Thermal Decomposition of Ammonium Perchlorate Single Crystals

P. W. M. JACOBS AND WEE LAM NG*

*Department of Chemistry, University of Western Ontario,
London 72, Ontario, Canada*

The thermal decomposition of large single crystals of pure ammonium perchlorate and ammonium perchlorate doped with Ba^{2+} or SO_4^{2-} ions has been investigated over the temperature range 220–290°C. Comparative studies were also made with compressed pellets of the pure powder and with small single crystals containing macroscopic flaws. The kinetic results were analyzed using a computer technique which permits a very detailed examination of various kinetic models. This reveals that the "induction period" ($\alpha < \sim 0.01$) is very complex and comprises a desorption step, a linear process, an exponential process, and the beginnings of an Avrami process. The latter three processes are identified with (i) the inward growth of rapidly formed surface nuclei, (ii) "branching" of surface nuclei, and (iii) nucleation in the bulk crystal. Kinetic parameters are obtained for these three processes and also for the growth of nuclei in the bulk crystal. This model fits the kinetic data over the complete range of α (0–1), or $1 \times 10^{-5} < \alpha < 1$ if the desorption step is not included. The mechanism of the reaction and possible effects on this of Ba^{2+} and SO_4^{2-} doping are discussed briefly.

Introduction

The thermal decomposition of ammonium perchlorate (AP) has been investigated extensively, and much of this work is described in three reviews (1–3). Below about 300°C, plots of fractional decomposition (α) against time (t) are sigmoid in character as is commonly so in the decomposition of solids (4, 5). Ammonium perchlorate is unusual, however, in that decomposition is incomplete, a white porous residue remaining even when the reaction rate has fallen to zero (6). Decomposition is accompanied by sublimation (6, 7). Several different equations have been used to describe the kinetics of the low-temperature reaction. The principal ones are the Prout–Tompkins equation (8)

$$\ln[\alpha/(1-\alpha)] = kt + c \tag{1}$$

used by Bircumshaw and Newman (9), the power law (4)

$$\alpha = (kt)^n \tag{2}$$

used by Bircumshaw and Newman (9) and

Schultz and Dekker (10), the contracting volume equation (4)

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

used by Schultz and Dekker (10), and the Avrami–Erofeev equation (11, 12)

$$[-\ln(1-\alpha)]^{1/n} = \bar{k}_n t \tag{4}$$

used by Jacobs and coworkers (13–15) and Herley and Levy (16, 17).

Bircumshaw and Newman (6) were the first to observe that reaction commences at discrete spots on the surface of an AP crystal. Random nucleation followed by uniform three-dimensional growth of these nuclei is the model which leads (11) to the Avrami equation

$$-\ln(1-\alpha) = (6\sigma N_0 k_2^3/V_0 k_1^3)[\exp(-k_1 t) \\ -1 + k_1 t \\ -\{(k_1 t)^2/2!\} + \{(k_1 t)^3/3!\}], \tag{5}$$

where σ is a shape factor, N_0 is the total number of potential nucleus-forming sites at $t = 0$, V_0 is the final volume of product, k_1 is the rate constant for nucleation, and k_2 the linear (assumed isotropic) rate of growth of the nuclei. In AP, the

* Present address: Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia.

Physical form	n	Range in which Eq. (4) fits the data
Small whole crystals	4	$0.02 < \alpha < 0.20$
	3	$0.20 < \alpha < 0.90$
Powder	4	$0.03 < \alpha < 0.70$
Pellet	3	$0.03 < \alpha < 0.87$
	2^a	$0.20 < \alpha < 0.89$
	2^b	$0.03 < \alpha < 0.85$
Small whole crystals	4	$0.025 < \alpha < 0.45$
	3	$0.42 < \alpha < 0.96$
Powder	4	$0.01 < \alpha < 0.90$

[a] Under products of decomposition volatile at 78°K.

[b] Under 730 Torr nitrogen + decomposition products.

