DECOMPOSITION AND COMBUSTION OF AMMONIUM PERCHLORATE

P. W. M. JACOBS AND H. M. WHITEHEAD*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Received August 2, 1968

Contents

I. Introduction

Perchlorates have long been of chemical interest as oxidizers, and several perchlorates have found technological application in explosives, pyrotechnics, and propellants. The enormous amount of research work done on ammonium perchlorate, in particular, in the last 15 years or so stems undoubtedly from its widespread use in solid rocket propellants. This review emphasizes the chemistry of the decomposition and combustion of ammonium perchlorate rather than mathematical or engineering aspects of rocket propulsion which are not discussed. For example, the important contemporary problems of combustion instability and erosive burning are not touched upon. It will be seen that the chemistry of ammonium perchlorate decomposition is dominated by the reactions of perchloric acid and by the oxidation of ammonia. In order to assess the relevance of certain reactions involving ammonia, perchloric acid, and oxides of chlorine, a brief account of these matters is given first in sections IV and V, before the mechanisms of the decomposition and combustion of ammonium perchlorate are discussed.

The systematic review of the literature was completed at the end of February 1968, but relevant papers which appeared in the commonly available journals since then up until June 10, 1968, together with some preprints and reports made available by their authors, have been included. While a conscientious attempt has been made to survey the open literature on the subject, not every paper and report traced has been mentioned, it being considered of greater value to couple a reasonably comprehensive coverage with a critical assessment of the various theories and hypotheses that have been formulated to explain these data, rather than to aim at a mere catalog, albeit a complete one.

The research scientist interested in ammonium perchlorate soon finds that much of the data of interest to him lies buried in reports from companies or from defense establishments, or from universities (usually directed to a sponsoring agency), or sometimes in unpublished conference proceedings. To avoid continued repetition of certain lengthy names the following abbreviations have been adopted in the references:

RPE = Rocket Propulsion Establishment, Westcott, Buckinghamshire, England

ERDE = Explosives Research and Development Establishment, Waltham Abbey, Essex, England

DDC = Defense Documentation Center, Cameron Station, Arlington, Virginia 22314, USA

AD = Astia Document, available from DDC; AD numbers of reports, where available, have been given in brackets

CPIA = Chemical Propulsion Information Agency, The Johns Hopkins University, Applied Physics Laboratory, Silver Spring, Maryland, USA

Where translations into English of the original papers are available, the source of these has been indicated in the references. To assist in the tracing of unpublished conference papers or reports, the titles of these have been given.

* Division of Building Research, National Research Council, Ottawa 7, Canada.

A. PHYSICAL PROPERTIES OF AMMONIUM PERCHLORATE

Ammonium perchlorate (AP) is a white crystalline solid which undergoes a reversible crystallographic transition from the low-temperature orthorhombic structure to a cubic structure at 240°.[1,2] This polymorphic change is attributable to the onset of free rotation of the perchlorate anions.[2,3] The low-temperature bipyramidal orthorhombic form has cell dimensions $a_0 = 9.202$ Å, $b_0 = 5.816$ Å, $c_0 = 7.449$ Å.[4] The cubic high-temperature form[5,6] contains four molecules per unit cell which has a cube edge of 7.63 Å. The calculated density[7] of the cubic form is 1.76 g/cm^3, as compared with 1.95 g/cm^3 for the measured density of the low-temperature form.[8]

A structure comprising an ordered, hydrogen-bonded arrangement of the NH_4^+ ions has been suggested from X-ray difference Fourier projections.[9] This arrangement, however, is not consistent with infrared measurements,[10] epr,[11] nmr,[12,13] and slow-neutron[14,15] studies, or with the neutron diffraction data,[16] all of which suggest that the ammonium ion undergoes free, or almost free, rotation. Ibers'[12] study of AP indicates reorientation in this compound at temperatures as low as 77°K with an activation energy of 2.0 ± 0.6 kcal/mole. Ibers predicted a line-width transition between 45 and 55°K, but Richards and Schaefer[13] did not observe such a transition at temperatures down to 20°K, and they accordingly estimated the potential barrier to reorientation as less than 1 kcal/mole. Confirmation of this latter value is to be found in the results of slow-neutron scattering experiments[14,15] and also from a study of the hyperfine splitting in the epr spectrum of the ion radical NH_3^+ in single crystals of AP at temperatures between 75 and 293°K which yielded a value for the potential barrier for rotation of 0.55 ± 0.05 kcal/mole.[11]

The phase transition is endothermic and is accompanied by a significant amount of decomposition with concomitant heat generation. Thus, calorimetric measurements of the enthalpy of transition of AP must involve resolution of a composite heat effect due to the endothermic phase transition and to the simultaneous endothermic dissociative sublimation and exothermic decomposition. Markowitz and Boryta[7] suppressed the decomposition and sublimation reactions by heating the AP samples under an atmosphere of ammonia gas. Using a differential thermal analysis technique, they computed a value of 2.3 ± 0.2 kcal/mole for the heat of transition from the orthorhombic to the cubic crystal structure. This value is to be preferred to that of 2.7 kcal/mole determined under less stringently controlled conditions.[17]

The specific heat of AP is 0.309 cal g^{-1} deg^{-1} between 15 and 240° and 0.365 cal g^{-1} deg^{-1} above the transition point.[17] Rosser, Inami, and Wise[18] have measured the thermal diffusivity of AP samples of porosity 0.023, sample density 1.90 g/cm^3, and particle size 43–61 μm. In the temperature range 50–240°, the thermal diffusivity is a linear function of temperature and can be expressed by the equation

$$\kappa = 3.59 \times 10^{-3} - (4.40 \times 10^{-6})T \quad \text{cm}^2/\text{sec} \qquad (1)$$

where T is the temperature in °K.

The effects of temperature and gaseous environment on the electrical conductivity of AP pellets have been investigated by Wise[19] and by Zirkind and Freeman.[20] At temperatures between 25 and 125°, argon and oxygen (at 1 torr pressure) depressed the conductivity of AP approximately one and two orders of magnitude, respectively. The activation energies[20] determined from the temperature dependence were 25.36, 26.75, and 32.27 kcal/mole for vacuum, oxygen, and argon, respectively. At higher temperatures (227–327°) the measured activation energy was 32 kcal/mole.[19] The conductivity was increased by the presence of ammonia, showing a first-order dependence on the partial pressure of NH_3 in the nitrogen carrier gas. The activation energy in the presence of NH_3 was 20 kcal/mole. A recent publication has reported[21] a complex temperature dependence for the electrical conductivity of single crystals of AP. Four distinct regions were observed with activation energies for conduction ranging from a high-temperature (T >255°) value of 45 kcal/mole to 4 kcal/mole at temperatures below 92°.

II. Decomposition Products

A. PURE AMMONIUM PERCHLORATE

AP is stable at room temperature but decomposes at measurable rates at temperatures greater than about 150°. At decomposition temperatures below approximately 300°, AP undergoes an autocatalytic reaction which ceases after about 30% decomposition. This is usually called the low-temperature reaction. The residue is quite stable at these temperatures unless rejuvenated by sublimation, recrystallization, or mechanical disturbance.[22–25] At temperatures above 350°, the high-temperature decomposition occurs; this reaction is not autocatalytic and decomposition is complete. Concurrently with these decomposition reactions, AP also undergoes dissociative sublimation.[22,24,25]

The chemical analysis of the decomposition products is

(1) W. Hueckel, "Structural Chemistry of Inorganic Compounds," Vol. II, Elsevier Publishing Co., Amsterdam, 1951, pp 667–670.
(2) D. Vorläender and E. Kaascht, *Ber.*, **56B**, 1157 (1923).
(3) C. Finbak and O. Hassel, *Z. Physik. Chem.*, **B32**, 130 (1936).
(4) C. Gottfried and C. Schusterius, *Z. Krist.*, **84**, 65 (1932).
(5) H. Braekken and L. Harang, *ibid.*, **75**, 538 (1930).
(6) K. Herrmann and W. Illge, *ibid.*, **75**, 41 (1930).
(7) M. M. Markowitz and D. A. Boryta, *J. Amer. Rocket Soc.*, 32, 1941 (1962).
(8) J. C. Schumacher and R. D. Stewart, "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 5, 2nd ed, Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1964, p 61.
(9) K. Venkatesan, *Proc. Indian Acad. Sci., Sect. A*, **46**, 134 (1957).
(10) T. C. Waddington, *J. Chem. Soc.*, 4340 (1958).
(11) A. V. Dubovitskii, N. Ya. Buben, and G. B. Manelis, *Zh. Strukt. Khim.*, **5**, 40 (1964); *J. Struct. Chem.*, **5**, 33 (1964).
(12) J. A. Ibers, *J. Chem. Phys.*, **32**, 1448 (1960).
(13) R. E. Richards and T. Schaefer, *Trans. Faraday Soc.*, **57**, 210 (1961).
(14) J. J. Rush, T. I. Taylor, and W. W. Havens, *J. Chem. Phys.*, **35**, 2265 (1961).
(15) J. J. Rush, T. I. Taylor, and W. W. Havens, *ibid.*, **37**, 234 (1962).
(16) H. G. Smith and H. A. Levy, *Acta Cryst.*, **15**, 1201 (1962).

(17) M. W. Evans, R. B. Beyer, and L. McCulley, *J. Chem. Phys.*, **40**, 2431 (1964).
(18) W. A. Rosser, S. H. Inami, and H. Wise, *AIAA J.*, **4**, 663 (1966).
(19) H. Wise, *J. Phys. Chem.*, **71**, 2843 (1967).
(20) P. Zirkind and E. S. Freeman, *Nature*, **199**, 1280 (1963).
(21) J. N. Maycock, V. R. Pai Verneker, and C. S. Gorzynski, *Solid State Commun.*, **5**, 225 (1967).
(22) L. L. Bircumshaw and B. H. Newman, *Proc. Roy. Soc.* (London), **A227**, 115 (1954).
(23) L. L. Bircumshaw and B. H. Newman, *ibid.*, **A227**, 228 (1955).
(24) L. L. Bircumshaw and B. H. Newman, "The Thermal Decomposition of Ammonium Perchlorate," ERDE Report No. 8/EMR/50, 1951.
(25) A. K. Galwey and P. W. M. Jacobs, *Proc. Roy. Soc.* (London), **A254**, 455 (1960).

Table I

Decomposition Products of AP and Their Dependence on Temperature

Temp, °C	Yield[a]								*Ref*
	O_2	N_2	N_2O	$Cl_2 + ClO_2$	Total H^+ [b]	HNO_3	HCl	NO [c]	
225	0.51	0.126	0.362	0.426	0.155				22
230	0.48	0.12	0.328	0.427	0.155				22
235	0.51	0.09	0.348	0.43	0.143				22
245	0.553	0.061	0.387	0.423	0.141				22
250	0.61	0.055	0.37	0.39		0.14	0.15	0.006	29
255	0.567	0.063	0.373	0.421	0.137				22
260	0.567	0.063	0.391	0.420	0.152				22
265	0.567	0.063	0.391	0.387	0.143				22
270	0.556	0.062	0.453	0.408	0.141				22
275	0.571	0.062	0.437	0.39	0.135				22
275	0.525	0.049	0.355	0.39		0.17	0.165	0.015	29
300	0.53	0.052	0.37	0.37		0.12	0.21	0.018	29
325	0.57	0.063	0.365	0.285		0.25[b]	0.28	0.032	29

[a] Moles of specified product per mole of AP decomposed. [b] Believed to be HNO_3 and $HClO_4$ in comparable amounts. [c] After Hg analysis.

rather complex. Dodé[26,27] was the first to publish detailed analyses of the gaseous products. He identified chlorine, chlorine dioxide (at temperatures below 300°), nitrogen, water, oxygen, nitrous oxide, nitric oxide, hydrogen chloride, and addition products of nitric oxide with chlorine and oxygen (nitrosyl chloride, nitrogen trioxide, and nitrogen dioxide). The distribution of the nitrogen between elemental nitrogen, nitrous oxide, and nitric oxide is temperature dependent. Below 300°, nitrous oxide predominates, but above this temperature the major nitrogen-containing species is nitric oxide.

Bircumshaw and Newman[22] confirmed Dodé's observation of a temperature-sensitive product distribution. In addition to the gases identified by Dodé, they found significant quantities of an acid other than hydrochloric acid; this they presumed to be perchloric acid. Their results indicated that a substantial redistribution of chlorine among the products was occurring in different temperature regimes. They found that at low temperatures almost all the chlorine appears as Cl_2 or ClO_2, whereas at high temperatures (380–450°) there is an almost equal distribution of chlorine between the acids and $Cl_2 + ClO_2$. Moreover, the stoichiometry of the decomposition could not be represented adequately by any simple equation. The following equations proposed by Dodé are therefore to be regarded as mere generalizations of the over-all product distribution.

$$T < 300°\text{: } 4NH_4ClO_4 = 2Cl_2 + 2N_2O + 3O_2 + 8H_2O \quad (2)$$

$$T > 300°\text{: } 2NH_4ClO_4 = Cl_2 + 2NO + O_2 + 4H_2O \quad (3)$$

Drops of liquid condensate from AP undergoing both sublimation and thermal decomposition at 300° have been observed,[28] and these were shown by a combination of infrared and wet chemical analysis to contain HNO_3, $HClO_4$, and HCl.

A thorough examination of the decomposition products from AP has also been made by Rosser, Inami, and Wise,[29] who used a flow method. Their results at <300° are generally in fairly good agreement with those of Bircumshaw and Newman, except that they found about 0.15 mole of HNO_3 (per mole of AP) and did not find any ClO_2. It is possible that the reported yields[22,24] of ClO_2 arose from the presence of NOCl, NO_2Cl, or Cl_2 in the volatile fraction. Rosser, Inami, and Wise also found small quantities of NO, somewhat less N_2O than Bircumshaw and Newman, and small quantities of either NO_2Cl or NO_3Cl.

A summary of the results of Bircumshaw and Newman[22] and of Rosser, Inami, and Wise[29] appears in Table I.

There have been seven reported investigations of the products from AP decomposition using mass spectrometry. Heath and Majer[30,31] heated AP in a small furnace adjacent to the ion source and at temperatures of 111–120° found ions due to NH_3, $HClO_4$, Cl_2, HCl, O_2, and oxides of nitrogen. Goshgarian and Walton[32] used a Knudsen effusion cell, again in the ion source chamber. Essentially the same configuration was used by Pellett and Saunders,[33] the AP powder being about 1 in. from the electron beam in their apparatus. The advantage of this procedure is that it should reveal the primary decomposition products since secondary reactions are minimized by the low ambient pressure in the ion source; the disadvantage is that, since sublimation is occurring simultaneously, it is virtually impossible to distinguish between the decomposition products of $HClO_4$ and of the AP. In an attempt to remedy this,[34,35] AP has been decomposed in a constant-volume system connected to a time-of-flight (TOF) mass spectrometer *via* a molecular leak. Isotopically labeled AP was used to eliminate ambiguities in some of the assignments of chemical species to observed peaks.

The results of Heath and Majer and of Goshgarian and

(26) M. Dodé, *Bull. Soc. Chim. France,* [5] **5,** 170 (1938).

(27) M. Dodé, *C. R. Acad. Sci., Paris,* **200,** 63 (1934).

(28) H. M. Cassel and I. Liebman, *J. Chem. Phys.,* **34,** 342 (1961).

(29) W. A. Rosser, S. H. Inami, and H. Wise, "Decomposition of Ammonium Perchlorate," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb 1967, CPIA Publication No. 138, Vol. I, pp 27–28; see also "Kinetics of Decomposition of Ammonium Perchlorate," Stanford Research Institute, PU 3573, Nonr-3415(00), Sept 1966 [AD 640 084].

(30) G. A. Heath and J. R. Majer, "A Preliminary Investigation by Mass Spectrometry of the Thermal Decomposition of Ammonium Perchlorate," RPE Technical Note No. 219, April 1963.

(31) G. A. Heath and J. R. Majer, *Trans. Faraday Soc.,* **60,** 1783 (1964).

(32) B. B. Goshgarian and J. A. Walton, "Mass Spectrometric Study of Ammonium Perchlorate," Technical Documentary Report AFRPL-TR-65-87, April 1965.

(33) G. L. Pellett and A. R. Saunders, "Mass Spectrometer Pyrolysis of Ammonium Perchlorate at Low Pressure," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb 1967, CPIA Publication No. 138, Vol. I, pp 29–38.

(34) J. N. Maycock, V. R. Pai Verneker, and P. W. M. Jacobs, *J. Chem. Phys.,* **46,** 2857 (1967).

(35) V. R. Pai Verneker and J. N. Maycock, *ibid.,* **47,** 3618 (1967).

Walton differ in some respects and also show considerable variations between runs with respect to the relative abundance of the various species. It is therefore difficult to draw quantitative conclusions. The principal products from AP decomposing at 230°, when $HClO_4$ is excluded, were found to be H_2O, N_2O, Cl_2, and O_2 in agreement with results of chemical analysis, together with significant amounts of HCl and N_2. It should be stressed that while this technique eliminated the complications due to concurrent sublimation, it permitted secondary reactions. Essentially the same conclusions were reached by Herley and Levy[36] from product analyses carried out using a quadrupole mass spectrometer. The most detailed investigations using mass spectrometry are those of Pellett and Saunders[33] who have established product yields (relative to Cl_2) for H_2O, O_2, N_2O, NO_2, and HCl, from which they deduce the equation

$$12NH_4ClO_4 = 4Cl_2 + 4N_2O + 4HCl + 4NO_2 + 7O_2 + 22H_2O \quad (4)$$

Subtraction of this equation for the stoichiometry from that of Dodé for orthorhombic AP (eq 2) yields the equation

$$2HCl + 2NO_2 = Cl_2 + O_2 + N_2O + H_2O \quad (5)$$

thus reconciling the apparent discrepancies between mass spectrometric and chemical analytical techniques provided the complications arising from the decomposition of $HClO_4$ by electron impact in the ion beam are not too serious. It is known that NO_2 reacts rapidly at moderate temperatures with the halogen acids; it is difficult, however, to obtain independent confirmation of the proposed reaction. Rosser and Wise[37] studied the oxidation of HCl by NO_2 in the temperature range 100–420°. Of the feasible over-all stoichiometries only

$$NO_2 + 2HCl = NO + H_2O + Cl_2 \quad (6)$$

was consistent with the following observations. At temperatures high enough to prevent the formation of significant quantities of NOCl from NO and Cl_2, the reaction proceeded without observable pressure change. The final change in optical density at 3300 Å, where both NO_2 and Cl_2 absorb light strongly, agreed precisely with that implied by eq 6. At temperatures less than about 300° the formation of some NOCl resulted in a slight pressure decrease as implied by the reaction

$$2NO + Cl_2 = 2NOCl \quad (7)$$

In connection with their recent important study of the behavior of AP + catalyst mixtures under pulsed ruby laser irradiation, using a Bendix TOF mass spectrometer to identify the products, Pellett and Saunders[38] have increased the temperature range of their earlier AP pyrolysis measurements. Their data now extend from 160 to 380° and must be considered the most detailed and reliable of the mass spectrometric measurements available on the decomposition of AP under high-vacuum conditions ($<10^{-6}$ torr). The principal feature of the new data above 240° is that the H_2O, O_2, Cl_2, N_2O, and NO_2 ratios (using HCl as the reference) all decrease smoothly with decreasing temperature. The simplest, but possibly too facile, interpretation of this result is that it is due principally to an increase in the proportion of HCl formed over this temperature range. Between 160 and 240°, the N_2O/HCl ratio decreases hardly at all, at the expense of the NO_2/HCl ratio, which falls by one-half in the same range, a fact of some relevance to the difficult problem of accounting for the N_2O formed in AP decomposition.

Majer and Smith[39] have studied the gas-phase reactions involved in the thermal decomposition of AP by passing the vapor from subliming AP through a reaction vessel in a second furnace, maintained at a higher temperature, and monitoring the reactions occurring by means of a mass spectrometer coupled to the reaction vessel *via* a pinhole leak. Major products detected were again H_2O, O_2, HCl, N_2, N_2O, NO_2, Cl_2, and NH_3 with traces of ClOH, ClO_2, and NH_2Cl. Inert gases (N_2, CF_4, and CO_2) initially increased slightly the partial pressure of NH_3, H_2O, HCl (N_2 only), and ClO_2 (CO_2 and N_2 only), but subsequently these decreased to zero. All other products showed an immediate decrease. Ammonia addition decreased all products except for NH_2Cl which increased rapidly as Cl_2 decreased. The effect of nitric oxide was more complicated: NH_3 and O_2 went through minima while NO_2, N_2O, Cl_2, and HCl passed through maxima and ClO_2 and ClOH decreased effectively to zero.

The kinetics of the decomposition of AP are usually investigated by measuring the pressure, P, of the permanent gases evolved as a function of time. Data so obtained are then converted to fractional decomposition, α, by dividing P by the final pressure, P_f. It is therefore important to establish whether or not this procedure is valid. Bircumshaw and Newman[22] have reported that the ratio of oxygen to nitrogen is constant over the duration of a run at any one temperature and nearly unchanged from the value of 9 to 1 over a large temperature range (240–320°). Also, the amount of gas produced per 10 mg of AP decomposed was reported to be almost constant. These claims, however, do not appear to be supported by the results published in ref 24. Most analyses were performed on product samples taken well after the completion of the reaction. Moreover, in the stated temperature range, the ratio of oxygen to nitrogen fluctuated randomly between 8:1 and 14:1. At temperatures below 240°, where most low-temperature studies are performed, the ratio was as low as 4:1.

The results of a recent study[29] show that while both the rates of formation of O_2 and N_2 vary with time, the ratio of the two is not constant. This ratio falls precipitously from an unknown initial value to a minimum which occurs at about the time of maximum total reaction rate. The subsequent increase is much slower than the initial decrease. There are, unfortunately, not enough data available to allow a final decision to be made on the vital issue of the proportionality of the mass decomposed to the pressure of permanent gas, although Davies, Jacobs, and Russell-Jones[40] have recently shown that, when corrections for sublimation are made, measurements of the fractional decomposition by weight loss, pressure of permanent gas, and pressure of total gas are in agreement over a substantial range of α.

(36) P. J. Herley and P. W. Levy, *J. Chem. Phys.*, **49**, 1493 (1968).
(37) W. A. Rosser and H. Wise, *J. Phys. Chem.*, **64**, 602 (1960).
(38) G. L. Pellett and A. R. Saunders, "Heterogeneous Decomposition of Ammonium Perchlorate-Catalyst Mixtures Using Pulsed Laser Mass Spectrometry," AIAA Sixth Aerospace Sciences Meeting, New York, N. Y., Jan 1968, AIAA Preprint 68-149.
(39) J. R. Majer and M. Smith, results quoted by G. Pearson in ref 75.
(40) J. V. Davies, P. W. M. Jacobs, and A. Russell-Jones, *Trans. Faraday Soc.*, **63**, 1737 (1967).

Table II

Variations in the Product Spectrum with the Nature of the Catalyst

Temp, °C	Catalyst[a]	Cat. concn, wt %	Moles of product/mole of AP decomposed O_2	N_2	N_2O	Cl_2	HNO_3	HCl	NO	Wt % decompn	Ref
250	...	0	0.61	0.055	0.37	0.39	0.14	0.15	0.006	19.8	29
250	CC	1.79	0.54	0.064	0.32	0.45	0.15	0.091	0.019	29.4	29
250	CC	3.99	0.54	0.078	0.30	0.43	0.15	0.11	0.026	31.0	29
275	...	0	0.52	0.049	0.36	0.39	0.17	0.16	0.015	26.6	29
275	CoO_x[b]	2.8	0.24	0.030	0.14	0.41	0.097	0.020	0.18[c]	100	29
275	Fe_3O_4	2.0	0.66	0.084	0.34	0.40	0.15	0.13	0.023	27.0	29
275	CC	1.03	0.56	0.073	0.29	0.41	0.17	0.12	0.14	35.3	29
275	CC	1.79	0.47	0.080	0.28	0.44	0.20	0.095	0.023	36.5	29
275	CC	2.73	0.47	0.090	0.26	0.44	0.20	0.10	0.026	36.2	29
275	CC	3.90	0.53	0.12	0.25	0.42	0.22	0.10	0.024	38.7	29
280	...	0	0.75	0.051	0.29	0.39		0.22	0.32	70.0	42
210–235	MnO_2	5.0	0.68	0.086	0.08	0.40		0.20	0.67	100	42
210–250	Co_2O_3	5.0	0.69	0.040	0.15	0.38		0.25	0.62	100	42
260–290	NiO	5.0	0.73	0.033	0.23	0.39		0.22	0.48	100	42
260–290	Fe_2O_3	5.0	0.73	0.050	0.23	0.40		0.21	0.44	100	42
270–300	Cr_2O_3	5.0	0.81	0.15	0.20	0.38		0.24	0.30	100	42

[a] CC = copper chromite. [b] 71.2 wt % Co, $\sim Co_2O_3$. [c] Believed to be derived from both NOCl and NO_2Cl.

B. EFFECT OF ADDITIVES ON DECOMPOSITION PRODUCTS

Additives influence both the temperature at which AP decomposition begins and the extent of the subsequent reaction. The available evidence[29,41,42] suggests that the additives also change the product distribution. In general, there appears to be a tendency for the very effective rate promoters to suppress the formation of certain products, *e.g.*, chlorine[41] and nitrous oxide.[42] However, the paucity of experimental data makes any further conclusions highly speculative.

At low temperatures the principal chlorine-containing product from the decomposition of AP is free chlorine, but with increasing temperature the amount of chlorine is reduced as the concentration of hydrogen chloride increases. The ratio of the quantity of chlorine evolved in the free state to that present as hydrogen chloride is not affected appreciably[42] by the presence of 5 wt % of Cr_2O_3, MnO_2, Fe_2O_3, NiO, or Cu_2O. However, these additives do suppress the formation of nitrous oxide and most of the nitrogen is evolved as nitric oxide. Zinc oxide is exceptional in that it strongly reduces the amount of hydrogen chloride and does not suppress nitrous oxide formation. Shmagin and Shidlovskii,[42] unlike Hermoni and Salmon,[41] did not detect appreciable quantities of chlorine dioxide in the gaseous decomposition products. The usual iodometric method used in the identification of chlorine dioxide appears to be subject to serious errors if the sample for analysis contains acidic components with volatility comparable to that of chlorine.

The yields given in Table II for chromite-containing samples represent the total products from two distinct reactions. The copper chromite (CC) catalyzed decomposition is limited to the early stages of the reaction and disappears as CC is oxidized by the products of the catalyzed reaction. The over-all product yield can, therefore, be considered as the sum of two reactions, one associated with the catalyzed process and another with the uncatalyzed reaction. The approximate product yield for the CC (3.9%) catalyzed reaction at 275° is: HCl, N_2O = 0, Cl_2 = 0.49, N_2 = 0.24, HNO_3 = 0.32, O_2 = 0.55, and NO (as NOCl) $\geq$ 0.04. Cobalt oxide is also chemically attacked during the AP decomposition, but unlike CC its catalytic effectiveness is not destroyed. Catalysis by cobalt oxide produces NOCl and NO_2Cl as major products and N_2O_3 in trace quantities.[29]

Since AP is transparent to the 6943-Å radiation from a ruby laser, it had to be mixed with carbon or metal oxides, and thus all the ruby laser work of Pellett and Saunders[38] refers to the catalyzed reaction. Since the carbon or oxide particles would be heated preferentially, decomposition is initiated at the AP–catalyst interface and so heterogeneous reactions predominate. NH_3 and $HClO_4$ are evolved within a fraction of a millisecond following the onset of irradiation and reach their peak intensities about 1 msec after the peak of the laser pulse. With the exception of ClOH, all major decomposition products appeared at the same time within a few tenths of a millisecond. With the three oxides studied (CC, Fe_2O_3, MnO_2) these products were (in decreasing order of ion intensity, measured as a ratio to HCl) H_2O, ClO_2, NO, ClOH, Cl_2, and NO_2. With carbon, O_2 and CO were also major products. Whereas the homogeneous decomposition of $HClO_4$ (section IV.A) at ordinary pressures leads principally to Cl_2, heterogeneous decomposition of $HClO_4$ under the high-vacuum conditions prevailing in the laser-induced pyrolysis experiment, leads to ClO_2 in large yield. This seems evidence for the initial step in the gas-phase decomposition of ClO_2 being bimolecular (see section IV.B.3). HCl is also a major product and is believed[38] to originate from the heterogeneous decomposition of $HClO_4$.

III. Sublimation of Ammonium Perchlorate

The sublimation of ammonium perchlorate was first recorded by Dodé.[26,27,43] Bircumshaw and Newman[22,23] found that decomposition and sublimation occurred simultaneously throughout both the high- and low-temperature decomposition regions. If the ambient pressure is increased, sublimation

(41) A. Hermoni and A. Salmon, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 656–662; see also *Bull. Res. Council Israel, Sect. A*, 9, 206 (1960).

(42) L. F. Shmagin and A. A. Shidlovskii, *Issled. v Obl. Khim. i Tekhnol. Mineral'n. Solei i Okislov, Akad. Nauk SSSR, Sb. Statei*, 112–114, (1965); RPE Translation 18, Aug 1967.

(43) M. Dodé, *Bull. Soc. Chim. France*, [5] 5, 176 (1938).

is replaced by chemical decomposition.[23,44] The fact that decomposition and sublimation occur concurrently complicates their experimental study. Bircumshaw and Phillips[45] studied the sublimation of AP residue at low temperatures under low pressures, using a gravimetric technique. From their rather limited data an activation energy of 21.5 ± 2.8 kcal/mole was deduced. Because the activation energy for the high-temperature decomposition of AP had been determined as 39 kcal/mole,[44] Galwey and Jacobs concluded[44] that sublimation and thermal decomposition must be competitive processes. Since the latter had been identified with a proton-transfer process (see section IX), they suggested tentatively that sublimation might involve an ion pair. This suggestion is now known to be incorrect. Mack, Tompa, and Wilmot[46,47] used the matrix isolation method to identify the gaseous species produced from subliming AP and found only NH_3 and $HClO_4$. Heath and Majer[30,31] decomposed AP in the ion source of a mass spectrometer and found ions due to NH_3, $HClO_4$, Cl_2, HCl, O_2, and oxides of nitrogen, with a "significant absence of $NH_4ClO_4^+$."

Support for a dissociative mechanism for sublimation also comes from the work of Inami, Rosser, and Wise[48] who measured the dissociation pressure of AP residue in the temperature range 250–342° by the transpiration method. The sublimate was found to contain equimolar quantities of NH_4^+ and ClO_4^-. This is consistent with the dissociative sublimation

$$NH_4^+ClO_4^-(s) = NH_3(g) + HClO_4(g) \tag{8}$$

The dissociation pressure P $(=p_{NH_3} + p_{HClO_4})$ is given by

$$\log P\,(\text{torr}) = 10.56 - (6283.7/T) \tag{9}$$

corresponding to an enthalpy of sublimation of 58 ± 2 kcal/mole which is in good agreement with the thermodynamic value.[49] If NH_3 was introduced into the gas stream, the sublimate consisted of equimolar amounts of NH_4^+ and Cl^-. This is attributed by the authors to reaction of Cl_2 (from decomposition of AP) with the NH_3, the sublimation of AP being entirely suppressed by the increased partial pressure of NH_3. That AP indeed sublimes by a dissociative mechanism can no longer be doubted: there remains the question of the activation energy.

