Notes

Synthesis and Characterization of a New Sulphate Derivative of Hydrazine, $N_2H_5HSO_4$ *

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Hydrazinium(1+) hydrogensulphate, $N_2H_5HSO_4$, has been prepared for the first time by the reaction of solid ammonium hydrogensulphate with hydrazine monohydrate. The compound has been characterized by chemical analysis, infrared spectra, and *X*-ray powder diffraction. Thermal properties of $N_2H_5HSO_4$ have been investigated using differential thermal analysis and thermogravimetric analysis and compared with those of $N_2H_6SO_4$ and $(N_2H_5)_2SO_4$.

Hydrazine is known [1,2] to form three sulphate derivatives namely, (*i*) hydrazinium(2+) sulphate, $N_2H_6SO_4$; (*ii*) dihydrazinium(1+) sulphate, $(N_2H_5)_2SO_4$; and (*iii*) hydrazine bis(sulphuric acid) $N_2H_4 \cdot 2H_2SO_4$. In aqueous solution the hydrazinium(2+) ion, $N_2H_6^{2+}$, of the hydrazinium salts dissociates according to equation (1). This has been attributed [2] to the small second ionization constant of the reaction (2).

$$N_2H_6^{2+} + H_2O \rightleftharpoons N_2H_5^+ + H_3O^+ \qquad (1)$$

$$N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^- \ (K_2 = 8.9 \times 10^{-16}) \qquad (2)$$

Hydrazinium(2+) sulphate, $N_2H_6SO_4$, mainly exists as $N_2H_5HSO_4$ in aqueous solution.[3] However, no attempt seems to have been made to isolate $N_2H_5HSO_4$ in the solid state. During the course of our study on hydrazine derivatives we have reported [4—6] the preparation of a number of hydrazinium salts by the reaction of solid ammonium salts with hydrazine monohydrate. As a part of this study we now report the preparation of hydrazinium hydrogensulphate, $N_2H_5HSO_4$, by the reaction of solid ammonium hydrogensulphate with hydrazine monohydrate. Formation of $N_2H_5HSO_4$ has been confirmed by chemical analysis, *X*-ray powder diffraction, and i.r. spectra. The physico-chemical properties of $N_2H_5HSO_4$ have been compared with those of $N_2H_6SO_4$ and $(N_2H_5)_2SO_4$.

Experimental

Both $N_2H_5HSO_4$ and $(N_2H_5)_2SO_4$ were prepared by reacting calculated amounts of the corresponding ammonium salts with hydrazine monohydrate as described earlier.[4—6] The compound $N_2H_6SO_4$ was available commercially (B.D.H., AnalaR) and used after recrystallization. The hydrazine content was determined volumetrically by titrating against standard (0.05 mol dm^{-3}) KIO_3 solution under Andrew's conditions.[4] The sulphate content was estimated gravimetrically as $BaSO_4$[7] [Found: N_2H_4, 24.40; SO_4, 72.85. $N_2H_5HSO_4$ requires N_2H_4, 24.65; SO_4, 73.80%. Found: N_2H_4, 39.45. $(N_2H_5)_2SO_4$ requires N_2H_4, 39.55%].

X-Ray powder diffraction patterns were obtained using a Phillips *X*-ray diffractometer, using Co-K_α radiation with an iron filter. Some values of the *d* spacings with intensity in parentheses are: (*i*) $N_2H_5HSO_4$, 4.361 (100), 3.059 (50), 4.089 (50), and 4.407 (40); (*ii*) $N_2H_6SO_4$, 4.129 (100), 3.537 (75), 3.257 (60), and 3.121 (50); and (*iii*) $(N_2H_5)_2SO_4$, 2.625 (100), 3.018 (90), 5.412 (80), and 4.949 (80).