"nuclei" are the porous residue, and V_0 is the final volume of residue. Equation (5) reduces to (4) under two specialized conditions: (a) $k_1 t \ll 1$, when $n = 4$ in Eq. (4) and (b) $k_1 t \gg 1$, when $n = 3$ in Eq. (4). The experimental evidence is summarized in Table I. The results of the two groups show a substantial measure of agreement. For whole crystals, $n = 4$ holds over the acceleratory period and $n = 3$ over the decay period—a classical example of the predictions based on Eq. (5). For powdered AP, $n = 4$ holds up to much higher values of α, implying that nucleation remains important right into the decay period. This is not unreasonable since the small particles would have to be nucleated individually. The values of n for pellets are not so easy to interpret. Discrepancies between the values at which $n = 4$ ceases to apply, for both crystals and powder, can be explained by the difficulty in distinguishing between even whole powers of n when graphical methods are used. When $k_1 t$ is of the order of unity, Eq. (4) ought not to hold, and the exact Avrami Eq. (5) should be used instead. And yet there appears to be no intermediate region of α marking the transition from $n = 4$ ($k_1 t \ll 1$) and $n = 3$ ($k_1 t \gg 1$), which again emphasizes the limitations of graphical procedures in kinetic analysis. We have recently developed a more powerful method of testing various kinetic models for solid state reactions, and a preliminary account of this has been given (18) together with results for pure AP pellets. In this paper, the method is applied to the

analysis of kinetic data for single crystals of pure AP and AP doped with Ba^{2+} and SO_4^{2-} ions.

It will be noted from the results in Table I that Eq. (4) was never found to hold below $\alpha = \alpha^* \simeq 0.01 - 0.03$. Thus, the equation being tested is really

$$[-\ln (1 - \alpha)]^{1/n} = \bar{k}_n(t - t_0), \quad \alpha > \alpha^*. \quad (6)$$

The period of the reaction prior to $\alpha = \alpha^*$ should be very interesting kinetically—it is termed the induction period and t_0 provides a useful quantitative measure of the induction period (15). In the course of testing various kinetic models, of which the first was the conventional Avrami model which leads to Eq. (5), it was found (18) that the induction period itself consists of three stages: (i) an instantaneous ($t < 1$ min) evolution of gas; (ii) a linear process; and (iii) an exponential process. These stages were followed by the main Avrami process described by Eq. (5). Even the Avrami Eq. (5) does not fit the data below $\alpha^* = 0.01$, showing that our previous identification of an induction period (15) was not a consequence of using the approximate Avrami (=Avrami-Erofeev) equation.

Experimental

Ammonium perchlorate powder of 99.99% purity was obtained from the Fisher Scientific Co. The only stated impurity was 0.002% by weight of ClO_3^-. This material was ground thoroughly in an agate mortar and compressed into cylindrical pellets of 94% crystal density in a manually operated press. This material is designated APP. Small plate-like crystals (APCB) ~ 10 mg in mass were kindly given to us by Dr. P. J. Herley, then at Brookhaven National Laboratory. These small crystals had been grown by slow evaporation of a saturated solution, and although they contained many visual faults, they were quite usable for decomposition studies. In order to make a detailed study of the induction period, large single crystals (APC) of good quality were required, and these were grown from solution using the technique described in another paper (19) in which conductivity measurements on these crystals are reported. These crystals were about $12 \times 12 \times 4$ mm in size, were visually glass clear, and could be cleaved readily to any desired size along the (001) and (210) cleavage planes. Crystals of AP doped with Ba^{2+} (APB) or SO_4^{2-} (APS) ions were grown by the same technique (19)

from solutions containing 1 mole% $Ba(ClO_4)_2$ or 0.1 mole% $(NH_4)_2SO_4$, respectively. Some of the crystals were analyzed amperometrically. However, the amounts of impurity incorporated were too small to be determined quantitatively, but upper limits of 0.01 mole fraction Ba^{2+} and 0.0001 mole fraction SO_4^{2-} could be fixed. Nevertheless, as the kinetic results will display, these impurities have a profound effect on the reaction rate. The thermal decomposition apparatus was conventional, the pressure of gas not condensed by liquid nitrogen being measured as a function of time using two calibrated McLeod gauges.

