalent to  $m = 12$  mg. The range of  $\alpha$  over which the equation fitted was then  $0.30 < \alpha < 0.90$ . This shows that the failure of equation (1) for low masses in the early stages of the reaction is due, not to the mass used, but to the pressure of gas evolved from the azide.

Plots of  $k$  and  $t_0$  against  $m$  at a constant temperature of 318° are shown in Fig. 2a and b. The rate constant  $k$  is seen to be independent of  $m$ , but the induction period decreases with increasing mass, becoming reasonably constant for  $m > 20$  mg. Plots of  $\log k$  and  $-\log t_0$

<sup>4</sup> Jacobs and Tompkins in "Chemistry of the Solid State," ed. Garner, Butterworths, London, 1955, p. 184 *et seq.*

against  $T^{-1}$  are shown in Fig. 3; in these runs, the sample mass lay in the range 15.4–22.0 mg. The values obtained for the activation energy  $E$  are 37.6 and 36.5 kcal./mole, respectively.

Samples of sodium azide (I) of mass in the range 11.7–16.7 mg. were decomposed under argon of pressure  $P$  in the range 0–500 mm. For  $P > 10$  mm. equation (1) holds for  $0.02 < \alpha < 0.60$ . Figs. 2c and d shows plots of  $k$  and  $t_0$  against  $P$  at constant temperature.

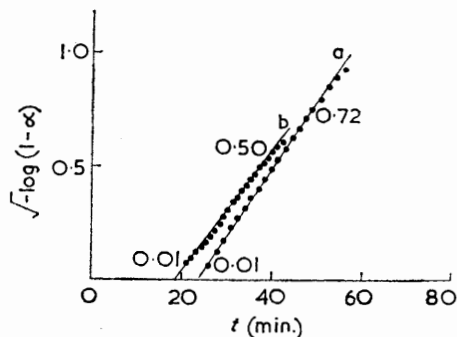


FIG. 1. Test of eqn. (1) for the thermal decomposition of sodium azide (a) *in vacuo* and (b) under 500 mm. argon. Numbers against the lines denote the range of  $\alpha$  over which the equation holds.

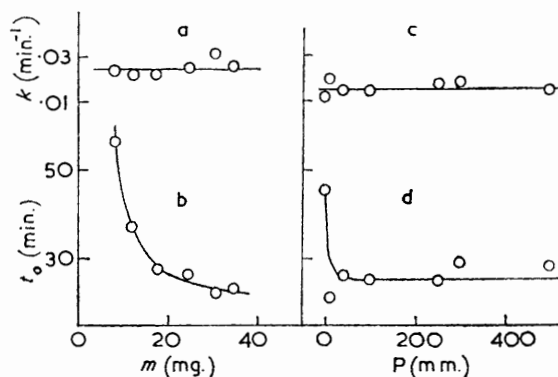


FIG. 2. Variation of the rate constant  $k$  and induction period  $t_0$  with the mass of sodium azide decomposed *in vacuo* (a, b) and with the pressure of argon (c, d).

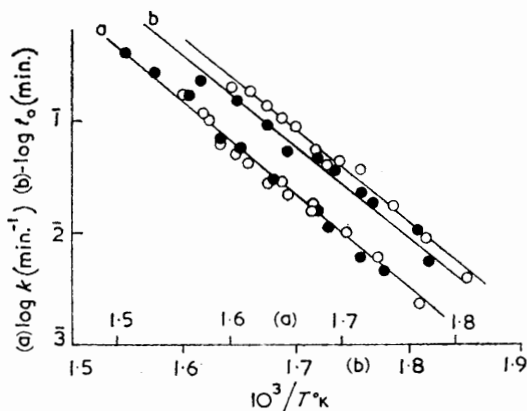


FIG. 3. Arrhenius plots for (a) the rate constant and (b) the induction period, determined by fitting the results to eqn. (1). Filled circles  $\bullet$ , *in vacuo*; open circles  $\circ$ , under 500 mm. argon.

