Thermal Decomposition of Ammonium Perchlorate

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1 Introduction

The thermal decomposition of ammonium perchlorate has been extensively studied because of its intrinsic chemical interest and more recently because of its application as an oxidizer in solid rocket propellants. This Review covers the literature on uncatalysed ammonium perchlorate.

The decomposition of ammonium perchlorate is influenced by many factors, but in a general way it may be divided into three regions, a low- and a high-temperature decomposition and deflagration or combustion. The low-temperature decomposition occurs in the range *ca.* 200—300° at atmospheric pressure and is characterised by an induction period, an acceleratory region, a rate maximum, and a deceleratory region. The decomposition stops before all the material is consumed. The high-temperature decomposition occurs between 350 and 400°. The initiation steps are immeasureably fast and the reaction shows a deceleratory region throughout at constant temperature. Deflagration or rapid combustion sets in at *ca.* 450° at atmospheric pressure.

A. Stoicheiometry of Thermal Decomposition.—Ammonium perchlorate was apparently first mentioned in the literature in 1831.[1,2] Its thermal decomposition has been investigated since 1869 when the equation

$$NH_4ClO_4 \rightarrow NH_4Cl + 2O_2$$

was proposed.[3] Later Berthelot[4] suggested the more complex equation

$$2NH_4ClO_4 \rightarrow 4H_2O + 2O_2 + Cl_2 + N_2$$

For explosion in a closed bomb, the equation[5]

$$4NH_4ClO_4 \rightarrow 6H_2O + 5O_2 + 4HCl + 2N_2$$

was given in 1910. In the same year, the use of MnO_2 and $NaNO_3$ was suggested[6–8] to inhibit the dangerous production of acid during decomposition.

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[1] G. S. Serullas, *Ann. Chim. Phys.*, 1831, **2**, 46.
[2] G. S. Serullas, *Ann. Chim. Phys.*, 1831, **2**, 304.
[3] P. Groth, *Liebigs Ann. Chem.*, 1868, **133**, 213.
[4] M. Berthelot, *Ann. Chim. Phys.*, 1882, **27**, 218.
[5] R. Escales, 'Die Chloratsprengstoffe', Viet and Co., Leipzig; *Chem Abstr.*, 1910, **4**, 3300.
[6] E. C. Carbonelli, *Ind. Chim.*, 1910, **10**, 209.
[7] E. C. Carbonelli, *Ind. Chim.*, 1910, **10**, 225.
[8] E. C. Carbonelli, *Ind. Chim.*, 1910, **10**, 245.

When free chlorine was detected[9] in the reaction products under explosive conditions, the equation proposed was

$$2NH_4ClO_4 \rightarrow N_2 + Cl_2 + 2O_2 + 4H_2O$$

The same authors also found some hydrogen chloride together with oxides of chlorine, and determined that moisture inhibits the explosive properties of the decomposing ammonium perchlorate.

In the first extensive investigation of the thermal decomposition of ammonium perchlorate, it was found [10-12] that the pure salt begins to sublime and decompose, *in vacuo*, at *ca.* 130° with deflagration occurring at *ca.* 400°. It was also realised that the decomposition occurred by more than one reaction mechanism. Below 300°, the decomposition could be represented mainly by the stoicheiometric equation

$$4NH_4ClO_4 \rightarrow 2Cl_2 + 8H_2O + 2N_2O + 3O_2 \qquad (1)$$

with traces of ClO_2, HCl, N_2, and other so-called 'nitrous gases'. Above 300°, the amounts of N_2 and 'nitrous gases' increased. In the high-temperature decomposition range, above 380°, the reaction became explosive and followed mainly the equation

$$2NH_4ClO_4 \rightarrow 4H_2O + Cl_2 + O_2 + 2NO \qquad (2)$$

The reaction products also included traces of Cl_2, O_2, NO_2, N_2O_3, N_2O_4, and NOCl. Below 380°, N_2O was obtained in excess over N_2, whereas above 400° NO is formed at the expense of N_2O and becomes the chief product.

A later definitive study[13] confirmed equations (1) and (2). Traces of $HClO_4$ were found, as well as of the previously reported products Cl_2, N_2O, N_2O_4, O_2, N_2, H_2O, HCl, ClO_2, and NOCl. Similar low-temperature gaseous products, together with NO, were identified[14] in a separately conducted Russian study. Nitric acid has also been reported[15] to be present as a product of the low-temperature decomposition, as well as trace quantities of NO_2Cl.[15-18]

A change in the reaction products with temperature has been noted, even within the individual decomposition ranges. Below 240°, chlorine evolves[19] mainly as Cl_2, but as the reaction temperature is increased the amount of HCl

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[9] P. Naoum and R. Aufschlager, *Z. ges. Schiess-Sprengstoffw.*, 1924, **19**, 121; *Chem. Abs.*, 1924, **18**, 3721.

[10] M. Dode, *Compt. rend.*, 1934, **200**, 63.

[11] M. Dode, *Bull. Soc. chim. France*, 1938, **5**, 170.

[12] M. Dode, *Bull. Soc. chim. France*, 1938, **5**, 176.

[13] L. L. Bircumshaw and B. H. Newman, *Proc. Roy. Soc.*, 1954, *A*, **227**, 115.

[14] L. D. Romodanova and V. I. Roshchupkin, *Zhur. fiz. Khim.*, 1962, **36**, 1554 (translation, AD 297566, Jan. 18, 1963).

[15] W. A. Rosser, S. H. Inami and H. Wise, Office of Naval Research Report, AD 640084, Contract Nonr-3415 (00), Sept. 29, 1966.

[16] K. Kuratani, *Rept. Aeronaut. Res. Inst. No.* 372, 1962, **372**, 79.

[17] K. Kuratani, *Rept. Aeronaut. Res. Inst. No.* 373, 1962, 103.

[18] K. Kuratani, *Rept. Aeronaut. Res. Inst. No.* 374, 1962, 115.

[19] L. F. Shmagin and A. A. Shidlovskii, *Issled. v Obl. Khim. i Tecknol. Mineral'n. Solei i Okislov, Akad. Nauk S.S.S.R., sb. Statei*, 1965, 112.

increases at the expense of the Cl_2. The perchloric acid was also found to increase[20,21] to a maximum at *ca.* 240°, and then to drop off above 250°. The ClO_2 was determined[20] to be in excess over Cl_2 at 300°, while above that temperature the Cl_2 increased. Recent decomposition studies,[15,18,22–24] however, have failed to find any ClO_2 as a stable reaction product and it has been concluded[15] to exist only as an intermediate.

Mass spectrometric analysis of the major products of the low-temperature decomposition has given divergent data. Goshgarian and Walton[22] found H_2O, O_2, Cl_2, HCl, NO, N_2O, and N_2. Other investigators[25] have shown the products to consist mainly of H_2O, O_2, Cl_2, N_2O, NO, NO_2, with possibly some N_2. The most recent studies,[23,24] however, have demonstrated that the previous data[22,25] were complicated by species derived from both sublimation and secondary reactions, and that the decomposition produces principally H_2O, O_2, Cl_2, and N_2O, together with significant quantities of HCl and N_2.

Nitrogen has also been claimed[26] as a major product by mass spectral analysis. It was suggested that the reaction

$$2NH_4ClO_4 \rightarrow 4H_2O + Cl_2 + N_2 + 2O_2 \qquad (3)$$

takes place simultaneously with equation (1). The latest published stoicheiometric investigations,[23,24] however, have attributed the excessive amounts of N_2 and HCl to secondary gas-phase reactions, and have reaffirmed equation (1) as substantially representing the low-temperature decomposition process.

The general features of the decomposition described above were also confirmed by kinetic studies[27] and by differential thermal analysis.[28] In the latter work, the known crystal transformation[29] from rhombic to cubic form was observed at 240°, followed by two distinct decomposition regions. The low-temperature decomposition occurred immediately after the crystal transformation and produced only a partial decomposition of the salt. The higher temperature decomposition resulted in a deflagration at 435° and left no solid residue.

The residue following the low-temperature decomposition was first thought[10,11] to be ammonium nitrate since some ammonium salts of oxygen containing anions do give ammonium nitrate as the chief product of their low-temperature decomposition, *e.g.* ammonium permanganate[30] and ammonium chlorate,[31]

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[20] H. Osada and E. Sakamoto, *Kogyo Kayaku Kyokaishi*, 1963, **24**, 236 (translation, NASA Accession No. N67-20309, Nov. 1966).

[21] H. Osada and S. Kakinouchi, *Kogyo Kayaku Kyokaishi*, 1965, **26**, 200 (translation, NASA Accession No. N67-20318, Nov. 1966).

[22] B. B. Goshgarian and J. A. Walton, AFRPL-TR-65-87 (1965).

