Tetrahedron Vol. 40, No. 10, pp. 1855 to 1856, 1984
Printed in Great Britain.

0040-4020/84 $3.00 + .00

PREPARATION AND REACTIONS OF MONOSULPHOMETHYLMELAMINE

I. Kunka and Z. Wirpsza*
Department of Chemistry Polytechnical University of Radom, Poland

(*Received in the UK* 26 *April* 1983)

Abstract—Melamine, formalin and sodium sulphite in aqueous solution gives monosulphonylmethylmelamine and its sodium salt. The properties of the compound and its salts were studied.

The sodium salt of sulphomethylmelamine (SSMSMM) may be an intermediate in the synthesis of sulfomethylated melamine resins but this has not yet been proved. Monosulphomethylmelamine (MSMM) and its salts have not yet been reported. Melamine hydroxymethanesulphonate, the salt of melamine and hydroxymethanesulphonic acid, has been described.[1] Obtaining and separating pure MSMM or its salts, containing two free amino groups would allow the synthesis of linear sulphomethylated melamine–formaldehyde resins. Besides, MSMM containing aromatic triazine ring and sulphonic group, could provide an interesting monomer for preparation of ionic polymers. MSMM was obtained through sulfomethylation of melamine with a stoichiometric amount of sodium hydroxymethanosulfonate which was obtained in exothermic reaction from stoichiometric amounts of acid sodium sulphite and formalin.

$$\mathrm{NaHSO_3 + CH_2O \rightarrow HOCH_2SO_3Na}$$

$$\mathrm{/CN/_3/NH_2/_3 + HOCH_2SO_3}$$

$$\mathrm{Na \rightarrow /CN/_3/NH_2/_2NHCH_2SO_3Na + H_2O.}$$

In order to maintain stoichiometric ratio of reagents the acid sodium sulphite was prepared immediately before the sulphomethylating reaction through saturating 5% aqueous NaOH by SO_2 to pH 6. It was found that satisfactory sulphomethylation can be accomplished only when the sodium hydroxymethanesulfonate, is prepared at a temperature not higher than 45°.

EXPERIMENTAL

Formalin (1 equiv) was added to aq sodium sulphite (pH = 10–11) at 45° for 20 min. Melamine (1 equiv) was added and the mixture was heated 80°. Unreacted melamine was filtered off (about 20% of the melamine used in the reaction), and the filtrate was allowed to cool to room temp. Sodium salt of MSMM, melamine, hydroxymethylmelamine and traces of hydrolysis of melamine products were precipitated. Products were identified by chromatographic methods.[2,3] R_f SSMSMM 0.60 as compared to 0.34 for melamine, was obtained. After bringing the pH to 8 the filtrate was concentrated under reduced pressure and the next part of precipitate was separated. SSMSMM was separated from the water solution of precipitate on strong alkaline anion exchanger Dowex 1 × 4, in acetate form. The hydroxide form causes partial hydrolysis of SSMSMM. SSMSMM was eluted from the column with aq 5% NaCl, concentrated under vacuum, and recrystallised out of water. SSMSMM (45% yield) a fine crystalline solid decomposing at 170°, soluble in water and dimethylsulfoxide, was obtained. Its water solubility was about 10 times higher than that of melamine (Table 1). It is not soluble in methanol, acetone and dimethylformamide. Elemental analysis of SSMSMM through combustion provided erroneous results, considerably decreased contents of particular elements (C, H, N) and different amount of ash from 40 to 54%. The sulfur contents in SSMSMM, determined as barium sulfate, was 13.1% (theoretical 13.2%). Elemental analysis through combustion of MSMM gave C, 21.23; H, 3.69; N, 37.27; S, 14.62; requires C, 21.30; H, 3.63; N, 38.10; S, 14.54%. MSMM was obtained through acidification of saturated aq SSMSMM with acetic acid to pH 4. Crystalline MSMM (solubility in water 0.06 g in 100 g of water at 20°) is then precipitated MSMM chromatogram developed by solvents containing ammonia is identical to that one of its sodium salt.

DISCUSSION

The constitution of MSMM is confirmed by the infra-red spectrum. It contains characteristic bands for the triazine ring (770 cm^{-1}) and sulphonic acid group (1170, 1030 and 600 cm^{-1}). The absorption band of MSMM attributed to triazine ring is shifted to lower frequency as compared to melamine (810 cm^{-1}). With in the range 3100–3400 cm^{-1}, 5–6 absorption bands of N–H bonds of substituted or nonsubstituted melamine amide groups appear. The most distinguishable of those bands (3450 cm^{-1}) is attributed to absorption of the SO_3H proton.[4]

MSMM starts to decompose endothermically at temperature about 270°. An endothermic maximum is associated with about 47% mass loss which corresponds to $-CH_2SO_3H$ group decomposition (weight fraction 48%). Further slower mass loss appears on heating to 360°, which is probably a result of melamine deamination. Beginning at 530°, the rate of mass loss increases (non-sharp exothermic maximum), attributed to oxidation of products of melam and melem decomposition. Complete disappearance of the compound occurs at 660°.

Besides sodium salt also other salts of MSMM have been obtained and their solubilities in water, dimethylsulfoxide and dimethylformamide have been

Table 1.

Temperature (°)	Solubility of SSMSMM (g/100 g water)	Solubility ratio of SSMSMM to melamine
20	3.3	10.5
40	7.5	10.9
60	15.0	10.2
80	23.0	10.1

Table 2. Solubility of MSMM salt, g/100 g solvent

Solvent	Na	K	NH_4	$N(CH_3)-CH_2-C_6H_5$	Ca	Mg	Ba	Zn	Al
Water	28	14	1	2	10	8.4	0.03	0.17	0.01
dimethylsulfoxide	2.5	1.2	0.08	10					
dimethylformamide	less than 0.1			1					

examined. Results are given in Table 2. The soluble postassium salt of MSMM was obtained similarly to sodium salt, using KCl solution for washing the sulphomethylated melamine of the anion exchange resin. Less soluble Ca, Mg, Ba, Zn, Al salts of MSMM were obtained through mixing stoichiometric quantities of saturated aqueous solutions of soluble salts of these metals and saturated aqueous MSMM, and the filtration of precipitates.

REFERENCES

[1] *British Pat* 885 529 (1961).

[2] E. Knappe and I. Rodhewal, *Z. Anal. Chem.* **223**, 174 (1966).

[3] K. Walczyk, M. Jaworski, and H. Szewczyk, *Chem. Anal.* **16**, 5 (1971).

[4] J. R. Dyer, *Absorption Spectroscopy in Organic Chemistry*. PWN, Warsaw, 1967.

[5] J. T. Thurston and J. R. Dudley, *J. Am. Chem. Soc.* **73**, 2981 (1951).