Results

Plots of α against t were sigmoid in character for all five samples studied, viz. compressed pellets (APP), the small single crystals (APCB), the large single crystals (APC), the Ba^{2+}-doped crystals (APB), and the SO_4^{2-}-doped crystals (APS). The decomposition of APCB was studied only in the cubic crystalline form about the phase transition which occurs at 240°C. Plots of $\alpha(t)$ for the decomposition of the other four samples at 230°C are shown in Fig. 1. It is at once apparent that the decomposition of compressed pellets is much faster than that of large single crystals and that doping both with Ba^{2+} and SO_4^{2-} ions accelerates the decomposition of single crystals. The continuous lines in Fig. 1 are not the best visual estimates through the experimental points
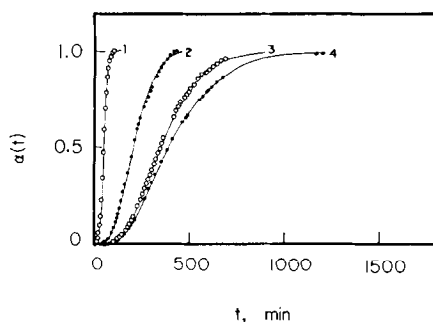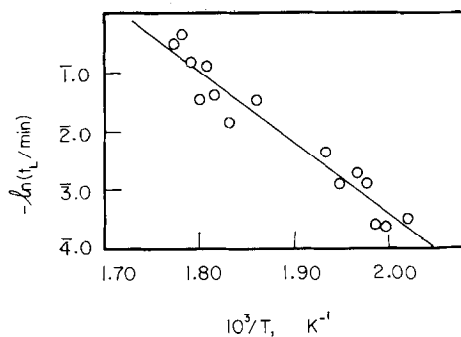

FIG. 2. Arrhenius plot for the duration of the linear process, t_L.

but actual fits to the data of the kinetic model used. The relevant equations are:

(i) Linear process

$$P = P_0 + k_L t, \quad 0 < t \leqslant t_L; \qquad (7)$$

(ii) Exponential process

$$P = C_3[\exp(k_3 t) - 1 - k_3 t], \quad t_L' \leqslant t \leqslant t_E; \qquad (8)$$

(iii) Avrami process

$$-\ln(1 - \alpha) = C_1[\exp(k_1 t) - 1 + k_1 t \\ - \{(k_1 t)^2/2!\} + \{(k_1 t)^3/3!\}], \quad t \geqslant t_A. \qquad (9)$$

C_1 and C_3 are constants for a given sample at constant temperature; k_L, k_1, k_2, and k_3 are the rate constants for the linear process, for nucleation, for growth, and for branching, respectively; P_0 denotes the pressure of gas evolved in the very rapid desorption process. Actually, three models based on these equations were tested (18):
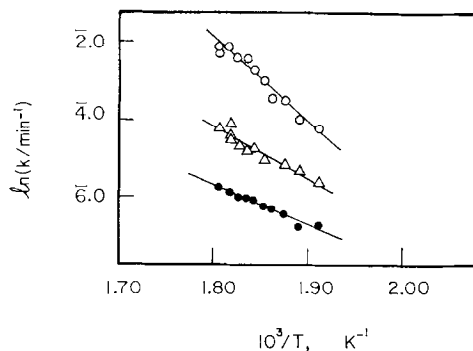

FIG. 1. Plots of fractional decomposition α against time t for the thermal decomposition of ammonium perchlorate at 230°C. Curve 1 is for a pellet of pure AP; curve 2 is for a Ba^{2+}-doped single crystal; curve 3 is for a SO_4^{2-}-doped single crystal, and curve 4 is for a large single crystal of pure AP.

