

## Reactions of Amidosulfuric Acid Salts with Formaldehyde

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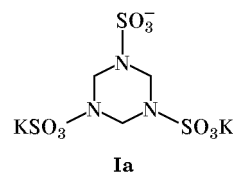
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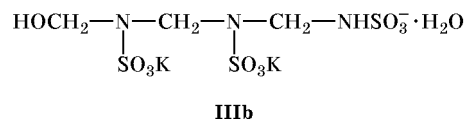
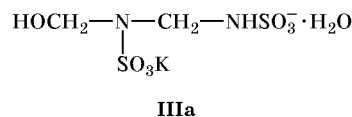
**Abstract**—Potassium amidosulfate reacts with formaldehyde at pH 7–12 to afford a mixture of dipotassium 4-hydroxy-1,3-diazabutane-1,3-disulfonate hydrate and tripotassium 6-hydroxy-1,3,5-triazahexane-1,3,5-trisulfonate  $\text{HO}(\text{CH}_2\text{NSO}_3\text{K})_n \cdot \text{H}_2\text{O}$  ( $n = 2, 3$ ). The reaction of the same compounds at pH 1–3 gives diammonium 1,3,5,7-tetraazabicyclo[3.3.1]nonane-3,7-disulfonic acid sulfate dihydrate.

Condensation of potassium amidosulfate with formaldehyde at pH 5 leads to formation of tripotassium 1,3,5-triazacyclohexane-1,3,5-trisulfonate (**I**) [1]. There are no published data on the effect of pH on the process. The goal of the present work was to study the condensation of amidosulfuric acid with formaldehyde over a wide range of pH values. First of all, we examined the reaction in the pH range from 7 to 12. Insofar as the reaction is reversible (in dilute solution the equilibrium is displaced toward initial compounds), the condensation was carried out using high reactant concentrations. Potassium amidosulfate was dissolved in 30% formaldehyde solution at 20 and 40°C. The concentration of potassium amidosulfate was 30 and 57% to ensure equimolar reactant ratio. Throughout the examined pH range the same products were formed (according to the IR spectra and elemental analyses), which were insoluble in organic solvents. In keeping with their elemental composition and results of determination of formaldehyde and amidosulfate ion, the products were assigned the structure of hydroxypoly(*N*-sulfomethyleneamine) potassium salt hydrate  $\text{HO}[\text{CH}_2\text{N}(\text{SO}_3\text{K})]_n \cdot \text{H}_2\text{O}$  (**II**). The molecular weight of **II** was determined by mass spectrometry using secondary ion–ion emission technique, which is based on generation of secondary ions like  $[M-H]^+$  or  $[M-H]^-$  by the action of cesium ion beam [2, 3]. Taking into account that this technique was not applied previously to potassium-containing derivatives of amidosulfuric acid, we initially tested it with tripotassium salt **I** as an example. The resulting spectrum contained a peak with  $m/z$  402, corresponding to quasimolecular ion **Ia**; we thus

concluded that the above method is applicable to potassium salts **II**.

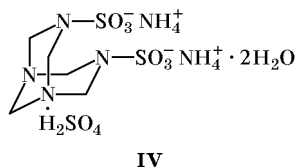


In the mass spectrum of product **II** we observed negative ion peaks with  $m/z$  values of 291 and 438, which correspond to anions derived from 4-hydroxy-1,3-diazabutane-1,3-disulfonic acid monopotassium salt hydrate (**IIIa**,  $n = 2$ ) and 6-hydroxy-1,3,5-triazahexane-1,3,5-trisulfonic acid dipotassium salt hydrate (**IIIb**,  $n = 3$ ).



Hence the reaction of formaldehyde with potassium amidosulfate gave a mixture of compounds **IIa** ( $n = 2$ ,  $M$  330) and **IIb** ( $n = 3$ ,  $M$  377). Judging by the IR spectra, analogous products were formed with other amidosulfuric acid salts with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Ba}^{2+}$  as cations.

In the reaction of potassium amidosulfate with formaldehyde at pH 3–5, the mixture also contained product **I**. Ammonium amidosulfate behaved differently. It is known that hydrolysis of amidosulfuric acid is a very slow process [4]. However, on addition of formaldehyde solution to a solution of ammonium amidosulfate at 0°C the pH of the medium jumps from 3.0 to 1.0–1.5, and diammonium 1,3,5,7-tetraazabicyclo[3.3.1]nonane-3,7-disulfonate sulfate dihydrate (**IV**) is formed in high yield.