[23] J. N. Maycock, V. R. Pai Verneker, and P. W. M. Jacobs, *J. Chem. Phys.*, 1967, **46**, 2857.

[24] V. R. Pai Verneker and J. N. Maycock, *J. Chem. Phys.*, 1967, **47**, 3618.

[25] G. A. Heath and J. R. Majer, *Trans. Faraday Soc.*, 1964, **60**, 1783.

[26] G. B. Manelis and Yu. I. Rubtsov, *Zhur. fiz. Khim.*, 1966, **40**, 770 (translation AD, 651748, May 1967).

[27] A. K. Galwey and P. W. M. Jacobs, *Proc. Roy. Soc.*, 1960, *A*, **254**, 454.

[28] S. Gordon and C. Campbell, *Analyt. Chem.*, 1955, **27**, 1102.

[29] D. Vorlander and E. Kaascht, *Ber.*, 1923, **56B**, 1157; *Chem. Abs.*, 1923, **17**, 2682.

[30] L. L. Bircumshaw and M. Taylor, *J. Chem. Soc.*, 1950, 3674.

[31] F. Fairbrother, *J. Amer. Chem. Soc.*, 1922, **44**, 2419.

the latter having already been noted by Dode.[10] However, a later investigation[13] showed the residue to be pure NH_4ClO_4. It was further established that the low-temperature decomposition gave a typical sigmoid curve even though the reaction was anomalous in that it stopped when only 28—30% of the salt had decomposed. The residue was porous in texture. Microscopic studies[32] showed that the decomposition started at various points on the surface of the crystal and then grew three-dimensionally to form a coherent interface which then progressed into the crystal interior. Sublimation was also found to occur over the entire decomposition temperature range.

In spite of the considerable amount of work done on the thermal decomposition of ammonium perchlorate, the stoicheiometry of the decomposition is still uncertain. The equation for the low-temperature region has remained essentially the same as when originally proposed in 1934[10] and later confirmed in 1954.[13] Investigators generally either avoid the issue of stoicheiometry by employing reaction mechanisms to account for the existence of decomposition products without regard to mass balance, or else simply accept equation (1) as representing the major products within their experimental error.

B. Stoicheiometry of Deflagration.—An early study[33] concluded that the products were well represented by equation (3). A later series of investigations[34–36] on ammonium perchlorate flame products at atmospheric pressure, suggested the equation

$$NH_4ClO_4 \rightarrow 1{\cdot}98H_2O + 0{\cdot}73O_2 + 0{\cdot}54NO + 0{\cdot}30HCl + 0{\cdot}085N_2 + 0{\cdot}35Cl_2 + 0{\cdot}14N_2O \qquad (4)$$

Another reported[37,38] the deflagration of ammonium perchlorate at 1000 psi to proceed by the equation

$$NH_4ClO_4 \rightarrow 0{\cdot}265N_2 + 0{\cdot}12N_2O + 0{\cdot}23NO + 1{\cdot}015O_2 + 1{\cdot}62H_2O + 0{\cdot}76HCl + 0{\cdot}12Cl_2 \qquad (5)$$

and at atmospheric pressure to follow the equation

$$NH_4ClO_4 \rightarrow 0{\cdot}55NO + 0{\cdot}10N_2O + 0{\cdot}125N_2 + 0{\cdot}5Cl_2 + 2H_2O + 0{\cdot}675O_2 \qquad (6)$$

A comprehensive review of the composition equations of ammonium perchlorate in 1963,[39] in which the equilibrium gas compositions at various pressures were calculated resulted in the formulation of two limiting reactions,

$$2NH_4ClO_4 \rightleftharpoons 4H_2O + O_2 + Cl_2 + 2NO \qquad (7)$$

[32] L. L. Bircumshaw and B. H. Newman, *Proc. Roy. Soc.*, 1955, *A*, **227**, 228.
[33] A. A. Shidlovskii, *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3**, 405.
[34] E. A. Arden, J. Powling, and W. A. W. Smith, *Combustion and Flame*, 1962, **6**, 21.
[35] J. Powling and W. A. W. Smith, *Combustion and Flame*, 1962, **6**, 173.
[36] J. Powling, Explosives Research and Development Establishment Report 15/R/65, AD 474311, July 13, 1965.
[37] R. Friedman, R. G. Nugent, K. E. Rumbel, and A. C. Schurlock, 'Sixth Symposium (International) on Combustion', Reinhold, New York, 1957, p. 612.
[38] J. B. Levy and R. Friedman, 'Eighth Symposium (International) on Combustion', Williams and Wilkins Co., Baltimore, 1962, p. 663.
[39] A. E. Simchen, *J. Appl. Chem.*, 1963, **13**, 369.

for zero pressure, and

$$4NH_4ClO_4 \rightleftharpoons 6H_2O + 5O_2 + 4HCl + 2N_2 \qquad (8)$$

for high pressures, within which the gas composition at equilibrium lies. Slight amounts of ClO_2 were thought to form below 300°, as well as some N_2O in place of NO. Simchen related the equilibrium of the Deacon process directly to the distribution of reaction products, and in this way determined the chlorine in equation (6) to be 60% in the form of hydrochloric acid. However, it has been noted[40] that the deflagration reaction of ammonium perchlorate does not necessarily proceed to equilibrium. The reaction

$$NH_4ClO_4 \rightarrow 3/2H_2O + HCl + 1/2N_2 + 5/4O_2 \qquad (9)$$

has also been proposed.[41]

Finally, the empirical equation

$$NH_4ClO_4 \rightleftharpoons (a/2 + 5b/4)N_2 + 1/6N_2O + (c - 3b/2)NO + (1/2 - 3a/2)Cl_2 + (3a)HCl + [3(b + c)/2 + 1]H_2O + (17/12 - 5c/4)O_2 \qquad (10)$$

has been postulated[42] as a means of calculating the product distribution of the ammonium perchlorate decomposition. The terms a and b represent the experimental values determined for HCl and N_2 respectively, and are related to c by the expression $a + b + c = 2/3$. Equation (10) was derived by summing various proposed reactions of ammonium perchlorate decomposition, both solid and gas phase. Knowing the experimental values of HCl and N_2, equation (10) readily produces the remaining reaction products in their correct stoicheiometric ratios. When the equation was fitted to previous data,[38] the results were in excellent agreement with experimental values.

2 Crystal Structure and Transformation

It has long been known that crystal structure plays an important role in the thermal decomposition of ammonium perchlorate. Early investigators[43–46] found crystals of ammonium perchlorate at room temperature to be orthorhombic, containing four molecules per unit cell with dimensions $a = 9{\cdot}202$, $b = 5{\cdot}816$, $c = 7{\cdot}449$ Å, and occurring in the space group *Pnma*. These facts were also substantiated in several[47–49] more recent crystal studies. Venkatesan,[48] by use of double Fourier projections, found the chlorine atom to be tetra-

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[40] R. Friedman, J. B. Levy, and K. E. Rumbel, AFOSR-TN 59-173, AD 211313, Feb. 5, 1959.

[41] D. Olfe and S. S. Penner, 'Eighth Symposium (International) on Combustion', Williams and Wilkins Co., Baltimore, 1962, p. 293.

[42] F. J. Cheselske, Aerojet-General Rept. 0372-01F, AD 458854, AF 49(638)-851, March 15, 1965.

[43] M. Volmer, *Liebig's Ann.*, 1924, **440**, 200.

[44] W. Bussem and K. Herrmann, *Z. Krist.*, 1928, **67**, 405.

[45] C. A. Schusterius, *Z. Krist.*, 1931, **76**, 455.

[46] C. Gottfried and C. A. Schusterius, *Z. Krist.*, 1932, **84**, 65.

[47] H. E. Swanson and E. Tatge, *Nat. Bur. Standards, Vol.* 7, *Cir.* 539, 1957, 6.

[48] K. Venkatesan, *Proc. Indian Acad. Sci.*, 1957, **46**, *A*, 134.

[49] H. G. Smith and H. A. Levy, *Acta Cryst.*, 1962, **15**, 1201.

hedrally surrounded by four oxygen atoms at a mean distance of 1·46 Å. The four hydrogen atoms were found to encompass each nitrogen atom, while the ammonium ion was surrounded by twelve oxygen atoms at distances varying between 2·89 and 3·39 Å. A later study[49] obtained slightly different values, reporting distances of 2·94—3·08 Å for eight of the twelve oxygen atoms, and 3·25—3·52 Å for the remaining four. The distance between the central chlorine and surrounding oxygen atoms was found to be 1·43 Å.

For ammonium perchlorate lattice energies[50,51] values of 149·4 kcal./mole for the electrostatic energy, and 143·8 kcal./mole for the total crystal lattice energy, have been calculated. The value of the Madelung constant was 3·3134.