FIG. 3. Arrhenius plots for small single crystals of ammonium perchlorate above the transition point. ● represent $\ln k_1$, where k_1 is the rate constant for nucleus formation; △ represent $\ln k_2$, where k_2 is the rate constant for nucleus growth; ○ represent $\ln k_3$, where k_3 is the rate constant for branching of surface nuclei.
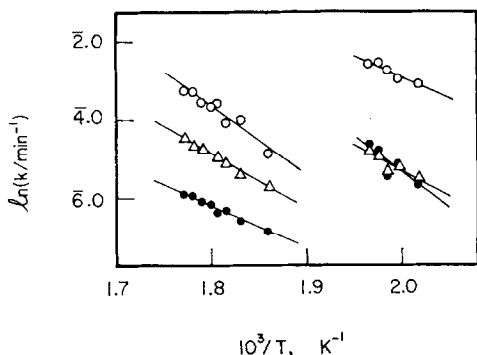
FIG. 4. Arrhenius plots for large single crystals of pure ammonium perchlorate. Symbols are defined in the caption to Fig. 3. Note the discontinuities at the transition point.

FIG. 6. Arrhenius plots for single crystals of ammonium perchlorate doped with SO_4^{2-} ions. Symbols are defined in the caption to Fig. 3.

$t_L = t_E = t_A$, $t_L = t_L' < t_E = t_A$, and $t_L = t_L' < t_A < t_E$, but only the third one gave satisfactory fits over the whole range of α. This model contains ten parameters, values for which were found by computer fitting the $\alpha(t)$ data to Eqs. (7–9) using a nonlinear least-squares program based on the Marquardt algorithm (20). Since reasonable estimates for four of these parameters, P_0, k_L, t_L, and P_A (=final pressure evolved in the Avrami process), could be determined by preliminary graphical analysis, the least-squares (LS) fitting was first carried out with these four parameters fixed and the other six parameters variable. When optimum values for these had been found, the LS fitting was continued with all ten parameters variable. The quality of the fits over the induction period cannot be judged from Fig. 1 but is displayed in Ref. (18) in figures with 300 and 4000 times the scale used for α in Fig. 1.
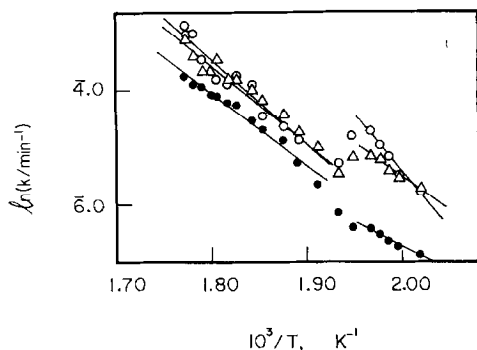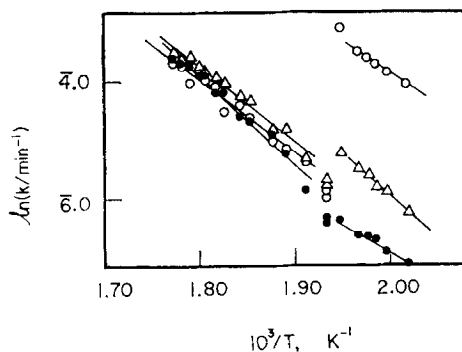
An Arrhenius plot for t_L for APC is shown in Fig. 2. Arrhenius plots for the rate constants k_1, k_2, k_3 for APCB, APC, APB, and APS appear in Figs. 3–6. The lines shown are linear LS fits to the data, separate analyses being made for results above and below the transition point, data very close to the transition point being omitted. The lines show accurately the points used in the LS fits. The activation parameters are given in Tables II and III. For APCB, the linear process was too brief and the temperature range used too short for reliable estimates of E_L and A_L to be obtained.

Discussion

The Linear Process

The initial pressure rise in the vacuum system to a value P_0 on commencing decomposition is attributed by us to desorption of permanent gases

FIG. 5. Arrhenius plots for single crystals of ammonium perchlorate doped with Ba^{2+} ions. Symbols are defined in the caption to Fig. 3.

