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Salts of sulfaminic and nitrosulfonic acids — their synthesis and thermal transformations

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Abstract

A crystalline potassium salt of sulfaminic acid and some fractions of amorphous potassium salts of nitrosulfonic acids were obtained from a nitro-oligomer of the polyisoprene rubber SKI-3 by treating it with potassium hydrogensulfite. Crystalline Ba, Pb, Cd and Mg salts were also obtained. Their behavior on dynamic heating in air and nitrogen was also studied. The crystalline salts under study as well as the free sulfaminic acid were found to have similar thermal transformations and considerable thermal stability: they retain their weight up to about 300°C. Some of these salts are crystal hydrates and are dehydrated in the temperature range 110–150°C. The initial decomposition temperature of the free sulfaminic acid according to the DTA curve is 230°C. The principal decomposition of amorphous potassium salts begins above 200°C, showing endothermal effects between 250 and 300°C and exothermal ones at about 300 and 410°C. The composition and the constituent functional groups of the obtained salts were determined using elementary and thermal analysis, as well as IR spectroscopy and chemical methods.

INTRODUCTION

Sulfaminic acids have been obtained by two methods: the treatment of amines with chlorosulfonic acid; and the interaction of nitro-compounds with hydrogensulfites [1].

Compounds having a general formula R_2NSO_3H have been obtained by sulfamination or *N*-sulfonation of N-containing organic compounds [2]. Aromatic nitro-compounds are capable of reacting with alkaline hydrogensulfites according to the Piria reaction, thus yielding sulfaminic acids. The addition of hydrogensulfites to nitroalkenes is a little used method for *N*-sulfonation of organic compounds, whereby 1,2-nitrosulfonic acids are transformed to 1,2-aminosulfonic acids [3]. Alcohols of the type RCH(OH)R′, where R = NO_2, C=O and R′ = H, R, interact with hydrogen sulfates to form nitrosulfonic acids [4].

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Polyfunctional nitro-oligomers and nitro-alcohols [5] on synthetic rubber bases are N-sulfonated with potassium hydrogensulfite yielding potassium sulfamates, which are characterized by their high thermal stability. Salts of sulfaminic acids are of considerable practical interest as complexing compounds, organic additives to electrolytes, surfactants, fire retardants for polymer compositions [6], etc. Their high thermal stability makes it possible to use them as stabilizers for chlorinated polyethylene [7].

The aim of the present work was to obtain crystalline potassium barium, lead, cadmium and magnesium sulfamates, as well as some amorphous salts of nitrosulfonic acids, on bases of a nitro-oligomer of the polyisoprene rubber SKI-3. The thermal transformations of the salts thus obtained were also studied.

EXPERIMENTAL

For the initial and end products, the following abbreviations will be used in the present work: NO, polyisoprene nitro-oligomer; SA-K, crystalline potassium salt of a sulfaminic acid; SA-Ba, SA-Pb, SA-Cd and SA-Mg, crystalline salts of metals; ASA, ASA-K, ASA-Ba and ASA-Pb, amorphous salts.

Nitration of polyisoprene rubber SKI-3 with nitric acid

In a 1 l triple-necked flask equipped with a stirrer, a reflux cooler and a hydraulic trap, 50 g of rubber were dissolved in dichloroethane with constant stirring at 60°C. To the solution thus prepared, 190 ml of 65% nitric acid were dropped from a separating funnel, over 3 h, at 70°C. The reaction was left to continue with constant stirring for two more hours, thus yielding 75 g of yellow amorphous nitro-oligomer (NO). The latter was filtered and purified by precipitating its 15% solution into 4 l of distilled water.