Jacobs and Russell-Jones[50] have shown that the rate of the high-temperature reaction measured gravimetrically is greater than that measured manometrically so that the activation energy measured by Galwey and Jacobs[44] refers to secondary gas-phase reactions. The activation energy for sublimation under 1 atm pressure is approximately 30 kcal/mole[50] so that a discrepancy between their value and that of Bircumshaw and Phillips[45] still exists. Later measurements[40] on the sublimation of the residue from the low-temperature reaction, at low temperatures, agreed well with those from the high-temperature region, and an activation energy of 28.04 ± 0.43 kcal/mole was obtained from sublimation rate constants which covered a range of more than 3 decades.

(44) A. K. Galwey and P. W. M. Jacobs, *J. Chem. Soc.*, 837 (1959).
(45) L. L. Bircumshaw and T. R. Phillips, *ibid.*, 4741 (1957).
(46) J. L. Mack, A. S. Tompa, and G. B. Wilmot, "Matrix Isolation and Infrared Determination of the Vapor Species of NH_4ClO_4," Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1962 (unpublished); *Spectrochim. Acta*, **18**, 1375 (1962).
(47) J. L. Mack and G. B. Wilmot, *J. Phys. Chem.*, **71**, 2155 (1967).
(48) S. H. Inami, W. A. Rosser, and H. Wise, *ibid.*, **67**, 1077 (1963).
(49) G. S. Pearson, *Advan. Inorg. Radiochem.*, **8**, 177 (1966).
(50) P. W. M. Jacobs and A. Russell-Jones, *AIAA J.*, **5**, 829 (1967).

The activation energy for sublimation is, therefore, undoubtedly close to half the enthalpy of sublimaton, calculated by Pearson[49] to be 29.2 kcal/mole.

The kinetics of sublimation have recently been studied in greater detail.[51] The rate constants referred to in the previous paragraph came from fitting the weight-loss data to the contracting-volume equation

$$1 - (1 - \alpha)^{1/3} = kt \tag{10}$$

where α is the fractional weight loss in time t and k is the rate constant. Jacobs and Russell-Jones[51] found, however, that the empirical expression

$$1 - (1 - \alpha)^{1/2} = kt \tag{11}$$

fitted the data distinctly better than eq 10 at high temperatures. A theoretical analysis which took account both of surface diffusion and of diffusion through the gas phase led to the development of a sublimation equation which fitted the data over the complete range of pressures and temperatures. Moreover, it was possible to see why eq 10 and 11 should fit the data approximately under certain conditions. The main contribution to the temperature dependence comes from the enthalpy of sublimation, and the values deduced for $\frac{1}{2}\Delta H$, 30.4 kcal/mole (from sublimation under 1 atm pressure of nitrogen) and 29.6 kcal/mole (from vacuum sublimation data), are in excellent agreement with the thermodynamic value derived by Pearson.[49]

Information on the sublimation of AP at much higher temperatures has been derived from linear pyrolysis studies. In these experiments[52–54] a hot plate is pressed against a compressed cylindrical strand of AP (or other material) and the linear rate of regression of the interface measured as a function of the temperature of the plate. There has been some controversy over the use of solid plates, because the radial flow of gas across the surface of the subliming solid might be expected to affect the sublimation rate.[55–58] The use of a porous plate[57,58] should alleviate this difficulty, and it apparently does yield more consistent results[59–61] although both the individual scatter and the discrepancies between the results of the various experimenters are rather large.[62] There is also some doubt

(51) P. W. M. Jacobs and A. Russell-Jones, *J. Phys. Chem.*, **72**, 202 (1968).
(52) W. H. Andersen, K. W. Bills, A. O. Dekker, E. Mishuck, G. Moe, and R. D. Schultz, *Jet Propulsion*, **28**, 831 (1958).
(53) M. K. Barsh, W. H. Andersen, K. W. Bills, G. Moe, and R. D. Schultz, *Rev. Sci. Instrum.*, **29**, 392 (1958).
(54) R. D. Schultz and A. O. Dekker, "Fifth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, pp 260–267.
(55) W. H. Andersen, *AIAA J.*, **2**, 404 (1964).
(56) R. H. Cantrell, *ibid.*, **1**, 1544 (1963).
(57) W. Nachbar and F. A. Williams, "Ninth Symposium (International) on Combustion," Academic Press, New York, N. Y., 1963, pp 345–356.
(58) F. A. Williams, "On the Analysis of Linear Pyrolysis Experiments," Lockheed Missiles and Space Division, Sunnyvale, Calif., AFOSR TN 683, June 1961.
(59) R. L. Coates, *AIAA J.*, **3**, 1257 (1965).
(60) R. L. Coates, "Linear Pyrolysis Rate Measurements of Propellant Constituents," First Combustion Instability Conference, Orlando, Fla., Nov 1962, CPIA Publication No. 68, Vol. I.
(61) M. Guinet, "Linear Velocity of Pyrolysis of Ammonium Perchlorate in One-Dimensional Flow," Office National d'Études et de Recherches Aérospatiales, France, T. P. 316, 1965; *Rech. Aérospatiale*, No. 109, 41–49 (1965).
(62) M. Barrère and F. A. Williams, "Analytical and Experimental Studies of the Steady State Combustion Mechanisms of Solid Propellants," 25th Meeting of the AGARD Combustion and Propulsion Panel, La Jolla, Calif., April 1965; Office National d'Études et de Recherches Aérospatiales, France, T. P. 240, 1965.

as to whether the measured plate temperature is really equal to the surface temperature of the AP.[58] Linear pyrolysis without a plate is also possible[68] by establishing a fuel-supported diffusion flame at the AP surface, the true surface temperature being obtained from infrared emission measurements. The distinction between this type of experiment and that in which a porous bed of AP is burned in a fuel stream is rather a fine one; nevertheless, the details of the latter type of experiment will be discussed in section X.

Despite the discrepancies between the results of various experimenters, there seems to be a broad measure of agreement that linear pyrolysis studies yield an activation energy of around 20 kcal/mole,[52,59,60–65] at least above 475°. At lower temperatures (415–475°) the linear pyrolysis studies appear to yield a much higher activation energy of $\sim$60 kcal/mole.[61] While $E < {}^1/_2\Delta H$ has been taken to indicate a multistep sublimation process,[51,54,66–68] the larger value ascribed to E at lower temperatures has not been explained satisfactorily.

At still lower temperatures, the activation energy for sublimation is $\sim{}^1/_2\Delta H$, indicating that the diffusion of ammonia and perchloric acid through the ambient gas is rate controlling.[51] A complete reconciliation of all the sublimation data would appear to require the assumption that diffusion control did not exist either in Bircumshaw and Phillips' experiments,[45] or in the various linear pyrolysis studies, or in Pellett and Saunders' mass spectrometric experiments[38] where an activation energy for perchloric acid formation of $\sim$21 kcal/mole was also deduced. An alternative, although possibly less charitable viewpoint, is that all these experiments (except the low-temperature isothermal sublimation experiments of Jacobs and Russell-Jones) simply did not yield very precise data. The apparent discrepancies between hot-plate pyrolysis, diffusion flame (and porous bed) pyrolysis, and isothermal sublimation have been examined recently by Jacobs and Powling[69] who conclude that, when appropriate corrections are made for the pressure dependence of the sublimation process, the combustion data are consistent with the isothermal sublimation data ($E \sim {}^1/_2\Delta H$), provided the evaporation coefficient β increases by a factor of about 3 over the temperature range (about 100°) separating the two sets of data. This is not physically unreasonable, although no temperature dependence for β was revealed over the limited temperature range of the isothermal sublimation measurements.[51]

IV. Thermal Decomposition of Perchloric Acid and of the Oxides of Chlorine

A. PERCHLORIC ACID

The perchloric acid molecule is tetrahedral in shape with a Cl–O bond length of 1.408 Å and a Cl–OH bond length of 1.630 Å.[70] The general properties of this acid have been extensively reviewed by Addison[71] and more recently by Schumacher[72] and by Zinov'ev.[73] The literature on the thermochemistry and the thermal decomposition in both the liquid and vapor phases has been critically evaluated by Cummings and Pearson.[74] In addition, Pearson has recently published a very full survey of the physical and inorganic chemistry of perchloric acid[49] and has reviewed recent determinations of various physical properties of $HClO_4$ in a comprehensive review entitled "Perchlorate Oxidizers."[75]

The study of the thermal decomposition of perchloric acid vapor is complicated by the large heterogeneous contribution to the reaction at temperatures below about 315°. Above this temperature the kinetics are those of a homogeneous reaction.[76] Sibbett and Lobato[77] studied the decomposition between 200 and 220° with initial acid pressures of 8.8–373.3 torr. They suggested that the reaction proceeded according to the over-all equation

$$HClO_4 = {}^1/_2H_2O + {}^1/_2Cl_2 + {}^7/_4O_2 \qquad (12)$$

although analyses of the reaction products by mass spectrometry, infrared spectrometry, and by a gas chromatographic technique were not considered to be completely successful. The kinetics were found to be of second order during the early decomposition stages and changed to first order as the reaction proceeded.

Levy[76] confirmed that the over-all reaction yields chlorine, oxygen, and water for the temperature range from 200 to 439°. Hydrogen chloride was not a product. The kinetics of the thermal decomposition from 200 to 350° were determined from colorimetric observations of the rate of chlorine formation. In the higher temperature range, the reaction was studied by a flow method. A first-order plot of the experimental data was linear for the first 50–90% of the reaction, falling off thereafter. The "goodness of fit" increased with increasing temperature; experiments performed at 294° indicated that water had a moderate inhibiting effect.

The data from 200 to 315° were quite scattered because of the heterogeneous nature of the reaction and the difficulty of reproducing unknown surface conditions. Nevertheless the Arrhenius curve could be seen to be quite flat, indicating an activation energy of perhaps 10 or 15 kcal/mole. The homogeneous reaction data obeyed the rate expression

$$k = 5.8 \times 10^{13} \exp(-45{,}100/RT)\ \text{sec}^{-1} \qquad (13)$$

The first-order nature of the reaction and the magnitude of the activation energy indicate that the rate-determining step is

$$HOClO_3 \longrightarrow HO + ClO_3 \qquad (14)$$

(63) J. Powling, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 447–456.

(64) W. H. Andersen and R. F. Chaiken, "The Detonability of Solid Composite Propellants," Part I, Aerojet-General Corp., Azusa, Calif., Technical Memo 809, Jan 1959.

(65) W. H. Andersen and R. F. Chaiken, *J. Amer. Rocket Soc.*, **31,** 1379 (1961).

(66) R. F. Chaiken, D. J. Sibbett, J. E. Sutherland, and D. K. Van de Mark, *J. Chem. Phys.*, **37,** 2311 (1962).

(67) R. D. Schultz and A. O. Dekker, *ibid.*, **23,** 2133 (1955).

(68) D. J. Sibbett, discussion on ref 57, "Ninth Symposium (International) on Combustion," Academic Press, New York, N. Y., 1963, p 357.

(69) P. W. M. Jacobs and J. Powling, *Combust. Flame*, **13,** 71 (1969).

(70) A. H. Clark, B. Beagley, and D. W. J. Cruickshank, *Chem. Commun.*, 14 (1968).

(71) C. C. Addison, "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, Part I, Longmans, Green and Co., London, 1956, Chapter II, pp 598–605.

(72) J. C. Schumacher, Ed., "Perchlorates, Their Properties, Manufacture, and Uses," Reinhold Publishing Corp., New York, N. Y., 1960, p 11.

(73) A. A. Zinov'ev, *Usp. Khim.*, **32,** 590 (1963); *Russ. Chem. Rev.*, **32,** 268 (1963).

(74) G. A. McD. Cummings and G. S. Pearson, "Perchloric Acid: A Review of Its Thermal Decomposition and Thermochemistry," RPE Technical Note No. 224, Oct 1963.

(75) G. S. Pearson, *Oxidation Combust. Rev.*, **4,** 1 (1969).

(76) J. B. Levy, "The Thermal Decomposition of Perchloric Acid," Atlantic Research Corp., Alexandria, Va., AFOSR TN 1555, Oct 1961 [AD 265 051]; *J. Phys. Chem.*, **66,** 1092 (1962).

(77) D. J. Sibbett and J. M. Lobato, "Investigation of the Mechanism of Combustion of Composite Solid Propellants," Aerojet-General Corp., Azusa, Calif., Aerojet Report No. 1782, April 1960 [AD 246 274].

the activation energy of 45.1 kcal/mole being ascribed to the energy required to break the HO–ClO_3 bond. The succeeding steps cannot be specified unambiguously. However, Levy[76] has proposed that the initial step is followed by the fast reactions

$$HO + HOClO_3 \longrightarrow H_2O + ClO_4 \quad (15)$$

$$2ClO_4 \longrightarrow Cl_2 + 4O_2 \quad (16)$$

$$2ClO_3 \longrightarrow Cl_2 + 3O_2 \quad (17)$$

The decomposition of ClO_3 and of the ClO_4 radicals is probably complex, involving formation and decomposition of lower chlorine oxides. Such chain reactions have been proposed[78,79] for the decomposition of Cl_2O_7 and of Cl_2O_6.

Sibbett and coworkers[80] have further studied the decomposition reaction between the temperatures of 150 and 260°. The amount of chlorine evolved was found to be directly proportional to the quantity of decomposed acid. They proposed the following mechanism.

$$2HClO_4 \xrightarrow{k_2} Cl_2 + {}^7/_2O_2 + H_2O \quad (18)$$

$$HClO_4 + H_2O \longrightarrow HClO_4 \cdot H_2O \quad (19)$$

$$HClO_4 \cdot H_2O \xrightarrow{k_1} {}^1/_2Cl_2 + {}^3/_2H_2O + {}^7/_4O_2 \quad (20)$$

Rate constants for the second-order reaction, k_2, and the first-order reaction, k_1, were computed from the initial and final data obtained by following the rate of pressure change. A computer solution of the simultaneous differential equations, which represent the above reaction scheme, demonstrated that the observed pressure could be computed from the calculated rate constants. Activation energies of the second- and first-order steps were 8.9 and 21.3 kcal/mole, respectively. Both reactions were surface catalyzed with a linear dependence of the two rate constants on the surface-to-volume ratio. Perchloric acid monohydrate is more stable than anhydrous perchloric acid;[49,78] it is therefore not obvious why the monohydrate should be an intermediate in the heterogeneous decomposition of perchloric acid vapor.

The mass spectrum of 72% perchloric acid has been recorded by Heath and Majer.[80,81] They deduced a value of 46 kcal/mole for the HO–ClO_3 bond strength. This value agrees favorably with that of 47.6 kcal/mole obtained entirely from thermochemical data and with Levy's[76] value of 45.1 kcal/mole for the activation energy of the homogeneous thermal decomposition of perchloric acid. Heath and Majer[80,81] also investigated the heterogeneous decomposition of $HClO_4$ vapor on a hot platinum wire placed adjacent to the ionization chamber of the mass spectrometer. The mass spectra showed that the hot platinum wire caused the reaction

$$HClO_4 \longrightarrow HCl + 2O_2 \quad (21)$$

The preponderance of the HCl^+ peak was a feature of both the spectrum of perchloric acid and of its decomposition products, and Pearson[49] has suggested that, at the temperatures and pressures used in these studies, the Deacon process would account for the production of large quantities of hydrogen chloride.

On admission of $HClO_4$ to a mass spectrometer,[81] there is an initial conditioning period of several hours during which the predominant peaks are those of HCl and O_2. These peaks gradually decrease to be replaced by a reproducible mass spectrum in which the principal ions are ClO_3^+, ClO_2^+, ClO^+, and $HClO_4^+$. The thermal decomposition produced mainly ClO and ClO_2, and Fisher[81,82] suggested that the ClO radicals were derived from the decomposition of ClO_3

$$ClO_3 \longrightarrow ClO + O_2 \quad (22)$$

and that production of ClO_2 arises from the alternative reaction

$$ClO_3 \longrightarrow ClO_2 + O \quad (23)$$

Laser-induced pyrolysis[38] of $HClO_4$ leads, as already remarked, to ClO_2 in large yield (of the same order as the amount of HCl) but little Cl_2.

The radiation chemistry of frozen aqueous solutions of $HClO_4$ has also been studied.[83]

B. OXIDES OF CHLORINE

The known oxides of chlorine are chlorine monoxide (Cl_2O), chlorine sesquioxide (Cl_2O_3), chlorine dioxide (ClO_2), chlorine hexoxide ($Cl_2O_6 = 2ClO_3$), and chlorine heptoxide (Cl_2O_7). In addition, the infrared absorption of a species observed in the photolysis of Cl_2O in a N_2 or an Ar matrix has been ascribed to Cl_2O_2.[84,85] The most stable of the chlorine oxides are Cl_2O[86,87] and Cl_2O_7.[78,88] They decompose homogeneously and must be heated to 100° or above to decompose at measurable rates. ClO_2 is much less stable and decomposes heterogeneously at 40–50°,[89,90] while Cl_2O_6, which dissociates almost completely into ClO_3 in the vapor phase, is even less stable and decomposes heterogeneously at room temperature.[79,91–93] Cl_2O_3[94] is the most unstable of the oxides of chlorine and decomposes slowly at −45° with the formation of O_2 and Cl_2. The extreme instability of this compound has been attributed to the presence in the molecule of a weak Cl–Cl bond which permits easy dissociation to yield the reactive ClO radical.

1. *Chlorine Heptoxide*

Figini, Coloccia, and Schumacher[78] studied the kinetics of the gas-phase decomposition of Cl_2O_7 at pressures of 1.5–80

(78) R. V. Figini, E. Coloccia, and H. J. Schumacher, *Z. Phys. Chem.* (Frankfurt am Main), **14**, 32 (1958); U. K. Ministry of Aviation, T.I.L. Translation T.5314, Nov 1962.
(79) H. J. Schumacher and G. Stieger, *Z. Anorg. Allg. Chem.*, **184**, 272 (1929).
(80) D. J. Sibbett, F. J. Cheselke, I. Geller, J. M. Lobato, F. E. Sutherland, and R. F. Chaiken, "Decomposition, Combustion and Detonation of Solids," Aerojet-General Corp., Azusa, Calif., abstracted in AFOSR 2348, April 1962 [AD 274 132].
(81) I. P. Fisher, *Trans. Faraday Soc.*, **63**, 684 (1967); see also **64**, 1852 (1968).
(82) I. P. Fisher, "A Mass Spectrometric Study of the Thermal Decomposition of Perchloric Acid and Chlorine Dioxide," R.P.E. Technical Report 66/13, Nov 1966.
(83) V. N. Belevskii and L. T. Bugaenko, *Zh. Fiz. Khim.*, **41**, 144 (1967); *Russ. J. Phys. Chem.*, **41**, 73 (1967).
(84) W. G. Alcock and G. C. Pimentel, *J. Chem. Phys.*, **48**, 2373 (1968).
(85) M. M. Rochkind and G. C. Pimentel, *ibid.*, **46**, 4481 (1967).
(86) J. J. Beaver and G. Stieger, *Z. Physik. Chem.*, **B12**, 93 (1931).
(87) C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **123**, 2730 (1923).
(88) E. Coloccia, R. V. Figini, and H. J. Schumacher, *Angew. Chem.*, **68**, 492 (1956).
(89) H. Booth and E. J. Bowen, *J. Chem. Soc.*, **127**, 510 (1925).
(90) H. J. Schumacher and G. Stieger, *Z. Physik. Chem.*, **B7**, 363 (1930).
(91) A. J. Arvia, W. H. Basualdo, and H. J. Schumacher, *Z. Anorg. Allg. Chem.*, **286**, 58 (1956).
(92) C. F. Goodeve and F. D. Richardson, *J. Chem. Soc.*, 294 (1937).
(93) J. W. T. Spinks and J. M. Porter, *J. Amer. Chem. Soc.*, **56**, 264 (1934).
(94) E. T. McHale and G. von Elbe, *ibid.*, **89**, 2795 (1967).

torr and at temperatures of 100–120°. The decomposition was followed manometrically since product analyses indicated that the reaction could be represented by the equation

$$Cl_2O_7 = Cl_2 + {}^7/_2O_2 \quad (24)$$

The reaction was homogeneous and unimolecular with an activation energy of 32.9 ± 1.5 kcal/mole. The effect of added chlorine or oxygen was to increase the decomposition rates. An initial decomposition into ClO_3 and ClO_4[78,88] was postulated

$$Cl_2O_7 \longrightarrow ClO_3 + ClO_4 \quad (25)$$

followed by transformation of these into ClO_2, Cl_2, and O_2 (see sections IV.B.5 and IV. B.6).

The liquid-phase decomposition of Cl_2O_7 has been investigated by Babaeva[95] at temperatures from 60 to 80°. The oxygen-liberation isotherms were very nearly linear, and the calculated activation energy was 32.1 kcal/mole. Additions of up to 5.5 wt % of carbon tetrachloride or trichloroacetic acid had no appreciable effect on the decomposition. However, small quantities (1%) of perchloric acid increased the rate of oxygen evolution and altered the shape of the oxygen-evolution curves.

2. Chlorine Monoxide

Accurate structural parameters for Cl_2O are known from microwave[96] and electron diffraction[97] measurements. Cl_2O is highly explosive if heated rapidly or overheated locally, but under conditions of careful temperature control the thermal decomposition proceeds at a conveniently measurable rate between about 100 and 140°. The decomposition of chlorine monoxide at temperatures below 140° has been studied by Hinshelwood[87,98] and by Beaver and Stieger.[86] Bodenstein and Szabó[99] have investigated the kinetics of the initial stages of the decomposition process. The thermal reaction is homogeneous, and the rate is not influenced by greatly increasing the area of the glass surface by adding glass wool to the reaction vessel. The rate accelerates as the reaction proceeds; however, this acceleration persists in the presence of an excess of oxygen or chlorine, and the reaction rate is not appreciably influenced by a fivefold excess of dry air, oxygen, or nitrogen.[87]

The mechanism of the reaction has not been determined with any degree of certainty. The reaction rate (excluding the slow initial induction period) is directly proportional to the initial pressure of the chlorine monoxide at temperatures between 100 and 130°.[86] At 140°[86] the reaction rate is of 0.75 order in chlorine monoxide. The shape of the pressure–time curves has been interpreted both on the basis of consecutive bimolecular reactions[98,100] and as a chain reaction.[86,99,101] In the first mechanism, the acceleration is attributed to the operation of at least two consecutive reactions, each essentially bimolecular, the first of which produces a pressure change less than that given by the subsequent reactions. These consecutive reactions would no doubt involve the formation of other oxides of chlorine. In contrast to this approach, the observation that an explosion frequently occurred toward the end of a slow thermal decomposition led to the postulate that the decomposition was a complicated chain reaction in which the Cl atom and the ClO radical were the chain carriers.[86,99,101]

3. Chlorine Dioxide

In the absence of light, chlorine dioxide undergoes thermal decomposition at a rate which increases considerably with increase in temperature.[90] Explosions are obtained at all temperatures above about 45°.[90,102] Inert gases shorten the induction period by impeding the diffusion of radicals to the walls where chain termination can occur.[102] The activation energy is 30.5 kcal/mole below 90° and 11.1 kcal/mole above this temperature.[102] Cl_2O has a slight inhibiting effect, being consumed in the slow reaction which precedes ignition,[90] but Cl_2O_7 has no effect on the induction times.[102] ClO_3 also has an inhibiting effect, presumably due to removal of ClO radicals by the reaction

$$ClO_3 + ClO \longrightarrow 2ClO_2 \quad (26)$$

ClO_2 which has been preirradiated with ultraviolet light is very sensitive to explosion.[102] It is known[94] that photolysis of ClO_2 at −45° leads to a mixture of Cl_2O_6 and Cl_2O_3, and addition of Cl_2O_3 to ClO_2 reduces the induction period considerably, thus identifying it as the active intermediate.[102]

McHale and von Elbe[102] have thus arrived at the following mechanism of the decomposition. Fission of the OCl–O bond requires ~57 kcal; therefore, the initial step is likely to be the heterogeneous reaction

$$ClO_2 + ClO_2 \longrightarrow ClO + ClO_3 \quad (27)$$

for which ΔH is +11 kcal/mole. ClO radicals are the principal chain carriers and react first with ClO_2 to form Cl_2O_3

$$ClO + ClO_2 \rightleftharpoons Cl_2O_3 \quad (28)$$

and then with Cl_2O_3

$$ClO + OCl\text{–}ClO_2 \longrightarrow ClOOCl + ClO_2 \quad (29)$$

$$ClOOCl \longrightarrow ClOO + Cl \longrightarrow 2Cl + O_2 \quad (30)$$

The chlorine atoms produced then undergo chain branching

$$Cl + ClO_2 \longrightarrow 2ClO \quad (31)$$

and chain termination reactions

$$Cl + Cl + \text{wall} \longrightarrow Cl_2 + \text{wall} \quad (32)$$

$$Cl + ClO_2 \longrightarrow Cl_2 + O_2 \quad (33)$$

4. The ClO Radical

Oxygen atoms react rapidly[103] with ClO_2 to form ClO

$$O + ClO_2 \longrightarrow O_2 + ClO \quad (34)$$

this reaction being about four times as rapid at room temperature as the corresponding reaction of O atoms with ClO radicals

$$O + ClO \longrightarrow O_2 + Cl \quad (35)$$

(95) V. P. Babaeva, *Zh. Neorg. Khim.*, **8**, 1809 (1963); *Russ. J. Inorg. Chem.*, **8**, 941 (1963).
(96) G. E. Herberich, R. H. Jackson, and D. J. Millen, *J. Chem. Soc., A*, 336 (1966).
(97) B. Beagley, A. H. Clark, and T. G. Hewitt, *ibid.*, 658 (1968). A more recent analysis has led to slight modifications of the parameters quoted in this paper: the latest values (A. H. Clark, private communication) are r_{Cl-O} = 1.695 Å, r_{Cl-Cl} = 2.799 Å.
(98) C. N. Hinshelwood and J. Hughes, *J. Chem. Soc.*, **125**, 1841 (1924).
(99) M. Bodenstein and Z. G. Szabó, *Z. Physik. Chem.*, **B39**, 44 (1938).
(100) H. Eyring, *ibid.*, **B7**, 244 (1930).
(101) Z. G. Szabó, P. Huhn, and F. Marta, *Trans. Faraday Soc.*, **55**, 1131 (1959).
(102) E. T. McHale and G. von Elbe, *J. Phys. Chem.*, **72**, 1849 (1968).

ClO radicals react similarly with nitric oxide[103]

$$ClO + NO \longrightarrow Cl + NO_2 \quad (36)$$

ClO radicals are quite stable, with a bond dissociation energy D(Cl–O) of 63 kcal/mole;[104] consequently a bimolecular decomposition mechanism

$$ClO + ClO \longrightarrow Cl_2 + O_2 \quad (37)$$

is favored.[103,105,106] ClO radicals are also formed in the reaction of oxygen atoms with Cl_2[107]

$$O + Cl_2 \longrightarrow ClO + Cl \quad (38)$$

and of Cl atoms with ClO_2 (eq 31), in the thermal decomposition of ClO_2 (eq 27), and in the flash photolysis of chlorine + oxygen mixtures,[106,108] chlorine dioxide,[109] and chlorine monoxide.[110]

5. *Chlorine Trioxide*

Chlorine trioxide is formed in the reaction of ClO_2 with ozone[79,87]

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2 \quad (39)$$

or by the photolysis of ClO_2 at $-45°$.[94] At low temperatures it forms an orange solid which melts at 3.5° to form a red oil which boils at 20.3°. In the liquid or solid state chlorine (VI) oxide exists as the dimer, dichlorine hexoxide, but in the gaseous state this dissociates completely to ClO_3[92,111,112] owing to the weak Cl–Cl bond which has a dissociation energy of ~2 kcal/mole.[111] ClO_3 is reported[91,113] to decompose bimolecularly in three possible ways

$$2ClO_3 \longrightarrow ClO_2 + O_2 \quad (40)$$

$$2ClO_3 \longrightarrow ClO_4 + ClO_2 \quad (41)$$

$$2ClO_3 \longrightarrow Cl_2 + 3O_2 \quad (42)$$

the activation energy for each of the reactions (eq 40–42) being about 12 kcal/mole. Under the high-vacuum conditions prevailing in a mass spectrometer,[81] the unimolecular decomposition of ClO_3 to ClO_2 or ClO has been suggested (see eq 22 and 23).

6. *Chlorine Tetroxide*

ClO_4 is apparently too unstable to have an independent existence, a reported preparation from $AgClO_4 + I_2$ having been shown to be incorrect.[114] It is formed as an intermediate, however, in the thermal decomposition of Cl_2O_7,[78,88] where the bond energy of the central Cl–O bond is 48 kcal/mole[88] in the reaction of chlorine with ozone[113] (but *cf.* ref 115), and in the decomposition of Cl_2O_6 where, in the presence of fluorine,[91] Cl_2O_7 is formed in substantial yield (20–25%) presumably by the reaction

$$ClO_3 + ClO_4 \longrightarrow Cl_2O_7 \quad (43)$$

At higher temperatures (as in the decomposition of Cl_2O_7 at ~100°) ClO_4 decomposes unimolecularly to the dioxide and oxygen.[78]

$$ClO_4 \longrightarrow ClO_2 + O_2 \quad (44)$$

V. *Oxidation of Ammonia*

Ammonia and oxygen react slowly in the temperature range 400–700°. In a flow system the fraction reacted increases rapidly as the ammonia concentration is decreased,[116] indicating that ammonia inhibits its own reaction with oxygen. Measurements[117] in a static system show that the kinetics change sharply at the equimolar mixture. For ammonia-rich mixtures, rates are roughly proportional to the product of ammonia and oxygen concentrations, whereas for ammonia-lean mixtures, the rate depends on the square of the oxygen concentration. There is a sharp change in rate as the ammonia: oxygen ratio is decreased. The low-temperature oxidation is an extremely complex reaction and has an activation energy of between 45 and 50 kcal/mole.[117,118] Hydrogen is one of the reaction products, particularly at low oxygen partial pressures.[119] Proposed mechanisms have been summarized by Marsh.[120] The high temperatures necessary to effect uncatalyzed oxidation by molecular oxygen renders it unlikely that this reaction is of any importance in the thermal decomposition of ammonium perchlorate. The oxidation of NH_3 at very high temperatures in shock waves has been studied recently.[121]

A. REACTION WITH ATOMIC OXYGEN

The reaction of NH_3 with atomic oxygen proceeds at an appreciable rate at relatively low temperatures. Wong and Potter[122,123] used a stirred-reactor technique to measure the reaction rates of ammonia with atomic oxygen at temperatures of 80–325°. A mass spectrometer capable of detecting atomic oxygen and hydrogen was used to analyze the reacting mixture in the stirred reactor. The stoichiometry of the reaction can be represented approximately by

$$NH_3 + 4.4O = NO + 0.5H_2 + 1.2O_2 + 1.0H_2O \quad (45)$$

Within experimental error, the rates of consumption of atomic oxygen were not affected by the presence or absence of excess molecular oxygen. Wong and Potter[123] suggested that the most plausible reaction steps were

$$NH_3 + O \longrightarrow NH_2 + OH \quad (46)$$

(103) M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, **62**, 1175 (1966).
(104) R. A. Durie and D. A. Ramsay, *Can. J. Phys.*, **36**, 35 (1958).
(105) M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc.* (London), **A303**, 207 (1968).
(106) G. Porter and F. J. Wright, *Discussions Faraday Soc.*, **14**, 23 (1953).
(107) M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, **62**, 2175 (1966).
(108) G. Burns and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A271**, 289 (1963).
(109) F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, *ibid.*, **A233**, 455 (1956).
(110) F. H. C. Edgecombe, R. G. W. Norrish, and B. A. Thrush, *ibid.*, **A243**, 24 (1957).
(111) J. Farquharson, C. F. Goodeve, and F. D. Richardson, *Trans. Faraday Soc.*, **32**, 790 (1936).
(112) Z. G. Szabó, *J. Chem. Soc.*, 1356 (1950).
(113) H. J. Schumacher, *Z. Phys. Chem.* (Frankfurt am Main), **13**, 353 (1957).
(114) R. N. Hazeldine and A. G. Sharpe, *J. Chem. Soc.*, 993 (1952).
(115) P. Huhn, F. Tudos, and Z. G. Szabó, *Magy. Tud. Akad. Kem. Tud. Oszt. Közlemén.*, **5**, 409 (1954).
(116) E. R. Stephens and R. N. Pease, *J. Amer. Chem. Soc.*, **72**, 1188 (1950).
(117) E. R. Stephens and R. N. Pease, *ibid.*, **74**, 3480 (1952).
(118) J. Verwimp and A. van Tiggelen, *Bull. Soc. Chim. Belges*, **62**, 205 (1953).
(119) H. Wise and M. F. Frech, *J. Chem. Phys.*, **21**, 948 (1953).
(120) J. D. F. Marsh, "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Supplement I, Part I, Longmans, Green and Co., London, 1964, pp 348–358.
(121) J. N. Bradley, R. N. Butlin, and D. Lewis, *Trans. Faraday Soc.*, **64**, 71 (1968).
(122) E. L. Wong and A. E. Potter, *J. Chem. Phys.*, **39**, 2211 (1963).
(123) E. L. Wong and A. E. Potter, *ibid.*, **43**, 3371 (1965).

$$NH_2 + O \longrightarrow NH + OH \quad (47)$$

$$NH + O \longrightarrow NO + H \quad (48)$$

$$OH + O \longrightarrow O_2 + H \quad (49)$$

$$OH + NH_3 \longrightarrow NH_2 + H_2O \quad (50)$$

$$H + NO + M \longrightarrow HNO + M \quad (51)$$

$$HNO + H \longrightarrow H_2 + NO \quad (52)$$

Using this proposed mechanism, the rate constant for reaction 46 was estimated to be $1 \times 10^{12} \exp(-4800/RT)$ cm^3 mole^{-1} sec^{-1}.

