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Note

THERMAL ANALYSIS OF HYDRAZINE PERCHLORATE HYDRATES AND AMMONIATES *

K.C. PATIL, C. NESAMANI and V.R. PAI VERNEKER

High Energy Solids Laboratory, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012 (India)

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The current interest in hydrazine perchlorates is due to their possible use as solid propellant oxidizers. The preparation and thermal properties of both hydrazine perchlorates $N_2H_5ClO_4$ (HP-1) and $N_2H_6(ClO_4)_2$ (HP-2) and their hydrates have already been described [1]. The thermal decompositions of $N_2H_5ClO_4$ [2,3] and $N_2H_6(ClO_4)_2$ [4] have recently been reported. The use of these perchlorates as solid propellant oxidizers is greatly handicapped by their shock sensitivity, hygroscopic nature and incompatibility. An attempt has been made to overcome this problem by stabilizing these compounds by complexing with ammonia. In this note we report the preparation and thermal properties of the hydrazine perchlorate ammoniates $N_2H_5ClO_4 \cdot NH_3$ and $N_2H_6(ClO_4)_2 \cdot 2\,NH_3$, and compare them with the corresponding hydrates.

EXPERIMENTAL

Hydrazine perchlorate hydrates $N_2H_5ClO_4 \cdot 0.5\,H_2O$ and $N_2H_6(ClO_4)_2 \cdot 2\,H_2O$ were obtained by the method described earlier [1]. Hydrazinium perchlorate monohydrate $N_2H_5ClO_4 \cdot H_2O$ was accidentally obtained by the addition of aqueous perchloric acid (60%) to the cold solution of hydrazine hydrate (99.5%). The hydrazine perchlorate ammoniates $N_2H_5ClO_4 \cdot NH_3$ and $N_2H_6(ClO_4)_2 \cdot 2\,NH_3$ were prepared by reaction of the respective hydrates with anhydrous ammonia gas. Both $N_2H_5ClO_4 \cdot 0.5\,H_2O$ and $N_2H_5ClO_4 \cdot H_2O$ yield $N_2H_5ClO_4 \cdot NH_3$ with ammonia gas. The compositions of the ammoniates were fixed by hydrazine analysis. The hydrazine content was determined by titration with 0.05 M potassium iodate solution under Andrew's condition [5]. The ammoniates were characterized by their IR spectra which were recorded using a Carl—Zeiss UR-10 spectrophotometer. The samples were prepared as Nujol mulls and KBr pellets. Differential thermal analysis (DTA) was carried out using a DTA-02 Universal Instrument.

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All DTA runs were made in air unless otherwise stated. The heating rate employed was 7°C min^{-1}. Platinum cups were used as sample holders; 25 mg samples were used for the DTA experiments.

RESULTS AND DISCUSSION

Thermal and analytical data for HP-1 hydrates, HP-2 dihydrate and HP-ammoniates are summarized in Table 1. Both HP-1 hemihydrate and HP-2 dihydrates are very hygroscopic and difficult to handle in air. HP-1 monohydrate is less hygroscopic and can be handled easily. The observed hydrazine content is in agreement with the chemical formula. The IR spectrum shows an absorption at 965 cm^{-1} characteristic of ν(N—N) of $N_2H_5^+$. The differential thermal analysis (DTA) is entirely different from those of HP-1 hemihydrate and HP-2 dihydrate. The first endotherm at 132°C was found to be due to partial dehydration and melting. The second exothermic peak in DTA at 263°C is due to decomposition. However, the DTA in vacuum gives anhydrous HP-1 which further decomposes at 226°C (exo) to ammonium perchlorate (AP). The two endotherms at 240 and 290°C have been assigned to AP-phase change and sublimation, respectively. This behaviour is similar to that reported for HP-2 [3], which is known to decompose initially to HP-1 (Fig. 1). The DTA's of HP-1 · 0.5 H_2O and HP-2 · 2 H_2O are in agreement with those which have been reported [3,6].

Complexing with ammonia has already been used [7] in stabilizing highly hygroscopic salts like lithium and magnesium perchlorates, so it was thought interesting to extend this idea to the very hygroscopic hydrazine perchlorates. However, liquid ammonia is known to react with hydrazine sulphate to give ammonium sulphate and anhydrous hydrazine

$$N_2H_6SO_4(s) + 2\,NH_3(l) \rightarrow (NH_4)_2SO_4(s) + N_2H_4(l) \qquad (1)$$

Our recent study [5] has shown that ammonium salts react with hydrazine

TABLE 1

Thermoanalytical data

Compound	% hydrazine		DTA peak temp. (°C) [a]
	Obs.	Calc.	
$N_2H_5ClO_4 \cdot 0.5\,H_2O$	22.38	22.61	86(endo), 224(exo)
$N_2H_5ClO_4 \cdot H_2O$	21.50	21.33	132(endo, m), 263(exo)[132(endo, m), 226(exo), 240(endo), 289(endo) [b]]
$N_2H_6(ClO_4)_2 \cdot 2\,H_2O$	11.37	11.85	100(endo), 273(exo)[198(exo), 209(endo, m), 230(exo), 240(endo), 290(endo) [b]]
$N_2H_5ClO_4 \cdot NH_3$	21.53	21.40	137(endo, m), 240(exo)
$N_2H_6(ClO_4)_2 \cdot 2\,NH_3$	12.04	11.98	100(endo, m), 218(exo)

[a] All DTA curves taken in air; *m* = melting.
[b] In vacuum.