As mentioned previously, at *ca.* 240° ammonium perchlorate undergoes a crystal transformation from the orthorhombic to the cubic form.[29] The high-temperature crystals (270°) possess a structure[52,53] somewhat resembling the sodium chloride lattice with each unit cell having $a = 7{\cdot}63$ Å and containing four molecules of ammonium perchlorate. The transition itself has been found[13,26] to have a marked effect upon the rate maximum in thermal decomposition. The maximum was shown to gradually rise with temperature, reaching a peak at *ca.* 240° then falling to a minimum at *ca.* 250°, and finally increasing again with temperature. This phenomenon has been attributed to several different factors, including crystal volume modifications[13,32] and alteration of the crystal imperfections.[21,27] The latter will be considered when reviewing proposed reaction mechanisms.

A decrease in lattice dimensions as a result of the transformation was first suggested[32] to account for the observed decrease in the maximum decomposition rate. Contraction of the lattice would reduce the number of interstitial ions which were considered to initiate the low-temperature decomposition, and hence would decrease the rate of decomposition. However, subsequent findings,[21,54] in which the crystal volume was found to increase rather than decrease, have disproved this theory. The orthorhombic form was determined[54] to have a density of 1·95 g./c.c. as compared to 1·76 g./c.c. for the cubic structure. The enthalpy of transition was also calculated from differential thermal analysis data and a value of 2·3 ± 0·2 kcal./mole was reported. A later value[55] is given as 2·7 kcal./mole. A recent kinetic investigation[26] has suggested that the phase transformation alters only the speed at which the reaction centres develop, and not the formation of the electronic traps responsible for decomposition. Thus a volume increase, by decreasing the velocity at which the reaction centres are produced, will reduce the rate of decomposition.

Single crystal diffraction studies[42] have led to the proposal of still another theory concerning the effect of the crystal transition upon the thermal decomposition. *X*-Ray data have shown the apparent existence of a second-order

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[50] A. Sevilla Benito and A. Perez Masia, *Anales. real Soc. españ. Fiz. Quím.*, 1962, **58**, *B*, 273.
[51] A. Sevilla Benito and A. Perez Masia, *Anales. real Soc. españ. Fiz. Quím.*, 1962, **58**, *B*, 283.
[52] H. Brakken and L. Harang, *Z. Krist.*, 1930, **75**, 538.
[53] K. Herrmann and W. Ilge, *Z. Krist.*, 1930, **75**, 41.
[54] M. M. Markowitz and D. A. Boryta, *Amer. Rocket Soc. J.*, 1962, **32**, 1941.
[55] M. W. Evans, R. B. Beyer, and L. McCulley, *J. Chem. Phys.*, 1964, **40**, 2431.

irreversible phase transition, apart from the reversible first-order orthorhombic to cubic phase transfer, occurring slightly below the known transformation temperature. This second-order transition has been suggested to account for the abnormal decomposition behaviour of ammonium perchlorate in the neighbourhood of 240°. Unlike a first-order transition which would normally be expected to occur rather suddenly, the second-order transition would occur over a range of temperature and affect the decomposition in the manner observed. Second-order transitions have been found in other ammonium salts,[56] and have been shown to alter solid-state decompositions.[42] The decrease in the maximum rate, to a minimum value at 250°, has also been ascribed[32] to either a slow phase transfer which does not reach completion until 250°, or to the fact that the maximum stability of the cubic form occurs at that temperature.

The ability of the two species present in the ammonium perchlorate lattice to rotate freely has been the topic of much discussion. Early decomposition studies[32] predicted the rotation of both the ammonium and perchlorate ions above 240°. One theoretical analysis[57] suggested the attainment of nearly free rotation of the perchlorate ion as a prerequisite to the formation of the activated complex below 250°. The ammonium ion was considered to rotate freely in both the cubic and orthorhombic crystalline forms. Nevertheless, these examinations were based solely on decomposition data and the only extensive crystal investigation[48] pointed to the formation of an ordered hydrogen bond configuration, yielding a weak nitrogen–hydrogen–oxygen bridge.

An i.r. study in 1958[58] failed to observe any combination band involving a torsional oscillation of the ammonium ion and concluded that the NH_4^+ was not altogether fixed in any set orientation in the crystal lattice. N.m.r. data[59] likewise indicated a random orientation of the ammonium ion. A value of 2·0 ± 0·6 kcal./mole was calculated for the potential barrier of reorientation. This was later modified[60] to probably less than 1 kcal./mole. The most recent estimate[61] is 0·55 ± 0·05 kcal./mole. The free rotation of the ammonium ion has also been shown to occur both by neutron diffraction data,[49,62] as well as by the spectrum obtained from measurements of inelestic neutron scattering.[63,64] Finally, a recent investigation on the ammonium perchlorate crystal transformation has shown[65] the phase transition at 240° to result from the ability of the perchlorate ions to commence free rotation. It was also found that the cation rotated freely below room temperature.

[56] J. C. Slater, 'Introduction to Chemical Physics', McGraw-Hill Book Co., New York, 1939, p. 293.

[57] R. D. Schultz and A. O. Dekker, 'Sixth Symposium (International) on Combustion', Reinhold, New York, 1957, p. 618.

[58] T. C. Waddington, *J. Chem. Soc.*, 1958, 4340.

[59] J. A. Ibers, *J. Chem. Phys.*, 1960, **32**, 1448.

[60] R. E. Richards and T. Schaefer, *Trans. Faraday Soc.*, 1961, **57**, 210.

[61] A. V. Dubovitskii, N. Ya. Buben, and G. B. Manelis, *Zhur. strukt. Khim.*, 1964, **5**, 40.

[62] H. G. Smith and H. A. Levy, Abstract K-6, American Crystallographic Association Annual Meeting, Cornel Univ., New York, July, 1959.

[63] J. M. Janik, *Inst. Nucl. Phys., Cracow Rept. No.* 360, 1964, 59.

[64] J. M. Janik, J. A. Janik, A. Bajorek, and K. Perlinski, *Phys. Status Solidi*, 1965, **9**, 905.

[65] M. Stammler, R. Bruenner, W. Schmidt, and D. Orcutt, *Adv. X-ray Anal.*, 1966, **9**, 170.

Thus, it now seems that both the ammonium and perchlorate ions undergo free rotation in the ammonium perchlorate unit cell. The ammonium appears to begin rotation somewhat below room temperature, whereas the perchlorate commences rotation around 240°. Ammonium perchlorate has also been reported[66] to undergo a probable first-order polymorphic transition at $-190°$.

The crystal transformation has also been found to profoundly affect the burning of ammonium perchlorate. The combustion velocity has been shown[67] to decrease with increasing pressure, accompanied by an unstable region of combustion. This unusual phenomenon has been attributed[68] to the requirement of the surface of the burning ammonium perchlorate to attain the phase-transition temperature at a particular pressure. Subsequent combustion studies[69,70] have shown the surface temperature to decrease, approaching 240° as the pressure was raised. It was suggested that the heat released by the condensed phase should fall to even a greater extent, as a result of heat absorption during phase transition, and this in turn could cause the observed decline of the combustion velocity.

3 Sublimation

Initial studies[13] found sublimation in the low-temperature range in a vacuum to be apparently independent of decomposition, increasing steadily as the temperature was increased. At roughly 280°, the rate of sublimation accelerated as the decomposition declined, the sample being *ca.* 28—30% decomposed. The sublimate contained traces of nitrate, nitrite, and hydrogen ions, but in all cases, was absent of any chloride ion. Sublimation was also found to occur at atmospheric pressure if the sample was heated under an inert gas stream. However, the rate was considerably reduced.

Ammonium perchlorate was originally postulated[32,40,71] to sublime *via* a proton transfer mechanism in which NH_3 and $HClO_4$ are formed, diffuse away, and subsequently recondense at a cold surface. The dissociation process was likened to that of ammonium chloride.[71] It was experimentally shown[32] that suppressing sublimation by the presence of an inert gas enhanced decomposition. A larger surface area which favoured sublimation, decreased the decomposition. The two processes were suggested[32,40] as competing with one another, sublimation becoming more favoured as the low-temperature decomposition progressed. An activation energy of 21·5 ± 2·78 kcal./mole was determined for the sublimation by use of rate constants derived from the equation[71] $dm/dt = k$.

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[66] M. Stammler, D. Orcutt, and P. C. Colodny, *Adv. X-ray Anal.*, 1962, **6**, 202.

[67] A. P. Glazkova, *Zhur. priklad. Mekhan. i. Tekhnich. Fiz.*, 1963, **5**, 121 (translation AD 614773, p. 193, Feb. 8, 1965).

