

### 956. *The Kinetics of the Thermal Decomposition of Ammonium Perchlorate.*

By L. L. BIRCUMSHAW and T. R. PHILLIPS.

Following a previous study by Bircumshaw and Newman,<sup>1</sup> the decomposition of ammonium perchlorate has been investigated under varying conditions of temperature and pressure. From 400° to 440° under 20 cm. of nitrogen, the decomposition had an activation energy of  $73.4 \pm 1.5$  kcal./mole, while at constant temperature the velocity constant of the decomposition was roughly proportional to (partial pressure of nitrogen)<sup>0.6</sup>. We suggest that at these temperatures the decomposition is that of the vapour following evaporation of the crystals, in contrast to the decomposition of solid which takes place at lower temperatures. Some experiments on the evaporation and sublimation of the salt are described. A little tetradeuteroammonium perchlorate was prepared and its decomposition compared with that of the ordinary salt in the range 230—280°.

BIRCUMSHAW and NEWMAN<sup>1</sup> found that the decomposition of ammonium perchlorate *in vacuo* at 220—280° was typical of many solid decompositions in that it spread throughout the crystals from surface nuclei yielding gaseous products, and left a residue which, however, was still almost pure ammonium perchlorate. Only approximately 30% of the salt decomposed in the first instance, but the residue could be decomposed further after treatment with a solvent vapour—a process which was named “rejuvenation.” The activation energy for decomposition was 18.9 kcal./mole above 240° and 29.6 below it, a change coinciding with a crystal transition from an orthorhombic to a cubic structure at 240°.

Two theories have been suggested to account for the progress of the decomposition. Bircumshaw and Newman<sup>1</sup> quoted a personal communication from Mr. L. A. Wiseman who suggested an electron-transfer process amongst the defects in the lattice resulting in the formation at the crystal surface of unstable perchlorate radicals; Schultz and Dekker<sup>2</sup> suggested that an initial step of proton transfer,  $\text{NH}_4^+ + \text{ClO}_4^- \rightarrow \text{NH}_3 + \text{HClO}_4$ , is followed by a reaction at an interface where constraining forces on the ions are unbalanced. Wiseman predicted that the mechanism would change at higher temperatures, the activation energy then having a value comparable to that observed in the decomposition of other inorganic perchlorates. Experiments have been made (a) with tetradeuteroammonium perchlorate to compare results with Schultz and Dekker's theory and (b) at high temperatures with the ammonium salt where the reaction characteristics differed from those previously described.

#### EXPERIMENTAL

*Material.*—Commercial ammonium perchlorate was thrice recrystallized from distilled water, and the crystals crushed and sieved. Most experiments at high temperature were made with samples of particle size 0.089—0.052 mm. radius (*i.e.*, mesh 85—150) and usually 0.100 g. was used; the few exceptions will be indicated.

<sup>1</sup> Bircumshaw and Newman, *Proc. Roy. Soc.*, 1954, *A*, 227, 115, 228.

<sup>2</sup> Schultz and Dekker, United States Air Force, Office of Scientific Research, Technical Note 55: 142.

Tetradeuteroammonium perchlorate was prepared by recrystallizing some of the above sample from 99.37% heavy water, the hydrogen atoms of ammonium ions being known to exchange rapidly with the solvent deuterium atoms, and the reaction having a separation factor of nearly unity.<sup>3</sup> Two recrystallizations gave a sample of calculated purity 99.1% which agreed well with the experimental value obtained from refractive-index measurements of the evaporated mother liquor. These crystals were crushed as before, but because of the small quantity made they were not sieved. Experiments on this material were compared with some made on ammonium perchlorate (sample "B") which had been prepared in exactly the same manner except that distilled ordinary water was used in place of the heavy water.

*Apparatus.*—The experiments on the deuterated salt and those with the ammonium salt were carried out by using gas accumulatory runs in the apparatus previously described.<sup>1</sup> At higher temperatures this method was unsuitable and we used the apparatus illustrated in Fig. 1. It consisted of a quartz spiral spring balance enclosed in a glass chamber, the pressure within which could be measured by gauges in a conventional high vacuum line. To start an experiment, the sample was lowered into free suspension by magnetic movement of the iron bobbin *M*.

