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THERMAL DECOMPOSITION OF HYDRAZINIUM MONOPERCHLORATE IN THE SOLID STATE

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ABSTRACT

Hydrazinium monoperchlorate (HP-1) has been shown to decompose thermally in the solid state according to the chemical equation:

$$5N_2H_5ClO_4 = 4NH_4ClO_4 + 1HCl + 3N_2 + 4H_2O$$

The activation energy for the evolution of HCl as determined mass spectrometrically is 8.05 kcal mol^{-1} in the temperature range of 80 to 120°C. The rate of decomposition is seen to be altered by doping HP-1 with small concentrations of SO_4^{2-}, Ca^{2+} and Al^{3+}.

INTRODUCTION

The thermal decomposition of HP-1 in the solid state does not seem to have been reported in the literature. During the dehydration of hydrazinium monoperchlorate hemihydrate at 70°C, it was observed that the time of dehydration determined the reproducibility of its thermal decomposition in the molten state. Irreproducibility in the behaviour of HP-1 has also been observed[1] in the studies on the burning rate of propellants using 95% of HP-1. HP-1 should also show similarities in chemical and physical behaviour to ammonium perchlorate. All these facts suggested that HP-1 could thermally decompose well below its melting point. Some preliminary data on the thermal decomposition of HP-1 in the solid state are presented in this investigation.

EXPERIMENTAL

Materials

High purity HP-1 was prepared by neutralizing 60% aqueous perchloric acid with 75% hydrazine at temperatures from 0 to 25°C. The salt precipitates from water at 0°C and was filtered cold through a sintered glass funnel. The fine white crystals were gently removed with a teflon spatula and placed in a drying tube at 70°C for 2 h at a constant vacuum of 0.05 mm of Hg to dehydrate the hemihydrate. Samples were titrated to a phenolphthalein end point with 0.1 N NaOH. The characteristic purity factor ranged from 99.2 to 99.8%.

The solid state decomposition of HP-1 is a very slow process requiring five days for the complete decomposition at 125°C. Hence, the bulk of the data has been obtained only on the very initial stages of decomposition, followed by an AEI-MS-10 mass spectrometer connected to a constant volume system via a molecular leak. For stoichiometric analysis, studies were also conducted on HP-1 in weighing bottles maintained at desired temperatures. The final residue was analyzed quantitatively for HP-1 and ammonium perchlorate by chemical methods and also by infrared (IR) spectra.

RESULTS

When 165 mg of $N_2H_5ClO_4$ are heated in a weighing bottle at 120°C, a weight loss is observed amounting to 29% at the end of the run shown in Fig. 1. An IR spectrum of the residue in Nujol mull shows the absence of HP-1 and the presence of NH_4ClO_4. Volumetric analysis confirms the IR observations.

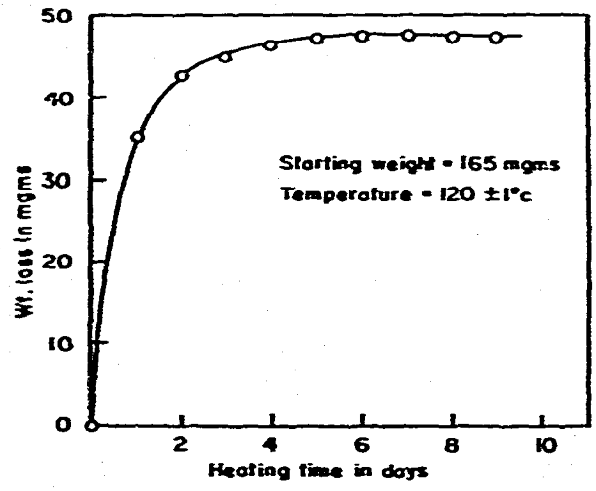

Fig. 1. Weight loss plotted against the time of heating HP-1 at 120°C.

The gaseous products of the thermal decomposition of HP-1 as analyzed by the mass spectrometer connected to a constant volume vacuum system (initial pressure of 1×10^{-5} torr) are listed in Table 1.

An analysis of the cracking patterns leads us to eliminate masses 14 and 17 leaving the parent peaks at masses 18, 28, 36 and 38. From the probable assignments made in Table 1, the final decomposition species seem to be water, nitrogen and hydrochloric acid.

