Technical Notes

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Thermal Decomposition of Ammonium Perchlorate

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Introduction

IN spite of the fact that the pyrolysis of ammonium perchlorate (AP) has been exhaustively studied,[1-3] two fairly important questions with respect to the decomposition process still remain; what are the exothermic reactions, if any, occurring in or on the surface of the solid and what are the rates and nature of gasification and subsequent gaseous reactions above the solid. In a recent publication by Wenograd and Shinnar,[4] it has been shown that the energy necessary to propagate the burning of AP is probably not solely governed by an endothermic evaporation followed by exothermic reactions in the gas phase close to the surface. It has also been suggested that perchloric acid alone might not be the only oxidizer in propagating the burning process,[5] but that probably some chlorine oxide may also be a participant in the flame-propagating process. The three most prominent species suggested are ClO, ClO_2, and ClO_3. We have designed a gas sampling system which approximates a collision-free molecular beam for the study of solid phase reactions. This system also has the added flexibility of being used as a Knudsen cell, where the products of solid phase processes are allowed to react in the gas phase at elevated temperatures. Experiments performed with this sampling system seem to indicate the occurrence of an exothermic surface reaction with ClO_2 as a major product resulting from the pyrolysis of AP between 200° and 400°C.

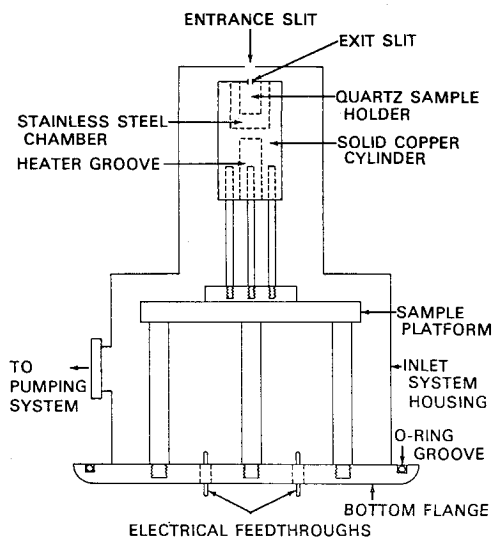

Fig. 1 Modified Bendix Knudsen inlet system.

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Experimental

The ammonium perchlorate (99.8% purity) was obtained from the Fisher Scientific Company. This material was recrystallized twice from a saturated solution at 60°C, by cooling over the course of an hour or so. A 25 wt % solution of this material was isothermally (31°C) recrystallized over a three-week period by critically controlled solvent evaporation. After crystal growth, only the very clear crystals were selected and used in these experiments.

The mass spectral observations were performed with a Bendix Time-Of-Flight Mass Spectrometer (Model 12-101) with a S14-107 source in conjunction with a modified Bendix Knudsen Inlet System shown in Fig. 1. The stainless steel sample platform was mounted on the bottom flange of the inlet system. This platform in turn supported the solid copper cylinder sample holder with three stainless steel rods $\frac{1}{8}$-in. diam. The cartridge-type heater (Model 900269, DuPont Instrument Products Division) and an iron-constantan thermocouple were imbedded in the solid copper cylinder. The 55-w heater was imbedded less than $\frac{1}{4}$-in. below the stainless steel chamber which contained the quartz sample holder. An additional thermocouple used for temperature measurement of the sample was placed adjacent to it between the quartz sample holder and the stainless steel chamber.

The stainless steel chamber was fitted with a screw-down cap which contained a central 1-mm hole, allowing both free evaporation and Knudsen-type experiments to be performed. The most important feature of this chamber was its use as a reaction vessel where evaporated products were allowed to leak into the mass spectrometer. Gold foil leaks (0.001 and 0.002 in. diam) were placed over the quartz sample holder and screwed down by the cap in such a way that the foil served both as a gasket and a leak. This arrangement allowed us to attain temperatures as high as 500°C with various evaporated gases still remaining in the sample cell.