[68] K. K. Andreyev and Sung Ts'uan-Ts'ai, 'Research on Thermal Decomposition of Ammonium Perchlorate and Certain Mixtures Based On It', Dissertation, Moscow, 1961.

[69] V. K. Bobolev, A. P. Glazkova, A. A. Zenin, and O. I. Leypunskiy, *Zhur. priklad. Mekhan. i Tekhnich. Fiz.*, 1964, 3 (translation AD 636992, p. 262, Feb. 1966).

[70] V. K. Bobolev, A. P. Glazkova, A. A. Zenin, and O. I. Leypunskiy, *Doklady. Akad. Nauk. S.S.S.R.*, 1963, **151**, 604 (translation NASA Accession No. 64-18141, Jan. 1964).

[71] L. L. Bircumshaw and T. R. Phillips, *J. Chem. Soc.*, 1957, 4741.

In the high temperature range, 380—440°, both decomposition and sublimation were attributed[71] to evaporation, with increased pressure reported to promote decomposition. The pressure effect was ascribed to hindering diffusion, thereby suppressing sublimation. At temperatures greater than 400°, less sublimate was recovered than at 350°. This was related to the thermal decomposition of the cation.

Rather large differences were found in the activation energies for the two processes competing at high temperatures, 21·5[71] for sublimation and 30·0 kcal./mole[72] for the high-temperature decomposition, when a similar rate expression was utilised. This led to the conclusion[72] that the two processes must possess different rate-determining steps. As proton transfer was believed responsible for the high-temperature decomposition, the formation of an ion-pair was suggested as being the initial step in the sublimation mechanism. This was based on the capability of the perchloric acid to donate a proton, and the stabilisation of the species formed through hydrogen bonding. Dissociation was considered unlikely in such a strong acid. In a separate investigation[73] attempting to prove this postulate, only one-sixth of the sublimation reaction was found to be simple dissociation. The remaining five-sixths of the ammonium perchlorate was reported to dissociate according to the reaction

$$NH_4ClO_4 \rightleftharpoons HNO_3 + HCl + H_2O \tag{11}$$

Linear pyrolysis measurements of ammonium salts[74] also showed the sublimation equilibrium to be comprised of only a limited amount of dissociation. The heat of sublimation was found to be 25 kcal./mole.

In 1963, a comprehensive examination of the dissociation pressure of ammonium perchlorate[75] in the temperature range 247—347°, cast doubt on the above reaction scheme. It was proposed that sublimation occurred entirely through the simple dissociation

$$NH_4ClO_4 \rightleftharpoons NH_{3(g)} + HClO_{4(g)} \tag{12}$$

Thermal decomposition and sublimation were observed simultaneously and, as reported earlier,[13] were independent. The sublimate was found to contain traces of chloride ion, contrary to the previous finding,[13] as well as equimolar amounts of ammonium and perchlorate ions. Chloride ion was suggested as resulting from the reaction of ammonia with chlorine

$$8NH_3 + 3Cl_2 \rightleftharpoons 6NH_4Cl + N_2 \tag{13}$$

This was substantiated by sublimation experiments conducted in an ammonia atmosphere. The sublimate contained equimolar quantities of NH_4^+ and Cl^-. This was shown to be due to the suppression of perchloric acid vaporisation by

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[72] A. K. Galwey and P. W. M. Jacobs, *J. Chem. Soc.*, 1959, 837.

[73] H. M. Cassel and I. Liebman, *J. Chem. Phys.*, 1961, **34**, 343.

[74] W. Nachbar and F. A. Williams, 'Ninth Symposium (International) on Combustion' Academic Press, New York, 1963, p. 345.

[75] S. H. Inami, W. A. Rosser, and H. Wise, *J. Phys. Chem.*, 1963, **67**, 1077.

the ammonia. Several recent studies[22,25,42,76–81] have also shown that ammonium perchlorate sublimes by first dissociating into ammonia and perchloric acid. Mass spectrometric[22–25] and i.r.[76,77] data have failed to find any evidence for the existence of an ion-pair.

A recent detailed kinetic investigation[81] of ammonium perchlorate sublimation, has postulated the first comprehensive theory concerning the sublimation process. The initial step is the transfer of a proton from the ammonium to the perchlorate ion at a kink site on the surface of the crystal. The two molecules, NH_3 and $HClO_4$, then will either diffuse to different surface crystal sites, or recombine *via* the reversible proton-transfer process. Once at separate sites, the molecules can desorb into the gas phase, and reunite to form the sublimate. The significance of ammonia and perchloric acid diffusing on the surface of the crystal was shown by subjecting the system to nitrogen pressure.

When fitted to an equation relating surface diffusion to evaporation coefficient, the data produced the expected linear plot.

A new kinetic sublimation expression was also formulated and found to fit the experimental data. The equation, derived from Fuchs' modification of Langmuir's sublimation theory, resulted in values of 60·8 and 59·2 kcal./mole for the heats of sublimation at 1 atm. pressure and *in vacuo*, respectively. These are in close agreement with previous values of 58 ± 2 kcal./mole from dissociation pressure measurements,[75] 56 kcal./mole from the relationship between the surface temperature and the ambient pressure,[82] 58·4[83] and 56 kcal./mole[35] from thermodynamic analysis, and 56 ± 1 kcal./mole[80] from a kinetic study utilising the contracting cube equation. All the values were determined on the assumption that sublimation occurs by the dissociation process (12). The agreement in the data, therefore, indicates that ammonium perchlorate sublimes entirely through the dissociation process on the surface of the crystal.

The activation energy for sublimation has recently been shown to be much higher than the initial value of 21·5 kcal./mole from weight-loss measurements,[71] and 22·0 kcal./mole from linear pyrolysis data.[84] It has been found possible to eliminate anomalies in the rate data[85] to give an activation energy of 30 kcal./mole by weight loss in both high- and low-temperature regions in a predecomposed sample.[79–81,85] Surface temperature measurements have also given an activation energy of *ca.* 30 kcal./mole.[36]

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[76] J. L. Mack, A. S. Tompa, and G. H. Wilmot, 'Symposium on Molecular Structure and Spectroscopy', Ohio State Univ., Columbus, Ohio, 1962.

[77] J. L. Mack, A. S. Tompa, and G. H. Wilmot, *Spectrochim. Acta*, 1962, **18**, 1375.

[78] V. R. Pai Verneker and J. N. Maycock, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2723.

[79] P. W. M. Jacobs and A. Russell-Jones, *AIAA J.*, 1967, **5**, 829.

[80] J. V. Davies, P. W. M. Jacobs, and A. Russell-Jones, *Trans. Faraday Soc.*, 1967, **63**, 1737.

[81] P. W. M. Jacobs and A. Russell-Jones, *J. Phys. Chem.*, 1968, **72**, 202.

[82] J. Powling and W. A. W. Smith, *Combustion and Flame*, 1963, **7**, 269.

[83] G. S. Pearson, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 177.

[84] W. H. Anderson and R. F. Chaiken, *Amer. Rocket Soc. J.*, 1961, **31**, 1379.

[85] A. Russell-Jones, 'Mechanism of the Decomposition of Inorganic Perchlorates', Dissertation, Imperial College of Science and Technology, London, 1964.

4 Decomposition Reaction Mechanisms

A. Low-temperature Mechanisms.—(i) *Electron transfer.* The first kinetic investigation[32] of ammonium perchlorate decomposition in the temperature region 200—300°, led to a mechanism involving transfer between an anion and an interstitial cation, with the NH_4 radical thus produced undergoing dissociation.

$$ClO_4^- + NH_4^+ \rightarrow ClO_4 + NH_4 \qquad (14)$$

$$NH_4 \rightarrow NH_3 + H \qquad (15)$$

The ClO_4 radical in the interior of the crystal is stabilised by crystalline force fields and either picks up an electron from a nearby ClO_4^- ion or from a hydrogen atom formed by reaction (15).

$$H + ClO_4 \rightarrow HClO_4 \qquad (16)$$

The hydrogen atom can also react with a $HClO_4$ molecule

$$H + HClO_4 \rightarrow H_2O + ClO_3 \qquad (17)$$

producing ClO_3 radicals which act as electron traps, thereby increasing the decomposition. This reaction was used to account for the catalytic effect of $HClO_4$. However, a later study[86] has reported that ClO_3 radicals decompose in the low-temperature region. Irradiation investigations,[87–89] on the other hand, have supported Bircumshaw and Newman, showing that ClO_3^- ions are thermally stable below 300°.

