SUBLIMATION OF AMMONIUM PERCHLORATE

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ABSTRACT

The sublimation of ammonium perchlorate has been investigated using simultaneous differential thermal analysis and thermogravimetric analysis. Critical evaluation of isothermal kinetics of data obtained by thermobarogravimetric technique indicate that the kinetics are consistent with an expression for a contracting cylinder rather than a contracting sphere model. The activation energy for sublimation obtained experimentally is in good agreement with that derived from the Schultz–Dekker theory $(18 \pm 2 \, \text{kcal} \cdot \text{mole}^{-1})$. An analogy of the sublimation process in ammonium perchlorate to that in ammonium halides is also presented. It is shown that a previously reported value of $30 \, \text{kcal} \cdot \text{mole}^{-1}$ for the activation energy was obtained under conditions where decomposition dominated.

INTRODUCTION

Quantitative measurements on the sublimation of ammonium perchlorate (AP) were first made by Bircumshaw and Phillips[1]. Because AP decomposition is a competing process, they first decomposed 30% of the AP at low temperatures and then studied the rate of sublimation in vacuum from 260 to 320°C by a weight loss technique. The activation energy is reported to be $21.5 \pm 2.8 \, \text{kcal} \cdot \text{mole}^{-1}$. They advocated proton transfer as the rate determining step in the sublimation process. Later Inami *et al.*[2] using the transpiration method studied the dissociation pressure of AP and concluded that AP undergoes congruent dissociative sublimation by the process

$$NH_4ClO_4(s) \rightleftharpoons NH_3(g) + HClO_4(g)$$

with a heat of dissociation of $58 \pm 2 \, \text{kcal} \cdot \text{mole}^{-1}$. These data show a very reasonable analogy to the sublimation process in ammonium halides. Chaiken *et al.*[3] experimentally determined the Arrhenius rate parameters for the sublimation of ammonium halides and noted that the activation energy increases linearly with increasing molecular weight and is approximately one-third the heat of sublimation. Similarly from the above data the activation energy for the sublimation of AP is one third of its heat of dissociation and is proportional to its molecular weight when compared with the ammonium halides.

However, Jacobs and Rusell-Jones[4] have recently remeasured the activation energy for the sublimation of AP, using the same approach as that of Bircumshaw and Phillips[1], and found the value of the activation energy to be 30 kcal·mole[-1]. They analyzed their vacuum sublimation data using the contracting sphere relation. By overlooking the kinetics of the processes which lead to the proton transfer they argued that the value of their activation energy was correct since it was one half of the heat of sublimation. They discarded the value of Bircumshaw and Phillips[1] of 21 kcal·mole[-1] based on the fact that it was derived from a limited study. Guirao and Williams[5] have, since then, discussed theoretically various models for the sublimation mechanism of pure AP and as a result have suggested that the results of Jacobs and Russell-Jones[4] on the sublimation of AP may be influenced by continuing low temperature decomposition. The results of Jacobs and Russell-Jones also make the analogy between the sublimation parameters of AP and of other ammonium halides invalid. To help clarify this discrepancy, we have studied the thermal decomposition as well as the sublimation of AP simultaneously from 200 to 380 °C using the thermobarogravimetric (TBGA) technique[6]. This has been supplemented by a calculation of the activation energy based on the Schultz–Dekker linear theory[3] for sublimation.

EXPERIMENTAL

The apparatus used in this work has been described previously[6]. Essentially it consists of a Mettler thermoanalyzer to which is connected a M.K.S. Baratron differential pressure gauge on the gas outlet system. From a knowledge of the weight loss of the sample, the effective leak rate of the system and the pressure, the reactive contributions of sublimation and conventional decomposition to the total weight loss could be ascertained. Analytical grade AP obtained from Fisher was recrystallized once from distilled water. All samples used were of one particle size range (88–125 μ), except for the experiments done on single crystals.