N-sulfonation of polyisoprene nitro-oligomer with potassium hydrogensulfite

100 ml of 5% aqueous solution of potassium hydroxide were dissolved in a 1 l triple-necked flask, equipped with a stirrer and a reflux condenser. Sulfur dioxide was blown through the solution at 30–40°C until pH 6–7 was reached. Then 10 g of NO dissolved in 200 ml of a 2% aqueous solution of potassium hydroxide were added from a separating funnel with stirring at 40°C. The reaction continued for about three more hours at the same temperature and pH sulfur dioxide being blown periodically through the solution. On completion of the process, the solution was neutralized with hydrochloric acid. The chief product was 5–7 g of the crystalline potassium

salt of sulfaminic acid (SA-K). It was separated from the solution either by cooling or by concentrating in a vaccuum. SA-K was then purified by recrystallization from its ethanol–water solution. Ethyl alcohol was added in two-fold excess to the solution, which was then concentrated. Finally, four amorphous fractions of potassium salts of nitrosulfonic acids (ASA-K-1, ASA-K-2, ASA-K-3 and ASA-K-4) were subsequently isolated. The total yield was 4 g. When the initial NO was doubly precipitated (by separating the low molecular weight fractions) only amorphous products were obtained.

Preparation of sulfaminic acid metal salts and free sulfaminic acid

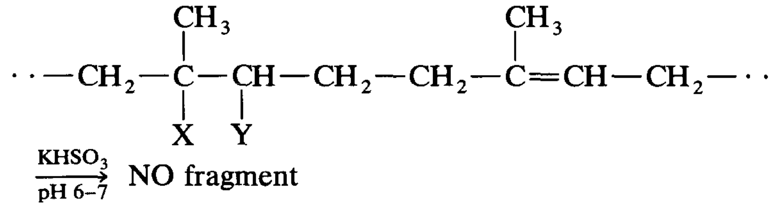
Ten grams of SA-K were treated with, in turn, 14 g of lead acetate, 9.2 g of barium chloride, 9.2 g of cadmium sulfate and 5.2 g of magnesium sulfate. The latter were added in equivalent quantities with respect to the sulfur content of the initial potassium sulfamate (SA-K). The crystalline metal salts were purified by recrystalization from their ethanol–water solutions. The ethanol to water ratio was 2:1 parts by volume and inorganic impurities were separated by precipitation from ethanol. The amorphous barium and lead salts (ASA-Ba and ASA-Pb) were obtained from the filtrate by a similar way.

The free sulfaminic acid was obtained by letting the aqueous solution of crystalline potassium salt pass through a highly acidic cation exchanger (Woffatit KS-10) with subsequent recrystallization from ethanol–water solution. The sulfaminic acid thus obtained is a white, crystalline, highly hygroscopic substance.

The products obtained were studied by means of IR spectroscopy, DTA, TG, DTG, and elementary and chemical analyses. The SA-K potassium content was determined using atomic absorption spectroscopy, while the contents of the other metals were determined complexometrically. The IR spectra were recorded on a UR-20 spectrophotometer using KBr discs (3 mg per 100 mg). A derivatograph (F. Paulik, L. Paulik, L. Erdey) was employed for thermal and thermogravimetric analyses. The heating rate was 8 K min^{-1}, sample weight was 100 mg and the atmosphere was either air (static) or nitrogen (flowing over the sample at a rate of 15 l h^{-1}). Weight changes were determined within an experimental error of ±1 mg.

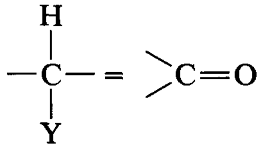
RESULTS AND DISCUSSION

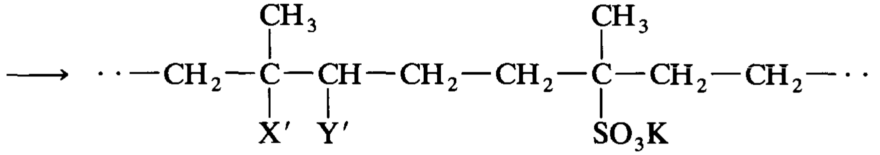
The major reaction centers of the polyisoprene SKI-3 rubber nitro-oligomer (NO) with respect to potassium hydrogensulfite are the nitro, ketone and hydroxyl groups. The interaction between the polydisperse NO, with $\overline{Mn}$ = 1200–2300, and a sulfonating agent yields crystalline potassium salts of sulfaminic acids and amorphous potassium salts of nitrosulfonic acids, according to the reaction scheme



