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THERMAL BEHAVIOR AND IR ABSORPTION SPECTRA OF THE SODIUM SALTS OF 1-NITROSO-2-NAPHTHOL-6-SULFONIC ACID AND 2-NITROSO-1-NAPHTHOL-6-SULFONIC ACID

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ABSTRACT

IR absorption spectra and thermal behavior were investigated for the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid. The infrared spectra of both salts show characteristic strong bands at 1200–475 cm^{-1} due to the sulfonato group and at 1480–1420 cm^{-1} due to the nitroso group. The IR spectra were recorded in KBr.

Dynamic studies on the thermal behavior of the two salts showed that their decomposition in nitrogen atmosphere proceeds in a similar manner, in three steps: dehydration at 50–150°C, formation of the sodium salts of 1- or 2-naphthol-6-sulfonic acid at 250–300°C, and the final weight loss associated with the formation and sublimation of 1- or 2-naphthol and the formation of sodium sulfate at 340–650°C. For both salts the DSC studies show two peaks the first of which is endothermic and the second exothermic. The first is due to the loss of water and the second to the decomposition of the salt.

INTRODUCTION

The thermal decomposition of sulfo-substituted aromatic ortho hydroxycarboxylic acids has been described earlier [1–3]. The sulfonic acid derivatives of α- and β-nitrosonaphthols have found wide use in spectrophotometric and potentiometric titrations because of their ability to form stable and colorful complexes with many metal ions in aqueous solutions [4–17]. In particular, 2-nitroso-1-naphthol-4-sulfonic acid has proved to be an excellent ligand in ion pair extraction for the spectrophotometric determination of nickel in iron and steel [18].

1-Nitroso-2-naphthol-6-sulfonic acid (126NNS) is a weaker acid in aqueous phase than 2-nitroso-1-naphthol-6-sulfonic acid (216NNS) [8,18]. The strong inductive effect on the oxygen in the ortho position of the naphthalene ring [19] in 216NNS makes the hydrogen bond weaker and, as a result, gives rise to stronger acid properties. Tautomeric effects influence the

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ring as well. Probably, the formation of intramolecular hydrogen bonds further increases the acidity of 2-nitroso-1-naphthol-6-sulfonic acid.

The aim of the present study was to investigate the structures, the decomposition mechanisms in nitrogen atmosphere, and the infrared absorption properties of the two solid isomers, sulfo-substituted α- and β-nitrosonaphthols.

EXPERIMENTAL

Reagents

The sodium salt of 1-nitroso-2-naphthol-6-sulfonic acid (Fig. 1) was synthesized as described in the literature [20]. The crude yellowish product was recrystallized three times from water–ethanol (1 : 1, v/v). (Found: C, 41.05; H, 2.80; N, 4.72; S, 11.0; O, 32.0; Na, 7.77. $C_{10}H_6NO_5SNa \cdot H_2O$ requires: C, 40.96; H, 2.75; N, 4.78; S, 10.9; O, 32.7; Na, 7.84%) The sodium salt of 2-nitroso-1-naphthol-6-sulfonic acid (Fig. 1) was synthesized as described earlier [12] and was purified as above. (Found: C, 36.51; H, 3.69; N, 4.26; S, 9.63; O, 38.2; Na, 6.87. $C_{10}H_6NO_5SNa \cdot 3H_2O$ requires: C, 36.48; H, 3.67; N, 4.25; S, 9.74; O, 38.9; Na, 6.98%).

Apparatus

The gravimetric analyses were made with a Mettler TA 3000 TG 50 thermobalance. The TG calibration was made with alumel, mumetal, and trafoperm for which the Curie points were 149.3, 392.4 and 745.6°C, respectively. The calorimetric measurements were performed with a Mettler TA 3000 DSC 20 system, calibrated with pure indium (99.999%). A Perkin-Elmer model 577 infrared spectrophotometer was used to record the IR spectra. In all cases, samples were weighed on a Mettler M 3 electronic microbalance.