In the above mechanism a ClO_4 radical will eventually be produced on the surface of the crystal and decompose, leaving a positive hole. This excess of positive charge is then either removed by an electron from the crystal interior, or by migration of an NH_4^+ ion from a nearby lattice site. Thus, decomposition centres form through the crystal surface. The decomposition process disorganises the crystal lattice and allows sublimation [reaction (12)] to increase because of the increasing surface area. As both processes compete for ClO_4^- ions on the surface, the decomposition eventually reaches a stage where sublimation is so much more rapid that the decomposition process ceases. This explains the cessation of the low-temperature reaction after only 30% decomposition.

Probably the most widely quoted early mechanism[27] involves the formation of a molecular complex, $[NH_4ClO_4]$, on the surface of the crystal at a kink site where an electron and a positive hole are mutually trapped. The molecular complex has a definite lifetime, in which it either decomposes or reverts back to the original ionic form. The mechanism is, therefore, a variation of the electron-transfer process, with the formation of the positive hole as the rate-determining

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[86] J. C. Petricciani, S. E. Wiberley, W. H. Bauer, and T. W. Clapper, *J. Phys. Chem.*, 1960, **64**, 1309.

[87] V. F. Komarov, V. V. Boldyrev, V. K. Zhuravlev, and G. V. Ivanov, *Kinetika i Kataliz*, 1966, **7**, 788.

[88] A. V. Rayeskiy, G. B. Manelis, V. V. Boldyrev, and L. A. Votinova, *Doklady Akad. Nauk. S.S.S.R.*, 1965, **160**, 1136.

[89] E. S. Freeman and D. A. Anderson, *J. Phys. Chem.*, 1961, **65**, 1662.

step. When an NH_4ClO_4 complex does decompose, it eliminates H_2O, which leaves a nitrogen atom and a ClO_2 molecule. The nitrogen atoms then combine, through a third body, to form molecular nitrogen

$$NH_4ClO_4 \rightarrow N + ClO_2 + 2H_2O \tag{18}$$

$$N + N + M \rightarrow N_2 + M \tag{19}$$

while the ClO_2 molecules go on to form chlorine and oxygen.

$$ClO_2 \rightarrow ClO + O \tag{20}$$

$$2ClO \rightarrow Cl_2 + O_2 \tag{21}$$

Nitrogen molecules react with the oxygen atoms from reaction (20) to form N_2O *via* a third-body reaction. The remaining trace products, *e.g.* HCl, $HClO_4$, and NOCl, are formed by side-reactions involving H_2O, N_2O, ClO, O_2, N_2, and ClO_2. Hence the decomposition is initiated at the surface at a junction of mosaic blocks, and spreads through the intergranular material. The reaction ceases when only loosely attached blocks remain, presumably at *ca.* 30% decomposition.

With regard to this variation of the electron transfer mechanism, evidence for the formation of a molecular complex has been discounted by several recent investigators,[37,90] as well as by the failure of mass spectrometric[22–25] and i.r.[76,77] studies to find any confirmation of the existence of the NH_4ClO_4 complex.

Microcinematography[91] of decomposing crystals has also led to the suggestion of an electron-transfer mechanism. In this case, ClO_4 radicals are produced by transfer of electrons from ClO_4^- ions into the conduction band of the crystal. The electrons may subsequently be captured by 'traps' resulting in the eventual formation of (NH_4) (ClO_4) radical pairs. The reaction rate is controlled by the decomposition of the complex or of the ClO_4 radical. The action of electron donor or acceptor catalysts is explained by their effect on the semiconductor properties of the crystal. A change in electron density changes the concentration of ClO_4 radicals and hence the decomposition rate. Metals which undergo change of valence readily, should be active catalysts.

The electron-transfer mechanism for pure ammonium perchlorate decomposition has in general received support from studies of catalysed reactions.[16,78,92–102]

[90] S. A. Inami, W. A. Rosser, and H. Wise, *Trans. Faraday Soc.*, 1966, **62,** 723.

[91] A. V. Rayevskiy and G. B. Manelis, *Doklady Akad. Nauk. S.S.S.R.*, 1963, **151,** 886 (translation AD 608052, Oct. 6, 1964).

[92] F. Solymosi and E. Krix, *J. Catalysis*, 1962, **1,** 468.

[93] F. Solymosi and K. Dobe, *Magyar Kém. Folyóirat*, 1966, **72,** 124.

[94] F. Solymosi and M. Ranics, *Magyar Kém. Folyóirat*, 1965, **71,** 556.

[95] A. Hermoni and A. Salmon, 'Eighth Symposium (International) on Combustion', Williams and Wilkins Co., Baltimore, 1962, p. 656.

[96] F. Solymosi, *Combustion and Flame*, 1965, **9,** 141.

[97] F. Solymosi and L. Reves, *Nature*, 1961, **192,** 64.

[98] F. Solymosi and L. Reves, *Z. anorg. Chem.*, 1963, **322,** 86.

[99] F. Solymosi and L. Reves, *Kinetika i Kataliz*, 1963, **4,** 88.

[100] A. K. Galwey and P. W. M. Jacobs, *Trans. Faraday Soc.*, 1959, **55,** 1165.

[101] A. K. Galwey and P. W. M. Jacobs, *Trans. Faraday Soc.*, 1960, **56,** 581.

[102] P. W. M. Jacobs and A. R. T. Kureishy, *J. Chem. Soc.*, 1962, 556.

However, it has been pointed out[103] that since N_2O and HCl are usually not products of catalysed reactions, the mechanisms need not be similar.

Early mass spectrometric studies[22,25] tended to disprove the electron-transfer mechanism but more recent work,[23,24] using an instrument coupled directly to a conventional vacuum reaction system, indicates that the rate controlling step in the decomposition is the formation of a ClO_4 radical and an electron from ClO_4^-. In addition, the electron-transfer mechanism has been shown to account[78] for the influence of various reaction parameters such as particle size, ageing of crystals, and effect of product gases, on the low-temperature decomposition rate.

The activation energy for the low-temperature region, 32 kcal./mole,[27,92,97,104] has been associated with promotion of electrons into the conduction band of the crystal.

Irradiation investigations[87,89,105–109] also support the electron-transfer mechanism. Irradiation shortens the induction period,[110] and lowers the activation energy in the acceleratory region,[109] but does not effect the activation energy of the deceleratory region.[109] Since irradiated ammonium perchlorate has been suggested as decomposing through an initial electron transfer step,[87,105,107–109] it has been postulated that un-irradiated ammonium perchlorate must also decompose by a similar mechanism. Irradiation simply catalyses the process by introducing defects and catalytic impurities such as ClO_3^-, which increases both the number of initial decomposition centres and the number of potential electron traps.

(ii) *Proton transfer.* Variations of this general mechanism are all based on the reaction

$$NH_4^+ClO_4^- \rightarrow NH_3 + HClO_4 \qquad (22)$$

occurring in the crystal lattice or on the surface. The earliest version[57] was put forth in connection with the application to previous data[13,32] of a kinetic analysis based on the linear rate of progression of the decomposition interface. The rate determining step in the decomposition of orthorhombic crystals below 250° was assumed to be the attainment of nearly free rotation by the perchlorate ion. For the cubic form above 250°, it was desorption of the $NH_3,HClO_4$ complex at the decomposition interface. Mathematical analyses of both the acceleratory and deceleratory portions of the decomposition rate curve were carried out successfully on the basis of these postulates.

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[103] W. A. Rosser, N. Fishman, and H. Wise, *AIAA J.*, 1966, **4**, 1615.

[104] P. W. M. Jacobs and A. R. T. Kureishy, 'Eighth Symposium (International) on Combustion', Williams and Wilkins Co., Baltimore, 1962, p. 672.

[105] E. S. Freeman, D. A. Anderson, and J. J. Campisi, *J. Phys. Chem.*, 1960, **64**, 1727.

[106] E. S. Freeman and D. A. Anderson, *J. Phys. Chem.*, 1959, **63**, 1344.

[107] J. E. Flanagan and J. C. Gray, *J. Spacecraft Rockets*, 1966, **3**, 135; *Chem. Abs.*, 1966, **64**, 12453.

[108] Yu. M. Boyarchuk, N. Ya. Buben, A. V. Dubovitskii, and G. B. Manelis, *Kinetika i Kataliz*, 1964, **5**, 823.

[109] E. S. Freeman and D. A. Anderson, *Amer. Soc. Testing Mat. Spec. Tech. Publ., No.* 359, 1963, 58.

[110] P. J. Herley and P. W. Levy, *Nature*, 1966, **211**, 1287.