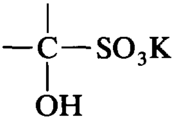
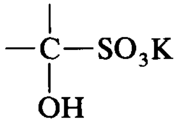
$$\cdots-CH_2-\underset{X}{\overset{CH_3}{C}}-\underset{Y}{CH}-CH_2-CH_2-\overset{CH_3}{C}=CH-CH_2-\cdots$$

$$\xrightarrow[\text{pH 6–7}]{KHSO_3} \text{NO fragment}$$

where X = ONO$_2$, OH, NO$_2$, Y = NO$_2$, OH and  $\underset{Y}{\overset{H}{-C-}} = {>}C=O$



$$\longrightarrow \cdots-CH_2-\underset{X'}{\overset{CH_3}{C}}-\underset{Y'}{CH}-CH_2-CH_2-\underset{SO_3K}{\overset{CH_3}{C}}-CH_2-CH_2-\cdots$$

where X′ = SO$_3$K, NHSO$_3$K and Y′ = NHSO$_3$K, SO$_3$K,  $-\underset{OH}{\overset{|}{C}}-SO_3K$ in the SA-K fragment; or X′ = OH, NO$_2$ and Y′ = NO$_2$, OH,  $-\underset{OH}{\overset{|}{C}}-SO_3K$ in the ASA-K fragment.

The nitrating reaction is a complicated process, involving destruction of the rubber macromolecule, aliphatic chain nitration at the C=C double bond, oxidation, etc. Consequently, the isoprene rings of NO containing the functional groups mentioned, as well as those in the products obtained are randomly situated.

The results of the elementary analyses for the crystalline and amorphous salts are given in Tables 1 and 2.

TABLE 1

Elementary composition of crystalline metallic salts of polyisoprene nitro-oligomer sulfaminic acids

No.	Salt	S (%) Schoniger	N (%) Kjeldahl	Me (%)
1	SA-K	9.9	3.3	12.1
2	SA-Ba	10.4	3.7	22.3
3	SA-Pb	8.9	3.8	28.8
4	SA-Cd	8.5	4.2	14.9
5	SA-Mg	10.3	3.5	17.1

TABLE 2

Elementary composition of amorphous metallic salts of polyisoprene nitro-oligomer nitrosulphonic acids

No.	Salt fraction	S (%) Schoniger	N (%) Kjeldahl
1	ASA-K-1	6.6	4.5
2	ASA-K-2	8.1	3.6
3	ASA-K-3	8.6	4.8
4	ASA-K-4	9.1	5.1
5	ASA-Ba	7.8	3.6
6	ASA-Pb	7.3	5.5

The reactions taking place during nitro-oligomer *N*-sulfonation may be clarified to some extent by means of IR spectroscopy (Table 3). It is interesting to note that potassium hydrogensulfite reduced the nitro group and, therefore, both $\nu(NO_2)$(as) at 1550 cm^{-1} and $\nu(NO_2)$(s) at 1360 cm^{-1} were absent from the spectrum of SA-K (as well as from the spectra of the other salts). In the course of the reaction, alkylhydroxylamine derivatives are probably formed, reacting thereafter with hydrogensulfite to form sulfamine groups. The latter were determined qualitatively with sodium nitrite and barium chloride [8]. The sulfamine group in the metallic sulfamates under study is characterized by δ(NH) at 1620–1570 cm^{-1} and the stretching vibration ν(NH) at 3230 cm^{-1}, but for some of the salts certain shifts can be observed. There is no ketone group vibration at 1700 cm^{-1}, due to the nucleophilic addition of potassium hydrogensulfite to the ketone groups, yielding secondary hydroxyl groups with δ(OH) at 1300 cm^{-1}.

Both the sulfo and sulfaminic groups in SA-K have $\nu(SO_2)$(as) at 1180 cm^{-1}, $\nu(SO_2)$(s) at 1050 cm^{-1} and ν(S–O) at 630 cm^{-1}. The characteristic bands of the other sulfamates are given in Table 2.

No bond vibrations at 1700 cm^{-1} for ν(C=O) or at 1620 cm^{-1} corresponding to δ(N–H) were found in the IR spectra of the amorphous potassium salts of the first and second fractions. For the third and fourth fractions, these vibrations are observed, but they are less intense.