B. HETEROGENEOUS OXIDATION OF AMMONIA

The effect of a metal oxide catalyst on the oxidation of NH_3 is twofold in that the activity, as well as the selectivity, can be altered by the electronic character of the metallic oxide. In general, it appears that the order of increasing catalytic activity is[124–126] p-type > n-type > insulators. Similarly, the selectivity of the reaction, in terms of N_2O yield, increases with increasing p-type character of the semiconductor.[124,125,127]

There are at least three hypotheses which have been advanced to explain the mechanism of the heterogeneous $NH_3 + O_2$ reaction. Bodenstein[128] and Krauss[129] postulated that the initial step is the reaction of ammonia with adsorbed oxygen to form hydroxylamine. Andrussow[130] suggested an initial reaction between ammonia and molecular oxygen in which nitroxyl (HNO) is formed. Zawadzki,[131] in a critical evaluation of the proposed mechanisms, rejected both of these hypotheses and proposed an "imide theory." Most recent work, however, has been interpreted in terms of the formation of hydroxylamine.

C. REACTION OF AMMONIA WITH OXIDES OF NITROGEN

Ammonia can also be oxidized by oxides of nitrogen. The reaction between NO_2 and NH_3 can be divided conveniently into two temperature regions. At temperatures below melting point of NH_4NO_3, the major products are N_2, H_2O, and NH_4NO_3.[132,133] At temperatures between 25 and 200°, Falk and Pease[132] reported that the reaction is initially third order with a large negative temperature coefficient, suggesting that N_2O_4, not NO_2, is the reactive species. At higher temperatures (>330°) the course of the reaction changes, and neither NH_4NO_3 nor its principal decomposition products are observed. Rosser and Wise[134] found the reaction to be bimolecular in the temperature range 330–530° with a measured activation energy of 27.5 kcal/mole. The oxidation is inhibited by NO, and the reaction products contain N_2, NO, and N_2O, the NO and N_2 being produced in approximately equimolar concentrations. The kinetics of the oxidation of NH_3 by N_2O[135] and by NO[136–139] are complicated, and the results of kinetic studies of the NH_3 + NO reaction are conflicting. However, there is general agreement that these reactions require much higher temperatures than are commonly encountered in thermal decomposition studies of AP.

D. REACTION BETWEEN AMMONIA AND PERCHLORIC ACID

The vapor-phase reaction of ammonia with perchloric acid has been studied briefly. Sibbett and Lobato[77] studied this reaction at 25.0, 48.4, and 60.0°, using 15:1, 10.6:1, and 3.4:1 mole ratios of ammonia to perchloric acid. Reaction was initiated by rupturing a break-seal between two Pyrex vessels at zero time, and conditions were so arranged that a jet of ammonia gas always passed rapidly into the acid vapor to start the reaction. The reaction appeared to be instantaneous since the pressure-measuring system showed a single pressure rise to a final level. Analysis of the product indicated simultaneous oxidation of the ammonia by the perchloric acid along with direct combination to yield ammonium perchlorate. The solid product contained substantial quantities of Cl^- ion, the $Cl^-:ClO_4^-$ mole ratios varying from a low of 0.93 at 25° to a high of 12 at 60°. Results at 230°[140] indicated that the ammonia triggered the decomposition of the acid.

Friedman and Levy[141,142] performed a preliminary investigation of this reaction at 367°. Separate streams of ammonia–nitrogen and perchloric acid–nitrogen were mixed and passed through a reaction vessel at a fixed temperature; the emerging products were absorbed in a series of traps. Analyses were performed for chloride (no hypochlorite was found) and perchlorate ion. The principal problem was that of mixing the two reactants completely in a time short in comparison to the residence time (*ca.* 2 sec). The results confirmed Sibbett and Lobato's observation that reaction occurs between perchloric acid and ammonia as well as by direct decomposition of the former. They deduced a value for the rate constant at 367° of about 2×10^6 cm^3 mole^{-1} sec^{-1} on the assumption that the ammonia–acid reaction is first order in each reactant. An approximate value of 60 kcal/mole for the heat of vaporization of AP was obtained from the observation that solid formation occurred in the mixing chamber at 362° but not at 367°.

Nitrogen[142] was passed over solid AP at 400° and the vapor was condensed, either on a cold finger very close to the solid (residence time ~0.1 sec) or after the vapor had passed through a large volume at the same temperature as the AP (residence time 10–15 sec). In the former experiment, there was no decomposition; in the latter, there was substantial

(124) N. Giordano, E. Cavaterra, and D. Zema, *Chem. Ind.* (Milan), **45**, 15 (1963).
(125) H. F. Johnstone, E. T. Houvouras, and W. R. Schowalter, *Ind. Eng. Chem.*, **46** 702 (1954).
(126) N. Morita, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **65**, 542 (1944).
(127) N. Giordano, E. Cavaterra, and D. Zema, *J. Catal.*, **5**, 325 (1966).
(128) M. Bodenstein, *Z. Electrochem.*, **47**, 501 (1941).
(129) W. Krauss, *Z. Physik. Chem.*, **B39**, 83 (1938).
(130) L. Andrussow, *Z. Angew. Chem.*, **39**, 321 (1926).
(131) J. Zawadzki, *Discussions Faraday Soc.*, **8**, 140 (1950).
(132) R. Falk and R. N. Pease, *J. Amer. Chem. Soc.*, **76**, 4746 (1954).
(133) M. Patry, R. Garlet, and S. Pupko, *C. R. Acad. Sci., Paris*, **225**, 941 (1947).
(134) W. A. Rosser and H. Wise, *J. Chem. Phys.*, **25**, 1078 (1956).
(135) A. Volders and A. van Tiggelen, *Bull. Soc. Chim. Belges*, **64**, 736 (1955).
(136) C. P. Fenimore and J. R. Kelso, *J. Amer. Chem. Soc.*, **74**, 1593 (1952).
(137) D. P. Poole and W. M. Graven, *ibid.*, **83**, 283 (1961).
(138) A. Volders and A. van Tiggelen, *Bull. Soc. Chim. Belges*, **63**, 542 (1954).
(139) H. Wise and M. F. Frech, *J. Chem. Phys.*, **22**, 1463 (1954).
(140) G. S. Pearson, "Perchloric Acid: A Review of the Physical and Inorganic Chemistry," RPE Technical Memo No. 352, March 1965.
(141) R. Friedman and J. B. Levy, "Research on Solid Propellant Combustion," Atlantic Research Corp., Alexandria, Va., Final Technical Report AFOSR 2005, Dec 1961.
(142) J. B. Levy, Comment on a paper by G. A. McD. Cummings and A. R. Hall, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, p 1371.

decomposition, >50%. Comparison of these data with that obtained from the decomposition of perchloric acid vapor revealed that the gas-phase reaction of NH_3 and $HClO_4$ is not determined by the thermal decomposition of the acid alone. A similar conclusion has been reached from the result of studies on perchloric acid decomposition flames.[143] Thus the thermal decomposition of perchloric acid is not necessarily a preliminary step in the oxidation reaction; in fact, perchloric acid is a stronger oxidizing agent[144,145] than is oxygen.

VI. Low-Temperature Thermal Decomposition of Ammonium Perchlorate

There have been numerous investigations of the kinetics of the low-temperature, uncatalyzed thermal decomposition of AP. In common with many solid-state decompositions, the reaction exhibits an induction period, the duration of which depends on the temperature[22,24] and past history[146] of the sample. Ammonia inhibits the decomposition, whereas small amounts of adsorbed perchloric acid shorten the induction period.[22,24] The induction period is also shorter, and the rate of decomposition is higher for sublimate[40] than they are for AP obtained by crystallization from aqueous solution in the usual way.

The induction period is followed by a rapidly accelerating reaction which attains a maximum rate and then gradually decelerates. The extent of the decomposition is then commonly about 30%,[22,24] but apparently it may depend on the volume of the system[147] (for unconfined decomposition at an ambient pressure of 1 atm the extent of decomposition is certainly remarkably consistent and close to 30%). The residue from the low-temperature reaction is apparently identical with the original salt except for an increase in surface area.[24,25] To account for this rather unique feature of the reaction, it was once assumed[25,148] that decomposition is limited to strained intermosaic material in the AP crystals and that the reaction at low temperatures does not penetrate into the interior of the mosaic blocks. The residue would then consist of a very loose aggregate of small AP crystallites which contain few crystal imperfections and with a total surface area much greater than that of the original samples. The experimental fact that reactivity could be restored by grinding[25] or by exposure of the residue to solvent vapors[22,24] could then be understood because of the lattice reorganization induced by these procedures. This explanation is not entirely satisfactory particularly with respect to the reason why the reaction ceased; an alternative recent proposal[40] is that the low-temperature reaction stops because it is inhibited by an adsorbed layer of ammonia on the surface. No particular correlation of the decomposed regions with intermosaic structure is then to be expected, and instead the observed increase in the specific surface area with partial decomposition[25] would result from a "worm-eaten" structure caused by the propagation of the reaction from nuclei and its continual inhibition behind the reaction front. Striking electron micrographs[149] show that the residue maintains the original structure with numerous decomposed blocks of material of various sizes but of the order of 1 μm in linear dimension, and with several larger "holes" where blocks have coalesced. Exposure to water vapor causes a loss in crystallinity[149] associated with a coalescence of the surviving AP bridges.

The reaction begins[22,24] with the formation of nuclei at isolated centers on or near the crystal surface. These nuclei then grow three dimensionally and eventually coalesce to form a continuous interface which moves uniformly inward toward the center of the crystal. (It should be clearly understood that these nuclei consist of AP residue.) Decomposition ceases at the point of furthest penetration into the crystal. The induction period and the acceleratory stage can, therefore, be associated with nucleus formation and growth. As the reaction zones begin to interfere with each other, the reaction rate decreases.

Random nucleation followed by a constant growth rate of nuclei in three dimensions should result in kinetics which obey the Avrami–Erofeev equation[150]

$$[-\ln (1 - \alpha)]^{1/n} = kt \tag{53}$$

with $n = 4$, α being the fractional decomposition in time t with k the rate constant. Interference of nuclei, and the setting up of a contracting interface, results in a reduction of n from 4 to 3. In practice, the kinetic data seem to fit eq 53 better than other equations which have been tried[22,24,25,36,40,151–153] although the value of n is often found to be 3 or 2, except for the early stages of the decomposition of whole crystals.[25,36,151,152]

There is some uncertainty as to the effect of the phase transition on the kinetics of the AP decomposition. Bircumshaw and Newman[23] first observed that the maximum decomposition rate rose sharply to a maximum at 238°, then fell to a minimum at 250°, and finally increased again. Rate constants for the cubic form were substantially lower than those for the orthorhombic form. Shidlovskii, *et al.*,[154] and Manelis and Rubtsov[153] have also reported that the kinetic description of the decomposition curves depends on the crystal form.

In the microscopic study of the formation and growth of nuclei in small single crystals (0.5–5 mm in diameter) of AP, Raevskii and Manelis[155] found that decomposition centers consist of a large number of spherical nuclei 1–2 μm in size. The nuclei are not stationary, each decomposition center being formed by the aggregation of the nuclei within the immediate neighborhood of the center. Nuclei can move dis-

(143) G. A. McD. Cummings and A. R. Hall, "Flames Supported by Perchloric Acid. Part I. Premixed Flames with Methane," RPE Technical Note No. 222, June 1963.

(144) G. S. Pearson and D. Sutton, "Composite Solid Propellant Ignition. Ignition of Ammonia and Other Fuels by Perchloric Acid Vapour," RPE Technical Report No. 66/8, June 1966.

(145) G. S. Pearson and D. Sutton, *AIAA J.*, **4**, 954 (1966).

(146) V. R. Pai Verneker and J. N. Maycock, *J. Inorg. Nucl. Chem.*, **29**, 2723 (1967).

(147) B. S. Svetlov and V. A. Koroban, *Kinet. Katal.*, **8**, 456 (1967); *Kinetics Catalysis* (USSR), **8**, 393 (1967).

(148) R. D. Schultz and A. O. Dekker, "Sixth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1957, pp 618–626.

(149) J. D. Hightower and K. Krautle, personal communication.

(150) P. W. M. Jacobs, "Kinetics of Reactions in Ionic Systems," Materials Science Research, Vol. 4, T. J. Gray and V. D. Fréchette, Ed., Plenum Press, New York, N. Y., 1968, pp 37–52.

(151) P. J. Herley and P. W. Levy, *Nature*, **211**, 1278 (1966).

(152) P. J. Herley and P. W. Levy, *J. Chem. Phys.*, **49**, 1500 (1968).

(153) G. B. Manelis and Yu. I. Rubtsov, *Zh. Fiz. Khim.*, **40**, 770 (1966); *Russ. J. Phys. Chem.*, **40**, 416 (1966).

(154) A. A. Shidlovskii, L. F. Shmagin, and V. V. Bulanova, *Izv. Vyssh. Ucheb. Zaved. SSSR, Khim. i Khim. Tekhnol.*, **8**, 533 (1965); RPE Translation 18, Aug 1967.

(155) A. V. Raevskii and G. B. Manelis, *Dokl. Akad. Nauk SSR*, **151**, 886 (1963); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **151**, 686 (1963).

tances of about 200 μm at speeds which are of the order 7–10 μm/min at 230°. The direction of motion is along the principal diagonal of the rhombohedron.[155a] Viewed from a rhombic face the decomposition centers have the appearance of ellipsoids of revolution. The rate of growth of the decomposition centers is about ten times greater in the longitudinal direction than in the transverse direction, a difference which seems to be due to a difference in activation energies, 31 $\pm$ 1 kcal/mole in the longitudinal direction and 33 $\pm$ 1 kcal/mole in the transverse direction. Viewed from rectangular faces of the crystal, the decomposition centers appear hemispherical in form. The rate of decomposition, as measured by weight loss, is greater and the induction period is shorter for crystals with a greater ratio of the area of rhombic to rectangular faces.

In the decomposition of the cubic modification above 240°, decomposition centers are initiated by growth of a single nucleus (rather than by aggregation), are spherical in form, and are randomly distributed throughout the body of the crystal. The activation energy for nucleus growth is 17 $\pm$ 1 kcal/mole.

The presence of water vapor apparently affects the thermal decomposition of AP.[22,147] Boldyrev, *et al.*,[156] studied the growth kinetics of centers during thermal decomposition at 230° under different pressures of water vapor. Decomposition centers which were ellipsoidal in shape were observed, in agreement with Raevskii and Manelis.[155] The number of centers depends markedly on the crystal's prehistory, size, and shape. If the AP crystals were fine plates grown at low supersaturations so that they had a minimum number of defects, then the number of centers formed initially remained constant. Consequently thermal decomposition is governed mainly by the number of centers formed at $t = 0$ at a given number of decomposition sites. Growth of this fixed number of centers continues at a constant rate until overlapping occurs with the formation of a continuous reaction interface. Although changes in the partial pressure of water vapor do not affect the anisotropy of the growth rate (the rate parallel to the c axis is greater than the rate perpendicular to the c axis), they do influence the velocity of center growth in a complex manner. At low concentrations of water vapor the growth rate decreases, but with further increases in water concentration the growth velocity increases, then passes through a maximum, and finally decreases again. This behavior is very similar to that of the over-all thermal decomposition velocity at different water vapor pressures, and so it is concluded that the variations in the over-all rate with varying water vapor content of the ambient atmosphere are due primarily to a change in nucleus growth rate rather than a change in the number of centers.

There has been little work done on the possible role of dislocations in the decomposition of AP. Raevskii, Manelis, Boldyrev, and Votinova[157] found that dislocations in AP crystals could be revealed by etching the surface of the crystals with 95.5% ethyl alcohol. The etching process was followed continuously by microscopic observation. In most crystals the etch pits were aligned along the main diagonal of the rhombic face which is the same direction, ⟨010⟩, as that in which the maximum rate of development of the decomposition centers had been observed.[155] In other crystals, however, the pits were arranged in a random fashion.

To prove that the etch pits are not associated with surface defects only, the crystals were etched to a considerable depth. Etching of the lateral (rectangular) faces also showed the presence of defects, while etching the cleavage plane disclosed a network of interacting dislocations. Moreover, in many crystals the dislocations were associated with growth defects and points of mechanical damage. The average dislocation density on a rhombohedral face is $\sim 10^6$ cm^{-2}. This figure varies considerably from one crystal to another, however, and it may also vary on the same crystal face as a result of the irregular distribution of dislocations. The dislocation density was found to be extremely sensitive even to slight mechanical disturbance, and it showed a tendency to increase during prolonged work with a crystal.

The effect of heating AP to the decomposition temperature is to increase the dislocation density in the vicinity of a nucleus. The authors thus conclude that the catalytic influence of the reaction product (residue) on the reaction rate may be due to the additional number of dislocations which are produced in that part of the crystal which is in contact with the reaction product. The authors also regard as significant the anisotropy which is apparent both in the arrangement of the dislocations and in the growth of decomposition centers. Both these phenomena, however, might stem from the same cause (namely the crystal structure of orthorhombic AP), and the assumption of a causal relation between them is not really justified on the strength of the limited observations available.

Davies, Jacobs, and Russell-Jones[40] have recently made a careful analysis of all the low-temperature kinetic data obtained by their group.[25,40,158] Although subjectively it appears that there is a slight decrease in reaction rate at the transition point and that this is associated with a decrease in activation energy, this conclusion is hardly supported by the statistical evidence. Least-mean-square values for the activation energies are 33.91 $\pm$ 1.64 kcal/mole for orthorhombic AP and 26.97 $\pm$ 2.36 kcal/mole for the cubic modification, or 26.63 $\pm$ 0.87 kcal/mole for both sets of data. The question of the precise effect of the phase transition on the decomposition is still an open one, therefore; a thorough analysis of existing data is handicapped by possible slight dependence of rate constants on AP purity, particle size, ambient pressure, and the presence of gaseous products, although none of these parameters appear to affect the rate by amounts greater than the experimental uncertainty in measuring an individual value for the rate constant.[40]

There is a considerable variation in the literature values for the activation energy of the low-temperature decomposition of AP. The values for the orthorhombic form vary from 41 to 20 kcal/mole. Corresponding values for the cubic form lie between 30 and 17 kcal/mole (see Table III). Some of this variation is undoubtedly due to the widely different kinetic analyses employed in the calculations of rate constants. Several mathematical models have been proposed to describe the course of the thermal decomposition of solids.[150,159]

(155a) This description of the moving nuclei is based on the published translation of the Russian text. An independent translation obtained later gave essentially the same meaning.

(156) V. V. Boldyrev, Yu. P. Savintsev, and V. F. Komarov, *Kinet. Katal.*, **6**, 732 (1965); *Kinetics Catalysis* (USSR), **6**, 650 (1965).

(157) A. V. Raevskii, G. B. Manelis, V. V. Boldyrev, and L. A. Votinova, *Dokl. Akad. Nauk SSSR*, **160**, 1136 (1965); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **160**, 158 (1965).

(158) P. W. M. Jacobs and A. R. T. Kureishy, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 672–677.

(159) P. W. M. Jacobs and F. C. Tompkins, "Chemistry of the Solid State," W. E. Garner, Ed., Butterworth & Co., Ltd., London, 1955, Chapter VII.

Table III

Summary of Kinetic Investigations of the Low-Temperature Thermal Decomposition of AP[a]

Authors	Ref	Material[b]	Exptl method[b]	Kinetic analysis[b]	Arrhenius parameters Log (A/min^{-1})	E, kcal/mole
Bircumshaw	22–24	2R, powder, O	P (*in vacuo*)	PT		27.8
and Newman		C				18.9
Galwey and	25	2R, crystal, O	P (*in vacuo*)	AE, $n = 4$		20.6
Jacobs		powder, O		$n = 4$		24.6
		pellet, O		$n = 3$		30.1
		crystal, C		$n = 2$		25.3
		powder, C		$n = 2$		24.8
		pellet, C		$n = 2$		29.9
Jacobs and Kureishy	158	BDH, pellet O	P (250 torr of N_2)	AE, $n = 3$	12.40	32.6
		(152–178 μm) C		$n = 2$	9.86	27.2
		BDH, pellet O		AE, $n = 3$	12.34	32.6
		(<66 μm) C		$n = 2$	9.96	27.2
Gross and Amster	165	O, C	Adiabatic			41.2
Raevskii and	155	2R, crystal, O, L	M	Linear growth		33
Manelis		O, T				31
		C				17
Manelis and Rubtsov	153	2R, powder, O, C	W[c]	MR, k_1	7.75	30.0
		(50–100 μm) O		$n = {}^3/_2$, k_2	10.1	30.0
		C		$n = 2$, k_2	4.5	18.2
Osado and	161	3R, powder, C	W	First order		
Sakamoto		80 μm				21.5
		56 μm				21.5
		27.8 μm				23.3
Inami, Rosser, and	166	MCB, C, 88–124 μm	Adiabatic	AE, $n = 4$ (PT)		23.6 (20.9)
Wise		61–88 μm				23.4 (20.3)
		43–61 μm				21.4 (19.4)
		<43 μm				20.0 (17.0)
Shidlovskii, *et al.*	154	1R, powder, O	W	AE, $n = 4.5$		40.1
		C				25.1
Herley and Levy	151	Crystals, O	P (*in vacuo*)	AE, $n = 4$		29.8
				$n = 3$		26.9
Solymosi and Révész	160	Merck, powder, O	P (760 torr of air,	PT (decay period)		32.7
			in vacuo)	first order		29.6
				AE, $n = 3$		34.9
Davies, Jacobs,	40	BDH, pellet,[d] O + C	W	AE, $n = 2$	11.51	31.3
and Russell-Jones		100 mg			11.54	30.0
		BDH 2R, pellet, O + C			11.42	31.5
		MCB, pellet, O + C			11.69	31.5
		BDH, pellet, O + C	P (730 torr of air)		11.26	30.3
		Sublimate			12.24	31.2
		FS, pellet, O	P (*in vacuo*)	AE, $n = 3$	13.04	34.1
			W (700 torr of N_2)	AE, $n = 2$	11.25	30.2
Jacobs, *et al.*	40	Pellets, O	W P	AE, $n = 3$	12.73 ± 0.38	33.49 ± 0.82
(reanalysis of data)	25	Pellets, O		AE, $n = 2$	13.00 ± 0.72	33.91 ± 1.64
	158	Pellets, C		AE, $n = 2$	9.89 ± 0.96	26.97 ± 2.36
		Pellets, O + C		AE, $n = 2$	9.78 ± 0.37	26.63 ± 0.87
Herley and Levy	152	3R, crystal, O	Pt	AE, $n = 4, 3$		28.7 (a), 29.2 (d)
			Pnc	t_0		29.8
				AE, $n = 4, 3$		26.9 (a), 26.4 (d)
		Powder, O (<53 μm)	Pt			30.3 (a), 28.3 (d)
			Pnc			29.0 (a), 26.7 (d)

[a] Abbreviations used: O = orthorhombic, C = cubic, L = longitudinal, T = transverse, 2R = twice recrystallized, BDH = British Drug Houses, FS = Fisher Scientific, MCB = Matheson Coleman Bell, P = pressure increase (with pressure of inert gas given in parentheses), Pt = total pressure of all gases evolved, Pnc = pressure of noncondensable gases, W = weight loss, MR = $d\alpha/dt = k_1(1-\alpha)^n + k_2\alpha(1-\alpha)^n$, AE = Avrami–Erofeev equation, PT = Prout–Tompkins equation, M = direct measurements under microscope, t_0 = induction period, a = acceleratory period, d = decay period. [b] Where an entry is not repeated under the same author, it is to be concluded that the same information applies. [c] In metal ampoules and possibly affected by catalysis. [d] 40 mg unless stated otherwise.

No less than six of these have been pressed into service to describe the kinetics of this complex reaction. The data of Solymosi and Révész[160] show that differences of as much as 5 kcal/mole can arise in this way. To add to an already complicated situation, the observed activation energy appears to be dependent on particle size[161] and physical form.[25]

(160) F. Solymosi and L. Révész, *Kinet. Katal.*, 4, 88 (1963); machine translation available from DDC [AD 605 590].

(161) H. Osado and E. Sakamoto, *Kogyo Kayaku Kyokaishi*, 24, 236 (1963); U. K. Ministry of Aviation TIL Translation T.5597, Nov 1966.

Table IV

Ammonium Perchlorate Radiolysis Products

Product	*G value, mole/100 eV*
ClO_3^-	1.3
ClO_2	<0.02
ClO_2^-	<0.02
ClO^-	0.45
Cl_2	1.2
Cl^-	2.5
$NO_3^- + NO_2^-$	<0.05

Finally, the possible effects of the gaseous products and of the ambient pressure of an inert gas need to be further explored. Such effects have been sought,[40,147] and they may, at least in part, be responsible for the discrepancies between the results of various investigators. In this connection, Strunin and Manelis[162] have concluded that the kinetics of the thermal decomposition of AP at 230 and at 260° are not changed under the influence of a pressure of 100 atm of inert gas. Kinetic effects due to particle size,[163] aging,[146] and the temperature of recrystallization[164] have also been noted and these effects should be examined further.

The various kinetic investigations of the low-temperature thermal decomposition of AP are summarized in Table III.[22–25,40,151–155,158,160,161,165,166]

A. THERMAL DECOMPOSITION OF IRRADIATED AP

The X-radiolysis of potassium chlorate[167,168] and the γ-radiolysis of the alkali and alkaline earth metal chlorates[169,170] and perchlorates[171,172] have been studied. Odian and coworkers[173,174] studied the products from the ^{60}Co γ-radiolysis of AP over the dose range of 0–120 Mrads. The irradiated AP was dissolved in water, and analyses were performed for chlorate, chlorine dioxide, chlorite, hypochlorite, chlorine, chloride, and the total amount of nitrite and nitrate. The radiolytic decomposition of AP was found to be greater than that of the alkali or alkaline earth perchlorate by a factor of 2–5 (depending on the particular metal perchlorate considered). Chlorine is a major product of AP radiolysis but is not found in the product spectrum from the irradiated metal perchlorates. The other major products from AP are Cl^-, ClO_3^-, and ClO^-. All yields, except that of ClO_3^-, increased linearly with radiation dose. The ClO_3^- yield decreased at higher radiation doses, presumably because it itself was decomposed by the γ-radiation. The G values for AP radiolysis appear in Table IV.

Epr investigations[175–177] of irradiated monocrystals of AP have demonstrated the presence of two paramagnetic species: the NH_3^+ ion and the ClO_3 radical. Boyarchuk, *et al.*,[178] studied the formation and recombination of these metastable centers in electron-irradiated pure AP and in AP with added CaO, MnO_2, and $KMnO_4$. They reported that in pure AP the NH_3^+ recombination reaction is second order with an activation energy of 8.3 ± 0.3 kcal/mole. This second-order kinetics is also exhibited by AP with added CaO or $KMnO_4$. However, in admixtures of AP with MnO_2 the reaction is first order with an activation energy of 8.7 ± 0.2 kcal/mole. In the system, AP + 2% CaO, the recombination of ClO_3 radicals is of second order, and the observed activation energy was 20 ± 1 kcal/mole. A further paramagnetic center responsible for a broad singlet in the epr spectrum anneals out between 150 and 270°K. This unstable center was ascribed by the authors to an electron trapped at a lattice defect.

Preirradiation with X-rays,[179,180] γ-rays,[151,181] or ultraviolet light[45,16] has a considerable effect on the subsequent thermal decomposition of AP. Freeman and Anderson[179,181] demonstrated that irradiation with 40-kV X-rays or with γ-radiation from a ^{60}Co source, in doses from 10^6 to 10^7 rads, leads to a substantial change in the thermal stability of AP, as evidenced by changes in the differential thermal analysis (dta) thermograms. Photomicrographs[180,182] taken under transmitted light show a significant difference between the appearance of partially decomposed irradiated and unirradiated AP. In unirradiated AP, the disruption pattern of the surface indicates preferential regions of reaction (*cf.* ref 149), but in X-ray irradiated AP, the reaction sites apparently occur in a homogeneous manner throughout the crystal. The principal effect of preirradiation seems, therefore, to be to increase the number of nuclei, and this would result in both the observed kinetic effects, the decrease in the induction period, and the increase in the rate constant for the acceleratory period.[151]

The most detailed kinetic study of preirradiation effects so far is that of Herley and Levy.[36,152] These authors found that the activation energy for the decomposition of AP was unchanged by irradiation at 28.4 ± 2.5 kcal/mole (*cf.* Table III) and that the increased rate of decomposition of irradiated material could be ascribed to both an increase in the nucleation rate constant and to an increase in the product of the number of nucleation sites (N_0) and the nucleus growth rate constant. Microscopic observation confirmed the increase in N_0 on γ-irradiation, but it was not possible to obtain independent evidence for a change in the rate constant for nucleus growth.