A proton-transfer step has been invoked in discussing the results of a qualitative isothermal kinetic decomposition study[20] and to explain some mass spectrometric results.[22,25] In a more detailed analysis, it has been suggested[111,112] that the decomposition can be thought of in terms of hard and soft acids and bases. Initially, the proton, being a very hard acid, tends to combine with the ammonia molecule, a hard base, rather than the ClO_4^- ion, only a moderately hard base. However, as the temperature is raised the polarisability of the NH_3 is readily increased, and its hard-base character begins to soften at a much greater rate than that of the ClO_4^- ion. Thus, at a high enough temperature, *ca.* 150°, the ClO_4^- ion will become harder in nature than the ammonia molecule, and hence will extract the proton from it. The unbalanced perchloric acid molecule then decomposes according to the equation

$$HClO_4 \rightarrow ClO_3 + OH \tag{23}$$

Hydroxyl radicals abstract hydrogen from ammonia until free nitrogen atoms are produced. These then dimerise. Both the production of water and of nitrogen are highly exothermic reactions which supply the energy necessary to maintain the reaction.

This mechanism clearly requires that the recombination reaction

$$NH_3 + HClO_4 \rightarrow NH_4^+ + ClO_4^+ \tag{24}$$

be sufficiently slow compared to the dissociation, that the lifetime of the individual $HClO_4$ molecules permits their unimolecular decomposition. In the case of the catalysed decomposition, the function of the catalyst is claimed to be to complex NH_3 or $HClO_4$ molecules and impede the recombination. Catalysts weaken the N–H bond by withdrawing electrons from nitrogen, and facilitate the extraction of hydrogen from ammonia by hydroxyl radicals.[111–114] Whether these considerations can be applied to the uncatalysed decomposition may need further consideration.

Adiabatic investigations[15,90] have supported a mechanism involving adsorbed NH_3 and $HClO_4$. In one research,[115] an analogy is drawn between ammonium perchlorate and ammonium nitrate decompositions, both being dependent upon dissociation products. A mechanism is suggested in which ammonia and perchloric acid are absorbed on the surface of the crystal.

$$\begin{array}{rcc} NH_4^+ + ClO_4^- \rightleftharpoons & NH_{3(s)} & + \; HClO_{4(s)} \\ & \updownarrow & \updownarrow \\ & NH_{3(g)} & + \; HClO_{4(g)} \end{array} \tag{25}$$

Evaporation of the species results in sublimation, whereas decomposition of the

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[111] J. E. Land, NASA Accession No. N65-31598, AD 466956 (1965).
[112] J. E. Land, AD 631593 (1966).
[113] J. E. Land, AD 625191 (1965).
[114] J. E. Land, AD 626805 (1965).
[115] W. A. Rosser, S. A. Inami, and H. Wise, *J. Phys. Chem.*, 1963, **67**, 1753.

adsorbed $HClO_4$ yields reactive intermediates

$$2HClO_{4(s)} \rightleftharpoons ClO_3^+ + ClO_4^- + H_2O_{(s)} \tag{26}$$

These can then oxidise the ammonia to give products and additional reactants, which through a variety of reactions produce the final products. Inhibition by ammonia is attributed to the reversal of reaction (25), while the reversal of reaction (26) is responsible for inhibition by water. Perchloric acid catalysis can be ascribed to the enhancement of reaction (25). Termination of the reaction is attributed to depletion of favourable reaction sites. A mechanism such as this can account qualitatively for the many nitrogen-containing products, *e.g.* N_2, N_2O, HNO_3, and traces of NOCl.

A recent publication[80] measuring the thermal decomposition by both weight loss and pressure gain, has shown the rate to be independent of the method of measurement. Also, the sublimation and low-temperature processes possess identical activation energies.[80,81] This has led to the suggestion[79,80,116] that the two processes occurring in the low-temperature region, operate by a single proton-transfer mechanism. The rate being independent of the method of measurement indicates that gas phase reactions are not rate-determining. This, in addition to the observation that the sublimation rate is slower than decomposition rate, suggests that the low-temperature decomposition proceeds through adsorbed NH_3 and $HClO_4$, as proposed earlier.[15,90]

A mechanism similar to reaction (25) was therefore proposed[79,80] in which either the adsorbed ammonia and perchloric acid sublime, or the $HClO_4$ decomposes on the surface, forming intermediates which react with the adsorbed NH_3. The perchloric acid decomposes by a bimolecular reaction

$$2HClO_{4(a)} \rightarrow H_2O + ClO_3 + ClO_4 \tag{27}$$

The oxides of chlorine decompose through a series of reactions, producing products and radical intermediates which oxidise the ammonia. The net result of these reactions are products which agree well with previous studies.[15,32] The proposed mechanism also is in agreement with the fact that perchloric acid increases the reaction rate and ammonia decreases it. The fact that $HClO_{4(a)}$ desorbs more rapidly than $NH_{4(a)}$, and that the latter is not rapidly oxidised, explains why the low-temperature reaction ceases after only 30% decomposition. The role of a catalyst in this mechanism has been attributed[79] to formation of ammines which tie up the ammonia. This is similar to an earlier theory,[111–114] except that the ammine complex inhibits a different reaction.

(iii) *Activation energy*. The first kinetic study[32] used pressure increase as a measure of decomposition rate in the interval 215—275°. Data for the acceleratory region were fitted to a power law $p = (kt)^6$ and for the deceleratory region to the equation

$$-\ln(P_f - p) = kt + C \tag{28}$$

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[116] P. W. M. Jacobs and A. Russell-Jones, 'Eleventh Symposium (International) on Combustion', The Combustion Institute, Pittsburg, 1966, p. 457.

where P_f is the final pressure at 30% decomposition. Use was also made of the modified autocatalytic Prout–Tompkins equation[117]

$$\ln[p/(P_f - p)] = kt + C \qquad (29)$$

Activation energies of 27·8 kcal./mole for the orthorhombic form and 18·9 kcal./mole for the cubic form were obtained.

In a more recent investigation,[27] also employing a manometric method, activation energies for the orthorhombic and cubic forms were found to be nearly equal, as shown in Table 1.

Table 1 *Activation energies for low-temperature decomposition*[27]

	Orthorhombic			*Cubic*		
	α	E_a(kcal./mole)	n	α	E_a(kcal./mole)	n
Powder	0·05—0·70	24·6	4	0·15—0·80	24·8	2
Pellets	0·05—0·70	30·1	3	0·15—0·80	29·9	2
Crystals	0·02—0·20 (acceleratory)	20·6	4	0·04—0·86	25·3	2
Crystals	0·20—0·90 (deceleratory)	16·9	3			

In this case, the Avrami–Erofeyev equation[118–121]

$$[-\ln(1 - \alpha)]^{1/n} = k(t - t_0) \qquad (30)$$

was used, where t_0 is the induction period and α the fraction decomposed. This is based on random nucleation followed by three-dimensional growth.

An E_a of 30 kcal./mole was obtained in still another manometric study[68] by use of several methods of calculation. Pressure measurements, when used to follow the decomposition of whole crystals,[110] produced an E_a of 24·6 kcal./mole for the decay ($n = 4$) and 26·9 kcal./mole for the acceleratory period ($n = 3$), by use of equation (30). A value of 29·8 kcal./mole was obtained from induction periods, by use of the equation

$$\alpha = kt + C \qquad (31)$$

Neither equations (28), (29), nor a modified version[122] of (29) would fit the data in the decay period. Other investigations[99,104] utilising equation (30) have given E_a values of 31·6 and 27 kcal./mole for temperatures >240° and 30·1 kcal./mole[55] <300°.

The low-temperature reaction was found[20] to be first order and an E_a of 21·5

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[117] E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.
[118] M. Avrami, *J. Chem. Phys.*, 1939, **7**, 1103.
[119] M. Avrami, *J. Chem. Phys.*, 1940, **8**, 212.
[120] M. Avrami, *J. Chem. Phys.*, 1941, **9**, 177.
[121] B. V. Erofeyev, *Compt. Rend. Acad. Sci. U.R.S.S.*, 1946, **52**, 511.
[122] E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, 1946, **42**, 468.

kcal./mole was calculated from the equation

$$\mathrm{d}x/\mathrm{d}t = k(1 - x)^n \tag{32}$$

which neglects autocatalysis. Little difference was noted in E_a as the particle size increased. This agrees with a recent adiabatic study,[90] in which only a slight increase was found to occur in E_a with respect to particle size. Mean activation energies of 22·1 and 19·1 kcal./mole were obtained using modified forms of equations (30) and (29) respectively. Studying the decomposition adiabatically permitted the elimination of self-heating of the sample.