These results show that the sulfonating agent reacts preferentially with the NO ketone groups: totally in the case of the first and second fractions, or partially with the third and fourth fractions. Potassium hydrogensulfite does not interact with the nitro groups (first and second fractions) but does cause partial sulfamination (third and fourth fractions). In these reactions the higher molecular weight NO fractions are involved, yielding amorphous salts of nitrosulfonic acids. The lower molecular weight NO fractions undergo N-sulfonation and nucleophilic addition of the sulfonating agent, yielding crystalline salts of sulfaminic acids.

The results of the thermal analysis in air (Fig. 1) show that the crystalline salts release 1–2% of water on heating to 100°C. From the nature of the peaks on the DTA and TG curves, this is physically bound water. The distinct endothermic peaks observed in the range 100–160°C and accompanied by 2–12% weight losses, are due to the liberation of crystallization water. As seen in Fig. 1, the amount of crystallization water is maximal for the Cd and Mg salts. This was confirmed by IR spectral data (Table 3) for the initial salts and those heated to 180°C, where the only difference in comparison with the initial structure of the sulfaminates is the absence of a band at 1320 cm^{-1}. The release of water and, hence, the reduced possibility of forming hydrogen bonds result in the absorption bands of $\nu(\mathrm{NH})$ at 3200–3100 cm^{-1} being more clearly defined. At temperatures above 170°C, all salts are characterized by a number of exothermal peaks, the sample weights increasing by about 3%. These processes are influenced strongly by the conditions of analysis, the contact surface area and the size of the sample particles. It is assumed, therefore, that these endothermal peaks are due to absorption of oxygen from the air which is desorbed on further heating. This is the probable reason for the absence of more oxygen-containing groups in the spectra of the salts heated at 280°C. At 280°C sulfamine groups are still partially retained (3150 cm^{-1}) because of the high thermostability of the salts.

The decomposition of the initial product of all the salts is preceded by a major endothermal peak of intense boiling which is complete at about 400°C. The final stage of combustion of the carbonized residue takes place only in air within the range 500–600°C.

There are distinct exothermal peaks with no weight increase in the range 180–280°C in a nitrogen medium, which indicates that oxidation takes place. The introduction of oxygen at the initial stages of decomposition to some extent hinders these processes because the weight loss in a nitrogen medium at 500°C proved to be somewhat greater than the weight loss in air.

DTA and TG curves of sulfaminic acid (Fig. 1) are similar to those of metallic salts, one difference being that an endothermal peak of sulfaminic acid melting is observed at 230°C. In addition, the weight losses for the thermal decomposition of the salts up to 600°C are lower, because of thermostable metallic oxides being formed.

In order to elucidate the mechanism of the thermal and thermo-oxidizing decomposition of the sulfamates, their residues after heating to 600°C in air and in nitrogen were analyzed. Their IR spectra were recorded and their composition was studied. Carbonized residue as well as a greater amount of metallic sulfide (in nitrogen) and metallic sulfate (in air) were found in all salts. Potassium polysulfides were found in the potassium salt residue, while lead oxide and cadmium oxide were found in the lead and cadmium salt residues.

TABLE 3

Characteristic absorption bands (cm^{-1}) in IR spectra of metallic salts of sulfaminic and nitrosulfonic acids in KBr disks (1 mg/300 mg)