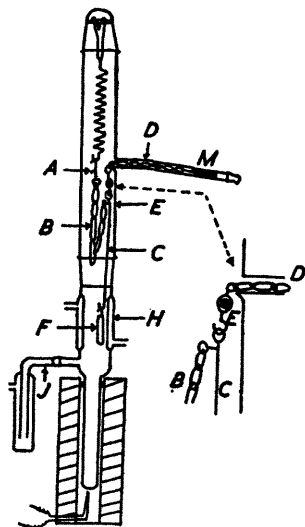


FIG. 1. *Decomposition apparatus.*  
A, Pointers; B and D, glass chains; C, glass fibre; F, sample tube; E, weighted glass hook; J, vacuum line; M, iron bobbin.

Subsequent decomposition in the temperature-controlled oven was followed by observing the contraction of the spring.

*Decomposition of Tetradeuteroammonium Perchlorate.*—The salt was decomposed in an initially evacuated apparatus and the increase in pressure observed at regular intervals. Pressure-time curves were sigmoid and similar to those obtained on decomposing the ammonium salt (sample B); for both salts velocity constants for the deceleratory part of the reaction were calculated from the "contracting sphere" equation  $^4 kt = \text{Const.} - [(100 - x)/100]^{\frac{2}{3}}$ , where  $t$  is the time at which  $x\%$  decomposition has occurred. Minimum values of  $k$  were obtained for both salts at approximately 240°, above which the ratios  $Z$  of the average velocity constant for  $\text{NH}_4\text{ClO}_4$  to that for  $\text{ND}_4\text{ClO}_4$  are as shown in Table I.

TABLE I. *Ratios of velocity constants for decomposition of  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$ .*

Temp. ....	245°	250°	255°	260°	270°
Z .....	0.732	0.798	0.905	0.787	0.744

These values are not those expected; Bigeleisen<sup>5</sup> indicated that usually a greater rate constant is observed in reactions involving "light" molecules, but exceptions to this rule are known especially for compounds containing hydrogen isotopes. Bigeleisen also states that at high temperatures the difference in activation energy between two isotopic reactions will become

<sup>3</sup> Bonhoeffer and Brown, *Z. phys. Chem.*, 1933, B, **23**, 171.

<sup>4</sup> Fischbeck and Spingler, *Z. anorg. Chem.*, 1939, **241**, 209.

<sup>5</sup> Bigeleisen, *J. Chem. Phys.*, 1949, **17**, 675.

vanishingly small. This is confirmed here where the activation energies for decomposition of  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$  are  $13.60 \pm 1.99$  and  $13.85 \pm 1.52$  kcal./mole respectively. The value of  $Z$  can be calculated from Schultz and Dekker's theory<sup>2</sup> where the expression for the velocity of penetration of the interface at which decomposition occurs is given by

$$B = (LkTF'/hF) \exp(-E/RT)$$

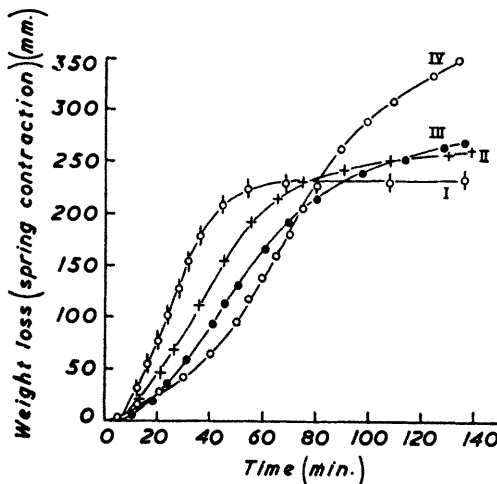
where  $L$  is the sum of the ionic radii,  $F'$  the partition function of activated complex over all degrees of freedom except for translation along the decomposition co-ordinate, and  $F$  the partition function for the normal state of the reactants. As  $B$  can be shown to be proportional to the velocity constant,  $Z$  is the ratio of  $B$  for  $\text{NH}_4\text{ClO}_4$  to that for  $\text{ND}_4\text{ClO}_4$ . For the cubic form of the crystals

$$F'/F = [1 - \exp(-h\nu_2/kT)]/[1 - \exp(-h\nu_3/kT)],$$

$\nu_2$  and  $\nu_3$  being the vibration frequencies of the normal states of the positive and perchloric ions respectively along the decomposition co-ordinate. The positive-ion frequencies were calculated

FIG. 2. Decomposition at 280° at different nitrogen pressures.