(162) V. A. Strunin and G. B. Manelis, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 2226 (1964); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2127 (1964).

(163) A. E. Simchen and L. Inbar-Rozem, *Israel J. Chem.*, **4**, 39p (1966).

(164) J. N. Maycock, V. R. Pai Verneker, and L. Rough, *Inorg. Nucl. Chem. Lett.*, **4**, 119 (1968).

(165) D. Gross and A. B. Amster, Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 728–734.

(166) S. H. Inami, W. A. Rosser, and H. Wise, *Trans. Faraday Soc.*, **62**, 723 (1966).

(167) H. G. Heal, *Can. J. Chem.*, **31**, 91 (1953).

(168) H. G. Heal, *ibid.*, **37**, 979 (1959).

(169) C. E. Burchill, P. F. Patrick and K. J. McCallum, *J. Phys. Chem.*, **71**, 4560 (1967).

(170) P. F. Patrick and K. J. McCallum, *Nature*, **194**, 766 (1962).

(171) L. A. Prince and E. R. Johnson, *J. Phys. Chem.*, **69**, 359 (1965).

(172) L. A. Prince and E. R. Johnson, *ibid.*, **69**, 377 (1965).

(173) G. Odian, T. Acker, T. Pletzke, E. Henley, and R. F. McAlevy, "Radiation-Induced Solid Propellant Decomposition," Radiation Applications Inc., Long Island City, N. Y., RAI 331, AFOSR 64–1448, Jan 1965 [AD 604 475]; see also RAI 314, Jan 1963 [STAR N63-14852] and RAI 347, Jan 1965 [AD 612 536].

(174) G. Odian, T. Acker, and T. Pletzke, *J. Phys. Chem.*, **69**, 2477 (1965).

(175) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

(176) M. Fujimoto and J. R. Morton, *Can. J. Chem.*, **43**, 1012 (1965).

(177) J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961).

(178) Yu. M. Boyarchuk, N. Ya. Buben, A. V. Dubovitskii, and G. B. Manelis, *Kinet. Katal.*, **5**, 823 (1964); *Kinetics Catalysis* (USSR), **5**, 723 (1964).

(179) E. S. Freeman and D. A. Anderson, *J. Phys. Chem.*, **63**, 1344 (1959).

(180) E. S. Freeman and D. A. Anderson, *ibid.*, **65**, 1662 (1961).

(181) E. S. Freeman, D. A. Anderson, and J. J. Campisi, *ibid.*, **64**, 1727 (1960).

(182) E. S. Freeman and D. A. Anderson, quoted in *Chem. Eng. News*, 40 (Oct 30, 1961).

Table V

Summary of Kinetic Investigations of the High-Temperature Thermal Decomposition of AP[a]

Authors	Ref	Material	Exptl method	Inert gas pressure, torr	Temp range, °C	Kinetic analysis[b] Table VI	Arrhenius parameters Log (A/min^{-1})	E, kcal/mole
Bircumshaw and Newman	23	2R, powder	P	10–40	380–450	Power law		
Bircumshaw and Phillips	45	3R, powder 104–178 μm	W	200	400–440	$\gamma = ^3/_2$	20.72	73.4
Galwey and Jacobs	44	2R, crystal pellet residue	P	400	380–440	$\gamma = 3$		38.8
Kuratani	186	3R, pellet, 26–37 μm	P	760	380–440	$\gamma = 3$	11.28	44.8
Jacobs and Russell-Jones	187 51	BDH, MCB, and 2R BDH pellets	W	760	287–375	$\gamma = 3, 2$	8.59	3.06
Osado and Sakamoto	161	3R, powder	W	760	370–400	$\gamma = 2$		
		80 μm						46.7
		56 μm						35.7
		28 μm						31.0
Shidlovskii, *et al.*	154	1R, powder	W	760	330–450	AE, $n = 0.8$		28.3
		residue				$n = 1.1$		23.7
						$n = 0.6$		39.1
						$n = 1.0$		35.5
Solymosi and Révész	160	Merck, powder, 46 μm	P	?	320–377	$\gamma = 3$		40.9

[a] Value of γ in the equation $1 - (1 - \alpha)^{1/\gamma} = kt$.

The addition of small quantities of chlorate ion[183,184] accelerates the decomposition of AP. Freeman and Anderson,[180] on the basis of this observation and on the observed similarity of the decomposition patterns of irradiated AP and of unirradiated samples precipitated from a solution containing a small concentration of chlorate ion, concluded that the decreased thermal stability of irradiated AP is primarily due to the formation of chlorate ion. Recent comparative studies[185] of AP samples containing coprecipitated chlorate ion, and of specimens with chlorate produced as a result of irradiation, showed that the decomposition of the irradiated samples proceeds at a greater rate than that of preparations containing a higher concentration of coprecipitated chlorate. Similarly, in experiments in which Cl^- ions were introduced into AP to the same extent as formed during irradiation, it was shown that the Cl^- ions were not responsible for the accelerated decomposition of irradiated ammonium perchlorate. Thus although ClO_3 radicals are produced by preirradiation and ClO_3^- impurity has been shown to enhance the decomposition of AP, whether or not the ClO_3 radicals are the sole effective catalysts and what their *modus operandi* is, remain open questions.

VII. High-Temperature Thermal Decomposition of Ammonium Perchlorate

Bircumshaw and Newman[23] made a brief study of the thermal decomposition of AP in the temperature range 380–450° under a small pressure of inert gas of 10–40 torr to reduce sublimation. The reaction was deceleratory throughout, with no induction period, and resulted in complete decomposition of the salt. The kinetics were found to obey the power law

$$p = kt^n \tag{54}$$

although the value of the exponent n varied somewhat irregularly between 0.5 and 1.0. Galwey and Jacobs[44] found that eq 54 was not a satisfactory representation of the kinetics since below 425° two values of n had to be used to fit the experimental data. It was found that n varied considerably with temperature although this variation was less marked for AP residue than for salt which had not been decomposed at lower temperatures first. Three values of n were needed for residue at the low-temperature end of the range studied. They therefore suggested the use of the equation

$$1 - (1 - \alpha)^{1/\gamma} = kt \tag{55}$$

and found indeed that $\gamma = 3$ gave an excellent fit to all their data for whole crystals, pellets, and residue, with an activation energy for k of 38.8 kcal/mole. They also established that the rate of decomposition was unaffected by molecular oxygen.

Both Bircumshaw and Newman[23] and Galwey and Jacobs[44] followed the reaction by pressure measurements. Bircumshaw and Phillips[45] followed the decomposition by measuring the loss in weight of AP samples. They used eq 55 with $\gamma = ^3/_2$, but the activation energy deduced (73.4 kcal/mole) appears to be much too high. Kuratani[186] again used pressure measurements, and his results ($\gamma = 3$, $E = 44.8$ kcal/mole) are in moderate agreement with those of Galwey and Jacobs.

All the above workers had experienced difficulty with the irreproducibility of the kinetics at $T < 380°$, and this certainly seems to be a feature of the reaction when followed by pressure changes. Jacobs and Russell-Jones[51,187] have made a

(183) J. C. Petricciani, S. E. Wiberley, W. H. Bauer, and T. W. Clapper, *J. Phys. Chem.*, 64, 1309 (1960).

(184) W. G. Schmidt, "The Effect of Solid Phase Reactions on the Ballistic Properties of Propellants," Aerojet-General Corp., Sacramento, Calif., NASA CR-66457, Sept 1967.

(185) V. F. Komarov, V. V. Boldyrev, V. K. Zhuravlev, and G. V. Ivanov, *Kinet. Katal.*, 7, 788 (1966); *Kinetics Catalysis* (USSR), 7, 697 (1966).

(186) K. Kuratani, "Some Studies on Solid Propellants. I. Kinetics of Thermal Decomposition of Ammonium Perchlorate," Aeronautical Research Institute, University of Tokyo, Report No. 372, Vol. 28, 1962, p 79.

thorough study of the kinetics in this temperature region using both thermogravimetry and direct weight-loss measurements. Reproducibility was excellent; AP from different commercial suppliers and twice-recrystallized material all gave essentially the same results (see Table V). The data could be fitted to eq 55 with either $\gamma = 3$ or $\gamma = 2$ although $\gamma = 2$ gave the better fit over a substantially wider range of α. The activation energy was found to be 30.6 kcal/mole. Unfortunately, their data do not overlap the earlier pressure measurements,[44] but extrapolation of these would give a reaction rate lower than that determined by weight loss. The implication is that in the "irreproducible" region below 380°, gas-phase reactions are rate determining.

An apparent dependence of the activation energy on particle size[161] and on extent of reaction[154] has been found by Osada and Sakamoto and by Shidlovskii, respectively, but the latter effect is almost certainly due to the use of an inappropriate equation to describe the kinetics. The various studies that have been made of the kinetics of the high-temperature thermal decomposition of pure AP are summarized in Table V.

VIII. Catalyzed Thermal Decomposition of Ammonium Perchlorate

AP which has been specially purified shows a much longer induction period than that characteristic of the commonly commercially available material.[188,189] The effects of a wide variety of additives on the thermal decomposition of AP have been studied, and a list of references to this work appears in Table VI.[22–24,29,41,42,146,154,160,161,183,184,186,190–206] The results of kinetic investigations are summarized in Table VII. Bircumshaw and Newman[22,24] found that the addition of NH_4Cl to AP increased the induction period (t_0) of the low-temperature reaction. Whereas the addition of 10% of Al_2O_3 (all per cent compositions are by weight unless stated to the

Table VI

List of Papers Dealing with the Effect of Additives on the Thermal Decomposition of Ammonium Perchlorate

Additive	*Reference*
	Halides
NH_4Cl	22, 24
NH_4Br	193
NH_4I	193
NaCl, KCl, $MgCl_2$, $CaCl_2$	161
CuCl	154, 186
$CuCl_2 \cdot 2H_2O$	154, 161
$FeCl_3$	268
	Oxides
MgO	22, 24, 41, 194
CaO	22, 24
ZnO	42, 154, 186, 195–197
CdO	194, 195, 198
Al_2O_3	22, 24, 186
PbO	195
Cu_2O, CuO	42, 154, 158, 186, 192, 196, 199, 200
Cr_2O_3	41, 42, 154, 161, 186, 201, 202
MnO_2	22–24, 29, 41, 42, 154, 186, 190, 196, 203
Fe_2O_3	22, 24, 29, 42, 154, 160, 186, 195, 196, 201, 204
NiO	41, 42, 154, 186
Cobalt oxides	29, 41, 42, 154
TiO_2	186, 202
V_2O_5	154, 186
Copper chromite	29, 184, 186, 192, 201, 203, 204
	Oxy Salts
$LiClO_4$	205
$AgClO_4$	193
$Ca(ClO_4)_2$	146
$TlClO_4$	196
$Cu(ClO_4)_2$	193
$Fe(ClO_4)_3$	193
$Zn(ClO_4)_2$	206
$Cd(ClO_4)_2$	206
$Mg(ClO_4)_2$	206
K_2CrO_4	161
$(NH_4)_2CrO_4$	146
$CaCrO_4$	196
$K_2Cr_2O_7$	146, 161, 192
$KMnO_4$	196
KIO_3, KIO_4	196
$KClO_3$	183, 184
$CuCO_3$	154
$(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$	184
	Miscellaneous
Compounds of chromium	154
Compounds of manganese	154
Compounds of iron	154, 184, 196
Compounds of cobalt and nickel	154
Compounds of copper	184
	Carbon and fuels
Carbon	191, 192, 201, 203, 204
Fuels	201, 204

(187) A. Russell-Jones, "The Thermal Decomposition of Some Inorganic Perchlorates," Ph.D. Thesis, University of London, Oct 1964.

(188) G. D. Sammons, "Application of Differential Scanning Calorimetry to the Study of Solid Propellant Decomposition," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Oct 1966, CPIA Publication No. 138, Vol. I, pp 75–83.

(189) G. D. Sammons, "Study of the Thermal Behaviour of Solid Propellants by Differential Scanning Calorimetry," 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(190) A. K. Galwey and P. W. M. Jacobs, *Trans. Faraday Soc.*, **55**, 1165 (1959).

(191) A. K. Galwey and P. W. M. Jacobs, *ibid.*, **56**, 581 (1960).

(192) P. W. M. Jacobs and A. Russell-Jones, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 457–462.

(193) F. Solymosi and K. Dobo, "Fifth International Symposium on the Reactivity of Solids," Elsevier Publishing Co., Amsterdam, 1965; see also *Magy. Kem. Foly.*, **72**, 124 (1966).

(194) F. Solymosi, *ibid.*, **73**, 358 (1967).

(195) A. V. Boldyreva and V. N. Mozzhova, *Kinet. Katal.*, **7**, 734 (1966).

(196) W. G. Schmidt and M. Stammler, "Thermal Decomposition of Catalyzed Ammonium Perchlorate," 21st Interagency Solid Propulsion Meeting, June 1965, Vol. I, pp 71–88.

(197) F. Solymosi and L. Révész, *Nature*, **192**, 64 (1961); see also *Z. Anorg. Allg. Chem.*, **322**, 86 (1963).

(198) F. Solymosi and K. Fónagy, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 429–437.

(199) P. W. M. Jacobs and A. R. T. Kureishy, *J. Chem. Soc.*, 556 (1962).

(200) F. Solymosi and E. Krix, *J. Catal.*, **1**, 468 (1962).

(201) S. H. Inami, W. A. Rosser, and H. Wise, *Combust. Flame*, **12**, 41 (1968); see also H. Wise, Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, p 446.

(202) F. Solymosi, *Combust. Flame*, **9**, 141 (1965).

(203) A. Hermoni and A. Salmon, "The Catalytic Decomposition of Ammonium Perchlorate in the Gaseous Phase," Proceedings of the XXXIII Meeting of the Israel Chemical Society, Vol. 1, 1963, p 313 (abstract only available).

(204) J. Wenograd and R. H. W. Waesche, "The Effects of Pressure and Additives on Kinetics of Decomposition of Ammonium Perchlorate," The Combustion Institute Western States Section Spring Meeting, University of California at San Diego, La Jolla, Calif., April 1967.

(205) F. Solymosi and M. Ránics, *Combust. Flame*, **10**, 398 (1966).

(206) F. Solymosi, *Magy. Kem. Foly.*, **73**, 366 (1967).

Table VII

Summary of Kinetic Investigations of the Thermal Decomposition of AP + Catalyst Mixtures

Authors	*Ref*	*Catalyst[a] (concn, %)*	*Temp range, °C[a]*	*Kinetic analysis[a,b]*	*Arrhenius parameters Log (A/min⁻¹)*	*E, kcal/mole*
Galwey and Jacobs	190	MnO_2 (10)	177–212	$p = mkt$	...	33.2
		(34–90)	137–162	CA	...	31.5
Galwey and Jacobs	191	C (3–17)	195–240	PT	...	32.1
Solymosi and	197	ZnO (1–50)	215–240	PT, AE, etc.	...	27.9–34.1
Révész	160	Fe_2O_3 (2–50)	180–200	PT,AE	...	27.6–35.6
Jacobs and Kureishy	158	Cu_2O (5)	240–270	$p = c\ \exp(kt)$	...	29
Solymosi and Krix	200	CuO (16–50)	180–200	PT, AE	...	28.9–32.9
Kuratani	186	Cu_2O (1)	260–280	$p = c\ \exp(kt)$	12.54	36.0
		MnO_2 (1)	317–340	CV	7.76	31.0
Hermoni and Salmon	41	MnO_2 (13)	170–200	CV	8.60	28
		NiO			12.48	33
		$Co_2O_3 + Co_3O_4$			13.95	33
		Cr_2O_3	210–230		9.00	26.7
		MgO	215–235		11.2	31.4
				PT	10.8	29.2
Solymosi and Dobo	193	$AgClO_4$ (0.1)	200–240	PT	...	27.7
		$Cu(ClO_4)_2$ (1–5)		CV, AE	...	25.0–30.4
		$Fe(ClO_4)_3$ (1–5)		ME	...	28.9–34.0
		NH_4Br (0.1)			...	33.5
		NH_4I (0.1)			...	27.5
Shidlovskii, Shmagin, and Bulanova	154	MnO_2	214–245	AE	12.70	33.7
		Co_2O_3	215–245		14.87	38.3
		CuO	239–270		20.70	53.5
		Cu_2O	250–270		17.15	45.5
		Fe_2O_3	250–296		14.42	41.0
		NiO	270–296		17.80	49.2
		V_2O_5	250–303		15.20	43.7
		Cr_2O_3	260–309		9.90	30.1
Schmidt and Stammler	196	$KMnO_4$ (2)	215–290	Time to $\alpha = 0.03$	...	20
		$CaCrO_4$	245–265		...	16
Jacobs and Russell-Jones	192	CC[e] (0–5)	207–277	AE	11.82	31.6
		CC (0.5–5)	283–315	CA	15.67	47.7
		Cr_2O_3 (0.85)	306–348	CV	8.80	31.3
		$K_2Cr_2O_7$ (1.64)	312–339	CA	14.79	47.7
		CuO (4.1)	260–289		16.60	47.7
Inami, Rosser, and Wise	201	CC (2.9)	...	Adiabatic	13.8	40
		CC (4.8)[c]	...		16.5	43
		CC (4.8)[d]	250–308		17.7	46
		Cr_2O_3 (4.8)	...		27.3	68
		C (2.5)	...		19.9	52.5
		Fe_2O_3 (4.8)[c]	...		12.9	34.3
		Fe_2O_3 (4.8)[d]	...		13.8	36.6
Wenograd and Waesche	204	CC (0.5–5)	300–350	CA	...	48
Solymosi and Fónagy	198	CdO (6)	200–240	PT	...	26.7
		$Cd(ClO_4)_2$ (9)	200–230	PT, etc.	...	28.7–29.3
Solymosi and Ránics	205	$LiClO_4$ (5–50)	200–270	First order	...	28.2–32.0
Solymosi	194	CdO	206–328	PT, etc.	...	25–33
		MgO	206–324			30.3
Solymosi	206	$Cd(ClO_4)_2$	210–231	PT, etc.	...	29–33
		$Mg(ClO_4)_2$	201–231		...	25–32

[a] In these three columns, an entry is not repeated under the same author when the same information applies. [b] CA means the equation $1 - (1 - \alpha)^{1/2} = kt$; CV means the equation $1 - (1 - \alpha)^{1/3} = kt$; PT = Prout–Tompkins equation; AE = Avrami–Erofeev equation. [c] AP, 88–124-μm particle size. [d] AP, 43–61-μm particle size. [e] CC = copper chromite.

contrary) had no effect, the same amount of CaO retarded the reaction, increasing t_0, while Fe_2O_3 and MnO_2 were positive catalysts decreasing t_0 to zero, and increasing both the reaction rate and the extent of decomposition. For the MnO_2 + AP mixtures the extent of the low-temperature reaction rose to 100% provided the reactant were in the form of a loose powder. If they are compacted into a hard pellet, the catalyzed reaction ceases after a while presumably because of loss of contact.[190] There is also a change in the products of decomposition in the presence of MnO_2,[22,190] little oxygen being evolved. Mass spectrometric analyses of the permanent gases produced in the catalyzed reaction, using ^{18}O-enriched MnO_2, showed no ^{18}O content in the small amount of oxygen formed.[190] This experiment would seem to constitute evidence against a mechanism involving oxidation–reduction of the MnO_2 on a macroscopic scale.[23,190] The low-temperature decomposition of AP is unaffected by mixing the AP with carbon,[191,192] but the high-temperature reaction is evidently catalyzed and mild explosions can occur above 260°.

Solymosi and coworkers have studied the catalytic effect of a number of metal oxides; much of their data have been interpreted in terms of an electron-transfer mechanism for the low-temperature decomposition. Solymosi and Révész[197] found ZnO to be an effective catalyst. Activation energies (Table VII) of about 32 kcal/mole were obtained between 200 and 300°. This value is much the same as that for pure AP, but the extent of reaction is increased from the usual 29% up to around 80%. The most spectacular effect was perhaps the lowering of the ignition temperature by about 150°. Solymosi and Révész state[197] that the catalytic effect of ZnO is enhanced by doping it with Al_2O_3 and decreased by doping it with Li_2O. Ferric oxide[160] also reduces the induction period and increases the extent of the reaction. Below 270° a variety of activation energies around about 31 kcal/mole was calculated by Solymosi and Révész.[160] Above 330° the low-temperature decomposition is succeeded by the high-temperature reaction, and the activation energy for this decreased with increasing Fe_2O_3 content from 41 kcal/mole for pure AP to 22 kcal/mole for 22% Fe_2O_3. Above 380°, explosions occur. Both copper(I) and copper(II) oxide catalyze the AP decomposition,[158,199,200] being particularly effective at promoting ignition. Copper(II) oxide is clearly the better catalyst of the two[199] and is superior to copper chromite and to chromium(III) oxide, using the criterion of the increase in the rate constant for the high-temperature decomposition.[192] Solymosi and Krix[200] found that if copper(II) oxide is doped with lithium oxide (which makes it more p-type) the reaction rate is increased and the induction period shortened, but if made more n-type, by doping with chromium(III) oxide, then the reverse effect occurs. Above 200°, an increase in E to 41 kcal/mole was associated with a change in mechanism to Cl–O bond fission. In a later paper,[197] Solymosi and Révész interpret the role of zinc oxide to be the promotion of melting of the AP. The presence of a water-soluble zinc salt in the reaction residue was cited as evidence for reaction of ZnO with NH_4ClO_4; furthermore, the addition of $Zn(ClO_4)_2$ and $ZnCl_2$ to AP also increases the decomposition rate and induces thermal explosions above 240°. The result of doping was therefore attributed to its effect on the solid-state reaction between ZnO and AP.

Kuratani[186] has compared the effects of a number of salts (chiefly oxides) and drawn the following conclusions: (i) Cu_2O, CuO, CuCl, and ZnO catalyze both the low-temperature and high-temperature reactions; (ii) NiO and Cr_2O_3 promote mainly the low-temperature reaction; (iii) MnO_2 and copper chromite catalyze mainly the high-temperature reaction; (iv) Al_2O_3, TiO_2, Fe_2O_3, and V_2O_5 are ineffective in both temperature regions. Kuratani concludes that p-type catalysts are more effective than n-type but admits that ZnO does not fit into this scheme.

The catalytic effect of a similar range of compounds has been investigated by Hermoni and Salmon.[41] They found that the presence of oxides of manganese(IV), cobalt(II) + cobalt(III), nickel(III),[207] or chromium(III) all enabled the low-temperature decomposition to go to completion. Below 200° the activation energy was generally about 30 kcal/mole, and this was taken as support for the electron-transfer mechanism. Above about 240° (210° for the oxides of nickel and cobalt), the activation energy increases and this was taken as evidence for a new decomposition mechanism; rupture of the Cl–O bond in the perchlorate anion was suggested. It would seem that this effect might well have been due to self-heating, however (*cf.* ref 191). The effect of catalysis on the product distribution was also examined; in general, the proportion of free oxygen in the products is decreased by the presence of catalysts. The authors also state that the proportion of ClO_2 is increased by the presence of catalyst, but they used Bircumshaw and Newman's method of analysis[22,24] which is not reliable for ClO_2.[29] An important type of experiment was devised by Hermoni and Salmon[203] in an attempt to distinguish between the catalysis of solid-phase and gas-phase reactions. AP sublimate was passed over a catalyst in a closed system and the pressure increase due to decomposition measured. It was concluded that carbon, manganese(IV) oxide, and copper chromite mainly influence solid-phase reactions while chromium(III) oxide and copper(I) oxide influence reactions occurring in the gas phase. Magnesium oxide[41] was found to react with AP.

Solymosi[202] found that whereas chromium(III) oxide was an effective catalyst, titanium(IV) oxide was practically ineffective. Moreover, doping Cr_2O_3 with TiO_2, which makes it less p-type, increases the induction period for ignition. Conversely, doping TiO_2 with Cr_2O_3 reduces the explosion temperature. These results were taken as evidence for the electron-transfer mechanism,[23,190] but clearly other interpretations (see section IX) are possible.

Solymosi and Dobo[193] have investigated the effect of additions of ammonium iodide or bromide, or silver(I), copper(II), or iron(III) perchlorates, on the thermal decomposition of AP. Below 240° all these additives decrease the induction period and increase the rate constant. Activation energies lay between 27.5 and 34.0 kcal/mole, and this was taken as evidence for the electron-transfer mechanism. Above 260° (298° for NH_4Br) thermal explosions occurred.

Osado and Sakamoto[161] noted that the low-temperature decomposition of AP was faster than that of recrystallized material and accordingly analyzed the AP spectrographically. Of the elements found (Cr, Fe, Cu, Si, Ca, Mg, Na) Ca, Mg, and Na were attributed to the AP and the remainder to the electrodes, reaction vessel, or some other source of contamination. The metallic chloride (20% by weight) was mixed with the AP. Dta traces showed that iron(III) chloride and copper(II) chloride accelerate the low-temperature reaction so much that no second stage appears at all. Chromium(III) oxide accelerates an exothermic process just above the phase transition, but $K_2Cr_2O_7$ and K_2CrO_4 are less effective. $CaCl_2$ and $MgCl_2$, and to a lesser extent NaCl and KCl, reduce the temperature at which the second big exotherm occurs in pure AP. Osado and Sakamoto stress the possibility of chemical reaction of the chlorides with AP to produce metal perchlorates which are the effective catalysts.

(207) The authors state[41] that they used Ni_2O_3; actually $Ni_2O_3 \cdot 2H_2O$ dehydrates with decomposition to give NiO.

Shidlovskii, Shmagin, and Bulanova[154] have studied the thermal decomposition of AP in the presence of metallic oxides, chlorides, carbonates, and oxalates. With the addition of MnO_2, $MnCO_3$, $MnCl_2 \cdot 4H_2O$, Co_2O_3, $CoCO_3$, CoC_2O_4, or $CoCl_2 \cdot 6H_2O$, AP decomposes completely at 210–220° with a much reduced induction period, and a sharply increased rate of decomposition. Copper salts ($CuCO_3$, Cu_2O, CuO, CuCl, and $CuCl_2 \cdot 2H_2O$) increase the maximum rate of decomposition below 240° but only affect slightly the extent of reaction. Compounds of iron (Fe_2O_3, FeC_2O_4, $FeCl_3 \cdot 6H_2O$), nickel (NiO, NiC_2O_4, $NiCO_3 \cdot 2Ni(OH)_2$, $NiCl_2 \cdot 6H_2O$), chromium (Cr_2O_3, $CrCl_3 \cdot 6H_2O$), and vanadium (V_2O_5) influence the decomposition kinetics only above 240°, decomposition being complete at 270–280°. The oxides of magnesium(II) and zinc(II) react with AP forming a liquid phase. The action of a particular metal additive depends on the compound added; for example, in the case of cobalt the order of effectiveness is carbonate $\simeq$ oxalate > oxide > chloride.

An important advance has been made by Schmidt and Stammler[184,196] in stressing the need to distinguish between *impurities* which can be substituted isomorphically into the AP lattice ($KMnO_4$, KIO_3, KIO_4, and $TlClO_4$) and those which are mixed mechanically with the AP. The inclusion of $TlClO_4$ had no effect on the decomposition at temperatures up to 330°. Of the substances tested $KMnO_4$ had the greatest effect on deflagration, cocrystallization of 2% $KMnO_4$ with AP causing it to deflagrate just above the phase-transition temperature; KIO_3 and KIO_4 cause a rapid acceleration of both low-temperature and high-temperature decompositions. The oxide catalysts studied can be divided into two groups: those like Fe_2O_3 and MnO_2 which accelerate the decomposition but do not lead to deflagration below 300° and those such as ZnO and Cu_2O which cause deflagration at temperatures between 245 and 265°. It is significant that if quenched samples are reheated the induction period is shorter by the amount of the initial heating. For AP + ZnO, this "memory effect" lasted at least 9 days, indicating that an irreversible chemical process was involved. The efficacy of various iron catalysts was not linked with the percentage iron in the catalyst, nor with its oxidation state (iron(II) or iron(III)); chelates showed the greatest catalytic activity of the compounds studied. The incorporation of ClO_3^- ions in AP[183,184] leads, as already remarked, to a reduced induction period and an accelerated rate of decomposition.

The distinction between incorporation of, and surface coating with, additives has been emphasized recently by Rhees and Hammar[208] who showed that very low concentrations of metal oxides were effective when used as surface coatings.

It is to be expected that the product distribution from the decomposition of AP will be altered by the presence of catalysts. Shmagin and Shidlovskii[42] have analyzed the gaseous products from the decomposition of mixtures of AP containing 5% of the oxides of chromium(III), manganese (IV), iron(III), cobalt(III), nickel(II), copper(II), or zinc(II). Similarly, Inami, Rosser, and Wise[29] have performed a very detailed analysis of products from the decomposition of AP mixed with copper chromite, cobalt oxides, or ferric oxide. Their detailed results have already been given in Table II, but it seems pertinent to remark that while ZnO has a particularly pronounced effect on the products, all the additives studied reduce the yield of nitrous oxide and increase the yield of nitric oxide. HCl is not a product of the copper chromite catalyzed reaction,[29] yet some other oxides hardly affect the $HCl:Cl_2$ ratio[42] within the experimental accuracy. In the copper chromite catalyzed reaction, Cr(III) is oxidized to Cr(VI) by some intermediate with consequent loss in catalytic activity although this can be prevented by excess NH_3. Their value for the activation energy for AP + copper chromite is in only fair agreement with that of 48 kcal/mole found in a detailed investigation of the isothermal kinetics of decomposition of AP + catalysts by Jacobs and Russell-Jones.[192] These authors found that while copper chromite had only a slight effect on the low-temperature reaction, its effect on the *high-temperature decomposition* was *profound*. The decomposition kinetics of AP with $K_2Cr_2O_7$, copper chromite (with or without carbon), or copper(II) oxide gave parallel Arrhenius plots with a common activation energy of 48 kcal/mole. The most effective of the catalysts tried was copper(II) oxide.

The technique of differential scanning calorimetry (dsc) has been applied recently by Wenograd and Waesche.[204] Their results with copper chromite confirm that, while the low-temperature decomposition is slightly affected, the high-temperature decomposition is accelerated considerably, and this effect is enhanced by increasing the concentration of catalyst. The activation energy found was 48 kcal/mole in agreement with the results of Jacobs and Russell-Jones.[192] Iron(III) oxide was found to be less effective than copper chromite.

Solymosi and Fónagy[198] have examined the effect of CdO on the decomposition of AP. Cadmium oxide, being an n-type semiconductor, they evidently expected it to be ineffectual as a catalyst; on the contrary it increases both the rate of the low-temperature decomposition and the extent of reaction. The activation energy is 29 kcal/mole. Doping the CdO with In_2O_3 increased the induction period erratically, but doping with Li_2O had hardly any effect. These results are hardly in accord with the conclusions of Kuratani and of Solymosi that it is p-type semiconductors that catalyze the thermal decomposition. Direct observation of the decomposing mixture on a hot-stage microscope showed partial melting of the reactant mixture, and subsequent analysis of the solid residue indicated the presence of a soluble cadmium salt. *Chemical reaction of CdO with AP was clearly indicated* and subsequent experiments proved cadmium perchlorate to be an effective catalyst. The role of cadmium perchlorate (like zinc perchlorate) was interpreted as the formation of a eutectic of lower melting point than that of pure AP which, of course, normally ignites before it melts, although evidence for a molten phase has been seen in the burning of pure AP under pressure.[209] The act of promoting melting through the formation of a eutectic would not of itself necessarily bring about an enhanced rate of decomposition, although the extent of the reaction would likely be affected. The stability of AP is actually increased by formation of a melt of the eutectic composition with $LiClO_4$.[205]

It seems almost incredible that evidence for direct chemical reaction between metal oxides and AP took so long to accumulate[197,198] since this method had been recommended for the preparation of anhydrous perchlorates of magnesium and

(208) R. C. Rhees and H. N. Hammer, "Effect of Surface Modification on the Properties of Ammonium Perchlorate," American Potash and Chemical Corp., Whittier, Calif., July 1966.