No.	Salt fraction	ν(N–H) δ(N–H)	$\nu(CH_3, CH_2)$ (as) $\nu(CH_3, CH_2)$ (s)	ν(C=C) γ(=CH)	$\nu(NO_2)$ (as) $\nu(NO_2)$ (s)	$\nu(SO_2)$ (as) $\nu(SO_2)$ (s) ν(S–O)	Sec-OH δ(OH) ν(C–O)	ν(C=O)
1	SA-K	3230	2930	1640		1180, 1020	1320	–
		1620	2860	870	–	630	1080	
		3222	2930	1640		1200, 1070	1300	
2	SA-Ba	1600	2860	870	–	690	1120	–
		3300	2930	1640		1180, 1050	1300	
3	SA-Pb	1570	2860	880	–	690	1120	–
		3110	2930	–		1200, 1010	1290	
4	SA-Cd	1580	2860	890	–	630	1080	–
		3200	2930	1640		1190, 1020	1290	
5	SA-Mg	1620	2860	890	–	630	1080	–
6	ASA-K-1	–	2930	1635	1560	1240, 1040	1260	
	ASA-K-2		2860	880	1380 [a] weak	630	1080	–
7	ASA-K-3	–1620 weak	2940	1640	1550	1220, 1040	1260 weak	1710 weak
	ASA-K-4	1620 weak	2860	–	1380 [a]	630	–	–
8	ASA-Ba	–	2930	1635	1550	1220, 1040	1260	–
			2860	875		630		
9	ASA-Pb	–	2930	1635	1550	1220, 1040	1240	–
			2860	880		630		
10	NO	–	2900	1640	1550	–		1700
			2870	850	1360 [a]		–	

[a] 1380 cm^{-1}, $\nu(NO_2)$(s) overlapping $\nu(CH_3)$(s).

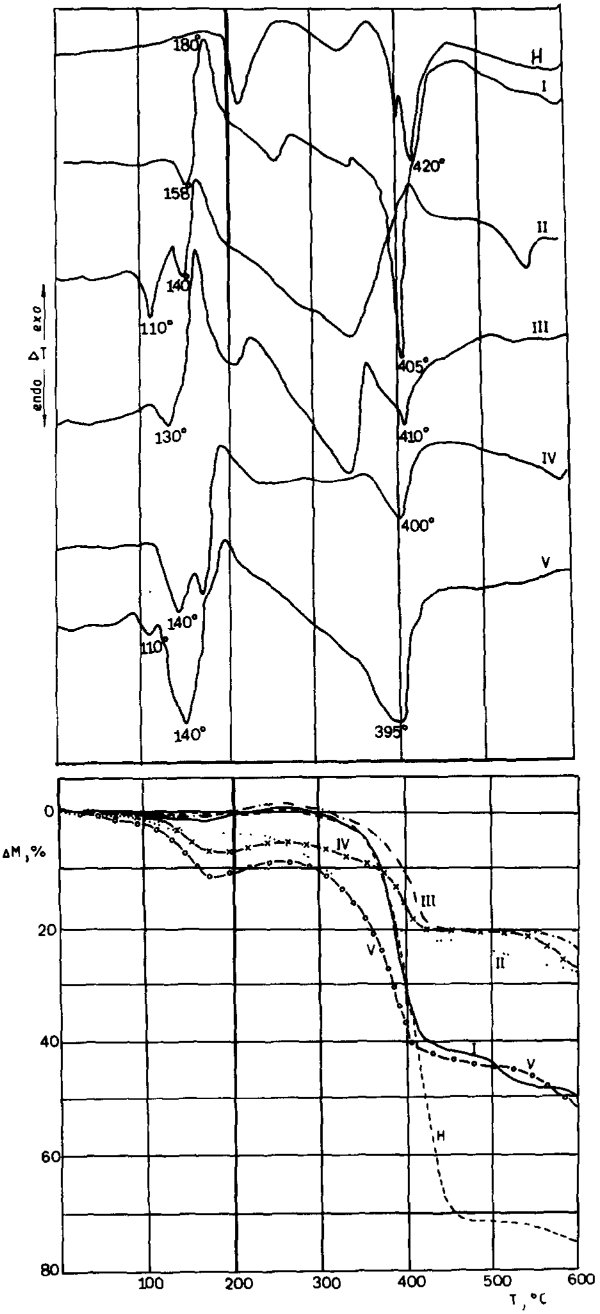


Fig. 1. DTA and TG curves of crystalline metallic salts of sulfaminic acids. H, sulfaminic acid; I, SA-K; II, SA-Ba; III, SA-Pb; IV, SA-Cd; V, SA-Mg.