RESULTS AND DISCUSSIONS

DTA and TGA

Any study of the reactivity of AP to heat has to define the exact experimental conditions so as to clarify whether the process under investigation is sublimation, decomposition or both. This can be done by simultaneous differential thermal analysis (DTA), thermogravimetric analysis (TGA) and gas pressure measurements. As can be seen from Figs. 1, 2 and 3, in one atmosphere of inert gas such as He or N_2 (the actual data were taken both in He as well as in air; the data in air are presented to reproduce Jacobs and Russell-Jones' experimental conditions) there is virtually no sublimation; all AP decomposes into gaseous products, exemplified by the exotherms on the DTA trace and the quantitative balance between the gas pressure and the weight lost. Below 20 torr there is no decomposition; all the AP sublimes as shown by
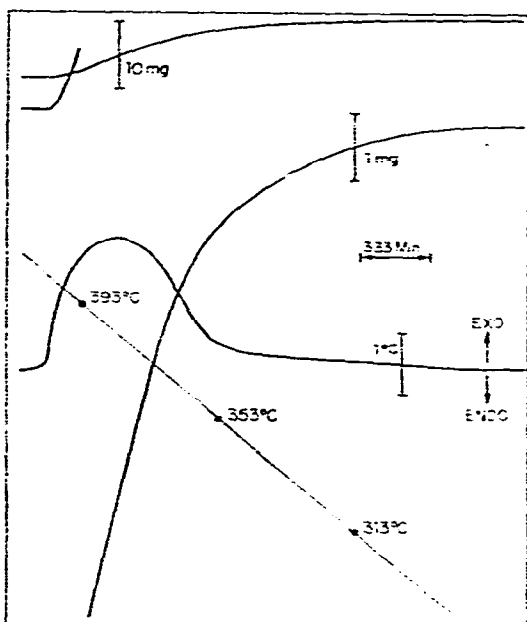
Fig. 1. Simultaneous DTA/TGA for ammonium perchlorate under one flowing atmosphere of air using a heating rate of $6°C \cdot min^{-1}$. The crystal change endotherm at 240°C does not appear in the figure due to the temperature scale used.

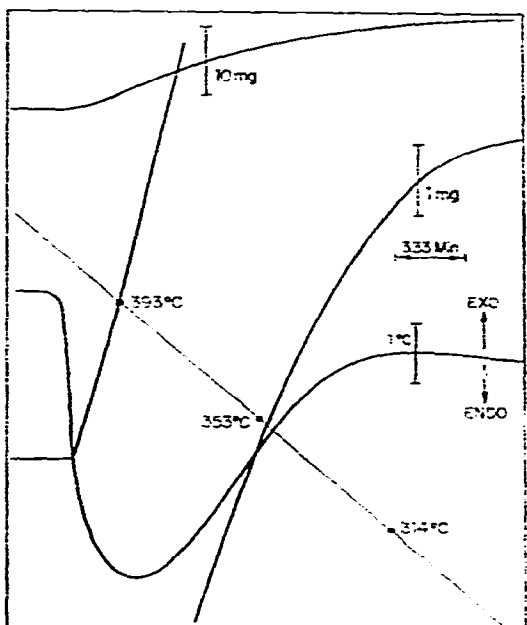Fig. 2. Simultaneous DTA/TGA for ammonium perchlorate under 10^{-4} torr atmosphere using a heating rate of $6°C \cdot min^{-1}$. The sublimation endotherm is clearly seen under these conditions.

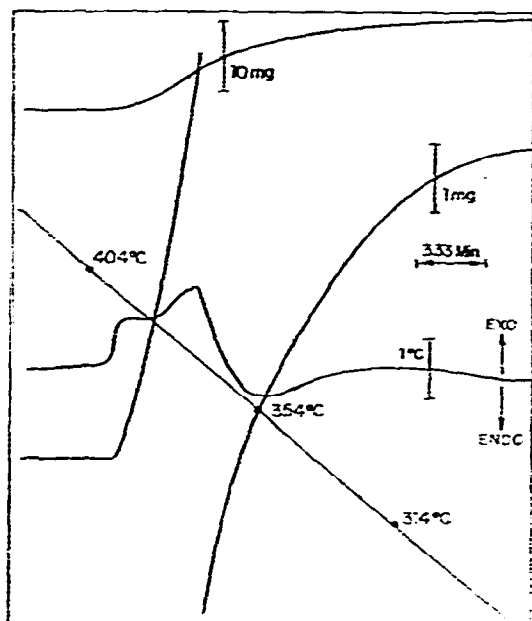Fig. 3. Simultaneous DTA/TGA for ammonium perchlorate in a static air atmosphere of 20 torr using a heating rate of $6°C \cdot min^{-1}$. Under this condition a composite exotherm–endotherm is displayed.

the typical sublimation endotherm and lack of gas pressure increase. Further, if the sublimed product is dissolved in water and recrystallized there is very good agreement between the initial weight of AP and the sublimed yield. Between these two extremes, one sees both sublimation and decomposition (Fig. 3). The DTA likewise shows both an exotherm and an endotherm.

