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THE NUCLEOPHILIC SUBSTITUTION REACTIONS IN s-TRIAZINIC SYSTEMS—I

KINETICS AND MECHANISM OF ALKALINE HYDROLYSIS OF THE MELAMINE

G. OSTROGOVICH, R. BACALOGLU and E. FLIEGL
Laboratory of Organic Chemistry, Polytechnic Institute, Timisoara, Roumania

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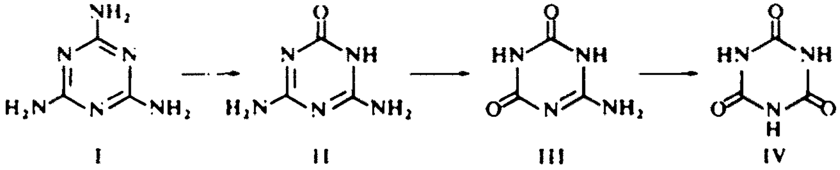
Abstract—It was established through kinetic determinations that the alkaline hydrolysis of melamine is an S_NAr2 mechanism scheme. The two process steps have near reaction rates, but as each depends upon the reaction conditions, the one or the other can determine the rate. In concentrated alkaline media (2·5M NaOH) the elimination step of the amide ion is slow, and in dilute alkali (0·01–1M NaOH) as well as in weak acids, the step involving a nucleophilic attack determines the rate.

THE kinetics of nucleophilic substitution reactions involving the s-triazinic nucleus, although widely used for preparative purposes, have recently been investigated but only to a limited extent. Consequently, the mechanism of these reactions has not been elucidated although several important aspects have been specified.[1]

It is known that in aqueous alkaline or acid solution, the three "cyanuric bases"—melamine (I), ammeline (II) and ammelide (III) are hydrolysed in the following sequence:[2,3]



(1)

The present paper forms part of a series directed to elucidate the mechanism of this sequence of reactions and checks the first step in an alkaline medium.

RESULTS

The pseudo-first-order constants concerning melamine were established by successive determinations of cyanuric bases from aliquots taken at certain intervals of time.

It was found that as the constants decrease linearily against the time, the alkaline concentration as well as the temperature increased (Fig. 1). Therefore, the k_1°—values of the extrapolated rate constants for the initial moment were considered to be significant (Table 1).

The dependence between these k_1°—constants and the alkaline concentration was found to be of the form:

$$k_1^\circ = k_2[\mathrm{OH}^-] + k_3[\mathrm{OH}^-]^2 \qquad (2)$$

The k_2 and k_3 constants may be determined by using the plotting $k_1^{\circ}/[\mathrm{OH}^-] = \varphi[\mathrm{OH}^-]$. Their values are given in Table 2, and are close to the values of the corresponding kinetic parameters.

These findings differ from those given by May and Onyon[4] who determined the ammonia produced during hydrolysis and found for the pseudo-first-order hydrolysis constant against melamine at 100°, and at relative decreased alkaline concentration (0·01–1M), the expression:

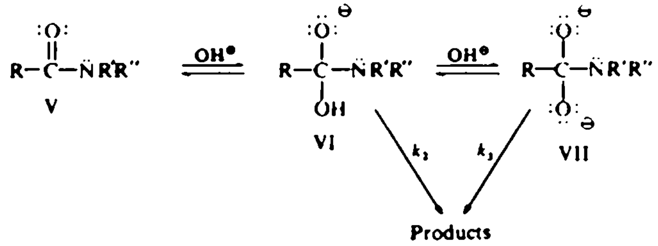
$$k_1 = 2{\cdot}28.10^{-3}\,[\mathrm{OH}^-]\,\mathrm{min}^{-1} \qquad (3)$$

We confirmed the results obtained by May and Onyon, reproducing their reaction conditions, but using different analytical means.