I, 0 cm. (accumulatory run); II, 3 cm.; III, 10 cm.; IV, 50 cm.



from the equation  $\nu_2 = 0.552(kT/md^2)^{1/2}$  where  $m$  is the mass of the positive ion and  $d$  the dimension of the unit cell. The values obtained were substituted in the equation

$$Z = [1 - \exp(-h\nu_2/kT)]_{\text{NH}_4} / [1 - \exp(-h\nu_2/kT)]_{\text{ND}_4}$$

and at 250° the value of  $Z$  obtained was 1.28, almost the exact inverse of the experimental value.

*Decomposition of Ammonium Perchlorate in the Presence of Inert Gas.*—Decomposition was followed by measuring the weight loss on heating the crystals. Sublimation can be<sup>1</sup> prevented by small pressures of inert gas, so various pressures of nitrogen were admitted into the apparatus before the start of an experiment.

*At 260—300°.* In 3 cm. of nitrogen, the results were similar to those obtained in accumulatory runs.<sup>1</sup> A sigmoid weight loss-time curve was obtained, *e.g.*, Fig. 2(II), the initial rate, maximum rate, and the total amount of decomposition increasing with temperature. The increase in pressure due to the non-condensable evolved gases was about 2 mm. The effect of increase of inert-gas pressure at 280° is shown in Fig. 2, its main effect being the increase of the final decomposition rate with pressure. The almost complete stoppage of the reaction after 30% decomposition, as in accumulatory runs, is not observed. For comparison, the results of an accumulatory run obtained by measuring pressure increase in the evacuated apparatus are shown in Fig. 2(I). To plot them on the same axes as the weight loss experiments a separate experiment was made to establish the relation between weight loss by decomposition and pressure increase within the apparatus. A long sample tube was suspended in the furnace from a fixed suspension. Its open end projected above the furnace and collected all the sublimate, so that the weight loss on heating the sample was due to decomposition alone. The final pressure was observed and, from the known sensitivity of the spring, a pressure

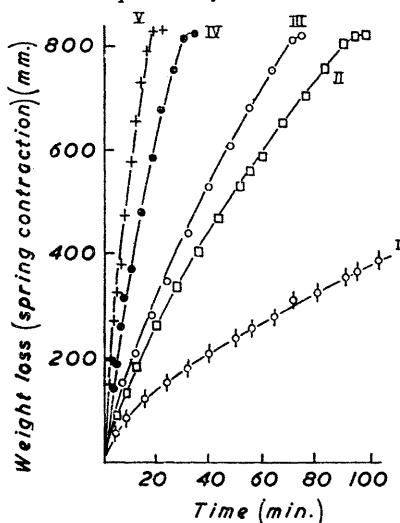
increase could then be represented by a contraction in spring length. For example, for a loss in weight of sample tube of 0.0284 g. the equivalent spring contraction, equal to weight loss multiplied by spring sensitivity, was 2.374 mm. The final pressure in the apparatus being 1.454 mm., 1 mm. (Hg) pressure increase corresponds with  $2.374/1.454 \equiv 1.632$  mm. spring contraction.

At 300—380°. None of the numerous experiments under various conditions gave reproducible results. Above 340°, the reaction became completely deceleratory, and at all temperatures there was no sign of its stopping before complete decomposition.

At 400—440°. The experiments were again reproducible and decomposition nearly complete, the residue never weighing more than 0.001 g. and appearing as a fragile network. Fig. 3 shows results of experiments at increasing temperatures and at a nitrogen pressure of 20 cm. At a constant temperature, 420°, but different nitrogen pressures, the results are shown in Fig. 4. Calculation showed that the velocity constants were approximately proportional to (partial pressure of  $N_2$ )<sup>0.6</sup>.