Measurement of the rate of growth of nuclei by slow motion microphotography,[91] gave an activation energy of 17 kcal./mole for single crystals above the transition point. Nucleation occurred randomly throughout the crystal. Below the crystal transformation, activation energies of 31 kcal./mole, for longitudinal, and 33 kcal./mole for transverse growth of the centre were recorded, with nuclei growing parallel to the principal diagonal of the rhomboid. Adiabatic measurements[90] gave a value of 43 kcal./mole for nucleation of pressed wafers, between 240 and 272°. When the decomposition of powdered ammonium perchlorate was followed through use of a thermoblance,[26] an activation energy of 30 kcal./mole was found below 236°. The data were analysed by the empirical equation

$$\mathrm{d}\alpha/\mathrm{d}t = k_1(1 - \alpha) + k_2\alpha(1 - \alpha) \tag{33}$$

where k_1 characterises the initial number of electron traps present and k_2 represents the speed of the development of the reaction centres. An activation energy of 30 kcal./mole was also found[109] for both the acceleratory and deceleratory stages of decomposition in the temperature range 161—266°, when weight loss data on whole crystals were plotted directly against $1/T$.

Activation energies have also been determined[111] by recording the heating rate and peak temperature of a sample during decomposition. The quantity $\ln(Hr/T_m^2)$ is plotted against $1/T$ where T_m represents the peak temperature and Hr is the heating rate. The slope of the straight line gives the activation energy. Values of E_a varied from 25 to 31 kcal./mole depending upon particle size.

In a kinetic study[123] by use of a gravimetric method of analysis and equation (29), activation energies of 40·1 kcal./mole ($n = 4{\cdot}5$, $\alpha = 0{\cdot}0$—$0{\cdot}12$) for the temperature range 214—236°, and 25·1 kcal./mole ($n = 1{\cdot}2$, $\alpha = 0{\cdot}0$—$0{\cdot}20$) for 250—300°, were obtained. These values are somewhat higher than previous investigations, but this was attributed to the decomposition being exposed to the air. This allowed the free removal of the decomposition gases and prevented side reactions from influencing the decomposition.

A recent kinetic investigation,[80] which made use of both pressure-change measurements and thermogravimetric methods, gave an activation energy of 26·6 kcal./mole by use of equation (30) with $n = 2$ or 3. The kinetics were found to be independent of both particle size and ambient atmosphere. Rate curves at 230 and 260°, have also demonstrated[124] that an inert gas pressure of 100 atm.

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[123] A. A. Shidlovskiy, L. F. Shmagin, and V. V. Bulanova, *Izvest. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1965, **8**, 533 (translation, NASA Accession No. N67-23401, 1967)

[124] V. A. Strunin and G. B. Manelis, *Izvest. Akad. Nauk. S.S.S.R. Khim.*, 1964, 2226.

has no effect upon the reaction kinetics. By use of the calculated induction periods (t_0), an activation energy of 30·1 kcal./mole was found.[80] It was further determined that pressure- and weight-loss curves become virtually identical up to $\alpha = 0{\cdot}7$, if the latter are corrected for sublimation. The least-square activation energies were 33·9 and 27·0 kcal./mole below and above the transition point respectively.

Thus it appears that while the decomposition mechanisms are identical for the orthorhombic and cubic crystals below 350°, the activation energies are not the same. The kinetics for the cubic structure are, in addition, less dependent on sample pretreatment. Both these observations are probably due to the reorganisation of the mosaic structure during the crystal phase transformation.

B. High-temperature Mechanisms.—High-temperature decomposition was first suggested[32] as resulting from the thermal breakdown of the perchlorate ion on the surface of the crystal. This would lead to an entirely deceleratory reaction as is the case in the high-temperature region. Further kinetic investigation[71] substantiated this theory, when an activation energy of 73·4 kcal./mole was obtained. The decomposition was compared to that of potassium perchlorate ($E_a = 69{\cdot}3$ kcal./mole), where a rupture of the Cl – O bond is thought to occur.[125] However, recent kinetic data[16,20,85,111] have shown the activation energy to be well below that found earlier[71] and it now seems unlikely that this is the mechanism.

A second mechanism has been proposed[72] in which the transfer, on the surface of the crystal, of a proton from the ammonium to the perchlorate ion is the rate-determining step. The perchloric acid then decomposes generating oxygen

$$2HClO_4 \rightarrow H_2O + Cl_2O_7 \qquad (34)$$

$$2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2 \qquad (35)$$

which subsequently oxidises the ammonia

$$4NH_3 + 5O_2 \rightarrow 6H_2O + 4NO \qquad (36)$$

Reaction (35) was suggested as being a chain reaction involving ClO_4, ClO_3, ClO_2, ClO, Cl, and O radicals. The reaction scheme accounts for the major decomposition products found earlier.[10–13]

Recently, a kinetic study[79,85,116] has shown that all three processes, high- and low-temperature decompositions and sublimation, possess identical activation energies of 30 kcal./mole. This suggests a common rate-determining step. The high-temperature rate constants were also found to be lower if measured by weight loss rather than pressure. This indicates gas-phase reactions to be rate determining. The mechanism advanced again consists of an initial proton transfer on the crystal surface, followed by evaporation into the gas phase. Perchloric acid, unstable at these temperatures,[126] decomposes and its reaction intermediates

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[125] T. R. Phillips, Ph.D. Thesis, Univ. of Birmingham, 1953.
[126] J. B. Levy, *J. Phys. Chem.*, 1962, **66**, 1092.

oxidise the gaseous ammonia to the final products. Introduction of an inert gas enhances the reaction by reducing diffusion and sublimation.[71]

The first high-temperature kinetic investigation[32] found that the reaction obeyed the power law $p = kt^n$ with $n < 1$ and depends on the temperature. A more extensive study,[71] utilising the equation

$$m^{2/3} = -kt + c \qquad (37)$$

where m is the mass decomposed in time t, gave an activation energy of 73·4 ± 1·5 kcal./mole. The reaction was studied under a nitrogen pressure of 20 cm. to prevent sublimation. The E_a was obtained from the temperature range 400—440°, since between 300° and 380° reproducibility of the data was poor. This was attributed to evaporation at the crystal surface. The fact that kinetic data in the range 300—380° are not reproducible was also demonstrated[72] in a later study. However, in this case the cause was attributed to a mixture of both the high- and low-temperature reactions occurring simultaneously. The decomposition in the range 380—450° was found to follow both the power law and the contracting cube expression,

$$kt = 1 - (1 - \alpha)^{1/3} \qquad (38)$$

an equation deduced from the contraction of an interface parallel to the crystal surface. In principle, however, because n in the power law varies with temperature, the use of equation (38) is preferable. An activation energy of 38·8 kcal./mole was calculated, over the range $\alpha = 0{\cdot}2$—$0{\cdot}8$, for pellets of both decomposed and undecomposed ammonium perchlorate. Other values for the high-temperature activation energy obtained by use of equation (38) are 44·8 kcal./mole[16] for the temperature range 350<440° and 31·6 kcal./mole[55] for 280—380°.

In an isothermal investigation,[20] the reaction was found to be of half-order and the activation energy, from equation (32), was found to be highly dependent upon particle size as shown in Table 2.

Table 2

Particle diameter (microns)	E_a(kcal./mole)
28	31·0
56	35·7
80	49·4

In a high-temperature investigation[111] using heating rates and decomposition peak heights, activation energies of 30 kcal./mole were calculated by use of the peak-height equation for particle diameters up to 162 microns. The samples were heated from ambient temperature to 450° in air. A recent kinetic study[123] found activation energies of 39·1 kcal./mole ($n = 0{\cdot}6$, $\alpha = 0{\cdot}0$—$0{\cdot}40$) and 35·5 kcal./mole ($n = 1{\cdot}0$, $\alpha = 0{\cdot}40$—$0{\cdot}80$), for decomposition of partly decomposed ammonium perchlorate over the temperature range 330—450°, when the data was fitted to equation (30). Values of 28·3 kcal./mole ($n = 0{\cdot}8$, $\alpha = 0{\cdot}10$—$0{\cdot}50$) and 23·7 kcal./mole ($n = 1{\cdot}1$, $\alpha = 0{\cdot}50$—$0{\cdot}90$) were calculated for undecomposed ammonium perchlorate in the temperature range 400—470°. A gravimetric method was used. The reason given for the much lower activation energy of the undecomposed sample, in contradiction of earlier results,[72] was that the intercrystalline material is much more difficult to decompose because favourable reaction sites have been lost during the low-temperature decomposition.

An activation energy of 30·6 kcal./mole has been recently obtained[85] when measuring the decomposition rate by weight loss. Differences from this value in the earlier work cited above, were attributed to gas-phase reactions being rate-limiting.[85,116]

Hence, reproducible kinetic data can be obtained only if the experimental system and procedure are carefully controlled.