For zero order or fractional order processes such as sublimation it has been found empirically and under certain restrictions justified theoretically[7] that the weight lost, W, as determined by TGA can be represented by

$$W = A \exp(-E/RT) \tag{1}$$

where E is the activation energy of the process and A depends on the heating rate, order of the reaction, etc.

Fig. 4 is a plot of log W versus the reciprocal temperature (data taken from Fig. 2) which yields an activation energy of 20 kcal·mole^{-1}. To check the experimental validity of this method used to obtain the activation energy for sublimation, similar studies were performed on ammonium bromide. In this case the so determined activation energy (13 kcal·mole^{-1}) was found to be in good agreement with the value of Chaiken et al.[3] obtained by conventional techniques. Fig. 5 is a similar plot for AP decomposition under 700 torr of air. Surprisingly enough one gets three regions characterized by the respective activation energies of 30, 20 and 45 kcal·mole^{-1}, which are in good agreement with the earlier work[8] using isothermal techniques. Clearly two distinct differences can be observed between Jacobs and Russell-Jones'
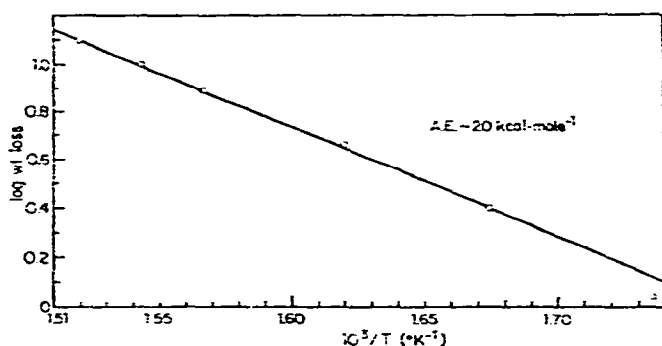
Fig. 4. Relationship for log W (wt. loss) against reciprocal temperature for ammonium perchlorate at 10^{-4} torr undergoing a $6°C \cdot min^{-1}$ heating program.

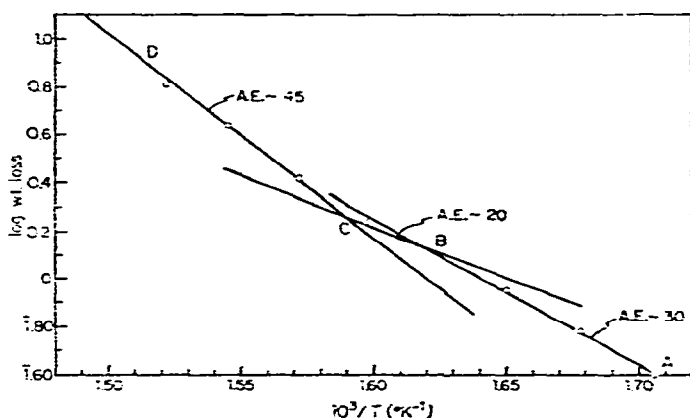
Fig. 5. Relationship for log W (wt. loss) against reciprocal temperature for ammonium perchlorate at 760 torr, air atmosphere undergoing a $6°C \cdot min^{-1}$ heating program. AB. BC and CD are the three regions of thermal decomposition.

work[4] and the present work: (1) They claim that under 700 torr of air AP sublimes. Our DTA and gas measurements (additionally we can see through the quartz furnace) demonstrate that AP decomposes under those conditions. (2) In vacuum our activation energy is 20 kcal·mole^{-1} whereas their activation energy is 30 kcal·mole^{-1}. It is possible that these differences are due to the fact that whereas we used undecomposed AP for sublimation studies, Jacobs and Rusell-Jones[4] first decomposed 30% of AP in air and then studied the sublimation of the residue. Experiments were therefore carried out on the residue of AP isothermally decomposed in air at 230°C. The results were identical to those on undecomposed AP. It is quite possible from these experiments that Jacobs and Russell-Jones[4] inadvertently studied thermal decomposition and interpreted the data as being relevant to sublimation processes. Secondly our experiments confirm that the original value of Bircumshaw and Phillips[1] for the activation energy (~ 21 kcal·mole^{-1}) is correct.