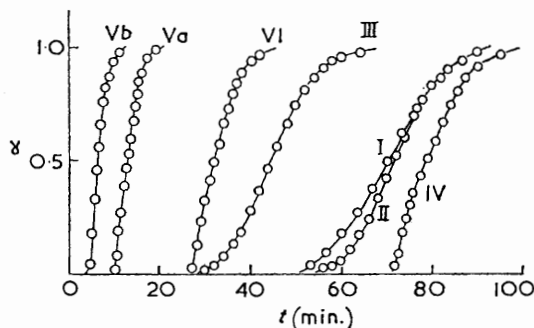


FIG. 4. Plots of fractional decomposition  $\alpha$  against time  $t$  for various preparations of sodium azide at  $311 \pm 0.5^\circ$ . Details of the methods of preparation are given in the text under "Materials."

Despite some scatter at low pressures,  $k$  is evidently independent of  $P$ , whereas  $t_0$  decreases sharply with increasing  $P$  at low pressures, all this decrease taking place from 0–10 mm. When the reaction is carried out under a pressure of 500 mm. of argon, varying the sample mass in the range 8–25 mg. does not affect the kinetics. The dependence of  $\log k$  and  $-\log t_0$  on  $T^{-1}$  for (I) decomposed under a pressure of 500 mm. of argon ( $m$  in the range 12–16 mg.) is also shown in Fig. 3. The independence of  $k$  with regard to  $P$  and the decrease of  $t_0$  with increasing ambient pressure are clearly shown. The fit of equation (1) seems to be rather better at low than at high temperatures: *c.g.*,  $0.02 < \alpha < 0.80$  at  $T = 291.6^\circ$  and  $0.05 < \alpha < 0.52$  at  $T = 345.7^\circ$ .

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Some preparations, *e.g.*, (II) and (IV), were not fitted so well by equation (1), and therefore a more general method of analysing the results was developed. This depends only on the applicability of a single kinetic equation, which need not even be known, over a finite range of the decomposition. Let the rate equation be of the general form

$$F(\alpha) = kt \quad (2)$$

where  $k$  is the rate constant and let  $\alpha_n, \alpha_{n+1}$  be the values of the fractional decomposition,  $\alpha$  at times  $t_n, t_{n+1}$ . Then from equation (2),

$$F(\alpha_{n+1}) - F(\alpha_n) = k(t_{n+1} - t_n) \quad (3)$$

Similarly at any different temperature, but at *the same values of*  $\alpha$ ,

$$F(\alpha_{n+1}) - F(\alpha_n) = k'(t'_{n+1} - t'_n) = \text{constant} \quad (4)$$

It follows that the plot of  $\log(t_{n+1} - t_n)$  against  $T^{-1}$  is linear with a slope of  $E/2.303R$ . This is a valuable method of obtaining the activation energy for a reaction when the kinetic equation is unknown, although clearly the pre-exponential factor cannot be found unless the form of  $F(\alpha)$  is known. Moreover, experience has shown that the method is sufficiently sensitive to indicate a change in the kinetic law in part of the temperature range investigated, if this should occur. The method is, of course, formally equivalent to that of superimposing decomposition curves by adjusting the time scale, but is more general in that it does not require a single kinetic law to hold over the whole range of  $\alpha$ .

Values of the activation energy for the decomposition of sodium azide obtained by this method are given in Table 1. The mean value of  $E$  for the decomposition of (I) evaluated by this method are 38.4 (*in vacuo*,  $0 < \alpha < 1$ ) and 38.1 (500 mm. argon,  $0 < \alpha < 0.7$ ) kcal./mole, in good agreement with the values obtained from the equation (1), *viz.* 37.6 kcal./mole (Fig. 2), thus supporting the validity of our analysis.