The TG curves of the sodium salts of 126NNS and 216NNS were studied in a nitrogen atmosphere (flow rate 100 ml min^{-1}) from 25 to 800°C with heating rates of 4 and 20 K min^{-1}. In the calorimetric measurements the

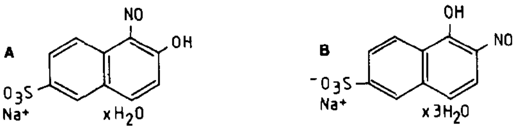

Fig. 1. The structures of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid (A) and 2-nitroso-1-naphthol-6-sulfonic acid (B).

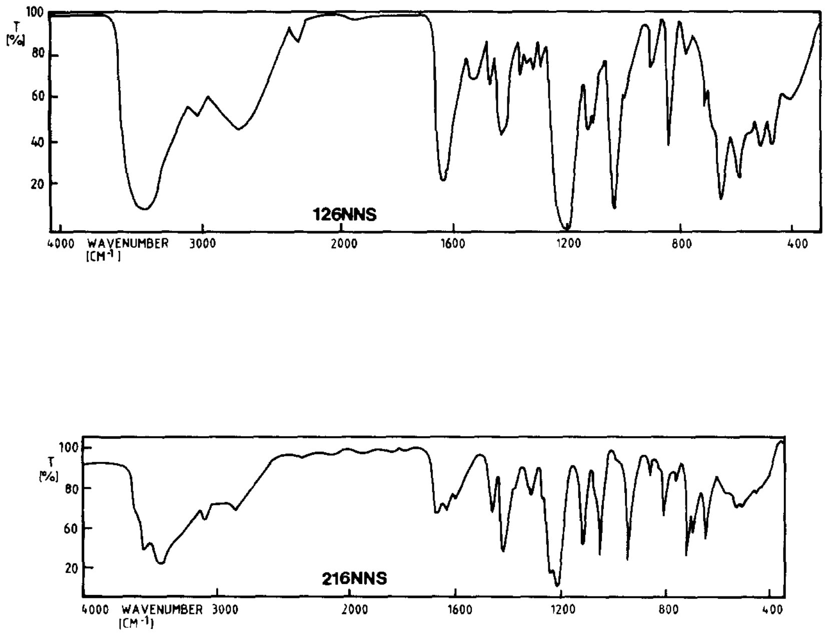

Fig. 2. The infrared spectra of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid in KBr.

samples were heated from 25 to 400°C at a heating rate of 4 K min^{-1}, in nitrogen atmosphere with a flow rate of 100 ml min^{-1}.

RESULTS AND DISCUSSION

The infrared spectra of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid are presented in Fig. 2. Both compounds show characteristic strong absorption bands for the functional groups, as listed in Table 1. From the spectra we can conclude that both compounds have a hydrogen bonded OH-group.

The dynamic studies on the thermal behavior of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid show that both compounds decompose in three weight loss steps (Table 2). The TG and DTG curves are presented in Fig. 3. The first weight decrease is due to the loss of water molecules, and the second step is the formation of the sodium salts of 1- and 2-naphthol-6-sulfonic acids. The final weight loss is associated with the formation and sublimation of 1- and 2-naphthol and formation of sodium sulfate. The weight losses are summed in Table 2.

The DSC curves of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid are presented in Fig. 4. The first endothermic peaks are due to the loss of one water molecule in the case

TABLE 1

The characteristic bands in infrared spectra of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic acid and 2-nitroso-1-naphthol-6-sulfonic acid

Ligand	$\bar{\nu}$ [cm^{-1}]	Group
126NNS	1200, 1040, 840, 660, 475	sulfonato stretching
216NNS	1205, 1050, 935, 715, 648	sulfonato stretching
126NNS	1660, 1445	nitroso stretching
216NNS	1665, 1620, 1410	nitroso stretching
126NNS	3060, 2920, 2840, 2615, 1290, 1110, 590	C–H bending of the napthalene skeleton
216NNS	3060, 2920, 2840, 1320, 1110, 806, 696	C–H bending of the napthalene skeleton
126NNS	1475, 1375, 1290	C=C stretching
216NNS	1450, 1319, 1218	C=C stretching
126NNS	3420, 1345, 780, 715	O–H stretching
216NNS	3590, 3510, 3410, 1405, 1240, 760	O–H stretching