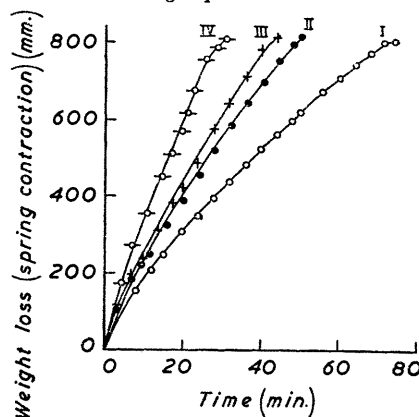
The equation  $m^{2/3} = -kt + \text{const.}$  (where  $m$  is the weight of undecomposed salt at time  $t$  and  $k$  a constant) represents the decomposition curves (Fig. 5). This equation is the

FIG. 3. *Decomposition at constant nitrogen pressure of 20 cm.*



I, 400°; II, 410°; III, 420°; IV, 430°; V, 440°.

FIG. 4. *Decomposition at 420° at different nitrogen pressures.*



I, 20 cm.; II, 35 cm.; III, 50 cm.; IV, 75 cm.

integrated form of the equation for weight loss of a spherical particle when the rate of weight loss is proportional to the radius. In 20 cm. of nitrogen the following values of  $k$  were obtained:

Temp. (° c) .....	400	400	410	420	420	430	440	440	440
$10^4 k$ .....	4.82	5.17	18.8	25.3	27.8	63.3	120	106	117

Calculation by the root-mean-square method gave the equation  $\log_{10} k = 20.72 - 16.06 \times 10^3/T$ , giving an activation energy of  $73.4 \pm 1.5$  kcal./mole.

Some experiments were also made at 420° and 240° in the apparatus described by Bircumshaw and Tayler<sup>6</sup> in which the salt was decomposed in a small chamber completely enclosed in a furnace, the products of the reaction accumulating in the chamber at the decomposition temperature. There was no indication of any catalysis or inhibition in these circumstances, apart from the higher reaction velocity associated with increased gas pressures.

*The Evaporation and Sublimation of Ammonium Perchlorate.*—*In vacuo*, ammonium perchlorate sublimes readily above 200°, but because of the onset of decomposition thereat the absolute vapour pressure and density could not be determined. Comparative measurements of the sublimation rates at different temperatures were made. The dissociation of ammonium chloride vapour<sup>7</sup> suggests that a similar mechanism may operate for the perchlorate, as

<sup>6</sup> Bircumshaw and Tayler, *J.*, 1956, 3405.

<sup>7</sup> Michalek and Rodebush, *J. Amer. Chem. Soc.*, 1929, 51, 746.

indicated by the fact that when calcium oxide was placed above the perchlorate in a tube in which sublimation was taking place, the amount of sublimate was considerably reduced, presumably because of adsorption of perchloric acid by the oxide.

*Rate of sublimation at low pressure.* Decomposition of the salt almost stops at 30% weight loss between 200° and 300°, so the loss of weight of the residue when further heated is almost entirely due to evaporation. Samples were therefore decomposed until gas evolution, as indicated by pressure measurements, ceased. The apparatus was re-evacuated and the subsequent weight loss observed. The rate of loss of weight remained fairly constant at a given temperature, the slight decrease observed towards the end of an experiment probably being due to the decrease in area of the evaporating surface. Values of the evaporation rate,  $r$ , obtained are shown in Table 3, and an activation energy for evaporation of  $21.5 \pm 2.78$  kcal./mole was calculated from the statistically determined equation  $\log_{10} r = 8.04 - 4.71 \times 10^3/T$ .

TABLE 3.

Temp. ....	260°	280°	300°	306°	320°
$r$ (mg./min.) .....	0.16, 0.13	0.346, 0.304	0.945, 1.11	0.712	1.04, 0.934

*Sublimation in the presence of inert gas.* The experiments were made in a horizontal furnace with long reaction tubes, the sublimate forming on the cool open end of the tubes which projected outside the furnace. The weight decomposed was obtained by weighing the tube before and after the experiment. The weight of sublimate was obtained by cutting off the portion of the tube on which it had formed, weighing it, dissolving the sublimate, and re-weighing. The results are shown in Table 4.