The inlet system, attached to the bottom flange of the source cross, was separated from the source region by a small thin gate valve and was separately evacuated with an auxiliary pumping system. The pumping system consists of a

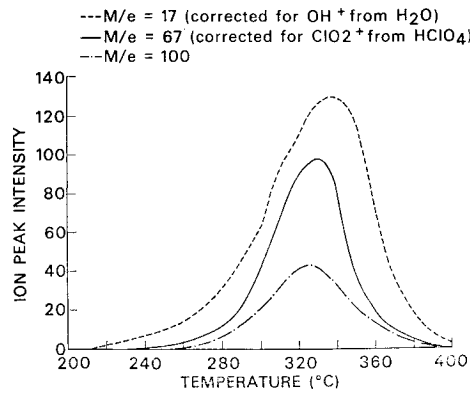

Fig. 2 Variation of some major spectral features with temperature from AP pyrolyses.

liquid N_2 trap (Type CT-200, Veeco Insts. Inc.), a water-cooled oil diffusion pump (Type PMCS-2C, Bendix Vacuum Division), and a 10 CFM Duo-Seal Mechanical Pump (Welch Model 1376). This system was capable of attaining vacua of 10^{-1} torr and maintained pressures in the 10^{-4}–10^{-6}-torr range in all the experiments performed. The pressure was monitored with a combination thermocouple-ionization gauge (CVC, Type Glc-11B).

The sample exit orifice was adjusted about $\frac{1}{4}$ in. directly below the 1-mm × 6-mm entrance slit. Thus, as long as the pressure of the inlet system was maintained below 10^{-4} torr, only material expelled on a direct flight from the sample orifice to the entrance slit was fed into the mass spectrometer.

Results

The pyrolysis of AP was investigated over the temperature range 200°–500°C. These studies were made using both a cell approximating free evaporation and a closed cell with 0.001 and 0.002 in. leaks.

Free-evaporation experiments

The powdered untreated AP sample (less than 0.10 g in all experiments) was slowly heated above room temperature in the quartz open cell. The auxiliary pumping unit maintained the sample region pressure less than 10^{-4} torr throughout these experiments. Therefore, any reactions between evaporated products were considered to be negligible. Furthermore, if any small amount of reaction did occur, there would be little probability of such products getting through the entrance slit into the mass spectrometer source region.

As the sample was heated over the temperature range from roughly 200° to 280°C, proportional growth features due to N_2, HCl, H_2O, Cl_2, O_2, N_2O, and a small amount of NO_2 were observed. As the temperature was further increased, a new spectral pattern began to develop indicating proportional growth features due to NH_3, $HClO_4$, and ClO_2, and a concurrent decrease of N_2, NO_2, and N_2O.

These changes in the relative spectral intensities occurred gradually over a 30° temperature interval. When the temperature reached 350°C, the major spectral features observed were due to $HClO_4$, ClO_2, HCl, O_2, H_2O, and NH_3. As the temperature was increased further, the spectrum began to decrease in intensity, and disappeared about 400°C. These results are shown in Fig. 2.

The pyrolysis of the recrystallized AP sample was carried out in a similar manner as described above. The products spectrum from decomposition was first observed at approximately 215°C. A minor pressure burst was observed at approximately 242°C, probably corresponding to the AP endotherm. As the sample was slowly heated above this temperature, growth features due to CO_2, NH_3, H_2O, N_2, Cl_2, HCl, O_2, ClO_2, and $HClO_4$ were observed. The source of CO_2 and possibly some of the other air components observed are probably from crystal voids where they were trapped during crystal growth. The presence of CO_2 complicated somewhat the positive identification of N_2O, which was confirmed using the powdered sample. When the temperature reached 279°C, NO_2 began to gradually increase. As the temperature was further raised, the proportion of ClO_2 relative to $HClO_4$ appeared to increase. Finally at 390°C, $HClO_4$ was no longer observed and the only chlorine species were ClO_2, Cl_2, and HCl. The complete loss of ClO_2 occurred at approximately 420°C, and the products spectrum consisted of Cl_2, N_2O, H_2O, HCl, O_2, N_2, and some NO_2. When the temperature reached approximately 500°C, all peaks due to AP decomposition disappeared.

