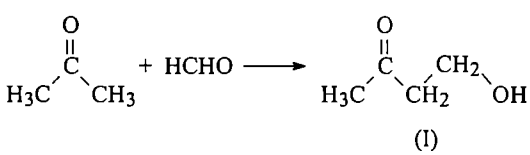
LESZEK WIANOWSKI*), ZDZISŁAW S. HIPPE**)

Computer simulations of the reactions of melamine with reactive solvents

Summary — Reactions with the reactive solvents, *viz.*, hydroxymethyl derivatives of acetone, can help bring melamine into the solution. These solvents are synthesized by the exhaustive reaction of 1 mol acetone with 1—12 mols of formaldehyde. At the reactant ratio of 1:8 (by mols), adduct (II) is likely to form. Computer simulations using Ugi-Dugundji's matrix model [3] of constitutional chemistry, involving reaction enthalpies (calculated by Allen's algorithm [4] and correlation factors [5]), were used to decide between postulated reaction schemes A and B. The calculated reaction enthalpies -12 up to 6 kcal/mol, favor the reaction of (hydroxymethyl)melamine with (hydroxymethyl)acetone. The simulations confirmed that melamine could be dissolved in the reactive solvents according to scheme B which has been suggested in [2].

Key words: melamine, reactive solvents obtained by acetone—formaldehyde reactions, hydroxymethyl derivatives of acetone, solubilization of melamine, computer simulations, reaction enthalpies, reaction mechanisms.

Despite its low solubility in standard organic solvents, melamine can be brought into solution by using the so-called reactive solvents, namely, hydroxymethyl derivatives of acetone [1]. The principal process proceeding in the synthesis of these solvents involves the exhaustive reaction of 1 mol of acetone with 1—12 mols of formaldehyde. As the first step, the product of the equimolar reaction of acetone with formaldehyde, *viz.*, mono(hydroxymethyl)acetone (I) is formed:

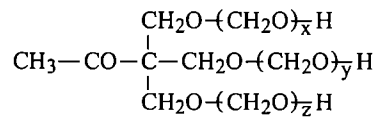


(1)

(I)

Then, in the excess of formaldehyde, all hydrogen atoms of the methyl group are stepwise substituted; this process is preferred at the low mole ratio of formaldehyde to acetone (i.e., < 1:4). The NMR study on the mechanism of the reaction discussed, performed at (8:1 by moles) formaldehyde—acetone [2], has proved the feasibility of the structural formula (II) of the resulting adduct.

Here, the number 3 indicates that the carbon atom of the methyl in the acetone molecule is bonded with three molecules of formaldehyde. These molecules do not participate in the unstable semi-formal structure, and are not released during the reaction.



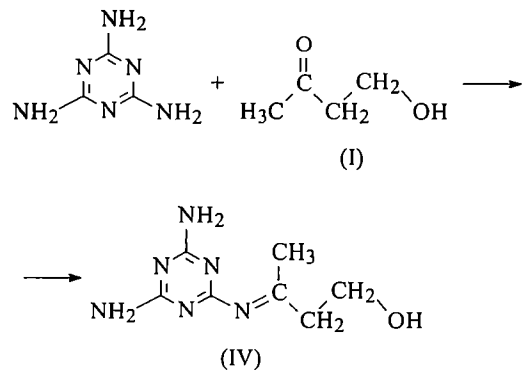
(II)

$x + y + z = n - 3$

n — number of mols of formaldehyde used in the reaction

The present study aims in the first place at confirmation of the mechanism of the reaction discussed, based on computer simulations using the Ugi-Dugundji matrix model [3] of constitutional chemistry.

According to the available literature, solubilization of melamine is a complex process that may be realized by following two different schemes. The first one, A, assumes the carbonyl group of a reactive solvent to react with the unsubstituted amine group of melamine (III), to yield Schiff's base (IV):



(2)

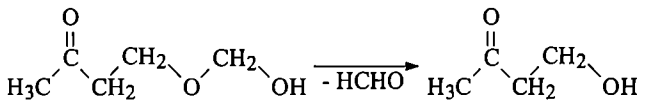
(I)

(IV)

*) Department of Science of Materials and Footwear Technology, University of Technology, Chrobrego 27, 26-600 Radom, Poland.