TABLE 1

THE DECOMPOSITION SPECIES OF HP-1 AT 100°C IN A CONSTANT VOLUME SYSTEM CONNECTED VIA A MOLECULAR LEAK TO THE MASS SPECTROMETER

m/e	*Probable assignments*	*Ion current* × 10^{13}
14	N^+	0.14
17	OH^+	2.20
18	H_2O^+	9.00
28	N_2^+	1.30
36	HCl^+	0.62
38	HCl^+	0.21

The peak heights (Table 1) are given in terms of ion current which is good for identification purposes. Relative partial pressures can, however, be obtained by the relationship:

$$\text{relative pressure } (P) = \frac{\text{ion current } (i)}{\text{relative cross-section } (\sigma)} \tag{1}$$

The relative cross-sections for the species involved in the present work, are available from the works of Otvos and Stevenson[2] and Pottie[3]. The relative pressures calculated from eqn (1) are given in Table 2.

TABLE 2

RELATIVE PARTIAL PRESSURES OF THE DECOMPOSITION SPECIES IN HP-1 AT 100°C

Species	*Relative cross-sections*	*Relative partial pressures*
N_2^+	2.82	0.46
HCl^+	4.85	0.17

TABLE 3

EFFECT OF DOPING HP-1 ON THE EVOLUTION OF HCl AT 110°C

Dopant	*Rate (min) (arbitrary units)*
Nil	65
NH_4^{1+} (1 M %)	65
Ca^{2+} (1 M %)	63
Al^{3+} (1 M %)	60
SO_4^{2-} (1 M %)	71
SO_4^{2-} (0.5 M %)	68

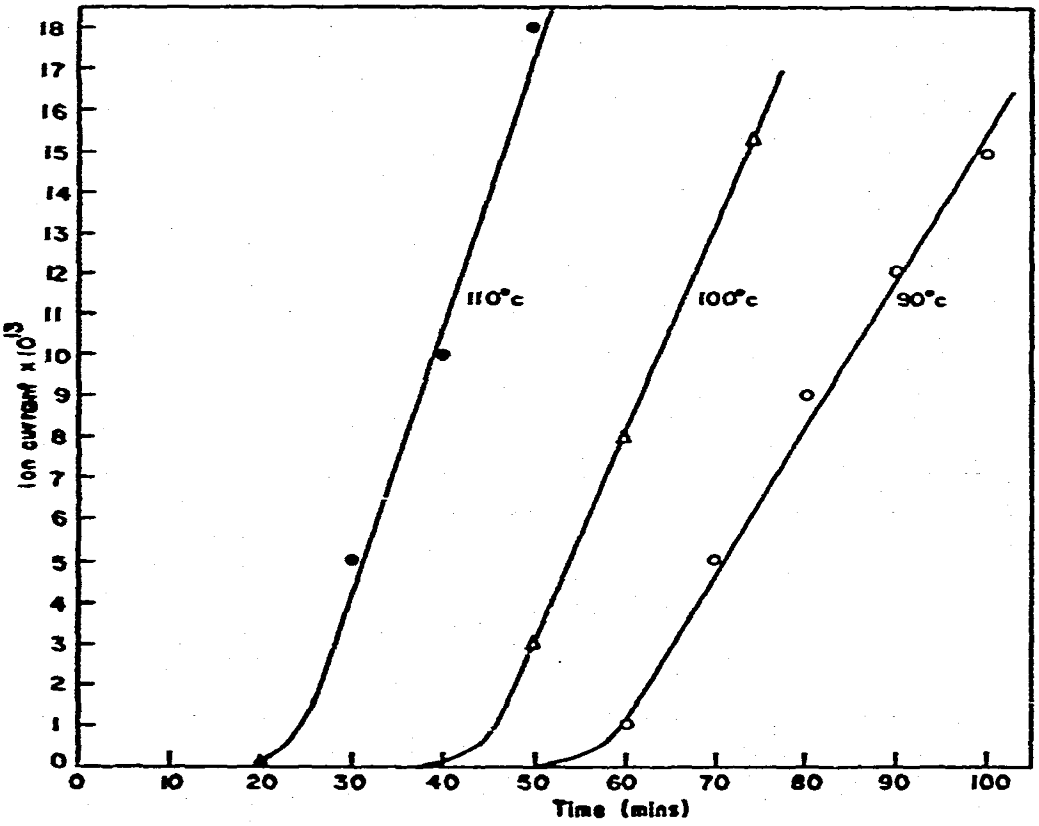

Fig. 2. Isothermal decomposition of HP-1 at 90°C (○); 100°C (△); and 110°C (●). Evolution of HCl expressed as ion current plotted against the time of heating.

