On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions.

III. Experimental Studies of the Rates of Hydrolysis of Monomethylol Urea

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The rates of monomethylol urea hydrolysis at 20° C are investigated. The reaction cannot be described by a simple first order reaction rate equation, and the rate constants were determined by means of an extrapolation method applied to the first order equation relationship.

The hydrolysis is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution is no simple function of the hydroxyl ion activity. The influence of the concentration of the reactants on the reaction rate constants is found to be small.

The rate of the hydrolysis of monomethylol urea:

was studied by Crowe and Lynch¹. The amount of liberated formaldehyde was determined by means of polarography directly in the reaction solutions. The experiment only included the hydrolysis of 0.00344 M monomethylol urea in 0.05 M LiOH; the reaction was studied by adding a monomethylol urea stock solution to an equal amount of 0.10 M LiOH. The time elapsed between the preparation of the stock solution and the addition to LiOH is not mentioned; thus it is not known if the hydrolysis occurring in the stock solution was controlled. No linear relationship was found when applying a first order reaction rate equation, but from the slope of the curve at zero reaction time, the constant was calculated.

From comparisons made between the hydrolysis rate constant obtained by this experiment and the corresponding constant of the equimolecular reaction between urea and formaldehyde an equilibrium constant of 20.5 was calculated by these authors. The equilibrium constant found from the latter of the reactions, extrapolated to infinite reaction time, was of the order 26. All data refer to 0.05 M LiOH.

The purpose of the following study is to investigate the rate of hydrolysis of monomethylol urea in comparatively concentrated solutions at 20° C with regard to the influence of pH, buffer and monomethylol urea concentration.

The experimental technique was the same as previously described (Landqvist ²). The monomethylol urea was prepared in accordance with Walter and Gewing ³. The cryoscopic molecular weight was found to be 90 ± 2 . All hydrolysis experiments were carried out at $20 \pm 0.1^\circ$ C, and all chemicals used were of A. R. quality. Dry monomethylol urea was added to a solution containing the buffer substances at the pH wanted and, if occurring, the very small change in pH was quickly adjusted. (The pH was re-checked during the reaction, and no changes observed, except for a reaction in an unbuffered solution with an initial pH of 6.70.) Solid monomethylol urea was added in order to prevent any influence of hydrolysis before mixing, *i. e.* in order to obtain a real zero reaction time. This time was calculated from the midpoint of the time needed for dissolving the monomethylol urea, which was of the order 30—60 seconds, since the maximum concentration of monomethylol urea was ≤ 1.0 M.

When neglecting the reaction between the hydrolysis products and a reaction between monomethylol urea and liberated formaldehyde producing dimethylol urea, we find the following reaction rate equation:

$$\frac{dx}{dt} = k' (C_0 - x) \quad t = 0, x = 0 \quad (1)$$

and

$$\ln \frac{C_0}{C_0 - x} = k' t \quad (2)$$

where x = the concentration of urea or formaldehyde, C_0 = initial concentration of monomethylol urea, t = time of reaction and k' = the rate constant of monomethylol urea hydrolysis.

If $x \ll C_0$ we obtain:

$$\frac{x}{C_0} = k' t \quad (3)$$

A complete reaction rate equation requires the consideration of all the factors mentioned above. Since the rates of dimethylol urea hydrolysis are unknown, the general case cannot easily be treated. However, the rate constants can, as previously mentioned, be determined from the slope of the function (2) at zero reaction time. This method does not permit a high degree of accuracy. If the slopes of the function (2), when plotted from experimental data, were determined graphically and then plotted as functions of reaction time logarithmically, it was found that

$$\sqrt{\frac{1}{d \ln [C_0/(C_0 - x)]/dt}} = f(t) \quad (4)$$

is a suitable function for linear extrapolations to zero reaction time in the present case. By applying this method, a better accuracy could be obtained.

Table 1. Experimental data of the hydrolysis of monomethylol urea in neutral and alkaline solutions at 20° C.