Potassium salt (ASA-K) amorphous fractions release from 2–8% of their hygroscopic moisture in the range 80–120°C (Fig. 2). The unreacted nitro groups were removed between 150 and 200°C. In the IR spectrum of the

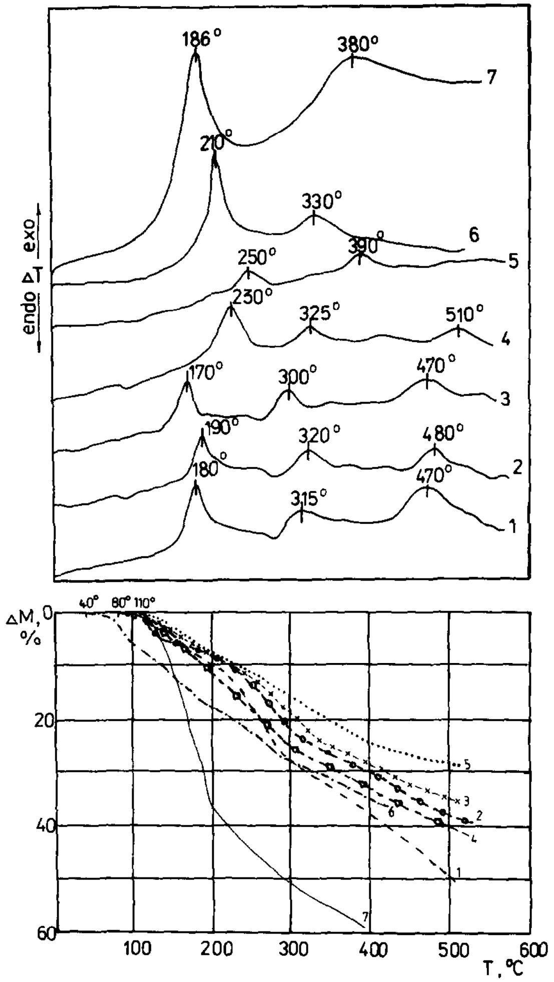


Fig. 2. DTA and TG curves of amorphous metallic salts of nitrosulfonic acids. 1, ASA-K-1; 2, ASA-K-2; 3, ASA-K-3; 4, ASA-K-4; 5, ASA-Ba; 6, ASA-Pb.

first fraction sample, heated up to 190°C, there was no vibration at 1550 cm^{-1}, but there were vibrations at 1250, 1120 and 1640 cm^{-1}.

Also, the recorded DTA curves showed characteristic exothermal effects with maxima at 170–190°C, as well as corresponding mass losses of 2–4%. For the initial NO, this process was recorded as an intense exothermal peak at 185°C, the corresponding mass loss being 18% of the initial sample. For the fourth fraction (Fig. 2, curve 4), where sulfonation has taken place to a greater extent ($\%S = 9.1$) an exothermal effect at 230°C can be observed. In the IR spectrum of the fourth fraction sample, heated up to 240°C, the vibration $\nu(as)$ 1550 cm^{-1} was absent and, moreover, most of the sulfo groups have been transformed into potassium sulfate (intense peak at 1120 cm^{-1}). A vibration at 1640 cm^{-1} was also observed. The main destruction of the amorphous potassium salts begins above 200°C (unlike the initial NO), showing endothermal effects between 250 and 300°C. Exothermal and oxidizing-destructive reactions occur, having DTA curve maxima at approx. 320 and 480°C, respectively.

The DTA curves of the Pb and Ba salts are similar (Fig. 2, curves 5 and 6). Characteristic, though low intensity, absorption bands for all functional groups, except hydroxyls, were found in the case of the amorphous Pb salt heated up to 240°C.

From the above considerations, it can be stated that the amorphous salts of nitrosulfonic acids have a greater relative thermostability than the initial NO.

CONCLUSIONS

Two types of products, crystalline salts of sulfaminic acids and amorphous salts of nitrosulfonic acids, were obtained from polyisoprene nitro-oligomer (molecular weight 1200–2300) and potassium hydrogensulfite, the type of the product depending on the fractional composition of the nitro-oligomer.

The crystalline salts of sulfaminic acids are thermally stable up to 300°C. The principal destruction of the amorphous salts of nitrosulfonic acids begins beyond 200°C.

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