Plots of  $\alpha$  against  $t$  for preparations (I), (II), (III), (IV), (Va), (Vb) and (VI) at  $T = 311 \pm 0.5^\circ$  are shown in Fig. 4. Certain qualitative features are evident. Precipitation of the azide from an unacidified solution (II) produces very little change in the decomposition characteristics, apart from a slight lengthening of the induction period and a slight speeding up of the accelerative process. The latter is a genuine effect for, while the activation energy for  $t_0$  has the "normal" value (36.1 kcal./mole), after 5% of decomposition  $E$  falls to around 22 kcal./mole until 50% of decomposition, when  $E$  starts to increase again. The shape of the plots of  $\alpha$  against  $t$  is rather irreproducible, and the activation-energy plots not as good as for the other preparations.

TABLE 1.

The values of activation energy,  $E$ , for the thermal decomposition of different preparations of sodium azide.

Sample .....	(I)	(I)	(II)	(III)	(VI)	(III)
Mass, mg. ...	15—20	18—22	10—12	9—11	9—11	25—30
$P$ , argon, mm.	500	vacuum	vacuum	vacuum	vacuum	vacuum
$\alpha$ -Range, %	$E$ , kcal./mole	$E$ , kcal./mole	$E$ , kcal./mole	$E$ , kcal./mole	$E$ , kcal./mole	$E$ , kcal./mole
$t_0$	35.2	34.3	36.1	28.4	26.6	37.4
0—5	38.8	36.6	32.2	43.5	38.8	37.0
5—10	39.1	39.2	20.6	45.3	38.8	37.7
10—15	41.1	37.9	20.1	43.5	41.6	38.8
15—20	40.9	39.2	22.4	38.4	40.2	36.8
20—30	38.6	38.4	23.8	39.3	37.5	39.5
30—50	38.8	39.2	26.1	38.8	37.0	39.8
50—70	32.4	39.5	28.4	36.4	36.6	—
70—90	27.6	38.8	31.3	38.0	38.4	—
90—95	$\approx 24.7$	40.9	33.4	37.3	38.8	—

For (III), however, the results were reproducible and it was therefore studied in greater detail. The activation energy for  $t_0$  (see columns 5 and 7 in Table 1) is 28 kcal./mole, and for the main reaction about 39 kcal./mole, although there is evidence that, for low masses

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(9–11 mg.) and small  $\alpha$  ( $< 0.15$ ),  $E$  is somewhat greater than the "normal" value,  $\sim 38$  kcal./mole (see column 5 in Table 1). The most striking feature of the decomposition of sodium azide precipitated from solutions acidified with hydrazoic acid, however (apart from the reproducibility of its behaviour) is the reduction in the induction period  $t_0$ , compared with those of samples (I) and (II) (Fig. 4).

A further reduction in induction period is achieved by doping with  $\text{Fe}^{3+}$ . We have no knowledge of the actual amount of iron incorporated or of the configuration of the  $\text{Fe}^{3+}$  in the azide crystal, but some uptake of  $\text{Fe}^{3+}$  is shown by the colour of (V), pale orange for (Va) and reddish-brown for (Vb). Fig. 4 also shows that, as well as a decrease in  $t_0$ , there is an increase in the rate of reaction for samples doped with  $\text{Fe}^{3+}$ . To check whether these effects were due to the presence of iron in a co-precipitated but separate phase, a mechanical mixture of ferric oxide and sodium azide (VII) was made. For this mixture  $t_0$  is nearly the same as that of (III) but the reaction, once started, goes at a much faster rate than it does with the pure azide. The activation energy for  $t_0$  is low for all three "acid" samples (Table 1), being 26.6 kcal./mole for (Vb), but "normal" (38.7 kcal./mole) for the main reaction in (Vb).