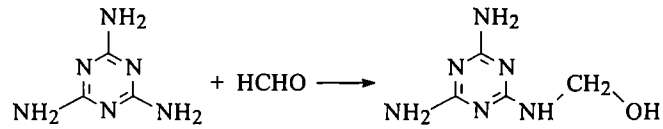
**) Department of Computer Chemistry, University of Technology, Powstańców Warszawy 6, 35-041 Rzeszów, Poland.

The second scheme, B, is presumably the following: at the first step the formaldehyde molecules is released from the terminal hydroxymethyl group of the reactive solvent (V):



(V) (3)

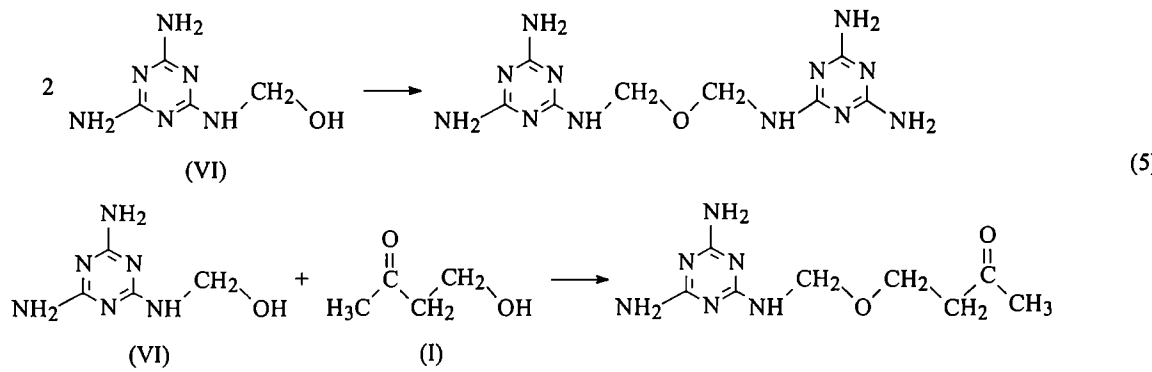
Then, the aldehyde reacts with the amine group of melamine (III) to form the hydroxymethyl derivative (VI).



(III) (VI) (4)

This compound can react either with (hydroxymethyl)melamine or hydroxymethyl derivative of acetone (I). In each case, condensation proceeds with participation of hydroxymethyl groups of compounds (VI) or (VI) and (I).

Computer simulations of the reaction of hydroxymethyl derivative of melamine (VI) with (hydroxyme-