Isothermal results

To provide confirmatory evidence, the sublimation of powdered AP was carried out in vacuum isothermal conditions from 200 to 380°C. Initial evaluation of the data was made using the equation

$$kt = 1 - (1 - x)^n \tag{2}$$

where x is the fraction decomposed and the exponent n was taken as 1/3. Up to x of about 0.93, i.e. $1 - (1 - x)^{1/3} = 0.6$, plots of $1 - (1 - x)^{1/3}$ vs. t were satisfactorily linear, however marked deviations were apparent for larger values of x (see Fig. 6). The activation energy for k determined from the linear range was 18.6 kcal·mole[-1]. Jacobs and Russell-Jones[4] found that their vacuum sublimation data for experiments in the range 218–270°C could be fit by the same equation up to at least, $x = 0.9$. They, however, reported an activation energy of 30.0 kcal·mole[-1].
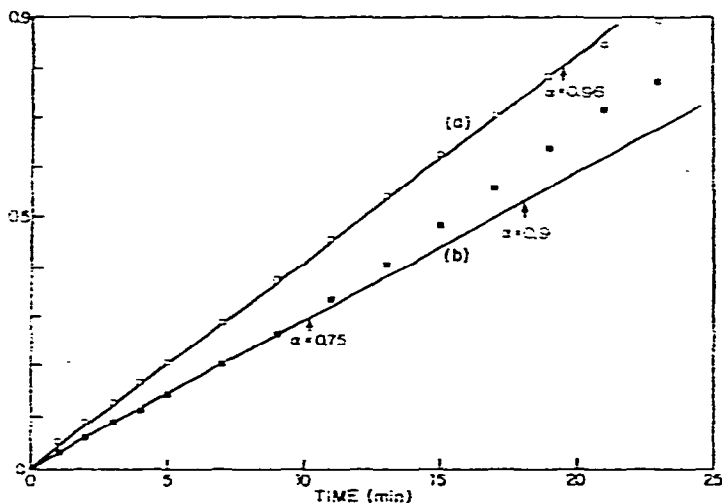

Fig. 6. A plot of (a) $1 - (1 - x)^{1/2}$ against time and (b) $1 - (1 - x)^{1/3}$ against time at 310°C. The figure clearly shows the superiority of 1/2 over 1/3 for the exponent.

The values of $1 - (1 - x)^{1/3}$ predicted by extrapolation from the region where $x < 0.9$ were always in the direction such that the source of the deviations could not be gas phase diffusional effects. It should be noted that at the highest pressures encountered we estimate that diffusional effects should have been undetectable. That there were consistently uniform deviations from Eqn. (2) with $n = 1/3$ is quite convincing evidence that this equation is not of fundamental significance in the sublimation. Several different models were tested to see if the discrepancies would have resulted from the kinetics of surface reactions. Some success was encountered here, in that the data for any single run could be fit using a two parameter relation predicted from a proposed model. Nonetheless, this model had to be discarded since the relative behavior of the calculated parameters for different runs did not behave as predicted. An excellent fit of the data could be obtained using Eqn. (2) with an

exponent $1/2$ (see Fig. 6). This result is in conflict with the results of Jacobs and Russell-Jones who found $n = 1/2$ worked well for their sublimation (decomposition?) data under 1 atm of air but used $n = 1/3$ for vacuum sublimation.

Since the differences between the experimental points and the best straight line through the points when plotted according to Eqn. (2) (with $n = 1/2$) were within experimental error it is clear that any acceptable model must predict Eqn. (2). This eliminates the bulk of the possible models suggested by Guirao and Williams[5]. In the case of vacuum sublimation the only rate processes which should be considered are the step or steps leading to the proton transfer and the two desorption steps. Clearly the desorption takes place from the crystal surface, however, it is not, a priori, necessary that the proton transfer process occurs only at the surface. For example, proton transfer could take place in the bulk according to