TABLE II

ARRHENIUS PARAMETERS FOR THE LINEAR PROCESS DETERMINED FROM LS FITS TO PLOTS OF $ln\,t_L$ AGAINST T^{-1}[a]

Sample	E_L/kcal mole^{-1}	$Log(A_L$ min$^{-1})$
APP	18.9 ± 2.3	6.1 ± 0.8
APC	28.1 ± 2.1	9.1 ± 0.8
APCB	—	—
APB	26.5 ± 4.6	8.4 ± 1.7
APS	23.9 ± 2.8	7.3 ± 1.0

[a] The errors quoted for the parameter estimates are the marginal standard deviations (21).

TABLE III

ARRHENIUS PARAMETERS FOR THE NUCLEATION (k_1), GROWTH (k_2), AND BRANCHING (k_3) PROCESSES IN THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE[a]

Sample	Crystal form[b]	E_1	Log A_1	E_2	Log A_2	E_3	Log A_3
APC	o	37.0 ± 14.4	13.9 ± 6.3	24.9 ± 9.1	8.6 ± 4.0	22.1 ± 5.5	8.4 ± 2.4
APCB	o	—	—	—	—	—	—
APB	o	17.0 ± 1.7	4.5 ± 0.8	22.6 ± 3.1	7.5 ± 1.3	41.0 ± 4.9	15.5 ± 2.1
APS	o	22.3 ± 2.2	6.7 ± 1.0	28.5 ± 2.7	9.9 ± 1.2	21.7 ± 1.0	7.8 ± 0.4
APC	c	22.1 ± 1.5	6.0 ± 0.6	28.5 ± 1.6	9.1 ± 0.6	35.0 ± 4.6	12.2 ± 1.8
APCB	c	20.4 ± 1.1	5.6 ± 0.4	27.5 ± 2.8	9.0 ± 1.2	43.7 ± 2.4	16.4 ± 1.0
APB	c	25.4 ± 1.2	8.2 ± 0.5	24.5 ± 1.5	8.1 ± 0.6	29.3 ± 2.2	10.0 ± 0.9
APS	c	30.5 ± 1.7	10.3 ± 0.7	25.3 ± 1.5	8.5 ± 0.6	24.8 ± 1.6	8.0 ± 0.7

[a] The units of A are min^{-1} and E are kcal/mole. The errors quoted for the parameter estimates are the marginal standard deviations (21).

[b] o = orthorhombic, c = cubic.

(nitrogen, oxygen). This view is strengthened by the fact that the initial gas evolution occurs very rapidly within 1 min of dropping the crystal into the reaction vessel and that no time dependence outside this range was ever observed. Doubtless, water is also desorbed but would not have been recorded. No significance as to the subsequent thermal decomposition is attached to P_0; it is merely a necessary parameter that must be introduced in order to fit the decomposition curves over the whole range of α.

The activation energy for the linear process was determined from t_L (e.g., Fig. 2) because values of the rate constant k_L in Eq. (7) showed a tremendous scatter. Three models for the linear process were considered, all based on random nucleation at N_{0s} potential nucleus-forming surface sites. One knows from direct microscopic observation (22) that nucleation commences first on the surface of single crystals and that the nuclei are approximately circular in shape and remarkably uniform in size. This would imply rapid surface growth up to a limited size after which the nuclei penetrate more slowly into the interior of the crystal. In general, if nucleation occurs randomly at N_0 sites with rate constant k_1 and $G_1(x_1')$ is the rate of growth in the x_1 direction at time $t = x_1'$ then the size of a nucleus which commenced growth at $t = t'$ is, at time t,

$$v(t, t') = \sigma \int_{t'}^{t} G_1(x_1') dx_1' \int_{t'}^{t} G_2(x_2') dx_2' \times \int_{t'}^{t} G_3(x_3') dx_3', \quad (10)$$

where σ denotes the shape factor. The total fractional decomposition volume of all nuclei is then

$$\bar{V}(t) = V(t)/V(\infty) = \int_0^t v(t, t')[dN/dt]_{t=t'} dt', \quad (11)$$