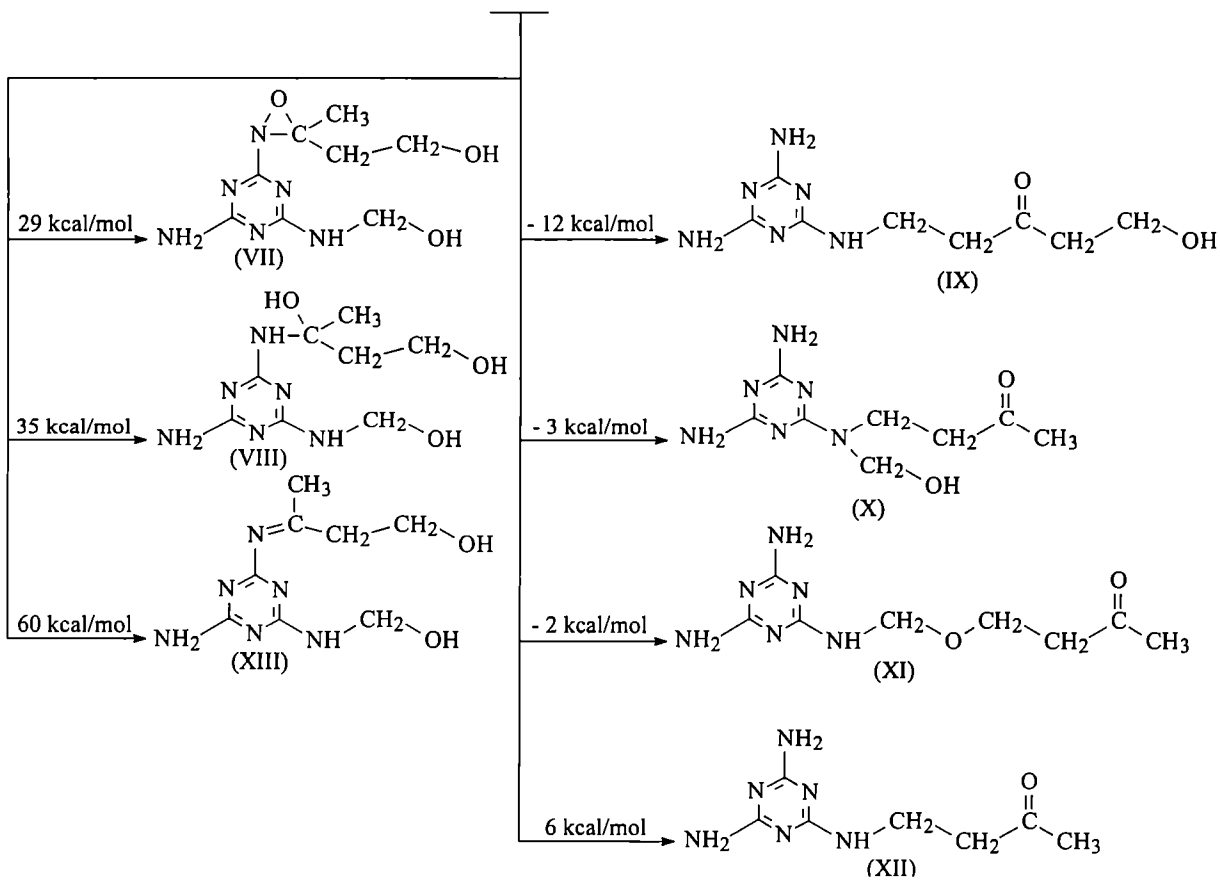


(VI) (5)

(VI) (I)

Scheme 1

A B



(VII) (VIII) (XIII) (IX) (X) (XI) (XII)

thyl)acetone (I) seemed to confirm the feasibility to dissolve melamine in reactive solvents according to scheme B, by assuming the hydroxymethyl groups of the educts (i.e. starting chemicals) to be involved in the reaction. The following observations may support our conclusion: the reaction enthalpies calculated for each scheme favor the condensation of (hydroxymethyl)melamine (VI) with (hydroxymethyl)acetone (I), because the values of the enthalpies of these reactions are contained within the range -12 to 6 kcal/mol. Therefore, the reaction of the released formaldehyde with melamine and the subsequent condensation of the products obtained in this way can be executed considerably earlier than the reaction in which it is necessary first to activate the carbonyl group. This observation is additionally confirmed by an attempt to simulate this transform by using restricted control parameters (basic medium of the reaction was chosen only). In that case, the process in which the carbonyl group does participate (i.e. according to scheme A) is excluded. Products (VII), (VIII) and (XIII) (theoretically expected *via* scheme A) have been obtained by computer simulation, however, only when the reaction medium was set as unknown. Product (VII), involving the lowest estimated enthalpy of reaction (29 kcal/mol), includes the oxaziridine ring containing two strongly electronegative atoms (nitrogen and oxygen), hence, this compound is likely to be unstable; the lowest value of the enthalpy of atomization of compound (VII) (5339 kcal/mol) seems to confirm this fact. On the other hand, the Schiff base (XIII), assumed in scheme A, can be obtained by a very endothermic reaction (60 kcal/mol), hence, this route seems to be rather unlikely.

Simulation research along scheme B has unexpectedly shown the most favored conversion of melamine in the reactive solvent tested to be the reaction of compound (VI) with the methyl group of (hydroxymethyl)acetone (I), resulting in compound (IX). The estimated enthalpy of the reaction pointed out that the unsubstituted hydrogen atom bonded to nitrogen, connected with hydroxymethyl group in melamine derivative, is more reactive than the second hydrogen atom in the same hydroxymethyl group. This assumption was proved by generating structure (X) during the simulation. The reaction discussed may be of paramount importance for the crosslinking process of melamine resins. It was also found that condensation of hydroxymethyl groups of compounds (VI) and (I) can effectively create molecules (XI) and (XII).

The above conclusions were drawn on the basis of the calculations of enthalpies of reactions obtained by Allen's algorithm [4] and by utilizing the correlation factors collected by Cox and Pilcher [5].

Computer simulations of the reaction of melamine with a reactive solvent such as hydroxymethyl derivative of acetone, allowed to support the mechanism proposed by Kucharski and Lubczak [2] (scheme B) as thermodynamically preferable to scheme A.

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