DISCUSSION

Kinetic expressions for the alkaline hydrolysis of the Eq. 2 are known for N-methylanilides of some carboxylic acids,[5] chloroacetamide,[6] N-methylacetamide[7] as well as lactams[8] and urea.[9]

In all cases it is agreed that there are two intermediate ions and hydrolysis takes place simultaneously by both of them, according to:



(4)

Thus the hydroxylic ion acts as a nucleophilic agent as well as a nucleophilic catalyst during the elimination step of the NR′R″-amide ion.

In support of the above mechanism evidence has been provided by Taft and Bichler[5] who checked the influence of the R radical upon the k_3/k_2 ratio, and found that the process which takes place by the intermediate VII is favoured by the attractive effect of the R radical electrons, and not favoured by its steric effect—the polar factor being more important than the steric one. These data are in agreement with the considered mechanism since the attraction of the R radical increases the ion acidity VI, and its steric effect inhibits solvation. This is more important in case VII than in case VI.

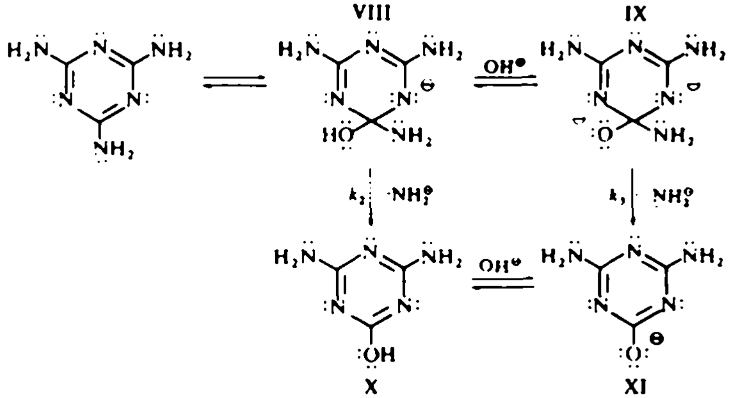
Finally, Vinnik *et al.*[10] by means of UV and IR spectral measurements performed during the reaction, confirmed the evidence in favour of ion VII.

If this mechanism is applied to the hydrolysis of melamine in strong alkaline media, it can be formulated as in the (S_NAr2) mechanism.

The decrease in the rate constant with time can only be understood if we consider that during hydrolysis, a secondary reaction involving melamine, may occur.

It is well known that nucleophilic substitutions take place with azines and especially in the case of s-triazines, in reactions which open the ring. Such secondary reactions have been emphasized in the hydrolysis of several amino-pyrimidine[11-13] or dichloro-s-triazine[14] derivatives. They are of primary importance even in the case of

Mechanism scheme



s-triazine, which behaves like a methynation agent.[15] It is considered that during hydrolysis of melamine the lowering of pseudo-unimolecular constants with time is due to the opening of the ring, yielding CO_2 and NH_3 as final products.

The possibility that ion VIII may be transformed in directions other than ammeline, proves that it has an independent existence in the system. Thus, the elimination step in the nucleophilic substitution is relatively slow.

TABLE 1. PSEUDOMONOMOLECULAR CONSTANTS OF MELAMINE HYDROLYSIS TO AMMELINE

NaOH M	Melamine M	Temp. °C	$k_1' \cdot 10^3$ min^{-1}
2	0·159	100	1·20
3	0·159	100	2·48
	0·079	90	1·20
	0·040	80	0·480
4·38·	0·159; 0·040	100	5·35
	0·079	90	2·45
	0·040	80	0·925
5	0·159	100	6·50