and this is just equal to α if overlapping of growing nuclei is neglected, as it can be for surface nuclei (see the photographs in 22). If the rate of growth into the interior of the crystal is constant, $G_1(x_1') = k_{21}$, and much smaller than that in the surface of the crystal ($k_{21} \ll k_{22} \sim k_{23}$) and assuming random nucleation

$$dN/dt = k_1 N_{0s} \exp(-k_1 t),$$

then Eq. (11) yields

$$\bar{V}(t) = (\sigma N_{0s} k_{21}/k_1)\{\exp(-k_1 t) - 1 + k_1 t\}, \quad (12)$$

which for $k_1 t \gg 1$ becomes

$$\alpha = \sigma N_{0s} k_{21} t. \quad (13)$$

This equation is of the appropriate form to describe the linear process, Eq. (7), and identifies the experimental rate constant k_L with $\sigma N_{0s} k_{21} P_F$, where P_F is the final pressure. Thus, we conclude that the linear process is explained satisfactorily by the penetration of nuclei of approximately constant area into the bulk from the surface and that surface nucleation is instantaneous or at least very rapid.

The irreproducibility of k_L is explained by it containing the factor N_{0s} which will be very structure sensitive if nucleation occurs, as seems most likely, at defect sites. However, if the nuclei only penetrate to a certain depth which is roughly independent of temperature and then cease growing, Eq. (7), then t_L will be $\propto k_{21}^{-1}$, and so the activation energy for inward growth of surface nuclei will be obtained from a plot of $-\ln t_L$ against T^{-1}. The cessation of the linear process at t_L was checked by allowing the linear process to continue rather than terminate at the beginning of the exponential period (i.e., $t_L > t_L'$). Satisfactory fits could not, however, be obtained. The values for the Arrhenius parameters in Table II show that nucleation, quite understandably, is easier in compressed pellets than in large single crystals. The mean activation parameters for APC, APB, and APS are $E = 26.2$ kcal/mole and $\log(A \ min^{-1}) = 8.3$. There are evidently no effects on k_{21} which can be ascribed to cation or anion doping when account is taken of the estimated errors in the parameters.

The Exponential Process

The linear stage is succeeded by one in which the extent of reaction increases exponentially with time. (There are two other terms besides the exponential one in Eq. (8), but for brevity we refer to this stage as the "exponential process".) An exponential time dependence implies branching of nuclei (4), never a very favored mechanism in solid state decompositions. However, AP may be one of few materials in which a physical realization of something very like nucleus branching has been identified (22). As the surface nuclei cease growth, new nuclei appear. These new nuclei seem to be adjacent to one another like beads on a string and are strongly aligned in directions which have projections along [$\bar{1}$24] and [$\bar{1}$2$\bar{4}$] on (210) (Figs. 6f, 7a, and 7b of Ref. 22). Two branches of these nuclei invariably seem to originate from a single surface nucleus, and it is this stage of nucleus development which seems to correspond with the exponential stage in the kinetics.

The activation energy for branching in the orthorhombic phase of APC and APS is 22 kcal/ mole but higher for APB. We would not wish at this stage to speculate on possible reasons why Ba^{2+} ions should inhibit the branching process, but a first step would be to see if the dislocation properties of APC and APB showed any differences. Such an investigation is planned.

