

SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Synthesis, Spectral Characteristics, and Some Properties
of Methylammonium Sulfamate Monohydrate. A New Route
to Sulfamic Acid Derivatives

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Abstract—Redox transformations of the products of reactions of the $\text{CH}_3\text{C}(\text{S})\text{NH}_2\text{—SO}_2\text{—H}_2\text{O}$ system components yield methylammonium sulfamate monohydrate $[\text{CH}_3\text{NH}_3]^+[\text{OSO}_2\text{NH}_2]^- \cdot \text{H}_2\text{O}$ and elemental sulfur. The synthesized compound was characterized by IR, ^1H and ^{13}C NMR, and mass spectroscopy and some of its properties were studied.

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It is known that sulfamic acid (HOSO_2NH_2), its salts and derivatives are used as medical drugs [1], disinfectants [2], herbicides [3], and reagents and catalysts of organic reactions [4–6]. Sulfamic acid is produced using corrosive compounds, for example, by the reaction of oleum with carbamide; SO_3 with NH_3 in anhydrous medium; sulfuryl chloride, SO_2 , and hydroxylamine [7].

This communication describes an original method for the synthesis of methylammonium sulfamate, which was prepared and characterized by Goodson [8]. Thioacetamide ($\text{CH}_3\text{C}(\text{S})\text{NH}_2$) and sulfur dioxide were used as the reactants, and water was used as the reaction medium.

EXPERIMENTAL

A suspension of thioacetamide (0.075 mol, 5.63 g) in water (5.0 mL) was placed into a 50-mL reactor, cooled to 0°C , and kept at this temperature for 30 min. Then SO_2 was bubbled through the suspension for 1 h at a flow rate of 50 mL min^{-1} . This was accompanied by dissolution of thioacetamide with simultaneous formation of a finely dispersed white-yellow precipitate. On further storage of the reaction mixture for 2 to 3 days, additional precipitation took place. Recrystallization of the water-insoluble precipitate from benzene gave yellow crystals (**I**) (1.73 g). The decanted aqueous solution was concentrated in air at room temperature until white crystalline compound (**II**) formed

(3.56 g, yield 64.93% relative to N). The product was purified by recrystallization from water.

The nitrogen, carbon, and hydrogen contents were determined using a CHN-analyzer; sulfur was quantified by the Schoeniger method [9]. The IR spectra were recorded on a Perkin-Elmer Spectrum BX II FT-IR System spectrophotometer in the range of $4000\text{—}350 \text{ cm}^{-1}$ (samples were prepared as KBr pellets); the ^1H and ^{13}C NMR spectra were recorded as a Bruker WM 400 radiospectrometer; EI mass spectra were run on an MX-1321 instrument (direct sample injection to the source; ionizing electron energy of 70 eV). The specific electrical conductivity of 10^{-3} M solutions of compound **II** in anhydrous CH_3OH , $(\text{CH}_3)_2\text{SO}$, $\text{C}_2\text{H}_5\text{OH}$, and CH_3CN and in distilled water was measured using an Expert 002 conductometer. The potentiometric measurement was carried out on a pH-150M pH-meter

RESULTS AND DISCUSSION

According to mass spectrometry data, the yellow-colored crystals of **I** represent elemental sulfur: the mass spectrum of this product exhibits peaks for S_8^+ ions ($m/z = 256$, $I = 7\%$) and S_6^+ ($m/z = 192$, $I = 8\%$), S_5^+ ($m/z = 160$, $I = 16\%$), S_4^+ ($m/z = 128$, $I = 18\%$), S_3^+ ($m/z = 96$, $I = 10\%$), and S_2^+ ($m/z = 64$, $I = 100\%$) fragment ions.