$$NH_4^+ + ClO_4^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} NH_3 + HClO_4 \tag{3}$$
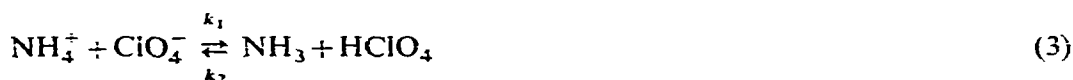
followed by the diffusional processes

$$NH_4^+ + NH_3 \quad \rightarrow \quad NH_3 + NH_4^+ \tag{4}$$

$$ClO_4^- + HClO_4 \quad \rightarrow \quad HClO_4 + ClO_4^- \tag{5}$$

followed by desorption of NH_3 and $HClO_4$ from the surface. Closed form solution of the resulting time dependent equation for this mechanism does not exist. Consideration of the relatively slow rates at which the crystal dimensions change indicates that an excellent approximation to the time dependent rate can be obtained by solving the steady state problem with constant crystal dimensions and then using this result to solve the time dependent equation relating the fractional decomposition α, time rate of change to the crystal dimensions. Even this simplified problem involves the solution of a non-linear partial differential equation, i.e.

$$D \nabla^2 N_A = -k_1(N^0 - N_A)^2 + k_2 N_A^2 \tag{6}$$

Boundary condition $-D(\nabla N_A)$ normal to surface $= k_4 N_A(S)$ where N^0 is the number density of NH_4^+ or ClO_4^- ion sites, A stands for either NH_3 or $HClO_4$, D is the diffusion coefficient of the NH_3–$HClO_4$ pair (note that the requirements of local electrical neutrality requires that there be only a single diffusion coefficient for the two species), k_4 is the rate constant for desorption and $N_A(S)$ is the value of N_A at the crystal surface. To avoid writing two equivalent equations the rate constants for NH_3 and $HClO_4$ have been taken to be equal. Fig. 7 is an Arrhenius plot of the rate constants determined from the data using Eqn. (2) with $n = 1/2$. The absence of any changes in slope above the phase change at $250°C$ is indicative of there being only a single rate determining step in the temperature range investigated. Therefore, Eqn. (6) is of interest only in the limiting cases where the kinetics are dominated by either diffusion, or desorption, or the reaction forming NH_3 and $HClO_4$. It is readily shown
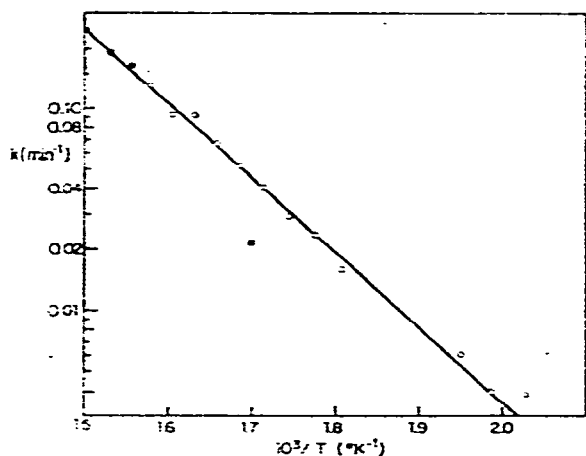
Fig. 7. An Arrhenius plot for the sublimation of powdered ammonium perchlorate. The data for the two ● points (at 370 and 380 °C) show some evidence for the lack of thermal equilibrium of the sample. The point, ■, is for a single crystal of ammonium perchlorate.

that in the latter case $d\alpha/dt$ will be proportional to the instantaneous volume of the crystal, while for the former two cases $d\alpha/dt$ would be proportional to the surface area of the crystal. In the case of compact solids such as cubes or spheres, where the ratio of the minimum to the maximum dimension is close to unity, if $d\alpha/dt$ is proportional to volume it follows that $kt = -\ln(1-\alpha)$, and if $d\alpha/dt$ is proportional to surface area then $kt = 1-(1-\alpha)^{1/3}$. For highly elongated solids if $d\alpha/dt$ is proportional to volume then $kt = -\ln(1-\alpha)$ however, if $d\alpha/dt$ is proportional to surface area then $kt = 1-(1-\alpha)^{1/2}$. It therefore follows that the observed kinetics are consistent with proton transfer in the bulk of an elongated solid with either surface desorption or diffusion being rate determining. The latter case is equivalent to requiring that the reactions can only occur on the surface, (if an elongated crystal) with either desorption or reaction being the rate controlling step.

