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SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF MELAM

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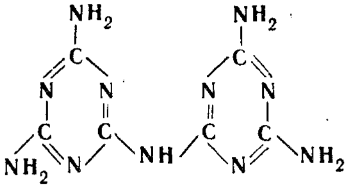
Fusing melamine with 2, 4-diamino-6-chloro-s-triazine gives melam. From its UV and IR spectra, it is assigned structure II. Thermographic studies showed that melam is not an intermediate product, but a side product, of thermal deamination of melamine.

Liebig [1] was the first to give information regarding the possibility of preparing melam. Later papers appeared dealing with the possibility of preparing mixed melam-melem by heating ammonium thiocyanate [2], dicyanodiamide [3], and melamine [4, 5]. A paper [6] first described the isolation and identification of melam using ion exchange chromatography and UV spectra. A structural formula I ascribed to melam [5], has long been accepted by all workers:



I

It was considered [2, 3], that melam is the first product of thermal deamination of melamine according to the following sequence:

$$\text{melamine} \rightarrow \text{melam} \rightarrow \text{melem} \rightarrow \text{melon} \qquad (1)$$

However, investigation of the thermal decomposition of melamine at 325-435° under atmospheric pressure showed [7] that melem is the first product of pyrolysis. Another paper [6] also indicates that it is rather difficult to prepare melam by heating melamine, although a certain amount of it is formed in this reaction, and can be isolated by ion-exchange chromatography. So the steps in the decomposition of melamine must be:

$$\begin{tikzcd}
\text{melamine} \arrow[r] \arrow[dr] & \text{melem} \arrow[r] & \text{melon} \\
 & \text{melam} \arrow[u] &
\end{tikzcd} \qquad (2)$$

A paper [8] describes the results of studying the thermal decompositions of melamine and melam,* isolated from the pyrolysis. The authors base their treatment of the experimental results on scheme 1 above. In this connection we repeated their experiments, giving special attention to the temperature at which the pyrolysis of melamine and melam began. Actually, [8] indicates a starting temperature of 345°, while in another paper [7] pyrolysis is observed to start at 325°.

We also repeated experiments on preparing melamine by pyrolysis of dicyanodiamide. However, in three experiments melamine was not obtained by this method.

In this connection it was of interest to synthesize melam by other methods, and to study its physicochemical properties in greater detail. To a considerable extent this work was facilitated by the appearance of a paper [9] describing a method of preparing alkyl and aryl substituted melams.

We synthesized melam by fusing together equimolecular amounts of melamine and 2, 4-diamino-6-chloro-s-triazine, gradually raising the temperature to 300°. Heating was continued until evolution of HCl ceased (about 20-30 min). A quantitative yield of melam was obtained. The reaction product was purified by recrystallizing from alkali [10]. 2, 4-Diamino-6-chloro-s-triazine was prepared by passing ammonia for 40-50 min through a benzene solution of cyanuric chloride at 50°.

The most trustworthy method of checking purities of starting materials and end products was comparison of their

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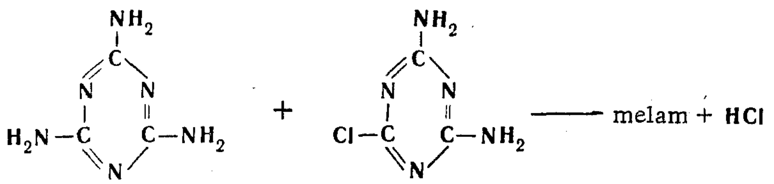
*The paper [8] incorrectly cites a paper by one of us [7] in connection with temperature range and experimental conditions (no pressure) and conclusions.

spectra with the data given in the literature. The UV spectrum of melam in various solvents completely agrees with that of a product isolated by Takimoto [6]. The IR spectrum of 2, 4-diamino-6-chloro-s-triazine agrees with the literature data. The synthesis of melam can be represented as follows:



The reaction product is a white powder, very sparingly soluble in water, but somewhat more soluble in acids and alkalies.