Table 1. Wave numbers (cm^{-1}) of the absorption maxima in the IR spectra of thioacetamide and compound **II**

Thioacetamide	II	Assignment
	3400 sh	$\nu(\text{NH}_2)$, $\nu(\text{NH}_3^+)$
3295 m.br		$\nu(\text{NH}_2)$
	3260 m.br	$\nu(\text{NH}_2)$, $\nu(\text{NH}_3^+)$
	3140 s.br	$\nu(\text{NH}_2)$, $\nu(\text{NH}_3^+)$
3085 s		$\nu(\text{NH}_2)$,
	3070 sh	$\nu(\text{NH}_2)$, $\nu(\text{NH}_3^+)$
2975 m		$\nu(\text{CH}_3)$
2921 m		$\nu(\text{CH}_3)$
	2670 sh	$\nu(\text{NH}_2)$, $\nu(\text{NH}_3^+)$
	1660 m	$\delta_{as}(\text{NH}_3^+)$, $\delta(\text{NH}_2)$
1650 s		$\delta(\text{NH}_2)$
	1608 sh	$\delta_{as}(\text{NH}_3^+)$, $\delta(\text{NH}_2)$
	1480 sh	$\delta_{as}(\text{CH}_3)$
1481 s		$\delta_{as}(\text{CH}_3)$
1446 sh		$\delta_{as}(\text{CH}_3)$
1423 w		$\delta_{as}(\text{CH}_3)$
	1402 s	$\nu(\text{CN})$
1395 sh		$\nu(\text{CN})$
1368 s		$\delta_s(\text{CH}_3)$
1305 s		$r(\text{NH}_2) + [\nu(\text{CC}) + \nu(\text{CS}) + \delta(\text{NCS})]$
	1240 sh	$\nu_{as}(\text{S=O})$
	1113 s	$\nu_s(\text{S=O})$, $\nu(\text{S-N})$, $\omega(\text{NH}_2)$
1030 m		$r(\text{NH}_2)$, $r(\text{CH}_3)$
	1020 sh	$r(\text{NH}_2)$, $r(\text{NH}_3^+)$, $r(\text{CH}_3)$
	1000 sh	$r(\text{NH}_2)$, $r(\text{NH}_3^+)$, $r(\text{CH}_3)$
975 s		$\nu(\text{CS}) + \nu(\text{CC}) + r(\text{CH}_3)$
	980 sh	$r(\text{NH}_2)$, $r(\text{NH}_3^+)$, $r(\text{CH}_3)$
751 m		$\nu(\text{CS}) + \nu(\text{CC})$
710 s		$\omega(\text{NH}_2)$, $r(\text{NH}_2)$
	670 w	$\nu(\text{S-O})$
	618 m	$\delta_s(\text{SO}_2)$, $\delta_s(\text{NSO})$
	542 sh	$\delta_{as}(\text{NSO}_2)$
513 m		$\pi(\text{CC})$
472 m		$\delta(\text{NCS})$
	465 w	$\delta_s(\text{NSO}_2)$
460 m		$\delta(\text{NCS})$

The composition of **II** according to elemental analysis data was as follows:

For $\text{CH}_{10}\text{N}_2\text{O}_4\text{S}$ anal. calcd. (%): C, 8.22; N, 19.17; S, 21.94; H, 6.90.

Found (%): C, 7.89; N, 19.06; S, 22.32; H, 6.31.

The mass spectrum of **II** contains peaks with $m/z = 97$, $I = 4\%$ and $m/z = 80$, $I = 100\%$, which were assigned to the $[\text{M}]^+[\text{H}_3\text{NO}_3\text{S}]^+$ molecular ion of sulfamic acid and the $[\text{M}-\text{NH}_3]^+$ fragment ion, respectively. This assignment is confirmed by good agreement of the mass spectrum recorded for **II** and the tabulated mass spectrum of sulfamic acid [10].

^1H NMR (DMSO- d_6 , 400 MHz), δ , ppm (J , Hz): 1.75 (s, 3H, $\text{NH}-\text{CH}_3$), 6.70 (s, 1H, NH), 7.12 (s, 1H, NH^+), 7.30 (s, 1H, NH). ^{13}C NMR (DMSO- d_6 , 100 MHz), δ , ppm: 22.89 (s, 1C, CH_3).

The ^1H NMR spectrum (DMSO- d_6 , 400 MHz) exhibits signals for the methyl protons (singlet at 1.75 ppm) and signals of nonequivalent amino-group protons (6.70, 7.30 ppm) and ammonium protons (7.12 ppm) broadened due to exchange with water. The proton-decoupled ^{13}C NMR spectrum shows a singlet for the methyl group (22.89 ppm).

The results of IR-spectroscopic study of product **II** and, for comparison, characteristic frequencies of crystalline thioacetamide, which were assigned resorting to published data [11], are presented in Table 1.