C. Effect of Impurities and Defects.—(i) *Impurities.* In comparison to the recrystallised salt, commercial grade ammonium perchlorate has been found to possess a lower decomposition temperature[20] and an increased reaction rate[20,55] in the low temperature range. The high-temperature decomposition was unaffected by recrystallisation. The effects were attributed to impurities. Recent experiments on specially purified ammonium perchlorate[127] have shown the low-temperature decomposition to be markedly suppressed. It has been suggested[79] that foreign ions are the prime decomposition initiation sites. In a study[78] in which ammonium perchlorate was doped with chromate and dichromate ions, it was found that the decomposition was accelerated. If, however, the sample was doped with Ca^{+2} ions, an inhibitory effect resulted. These effects were interpreted in terms of an electron-transfer mechanism, in which an excess of cation vacancies, Ca^{+2}, decelerates the reaction, whereas the addition of anion vacancies, chromate and dichromate, increases decomposition. Similar findings have been reported[91–94] by various other investigators. Coloured impurities have also been suggested[78] as catalysing the reaction by introducing localised perturbations into the energy levels of the ammonium perchlorate.

Adsorption of a surfactant on the crystals has been reported to increase the rates of both low- and high-temperature decomposition.[128–130] An increase in the number of crystalline defects was considered responsible.

(ii) *Particle size.* Variations in particle size have been shown to affect both the low- and high-temperature decompositions of ammonium perchlorate. In the low-temperature region, the velocity[10,32,78] and amount[20] of decomposition were found to increase as the particle size was decreased. The rate, however, was observed[32,78] to attain a maximum value, after which further decreases in the particle size, resulted in a lowering of the decomposition rate. The rise in decomposition rate with diminishing grain size was attributed[32] to the increase

G[127]. Sammons, NASA Third Interagency Chemical Rocket Propulsion Group Combustion Conference, John F. Kennedy Space Center, Oct. 1966.

[128] B. G. Moser, R. E. Wiech, and R. F. Landel, Western States Section of the Combustion Institute, Paper WSCI 65-36, 1965.

[129] K. Ito and T. Hikita, *Kogyo Kayaku Kyokaishi*, 1965, **26**, 124.

[130] K. Ito and T. Hikita, *Kogyo Kayaku Kyokaishi*, 1965, **26**, 131.

in particle surface area available for nucleation. Also, a reduction in the grain size gives rise to an increase in crystal imperfections.[20] However, as the particle size is decreased still further, the escape of decomposition gases which inhibits the reaction becomes retarded, owing to the smaller distances between particles. In addition, the interference between expanding reaction zones increases, and overcomes the effect of an enlarged surface area.[32]

The activation energy of the low-temperature decomposition, as discussed earlier, is only slightly affected by changes in grain size.[20,80] This was explained[20] on the basis that changes in grain size alter only the number of crystal defects but not their individual decomposition activation energy. In the high-temperature region, a decrease in particle size lowers both the activation energy and the temperature at which decomposition begins to occur.[20] Again this is reasonable, since the high-temperature decomposition energy is dependent upon the surface area and surface energy of the crystals.

(iii) *Lattice defects.* The vital role played by imperfections in the crystal structure was first indicated in 1955, when nucleation was found to occur, suggesting preferential sites for initiation of decomposition.[32] This was subsequently supported by a series of investigations[42,87–89,91,109,131–133] in which preferred regions of reaction were observed along the intermosaic boundaries where crystal defects occur. Slow motion microphotography[88,91] revealed a great similarity between the anisotropy of the distribution of imperfections and the anisotropy of the nuclear decomposition growth of the nuclei.

A change in the activation energy can be brought about by modifications in the ammonium perchlorate physical form. Activation energies for decomposition nucleus growth in the orthorhombic form have been observed[27] to increase as the amount of sample reorganisation is decreased. For single crystals, $E_a = 17$, for powders $E_a = 22$, and for pellets $E_a = 30$ kcal./mole. This has been ascribed to a decrease in the crystalline defects as the sample is mechanically worked. With the cubic structure, however, all three physical forms possessed identical activation energies. Values of *ca.* 25 kcal./mole, were determined for whole crystal and powdered forms, and 27 kcal./mole was calculated for pellets. This was attributed[27] to a reorganisation of the lattice during crystal transformation, making it independent of the initial preparation. The activation energy for the high-temperature decomposition was also determined to be apparently independent of the physical form.[72]

The prehistory of the ammonium perchlorate sample has been found to affect the low-temperature decomposition almost exclusively. This is because modifications in the method of crystal formation markedly alter the lattice imperfections which are presumed responsible for decomposition in the low-temperature region. It has been shown[133] that the number of decomposition nuclei depends

[131] R. F. Chaiken, J. F. Cheselske, I. Geller, J. H. Lobata, K. Schneider, D. J. Sibbett, J. E. Sutherland, and A. Wheeler, AFOSR Second Contractor's Meeting on Solid Propellant Combustion, AD 239150, Alexandria, Virginia, June 7, 1960.

[132] E. S. Freeman, D. A. Anderson, and J. Campisi, *Chem. Eng. News*, 1961, 39, 40.

[133] V. V. Boldyrev, Yu. P. Savintsev, and V. F. Komarov, *Kinetika i Kataliz*, 1965, **6**, 732.

solely upon the conditions and methods under which the crystals are grown. Also, changes in the acidity of the solvent used in crystallisation produce a change in the decomposition rate.[21]

A decrease in the decomposition rate with time since crystal synthesis, has indicated that ageing also influences the low-temperature decomposition.[78] Again, this has been attributed[78] to imperfections. It was suggested that the defects are annealed out of the crystal lattice as a function of time.

The gaseous decomposition products, as a whole, have been reported to both increase and decrease further decomposition. In the low-temperature region, the reaction products escaping to the surface create new defects in the crystal lattice.[26,21] Water, one of the major decomposition products, was first found[13] to display a rejuvenating effect toward the low-temperature decomposition. Adding the condensed water back into the decomposing salt caused an increase in the amount of decomposition. The effect was attributed to the reorganisation of the crystal lattice by the solvent, reproducing the crystalline voids and defects removed during decomposition. These imperfections were suggested[32] to be responsible for decomposition. Later studies,[15,133,134] however, have shown water to definitely inhibit the thermal reactions. It has been postulated[78] that the overall suppression of the decomposition by the product gases is due to the inhibiting effect of the water vapour alone.

Microphotographic measurements[133] have found water vapour to affect only the rate of growth of decomposition nuclei, and not to influence the initial number of nuclei formed. This would indicate that the decomposition process must be primarily determined by growth rate, rather than the number of nuclei present. The latter depends upon crystal prehistory.

The structural defects found in the ammonium perchlorate crystal lattice are of two basic types, Schottky, or Frenkel. The Schottky type occurs when some of the cation or anion sites in the lattice are void, while the Frenkel type occurs when an ion is found in an interstitial position. Due to several contributing factors, including a high dielectric constant and a high van der Waals energy for the interstitial ion, it was first thought[135] that ammonium perchlorate crystal imperfections were of the Frenkel type. From the variation of the ionic conductivity with temperature, the energy for formation and migration of lattice defects was found to be 24 and 20 kcal./mole, respectively.[135,136] A similar investigation[137] gave a value of 11·5 kcal./mole for the defect migration energy, based on the prevalence of Frenkel disorders in the orthorhombic crystalline form and the Schottky defect structures in the cubic form. The energies of formation of a defect pair were calculated as 13·8 and 69·1 kcal./mole, respectively.

The electrical conductivity of ammonium perchlorate is abnormally high compared to the alkali halides.[135,136] It has been found to increase with increase in number of lattice defects[130] as would be expected. The conductivity has also

[134] B. S. Svetlov and V. A. Koroban, *Kinetika i Kataliz*, 1967, **8**, 456.

[135] H. Wise, Office of Naval Research Report, AD 639222, Sept. 15, 1966.

[136] H. Wise, *J. Phys. Chem.*, 1967, **71**, 2843.

[137] J. N. Maycock, V. R. Pai Verneker, and G. A. Gorzynski jun., *Solid State Comm.*, 1967, **5**, 225.

been found to increase with addition of gaseous ammonia. As a result of these observations, it has been suggested[135,136] that the electrical conductivity of the solid crystal is due to effective ion transport which is brought about by a charge-transfer process.

The mechanism advanced consists of a proton moving from an ammonium ion to an ammonia molecule situated in a Schottky or Frenkel defect. It was further suggested[135] that this proton transfer might be the key step in the thermal decomposition. Transfer of a proton to a perchlorate anion would lead to decomposition, whereas transfer to an ammonia molecule would bring about charge transport.

The cessation of the low-temperature reaction after only partial decomposition, has also been attributed to crystal imperfections. It has been suggested[15,20,27,57] that the decomposition occurs only in the disordered regions of the crystal, through some annealing reaction of lattice defects. Once these crystal imperfections are removed the reaction stops. Hence, the decomposition proceeds solely through the intermosaic structure which constitutes *ca.* 30% of the crystalline mass.

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