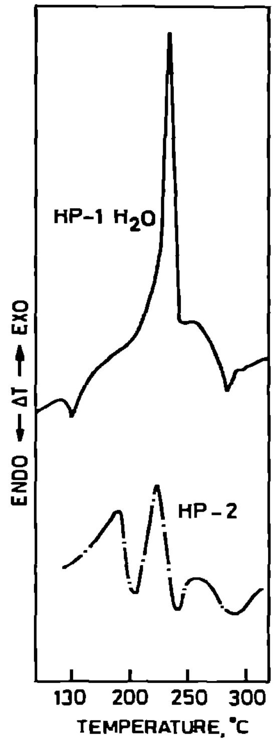

Fig. 1. DTA curves of hydrazine perchlorates in vacuum (below 20 torr).

hydrate to give the corresponding hydrazinium salts

$$NH_4X(s) + N_2H_4 \cdot H_2O(l) \rightarrow N_2H_5X(s) + NH_3(g) + H_2O(g) \qquad (2)$$

where $X = F^-, Cl^-, Br^-, NO_3^-$ and ClO_4^-, etc. A similar reaction is also possible with anhydrous hydrazine, so that reaction (1) appears to be reversible. In the light of this, we attempted to prepare HP-ammoniates by the reaction of HP-hydrates with ammonia gas and ammonia liquid. We were able to isolate HP-ammoniates only when the reaction was carried out with $NH_3(g)$. The products with liquid ammonia were mixtures of AP and HP. The reactions with $NH_3(g)$ can be written

$$N_2H_5ClO_4 \cdot H_2O(s) + NH_3(g) \rightarrow N_2H_5ClO_4 \cdot NH_3(s) + H_2O(g) + \text{heat} \qquad (3)$$

$$N_2H_6(ClO_4)_2 \cdot 2\,H_2O(s) + 2\,NH_3(g) \rightarrow N_2H_6(ClO_4)_2 \cdot 2\,NH_3(s) + 2\,H_2O(g) + \text{heat} \qquad (4)$$

This reaction is exothermic, as shown by the heating of the reaction flask. The crystalline salts swell in size when $NH_3(g)$ is absorbed and become amorphous and non-hygroscopic.

The HP-ammoniates were characterized by hydrazine analysis (Table 1) and their IR spectra (Table 2). The IR frequencies observed are similar to those observed for $M(NH_3)_2(ClO_4)_2$ [8]. Characteristic bands due to coordinated ammonia are observed ~1400 and 750 cm^{-1} and are assigned as $\delta(NH_3)$ and $\rho_r(NH_3)$, respectively. Both the HP-ammoniates are non-hygroscopic and can be stored without decomposition. They are not shock-sensi-

TABLE 2

Infrared absorption frequencies of hydrazine perchlorate hydrates and ammoniates (cm^{-1})

Assignment	$N_2H_5ClO_4 \cdot 0.5\ H_2O$	$N_2H_5ClO_4 \cdot H_2O$	$N_2H_6(ClO_4)_2 \cdot 2\ H_2O$	$N_2H_5ClO_4 \cdot NH_3$	$N_2H_6(ClO_4)_2 \cdot 2\ NH_3$
ν(O—H)	3400—3600	3400—3600	3400—3600		
ν(N—H)	3240	3240	3240	3240, 3380	3240, 3380
$\delta(H_2O)$	1600	1600	1600		
$\delta(NH_3)$				1400—1410	1410
$\rho_r(NH_3)$				750	750
Perchlorate bands					
ν_3	1100	1100	1100	1100	1100
ν_1	945	945	940	945	940
ν_4	630	630	630	630	630
ν(N—N)	965	965	985	965	985

tive. The thermal properties of HP-ammoniates are quite different from those of the corresponding hydrates. Both the ammoniates melt and decompose exothermally and explosively; both the HP ammoniates are thermally less stable than the corresponding hydrates, as seen by the lower decomposition temperatures in DTA. The difference in the decomposition temperatures of HP-2 hydrate and ammoniate is quite appreciable (~50°C). This is quite natural, since HP-ammoniates behave like monopropellants, having oxidizing (ClO_4^-) and reducing (N_2H_4, NH_3) groups in the same molecule.

In conclusion, HP-ammoniates can be prepared by reaction of the corresponding hydrates with ammonia gas. The HP ammoniates are non-hygroscopic, stable and are not shock-sensitive.

Further work on the compatibility of these salts with conventional polymers and their possible use as solid propellant oxidizers is in progress.

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