Closed-cell experiments

As the enclosed sample (powdered AP) was heated above room temperature, the pressure in the surrounding region was kept below 10^{-4} torr by the auxiliary pumping unit. When the temperature reached approximately 263°C, a products spectrum began to develop corresponding to H_2O, Cl_2, O_2, N_2O, and N_2. When the temperature reached approximately 290°C, mass spectral peaks due to HCl, NO_2, and possibly HNO_3 began to grow in intensity along with the concurrent growth of the aforementioned products. As the temperature was gradually raised to 400°C, the dominant features in the mass spectrum were due to H_2O, N_2, O_2, Cl_2, HCl, NO_2, and possibly some N_2O (Fig. 3). This pattern began to decrease in intensity at about 450°C and disappeared completely slightly above 500°C.

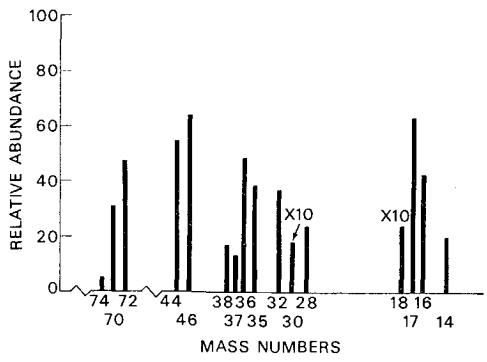

Fig. 3 Mass spectrum of thermally dissociated ammonium perchlorate at 400°C (Knudsen-type experiment).

Discussion

The products of the thermal decomposition of the powdered AP sample over the low-temperature range are in general agreement with the results observed by Verneker and Maycock[6] and Rubstov.[7] The latter proposed the following decomposition processes:

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

and

$$2\ NH_4ClO_4\ (c) \rightarrow 4\ H_2O + Cl_2 + 2\ O_2 + N_2 \quad (2)$$

which agrees well with the observations of these experiments with the exception of HCl. However, above 280°C, new product peaks appear, among which are NH_3 and $HClO_4$. The appearance of these species naturally suggests the well-accepted proton-transfer mechanism followed by desorption of NH_3 and $HClO_4$.

$$NH_4ClO_4\ (c) \rightarrow NH_3\ (g) + HClO_4\ (g) \quad (3)$$

The appearance of other degradation products in the free-evaporation experiments strongly implies the occurrence of another surface reaction, since the probability of gaseous collisions above the solid are very small. On the basis of the observed products and the fact that NH_3 desorbs intact, one possibility is the disproportionation of $HClO_4$,

$$3\ HClO_4\ (\text{adsorbed}) \rightarrow 2\ ClO_2 + HCl + \tfrac{7}{2}\ O_2 + H_2O \quad (4a)$$

Similar free-evaporation experiments[8] performed on a series of methyl-substituted amine-type perchlorates which presumably dissociated into adsorbed $HClO_4$ and the corresponding methyl-substituted amine gave the same products as those observed in reaction Eq. (4a).

This reaction establishes two possible processes for the adsorbed $HClO_4$ molecule (desorption and disproportionation). The two processes appeared to be comparable in rate over the temperature range observed with the powdered sample.

The results of the study involving the recrystallized AP sample are similar to the observations of Bircumshaw and Newman.[9,10] Apparently, decomposition, sublimation, and probably the disproportionation of $HClO_4$ are all occurring simultaneously. The products observed over practically the entire temperature range correspond to the combination of reactions of Eqs. (1–4a). As the temperature increased,

reaction (4a) seemed to occur at a faster rate than Eq. (3). Above 420°C the decomposition of the AP crystal became the dominant process.