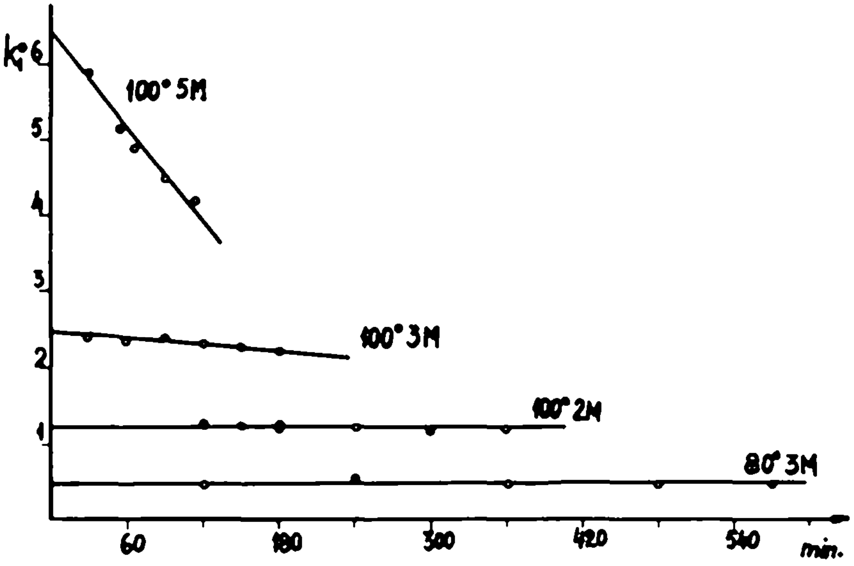
TABLE 2. CONSTANTS k_2 AND k_3

Temp. °C	$k_2^{\circ} \cdot 10^3$ l/mol min	$k_3^{\circ} \cdot 10^3$ $l^2/mol^2 min$
100	16·0	23·4
90	8·0	10·8
80	4·0	4·0
Kinetic	$\Delta H^{\ddagger}$ 18·3 Kcal/mol	23·2 Kcal/mol
Parameters	$\Delta S^{\ddagger}$ − 27·5 cal/mol degree	− 14·6 cal/mol degree

Since the particularly low activation entropy determines reaction rate in the uncatalyzed process, presumably amide ion formation is dependent on an intense solvation. As the activation entropy increases considerably with nucleophilic catalysis ($\Delta S^{\ddagger} = -14{\cdot}6$ cal/mol. degree) this suggests that the accumulation of two negative charges, even when special solvation of the amide group is lacking, can bring about elimination of the amide ion. Obviously, the increased negative charge is also responsible for an increase of the enthalpy of activation (from 18·3 Kcal/mol up to 123·2 Kcal/mol).

Finally, we think that the higher value of the bimolecular rate constant in dilute alkaline solutions as compared with the value in concentrated alkaline solutions may be due to a general acid catalysis of the solvent (H_2O) which favours the subsequent nucleophilic attack of the OH ion. It is well known that the s-triazine 2,4,6-trisubstituted systems readily undergo nucleophilic substitution in the presence of acidic catalysts,[16] and this has been shown in the case of melamine.[4] This has been emphasized in the electrophilic catalysis of a nucleophilic addition of hydrocarbon anion R^- to cyanuric chloride[17] by means of Mg^{2+}.

In conclusion, the sensitivity of the initial product in this electrophilic catalysis may be an indication that the first step of hydrolysis is probably slow and if the OH^- concentrations are not too high it may even determine the rate.



EXPERIMENTAL

The hydrolysis was carried out in a 3-neck flask of 2 L equipped with an ascending condenser and a thermometer Höppler U-10 thermostat or electric heating were used to obtain a temp ±0·5. 100-200 ml aliquots were immediately acidulated with glacial AcOH, and analysed by a method[18] which is accurate but laborious.[19]

The rate constant k_1 was determined by using the expression:

$$k_1 = \frac{1}{t} \ln \frac{[M]}{[M_0]}$$

where M represents the melamine concentration in the moment t and M_0 the melamine concentration in the moment O, considered to be equal with the sum of the determined melamine, ammeline and ammelide concentrations.

The activation energy and the preexponential factor, determined on the basis of the Arrhenius equation, were used to calculate the enthalpy and the entropy of the reaction at 300°K using the known expressions:

$$\Delta H \approx \Delta E \qquad \Delta S^{\ddagger} = R \ln A \frac{h}{\mathrm{kT}}$$

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