(209) J. D. Hightower and E. W. Price, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 463–472.

the alkaline earth metals as far back as 1935.[210] Recently, rather direct evidence of such reaction in the kind of mixtures usually employed in AP decomposition studies has been obtained by Boldyreva and Mozzhova.[195] With ZnO, PbO, and CdO visual observation indicated melting, while infrared spectra taken before and after decomposition confirmed that $Zn(ClO_4)_2$, $Pb(ClO_4)_2$, and $Cd(ClO_4)_2$ are formed.

IX. Mechanism of the Decomposition of AP

Bircumshaw and Newman[22,24] considered three possible mechanisms for the decomposition of AP. These are (a) electron transfer from a ClO_4^- anion to an (interstitial) NH_4^+ cation; (b) proton transfer from NH_4^+ to ClO_4^-; and (c) thermal breakdown of ClO_4^- anions by rupture of a Cl–O bond. They ascribed the high-temperature reaction to (c), sublimation to (b), and the low-temperature reaction to (a). Galwey and Jacobs[44] measured the activation energy for the high-temperature reaction by following the reaction rate by the increase in pressure in a closed system and found a value of 39 kcal/mole, in contrast to Bircumshaw and Phillips' value[45] of 73 kcal/mole. They therefore discarded the Cl–O bond rupture mechanism and proposed[44] instead that the high-temperature reaction proceeds by proton transfer, followed by evaporation of NH_3 and $HClO_4$ into the gas phase, decomposition of $HClO_4$ in the gas phase, and oxidation of NH_3 by radicals resulting from the $HClO_4$ decomposition. Because Bircumshaw and Phillips[45] had reported an activation energy of 21 kcal/mole for sublimation, a different mechanism for sublimation was indicated. At that time (1959) there was no quantitative information on the gas-phase decomposition of $HClO_4$; Galwey and Jacobs[44] assumed (unjustifiably, as it later turned out) that $HClO_4$ would be very unstable and thus made the tentative suggestion that sublimation might involve an NH_4ClO_4 "molecule" or ion pair, stabilized by hydrogen bonding. It is now abundantly clear that this suggestion was incorrect. Levy's work[76] on the gas-phase thermal decomposition of $HClO_4$ has shown that it is quite possible for AP to sublime as free $HClO_4$ and NH_3 in the expected manner (*cf.* NH_4Cl). Furthermore, infrared[46,47] and mass spectrometric[30,31] investigations have failed to reveal any evidence for a molecular NH_4ClO_4 species.

The activation energy anomaly was resolved by Jacobs and Russell-Jones[51] who found that when the high-temperature reaction is followed by weight loss the activation energy is close to 30 kcal/mole and that this is also the value for the sublimation process, determined over a very wide temperature range.[40,51] Galwey and Jacobs' value of 39 kcal/mole,[44] having been obtained from pressure measurements, therefore refers to the gas-phase reactions which are rate limiting in the temperature range covered by the measurements (380–440°). Jacobs and Russell-Jones[50] were thus led to a unified mechanism for the decomposition of AP which is summarized in the reaction scheme of eq 56.

$$\begin{tikzcd}
NH_4^+\,ClO_4^- \arrow[r, shift left, "1"] & NH_3(a) \arrow[l, shift left, "-1"] \arrow[d, shift left, "3"] & + & HClO_4(a) \arrow[r, squiggly, "2"] \arrow[d, shift left, "4"] & \text{products} \\
\text{sublimate} & NH_3(g) \arrow[l, "6"'] \arrow[u, shift left, "-3"] & + & HClO_4(g) \arrow[r, squiggly, "5"] \arrow[u, shift left, "-4"] & \text{products}
\end{tikzcd} \qquad (56)$$

(210) C. F. Smith and V. R. Hardy, *Z. Anorg. Allg. Chem.*, **223**, 1 (1935).

A. LOW-TEMPERATURE DECOMPOSITION

The fundamental step is proton transfer (1) which results in adsorbed ammonia and perchloric acid on the surface of the AP. Since the low-temperature decomposition of AP is faster than the vacuum rate of sublimation,[40,51] it must therefore involve the adsorbed species $NH_3(a)$ and $HClO_4(a)$. Furthermore, the thermal decomposition reaction is unaffected by changes in the ambient pressure,[40,162] whereas the sublimation process is very pressure dependent.[51] These two sets of observations show that the low-temperature reaction is initiated on the surface, although it may be completed in the gas phase. Since the reaction is catalyzed by $HClO_4$ and retarded by NH_3, it was proposed[40,50] that decomposition at low temperatures proceeds *via* the bimolecular reaction of adsorbed perchloric acid molecules

$$2HClO_4(a) \longrightarrow H_2O + ClO_3 + ClO_4 \qquad (57)$$

followed by the rapid decomposition of the unstable chlorine oxides (section IV) to yield O atoms and ClO radicals, which oxidize NH_3, the reaction commencing in the adsorbed phase. Earlier[187] they had considered the possibility of direct reaction between NH_3 and $HClO_4$. This is still a viable possibility, and there is little evidence on which to eliminate either the direct reaction or the decomposition of perchloric acid. The kinetics[40] indicate a bimolecular reaction which would accord with either mechanism. The problem of accounting for the undecomposed residue (see later) favors slightly decomposition of $HClO_4$ rather than direct reaction of $HClO_4$ with NH_3, but the latter is not inconsistent with the experimental facts so far as they are known.

Further details are largely a matter of conjecture. While recognizing the possible role of ClO as the oxidant (as suggested by Pearson[211,212]), Davies, Jacobs, and Russell-Jones[40] wrote a typical reaction mechanism only for O atoms. There appear to be two objections to this: the absence of H_2 in the products, as found by Wong and Potter[123] in their study of the NH_3 + O reaction (see the reactions represented by eq 48, 51, and 52) and the fact that the major N_2-containing product is N_2O rather than NO (see Table I). However, AP is oxidant rich, so that hydrogen is an unlikely end product. The appearance of N_2O was explained[40,187] by the bimolecular decomposition of nitroxyl

$$2HNO \longrightarrow H_2O + N_2O \qquad (58)$$

This could only be the major route if the H-atom concentration were low, for otherwise[123,213]

$$H + HNO \longrightarrow H_2 + NO \qquad (52)$$

A low H-atom concentration is presumably a justifiable assumption since H_2 is not an end product. Conceivably H atoms would be removed by NO (heterogeneously) to form nitroxyl[213–215]

$$H + NO + M \longrightarrow HNO + M \qquad (51)$$

An alternative explanation for the appearance of N_2O

(211) G. A. Heath and G. S. Pearson, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, p 967.

(212) G. S. Pearson, *Nature*, **208**, 283 (1965).

(213) M. A. A. Clyne, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 311–316.

(214) M. Z. Hoffman and R. B. Bernstein, *J. Phys. Chem.*, **64**, 1753 (1960).

(215) H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944).

rather than NO as a product is that NO and NO_2 are indeed formed but are subsequently reduced by reaction with NH_3, HCl, or some other species. However, NO_2 + HCl yields[37] NO, while $NH_3 + NO_2$ yields NO + N_2 in equimolar amounts.[134] More feasible suggestions are that NO_2 reacts with NH_2[216–218] or that NO reacts with nitroxyl.[213]

$$NO + HNO \longrightarrow OH + N_2O \qquad (59)$$

The termolecular reactions[219, 220]

$$2NO + HNO \longrightarrow N_2 + H + NO_2 \qquad (60)$$

$$2NO + HNO \longrightarrow N_2 + HNO_3 \qquad (61)$$

are less likely to occur unless the NO concentration is high. It is possibly significant that the NO yield increases at the expense of N_2O in the presence of some catalysts, notably copper chromite and cobalt oxide.

A reconsideration of the proposal that oxidation of NH_3 occurs with O atoms[40] shows that several major objections exist. Recent work on the decomposition of $HClO_4$[81,82] and ClO_2[82, 102] suggests that O atoms may not in fact be produced in major yield and that the primary products, after decomposition of the unstable chlorine oxides, will be ClO and O_2 as well as H_2O.

$$ClO_4 \longrightarrow ClO_2 + O_2 \qquad (44)$$

$$ClO_2 + ClO_2 \longrightarrow ClO + ClO_3 \qquad (27)$$

$$ClO_3 \longrightarrow ClO + O_2 \qquad (22)$$

In addition there are Wong and Potter's observations[123] that NO and H_2 are products of the NH_3 + O reaction, and the difficulty of accounting for N_2O, although the latter is also a feature of all likely mechanisms. Thus Pearson's proposal[211, 212, 221] that ClO is the oxidizing species in perchloric acid flames seems likely to hold also in the thermal decomposition of AP. If this is so then a reasonable mechanism is

$$NH_3 + ClO \longrightarrow NH_2 + ClOH \qquad (62)$$

$$NH_2 + O_2 \longrightarrow NO + H_2O \qquad (63)$$

$$NH_2 + O_2 \longrightarrow HNO + OH \qquad (64)$$

$$2HNO + H_2O + N_2O \qquad (58)$$

with Cl_2 and HCl coming from further reactions of ClOH and ClO, and N_2 from the reaction of NO with NH_2.[216–218]

$$NH_2 + NO \longrightarrow N_2 + H_2O \qquad (65)$$

Thus the details of the heterogeneous and homogeneous reactions following proton transfer remain to be elucidated. Of particular interest are the comparative roles of $HClO_4$ molecules, O atoms, and ClO radicals in the oxidation of NH_3, and the absence of NO as a major product. A reaction step involving reduction of NO_2 seems the only likely alternative to the formation of N_2O *via* nitroxyl.

In contrast to the necessarily speculative nature of proposals regarding the oxidation of NH_3 and subsequent reactions, the initial step (proton transfer to give adsorbed NH_3 and $HClO_4$) seems to be fairly well established. The activation energy probably lies in the range 27–34 kcal/mole (see Table III) and is thus close to that for sublimation (29–30 kcal/mole, section III) which involves proton transfer followed by desorption of NH_3(a) and HCl_4(a), although this may be a coincidence. A theoretical analysis[51] shows that the activation energy for sublimation should be close to $^1/_2\Delta H$, and this is well borne out by the experiments: in the low-temperature reaction there is no question of step 2 of reaction eq 56 being reversible and so the over-all E depends on E_1, E_{-1}, and E_2. The most convincing evidence for a proton-transfer mechanism comes from the effect of NH_3[29, 40, 222] which increases the induction period, reduces the reaction rate, and suppresses sublimation completely. Water has a slight inhibiting effect[22, 29, 147, 156] due to its adsorption by the decomposing AP and possibly to stabilization of the $HClO_4$ through formation of the more stable hydrates.[49,73]

Although various interesting experiments on the formation and growth of nuclei in AP have been performed,[22, 24, 149, 152, 155–157] it is still too early to attempt to interpret these in any detail. A final synthesis of the chemistry and of the topochemistry of this complex reaction has yet to be made.

B. HIGH-TEMPERATURE DECOMPOSITION

If the oxidation of ammonia proceeds with less than 100% efficiency, through desorption of the perchloric acid, of the chlorine oxides, or of the radicals performing the oxidation (O, ClO), then NH_3 will accumulate on the surface, thus suppressing the reversible proton-transfer process to the stage where this ceases altogether on an NH_3-covered surface. The failure of the low-temperature reaction to go to completion thus finds a rational basis in the unified mechanism.[50] As the temperature is raised, desorption of NH_3 occurs, dissociation recommences, and a situation develops in which NH_3 and $HClO_4$ molecules are both desorbing into the gas phase rather than reacting on the surface (see eq 56). At low ambient pressures they diffuse sufficiently rapidly to get out of the heated zone of the reaction vessel before substantial decomposition of $HClO_4$ can occur. The NH_3 and $HClO_4$ then recombine on any cold surface to complete the sublimation process (step 6 in the reaction scheme represented by eq 56). As the ambient pressure increases, the rate of diffusion of NH_3 and $HClO_4$ through the gas phase decreases, and their residence time in the reactor is sufficiently long for decomposition of $HClO_4$ followed by oxidation of ammonia to occur.

The reaction mechanism is thus similar to the low-temperature reaction except that the initial decomposition of $HClO_4$ is homogeneous rather than heterogeneous. As the temperature is raised, the NO/N_2O ratio increases, showing that the subsequent reactions also differ in detail. A possible reason for the appearance of NO is the instability of NO_2 at higher temperatures. The possibility of direct reaction between NH_3 and $HClO_4$ rather than, or in addition to, decomposition of $HClO_4$ cannot be ignored.

An interesting new development[223] is the application of the flash photolysis technique to AP. Care must be taken in applying the results directly to the thermal decomposition of AP, however, since the flash also causes photochemical decomposition of ClO_2 (yielding O atoms and ClO radicals)

(216) G. K. Adams, W. G. Parker, and G. H. Wolfhard, *Discussions Faraday Soc.*, **14**, 97 (1953).
(217) C. H. Bamford, *Trans. Faraday Soc.*, **35**, 568 (1939).
(218) J. B. Levy and R. Friedman, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 663–672.
(219) E. A. Arden and L. Phillips, *Proc. Chem. Soc.*, 354 (1962).
(220) O. P. Strausz and H. E. Gunnings, *Trans. Faraday Soc.*, **60**, 347 (1964).
(221) G. S. Pearson and D. Sutton, *AIAA J.*, **5**, 2101 (1967).
(222) R. L. Stone, *Anal. Chem.*, **32**, 1582 (1960).
(223) R. V. Petrella and T. L. Spink, *J. Chem. Phys.*, **47**, 1488 (1967).

and of NH_3 (yielding H atoms and NH_2 radicals). The preponderance of NO over N_2O in these experiments may be due to high temperatures induced by irradiation with the flash or to a higher (relative) concentration of O atoms and H atoms than exists in the purely thermal decomposition.

C. CATALYZED REACTION

Early speculations[23,190] regarding the mechanism of the catalyzed decomposition involved electron transfer, and this has been much used in subsequent work. Jacobs and Russell-Jones[192] have shown, however, that a consistent interpretation of the role of catalysts can be provided in terms of the proton-transfer mechanism, and this has recently received strong support from the experiments of Pearson and Sutton[221] on the catalyzed ignition of composite propellant fuels.

An analysis of the data available at the present time suggests that probably there is no single mechanism by which the rate of AP decomposition can be altered by catalysts. Three groups of catalysts can be distinguished. Of particular interest are those in group I, comprising copper chromite and other metal oxides which do not react with AP. Copper chromite alters the low-temperature reaction rate only slightly[192] but accelerates the high-temperature reaction considerably. Copper(II) oxide is even more effective. This acceleration is associated with a change in the activation energy from 30 to 48 kcal/mole. Since the rate of the catalyzed reaction exceeds the sublimation rate at the same pressure, Jacobs and Russell-Jones[192] proposed that perchloric acid migrates to the catalyst surface by surface diffusion and there decomposes heterogeneously. Subsequent steps involve the oxidation of ammonia and this may, in part, also be heterogeneous. Support for this mechanism comes from recent work by Boldyreva, Bezrukov, and Boldyrev[224] who showed that NiO, ZnO, Cr_2O_3, Co_3O_4, and CuO can catalyze the decomposition of AP when separated physically from it. In these experiments the $HClO_4$ molecules must diffuse to the catalyst through the vapor phase before decomposing heterogeneously on the oxide. The experiments of Schmidt,[184] in which $KClO_4$ + catalyst mixtures, heated in a stream of NH_3, were shown not to deflagrate even at temperatures above that at which AP deflagrated, also support the Jacobs and Russell-Jones mechanism, since they show that the catalyst acts on $HClO_4$ and not on the ClO_4^- anion.

The low-temperature reaction is catalyzed by a number of foreign ions (group II) of which Ag^+ and Cd^{2+} are typical examples among the cations.[193,198] Among anions, MnO_4^-, ClO_3^-, I^-, and Br^-, for example, are effective.[180,183–185,193,196] Little work has been done on the effect of anions in solid solution (see Table VI) and no concrete proposals regarding their action have been made. One knows, of course, that NH_4ClO_3 is much less stable than AP, but this does not explain its effectiveness as a catalyst, unless $HClO_3$ is less stable than $HClO_4$ or attacks NH_3 more readily. The cations, in contrast, may facilite the proton-transfer process through forming ammines.[50,225]

Certain metal oxides (forming a third group of catalysts), of which MgO, CdO, ZnO, and PbO[41,195,198] are examples, react with AP to form the metal perchlorate which then forms a molten phase with the AP. At the high pressures typical of propellant combustion, AP will melt without a catalyst as shown by the elegant experiments of Hightower and Price.[209] There seems no reason to suppose that decomposition in the melt is any different chemically from that at the surface of the solid. (Hydrazine perchlorate melts prior to decomposition, and the mechanism here too is believed to involve proton transfer.[226]) The mechanism of catalysis of AP decomposition by group III catalysts is probably that proton transfer occurs very readily in the melt.

D. DECOMPOSITION OF IRRADIATED AP

The effect of high-energy ionizing radiation on an ionic solid is to elevate electrons from the valence band to the conduction band of the crystal. In NaCl, for instance, the highest occupied electron levels in the valence band come from the 3p levels on the free Cl^- ion, and it is from these levels that electrons are excited by radiation to give Cl atoms. The sodium 2p valence band lies well below the chlorine 3p valence band and is not affected. The band structure of AP has not been calculated, and the relative positions of the NH_4^+ and ClO_4^- valence bands are therefore unknown. The esr evidence suggests that both bands are involved when AP is exposed to ionizing radiation, for then one expects the reactions

$$NH_4^+ \longrightarrow NH_4^{2+} + e^- \quad (66)$$

$$NH_4^{2+} \longrightarrow NH_3^+ + H^+ \quad (67)$$

$$ClO_4^- \longrightarrow ClO_4 + e^- \quad (68)$$

$$ClO_4 \longrightarrow ClO_3 + O \quad (69)$$

Since H atoms are not detected by esr, electrons are trapped predominantly by ClO_3 and by its further decomposition products ClO_2, ClO, and Cl although lattice defects (anion vacancies?) may also be involved.[178] ClO_3 and NH_3^+ have both been identified with the aid of esr.[175–177] The protons are presumably trapped with high efficiency by ClO_4^- ions to form perchloric acid.

$$ClO_4^- + H^+ \longrightarrow HClO_4 \quad (70)$$

The principal products of prolonged radiolysis are Cl_2, Cl^-, ClO_3^-, and ClO^- (Table IV).

Preirradiation with X-rays and γ-rays has a considerable effect on the thermal stability of AP,[36,151,152,179–181] and it seems likely that this is due to the production of ClO_3^-[180,185] ions although the irradiated salt is more unstable than that containing a higher concentration of coprecipitated chlorate. Possibly this may be indicative of the need for ClO_3^- to be actually present in the lattice in solid solution and not merely coprecipitated, when only a small fraction of the impurity may go substitutionally into the lattice. Alternatively, or in addition, the enhanced catalytic effect may be due to the production of $HClO_4$ during preirradiation. The stability of AP is also affected by preirradiation with ultraviolet light,[45,161] but there is no information available on whether or not ClO_3^- ions are formed during irradiation.

The mechanism of the decomposition of AP has also been

(224) A. A. Boldyreva, B. N. Bezrukov, and V. V. Boldyrev, *Kinet. Katal.*, **8**, 29 (1967); *Kinetics Catalysis* (USSR), **8**, 258 (1967).
(225) L. Dauerman, *AIAA J.*, **5**, 192 (1967).
(226) P. W. M. Jacobs and A. Russell-Jones, *Can. J. Chem.*, **44**, 2435 (1966).

Table VIII

Summary of Investigations of the Thermal Ignition of AP and of AP + Catalyst Mixtures

Authors	*Ref*	*AP + catalyst (concn, %)*[a,b]	*Minimum ignition temp, °C*[c]	*Pellet mass, mg*[a]	*Activation energy, kcal/mole*
Glasner and Makovky	231	Baker CP	440	70	31.0
		$+CuO$	345		
		$+MoO_3$	400		
Galwey and Jacobs	229	2R	427	50	41.1
Galwey and Jacobs	191	2R + C (20)	260	16	40.0
Solymosi and Révész	197	Merck + ZnO	224	200	17–34
Jacobs and Kureishy	158	BDH + Cu_2O (6.7)	248	30	28.1
	199	(29)	258		...
		(50)	253		31
Solymosi and Krix	200	+ CuO	255	...	29–31
Kuratani	186	3R	430	100	...
		+ MnO_2 (1)	336		33.5
		+ MgO (1)	330		43.5
		+ CuCl (1)	297		36.0
		+ Cu_2O (1)	269		38.1
		+ CuO (1)	258		31.0
		+ ZnO (1)	247		29.5
Hermoni and Salmon	41	1R + Co_2O_3 + Co_3O_4	241	150	46.6
Shidlovskii, *et al.*	154	1R + MnO_2 (5)	265	150	...
	232	+ CuCl (5)	290		
Solymosi and Dobo	193	2R + $AgClO_4$	277	100	16–19
		+ $Cu(ClO_4)_2$	270		22.6
		+ $Fe(ClO_4)_3$	276		29.6
		+ NH_4Br	298		22–24
Solymosi	202	+ Cr_2O_3	251	100	24–29
		+ TiO_2	269		29–30
Schmidt and Stammler	196	+ KIO_3	355		
		+ KIO_4	310		
		+ CuO	>300		
		+ ZnO	240		
		+ $KMnO_4$	240		
Osada and Sakamoto	161	AP		50	23–69
Jacobs and Russell-Jones	192	MCB + CC (0.5)	300	40	12.2
		(2.5)	287		13.8
		(5)	290		14.0
Solymosi and Fónagy	198[d]	2R + CdO	260		23.5
		+ $Cd(ClO_4)_2$	257		26–31
Solymosi and Ránics	205	+ $LiClO_4$	290		
Solymosi	233	+ SnO_2	370–400	...	...
		+ SnO_2 + Cr_2O_3	280		15–18

[a] In these columns, an entry is not repeated under the same author when the same information applies. [b] BDH = British Drug Houses; CC = copper chromite; MCB = Matheson Coleman and Bell; *n*R = recrystallized *n* times. [c] The minimum ignition temperature depends on the mass of the reactant (see ref 158 and 199); it also depends on the concentration of additive where a concentration range is specified. [d] Compare also ref 194 and 206.

discussed recently in two reports by Pittman[227] and by Hall and Pearson.[228]

(227) C. U. Pittman, "The Mechanism of Decomposition of Ammonium Perchlorate: A Review," U. S. Army Missile Command, Redstone Arsenal, RK-TR-66-13, Aug 1996.

(228) A. R. Hall and G. S. Pearson, "Ammonium Perchlorate: A Review of Its Role in Composite Propellant Combustion," R.P.E. Technical Report 67/1, 1967; see also "Oxidation and Combustion Reviews," Vol. III, C. F. H. Tipper, Ed., Elsevier Publishing Co., Amsterdam, 1968, p 129.

X. Combustion of Ammonium Perchlorate

A. THERMAL EXPLOSION

At temperatures above about 440° the decomposition of AP is too fast to be followed manometrically;[229] after an induction period there is a sudden large pressure change which clearly

(229) A. K. Galwey and P. W. M. Jacobs, *J. Chem. Soc.*, 5031 (1960).

Table IX

Summary of Experimental Investigations of the Ignition of AP Propellants

Source of heat	*Authors*	*Ref*	*Propellant[a] fuel and catalyst*	*Flux, cal cm^{-2} sec^{-1}*	*Ignition time, msec*	*Surface temp, °C*	*E, kcal/mole*
Hot wire	Altman and Grant	236	...	...	10^3–2×10^4	390	...
	Baer	237	PBAA CC	...	10–1×10^4	400	...
Hot plate	Marklund	238	Nil	...	100–1×10^5	280–470	41
Conduction from hot gases	Summerfield, *et al.*	239–245	Polystyrene or epoxy resin ferric oxide	...	0.2–4[b]	160	...
Convection from hot gases	Ryan, *et al.*	246–251	Polysulfide, PBAA, rubber, or polyurethan CC[c]	10–120	...	...	30
	Kling, Maman, and Brulard	252	...	40–150	...	...	5
	Niessen and Bastress	253	PBAA	17–120	...	...	
Hypergolic (ClF_3)	Allen and Pinns	254	Polysulfide, polyurethan, or PBAA	...	0–3	...	
Radiation	Ryan, *et al.*	246 247 251 255	Polysulfide, PBAA, rubber, or polyurethan CC[c]	1–13	300–2×10^4	320–380	28
	Beyer and Fishman	256	Polysulfide	5–160	50–100	...	...
	Price, *et al.*	257	PBAA	4–100	...	480	
	Evans, *et al.*	17 258 259	CC Carbon + CC	9–63	20–400	380 260	
	Rosser, *et al.*	260	CC Carbon + CC	20–120	5.2	360–480[d] 260–340	
	Sutton and Wellings	261	PIB	2–300	40–1300	...	

[a] AP concentration in the range 75–88%, except when pure AP is used. PBAA denotes polybutadiene–acrylic acid copolymer; PIB denotes polyisobutylene. [b] No ignition except in presence of oxygen. [c] An unidentified iron compound was the catalyst in the polysulfide and polyurethan propellants. [d] In nitrogen; higher in helium.

marks the onset of deflagration. While direct measurements of self-heating have only been made for mixtures of AP + catalysts,[199] there is no doubt that the explosions have a thermal origin. Simplified theories of self-heating[229,230] predict that the induction period τ should conform to the equation

$$\log (\tau/T_0^2) = \log B - \frac{E}{2.303RT_0} \tag{71}$$

where $B = C_pRT_0^2/QAE$, T_0 is the temperature of the reaction vessel, Q is the heat of reaction, $A \exp(-E/RT_0)$ is the rate constant of the reaction, and C_p is the heat capacity of the reactant. Frequently, thermal explosion data are analyzed using the empirical expression

$$\log \tau = \log B' - \frac{E}{2.303RT_0} \tag{71'}$$

which usually provides an equally good fit to the data but will yield a slightly different value for the activation energy E. Corrections for the heat-up time, τ_0, if significant, should be made.[192,199,229]

In general, incorporation of a catalyst lowers the minimum ignition temperature. The results of investigations of the thermal explosion of pure AP and of AP + catalysts are summarized in Table VIII.[41,154,158,161,186,191–200,202,205,229,231–233]

The activation energies deduced cover a wide range of values (12.2–46.6 kcal/mole, with even a lone value at 69 kcal/mole), and while the results are probably not very accurate some general expectations can be formulated. With pure AP the low-temperature reaction occurs first,[229] and thermal explosion involves the residue. The mechanism of decomposition (section IX) consists for the formation of NH_3 and $HClO_4$ molecules on the surface, their desorption into the gas phase, and their reaction there with an activation energy of ~40 kcal/mole. These gas-phase reactions are exothermic and heat conducted to the AP results in a rise in temperature, accelerated decomposition, and eventually deflagration. One would expect then that the activation energy obtained from measurements of ignition times as a function of T_0 would also be approximately 40 kcal/mole, and this expectation is fulfilled[229] provided corrections for the heat-up time τ_0 are

(230) P. Gray and M. J. Harper, *Trans. Faraday Soc.*, **55**, 581 (1959).

(231) A. Glasner and A. Makovky, *J. Chem. Soc.*, 1606 (1954).

(232) A. A. Shidlovskii and L. F. Shmagin, *Izv. Vyssh. Ucheb. Zaved. SSSR, Khim. i Khim. Teckhnol.*, **5**, 529 (1962); available as RPE Translation 5, Sept 1963.

(233) F. Solymosi, "Initiation of Ammonium Perchlorate Ignition by Tin IV Oxide-Chromium III Oxide Catalysts," to be published.

made.[161,199] It should be borne in mind that eq 71 is an approximate one and is based on the assumption of first-order kinetics; however, it is probably no more inaccurate than the experimental data if B is taken as an empirical parameter.

When catalysts are present E generally lies between about 30 and 40 kcal/mole but is occasionally much lower than this.[192,193] The reactions involving NH_3 and $HClO_4$ now occur at least partly catalytically (sections VIII and IX) although they are completed in the gas phase. A wide variety of activation energies might therefore be expected depending on which step is rate controlling. Unfortunately there have been few attempts at correlating thermal explosion data with pre-ignition kinetics.[158,197,234] In at least one important example, the copper chromite catalyzed decomposition of AP, the activation energies for thermal ignition and for isothermal decomposition differ[192] by an extent far greater than likely experimental error, showing that ignition is controlled by the exothermic gas-phase reactions which complete the chemical process (~13 kcal/mole), whereas the isothermal decomposition is controlled by the second step, namely the heterogeneous decomposition of $HClO_4$ (and/or the first stages of the heterogeneous oxidation of ammonia), ~48 kcal/mole.

A "memory" effect in the catalysis of the thermal explosion of AP by some metal oxides (*e.g.*, ZnO) has been reported.[196,235] This is only to be expected when the oxide reacts with AP to form the corresponding perchlorate for, on reheating the quenched reactant mixture even after a long time interval, the metal perchlorate will already be present, and thus the first stage of the pre-ignition reaction having already taken place, a reduced ignition time is to be expected.

B. IGNITION

The firing of a composite rocket propellant, consisting of AP, fuel, and catalyst, is achieved by the combustion of an igniter which heats localized areas of the propellant to temperatures sufficient to bring about their ignition. These burning areas spread until the whole surface is ignited, and, when the chamber pressure reaches its steady-state value, steady burning of the whole propellant results. Several mechanisms for the transfer of energy to the propellant surface may be exploited, namely (i) heat transfer from hot gases; (ii) diffusion of condensable vapors or reactive chemical species; (iii) scattering of hot refractory particles; (iv) radiation from hot igniter products. The operation of practical igniters is simulated in laboratory ignition tests by the transfer of energy to the propellant by conduction from hot wires, by conductive or convective heating, by hot gases, and by thermal radiation. Hypergolic ignition (spontaneous ignition when an oxidizer and fuel are brought into contact) has also been employed. These experiments are summarized in Table IX.[17,236–261]

The low surface temperature of 160° found by the Summerfield group in their experiments on propellant ignition by shock-heated gases, and the failure of the propellants to ignite unless oxygen was present, led to the proposal that the source of heat in ignition is a homogeneous gas-phase reaction between fuel vapor and oxygen.[239–245,262–264] This mechanism

(234) P. W. M. Jacobs and A. R. T. Kureishy, "Ninth Symposium (International) on Combustion," Academic Press, New York, N. Y., 1963, pp 366–370.

(235) D. Sutton and P. C. Wellings, unpublished data quoted by A. R. Hall and G. S. Pearson in ref 228.

(236) D. Altman and A. F. Grant, "Fourth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1953, pp 158–161.

(237) A. D. Baer, "Recent Results Concerning the Hot Wire Ignition of Composite Propellants," The Combustion Institute Western States Section, Paper WSCI 64–28, Oct 1964; see also *Pyrodynamics*, 3, 15 (1965).