In order to obtain some idea as to whether or not reaction Eq. (4a) might be exothermic, we considered the gas phase reaction,

$$3\ HClO_4\ (g) \rightarrow 2\ ClO_2 + HCl + \tfrac{7}{2}\ O_2 + H_2O \qquad (4b)$$

The heats of formation of $HClO_4$ and ClO_2 were taken as 2 kcal/mole and 24.7 kcal/mole, respectively,[11] and the values of the other compounds were taken from standard thermodynamic tables. The calculated H° of the reaction (4b) is − 37 kcal/mole. This value plus the endothermicity of desorbing three moles of $HClO_4$ gives the overall H° of reaction (4a). Since $HClO_4$ is presumed to physically adsorb on the AP crystal surface[12] upon dissociation, the total energy necessary to desorb or evaporate three moles is probably less than 10 kcal. If disproportionation of $HClO_4$ is indeed occurring on the crystal surface, this calculation indicates that it is probably exothermic. These results support the arguments of Wenograd and Shinnar[4] cited earlier.

The results of the closed cell experiments provide some insight into the gaseous reactions that occur when the volatile products remain trapped. It appears that a complicated system of oxidation-reduction reactions is occurring. Both $HClO_4$ and ClO_2 serve as the major oxidizers, while NH_3 appears to be the major species which is oxidized. $HClO_4$ and ClO_2 appear to be reduced to Cl_2 and HCl, while NH_3 is oxidized to N_2, NO_2, and N_2O.

Conclusion

When AP is heated between 200° and 400°C, both decomposition and dissociative sublimation occur simultaneously on/in the crystal surface. An additional exothermic reaction occurring on the surface appears to be the disproportionation of adsorbed $HClO_4$ producing ClO_2 as a major product. The gaseous products of the various pyrolytic reactions are observed to undergo a complex series of oxidation-reduction reactions.

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New Outer Boundary Conditions for the Similar Boundary-Layer Equations

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In the numerical integration of the similar boundary-layer equations, the outer boundary conditions, which should be applied at infinity, are necessarily applied at some reasonable finite distance with a resulting loss of accuracy. (In some methods of solution, this also leads to loss of uniqueness of the solution e.g., see Ref. 1.) This inaccuracy can, in principle, be reduced to any desired degree by applying the outer boundary conditions at a sufficiently large distance from the surface. However, an attractive alternative was introduced by Libby and Chen[2] that consists of matching a numerical inner solution to an asymptotic series for the outer solution. This procedure was applied by Libby in Refs. 2 and 3 to the quasilinearization method of integrating the similar boundary-layer equations with unit Prandtl number. In this paper, we treat the outer boundary conditions in a more general manner, not tied to any particular numerical method of solution. We show the derivation of outer boundary conditions from the asymptotic form of the similar boundary-layer equations with unit Prandtl number, and also note results for the incompressible case with arbitrary Prandtl number.

The laminar similar boundary-layer equations for steady two-dimensional ideal gas flows with unit Prandtl number and constant wall temperature are[4]

$$f''' + ff'' + \beta(1 + S - f'^2) = 0 \qquad (1)$$

$$S'' + fS' = 0 \qquad (2)$$

subject to the inner and outer boundary conditions

$$f(0) = f'(0) = 0,\ S(0) = S_w$$
$$f'(\infty) = 1,\ S'(\infty) = 0 \qquad (3)$$

where f and β are defined as usual, primes denote differentiation with respect to η, and S is defined in terms of the stagnation enthalpy $S = (h_s/h_{se}) - 1$.

To find an outer solution we first introduce a new variable $\phi = 1 - f'$ in terms of which

$$f = \eta - \int_0^\eta \phi d\eta = \eta - \eta_0 + \int_\eta^\infty \phi d\eta$$

where we have defined

$$\eta_0 = \int_0^\infty \phi d\eta$$

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