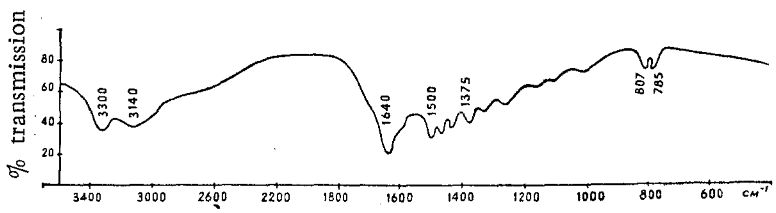
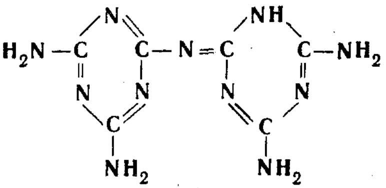


Fig. 1. IR spectrum of melam.

In the UV spectrum of melam, long wave bands of high intensity stand out. Thus in alkali there is an absorption band λ_{max} 285 mμ, in acid one at 260 mμ. In the UV spectrum of melamine, the actual long wave band has λ_{max} 236 mμ. The shift of absorption maxima indicates a longer system of conjugated bonds than for melamine, consequently formula II, previously advanced for melam [11], must be ascribed to it.



II

The IR spectrum of melam (Fig. 1) is obtained with a UR-10 spectrophotometer, the compound being tabletted with KBr. The spectrum clearly exhibits the bands characteristic of the NH_2 group (3330, 3140, and 1540 cm^{-1}), and of the triazine ring (1590 shoulder, 1635 shoulder, 1500, 807 and 785 cm^{-1}). Corresponding bands for the aminooxy derivatives are in the regions 1490-1560 cm^{-1} and 770-810 cm^{-1} [12].

The NH_2 group bands in the spectrum of melam are very intense and wide. Probably they overlap with a comparatively weak band of the ring NH group, not observed separately in the spectrum. Hence, it can be concluded that

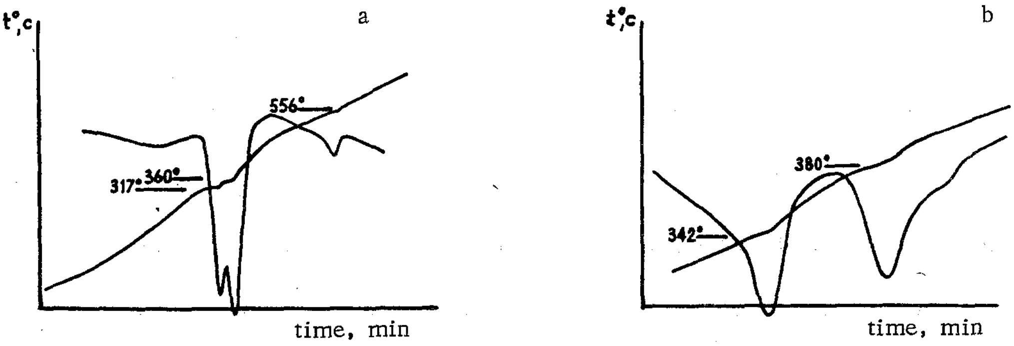


Fig. 2. Thermograms: a) melamine, b) melam.

the IR spectrum data are also in accord with structure II.

Thermograms (Fig. 2) of the decomposition of melamine and melam enable conclusions to be drawn regarding the part played by melam in the deamination of melamine. It can be seen from the thermogram that the reconstituting of the melamine molecule to give melam starts at 317°. At the same time, melam is completely stable in that temperature range, and as with all other compounds of that kind, it is only starting at 342° that it changes into melon, identified by its IR spectrum [13]. Were melam an intermediate product of melamine decomposition, it would have been possible to obtain a large yield of melam by carrying out the pyrolysis at 320-325°, and this was not observed.

Hence it follows that melam formation can only proceed parallel to melem formation. So melam is, as scheme 2 shows, a side product, and not an intermediate one in the thermal deamination of melamine.

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