(238) T. Marklund, "Ignition of Ammonium Perchlorate at Various Pressures," Swedish Defence Institute Report FOA 2, A 2322-242, Feb 1965; RAE Translation 1245, Aug 1967.

(239) P. L. Cowan, "Experiments on the Ignition of Composite Solid Propellants," MSE Thesis, Department of Aeronautical Engineering, Princeton University, Jan 1960 [AD 293 914].

(240) C. E. Hermance, J. Wenograd, K. P. Hall, and M. Summerfield, "Research on the Ignition of Solid Propellants," Princeton University Department of Aeronautical Engineering Report No. 588, Dec 1961 [AD 270 112].

(241) R. F. McAlevy, "The Ignition Mechanism of Composite Solid Propellants," Ph.D. Thesis, Princeton University Department of Aeronautical Engineering Report No. 557, June 1961, AFOSR TN 1220 [AD 263 440].

(242) R. F. McAlevy, P. L. Cowan, and M. Summerfield, "A Technical Report on the Mechanism of Ignition of Composite Propellants by Hot Gases," Princeton University, Department of Aeronautical Engineering Report No. 505, April 1960, TN 60-335 [AD 235 023].

(243) R. F. McAlevy, P. L. Cowan, and M. Summerfield, "Progress in Astronautics and Aeronautics," Vol. I, "Solid Propellant Rocket Research," Academic Press, New York, N. Y., 1960, pp 623–652.

(244) M. Summerfield and R. F. McAlevy, *Jet Propulsion*, 28, 478 (1958).

(245) M. Summerfield, R. Shinnar, C. E. Hermance, and J. Wenograd, "A Critical Review of Recent Research on the Mechanism of Ignition of Solid Rocket Propellants," Princeton University, Department of Aeronautical Engineering Report No. 661, Aug 1963 [STAR N63-21713; AD 416 332].

(246) A. D. Baer, N. W. Ryan, and D. L. Salt, "Progress in Astronautics and Aeronautics." Vol. I. "Solid Propellant Rocket Research," Academic Press, New York, N. Y., 1960, pp 653–672.

(247) A. D. Baer, N. W. Ryan, and D. L. Salt, "Ignition of Composite Propellants," University of Utah, AFOSR TN 59-516, March 1959 [AD 216 291].

(248) J. A. Keller, A. D. Baer, and N. W. Ryan, "The Ignition of Composite Solid Propellants by Hot Gases," The Combustion Institute Western States Section, Paper WSCI 64–27, Oct 1964; see also *Pyrodynamics*, 3, 1 (1965).

(249) J. A. Keller, A. D. Baer, and N. W. Ryan, "Ignition and Combustion of Solid Propellants," University of Utah, AFOSR 65-0936, Sept 1964 [AD 615 103].

(250) J. A. Keller, A. D. Baer, and N. W. Ryan, *AIAA J.*, 4, 1358 (1966).

(251) R. C. Mitchell, J. A. Keller, A. D. Baer, and N. W. Ryan, "Ignition and Combustion of Solid Propellants," University of Utah, AFOSR 2225, Sept 1961 [AD 274 624]; AFOSR 5316, Sept 1962 [AD 419 883]; AFOSR 64-1665, Sept 1963 [AD 605 729].

(252) R. Kling, A. Maman, and J. Brulard, "The Kinetics of Ignition of Composite Solid Propellants Submitted to High Heat Fluxes," La Recherche Aérospatiale No. 103, 1964, pp 3–10.

(253) W. R. Niessen and E. K. Bastress, "Solid Propellant Ignition Studies," A. D. Little, Inc., Cambridge, Mass., Reports AFRPL-TR-136, July 1965; AFRPL-TR-65-197, Oct 1965; AFRPL-TR-66-32, Feb 1966.

(254) H. Allen and M. L. Pinns, "Relative Ignitability of Typical Solid Propellants with Chlorine Trifluoride," NASA TN D-1533, Jan 1963.

(255) A. D. Baer and N. W. Ryan, *AIAA J.*, 3, 884 (1965).

(256) R. B. Beyer and N. Fishman, "Progress in Astronautics and Aeronautics," Vol. I, "Solid Propellant Rocket Research," Academic Press, New York, N. Y., 1960, pp 673–692.

(257) E. W. Price, H. H. Bradley, J. D. Hightower, and R. O. Fleming, "Ignition of Solid Propellants," AIAA Solid Propellant Rocket Conference, Palo Alto, Calif., 1960, AIAA Preprint 64-120.

(258) D. B. Moore and M. W. Evans, "Ignition of Solid Rocket Propellant Surfaces," Stanford Research Institute, Technical Report, May 1965.

(259) M. W. Evans, D. B. Moore, and R. C. McCarty, "Error Analysis of Data from Arc Image Furnace Ignition Experiments," AIAA Second Propulsion Joint Specialist Conference, June 1966, AIAA Preprint 66-669.

(260) W. A. Rosser, N. Fishman, and H. Wise, "Ignition of Simulated Propellants Based on Ammonium Perchlorate," Stanford Research Institute Report PU-3573, July 1965 [AD 619 067]; *AIAA J.*, 4, 1615 (1966).

(261) D. Sutton and P. C. Wellings, "The Ignition of Solid Propellants by Radiant Energy," RPE Technical Report 66/4, 1966.

(262) C. E. Hermance, R. Shinnar, and M. Summerfield, *AIAA J.*, 3, 1584 (1965).

(263) C. E. Hermance, R. Shinnar, and M. Summerfield, "Ignition of an Evaporating Fuel in a Hot Oxidizing Gas, Including the Effect of Heat Feedback," Princeton University, Aerospace and Mechanical Sciences Report No. 752, Sept 1964, AFOSR 66-0409 [AD 628 931]; *Astronaut. Acta*, 12, 95 (1966).

(264) R. F. McAlevy, S. Y. Lee, and R. S. Magee, *ibid.*, 11, 144 (1965).

may well be valid for the model experiments using shock-heated gases but is not so clearly applicable when the propellant has to supply both the oxidant and the fuel. The initial step in both the decomposition and sublimation of AP is the formation of adsorbed NH_3 and $HClO_4$ (eq 56). The further reaction of these, if no catalysts are present, requires an induction period at low temperatures, but surface diffusion on to catalyst particles can occur so that one would expect heterogeneous reactions, the catalytic decomposition of $HClO_4$[192] and the heterogeneous oxidation of fuel by an oxygen-containing product (ClO?),[221] to be important. It is significant that in experiments involving convective heating by shock-heated gases[248,251] ignition times were longer for samples covered with a thin, smooth, polymer layer than for freshly cut surfaces, while they were shorter for cut surfaces sprinkled with AP. These experiments point to the important role of AP decomposition but do not necessarily indicate that this alone is important in ignition, as in the thermal ignition theory of Hicks.[265] Although the activation energies obtained by Ryan and his group (Table IX) from thermal ignition data are close to that for thermal decomposition, other exothermic processes besides the decomposition of AP[266-268] (the oxidation of fuel by $HClO_4$ or ClO, for example) may be all-important in causing ignition. The importance of heterogeneous processes is emphasized in the theory proposed by Anderson, *et al.*,[269-273] based on studies of hypergolic ignition of propellants by F_2 and ClF_3. In normal ignition without the added powerful oxidant, it is the gaseous decomposition products of AP which are supposed to react with the solid fuel.[274]

The situation with respect to the influence of oxygen is evidently complicated. Whereas Summerfield, *et al.*,[239-245] failed to achieve ignition by conductive heating from shock-heated gases, unless oxygen was present, Kling, *et al.*,[252] using convective heating, found the ignition time τ independent of oxygen content except at high partial pressures when τ decreased with increasing oxygen content. Since copper chromite reduces[252] τ only in the range in which it is independent of oxygen mole fraction, it seems that ignition may occur by two different mechanisms. Sutton and Wellings[275] also found oxygen content to be of little importance in the ignition of AP propellants by a hot stream of gas in the temperature range 300–500°. In ignition experiments with arc image furnaces,[256] the energy required for ignition is independent of the oxygen content of the ambient atmosphere up to about 0.6 mole fraction, but it decreases sharply at higher oxygen concentrations. Copper chromite reduces the critical energy for ignition,[257] but this does not of itself necessarily indicate catalysis since the reflectivity of the propellant will be reduced drastically.[17] Sutton and Wellings[261] found that the ignition times of AP propellants (containing PIB fuel) exposed to radiant energy to be very dependent on the oxygen partial pressure especially for high fluxes and at high pressures. High-speed photography has revealed considerable vaporization of fuel before ignition[261] in oxygen and also that the flame is formed initially away from the surface.[256]

A series of particularly illuminating ignition experiments has been performed by Pearson and Sutton,[144,145,221,276] who showed[145] that when a stream of either oxygen or the vapor from 72% perchloric acid is directed on to fuels typical of those used in solid rocket propellants, ignition occurs with oxygen at about 400° but with perchloric acid at 200–300°. With gaseous fuels (NH_3 and simple hydrocarbons)[144,276] ignition was only achieved heterogeneously, for example, on a copper chromate catalyst. In their most recent paper[221] it is shown that fuels, which are ignited only with difficulty by perchloric acid vapor at 200–250°, ignite very readily in the presence of a catalyst. Moreover, the relative effectiveness of various catalysts in the ignition process is in general agreement with their effectiveness in promoting thermal decomposition of AP.[192,221,227,228]

The varied, and sometimes conflicting, data on ignition of AP propellants and the differently based theories of ignition (thermal theory of Hicks[265], the homogeneous gas-phase theory of Summerfield, *et al.*,[262,263] and the heterogeneous reaction theory of Anderson, *et al.*,[269-273] and of Williams[274]) can be reconciled when one appreciates that more than one possible mechanism of ignition exists and that different types of experiments and different types of composite propellants accentuate one or more of these mechanisms. The shortest ignition times (Table IX) are obtained in hypergolic ignition using gaseous ClF_3, and it seems tolerably certain that here the gaseous oxidant attacks the solid fuel heterogeneously, and that the heat liberated from this reaction leads to ignition.

In the experiments of Summerfield, *et al.*,[239-245] in which the propellant is heated by conduction from hot gases containing oxygen, the ignition times are also very short (of the order of 1 msec) and the surface temperatures certainly too low for the thermal decomposition of AP to play any significant part in the process. Consequently the oxidant had to be supplied externally (gaseous oxygen), and a diffusion flame supported by fuel vaporizing into the hot oxidizing gas is the start of the ignition process. This mechanism also applied to the radiant energy experiments of Sutton and Wellings[261] with oxygen, but they, like Evans, Beyer, and McCulley,[17] also used nitrogen as the ambient gas so that here the oxidant has to come from the AP. The surface temperatures[17] of ~380° for AP + copper chromite and ~260° for AP + CC + carbon (*cf.* ref 260 for more extensive data) are compatible with thermal decomposition of AP, but too low for the thermal ignition of pure AP[229] (which occurs because of heat generated in the homogeneous gas-phase oxidation of NH_3 by $HClO_4$ and/or its decomposition products). In any event the experiments of

(265) B. L. Hicks, *J. Chem. Phys.*, 22, 414 (1954).
(266) J. T. Cheng, L. S. Bouck, J. A. Keller, A. D. Baer, and N. W. Ryan, "Ignition and Combustion of Solid Propellants," University of Utah Technical Report, Sept 1965, AFOSR 40-65.
(267) R. G. Mantyla, J. T. Cheng, L. S. Bouck, J. A. Keller, A. D. Baer, and N. W. Ryan, "Ignition and Combustion of Solid Propellants," University of Utah Technical Report, Sept 1966, AFOSR 67-1901 [AD 655 781].
(268) H. Wise, S. H. Inami, and L. McCulley, *Combust. Flame*, **11**, 483 (1967).
(269) R. Anderson, R. S. Brown, and L. J. Shannon, "Ignition Theory of Solid Propellants," AIAA Solid Propellant Rocket Conference, Palo Alto, Calif., Jan 1964, AIAA Preprint 64-156.
(270) R. Anderson, R. S. Brown, and L. J. Shannon, *AIAA J.*, **2**, 179 (1964).
(271) R. Anderson, R. S. Brown, and L. J. Shannon, *Chem. Eng. Progr., Symp. Ser.*, No. 61, **62**, 29 (1966).
(272) R. Anderson, R. S. Brown, G. T. Thompson, and R. W. Ebeling, "Theory of Hypergolic Ignition of Solid Propellants," AIAA Heterogeneous Combustion Conference, Palm Beach, Fla., Dec 1963, AIAA Preprint 63-514.
(273) R. S. Brown, T. K. Wirrick, and R. Anderson, "Theory of Ignition and of Ignition Propagation of Solid Propellants in a Flow Environment," AIAA Solid Propellant Rocket Conference, Palo Alto, Calif., Jan 1964, AIAA Preprint 64-157.
(274) F. A. Williams, *AIAA J.*, **4**, 1354 (1966).
(275) D. Sutton and P. C. Wellings, unpublished results quoted by A. R. Hall and G. S. Pearson in ref 228.
(276) G. S. Pearson and D. Sutton, *AIAA J.*, **5**, 344 (1967).

Pearson and Sutton[144,145,221,276] clearly indicate the importance of heterogeneous reactions and support a mechanism in which proton transfer is followed by heterogeneous decomposition of $HClO_4$[192] and then by oxidation of fuel. Since ignition was not observed for fuels exposed to $HClO_4$ vapor when catalyst and fuel were physically separated,[221] ignition must involve oxidation of solid fuel heterogeneously by a reaction product from the decomposition of $HClO_4$ which has a relatively short lifetime (ClO radicals). Rather direct support for the heterogeneous decomposition mechanism of ignition during arc image irradiation derives from the recent experiments of Fishman[277] which have disclosed a surface exotherm preceding ignition at high heat fluxes, where the ignition time is pressure dependent. This exotherm is clearly associated with surface reactions, the heterogeneous decomposition of $HClO_4$, and the heterogeneous oxidation of fuel. As the ambient pressure is decreased, desorption of $HClO_4$ becomes competitive with surface decomposition, and the ignition time consequently increases.

For a unified treatment of the mathematical theories of ignition, the reader is referred to the survey article by Price, Bradley, Dehority, and Ibiricu.[278] A promising simplified model for ignition, which includes the essential feature of a heat flux generated at or near the surface, has been put forward by Baer and Ryan,[279] and a critical analysis of arc image ignition has been given by Ohlemiller and Summerfield.[280]

C. COMBUSTION

The deflagration of pure ammonium perchlorate has been investigated intensively in an effort to gain a basic understanding of this process and hence of the combustion of rocket propellants that contain AP as the oxidizer. These studies have proceeded along two general lines: one is the investigation of the effects of pressure, catalyst, and added radiant energy on the burning rate; the other is the study of the chemistry of the deflagration process.

The combustion of AP is usually investigated on a laboratory scale in some type of strand burner. The powdered AP, possibly with added catalyst and fuel, is compressed into long pellets or "strands" in steel presses. If sufficiently high pressures are used, the density of strands of pure AP can approach the single-crystal value. The strands are mounted vertically in a Crawford bomb and ignited on the top surface by a hot wire often with the aid of a chemical igniter. If burning is confined to the top surface, its rate of regression can be measured to give the linear deflagration rate. Although the regression of the surface can be detected electrically by embedding wires in the AP, direct observation of the combustion as well is recommended so as to ensure that linear burning conditions prevail without any spreading of the flame to the sides of the propellant. The flame has an orange tinge and occurs very close to the surface of the AP. The pressure of inert gas in the bomb is adjusted to some suitable value during combustion and the results are generally expressed by giving the dependence of the linear burning rate on pressure, $r(P)$.

(277) N. Fishman, *AIAA J.*, **5**, 1500 (1967).
(278) E. W. Price, H. H. Bradley, G. L. Dehority, and M. M. Ibiricu, *ibid.*, **4**, 1153 (1966).
(279) A. D. Baer and N. W. Ryan, *ibid.*, **6**, 872 (1968).
(280) T. J. Ohlemiller and M. Summerfield, *ibid.*, **6**, 878 (1968).

1. Products of Combustion of AP

A summary of analytical data[218,281–283] on the products of combustion is presented in Table X. The flame temperatures measured with fine thermocouples (Table X) are some 150–200° below the theoretical flame temperature of 1112° for the adiabatic decomposition of AP according to the equation

$$NH_4ClO_4 \longrightarrow {}^1/_2N_2 + {}^3/_2H_2O + HCl + {}^5/_4O_2 \qquad (72)$$

for which $\Delta H = -38.4$ kcal/mole. These discrepancies find 0 natural explanation in the presence of NO ($\Delta H_f° = 21.6a$ kcal/mole) and N_2O ($\Delta H_f° = 19.49$ kcal/mole). At high pressures less NO is formed.[282] The addition of copper chromite[218] or copper(I) oxide[282] reduces the amount of N_2O formed. Apart from this, a wide range of the usual AP catalysts (CuO, CuCl, MgO, ZnO, Cr_2O_3, MnO_2, NiO, Fe_2O_3, V_2O_5, Al_2O_3) have remarkably little effect on the product distribution.[282] It has been suggested by Levy and Friedman[218] that N_2O and N_2 result from the reduction of NO_2 and NO, respectively, by NH_2 radicals.[216–218,284]

$$NO_2 + NH_2 \longrightarrow N_2O + H_2O \qquad (73)$$

$$NO + NH_2 \longrightarrow N_2 + H_2O \qquad (65)$$

The former reaction is more probable in the cooler regions, especially in the oxidizing atmosphere of the decomposing AP, for in the flame zone NO_2 would decompose spontaneously to NO and O_2. These last two reactions (*cf.* section IX.A) are also relevant to the mechanism of decomposition of AP at lower temperatures where (73) might provide an alternative explanation for the formation of N_2O, in the low-temperature decomposition. However, its production *via* nitroxyl, eq 58, seems more probable.

2. Mechanism of Combustion of AP

While the details are far from clear at this stage, a general scheme for the chemical reactions associated with the self-sustained combustion of AP may be formulated. The surface temperature must be high enough to permit sublimation of AP as NH_3 and $HClO_4$. The $HClO_4$ decomposes in the gas phase producing initially ClO_3 and OH radicals (eq 14). Chlorine trioxide is very unstable and will decompose either bimolecularly to ClO_2 and O_2 (eq 40), or unimolecularly to ClO_2 and O atoms, or to ClO radicals and O_2 (eq 22 and 23). Either one of these routes will result in ClO radicals and possibly O atoms. (Although the bimolecular decomposition of ClO_2 is favored at low temperatures, the temperature gradient in the zone between the AP surface and the flame is so high that collisions with neutral molecules may be sufficiently energetic to supply the 57 kcal/mole needed to break the O–ClO bond.) The next stage is clearly radical attack on ammonia molecules, principally by ClO and possibly also by OH and by O atoms, to give NH_2

$$NH_3 + ClO \longrightarrow NH_2 + ClOH \qquad (62)$$

$$NH_3 + O \longrightarrow NH_2 + OH \qquad (46)$$

(281) E. A. Arden, J. Powling, and W. A. W. Smith, *Combust. Flame*, **6**, 21 (1962).
(282) K. Kuratani, "Some Studies on Solid Propellants. III. Analytical Results of the Combustion Gases," Aeronautical Research Institute, University of Tokyo, Report No. 374, Vol. 28, 1962, p 115.
(283) J. Powling, "The Combustion of Ammonium Perchlorate-Based Composite Propellants: A Discussion of Some Recent Experimental Results," ERDE Report 15/R/65, July 1965 [AD 474, 311].
(284) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **65**, 298 (1961).

Table X

Products of Combustion of Ammonium Perchlorate

Authors	Ref	Pressure, psig[a]	Catalyst	Moles of product/mole of AP: NO^{b}	N_2O	N_2	O_2	HCl	Cl_2	Measured flame temp, °C
Levy and Friedman	218	0[c]	...	0.55	0.10	0.11	0.65		0.50	
		500	...	0.31	0.11		0.75			
		1000		0.23	0.12		0.80			925
		2000		0.23	0.05		0.80			940
		1000	3% CC	0.24	0.012					950
Arden, Powling, and Smith	281	0[d]	...	0.69	0.11	0.07	0.68	0.25	0.39	970
		1050	...	0.01	0.11		0.78	0.55	0.08	930
Kuratani	282	0[e]	...	0.38	0.12	0.19	0.75		0.31	
		0	1% CC	0.35	0.14	0.19	0.75		0.33	
Powling	283	0[d]	2.9% copper chromate	0.42	0.06	0.17	0.87	0.39	0.29	900
		0[f]	2.9% $CaCO_3$	0.42	0.15	0.17	1.03	0.29	0.25	

[a] That is, the pressure in lb/in.^{2} above atmospheric pressure. [b] Appears in the products as NO_2, NOCl, NO_2Cl, or HNO_3 due to secondary reactions. [c] With the aid of radiation. [d] Preheated to 280° (250° when copper chromate present). [e] With external heating until ignition. [f] AP + $CaCO_3$ will also undergo self-sustained combustion at atmospheric pressure when preheated to only 60°; the gas phase and (liquid) surface temperatures are ~400°, and the nitrogen-containing products are N_2O (0.47), N_2 (0.17), and NO (0.09).

$$NH_3 + OH \longrightarrow NH_2 + H_2O \quad (50)$$

ClOH can react with O atoms or with OH radicals

$$ClOH + OH \longrightarrow ClO + H_2O \quad (74)$$

$$ClOH + O \longrightarrow ClO + OH \quad (75)$$

to regenerate ClO radicals. Repeated hydrogen abstraction from NH_2, or reaction of NH_2 with O_2, gives NO which may then react further as indicated above, eq 65.

Although oxidation of NH_3 by O_2, NO, or N_2O is unimportant in the thermal decomposition of AP, these reactions may well play a role at the higher temperatures prevailing in combustion.[285,286] Although NO is less reactive than O_2, it is of importance in the oxidation of NH_3 because of the ease with which it reacts with NH_2 radicals[216,217,287] (see eq 65). This must certainly be the mechanism by which N_2 is formed, since the decomposition of NO is too slow at these temperatures.[288] The only feasible source of N_2O lies in the reactions represented by eq 58 and 73; if the latter, then NO_2 must have at least a transient existence in the cooler parts of the reaction zone (*e.g.*, at the strand edges). Perhaps sampling with fine probes would help to settle this difficult question.

This mechanism of combustion of pure AP will undergo modification in the presence of catalysts or fuels. In particular, heterogeneous reactions assume a much greater importance.

Solid propellant fuels are usually polymers which at elevated temperatures undergo depolymerization and pyrolysis to produce oxidizable chemical fragments. The pyrolysis and combustion of fuels are considered in later sections.

3. *Pressure Limits*

The decomposition flame of pure AP is self-sustaining at high pressures, and added fuel is not essential to the process. Steady deflagration of AP strands cannot be achieved, however, unless the ambient pressure exceeds a minimum critical value. Friedman, *et al.*,[289] have studied the upper and lower pressure limits of combustion. The lower deflagration limit was found to be very sensitive to particle size and the temperature to which the AP strands had been preheated. Thus, at an ambient temperature of 21°, strands pressed from AP powder with a wide distribution of particle sizes could not be ignited at pressures below 45 atm. Tests with perchlorate pressed from AP particles of sizes between 74 and 105 μm gave a lower limit of 90 atm. When pellets were preheated before ignition to 70° instead of 21°, the deflagration rates were increased at all pressures, and deflagration could be maintained down to nearly 20 atm. Precooling to −18° resulted in a pellet which could not be ignited at any pressure from 70 to 270 atm.

In a subsequent study, using a much more efficient ignition technique, Friedman, *et al.*,[290] were able to accomplish steady deflagration at ambient temperatures at pressures of 22 atm. This lower limit was believed to be independent of ignition energy, since specimens ignited at the limit pressure with this powerful igniter would often burn partially before extinction. Experimental data on pressure limits are summarized in Table XI.[290–296] Certain general features of the results can be

(285) J. W. Armitage and P. Gray, *Combust. Flame*, **9**, 173 (1965).

(286) R. F. Chaiken and F. J. Cheselke, "Investigations of the Mechanisms of Decomposition, Combustion and Detonation of Solids," Aerojet-General Corp., Sacramento, Calif., Report No. 0372-01-20Q, Jan 1965 [AD 610 802].

(287) W. G. Parker and H. G. Wolfhard, "Fourth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1953, pp 420–428.

(288) H. Wise and M. F. Frech, *J. Chem. Phys.*, **20**, 22 (1952).

(289) R. Friedman, R. G. Nugent, K. E. Rumbel, and A. C. Scurlock, "Sixth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1957, pp 612–618.

(290) R. Friedman, J. B. Levy, and K. E. Rumbel, "The Mechanism of Deflagration of Pure Ammonium Perchlorate," Atlantic Research Corp., Alexandria, Va., AFOSR TN 59-173, Feb 1959 [AD 211 313].

(291) G. K. Adams, B. H. Newman, and A. B. Robins, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 693–705.

(292) L. D. Romodanova and V. I. Roschupkin, *Zh. Fiz. Khim.*, **36**, 1554 (1962); *Russ. J. Phys. Chem.*, **36**, 834 (1962).

(293) A. P. Glazkova, *Zh. Prikl. Mekhan. i Tekhn. Fiz.*, 121–125 (1963); translation available from DDC [AD 614 773, pp 193–202].

(294) A. A. Shidlovskii, L. F. Shmagin, and V. V. Bulanova, *Izv. Vyssh. Ucheb. Zaved. SSSR, Khim. i Khim. Tekhnol.*, **7**, 862 (1964); RPE Translation 18, Aug 1967.

(295) N. N. Bakhman, A. F. Belyaev, G. B. Lukashenya, and D. P. Polikarno, *Zh. Prikl. Mekhan. i Tekh. Fiz.*, 131–134 (1964); translation available from DDC [AD 615 211, pp 217–223].

(296) É. I. Maksimov, Yu. M. Grigor'ev, and A. G. Merzhanov, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 422 (1966); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 398 (1966).

Table XI

Pressure Limits for the Combustion of Ammonium Perchlorate

Authors	*Ref*	*AP*[a]	*Particle size, μm*[b]	*Strand size, mm*[b]	*Strand density, g/cm³*[b]	*Additive (concn, %)*	*Pressure limits, atm Lower*	*Upper*
Adams, Newman, and Robins	290	R		5 × 5			70	
Friedman, *et al.*	218	RG		4 × 4			22	250
	289						1[c]	
	291					Platinum black (0.025)	120	
						CC (0.0001)	22	250
						CC (0.001)	25	250
						CC (0.01)	110	260
						CC (0.1)	160	>340
						CC (1)	140	
						CC (10)	15	
						CC (50)	1	
Arden, Powling, and Smith	281	R	76–104	5 × 5			100	
							1[d]	
Romodanova and Roschupkin	292		200–350	8	1.51		53	
					1.67		48	
					1.92		38	
					1.92	Water (>2)	150	
				12.7	1.92		33	
			3–7	8			115	
			55–95				66	
			1000				24	
Shidlovskii and Shmagin	232		<100	22	1.1–1.2	Cu_2Cl_2 (1)	<1	
						MnO_2 (5)	<1	
						$KMnO_4$ (5)	<1	
Glazkova	293	AG		5	1.93		>50	250
				7			30	None
Shidlovskii, Shmagin, and Bulanova	294	RG	<100	18	1.2–1.25	Cu_2O (5)	<1	
						CuO (5)	<1	
						$MnCO_3$ (5)	<1	
						$CuCO_3$ (5)	<1[e]	
						$MnCl_2 \cdot 4H_2O$ (5)	<1[e]	
						Co_2O_3 (5)	<1[e]	
						ZnO (5)	<1[e]	
Bakhman, *et al.*	295		~15	10	0.75–1.6	Cu_2O (2)	<1	
Maksimov, Grigor'ev, and Merzhanov	296	RG, R	<50	8			110 (50, 30)[f]	
			50–63				70	
			63–100				70 (20, 20)	
			100–160				80	
			160–250				40	
			250–315				23 (18, 18)	
			315–400				20	
Hightower and Price	209	R	Single crystals				19	

[a] RG = reagent grade, AG = analytical grade, R = recrystallized. [b] In these columns, an entry is not repeated under the same author where the same information applies. [c] When irradiated with a flux of >10 cal cm^{-2} sec^{-1}. [d] Preheated to give a final flame temperature of 930°, or with added fuel. [e] If heated to 100°. No combustion at atmospheric pressure even at 100° for AP containing 5% of Fe_2O_3, Ni_2O_3 (see ref 207), Cr_2O_3, CC, CdO, or MgO. [f] Low pressure limits obtained by Maksimov, *et al.*, for AP preheated to 60 and 120° respectively, are given in parentheses in this order.

distinguished. The lower limit is predictably dependent on strand size,[292,293] being lower for strands of larger diameter. The lower limit is also decreased by increasing the strand density[292] or by increasing the particle size of the AP.[296] The lower limit can be reduced to 1 atm or lower by preheating of the AP[281,296] or by the incorporation of catalysts.[218,232,290,294,295] Methods of increasing the low-pressure limit in practical propellants have been discussed by Peterson, Reed, and McDonald.[297]

The general conditions under which a nonadiabatic flame would be expected to possess a sharp flammability limit have

(297) J. A. Peterson, R. Reed, and A. J. McDonald, *AIAA J.*, **5**, 764 (1967).

been considered by Spalding,[298] Meyer,[299] and Williams,[300] and models for solid propellant burning have been discussed by Spalding,[301] Johnson and Nachbar,[302] and Steinz and Summerfield.[303] Levy and Friedman[218,290] attributed the upper limit to convective cooling by the ambient gas and the lower limit to radiative heat loss from the burning surface of the solid. The latter hypothesis was supported by the increase in the lower limit on incorporating small amounts of platinum black or copper chromite which increase the emissivity of the AP. (With increasing concentration of CC, the lower limit at first increases and then later decreases, due to catalytic effect of CC; see Table XI and Figure 2 of ref 218.) The fact that a reduction of the lower limit occurs on supplying the surface with additional radiant energy[218] was also considered to support the heat-loss theory. However, experiments[304] involving combustion on the inner surface of a cylinder of AP gave low-pressure limits similar to those obtained in the normal strand burner, and this casts some doubt on the radiative loss theory. Also the calculations of Johnson and Nachbar[302] show that neither the heat loss from the gaseous products[305] nor that by thermal radiation from the burning surface is large enough to account for the observed low-pressure limit. The main cause of low-pressure extinction in strand burners is now considered to be convective cooling by entrained ambient gas together with a decrease in combustion efficiency at reduced pressures.[306]

Although a quantitatively successful theory has not yet emerged, a simple model for the combustion of AP may be formulated. The primary process, sublimation of AP as NH_3 and $HClO_4$, is endothermic to the extent of 58 kcal/mole. Some of the heat produced in exothermic gas-phase reactions (decomposition of $HClO_4$ and oxidation of NH_3) is fed back to the surface by conduction with presumably radiation from the hot gas playing a minor role. The burning surface of the propellant is cooled by conduction of heat into the solid, by radiative heat loss, and by the endothermic sublimation process, so that a delicate heat balance exists. As the pressure is lowered, there is a fall in the heat flux to the surface because of the pressure dependence of the exothermic gas-phase reactions and convective cooling, so that this heat balance is upset and extinguishment occurs. This can be prevented by supplying additional radiant energy to the surface,[218] by heating the AP,[296] or by the use of catalysts,[218,232,294] the latter act by allowing heterogeneous exothermic reactions to occur actually on the surface, rather than away from it in the gas phase, thus maintaining the surface temperature and lowering the lower limit.