No other model whose kinetics were consistent with the observed rate expression was found. The relevance of the models which were found to be consistent with the experimental kinetics is subject to two criticisms: The activation energy is less than $\frac{1}{2}\Delta H_{subl.}$, and the crystallites of AP used did not qualify as highly elongated cylinders. That the experimental activation energy of 16.5 kcal·mole^{-1} is less than 29 kcal·mole^{-1}, the value of $\frac{1}{2}\Delta H_{subl.}$ is not *a priori* impossible since (contrary to the statement made by Jacobs and Russell-Jones[+]) the near equality of these two quantities can only be expected for systems which do not undergo dissociative sublimation. Even for these systems the measured activation energy for vacuum sublimation can exceed $\Delta H_{subl.}$ by the activation energy for adsorption.

Consider the following set of surface reactions leading to the sublimation of AP

$$A^+ P^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A-P \text{ proton transfer} \tag{7}$$

$$A-P \quad \overset{k_3}{\underset{k_4}{\rightleftharpoons}} \quad A+P \text{ surface diffusion} \tag{8}$$

$$A \quad \overset{k_5}{\underset{k_6}{\rightleftharpoons}} \quad A_g \text{ desorption} \tag{9}$$

$$P \quad \overset{k_7}{\underset{k_8}{\rightleftharpoons}} \quad P_g \text{ desorption} \tag{10}$$

Where A stands for NH_3, A^+ for NH_4^+, P for $HClO_4$, P^- for ClO_4^- and the subscript g for the gas phase. Irrespective of whether the first reaction is first order or second order the calculated value of $\Delta H_{subl.}$ is $E_1 - E_2 + E_3 - E_4 + E_5 - E_6 + E_7 - E_8$. For vacuum sublimation A_g and P_g are taken as 0. Because the surface area changes so slowly it is appropriate to make the steady state approximation on A–P, A and P. In the solution of the above set of equations there are several limiting cases of interest for which the activation energy, E, of the sublimation rate constant can be found:

if $b^2/4ac \ll 1$ and $E_1 > E_2$, $E \approx \frac{1}{2}(E_3 + E_5 + E_7 - E_4)$;

if $b^2/4ac \gg 1$ and $b \approx 1$, $E \approx E_1$

$\qquad\qquad\qquad\qquad\; b \approx k_1/k_2$, $E \approx E_2$

$\qquad\qquad\qquad\qquad\; b \approx k_1/k_5$, $E \approx E_5$

$\qquad\qquad\qquad\qquad\; b \approx k_1/k_7$, $E \approx E_7$

$b = 1 + k_1/k_3 + k_2/k_3 + \frac{1}{2}(k_1/k_5 + k_1/k_7)$

$a = k_4(k_1/k_3 + k_2/k_3)/(k_5/k_7)$

$c = k_1 C_0$.

It is clear that the possibility that $E < \frac{1}{2}\Delta H_{subl.}$ is not unreasonable.

That the kinetics are consistent with an expression for a contracting cylinder rather than a contracting sphere is somewhat surprising. However scanning electron microphotographs of partially decomposed AP which had been exposed to water vapor shows that the material is present as a fine grid[12]. Our observation of AP during sublimation indicates that the crystals rapidly take on a filamentous appearance. The rate at which the AP was heated to the temperature where the sublimation was to be investigated $(25\,^{\circ}C \cdot min^{-1})$ permitted some sublimation and decomposition to occur before the point where the value of α was taken as 0 for purpose of analysis. During this time the crystal could have undergone the changes necessary for the contracting wire expression to be approximately valid.

It is not evident whether formation or desorption is the rate controlling process. One experiment was done with a single 50 mg crystal which yielded a value of k about 50% lower than from the 100 μ crystallites usually used. Rough calculations indicated that the difference could be accounted for by non-thermal equilibrium of the larger crystal due to evaporation. Similar calculations showed that the smaller crystals should have been very close to the oven control temperature. The salient point

to note is that a twenty-fold increase in the diameter results in only a two-fold or less decrease in k. k decreased much less than inversely to the diameter as would be predicted by theories based on the geometric area which serves as added support for the filament hypothesis. In addition the similarity in the results for a single crystal and a pile of small crystals tends to show that adsorption is not an important part of our observed results.