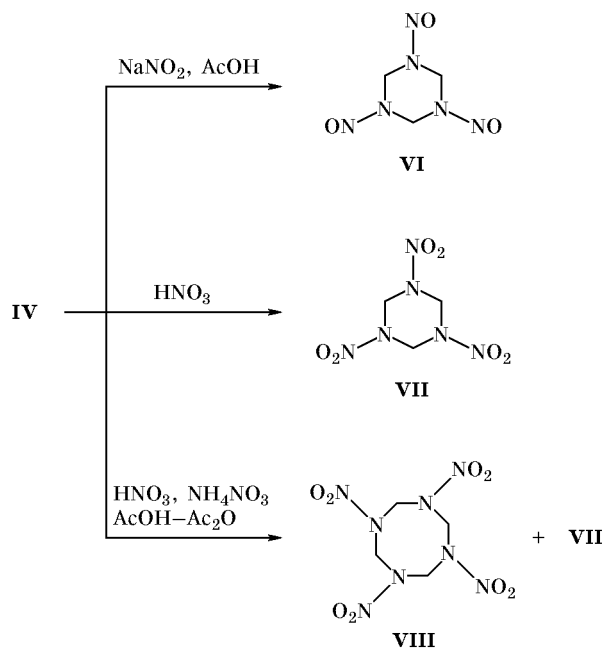
The IR spectrum of **IV** contains absorption bands due to the  $\text{NSO}_3^-$  group ( $1230\text{--}1200$ ,  $1020\text{ cm}^{-1}$ ), sulfate ion ( $1130\text{ cm}^{-1}$ ), and  $\text{NH}_4^+$  ion ( $1430$ ,  $3200\text{--}3300\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectrum we observed three groups of signals from  $\text{CH}_2$  groups at  $\delta$ , ppm: 5.1 s, 4.6 d, 4.35 d (intensity ratio 2:2:1). Potentiometric titration showed the presence of two acid equivalents in **IV**. Treatment of **IV** with an alcoholic solution of picric acid gives urotropine picrate.

Until recently, heterolysis of urotropine [5–7] was the only method for preparation of N-substituted

1,3,5,7-tetraazabicyclo[3.3.1]nonanes (**V**). Soon-Ben Teo and Siang-Guan Tech [8] recently proposed a template procedure for synthesis of bicyclononanes **V**, which is based on the reaction of amino acids with formaldehyde and ammonia in the presence of nickel, zinc, or copper salts. The reaction of ammonium amidosulfate with formaldehyde represents the second known (in addition to the synthesis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane [6]) case of noncatalytic cyclization with formation of bicyclononane **V**.

The structure of compound **IV** was confirmed by its transformations in reactions with some electrophilic reagents. Treatment of **IV** with sodium nitrite in aqueous acetic acid gave 1,3,5-trinitroso-1,3,5-triazacyclohexane (**VI**), and with nitric acid, 1,3,5-trinitro-1,3,5-triazacyclohexane (**VII**, hexogen) was formed. When the nitration was carried out in a mixture of acetic acid with acetic anhydride in the presence of ammonium nitrate, we obtained a mixture of compound **VII** and 1,3,5,7-tetra-nitro-1,3,5,7-tetraazacyclooctane (**VIII**, octogen) (Scheme 1), i.e., compound **IV** reacted like 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane [6]. The structure of **IV** was also proved by its reaction with acetic anhydride. Compound **IV** decomposes in acetic anhydride, but addition of acetic anhydride to a solution of **IV** in acetic acid, preliminarily treated with ammonium acetate to neutralize sulfuric acid, leads to formation of a mixture of 1,3,5-triacetyl-1,3,5-triazacyclohexane (**IX**, yield 18%), 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (**X**, 12%), and 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (**XI**, 8%) (Scheme 2).

**Scheme 1.**

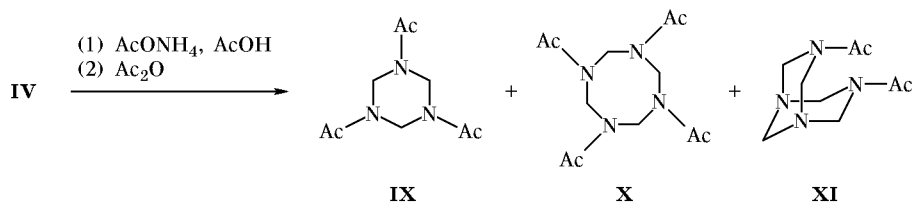


## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr. The  $^1\text{H}$  NMR spectra were obtained on a Bruker AM-300 (300 MHz) instrument in  $\text{DMSO-}d_6$  using HMDS as internal reference. Values of pH were measured with the aid of a pH-673 pH-meter-voltmeter. The elemental compositions were determined on a Hewlett-Packard 185 analyzer. The mass spectra were run on an MI-1201 instrument adapted for the secondary ion-ion emission technique [3]. Silicagel L 100/200  $\mu\text{m}$  (Chemapol) was used for column chromatography.