The outstanding feature of the early stages of the decomposition of sodium azide is undoubtedly the existence of the competing processes of nucleus formation and the evaporation of the first-formed sodium nuclei; if these can grow at a faster rate than that at which sodium is lost by evaporation, then an accelerative reaction is set up. All crystals contain imperfections at which reaction occurs preferentially; most probably, the decomposition of sodium azide is initiated at sites in the grain boundaries and spreads initially through the intergranular material at a roughly linear rate. As there are a finite number of sites of roughly equal activation energy for nucleus formation, nuclei are formed according to a unimolecular decay law, which is approximately linear in the initial stages. Thus, the overall reaction rate is a function of the square of the time, as observed experimentally for (I) under argon. Once the reaction has penetrated through the intermosaic network giving essentially linear filaments of sodium, these nuclei grow two-dimensionally, and thus expand into cylinders, which eventually overlap. As growth is two-dimensional the coefficient  $n$  in the Avrami-Erofeev equation is 2: interference of nuclei is taken care of in the usual way<sup>4</sup> by replacing  $\alpha$  by  $-\log(1 - \alpha)$ . In the later stages of the reaction, one has essentially a mass of sodium surrounding isolated pockets of the azide. As sodium is molten, it flows out of the pellet when this stage is reached, and the kinetic laws break down when about two-thirds of the azide has decomposed.

Our achievement of better reproducibility than that of previous workers is due partly to the generally better behaviour of sodium azide recrystallized from acid solutions, partly to our use of pellets and partly to our use of larger masses. Both the latter tend to inhibit the evaporation of sodium; in addition, the larger the mass the larger the pressure of nitrogen at equivalent fractional decompositions, and the more effective the inhibition of the evaporation of sodium. Similar conditions apply to the reaction under argon. (It should be noted that the reaction of sodium and nitrogen is too slow at the decomposition temperatures to affect the results. At the highest temperatures, a very slow decrease in the pressure attained at  $\alpha = 1$  could be observed if the gaseous products were left in contact with the sodium. Overnight, the pressure decreased by an amount corresponding to the reaction



but even at the highest temperatures employed this reaction is too slow to disturb the kinetics of the decomposition reaction.)

In the small plate-like crystals used by Secco,<sup>2</sup> evaporation is favoured and so, at low temperatures, the nucleus-forming sites are consumed but, the sodium nuclei evaporate at a faster rate than that of the growth reaction and so a stable residue of sodium azide results. At higher temperatures, the rate of the interface reaction exceeds that of the

destruction of nuclei and an accelerative reaction can start. Nevertheless, the importance of evaporation is clearly evident in the photographs published by Secco.

The reduction in the induction period of the reaction, which results from recrystallization from hydrazoic acid solution, may be due to an increase in the dislocation density or to the incorporation of  $\text{HN}_3$  molecules in the azide lattice. These would be expected to decompose more readily and could initiate the reaction if vacancies were effective for this purpose. As hydrochloric acid retards the reaction, it may be that foreign anions  $\text{OH}^-$ ,  $\text{Cl}^-$  impede the initiation of the reaction, possibly by precipitating out on dislocations.

The above interpretation of the effect of acid or alkali on  $t_0$  is rather speculative, but the role of  $\text{Fe}^{3+}$  seems more certain. Ferric ions will act as electron traps and thus are potential nucleus-forming sites. Therefore, the induction period is greatly reduced, as is the rate of the accelerative reaction. The experiment with ferric oxide seems to confirm that  $\text{Fe}^{3+}$  ions are incorporated in the lattice, or at least precipitated in the grain boundaries, in (Va) and (Vb). The activation energy for  $t_0$  is the same for azide doped with  $\text{Fe}^{3+}$  as for the other samples precipitated from acid solution. Thus, the increased reactivity is due to a change in the number of sites rather than to a lowering of the activation energy for nucleus formation. Catalysis of the decomposition of molten potassium azide has been confirmed by Egghart.<sup>5</sup>

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IMPERIAL COLLEGE, LONDON S.W.7.

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<sup>5</sup> Egghart, *Inorg. Chem.*, 1963, 2, 364.