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Thermoanalytical Properties of Hydrazinium Sulfite Monohydrate

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Hydrazinium sulfite monohydrate has been isolated as the product of the heterogeneous reaction between $N_2H_4.H_2O$ and SO_2 gas. The product is characterized by chemical analysis, infrared spectrum, X-ray diffraction and thermoanalytical properties studies.

INTRODUCTION

The reaction between hydrazine hydrate and sulfur dioxide gas has been investigated by many workers. However, the nature of the product reported differs[1-3] viz. $(N_2H_5)_2S_2O_5$, $HSO_2{\cdot}HN{\cdot}NH{\cdot}SO_2H$ and $N_2H_2(HSO_2{\cdot}N_2H_4)_2$, $(N_2H_5)_2SO_3$. Interestingly, a similar reaction with CO_2 gas, (in place of SO_2) has been studied[4] and there seems to be unanimity as for the nature of the product. A systematic attempt is therefore, made to reinvestigate this heterogeneous reaction with SO_2 gas. The product obtained is identified by chemical analysis, infrared spectrum and thermal analysis and the results are presented in this paper.

EXPERIMENTAL

The commercially available chemicals (AnalaR or equivalent grade) were used as such without purification. Hydrazine hydrate, $N_2H_4{\cdot}H_2O$, (99-100%) BDH was used.

Sulfur dioxide gas was generated by the addition of 1 : 1 HCl to Na_2SO_3. On bubbling this gas through hydrazine hydrate ($N_2H_4{\cdot}H_2O$), the product was precipitated by the addition of ethanol, which was washed with ether and dried over P_2O_5.

The usual volumetric method of determining hydrazine using 0.025 M KIO_3 solution under Andrews[5] conditions could not be used as sulfite also undergoes oxidation with KIO_3. Therefore, a modified procedure (method of difference) for the determination of N_2H_4 was developed. According to this procedure, the KIO_3 titration gives the combined value of hydrazine and sulfite from which the amount corresponding to sulfite alone (determined iodometrically by using excess of I_2 in acidic medium pH-4) was subtracted to determine the hydrazine content.

Infrared spectrum of the sample was recorded as nujol mull using a Perkin-Elmer-599 spectrophotometer. Simultaneous TG- DTG-DTA curves of the samples were recorded using a TGD-5000 RH thermobalance of ULVAC Sinku–Riko Japan. All experiments were carried out in air using 4–5 mg. of the sample. Heating rate employed was 20°C/min. X-ray powder diffraction patterns of the sample was recorded on a Philips PW 1050/70 diffractometer using Cuk_α radiation.

RESULTS AND DISCUSSION

Reaction between hydrazine hydrate and sulfur dioxide is exothermic and yields a syrupy liquid from which a solid is precipitated using ethanol. The product analysed for the composition is $(N_2H_5)_2SO_3 \cdot H_2O$ ($\% N_2H_4$: obsd. 39.14 reqd. 39.02; %S: obsd. 19.46 reqd. 19.51). The reaction can be represented as follows:

$$2N_2H_4 \cdot H_2O + SO_2 \rightarrow (N_2H_4)_2 \cdot H_2SO_3 \cdot H_2O.$$

$$(N_2H_4)_2 \cdot H_2SO_3 \cdot H_2O \rightarrow (N_2H_5)_2SO_3 \cdot H_2O.$$

The mechanism can be explained on the basis of addition of SO_2 to H_2O to form H_2SO_3 and subsequent formation of salt with N_2H_4.

$$H_2O + SO_2 \rightarrow H_2SO_3.$$

$$H_2SO_3 + 2N_2H_4 \cdot H_2O \rightarrow (N_2H_5)_2SO_3 \cdot H_2O + H_2O$$

Unlike in the case of the reaction of N_2H_4 (hydrazine) with CO_2 to form N_2H_3COOH, Sulfur dioxide does not yield N_2H_3SOOH. This may be obviously understood, since in the case of CO_2 the lone pair on N atom of N_2H_4 attacks the positive centre of (C atom) forming $N_2H_3COO^-$ ion. Salts and complexes of this ion are well known.[4] However, in the case of SO_2 sulfur atom has a free electron pair, which repels such an attack. And SO_2, owing to its greater affinity for H_2O, forms H_2SO_3 which subsequently gives hydrazine salt $(N_2H_5)_2SO_3$.