**Dipotassium 4-hydroxy-1,3-diazabutane-1,3-disulfonate hydrate (IIIa) and tripotassium 6-hydroxy-1,3,5-triazahexane-1,3,5-trisulfonate hydrate (IIIb).** To a solution of 15 g (0.11 mol) of potassium

Scheme 2.



amidosulfate in 25 ml of water we added with stirring 11.3 g (0.11 mol) of a 30% formaldehyde solution. The mixture was adjusted to pH 7–12 by adding a 10% solution of potassium hydroxide and was kept for 3 h at 25 or 40°C. The precipitate was filtered off, washed with ethanol, and dried in a vacuum desiccator over phosphoric anhydride. Yield 12.6 g (69%). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 960, 1000–1070, 1200 ( $\text{NH}\text{SO}_3^-$ ), 650, 1245 ( $\text{H}_2\text{O}$ ), 3290 (NH), 3380 ( $\text{H}_2\text{O}$ ), 3480 (OH). Found, %: C 7.67; H 2.10; N 8.71.  $\text{C}_2\text{H}_8\text{K}_2\text{N}_2\text{O}_8\text{S}_2$ . Calculated for  $n = 2$ , %: C 7.29; H 2.43; N 8.51.  $\text{C}_3\text{H}_{10}\text{K}_3\text{N}_3\text{O}_{11}\text{S}_3$ . Calculated for  $n = 3$ , %: C 7.55; H 2.10; N 8.88.

**Diammonium 1,3,5,7-tetraazabicyclo[3.3.1]nonane-3,7-disulfonate sulfate dihydrate (IV).** Ammonium amidosulfate, 27.3 g (0.24 mol), was added at 0–5°C to 48 ml (0.48 mol) of a 30% formaldehyde solution. The mixture was kept for 4 h at 0–5°C. The original pH value (3) changed to 1 (by the end of addition of ammonium amidosulfate) and then to 0.8 (by the end of the process). The mixture was poured with vigorous stirring into a 10-fold amount of acetone cooled to 0°C, and the mixture was stirred until complete crystallization. The precipitate was filtered off, washed with acetone, and dried in a vacuum desiccator over sulfuric acid. Yield 37.3 g (95%). Found, %: C 12.78, 12.79; H 5.52, 5.55; N 18.69, 18.61; S 20.45, 20.11.  $\text{C}_5\text{H}_{24}\text{N}_6\text{O}_{12}\text{S}_3$ . Calculated, %: C 13.16; H 4.82; N 18.42; S 21.05.

**1,3,5-Trinitroso-1,3,5-triazacyclohexane (VI).** To a solution of 3 g (0.0065 mol) of compound IV in 25 ml of 50% acetic acid we added at 0°C 1 g (0.014 mol) of sodium nitrite. The mixture was kept for 1 h at 0°C and poured into 50 ml of acetone, and the precipitate was filtered off. Yield 0.2 g (18%), mp 105°C (from ethanol) [6].

**1,3,5-Trinitro-1,3,5-triazacyclohexane (VII).** Compound IV, 1 g (0.0062 mol), was added to 10 ml of 98% nitric acid cooled to –40°C. The mixture was kept for 1.5 h at that temperature and poured into water. Yield 0.19 g (38%), mp 205°C (from acetone) [6].

**1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (VIII)** [9]. To a suspension of 9.2 g (0.02 mol) of compound IV in 25 ml of acetic acid, stirred at 50°C, we added over a period of 30 min simultaneously from two dropping funnels a solution of 0.8 g (0.01 mol) of ammonium nitrate in 6.02 g (0.02 mol) of 98% nitric acid and 10 g (0.035 mol) of acetic anhydride. The mixture was kept for 20 min at 70°C and poured into 100 ml of ice water. The product was filtered off, treated with hot water for 2 h at 100°C, and repeatedly washed with cold water. The isolated material, 1.33 g (40%), was a mixture of compound VII (0.93 g, 70%) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (VIII) (40 g, 30%). The composition of the mixture was determined by the procedure described in [10].

**Acetylation of diammonium 1,3,5,7-tetraazabicyclo[3.3.1]nonane-3,7-disulfonate (IV).** To a solution of 1.9 g (0.024 mol) of ammonium acetate in 15 ml of acetic acid we added 5.5 g (0.012 mol) of compound IV. The mixture was kept for 30 min, the precipitate was filtered off, the filtrate was cooled to 10°C, 3 ml (0.03 mol) of acetic anhydride was added, and the mixture was evaporated to dryness in a stream of air. The residue (0.7 g) was subjected to column chromatography. We isolated 0.3 g (16%) of 1,3,5-triacetyl-1,3,5-triazacyclohexane (IX), mp 94°C [11], 0.25 g (9%) of 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (X), mp 160°C [12], and 0.18 g (8%) of 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (XI), mp 195°C [8].

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