The Avrami Process

The bulk reaction is associated with the formation of small spherical holes that occur in bands which are aligned principally along the [010] direction (22, 23). These holes appear to have roughly the same size of about 2 μm in a crystal which has been decomposed at 217°C for 225 min ($\alpha = 0.15$]. The holes are embedded in a matrix of residue forming a coral-like structure, and it is this aggregate which forms the nucleus, at least in the Avrami sense. [Previously (2), the holes were called nuclei and the aggregates called decomposition centers, but this is now seen to be a poor nomenclature, and the original Russian terminology (23) is to be preferred.] The growth of these nuclei is anisotropic so that they appear, when viewed from the (001) face, as ellipsoids of revolution. The derivation of the Avrami equation does not require that growth be isotropic— only that the growth rate in each of three principal directions be constant and that nucleation be random (24). In view of the pronounced alignments of the internal nuclei, nucleation is not random in AP, taking the crystal as a whole. However, nucleation will occur randomly at the potential nucleus-forming sites within the band, and this may be a sufficient condition for the Avrami equation to be satisfied, i.e., nucleation is random in time, but the nuclei are not uniformly distributed in space. The values of E_2 in Table III do not reveal any significant effect due to doping with Ba^{2+} or SO_4^{2-}. The mean values of the activation energy for growth, E_2, are 25.3 kcal/mole for orthorhombic crystals and 26.5 kcal/mole for the cubic modification. These values are again equal within the estimated errors in the parameters so that an overall mean value of 26.0 kcal/mole may be associated with the growth of nuclei in the bulk. The limits on E_1 for APC are extremely large and if we omit that value and average the other two results for the orthorhombic phase, we arrive at a mean value of $E_1 = 19.6$ kcal/mole for orthorhombic crystals. The mean of the three values of E_1 for the cubic phase of APC, APCB, and APB is 22.6 kcal/mole, and the difference between this value and the orthorhombic mean is again not significant when account is taken of the standard deviations. However, that for cubic APS is significantly higher at 30.5 kcal/mole. From Figs. 4 and 5, we note that for both APB and APS, there is a slight increase in k_1, a decrease in k_2, and a large decrease in k_3 on passing through the transition

point, whereas for APC there is a large decrease in k_1 as well as decreases in k_2 and k_3. The detailed reasons for these changes are not understood at present.

Effects of Doping

The effects of added Ba^{2+} or SO_4^{2-} on the thermal decomposition of AP may be considered either energetically or phenomenologically. Summarizing the previous discussion of activation energies in Tables II and III, we may say that E_{21} and E_2 are unaffected by doping, that E_1 is larger for APS, and that E_3 is larger for APB. One's first impulse is to look for some correlation involving vacancies. However, the first important step in the thermal decomposition of AP is proton transfer (*25*)

$$NH_4^+(s) + ClO_4^-(s) \rightleftharpoons NH_3(a) + HClO_4(a). \quad (14)$$

Here (s) denotes ions at special sites, either the actual surface or internally at dislocations, and (a) an adsorbed molecule on either the external of an internal surface. Recently, the electrical conductivity of APC, APB, and APS has been studied (*19, 26*), and it was concluded that the dominant feature is the transfer of protons from NH_4^+ ions to $NH_3(a)$ or $H_2O(a)$ to give a proton defect (NH_3 molecule on a normal lattice cation site) which is responsible for the proton conductivity. Vacancies therefore appear to play a very small part in the proton transfer process. We must therefore search for possible chemical effects. SO_4^{2-} ions will act as excellent proton traps and thus inhibit the formation of free perchloric acid molecules. $HClO_4$ acts as a positive catalyst to the decomposition, but almost certainly this role is an indirect one because it aids the removal of NH_3 (by producing products—Cl_2 for instance— that react with NH_3), a negative catalyst (*15*). Almost certainly, NH_3 acts by suppressing the equilibrium (*14*). Thus, any other species that removes protons cuts down on the amount of $HClO_4$ and therefore indirectly enhances the NH_3 concentration and retards the reaction. Thus, E_1 might be expected to be increased by the presence of SO_4^{2-}. Ba^{2+} does not alter E_1 but shortens the induction period substantially (Fig. 1). One might suggest that NH_3 molecules complex with Ba^{2+} ions to some extent, even though stable complexes of Ba^{2+} with NH_3 are unknown, as they do with Ca^{2+}, for example. If this is so, Ca^{2+} should be an even more effective catalyst. If Ba^{2+} ions act by trapping NH_3, then they facilitate, but do not affect the energetics of,

the proton transfer reaction, and so the reaction rate is increased but E_1 unaltered. The same effects are noted for the surface reaction where SO_4^{2-} increases t_L but Ba^{2+} decreases t_L.