The sublimate formed at 400° was always less than that at 350°. This could result either from decomposition's being so fast at 400° that sublimation is prevented, or because the vapour of the perchlorate itself decomposes to a greater extent at 400°. The first alternative was disproved by decomposing a sample *in vacuo* at 400°; 80% sublimed, indicating that evaporation is the fastest process at this temperature.

TABLE 4.

Partial pressure of N <sub>2</sub> (cm.)	Temp.	Heating time (hr.)	Weight decomp. (mg.)	Weight subld. (mg.)	Partial pressure of N <sub>2</sub> (cm.)	Temp.	Heating time (hr.)	Weight decomp. (mg.)	Weight subld. (mg.)
3	350°	8	49.7	12.2	5	400°	8	92.3	5.0
5	350	8	52.0	10.8	10	400	8	96.0	1.7
10	350	20	65.7	2.8	15	400	8	97.6	1.3
15	350	8	85.2	0.8	0.0	400	2	20.0	80.0

*The simultaneous measurement of sublimation and decomposition.* Experiments were made by recording pressure increase in the initially evacuated apparatus simultaneously with the spring contraction. Using the relation (p 4744) 1.632 mm. contraction  $\equiv$  1 mm. pressure, we drew graphs of total weight loss and weight loss by decomposition. The difference at a given time was the weight loss by sublimation. Fig. 6 shows the curves obtained at 300° where the sublimation rate for the first 30 min. of the reaction just exceeds the rate of decomposition. At a higher temperature, the difference becomes larger, while at 280°, decomposition is the faster.

*The Ultraviolet Irradiation of Ammonium Perchlorate.*—The experiments were confined to studying the effect of pre-irradiation before heating the sample. The sample was irradiated *in vacuo* in a quartz-windowed cell at 15° and pushed magnetically without exposure to air into a decomposition furnace at 225°. The ultraviolet source was a low-pressure mercury discharge of unknown spectral distribution. The induction period, which was arbitrarily taken as the time for the pressure of decomposition products to reach 0.03 cm., was found to be considerably reduced:

Time of irradiation (min.) .....	0	20	40	80	120	160	240
Average induction period (min.) ...	38	34	26.5	25	20	22	21.5

Garner and Maggs<sup>8</sup> suggested that a similar effect on irradiation of barium azide was due to photochemical formation of nuclei, but microscopical examination of the perchlorate crystals

<sup>8</sup> Garner and Maggs, *Proc. Roy. Soc.*, 1939, A, **173**, 299.

gave no evidence of this. It is generally considered that when such effects are observed the ultraviolet light increases the number of surface defects, resulting in an increased probability of nucleus formation.

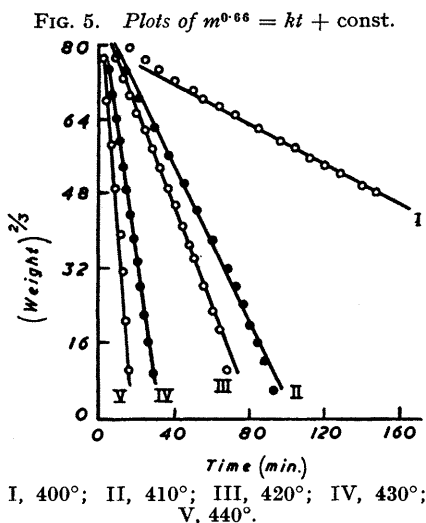
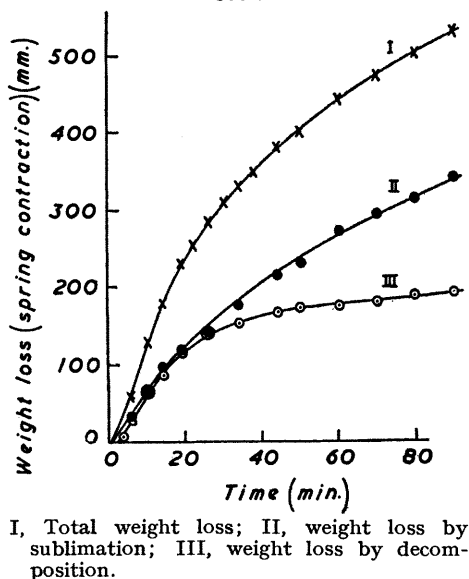


FIG. 6. Heating in evacuated apparatus at 300°.