The low-pressure limit decreases with increasing particle size,[296] that for AP particles in the range 315–400 μm being close to the single crystal value.[209] According to Romodanova and Roschupkin,[292] this is due to the variation of thermal conductivity of the strands with grain size and to the ease with which the hot gases can penetrate into the pores. The dependence of the low-pressure limit on strand density[292] supports their views. Thus not only the surface temperature, but also the temperature gradient below the surface, is of importance in determining the low-pressure limit for the combustion of AP. The possible contribution to this from subsurface thermal decomposition of AP has not yet been settled.

4. *Burning Rate*

The investigation of the linear burning rate of AP has been the subject of numerous investigations.[62,77,154,209,218,232,281–289,291,296,307–312] The principal interest has been the pressure dependence of the burning rate, but the effect of catalysts, AP particle size, strand density, and ambient temperature have all been examined. The data of the various investigators do not agree particularly well. It appears that AP at room temperature is probably burning near the limit of flammability at all pressures, and consequently erratic burning and poor reproducibility of the results are to be expected. It seems that better reproducibility is attainable with single crystals than with strands of AP since the recent data of Hackmann and Beachell[313] agree rather well with those of Hightower and Price.[209] There is general agreement that the burning rate increases with pressure (up to at least ~150 atm) but little as to the correct functional form which describes this increase. Adams, Newman, and Robins[291] fitted their results to the expression

$$r = bP^n \tag{76}$$

where r is the burning rate, P is the pressure, and b and n are constants, and found a value for the pressure exponent n of 0.5, although the rate did tend to fall with pressure near the lower limit more rapidly than according to this expression. Irwin, Salzman, and Andersen[309] used two exponents: n = 0.25 for P between 68 and 340 atm and n = 1.75 for P >340 atm. Originally the increase in the pressure exponent was attributed[309] to cracking of the surface due to shear stresses as a result of the high pressures, but in a later analysis[314] thermal stresses were regarded as responsible for cracking over the entire pressure range, these stresses becoming greater with the increasing temperature gradient near the solid surface. Arden, Powling, and Smith[281] favored the linear relationship

$$r = a + bP \tag{77}$$

(298) D. B. Spalding, *Proc. Roy. Soc.* (London), **A240**, 83 (1957).
(299) E. Meyer, *Combust. Flame*, **1**, 438 (1957).
(300) F. A. Williams, "Combustion Theory," Addison Wesley Publishing Co., Reading, Mass., 1965.
(301) D. B. Spalding, *Combust. Flame*, **4**, 59 (1960).
(302) W. E. Johnson and W. Nachbar, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 678–689.
(303) J. A. Steinz and M. Summerfield, "Solid Propellant Combustion. Mechanism Studies." Princeton University, Department of Aerospace and Mechanical Sciences, Report No. 4469, June 1965.
(304) M. D. Horton and E. W. Price, *J. Amer. Rocket Soc.*, **32**, 1745 (1962).
(305) D. B. Olfe and S. S. Penner, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 293–303.
(306) J. A. Steinz, P. L. Stang, and M. Summerfield, "Effects of Oxidizer Particle Size on Composite Solid Propellant Burning; Normal Burning, Plateau Burning and Intermediate Pressure Extinction," Princeton University, Department of Aerospace and Mechanical Sciences, Report No. 810, Oct. 1967; see also "The Burning Mechanism of Ammonium Perchlorate-Based Composite Solid Propellants," AIAA 4th Propulsion Joint Specialist Conference, Cleveland, Ohio, June 1968, AIAA Preprint 68-658.
(307) A. P. Glazkova, *Zh. Fiz. Khim.*, 37, 1119 (1963); *Russ. J. Phys. Chem.*, 37, 588 (1963).
(308) A. P. Glazkova, *Fiz. Goren. Vzryva*, No. 1, 1959 (1966).
(309) O. R. Irwin, P. K. Salzman, and W. H. Andersen, "Ninth Symposium (International) on Combustion," Academic Press, New York, N. Y., 1963, pp 358–365.
(310) L. J. Shannon and E. E. Petersen, *AIAA J.*, **2**, 168 (1964).
(311) A. F. Belyaev and G. B. Lukashenya, *Zh. Prikl. Mekhan. i Tekhn. Fiz.*, 114–120 (1963); translation available from DDC [AD 618 314, pp 183–194].
(312) A. G. Whittaker and D. C. Barham, *J. Amer. Rocket Soc.*, **32**, 1273 (1962).
(313) E. E. Hackmann and H. C. Beachell, *AIAA J.*, **6**, 561 (1968).
(314) O. R. Irwin, P. K. Salzman, and W. H. Andersen, *ibid.*, **1**, 1178 (1963).

which is also predicted by Chaiken's "thermal layer" theory[315] of the burning of composite propellants. Equations 76 and 77 can be regarded as two special cases of the empirical expression

$$r = a + bP^n \tag{78}$$

The data of Maksimov, *et al.*,[296] exhibit greater reproducibility than that of most other workers, and this is undoubtedly due to their use of an ambient temperature (T_0) of 60° (or higher) so that the AP was not as close to its limit of flammability as it is at room temperature. Over the whole pressure range their data do not obey eq 78, unless b and n are allowed to become pressure dependent, but for $P < 75$ atm, the linear relationship of Arden, Powling, and Smith[281] (*i.e.*, $n = 1$) is a fair representation of their data.

Adams, *et al.*,[291] reported a slight increase in the burning rate with particle size in the range 150–300 μm, although the earlier results of Friedman, *et al.*,[289] and of Adams, *et al.*,[316] both show a slight decrease in burning rate with increasing particle size in the range 0–105 μm. Romodanova and Roschupkin[292] found that the rates for all size fractions tended to a constant value at ~150 atm, and this same tendency was confirmed by Maksimov, *et al.*,[296] who also found that the burning rate increased with particle size (at $T_0 = 60°$) for small values of the particle diameter d but that the effect was small for $d > 250$ μm. At $T_0 = 20°$ their data showed no such clear trend although the rate again changed very slightly for $d > 250$ μm. Shannon and Petersen's data are probably the most comprehensive;[310] they found that the dependence of burning rate r on the particle diameter d at both 20 and 70° could be fitted to the expression

$$r^{-1} = k_1 + k_2d^{0.8} \tag{79}$$

which was based on a theoretical model. It is doubtful, however, if the accuracy of the data is really sufficient to distinguish small variations in the power of d. Hightower and Price[209] have shown that the data of Shannon and Petersen[310] can be represented by the empirical expression

$$\log r = k_1 - k_2d \tag{80}$$

and that the extrapolation of these isotherms to zero particle size gives burning rates in excellent agreement with their single crystal data. On the other hand, McAlevy and Lee[317] favored the expression

$$r^{-1} = k_1 + k_2d \tag{81}$$

to describe their data on the burning rate of loose mixtures of AP + polystyrene.

The burning rates of single crystals are independent of crystallographic orientation, for, within the accuracy of the data, no differences between burning rates measured normal to the m face, (210) plane, or to the c face, (001) plane, could be detected.[209,312]

Bakhman, *et al.*,[295] and Maksimov, *et al.*,[296] both found that the burning rate increased with increasing density of the AP strand. The latter authors also investigated[296] the effect of pressure, for three different particle size fractions, on the temperature coefficient of the rate of burning

$$\alpha = \frac{1}{r}\left(\frac{\partial r}{\partial T_0}\right)_P \tag{82}$$

and found that α decreases both with increasing particle size and with increasing pressure (but *cf.* ref 311).

The burning rate of AP can be altered drastically by certain additives. Friedman, *et al.*,[289,290] studied the effects of 3% copper chromite (Harshaw Chemical Co. Cu-0202; 85 wt % CuO and 15 wt % Cr_2O_3), CuO, Cr_2O_3, Fe_2O_3, MnO_2, and $NaMnO_4 \cdot 3H_2O$ on the deflagration of AP in the pressure range 40–340 atm. The greatest increase in deflagration rate was produced by copper chromite. AP with 3% copper chromite deflagrated faster than pure AP throughout the entire pressure range. The effect of concentration is complex:[290] below 0.1% CC has little effect on r, between 0.1 and 4% CC the rate at 204 atm increases from 0.36 to 5.25 cm/sec, and at higher concentrations the burning rate steadily decreases. Similar, but less marked, effects occur for AP propellants containing polystyrene[318] or polybutadiene,[319] while copper chromate has a pronounced catalytic effect on AP + PIB propellants.[320]

Glazkova[308] has studied the effect of potassium dichromate and of chromium oxide on the combustion rate of AP and of mixtures based on AP at pressures up to 1000 atm. Pellets of density approximately equal to that of pure AP were prepared from AP of particle size <250 μm and from additives (5%) with particle sizes <100 μm. The addition of the dichromate had little effect on deflagration rates at pressures less than 30 atm; for higher pressures, however, the deflagration rates of the catalyzed perchlorate increased much more rapidly than that of pure perchlorate. For pressures between 150 and 1000 atm the burning rate of the dichromate-catalyzed perchlorate was a linear function of pressure. Chromium oxide had its own peculiar pressure-dependent characteristics. At pressures up to 100 atm the effect was the same as for potassium dichromate, but with further increase in pressure the accelerating action of Cr_2O_3 decreased, and above 500 atm chromium oxide decreased the deflagration rate of the perchlorate.

Kuratani[321] studied the effect of numerous additives on the deflagration rate of an AP propellant containing 15% of a polyester fuel and 1% of the catalyst. The observed order of catalytic effectiveness was $MgO \sim Cu_2O \gg CuCl > CuO >$ copper chromite $\sim ZnO \sim Co_2O_3 \sim Cr_2O_3 > V_2O_5 > Fe_2O_3 \sim$ AP. Shidlovskii, *et al.*,[294] measured the burning rate of a large number of AP mixtures at atmospheric pressure. The mixtures contained 5% of additives and were compressed to a density between 1.20 and 1.25 g/cm³. At 20° the relative catalytic efficiency was $Cu_2O \sim CuO > Cu_2Cl_2 > MnO_2 > MnCO_3$. This order was dependent on the temperature to which the

(315) R. F. Chaiken, *Combust. Flame*, 3, 285 (1959).

(316) G. K. Adams, B. H. Newman, and A. B. Robins, "Selected Combustion Problems: Fundamentals and Aeronautical Applications," Butterworth & Co., Ltd., London, 1954, p 387.

(317) R. F. McAlevy and S. Y. Lee, "Further Studies of Ammonium Perchlorate Composite Propellant Deflagration by Means of Burner Analog Techniques," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb 1967, CPIA Publication No. 138, Vol. I, pp 95–98.

(318) M. Summerfield, G. S. Sutherland, M. J. Webb, H. J. Taback, and K. P. Hall, "Progress in Astronautics and Rocketry," Vol. I, "Solid Propellant Rocket Research," Academic Press, New York, N. Y., 1960, pp 141–182.

(319) M. Stammler and W. G. Schmidt, "Oxidizer Properties that Affect Combustion Rates of Solid Propellants," The Combustion Institute Western States Section Meeting, 1966, Paper WSCI 66-26.

(320) B. C. Howard and J. Powling, "The Use of Catalytic Surfactants in Plastic Propellants," ERDE Technical Memo 15/M/65, 1965.

(321) K. Kuratani, "Some Studies on Solid Propellants. II. Burning Rate of the Perchlorate-Polyester (Castable) Propellants," Aeronautical Research Institute, University of Tokyo, Report No. 373, Vol. 28, 1962, p 103.

specimens had been preheated. At 100°, $CuCO_3$, $MnCl_2 \cdot 4H_2O$, Co_2O_3, and ZnO promoted deflagration. Interestingly, under the reported experimental conditions, mixtures containing Fe_2O_3, NiO, Ni_2O_3, Cr_2O_3, copper chromite, CdO, and MgO, did not burn.

The presence of small quantities of NH_4Cl decreases the combustion rate and increases the observed flame temperature.[281,296] A stoichiometric mixture (70% NH_4ClO_4 and 30% NH_4Cl) could not be ignited. Maksimov, *et al.*,[296] suggested that the endothermic dissociation of NH_4Cl, occurring at a velocity approximately equal to the rate of decomposition of AP, leads to a decrease in the temperature of the reaction layer of the condensed phase. They ascribed the increase in the maximum deflagration temperature to the heat released in the oxidation of the NH_3 produced from the subliming NH_4Cl. However, the measured surface temperatures[281] for a 7.5% paraformaldehyde mixture with 5, 10, and 15% NH_4Cl were constant and, within experimental error, identical with those of other perchlorate fuel mixtures. Incorporation of 0.01% NO_2ClO_4 in AP single crystals leads to a 50% increase in burning rate.[313] Metal chelates and acetyl acetonates increase the burning rate of AP composite propellants, but basic amines reduce the burning rate and also affect its pressure dependence.[184] These results point to the importance of heterogeneous reactions involving perchloric acid in propellant combustion (section X.D.4).

When a porous plug of AP is burned in an environment of methane gas, the burning rate is apparently increased by preexposure of the AP to ^{60}Co γ-radiation.[173,322,323] The effect is not large: a 20% increase in burning rate occurs at a methane flow rate of 0.026 g cm^{-2} sec^{-1}, and at lower flow rates the effect is smaller.[173] Preirradiation actually decreases[173] the burning rate of polystyrene, but that of AP + PS mixtures is also increased slightly by exposure to γ-radiation. On the other hand, Caveny and Pittman[324] could find no indication of any effect of γ-irradiation on the burning rate of propellants containing 55–80% AP.

5. *Surface Temperature*

Friedman[325] has calculated the characteristic thickness of the thermal wave penetrating the condensed phase during combustion of a solid propellant to be of the order of 20 μm, and the height of the flame above the surface to be of the order of 10 μm, for burning rates of the order of 1 cm/sec. These extremely small distances show that the temperature gradients near the burning surface in both the condensed phase and the gas phase are extremely large and that the "surface temperature" will not only be exceedingly difficult to measure accurately, but that it may even not be conceptually well defined in the sense of being the temperature of a definite plane.

Two direct experimental methods have been used to measure surface temperatures, and both of these presumably measure an effective mean temperature of a surface of finite layer thickness which is not negligible on the scale of the temperature gradient given by the calculations by Friedman referred to above.[325] Bobolev, *et al.*,[326] and Sabadell, *et al.*,[327] have both measured temperature profiles with fine thermocouples. The Russian workers used thermocouples of tungsten + rhenium, 15 or 30 μm in diameter, and also plate-type thermocouples 3.5 or 7 μm thick. Their recorded values of the surface temperature of burning ammonium perchlorate show a decrease from ~400 to ~300° as the pressure is increased from 50 to 200 atm. Sabadell, *et al.*,[327] used noble metal thermocouples fabricated from wire 7.5 μm in diameter. They recorded surface temperatures in the range 550–650° at pressures between 1 and 15 atm for propellants containing ~25% PBAA. Strittmater and coworkers[328] synchronized a high-speed motion picture camera and a tiny thermocouple (5 μm) so that the temperature registered by the thermocouple could be measured at the instant it emerged from the surface of a burning propellant. A sharp break in the temperature profile occurred between 300 and 400° with all the composite propellants studied. This sharp increase in the slope of the temperature gradient began at about 40 μm from the surface. It was estimated that with the 5-μm junction used the thermocouple temperature was from 25 to 50° less than the temperature of the undisturbed surface.

An alternative method for the measurement of surface temperatures, developed by Powling and Smith,[63,283,329–331] utilizes the infrared emission from the burning surface. This method requires the use of an infrared wavelength at which the AP is as opaque as possible, so that the result will be a true measure of the surface temperature, affected as little as possible by radiation from the cooler subsurface layers. Also the wavelength employed should be one at which there is as little radiation as possible from the gaseous region which is at a higher temperature than the surface. Powling and Smith[329] used a special burner in which the products are rapidly removed sideways from the burning surface so as to minimize radiation from the gas flame. By this technique the surface was viewed through approximately 2 mm of flame gases so that the gas contribution at the selected wavelengths of 3.1, 7.1, and 9.0 μm (corresponding to maxima in the measured emissivity from AP) could be kept to a low value. Corrections were made for this residual gas contribution. The results[329] of these measurements show a surface temperature for both preheated AP and for AP burning in the presence of fuel vapors at 1 atm pressure, of ~495° with little dependence on burning rate over the range 0.03–0.14 cm/sec. Later measurements[330] at subatmospheric pressures showed a correlation between ambient pressure P and surface temperature T_S of the Arrhenius type with a corresponding enthalpy of 57 kcal/mole for AP + paraformaldehyde and 62 kcal/mole for AP + polystyrene. The burning rate varies linearly with ambient pressure in this pressure range and, because of the much lower

(322) T. Acker, E. Henley, R. F. McAlevy, and G. Odian, *AIAA J.*, **2**, 1165 (1964).

(323) J. E. Flanagan and J. C. Gray, *J. Spacecraft Rockets*, **3**, 135 (1966).

(324) L. H. Caveny and C. U. Pittman, "Contribution of Solid Phase Heat Release to Ammonium Perchlorate Composite Propellant Burning Rate," to be published.

(325) R. Friedman, *AIAA J.*, **5**, 1217 (1967).

(326) V. K. Bobolev, A. P. Glazkova, A. A. Zenin, and O. I. Leipunskii, *Dokl. Akad. Nauk SSSR*, **151**, 604 (1963); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **151**, 644 (1963).

(327) A. J. Sabadell, J. Wenograd, and M. Summerfield, *AIAA J.*, **3**, 1580 (1965).

(328) R. C. Strittmater, H. E. Holmes, and L. A. Watermeier, "Measurement of Temperature Profiles in Burning Solid Propellants," Ballistic Research Laboratories, Aberdeen Proving Ground, Md., Report No. 1737, March 1966.

(329) J. Powling and W. A. W. Smith, *Combust. Flame*, **6**, 173 (1962).

(330) J. Powling and W. A. W. Smith, *ibid.*, **7**, 269 (1963).

(331) J. Powling and W. A. W. Smith, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 1373–1380.

burning rates (of the order of 3×10^{-2} cm/sec), the characteristic distances in Friedman's calculation are about 1 mm rather than about 10 μm (*cf.* Figure 5 in ref 330).

In a later paper[331] the method was adapted to elevated pressures, and values in the range ~530–620° were obtained in the pressure range 3–19 atm; the general trend indicated an increase in surface temperature with pressure. More recently Powling[63] has correlated considerable data on the dependence of surface temperature on burning rate. He finds that for porous plugs of AP burning in gaseous fuels T_S varies with the mass rate of burning (at constant pressure); the data could be fitted to an Arrhenius expression with an activation energy of 29.6 kcal/mole (*cf.* ref 51). However, an activation energy of ~20 kcal/mole apparently gave a better fit to the accumulated data from linear pyrolysis (section III) and from diffusion flame experiments. Recently Jacobs and Powling[69] have shown that, when reasonable corrections are applied for the dependence of the sublimation rate on the ambient pressure, then all the combustion data[63,329,330] are consistent with an activation energy of $^1/_2\Delta H$ or ~30 kcal/mole. These results of Powling for particulate AP[63] differ from those of McAlevy and Lee,[332] who used the thermocouple method, with respect to both the range of T_S and the magnitude of the variation of T_S with burning rate.

There seems little doubt that, while both experimental methods which have been used become unreliable at high burning rates, the infrared method exploited by Powling, *et al.*, is superior to the thermocouple method because of the smaller effective dimension of the detector. The effective thickness seen by the infrared detector is 2 μm; the temperature gradient over even this small distance, while negligible at low pressures, will be about 50° at around 33 atm, and the upper pressure limit even for the infrared method is felt to be about 4 atm.

A third (and less direct) method of determining the surface temperature consists in assuming that a steady-state prevails in the conduction of heat from the surface into the AP propellant. The temperature at one point in the propellant is fixed from observations of the thickness of the layer of cubic AP caused by the phase transition which occurs at 240°. McGurk[333,334] has examined microtomed cross sections of quenched composite propellants under a microscope, using polarized light, and he has observed the presence of a phase transition zone. Beckstead and Hightower[335] measured the thickness of the phase transition layer, x_{tr}, in quenched single crystals of AP and found that x_{tr} was inversely proportional to burning rate. Thus T_S could be calculated using an integrated form of the heat conduction equation and values of x_{tr} found from the measured burning rate. Their results indicate a constant surface temperature of 560°, virtually independent of burning rate in the range 0.6–1.7 g cm^{-2} sec^{-1}.

A similar technique has been used by Selzer[336] who burned thin propellant specimens between crossed polarizing filters and photographed the light penetrating the specimen from a background lamp in order to locate the position of the phase transition surface with respect to the burning surface. A mean value of T_S of 610 ± 80° was derived, although the results cannot be very accurate since individual values deviated from the mean by as much as ±200°. Recently, Caveny and Pittman[324] have reanalyzed Beckstead and Hightower's data; using a model which includes the effects of subsurface heating, variable thermal properties, and transients after extinguishment, they calculated a surface temperature of 442 ± 30°.

One concludes inevitably from this work that although the measurement of the thickness the phase transition layer is potentially a useful method for determining surface temperatures, it cannot as yet approach the infrared method in accuracy.

6. *Observations during Burning*

Direct photography[337] of burning AP propellants showed a flame ~5 mm high at 15 atm and ~2 mm high at 120 atm. The brightness–emissivity method of measuring flame temperatures shows[318,338] that the maximum temperature is reached within 100 μm of the surface (*cf.* ref 325) for PBAA propellants burning at 4 atm pressure and that for fine AP particles (5–10 μm in diameter) the magnitude of this maximum temperature (2500°) was in good agreement with the theoretical value, although it was some 200° lower for coarse (150–200 μm) AP. This discrepancy is reduced at high pressures or on incorporating a Cu_2Cl_2 or Cu_2O catalyst.[339]

The principal emitters in propellant flames are OH, CH, NH, and CN, but excited N_2, C_2, and a carbon continuum have also been reported.[318,340–342] The presence of the CN and NH bands is assumed[318] to indicate that diffusional mixing of fuel and oxidizer occurs before oxidation and that the chemical reactions are therefore rate controlling (*i.e.*, that one has a premixed flame rather than a diffusion flame). Povinelli[343] has shown that the CN emission begins ~70 μm above the surface, reaches its maximum intensity at ~235 μm, and drops to half this intensity over ~2 mm for a PBAA propellant at atmospheric pressure.

The surface of burning solid propellants has been examined using microcinematography.[209,344–346] A mesh of individual (diffusion) flames emerging from the larger AP crystals were observed, with smaller (premixed) flames in the vicinity of these crystals.[346] Most modern composite propellants contain

(332) R. F. McAlevy and S. Y. Lee, "Progress in Astronautics and Aeronautics." Vol. 15, "Heterogeneous Combustion," H. G. Wolfhard, I. Classman, and L. Green, Ed., Academic Press, New York, N. Y., 1964, pp 583–608.

(333) J. L. McGurk, "Microscopic Observation of Propellant Combustion Surface Temperatures," First ICRPG Combustion Instability Conference, Orlando, Fla., Nov 1964, CPIA Publication No. 68, Vol. I, pp 345–360.

(334) J. L. McGurk, "Crystallographic Changes in Ammonium Perchlorate Related to Different Rates of Heating," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb 1967, CPIA Publication No. 138, Vol. I, pp 51–62.

(335) M. W. Beckstead and J. D. Hightower, "On the Surface Temperature of Deflagrating Ammonium Perchlorate Crystals," Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb 1967, CPIA Publication No. 138, Vol. I, pp 107–112; see also AIAA Fifth Aerospace Meeting, New York, N. Y., Jan 1967, Paper 67–68; *AIAA J.*, **5**, 1785 (1967).

(336) H. Selzer, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 439–446.

(337) R. W. Lawrence and A. O. Dekker, *Jet Propulsion*, **25**, 81 (1955).

(338) G. S. Sutherland, D. A. Mahaffy, and M. Summerfield, *ibid.*, **25**, 537 (1955).

(339) S. Tsuchiya, *Kogyo Kagaku Zasshi*, **65**, 843 (1962).

(340) H. Selzer, *Raketentech. Raumfahrtforsch.*, 7, 41 (1963).

(341) H. Selzer, "The Study of the Burning Mechanism of Solid Rocket Propellant," Deutsche Forschungsanstalt für Luft- und Raumfahrt, Institut für Strahltreibwerke, Hanover, Germany, Mitteilungen, 1966, pp 156–167.

(342) H. Selzer, *Astronautik*, **3**, 182 (1966).

(343) L. A. Povinelli, *AIAA J.*, **3**, 1593 (1965).

(344) R. Kling and J. Brulard, *Rech. Aeron.*, **80**, 3 (1961).

(345) K. P. McCarty, *Pyrodynamics*, **1**, 71 (1964).

(346) J. Vandenkerkhove and A. Jaumotte, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 689–693.

metals such as aluminum and beryllium. In such propellants patterns of agglomerated aluminum can be seen on the surface as the binder is gasified. These agglomerates melt and then coalesce into large aluminum drops (100–200 μm in diameter) which are then driven off by the combustion gases.[345] The combustion process in the gas phase can also be followed by microcinematographic techniques.[62] Clearly in metallized propellants the final combustion temperature in the flame must exceed the melting point of the metal oxide if full benefit is to be derived.

The most detailed results using this technique have been obtained by Hightower and Price[209] with pure AP crystals. During burning an intricate, pressure-dependent structure of ridges, troughs, and craters was observed, the depth of the latter being ~20 μm. The surface pattern on any one sample remained substantially unchanged as the surface receded, indicating that a stable three-dimensional combustion zone structure prevailed. The character of this pattern was disclosed in greater detail by microscopic examination of the quenched specimens[209,347,348] from different angles and with various types of illumination. Large portions of the surface of the quenched samples were covered by a frothy-looking layer. The hollow bubbles in the frothy layers had AP walls of thickness 2–4 μm. These observations provide convincing testimony for the presence of a surface melt.

D. COMBUSTION OF FUELS

1. *Pyrolysis of Fuels*

At low combustion pressures, the burning rate of AP with polymeric fuels of quite different thermal stabilities is remarkably constant.[63] This independence of the burning rate on the nature of the fuel is not preserved at higher pressures, however, and the burning rate becomes progressively more sensitive to the type of fuel employed as the combustion pressure increases.[349]

There is an extensive literature on the thermal degradation of polymers.[350,351] Most of these data were obtained by bulk-heating under relatively mild conditions. The need to extrapolate these data to situations of intense surface heating, such as are encountered in composite propellant burning and ignition, hybrid rockets, and atmospheric reentry, has led to some recent work on the behavior of polymers under simulated conditions.[266,352–354] A reasonable model[352] involves the depolymerization of polymer, followed by desorption of monomer from the surface. At low pyrolysis rates the apparent activation energy (~40–50 kcal/mole) is similar to that obtained in bulk degradation experiments;[350] at higher rates it decreases to 11 kcal/mole for poly(methyl methacrylate) (PMM)[252] and 12–14 kcal/mole for polystyrene (PS),[353] values which are reasonably associated with the evaporation of monomer. Although oxygen[355] does not affect the rate of gasification of PS, flowing Cl_2 or NO_2 through a bed of PS beads does do so,[353] and this indicates the need to consider chemical degradation as well as thermal degradation in composite propellant burning.

It should be pointed out that although the experiments described above are traditionally referred to as pyrolysis in the literature, the processes that are presumed to occur are depolymerization and monomer evaporation. The extent of any actual thermal decomposition (pyrolysis) which may occur prior to oxidation of the fuel in propellant burning is apparently unknown.

The infrared method[329,356] has been applied to the determination of surface temperatures of typical polymeric fuels burning in diffusion flames at 1 atm pressure. Results indicate that the surface temperatures are quite similar to that of AP so that in the burning of composite propellants, at least at pressures close to atmospheric, the surface temperature of both fuel and oxidizer is about 500°.

2. *Combustion of Fuels by Perchloric Acid*

At low pressures the flame above a composite propellant is probably a premixed flame supported by perchloric acid, ammonia, and fuel pyrolysis products.[283] A stable diffusion flame based on ammonia and perchloric acid has not been obtained,[77] but flames supported by perchloric acid and model fuels (principally, methane, ethane, and ethylene) have been studied extensively.[143,211,357–369] A decomposition flame is observed[370] when the vapor from 72% $HClO_4$ is heated to ~400°. From measurements of the burning velocity, Cum-

(347) J. D. Hightower and E. W. Price, "Two-Dimensional Experimental Studies of the Combustion Zone of Composite Propellants," ICRPG Second Combustion Conference, Nov 1965, CPIA Publication No. 105, 1966, pp 421–435.

(348) J. D. Hightower and E. W. Price, "Experimental Studies of the Combustion Zone of Composite Propellants," ICRPG/AIAA Solid Propulsion Conference, July 1966.

(349) E. K. Bastress, K. P. Hall, and M. Summerfield, "Modification of the Burning Rate of Solid Propellants by Oxidizer Particle Size Control," American Rocket Society Solid Propellant Rocket Conference, Salt Lake City, Utah, Feb 1961, Paper 1597-61; see also Princeton University, Department of Aeronautical Engineering Report No. 536, March 1961.

(350) N. Grassie, "Chemistry of High Polymer Degradation Processes," Butterworth & Co., Ltd., London, 1956.

(351) H. H. G. Jellinek, "Degradation of Vinyl Polymers," Academic Press, New York, N. Y., 1955.

(352) R. F. Chaiken, W. H. Andersen, M. K. Barsh, E. Mishuck, G. Moe, and R. D. Schultz, *J. Chem. Phys.*, **32**, 141 (1960).

(353) J. G. Hansel and R. F. McAlevy, *AIAA J.*, **4**, 841 (1966).

(354) B. Rabinovitch, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 1395–1404.

(355) R. F. McAlevy and J. G. Hansel, *AIAA J.*, **3**, 244 (1965).

(356) R. F. McAlevy, S. Y. Lee, and W. H. Smith, "The Linear Pyrolysis of Polymethylmethacrylate," The Combustion Institute, Western States Section, Spring Meeting, Denver, Colo., April 1966, Paper WSCI 66-24; see also *AIAA J.*, **6**, 1137 (1968).

(357) G. A. McD. Cummings and A. R. Hall, "Perchloric Acid Flames." III. "Some Flame Temperatures and Burning Velocities," RPE Technical Report No. 65/5, Sept 1965.

(358) G. A. McD. Cummings and A. R. Hall, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 1365–1372.

(359) G. A. McD. Cummings and G. S. Pearson, "Flames Supported by Perchloric Acid. II. The Decomposition Flame," RPE Technical Note 226, Oct 1963.

(360) G. A. McD. Cummings and G. S. Pearson, *Combust. Flame*, **8**, 199 (1964).

(361) G. A. Heath and G. S. Pearson, "The Chemical Structure of Methane-Perchloric Acid Flames," RPE Technical Memo 399, April 1966.

(362) G. S. Pearson, "Perchloric Acid Flames. IV. Methane-Rich Flames," RPE Technical Report No. 65/6.

(363) G. S. Pearson, "Perchloric Acid Flames. V. Ethylene-Rich Flames," RPE Technical Report No. 66/1.

(364) G. S. Pearson, "Perchloric Acid Flames. VI. Ethane-Rich Flames," RPE Technical Report No. 66/2, March 1966.