$\text{CH}_3\text{N.CO.NH.CH}_2\text{OH}$	Buffer substance ¹	C_{buffer}	pH	$k' \times 10^5$	$\frac{k'}{\bar{k}}$ from reaction rate data
1.00	—	—	6.70 ²	0.057	—
1.00	KH_2PO_4	0.100	6.70	0.60	0.037
1.00	KH_2PO_4	0.050	6.70	0.35	0.035
1.00	KH_2PO_4	0.025	6.70	0.22	0.034
1.00	borax	0.100	9.20	0.30	0.037
1.00	borax	0.050	9.20	0.23	0.038
1.00	borax	0.025	9.20	0.19	0.037
1.00	Na_2CO_3	0.100	10.00	0.76	0.040
1.00	Na_2CO_3	0.050	10.00	0.46	0.041
1.00	Na_2CO_3	0.025	10.00	0.35	0.035
0.50	Na_2CO_3	0.100	10.00	0.77	—
0.25	Na_2CO_3	0.100	10.00	0.77	—
1.00	Na_2CO_3	0.100	11.50	6.6	0.036
1.00	Na_2CO_3	0.050	11.50	5.8	0.036
1.00	Na_2CO_3	0.025	11.50	5.2	0.037
					Av. 0.037

¹ In all cases such amounts of a chloride of the buffer cation were added that a cationic strength corresponding to that of the most concentrated solution was obtained.

² Initial pH; the final pH was 7.05.

The compositions of the reaction solutions and the experimental results are given in Table 1. In this table the equilibrium constants, as calculated from the figures here obtained and the corresponding constants of the equimolecular reaction between urea and formaldehyde (Landqvist ²), can also be found. (These data are the inverse of the figures given by Crowe and Lynch ¹.) No influence of pH and the catalytic properties of the reaction solution on the equilibrium constants can be observed.

No experimental equilibrium constants have been determined, since they cannot be assumed to be similar to the constants calculated from the reaction rates. All the reactions previously mentioned might be included in the experimental equilibrium. When regarding the hydrolysis of monomethylol urea and the reaction between the liberated urea and formaldehyde, we have:

$$\frac{dF}{dt} = k' (C_0 - F) - k F^2 \quad (5)$$

where F = the concentration of liberated formaldehyde, k = the urea-formaldehyde reaction rate constant when the reaction product is monomethylol urea. Thus, at equilibrium we obtain:

$$k'/k = F_\infty^2 / (C_0 - F_\infty) \quad (6)$$

where F_∞ = the amount of free formaldehyde at equilibrium.

During the hydrolysis the amount of free formaldehyde reaches a maximum and then decreases asymptotically; the change is very small and is probably

Fig. 1. The eqn. (2) relationship of the hydrolysis of 1.0 M monomethylol urea in 0.100 M Na_2CO_3 , pH 10.00, 20° C.

Fig. 2. The extrapolation method applied to the curve of Fig. 1.

due to dimethylol urea and urea-formaldehyde reactions. However, the amount of free formaldehyde at maximum was only about 1/4 of the amount calculated from eqn. (6) and no linear relationship was found when applying the solution to eqn. (5) to experimental data. Such results are to be expected from the previous discussion.

Fig. 3. Relationship between the reaction rate constants of the hydrolysis of 1.0 M monomethylol urea and the concentrations of the buffer substances at 20° C. KH_2PO_4 , pH 6.70 ($\times$); borax, pH 9.20 ($+$); Na_2CO_3 , pH 10.00 ($\bullet$) and Na_2CO_3 , pH 11.50 ($\circ$).

Fig. 4. Relationship between the logarithm of the reaction rate constant, extrapolated to zero buffer concentration, and pH for the hydrolysis of 1.0 M monomethylol urea at 20° C.

Fig. 1 is an example of the eqn. (2) relationships obtained, and Fig. 2 shows the corresponding extrapolation curve according to eqn. (4).

If the reaction rate constants of the monomethylol urea hydrolysis were plotted as functions of the concentrations of the buffer substances at a constant cationic strength, a relationship as shown by Fig. 3 was obtained. By extrapolation of these curves to zero buffer concentration, a "zero reaction rate", k'_0 , can be determined. The relation between $\log k'_0$ and pH is shown by Fig. 4.

From these experiments the following conclusions might be drawn, as regards the ranges studied:

1. No linear relationship can be found when applying a simple first order reaction rate equation (Fig. 1).
2. The equilibrium of the reaction is not in agreement with the equilibrium constants calculated from the reaction rates, and this is probably due to the influence of other reactions including mono- and dimethylol urea formation and dimethylol urea hydrolysis.
3. The concentration of the reactant does not affect the reaction rate constant to any considerable extent (Table 1).
4. A linear relationship is present between the reaction rate constants and the concentration of the buffer substances at a constant cationic strength, *i. e.* the reaction is subject to an *acid-base catalysis* (Fig. 3).
5. A very low catalytic effect is present in the case of borate buffers (Table 1).
6. The equilibrium constant, as calculated from the reaction rates, of the reaction between urea and formaldehyde producing monomethylol urea, is 0.037 (Table 1).
7. No pH dependence of the equilibrium constant seems to be present.

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