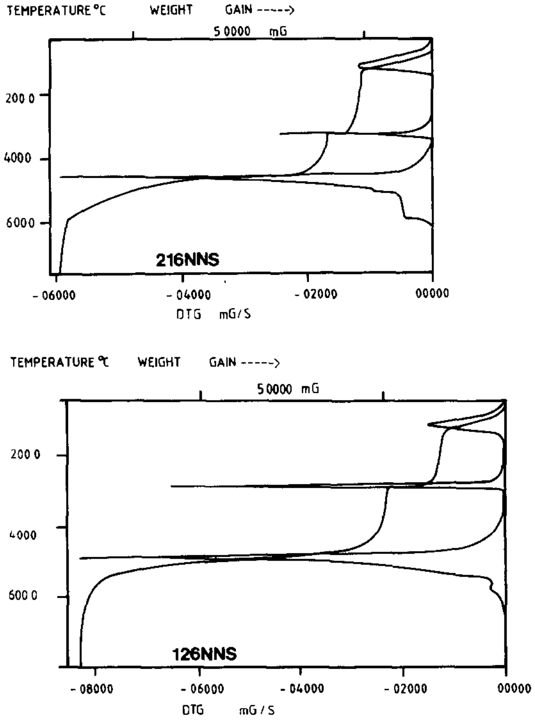

Fig. 3. TG and DTG curves of the sodium salts of 126NNS and 216NNS in nitrogen atmosphere. Heating rate 4 K min^{-1}.

TABLE 2

The TG and DSC data of the sodium salts of 126NNS and 216NNS

TG				DSC	
Compound	Weight loss (%)	Temperature range (°C)	Product	ΔH (kJ mol^{-1})	T (°C)
126NNS	6.3	50–150	$C_{10}H_6NO_5SNa$	76.5(7)	110
216NNS	16.6	50–150	$C_{10}H_6NO_5SNa$	144.9(3)	102
126NNS	9.1	230–300	$C_{10}H_7O_4SNa$	−94.3(5)	305
216NNS	10.0	250–300	$C_{10}H_7O_4SNa$	−115.0(3)	325
126NNS	63.1	340–650	$C_{10}H_8O+Na_2SO_4$		
216NNS	53.9	340–650	$C_{10}H_8O+Na_2SO_4$		

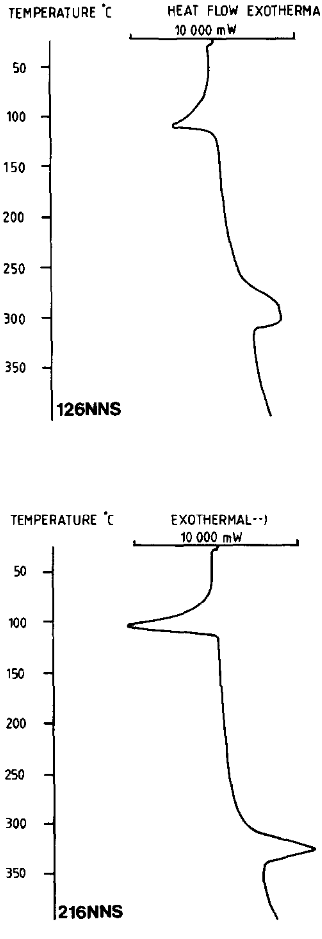

Fig. 4. DSC curves of the sodium salts of 126NNS and 216NNS in nitrogen atmosphere. Heating rate 4 K min^{-1}.

of 126NNS and of three water molecules when the sample is 216NNS. The second peaks are exothermic revealing the decomposition of the sodium salts of 126NNS and 216NNS.

According to these thermal studies, the sulfo-substituted β-nitrosonaphthol is slightly more stable than the α-substituted derivative: the decomposition of 216NNS begins about 20°C higher than that of 126NNS. However, the difference can be observed only by heating the samples very slowly.

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