The overall effects of the two added impurities are seen most clearly in Fig. 1 where SO_4^{2-} hardly affects the induction period but increases the maximum rate somewhat, whereas Ba^{2+} decreases the induction period and also accelerates the main reaction markedly. However, the detailed kinetic analysis of this paper shows that the term "induction period" may include several different processes: surface nucleation, growth of surface nuclei, branching processes, and nucleation in the bulk and that it is an extremely complex business to sort out the effect of some reaction parameter, like the concentration of an impurity, without consideration of the detailed mechanisms.

Acknowledgment

References

1. A. R. Hall and G. S. Pearson, *in* "Oxidation and Combustion Reviews" (C. F. H. Tipper, Ed.), Vol. III, No. 2, pp. 129–239, Elsevier, Amsterdam (1968).

2. P. W. M. Jacobs and H. M. Whitehead, *Chem. Rev.* **69**, 551 (1969).

3. A. G. Keenan and R. F. Siegmund, *Quart. Rev.* **23**, 430 (1969).

4. P. W. M. Jacobs and F. C. Tompkins, *in* "Chemistry of the Solid State" (W. E. Garner, Ed.), Chap. 7, Butterworths, London (1955).

5. D. A. Young, "Decomposition of Solids," Pergamon Press, Oxford (1966).

6. L. L. Bircumshaw and B. H. Newman, *Proc. Roy. Soc.* (*London*) A227, 115 (1954).

7. P. W. M. Jacobs and A. Russell-Jones, *J. Phys. Chem.* **72**, 202 (1968).

8. E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.* **40**, 488 (1944).

9. L. L. Bircumshaw and B. H. Newman, *Proc. Roy. Soc.* (*London*) A **227**, 228 (1955).

10. R. D. Schultz and A. O. Dekker, "Sixth Symposium (International) on Combustion," p. 618, Reinhold, New York (1957).

11. M. Avrami, *J. Chem. Phys.* **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).

12. B. V. Erofeev, *Compt. Rend. Acad. Sci. URSS* **52**, 511 (1946).

13. A. K. Galwey and P. W. M. Jacobs, *Proc. Roy. Soc.* (*London*) A **254**, 445 (1960).

14. P. W. M. JACOBS AND A. R. T. KUREISHY, "Eighth Symposium (International) on Combustion," p. 672, The Williams and Wilkins Co., Baltimore MD (1962).

15. J. V. DAVIES, P. W. M. JACOBS, AND A. RUSSELL-JONES, *Trans. Faraday Soc.* **63**, 1737 (1967).

16. P. J. HERLEY AND P. W. LEVY, *Nature (London)* **211**, 1287 (1966).

17. P. J. HERLEY AND P. W. LEVY, *J. Chem. Phys.* **49**, 1500 (1968).

18. P. W. M. JACOBS AND W. L. NG, *in* "Reactivity of Solids" (J. S. Anderson, M. W. Roberts, and F. S. Stone, Eds.), pp. 398–410, Chapman and Hall, London (1972).

19. P. W. M. JACOBS, F. E. LOVATT, AND W. L. NG, *Can. J. Chem.* **50**, 3154 (1972).

20. D. W. MARQUARDT, *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).

21. W. C. HAMILTON, "Statistics in Physical Science," pp. 129–132, The Ronald Press, New York (1964).

22. P. J. HERLEY, P. W. M. JACOBS, AND P. W. LEVY, *Proc. Roy. Soc. (London)* A **318**, 197 (1970).

23. A. V. RAEVSKII AND G. B. MANELIS, *Dokl. Akad. Nauk SSSR* **151**, 686 (1963).

24. P. W. M. JACOBS, *in* "Materials Science Research Vol. 4" (T. J. Gray and V. D. Frechette, Eds.), Chap. 3, Plenum Press, New York (1969).

25. P. W. M. JACOBS AND A. RUSSELL-JONES, *AIAA J.* **5**, 829 (1967).

26. P. W. M. JACOBS AND W. L. NG, *J. Phys. Chem. Solids* **33**, 2031 (1972).