Infrared spectra were recorded, using a Perkin-Elmer model 597 spectrophotometer, as KBr pellets. Differential thermal analysis (d.t.a.) experiments were carried out both in air and vacuum using the instrument fabricated in our laboratory [8] and fitted with an Omniscribe stripchart recorder. Thermogravimetric analysis (t.g.a.) experiments were carried out using a Stanton Redcroft TG-750 thermobalance. The heating rates of 10 °C min^{-1} for both t.g.a. and d.t.a. were employed. Platinum cups were used as sample holders. About 100 mg of sample was used for d.t.a. and 5—6 mg for t.g.a. experiments. All t.g.a. experiments (dynamic and isothermal) were carried out in a nitrogen atmosphere.

Results and Discussion

Ammonium hydrogensulphate reacts instantaneously with hydrazine monohydrate with the evolution of ammonia. The reaction can be represented by equation (3). Formation

$$NH_4HSO_4 + N_2H_4 \cdot H_2O \longrightarrow N_2H_5HSO_4 + NH_3 + H_2O \qquad (3)$$

of hydrazinium hydrogensulphate is confirmed by the chemical analysis, *X*-ray powder diffraction, and i.r. spectra (Table 1). In order to establish the identity of $N_2H_5HSO_4$ unequivocally and differentiate it from $(N_2H_5)_2SO_4$ and $N_2H_6SO_4$ in particular, a comparative study is made.

(*a*) *Infrared Spectra.*—Infrared absorption frequencies of $N_2H_5HSO_4$, $N_2H_6SO_4$, and $(N_2H_5)_2SO_4$ have been listed in Table 1. The assignments of the bands are made on the basis of earlier work.[9—15] It can be seen that both $N_2H_5HSO_4$ and $(N_2H_5)_2SO_4$ show characteristic absorptions of the $N_2H_5^+$ ion at ~1 600, ~1 400, 1 240, 980, and ~963 cm^{-1}. The ν_3 band of the SO_4^{2-} ion in $N_2H_5HSO_4$ is split into two bands at 1 105 and 1 080 cm^{-1} indicating C_{3v} symmetry of HSO_4^-. However, the absorption at 617 cm^{-1} (ν_4) does not show any splitting. The main distinguishing feature of $N_2H_5HSO_4$ from $N_2H_6SO_4$ is the presence of ν(N–N) of $N_2H_5^+$ at 963 cm^{-1} in the former compared to ν(N–N) of $N_2H_6^{2+}$ at 1 023 cm^{-1} in the latter. Although i.r. spectra of both $N_2H_5HSO_4$ and $(N_2H_5)_2SO_4$ are almost identical the hydrazium content is different.

(*b*) *Thermal Analysis.*—The results of the thermal analysis (t.g.a. and d.t.a.) of $N_2H_5HSO_4$, $N_2H_6SO_4$, and $(N_2H_5)_2SO_4$

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* *Non-S.I. unit employed:* 1 mmHg = (101 325/760) N m^{-2}.

Table 1. Infrared absorption frequencies (cm^{-1}) * of $N_2H_5HSO_4$, $N_2H_6SO_4$, and $(N_2H_5)_2SO_4$

$N_2H_5HSO_4$	$N_2H_6SO_4$	$(N_2H_5)_2SO_4$	Assignment
3 245m		3 245m	N–H stretching of NH_2 group (N–H · · · O)
3 149w		3 145w	
3 040w	3 080w	3 040w	N–H stretchings of NH_3^+ group (N–H · · · O)
2 970w	2 930w	2 970w	
2 690w	2 790w	2 690w	
2 575m	2 590w	2 575m	
	2 100w		NH_3^+ deformation
1 630m		1 630m	NH_2 deformation
1 604w	1 610m	1 600w	
1 576m	1 555m (sh)	1 578m	N–H bendings
1 510 (sh)	1 510s, br	1 510 (sh)	
1 496s		1 495s	
1 400s		1 410m	
		1 400m	$N_2H_5^+$ deformation
1 240s	1 147m, br	1 240m	
		1 180w (sh)	NH_3^+ rocking
1 105s, br	1 057m	1 110s, br	$\nu_3(SO_4)$
1 080 (sh)		1 082 (sh)	
980 (sh)		990w	
		980w	NH_2 rocking
970 (sh)	969m	970 (sh)	$\nu_1(SO_4)$
963s	1 023m	964m	N–N stretching
	640s (sh)		
617s	616s	619s	$\nu_4(SO_4)$
498s, br	513s	498s, br	Torsional mode
455 (sh)	466s	450 (sh)	$\nu_2(SO_4)$