At the present time it is not possible to differentiate between desorption and proton transfer as the slow step, or even whether the proton transfer steps take place in the bulk or on the surface alone. Suitably designed experiments in the sublimation of AP in the presence of very small overpressures of NH_3 and $HClO_4$ coupled with appropriate isotopic exchange studies could resolve these points.

Schultz–Dekker theory

Calculation of the activation energy for the sublimation of AP has also been made using the Schultz–Dekker linear theory[9] for sublimation which Chaiken *et al.*[3] have used very successfully for the ammonium halides. The activation energy E is given by the expression

$$E = \tfrac{1}{2}(\Delta H_{m,NH_3} + \Delta H_{m,HClO_4}) + (\Delta H_{s,NH_3} - RT_{s,NH_3}) + (\Delta H_{s,HClO_4} - RT_{s,HClO_4})$$

where

$\Delta H_{m,x}$ refers to the heat of fusion of x, NH_3 or $HClO_4$

$\Delta H_{s,x}$ refers to the heat of sublimation of x, NH_3 or $HClO_4$

$\Delta H_{m,NH_3}$ = 1.424 kcal·mole^{-1}(Ref. 10)

$\Delta H_{s,NH_3}$ = 5.581 kcal·mole^{-1}, 239.7°K (Ref. 10)

$\Delta H_{m,HClO_4}$ = 1.655 kcal·mole^{-1} (Ref. 11)

$\Delta H_{s,HClO_4}$ = 9.4   kcal·mole^{-1} (Ref. 2)

E, calculated this way, comes out to be 15.5 kcal·mole^{-1}. The agreement between the experimentally obtained values and the theoretically derived activation energy is very satisfactory as is shown in Table I.

TABLE I

	S.–D. theory	log W vs. 1/T	Contracting cylinder k vs. 1/T	Single crystal photomicroscope[12]
E	15.5	20	16.3	20

The table also lists the activation energy as obtained by Kraeutle[12] for what he claims to be the thermal decomposition of single crystals of AP studied by photo-microscopy. Single crystals of AP, when subjected to heat, primarily sublime independent of the over pressure in the system. Maycock *et al.*[13] have shown this clearly by DTA where the thermogram is purely endothermic. Secondly the small amount which does decompose (very little detected by DTA) does so with an activation energy of about 28 kcal·mole^{-1} in the temperature studied by Kraeutle[12]. It thus follows

that Kraeutle has in fact studied sublimation and this is why he gets good agreement between the weight loss (TGA) and the weight loss calculated from the growth of the nuclei. Clearly Kraeutle's activation energy value of 20 kcal·mole^{-1} obtained by TGA as well as photomicroscopy is not the activation energy for the decomposition process but is in fact the activation energy for the sublimation. This is therefore further evidence that the activation energy for sublimation of AP is about 18 kcal·mole^{-1} (± 2) and therefore it bears an analogy to the sublimation processes in ammonium halides. Fig. 8 shows a correlation of the activation energies for sublimation of these
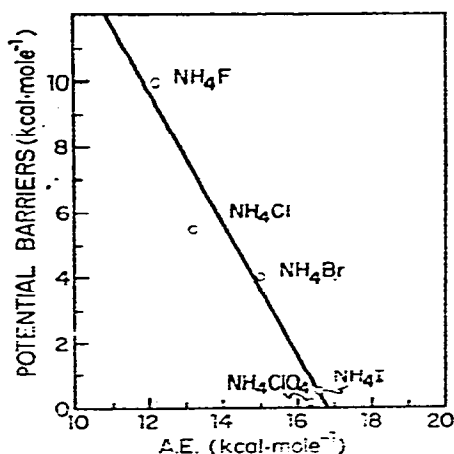

Fig. 8. Relationship between the potential barrier for NH$_4^+$ rotation against activation energy for sublimation of several ammonium salts.

ammonium salts and the potential barrier for the rotation of the ammonium ion. As the potential barrier increases, the activation energy for sublimation decreases. It is expected that the higher the potential barrier, the larger is the anion–cation interaction which predicts that the energy for the proton transfer will be lower as the anion–cation interaction increases.

In summary it has been shown that the activation energy for sublimation of AP is 18 ± 2 kcal·mole^{-1} with the sublimation process bearing an analogy to that in the ammonium halides and the activation energy is inversely proportional to the barrier for the rotation of the NH$_4^+$ ion.

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