(365) G. S. Pearson, "Perchloric Acid Flames. VII. Mixed Fuel-Rich Flames," RPE Technical Report No. 67/3, March 1967.

(366) G. S. Pearson, "Perchloric Acid Flames. VIII. Methane-Rich Flames with Oxygen," RPE Technical Report No. 67/5, May 1967.

(367) G. S. Pearson, *Combust. Flame*, **11**, 89 (1967).

(368) G. S. Pearson, *ibid.*, **11**, 97 (1967).

(369) G. S. Pearson, *ibid.*, **11**, 103 (1967).

(370) W. Dietz, *Angew. Chem.*, **52**, 616 (1939); RPE Translation 8, Jan 1964.

mings and Pearson[359,360] deduced that the activation energy of the rate-determining step (a first-order reaction) was close to 45 kcal/mole, in agreement with the value for isothermal decomposition of $HClO_4$ which Levy[76] had associated with the rupture of the $HO–ClO_3$ bond. Premixed flames with H_2 show a temperature dependence of burning velocity which corresponds to an activation energy of 15 kcal/mole, implying that the rate-determining step, which is of second order, is not acid decomposition but rather a reaction involving radical attack. Premixed flames with methane[143,211,357,358,366,367] and other fuels[357,358,362–365,368,369] have a greater burning velocity than have flames supported by the corresponding fuel and oxygen. The burning velocity (u) reaches a maximum on the fuel-rich side and is independent of pressure, indicating a second-order reaction. The spectra of perchloric acid flames show the same band systems as the corresponding flames with oxygen, but in addition methane flames show strong "cool-flame" bands due to excited formaldehyde. Halogenated hydrocarbons such as CF_3Br are not effective inhibitors as they are for fuel + O_2 flames. Furthermore u is greater than for the $HClO_4$ self-decomposition flame. All this evidence points to the presence in the decomposition products of $HClO_4$ of a more reactive oxidizer than molecular oxygen, which can initiate radical chain processes. The following mechanism is that proposed for the oxidation of methane[211,212,221,361,366,367] with ΔH values (kcal/mole) given in parentheses.

$$HClO_4 \longrightarrow OH + ClO_3 \quad (+48.3)$$
$$ClO_3 \longrightarrow ClO + O_2 \quad (-12.8)$$
$$CH_4 + ClO \longrightarrow CH_3 + ClOH \quad (+3.6)$$
$$CH_3 + ClO \longrightarrow CH_2O^* + HCl \quad (-105.8)$$
$$CH_2 + O_2 \longrightarrow OH + [CH_2O] \quad (-50.3)$$
$$[CH_2O] \longrightarrow H_2 + CO \quad (+1.3)$$
$$ClOH + OH \longrightarrow ClO + H_2O \quad (-21.0)$$
$$ClOH \longrightarrow Cl + OH \quad (+60.3)$$
$$CH_4 + Cl \longrightarrow CH_3 + HCl \quad (-1.2)$$
$$CO + OH \longrightarrow CO_2 + H \quad (-24.9)$$
$$H_2 + OH \longrightarrow H_2O + H \quad (+4.4)$$
$$H + ClOH \longrightarrow H_2O + Cl \quad (-60.0)$$
$$H + HClO_4 \longrightarrow H_2O + ClO_3 \quad (-71.7)$$
$$CH_3 + CH_3 + M \longrightarrow C_2H_6 + M \quad (-84.1)$$
$$Cl + Cl + M \longrightarrow Cl_2 + M \quad (-58.0)$$

The key feature is the use of ClO to initiate hydrogen abstraction from CH_4. While direct proof of this step is naturally hard to come by, the ClO radical would appear to have the necessary stability[104] (unlike higher oxides of chlorine). The reaction of ClO with CH_3 is sufficiently exothermic to produce formaldehyde in an excited state, CH_2O^*, and thus to account for the cool flame bands observed.[367]

Addition of oxygen to the premixed gases of a methane-rich perchloric acid flame[143,358,366,371] results in the formation of a second flame front which has the characteristics of a methane–oxygen flame, although much of the added oxygen does react in the first flame. This observation confirms that $HClO_4$ (through formation of ClO) is a more reactive oxidizer than molecular oxygen. A two-flame structure is also observed on adding nitrogen or argon as a diluent to methane–oxygen flames.[372]

Methane–ClO_2 flames[373] have also been studied recently, and these also show a maximum velocity on the fuel-rich side and also many other similar characteristics to the perchloric acid flame systems (cool flame bands, faster than oxygen flame,[374] etc.).

3. *Combustion in Particulate Systems*

The combustion of small spheres of AP (0.6–1.5 cm in diameter) in a stream of fuel gas has been examined by Barrère and Nadaud.[375,376] The spheres, supported on wire gauze, were ignited by means of an electrically heated wire on their upper surface. The flame first spread rapidly over the surface after which the spheres burned symmetrically. With propane a decomposition flame and two diffusion flames were observed, whereas with ammonia and with hydrogen only a diffusion flame appeared. Theoretical analysis suggests[375] that the variation of the diameter d of the sphere with time, during steady burning, should obey the equation

$$1 - (d/d_0)^n = kt \qquad (83)$$

with the exponent n between 1 and 2 (see ref 51 for a more detailed discussion). In propane and ammonia $n = 2$, indicating diffusion control, but for hydrogen and hydrogen–nitrogen mixtures $n = 3$, which was not explained by the theory.[375] The burning rate constant k varied with the pressure of the gas, the velocity of the gas, and temperature, and could be increased by incorporating 1% CC in the AP spheres. The pressure exponent was about 0.6, quite similar to that for the burning rate of composite propellants.

If a stream of fuel gas is passed through a porous bed of AP,[63,283,332,377–382] then a flat flame can be stabilized over the upper surface of the AP even down to very low pressures. (The converse system, in which an oxidizing gas is passed through a bed of fuel particles, has already been discussed in connection with fuel pyrolysis.) Burger and Van Tiggelen[378] concluded that the flames with various fuels (H_2, C_2H_2, C_2H_4, CH_4, C_3H_8) were premixed rather than diffusion flames.

(371) G. S. Pearson, *Combust. Flame*, **12**, 54 (1968).

(372) A. R. Hall and G. S. Pearson, "Perchloric Acid Flames. IX. Two Flame Structure with Hydrocarbons," Twelfth Symposium (International) on Combustion, Poitiers, July 1968.

(373) R. Moreau and J. Combourieu, *C. R. Acad. Sci. Paris*, **265**, 440 (1967); RPE Translation 17, Oct 1967.

(374) P. Laffitte, J. Combourieu, I. Hajal, M. Ben Caid, and R. Moreau, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, p 941.

(375) M. Barrère and L. Nadaud, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 1381–1394.

(376) L. Nadaud, *Rech. Aerospatiale*, **108**, 39–51 (1965).

(377) J. Burger, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides*, **20**, 1 (1965).

(378) J. Burger and A. Van Tiggelen, *Acad. Roy. Belg, Classe Sci. Mem.*, **34** (3), 1–47 (1964); RPE Translation 13, Jan 1965.

(379) J. Burger and A. Van Tiggelen, *Bull. Soc. Chim. Fr.*, [12] 3122 (1964).

(380) V. R. De Tingo, "An Experimental Investigation of Ammonium Perchlorate Deflagration Utilizing the Porous Plug Burner Technique at Elevated Pressures," M.E. Thesis, Stevens Institute of Technology, June 1965.

(381) R. F. McAlevy, S. Y. Lee, V. R. De Tingo, and F. A. Lastrina, "Fundamental Studies of Composite Propellant Deflagration by Experimental Analog Techniques," The Combustion Institute, Western States Section, Spring Meeting, April 1966, Paper WSCI 66-25.

(382) R. F. McAlevy, S. Y. Lee, F. A. Lastrina, and N. A. Samurin, "Further Studies of Ammonium Perchlorate Composite Propellant Deflagration by Means of Burner Analog Techniques," AIAA 5th Aerospace Sciences Meeting, New York, N. Y., Jan 1967, AIAA Preprint 67-101.

The variation of the burning rate of AP + CH_4 with pressure is apparently quite sensitive[380,381] to fuel concentration, but for mixture ratios near stoichiometric $d \log r/d \log p \sim 0.5$ as it is for AP spheres.

Instead of passing a gaseous fuel through a porous bed, a volatile fuel can be mixed with AP in a pressed strand.[61,63,281,283,290,307,329,330,377–379,381,383–387] This represents perhaps the closest two-phase approximation to the actual composite propellant in which particles of AP (and catalyst) are suspended in a polymeric binder forming a solid–solid colloid. Temperature measurements[281,379] show that the final flame temperature is only achieved some distance downstream from the beginning of the reaction zone, even in fuel-lean conditions. Product analysis[379] confirms that this is due to some slowness in the oxidation of CO. The flames appear to be homogeneous premixed flames[283] except for coarse particle sizes where the burning rate depends strongly on the type of fuel and diffusion flames also occur.[283] Adams, Newman, and Robins[291,316] suggested a model for this type of combustion in which each AP particle supports its own decomposition flame, this being succeeded by a diffusion flame supported by the gasified fuel and the oxidant-rich products of the AP decomposition flame. The temperature of the decomposition flame, and hence the rate of sublimation of AP, is affected by heat transfer from the diffusion flame. As the pressure increases the diffusion flame moves further away from the surface so that at very high pressures the combustion rate will be that of the AP alone; conversely, at very low pressures, diffusional mixing occurs so rapidly that the flame becomes a premixed one.

At low pressures[281,283] the burning rate of AP + PF (paraformaldehyde) mixtures obeys eq 77, and for fuel-lean mixtures the pressure exponent remains unity up to $\sim$60 atm. As the concentration of PF is increased up to $\varphi = 0.66$ (where $\varphi = 1$ corresponds to a stoichiometric composition) n decreases to 0.6 ($P < 70$ atm) in agreement with observations of Adams, *et al.*,[291] for stoichiometric AP + PF mixtures.

For loose beds of coarse particles of AP + PMM (poly(methyl methacrylate)), the maximum burning rate occurs near $\varphi = 1$, but for AP + PS (polystyrene) mixtures it corresponds to $\varphi > 1$.[381,383,384] The burning rate appears to depend more sensitively on the size of the fuel particle than on that of the oxidizer,[381] but the AP particle size certainly does have an effect on the burning rate.[307] With less volatile fuels[281] gradual departures from steady one-dimensional burning occur. Premixing of oxidant and fuel vapors is facilitated if the monomeric fuel is used rather than the polymer.[307] Direct observation[386,387] of the quenched strand surface shows that at low pressures with volatile fuels, AP particles project from the surface, but at pressures higher than the low-pressure limit for self-sustained combustion, AP is consumed more rapidly than fuel, resulting in craters in the surface.

These experiments, valuable as they are, serve to emphasize the complexity of the combustion process based on solid fuel and oxidizer. Apart from pressure and initial temperature, the burning rate also depends on fuel/oxidizer ratio, the particle size of each, and the nature (volatility) of the fuel. Such pressed strand systems are thus not much less complicated than the composite solid propellants for which they represent experimental models.

4. *Burning of Composite Propellants*

A composite propellant consists of fine particles of oxidizer (usually AP) and of catalyst (*e.g.*, CC, Fe_2O_3), distributed in a polymeric fuel binder, such as polyurethan, polyisobutylene, etc. Variants include the addition of metallic particles (to increase the final flame temperature), the addition of explosive oxidizers, and the use of active binders. Alternatives to ammonium perchlorate have been suggested: these include, *inter alia*, potassium perchlorate, ammonium nitrate, nitronium perchlorate, nitrosyl perchlorate, hydrazine perchlorate, hydroxylamine perchlorate, and hydrazine diperchlorate. The early work on composite propellants has been reviewed by Geckler,[388] Huggett,[389] and Schultz, Green, and Penner;[390] a recent review is that by Hall and Pearson.[228] Various models for the deflagration of composite propellants have been proposed, and these may be discussed conveniently within the framework of the following generalized model.

In the state of steady burning, the propellant surface is at an elevated, but not necessarily uniform, temperature; if fuel evaporates more readily than oxidizer, then AP particles will project above the surface and will consequently be hotter than the patches of fuel.[54,390–392] The system is clearly self-regulating for the average linear rates of removal of oxidizer and fuel must be equal. There is impressive evidence[209] for the existence of a surface melt on deflagrating AP crystals, but this may not necessarily be true for all composites and is evidently not so for some (*e.g.*, AP + styrene polyester copolymer).[318] The presence or absence of a molten AP phase has little effect on the chemistry of the surface reactions (except in the special instances of additives like $CaCO_3$, ZnO, etc., where catalysis proceeds in the molten phase) but may have important physical consequences in restricting or even preventing penetration of hot combustion gases below the surface into holes left by volatilizing fuel.[391] Fuel pyrolysis may also proceed *via* a liquid phase consisting of depolymerized monomer.[353]

The significant condensed-phase reaction is the endothermic dissociation of AP into NH_3 and $HClO_4$. Several alternative reaction paths exist, and although one or more of these may occur predominantly or even exclusively in certain propellants at certain pressures, it would be imprudent to ignore any of them in a complete analysis. (i) Firstly, NH_3 and $HClO_4$ evaporate into the gas phase and support a decomposition

(383) N. N. Bakhman, *Zh. Fiz. Khim.*, **39**, 764 (1965); *Russ. J. Phys. Chem.*, 39, 402 (1965).

(384) N. N. Bakhman, V. V. Evdokimov, and S. A. Tsyganov, *Dokl. Akad. Nauk SSSR*, **168**, 1121 (1966).

(385) N. N. Bakhman and Yu. A. Kondrashkov, *ibid.*, **142**, 377 (1962); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **142**, 44 (1962).

(386) P. F. Pokhil and L. D. Romodanova, *Zh. Fiz. Khim.*, **39**, 294 (1965); *Russ. J. Phys. Chem.*, **39**, 152 (1965).

(387) P. F. Pokhil and L. D. Romodanova, *Teplo i Massoperenos*, **4**, 183 (1966).

(388) R. D. Geckler, "Selected Combustion Problems AGARD," W. R. Hawthorn and J. Fabri, Ed., Butterworth & Co., Ltd., London, 1954, pp 289–339.

(389) C. Huggett, "High Speed Aerodynamics and Jet Propulsion," Vol. II, "Combustion Processes," B. Lewis, R. N. Pease, and H. S. Taylor, Ed., Princeton University Press, Princeton, N. J., 1956, pp 514–574.

(390) R. Schultz, L. Green, and S. S. Penner, "Combustion and Propulsion (Third AGARD Colloquium)," M. W. Thring, J. Fabri, O. Lutz, and A. H. Lefebvre, Ed., Pergamon Press, London, 1958.

(391) W. Nachbar, "Progress in Astronautics and Rocketry," Vol. I, "Solid Propellant Rocket Research," Academic Press, New York, N. Y., 1960, pp 207–226.

(392) W. Nachbar and J. M. Parks, "A Sandwich Burner Model for the Solid Composite Propellant," Lockheed Missile Systems Division, Palo Alto, Calif., LMSD-2191, AFOSR-TN 57-418, Sept 1957 [AD 132 497].

flame around each particle.[291] (ii) Secondly, NH_3 and $HClO_4$ migrate by diffusion to catalyst particles and there undergo decomposition and oxidation.[200,291] (iii) Thirdly, fuel reacts heterogeneously with $HClO_4$, and especially with its decomposition products, specifically ClO.[221] (iv) Fourthly, diffusional mixing of fuel vapor and the oxidant-rich products of the decomposition flame supports a diffusion flame which results in the attainment of the final gas temperature.

Various individual models have stressed different features. Adams, Newman, and Robins[290] considered the essential feature to be the self-sustained decomposition flame close to the oxidizer crystal surface and followed by the diffusion flame which increased the temperature of the decomposition flame to an extent dependent on the pressure. Andersen, *et al.*,[393] based their model on the two-temperature hypothesis[54] and considered the decomposition flame to be little influenced by the diffusion flame. This model was further elaborated by Chaiken:[315] to facilitate the calculation of heat transfer to the propellant surface, the distance between the first flame zone and the surface, designated a "thermal layer," was visualized as comprising the expansive movement of premixed gases with diffusion playing no part. The thermal layer theory, which was developed originally for ammonium nitrate composites, predicts a linear dependence of burning rate on pressure and thus cannot be applicable over a wide pressure range.

The theory which has been most successful in predicting the pressure dependence of the burning rate is the "granular diffusion flame" (GDF) theory of Summerfield, *et al.*[306,318] In this theory it is the rate of chemical reaction between fuel and oxidizer in the gas phase which is emphasized. Subsurface reactions and heterogeneous surface reactions between fuel and oxidant (or its decomposition products) are specifically excluded, the only condensed-phase chemical processes of any significance being judged to be the sublimation (or pyrolysis) of oxidizer and fuel. The essential feature of the theory is that the fuel vapor is released in the form of "pockets," the average mass of which is independent of pressure but is somehow related to the mass of the oxidizer crystals, although very much smaller. The pockets of fuel vapor are then consumed at a rate which is controlled by diffusional mixing and chemical reaction. The model is amenable to an exact analysis only in two extreme situations: at low pressures molecular diffusion is rapid and the flame is essentially a premixed one; at very high pressures, chemical reaction is very rapid and the burning rate is controlled by the rate of interdiffusion. The general case of intermediate pressures is treated by assuming that the flame thickness is a weighted arithmetic mean of the thicknesses that it would have if it were (a) reaction-rate controlled or (b) diffusion controlled. These assumptions lead to the expression

$$\frac{1}{r} = \frac{a}{P} + \frac{b}{P^{1/3}} \tag{84}$$

which describes the pressure dependence of burning rate rather well over a wide range of pressures. This is understandable since the model includes the principal effect of increasing the pressure, namely the gradual transition from chemical reaction control to diffusion control of the rate of the gas-phase processes.

The GDF theory breaks down at pressures above about 100 atm when the AP particles are of intermediate size (20–250 μm) and at pressures below 100 atm for very large-sized particles (>250 μm) because the flame can no longer be regarded as one dimensional.[306] In the original GDF theory it was assumed that the reaction between ammonia and perchloric acid (arising from sublimation of AP) gave rise to a reaction which occurred very close to the propellant surface, so close in fact that the reaction could be described mathematically as occurring right at the surface. Since this reaction is occurring in an infinitely thin zone, it cannot contribute to the pressure dependence of the combustion rate, which is due to the burning of the fuel droplets in the oxidizing atmosphere of the combustion products from the ammonia oxidation reaction, through a combination of diffusion control and reaction-rate control, as just described. In a recent modified version of the GDF theory,[306] the ammonia + perchloric acid flame is allowed to have a finite thickness. Thus at low pressures (<1 atm), one has essentially two successive premixed flames, the ammonia flame close to the surface and the fuel + oxidizer products flame (reaction rate controlled because diffusion is so very rapid at these low pressures). The modified GDF theory, including an extended ammonia flame, is in good agreement with all burning rate data down to 0.01 atm.

The assumption in the GDF theory of an effectively dry, planar burning surface breaks down when propellants contain small AP particles, low AP content, or fuels that melt readily. All these factors favor the formation of a molten fuel layer which leads to a plateau in the burning rate–pressure curve and even to extinction at intermediate pressures. The effect of initial propellant temperature on the burning rate at constant pressure has been discussed in terms of the GDF model by Glick.[394] In a further elaboration a diffusion flame burning at the interface between streams of fuel and oxidant emitted from the propellant surface is envisaged.[395]

A more detailed model has recently been presented by Hermance.[396,397] This includes substantial energy release at the burning surface through a heterogeneous reaction between fuel binder and a product of the initial oxidizer decomposition process (*cf.* (iii) above). In its original version[396] the theory neglected diffusional mixing in the gas phase, but this was latter remedied (in a manner similar to that of Summerfield[318]) by postulating that the times required for mixing and for chemical reaction together determine the flame height. The onset of turbulence in the mixing zone is also discussed.[397] This theory is capable of reproducing the essential features of the burning rate *vs.* pressure curves for a wide range of propellant compositions and particle-size distributions, although the parameters needed are not accurately enough known from independent sources to provide the ultimate check on the theory. Other burning models which in-

(393) W. H. Andersen, K. W. Bills, E. Mishuck, G. Moe, and R. D. Schultz, *Combust. Flame*, 3, 301 (1959).

(394) R. L. Glick, *AIAA J.*, 5, 586 (1967).

(395) J. B. Fenn, "A Phalanx Flame Model for the Combustion of Composite Solid Propellants," Princeton University, Project Squid Report PR-114-P, April 1967; see also *Combust. Flame*, 12, 201 (1968).

(396) C. E. Hermance, *AIAA J.*, 4, 1629 (1966).

(397) C. E. Hermance, "A Detailed Model of the Combustion of Composite Solid Propellants," 17th Canadian Chemical Engineering Conference, Niagara Falls, Ontario, Oct 1967.

clude heterogeneous reactions have been considered by Smith,[398] Anderson, *et al.*,[399–401] and Bakhman and Kondrashkov,[402] and a critique of gas-phase theories has been given recently by Wenograd and Shinnar.[403]

Considerable effort has been devoted to developing a theory for the burning of an AP monopropellant, not only because of the intrinsic interest of this problem but also in the hope that such a theory would assist in understanding the burning of composite propellants containing AP as the oxidizer. Johnson and Nachbar[302,404] considered a model consisting of an unopposed heterogeneous pyrolysis process at the surface of the solid and a one-step exothermic chemical reaction in the gas phase. This type of model has also been used by Rosen,[405] but Johnson and Nachbar's treatment is more detailed and accurate than Rosen's and includes nonadiabaticity and a discussion of deflagration limits. A detailed presentation of the Johnson and Nachbar model has been given by Barrère and Williams.[62] An excellent fit[302] to the burning rate data of Friedman, *et al.*,[290] is obtained with suitable choice of parameters, namely, $E = 60$ kcal/mole for the gas-phase chemical reaction and a total heat loss from the solid equivalent to 5 cal cm^{-2} sec^{-1} from the burning surface. This latter value appears to be much too large, and the need to use such a large value detracts from an otherwise elegant theory. Other unsuspected features may be contributing to the deflagration limit. A recent suggestion[406] is that, as the pressure is lowered, the flame temperature remains constant but the energy released in the frothy surface region increases, leading to a reduction in heat transfer to the surface and consequent inability of a flame to propagate in the gases issuing from the surface.

The unopposed surface gasification process assumed by Johnson and Nachbar is also unrealistic, for it implies that the concentration of NH_3 and $HClO_4$ molecules in the gas phase at a distance of the order of one mean free path from the surface is orders of magnitude less than the equilibrium concentration. If this assumption is not justified, then some modification in the boundary conditions used would be required.

The individual models described so far have all involved some variant of laminar flame theory and, although solid pyrolysis is used as a boundary condition in the Johnson and Nachbar theory, and heterogeneous reactions are treated by Hermance and also in some other theories, in the main the solid is seen primarily as a source of material to support the flame which it does through a mass flux at a rate equal to the mass burning velocity of the gas-phase flame. At the other extreme are those theories which attribute the combustion process to condensed-phase reactions.[204,407] Particularly relevant in this respect is the discovery of a so-called "flameless combustion" which propagates through certain polysulfide composite propellants after extinguishment of the gas-phase flame by lowering the ambient pressure.[408,409] The maximum temperature in such combustion waves is $\sim 300°$, and the propagation rate is dependent on pressure and particle size even though no gas-phase flame is present. Such observations support (but do not prove) the existence of an exothermic oxidation reaction taking place at the solid surface or even just below it, and point to the need to include the corresponding heat-release term in composite propellant combustion models. Bobolev, *et al.*,[326] on the basis of temperature profiles obtained from thermocouple measurements, reported a substantial condensed-phase heat release of 80–120 cal/g for pure AP burning at pressures of 50–150 atm, but Powling[63] has pointed out this could be due to the thermal lag being greater in the gas phase than in the condensed phase. Inami, Rosser, and Wise[201] have applied the adiabatic technique to the decomposition of AP with and without added fuel and catalyst and have concluded that there is substantial heat generation from exothermic reactions in the condensed phase. Caveny and Pittman,[324] however, contend that AP subsurface reactions are not an important factor in the control of burning rates.

Merzhanov[410,411] considers that strongly exothermic solid-phase reactions will normally be accompanied by considerable dispersion of the substrate and that this dispersion has a controlling effect on the burning rate. Maksimov, *et al.*,[296] placed a metal plate a distance of 0.5–1 cm above the surface of a burning strand of AP. Microscopic examination of the cooled plate revealed adhering particles in the center of the plate and an incrustation of crystals toward the (cooler) edges. This pattern was interpreted as evidence for simultaneous sublimation and thermal decomposition, the latter resulting in the dispersion of fine particles of AP which become entrained in the gas stream.

In the light of available evidence, it is unrealistic to discount completely condensed-phase (especially surface) chemical reactions in any model of solid propellant burning, although the extent to which they may exercise a controlling effect on the burning rate of composite solid propellants is yet to be assessed.

XI. Detonation of Ammonium Perchlorate

Ammonium perchlorate is friction sensitive and can be made to explode under the usual drop-weight tests. The impact sensitivity is such that 50% of trials using a weight of 2 kg from a height of 100 cm led to explosion, the comparable height for

(398) J. M. Smith, *A.I.Ch.E. J.*, **6**, 299 (1960).

(399) R. Anderson and R. S. Brown, "Structure of the Combustion Zone in Composite Propellant Burning," First Combustion Instability Conference, Orlando, Fla., Nov 1964, CPIA Publication No. 68, Vol. I, 1965, p 343.

(400) R. Anderson and L. J. Shannon, "Role of Solid Oxidizer and Polymer Binder in Composite Propellant Combustion," First Combustion Instability Conference, Orlando, Fla., Nov 1964, CPIA Publication No. 68, Vol. I, 1965, p 329.

(401) R. S. Brown and R. Anderson, "Pressure Coupling with Chemical Mechanism in the Combustion Zone in Composite Propellant Burning," First Combustion Instability Conference, Orlando, Fla., Nov 1964, CPIA Publication No. 68, Vol. I, 1965, p 381.

(402) N. N. Bakhman and Yu. A. Kondrashkov, *Dokl. Akad. Nauk SSSR*, **168**, 844 (1966); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **168**, 349 (1966).

(403) J. Wenograd and R. Shinnar, *AIAA J.*, **6**, 964 (1968).

(404) W. E. Johnson and W. Nachbar, *Arch. Rational Mech. Anal.*, **12**, 58 (1963).

(405) G. Rosen, *J. Chem. Phys.*, **32**, 89 (1960).

(406) F. E. C. Culick, J. D. Hightower, and E. W. Price, "Combustion of Ammonium Perchlorate and the Lower Deflagration Limits," to be published.

(407) R. H. W. Waesche, J. Wenograd, and L. R. Feinauer, "Investigation of Solid Propellant Decomposition Characteristics and Their Relation to Observed Burning Rates," Second ICRPG/AIAA Solid Propulsion Meeting, Anaheim, Calif., June 1967.

(408) W. J. Most, J. Wenograd, and M. Summerfield, "Solid Propellant Combustion: Mechanism Studies," Princeton University, Department of Aerospace and Mechanical Sciences, Report No. 446 p, June 1965.

(409) J. Wenograd, W. J. Most, and M. Summerfield, "Flameless Combustion of Polysulfide Ammonium Perchlorate Composite Propellants," First ICRPG Combustion Instability Conference, Nov 1964, CPIA Publication No. 68, 1965, pp 335–336.

(410) B. I. Khaykin and A. G. Merzhanov, *Dokl. Akad. Nauk SSR*, **173**, 1382 (1967); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **173**, 295 (1967).

(411) A. G. Merzhanov, *Dokl. Akad. Nauk SSSR*, **135**, 1439 (1960).

RDX being 33 cm.[412] The impact sensitivity of AP is increased considerably by cocrystallization of certain impurities, notably $KMnO_4$ and KIO_4[412] or NO_2ClO_4.[313] Steady-state detonations with a velocity of the order of 3 mm/μsec can be set up in AP using conventional detonators and a suitable booster such as tetryl.[413] The most thorough investigation of detonation velocity as a function of density and particle size is that by Price, *et al.*,[414] who have expressed their results in terms of the equation

$$D_i = -0.45 + 4.19\rho_0 \tag{85}$$

where ρ_0 is the density in g/cm^3 and D_i is the detonation velocity (in mm/μsec) corresponding to ∞ charge diameter. D_i is obtained by linear extrapolation of plots of detonation velocity D against the reciprocal of the charge diameter. Equation 85 is valid for $1.0 \leq \rho_0 \leq 1.26$ g/cm^3; other results[413, 415–417] are in reasonable agreement with it.

The data of Price, *et al.*,[414] support a grain-burning mechanism[418] in which reaction occurs sequentially in molecular layers, propagating inward from the surface of each particle until the entire particle is consumed. It is natural to associate this surface reaction with the sublimation of AP. Andersen and Pesante[413] felt that detonation reaction times τ of the right order could be calculated by extrapolating their linear pyrolysis measurements to the detonation temperature and using the equation from the grain-burning model[419]

$$\tau = d/2r = k^{-1} \tag{86}$$

where d is the mean particle diameter, r the linear rate of regression, and k the kinetic rate constant for sublimation (see, *e.g.*, eq 10 and 11). The same theory has been used to calculate critical diamaters for detonation of composite propellants.[64,65] However, Price, *et al.*, point out[414] that two commonly used equations of state[413, 415] predict detonation temperatures differing by over 500°K and this uncertainty in T (together with the doubts about the activation energy for sublimation at high temperatures, referred to earlier in section III) would appear to make any conclusions about reaction times drawn from eq 86 rather tenuous at the present time.

Acknowledgments. Grateful acknowledgment is made to the Naval Weapons Center, China Lake, California, for their sponsorship of the preparation of this review. We are greatly indebted to Dr. G. S. Pearson of the Rocket Propulsion Establishment, Westcott, Bucks, England, for supplying us with numerous references and several translations, and for helpful correspondence. We also thank several persons, notably Dr. Edward McHale and Mr. J. D. Hightower, for allowing us to refer to their work prior to its publication, and Mrs. Joyce Kilbourne for help with the preparation of the manuscript.

(412) M. Stammler and W. G. Schmidt, *Chem. Abstr.*, **65**, 18418*e* (1966); U. S. Patent 3,269,879 (1966).

(413) W. H. Andersen and R. E. Pesante, "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp 705–710.

(414) D. Price, A. R. Clairmont, and I. Jaffe, *Combust. Flame*, **11**, 415 (1967).

(415) M. W. Evans, B. O. Reese, L. B. Seely, and E. L. Lee, "Proceedings of the Fourth Symposium (International) on Detonation," U. S. Government Printing Office, Washington, D. C., 1967, ACR-126, pp 359–372.

(416) B. O. Reese, J. H. Blackburn, L. B. Seely, and M. W. Evans, *Combust. Flame*, **11**, 262 (1967).

(417) M. L. Pandow, K. F. Ockert, and H. M. Shuey, "Proceedings of the Fourth Symposium (International) on Detonation," U. S. Government Printing Office, Washington, D. C., 1967, ACR-126, pp 96–101.

(418) H. Eyring, R. E. Powell, G. H. Duffey, and R. B. Parlin, *Chem. Rev.*, **45**, 69 (1949).

(419) W. H. Andersen and R. F. Chaiken, *J. Amer. Rocket Soc.*, **29**, 49 (1959).