* br = Broad, m = medium, s = strong, sh = shoulder, and w = weak.

Table 2. D.t.a. and t.g.a. results of $N_2H_5HSO_4$, $N_2H_6SO_4$, and $(N_2H_5)_2SO_4$

		Thermogravimetry		
Compound	d.t.a. peak */°C	Temp. range/°C	% Wt. loss found (calc.)	Phenomena
$N_2H_5HSO_4$	105 (endo)			Melting
	250 (exo)	190—290	54 (53.15)	$10\ N_2H_5HSO_4 \longrightarrow 2\ (NH_4)_2SO_4 + 3\ NH_4HSO_4 + 6\ N_2 + NH_3 + 12\ H_2O + 4\ SO_2 + H_2S$
	324 (endo)	300—400	100 (100.0)	$(NH_4)_2SO_4 \longrightarrow NH_4HSO_4 \longrightarrow$ decomposition and volatilization
	404 (endo)			
$N_2H_6SO_4$	222 (endo)			Phase transformation
	265 (endo)			Melting with decomposition
	271 (exo)	270—290	56 (55.81)	$20\ N_2H_6SO_4 \longrightarrow 10\ NH_4HSO_4 + 4\ NH_3 + 13\ N_2 + 28\ H_2O + H_2S + 3\ S + 6\ SO_2$
	400 (endo)	300—450	100 (100.0)	$NH_4HSO_4 \longrightarrow$ decomposition and volatilization
$(N_2H_5)_2SO_4$	95 (endo)			Melting
	250 (exo)	180—280	57 (57.41)	$5\ (N_2H_5)_2SO_4 \longrightarrow 3\ NH_4HSO_4 + 6\ H_2O + 5\ N_2 + SO_2 + H_2S + 7\ NH_3$
	400 (endo)	300—450	100 (100.0)	$NH_4HSO_4 \longrightarrow$ decomposition and volatilization

* endo = Endothermic peak, exo = exothermic peak.

are summarized in Table 2. Both hydrazinium suphates melt at ~100 °C and decompose exothermically at 250 °C. Hydrazinium(2+) sulphate melts with decomposition at 265 °C. The d.t.a. of $N_2H_5HSO_4$ shows an additional endotherm at 324 °C which is not seen in the d.t.a.s of $N_2H_6SO_4$ and $(N_2H_5)_2SO_4$. This endotherm has been assigned to the decomposition of $(NH_4)_2SO_4$ to NH_4HSO_4.[16] The observed weight loss in t.g.a. (190—290 °C, 54%) for the decomposition of $N_2H_5HSO_4$ has been attributed to a mixture of $(NH_4)_2SO_4$ and NH_4HSO_4. Therefore, it appears that whereas $N_2H_5HSO_4$ decomposes to give a mixture of $(NH_4)_2SO_4$ and NH_4HSO_4, $N_2H_6SO_4$ and $(N_2H_5)_2SO_4$ both decompose to give NH_4HSO_4 which decomposes and volatalizes at 400 °C (endotherm). However, vacuum d.t.a. of the sulphate derivatives of hydrazine (Figure) show identical d.t.a. curves and thus it appears that all such compounds initially decompose to give $(NH_4)_2SO_4$ which further decomposes to NH_4HSO_4.