The $\nu(\text{NH})$ vibrations are manifested as a broad intense band with peaks at 3400, 3260, 3140, 3070, and 2670 cm^{-1} , which corresponds in the position and shape to the absorption of $-\text{NH}_2$ and $-\text{NH}_3^+$ groups involved in hydrogen bonding [12, 13]. The absorption bands at about 1660 and 1608 cm^{-1} can be assigned to bending vibrations of these groups. The shoulder of the asymmetric band of $-\text{CH}_3$ bending vibration at 1480 cm^{-1} is rather clear, whereas the $\nu(\text{CH})$ bands at 2975–2900 cm^{-1} are superimposed by more intense absorption of $\nu(\text{NH}_2)$ and $\nu(\text{N}^+\text{H}_3)$ modes.

It should be emphasized that the IR spectrum of **II** does not contain the absorption band at 751 cm^{-1} with predominant contribution of $\nu(\text{CS})$ vibrations typical of free thioamide.

The vibrational spectrum of the NOSO_2 fragment can be interpreted proceeding from a tetrahedral structure: the symmetry decreases from T_d (SO_4^{2-}) to C_1 (NOSO_2). According to the selection rules, the number of IR-active vibrations should increase from two to nine. Taking account of correlations [14] for sulfoxides and sulfones, it is assumed that in the spectrum of **II**, the absorption band at 1240 cm^{-1} should be assigned to asymmetric S=O stretching vibrations. The $\nu_s(\text{S=O})$ and $\nu(\text{S-N})$ vibrations probably make a contribution to the strong absorption band at 1113 cm^{-1} , which also includes the wagging bending vibrations of NH_2 groups.

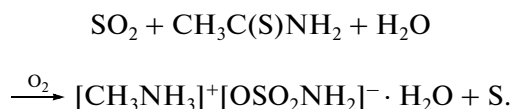
Table 2. Electrical conductivity 10^{-3} M solutions of **II** and pH of a 10^{-3} M aqueous solution of **II** at 25°C

$\lambda, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$					pH
$\text{C}_2\text{H}_5\text{OH}$	$(\text{CH}_3)_2\text{SO}$	CH_3CN	CH_3OH	H_2O	H_2O
6.2	7.6	8.0	14.1	352.8	4.25

The absorption band at 670 cm^{-1} can be identified as the S–O stretching vibration of the $^-\text{O}-\text{SO}_2$ fragment. The low-frequency shift of this band in the spectrum in question relative to the $870\text{--}810 \text{ cm}^{-1}$ range [14] expected for the sulfoxide $\text{HO}-\text{SO}_2$ group is related, apparently, to strengthening of the sulfur–oxygen single bond in the obtained product.

The compound nature of the medium-intensity band with a maximum at $\sim 618 \text{ cm}^{-1}$ is due, judging by published data [14], to the overlap of the symmetrical bending vibrations of the SO_2 and NSO fragments. The $\delta_{as}(\text{NSO}_2)$ and $\delta_s(\text{NSO}_2)$ bending modes are responsible for the shoulder at 542 cm^{-1} and a medium-intensity band at 472 cm^{-1} .

On the basis of elemental analysis data and spectroscopic studies, it can be stated that product **II** is methylammonium sulfamate monohydrate formed by the following route:



The obtained compound melts at $117\text{--}118^\circ\text{C}$, unlike the anhydrous salt ($\text{mp} = 91\text{--}93^\circ\text{C}$ [8]). The solubility in water at 20°C is 32.48 wt % (5.60 mol %). The molar electrical conductivity ($\lambda, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and pH of solutions of compound **II** are summarized in Table 2. Evidently, solutions of compound **II** in organic solvents are weak electrolytes (Table 2) [15]. The lower electrical conductivity values of a 10^{-3} M aqueous solution of methylammonium sulfamate compared to that of a 10^{-3} M aqueous solution of sulfamic acid ($\lambda \approx 384 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [16]) attest to complexation between HOSO_2NH_2 and CH_3NH_2 through H-bonding.

Thus, the developed method provides a route to sulfamic acid derivatives requiring mild conditions, low temperature, and no use of corrosive reagents. It is of interest that the reaction of the oxygen thioacetamide analog with sulfur dioxide in an aqueous solution in a similar situation is accompanied by condensation of $\text{CH}_3\text{C(O)NH}_2$ giving cyclic *o*-quinoid compound [17].

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