#### DISCUSSION

The experiments indicate that the mechanism of high-temperature decomposition is different from that operating at 200–300°. At high temperatures there is no induction period and the reaction is deceleratory throughout, the calculated activation energy is much higher, and there is no stable residue.

On heating ammonium perchlorate there are three competing reactions which can take place: (a) the "low" temperature reaction, (b) the "high" temperature reaction, and (c) sublimation. Process (a) has been shown<sup>1</sup> to be a true "solid" decomposition in which a decomposition interface moves through the crystal. From 380° to 440°, Table 4 shows that the predominant reaction is determined by the inert-gas pressure in the system. The sublimation experiments have shown that evaporation is the fastest reaction in this temperature range, and if there is no inert gas to impede the movement of the vapour molecules they will sublime rapidly to the cool parts of the reaction tube. In the presence of an appreciable pressure of gas, this escape is retarded, and the vapour decomposes (high-temperature reaction) with a resultant diminution of the amount of sublimate formed. Increase of gas pressure would increase this impedance, so resulting in a higher vapour concentration and explaining the enhanced decomposition rate observed.

The mechanism for decomposition is similar to that suggested for burning propellants, except that the heat transferred from the vapour decomposition to the solid is not itself sufficient to maintain the reaction. Ammonium perchlorate is only self-combustible above 68 atm.<sup>9</sup> so it is considered that the back-diffusion of heat to the solid at our pressures will not be important. The burning rate of ammonium perchlorate<sup>9</sup> shows almost the same dependence on pressure as the decomposition rate in these experiments, *i.e.*, proportional to  $p^{0.5}$ .

The rate-controlling process in the decomposition is probably the breakdown of the

<sup>9</sup> Adams, Newman, and Robins in Advisory Group of Aeronautical Research and Development (AGARD), "Selected Combustion Problems," Butterworths, London, 1954, p. 387.

perchlorate ion. Experiments on potassium perchlorate<sup>10</sup> at 500—550° gave an activation energy for decomposition of 69.3 kcal./mole which agrees well with that obtained for ammonium perchlorate. For the potassium salt, it is hard to envisage what reaction apart from the breakdown of the perchlorate ion could take place.

A similar vaporization process has been suggested to account for the decomposition of ammonium tri- and di-chromates, but in this case it was thought that the oxidation of ammonia was rate-controlling.<sup>11</sup>

The experiments on tetradeuteroammonium perchlorate do not give any additional support to Scultz and Dekker's theory, and the electron-transfer<sup>1</sup> theory is still preferred for decompositions at low temperatures. Proton transfer is more likely to lead to evaporation than decomposition. It is of interest that calculation of the rate of shrinkage of an evaporating sphere of perchlorate gives an answer of the same order as that for interface velocity in Schultz and Dekker's theory. Furthermore, while ultraviolet radiation affects the electronic structure of solids, it seems energetically improbable that it will cause proton transfer.

From 300° to 380° it is thought that the poor reproducibility of results is caused by the disruption of the crystal surface by evaporation, the reaction chains of the solid decomposition being broken. From the stability of the finely divided residue from the low-temperature experiments, it is clear that a certain degree of continuity is necessary for a "solid" reaction to take place. Schultz and Dekker suggested that decomposition takes place along the mosaic boundaries within the crystal, as occurs during the photolysis of silver halides.<sup>12</sup> From the appearance of the residue, this seems very probable, but it is not evident why the large increase in surface area which would then occur is not accompanied by an increase in evaporation rate.

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<sup>10</sup> Phillips, Thesis, Birmingham, 1953.

<sup>11</sup> Shidlovski and Oranzherev, *Zhur. priklad. Khim.*, 1953, **26**, 25.

<sup>12</sup> Mitchell and Hedges, *Phil. Mag.*, 1953, **44**, 357.

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