Further distinction between the thermal decomposition of $N_2H_5HSO_4$ and $N_2H_6SO_4$ has been made by kinetic studies. The kinetics of decomposition have been studied by isothermal t.g.a. in the temperature region 250—290 °C. The activation energy of decomposition has been calculated using the Jacobs-Kureishy equation.[17] The activation energies for decompositions are: $N_2H_5HSO_4$, $-\ E_a = 200.85$ kJ mol^{-1} ($\alpha = 0.1$—0.8); $N_2H_6SO_4$, $-\ E_a = 131.38$ kJ mol^{-1} ($\alpha = 0.1$—0.4), $-\ E_a = 165.27$ kJ mol^{-1} ($\alpha = 0.5$—0.9).

In conclusion, the reaction of solid NH_4HSO_4 with hydrazine monohydrate yields hydrazinium(1+) hydrogensulphate which has distinct chemical and thermal characteristics.

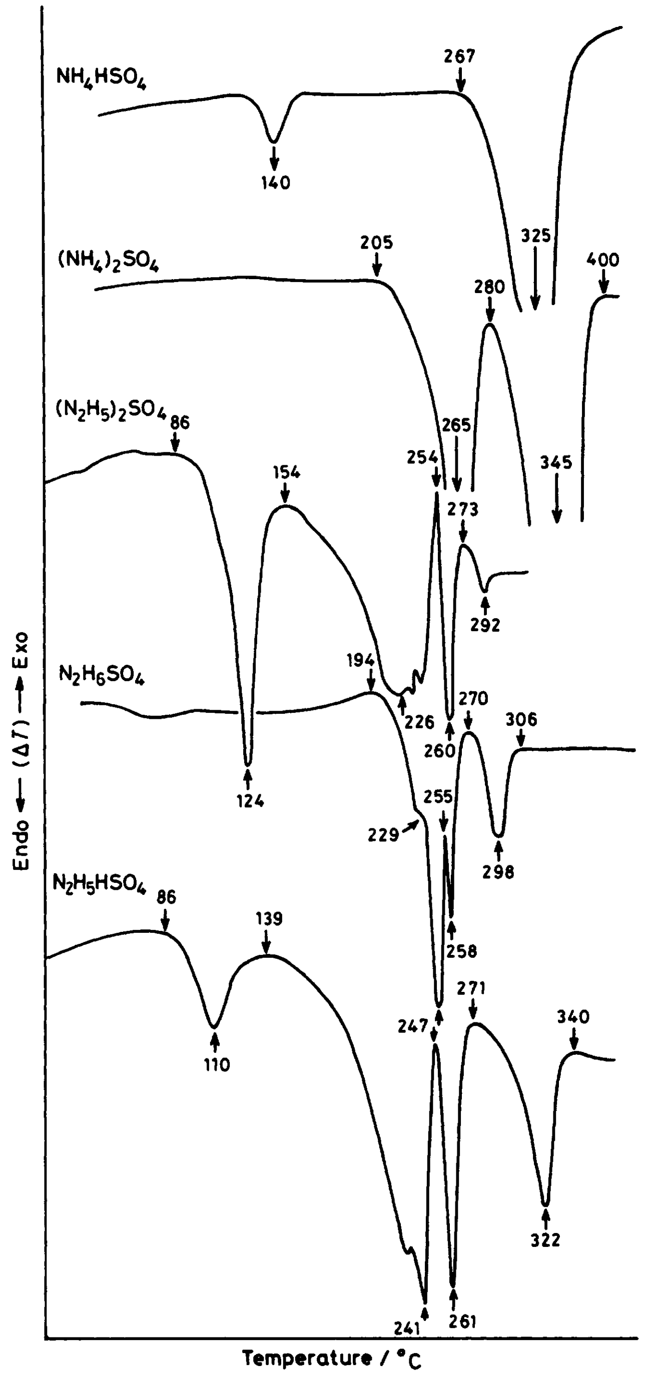

Figure. Differential thermal analysis (0.5 mmHg pressure) with a heating rate of 13 °C min^{-1}

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