TABLE 1

CALCULATED d VALUES OF $(N_2H_5)_2SO_3.H_2O$ USING X-RAY POWDER DIFFRACTION PATTERN

20	d-values	relative intensity
14.70	6.968	20.6
15.25	6.7458	16.36
28.00	3.6999	31.82
31.2	3.3285	26.06
32.05	3.2424	24.24
32.65	3.844	100.00
33.6	3.0969	27.3
34.65	3.0058	32.73

During the investigation it was noted that irrespective of the amount of SO_2 gas used, the end product invariably had the same N_2H_4 and S contents.[2]

Infrared spectrum of $(N_2H_5)_2SO_3{\cdot}H_2O$ shows characteristic absorption frequencies (Table 2) of $N_2H_5^+$ ion, SO_3^{2-} ion and H_2O. The absorptions at 3325 ($\nu_{asym\ NH}$), 3275 ($\nu_{sym\ NH}$), 1620 (δ_{NH_2}), 1560 ($\delta_{NH_3^+}$), 1300 ($\rho_{NH_3^+}$). 1170 (W_{NH_2}), 1120 (ν_{NH_2}), 970 (ν_{N-N}) cm^{-1} are attributed to various vibrational modes[6] of $N_2H_5^+$. The observed N–N stretching frequency at 970 cm^{-1} indicates the presence of ionic $N_2H_5^+$ in the solid. The structure of sulfite ion is known to be pyramidal with the S–O bands. The absorption at 965, 620 and 490 cm^{-1} are characteristic of ionic sulfite[7]. The bands at 3585 and 1640 cm^{-1} are due to O–H and H_2O respectively of water molecule, thus confirming the formula assigned to the compound.

TABLE 2

INFRARED ABSORPTION FREQUENCIES OF $(N_2H_5)_2SO_3.H_2O$ AND ASSIGNMENT

Absorption cm^{-1}	Assignment
3585(w)	Asym. O–H stretching
3325(b)	Asym. N–H stretching
3275(vb)	Asym. N–H stretching
2650(w)	N–H stretch. of NH_3^+
1700(m)	O–H bending
1680,	
1640(s)	NH_2 bending
1620,	
1560(s)	bending of NH_3^+
1300(m)	NH_3^+ rocking
1170(m)	NH_2 wagging
1135,	
1120(s)	NH_2 twisting
970(sb)	N–N stretching
770(s)	S–O stretching
620(s)	S–O sym. bending
490(m)	asym. bending

The analyses of simultaneous TG–DTG–DTA curve of $(N_2H_5)_2SO_3 \cdot H_2O$ is summarised in Table 3. The TG–DTG shows three distinct steps, DTA shows two endotherms and two exotherms. The sharp endotherm at 58°C is reversible and is assigned to melting. The first step in TG with a weight loss of 44.85% is attributed to the decomposition of $(N_2H_5)_2SO_3 \cdot H_2O$ to $(NH_4)_2SO_3$.

$$4(N_2H_5)_2SO_3 \cdot H_2O \rightarrow 3(NH_4)_2SO_3 + SO_2 + 4NH_3 + 5H_2O + H_2 + 3N_2$$

TABLE 3

THERMAL DECOMPOSITION DATA OF $(N_2H_5)_2SO_3.H_2O$

Step No.	Thermogravimetry temp. range °C	% Weight loss obsd. theor.	DTA peak temp. °C	Reaction
1.	—	—	58	Melting
2.	50–110	44.85 46.95	110	$4(N_2H_5)_2SO_3.H_2O \rightarrow 3(NH_4)_2SO_3 + H_2 + 3N_2 + SO_2 + 4NH_3 + 5H_2$
3.	120–200	80.5 80.0	162	$5(N_2H_5)_2SO_3.H_2O \rightarrow (NH_4)_2SO_4 + S$ + gaseous products
4.	200–290	100.0 100.0	300	broad peak $(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2SO_4$

This reaction is seen as an exothermic peak at 100°C. The decomposition of hydrazine salts to ammonium salts is known to be exothermic. The second step in TG with a weight loss of 80.5% may be attributed to the decomposition of $(NH_4)_2SO_3$ to $(NH_4)_2SO_4$.

Combustion Studies

$(N_2H_5)_2SO_3 \cdot H_2O$ when heated in a test tube, initially melts and then decomposes with the evolution of NH_3 and SO_2 and a decomposition of sulfur on cooler parts of the test tube. The melt exhibits colour display characteristic of thiosulfate, possibly due to the reaction of sulfite with S.

Hydrazinium sulfite monohydrate is highly soluble in water and the solution is acidic (pH *ca* 4). Aqueous solution of $(N_2H_5)_2SO_3 \cdot H_2O$ when treated with solutions of metal salts yields metal sulfite hydrazinate hydrates.

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