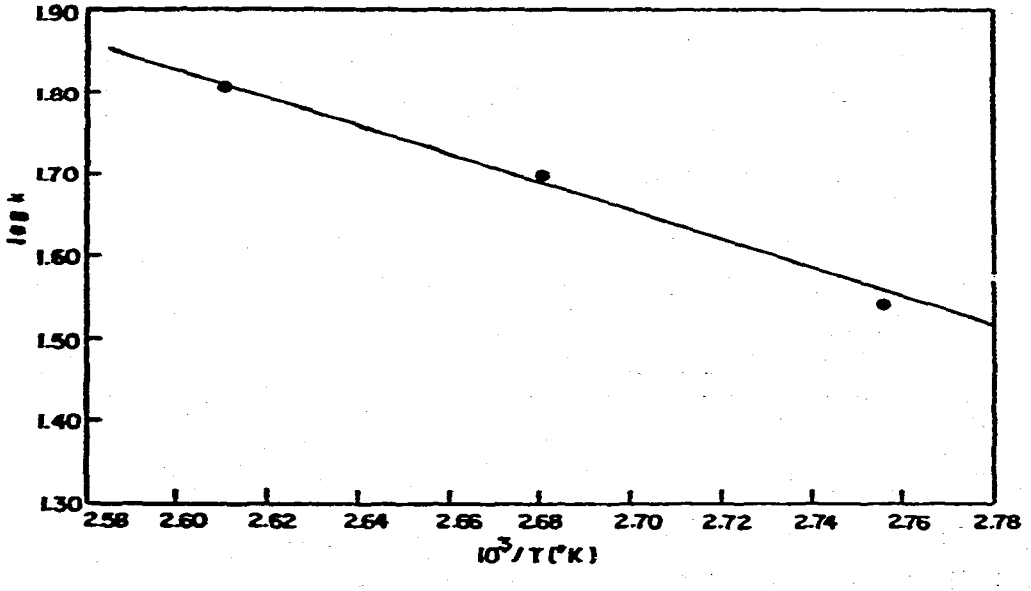

Fig. 3. Arrhenius plot for the decomposition of HP-1.

The decomposition species were also determined at 125°C and found to be the same as at 100°C.

The isothermal runs on the decomposition of HP-1 were carried out in the temperature range 90 to 110°C, monitoring the evolution of HCl. This is shown in Fig. 2. Activation energy (E_A) was calculated from the initial slopes of the α (t) plots. (shown in Fig. 3) and found to be 8.05 kcal mol^{-1}. The effect of doping HP-1 with SO_4^{2-}, NH_4^{1+}, Ca^{2+} and Al^{3+} in the subsequent rate of evolution of HCl is shown in Table 3.

DISCUSSION

The weight loss measurements (Fig. 1) and the mass spectrometric data (Tables 1 and 2) lead us to the following chemical reaction for the solid state thermal decomposition of HP-1:

$$5N_2H_5ClO_4 = 4NH_4ClO_4 + 1HCl + 3N_2 + 4H_2O \qquad (2)$$

With the available data it is difficult to put forth any definite mechanism. One could speculate that the mechanism involves a proton transfer leading to the formation of N_2H_4 and $HClO_4$. The evolution of N_2H_4 may be inferred from the presence of small concentrations (ion currents not listed in the mass spectrometric data presented in Table 1 because the concentrations are very small) of masses 15(NH), 16(NH_2), 30(N_2H_2), 31(N_2H_3) and 45(N_3H_3). The E_A of 8.05 kcal mol^{-1} may then refer to the E_A of the heterogeneous thermal decomposition of $HClO_4$. However, the effect of doping HP-1 with intentional impurities (Table 3) suggests that whereas anion vacancies sensitize the decomposition, cation vacancies desensitize the reaction. Univalent ions like NH_4^+ do not alter the decomposition rate. Assuming a Schottky defect structure, this could mean that the migrating species is the perchlorate ion. A Frenkel defect structure, on the other hand, would suggest the migration of an interstitial $N_2H_5^+$ ion. The low value of the E_A (8.05 kcal mol^{-1}) may well signify that the rate determining step involves the migration of one of the ions $N_2H_5^+$ or ClO_4^- to the preferential sites, where proton transfer could be envisaged.

REFERENCES

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