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

II. Experimental Studies of the Rates of the Equimolecular Reaction between Monomethylol Urea and Formaldehyde

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The paper includes the results of experimental studies at 20° C of the reaction between monomethylol urea and formaldehyde in comparatively concentrated solutions. The relationship between the amount of dimethylol urea produced by the reaction and the reaction time cannot be described by a simple second order reaction rate equation. However, an equation deduced with regard to the influence of dimethylol urea hydrolysis is in agreement with experimental results.

The reaction is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution to this catalysis is not a simple function of the hydroxyl ion activity. The influence of the concentration of the reactants on the reaction rate constants was found to be small.

A study of the rates of the reaction between monomethylol urea and formaldehyde,

is due to Květoň and Králová¹. In their investigations they used the hydroxylamine method for determining the amount of "free" formaldehyde of the reaction solutions. Since they found that this method, as it was described by Smythe², gives too low formaldehyde concentration data, the method was somewhat modified and highly standardized. The authors report an accuracy of $\pm 5\%$ when the hydroxylamine method is used as they recommend. (However, the results obtained by Landqvist³ in a critical analysis of some of the methods suitable for formaldehyde determinations in urea-formaldehyde reaction solutions, and the appearance of an initial rapid reaction in the experiments, as carried out by Květoň and Králová, gives the impression that $\pm 5\%$ might be a too optimistic figure when the modified method is more generally applied.)

According to Květoň and Králová, the accuracy is moderate if the later part of a reaction between urea and formaldehyde at a molar ratio of 1:2 is

used for an investigation of the reaction between monomethylol urea and formaldehyde. Thus, these authors also studied the reaction rates when starting from these latter compounds in 1 M solutions. In order to examine the influence of pH on the reaction rates, experiments were made at different pH in citric and boric acid buffers. (Corrections applied for the influence of the buffer substances on the results of the hydroxylamine titrations?) A minimum reaction rate was found at pH 6.5. All reaction rates were calculated by means of an equation corresponding to a second order reaction, and no regard was given to the influence of hydrolysis effects. Except for a rapid initial stage, the reactions were found to be of second order. However, only the middle part of the reaction was used for calculations, and when examining the rate constant data at long reaction times, deviations are found to be present. (Table 2 in the paper by Květoň and Králová.) Finally, an activation energy of 12.2 kcal was determined.

In the following the results of some experiments on the equimolecular reaction between monomethylol urea and formaldehyde are given. The purpose of these experiments has been to investigate the influence of pH and buffer substances on the reaction rates and the effect of the concentration of the reactants. A reaction rate equation will be deduced, with regard to the dimethylol urea hydrolysis.

The experimental technique was the same as previously described by Landqvist³. Monomethylol urea was prepared in accordance with Walter and Gewing⁴. The cryoscopic molecular weight of this monomethylol urea was 90 ± 2 . The monomethylol urea was dissolved in cold water and the cryoscopic measurements made immediately in order to prevent hydrolysis effects. All experiments were carried out at $20 \pm 0.1^\circ \text{C}$ and all chemicals were of A. R. quality, except for the formaldehyde, which was a Merck product of high purity, only containing traces* of formic acid and methyl alcohol.

The dry methylol urea was added to a solution containing formaldehyde and the buffer substances at the pH wanted. (The pH was then re-checked during the reaction, and no changes found, except for an experiment on an unbuffered solution, initial pH 6.70.) The addition of solid monomethylol urea was made in order to prevent any undesirable hydrolysis effects. The substance was brought into the solution and dissolved within 30–60 seconds; the reaction time was calculated from the midpoint of the time needed for complete dissolution. The maximum concentration used was 1 M, since the solubility of dimethylol urea is moderate.

When neglecting the hydrolysis of methylol ureas, we obtain the following reaction rate equation:

$$\frac{dx}{dt} = k_1 \cdot (C-x)^2 \quad t = 0, x = 0 \quad (1)$$

i. e.

$$\frac{x}{C \cdot (C-x)} = k_1 \cdot t \quad (2)$$

* $< 2 \times 10^{-4}$ M at 380 g/l formaldehyde.

where x = concentration of dimethylol urea, C = initial concentration of the reactants, t = time of reaction and k_1 = reaction rate constant.

However, when regarding the hydrolysis of dimethylol urea, but still neglecting that of monomethylol urea, we find:]

$$\frac{dx}{dt} = k_1 \cdot (C-x)^2 - k_2 \cdot x \quad t = 0, x = 0 \quad (3)$$

where k_2 = the rate constant of the dimethylol urea hydrolysis.

We write

$$k_2/k_1 = \sigma, \text{ i. e. the equilibrium constant.}$$

Since at equilibrium $d x/d t = 0$, we have:

$$\sigma = \frac{k_2}{k_1} = \lim_{t \rightarrow \infty} \frac{(C-x)^2}{x} \quad (4)$$

Under these conditions we obtain the following solution to eqn. (3)

$$k_1 \cdot t = \varphi = \frac{1}{\sqrt{4 \cdot C \cdot \sigma + \sigma^2}} \ln \frac{1 - 2 \cdot x / (2 \cdot C + \sigma + \sqrt{4 \cdot C \cdot \sigma + \sigma^2})}{1 - 2 \cdot x / (2 \cdot C + \sigma - \sqrt{4 \cdot C \cdot \sigma + \sigma^2})} \quad (5)$$

In each experiment the equilibrium constant was determined by extrapolation of the amount of "free" formaldehyde of the reaction solution to infinity reaction time.

Fig. 1. Reaction between 1.0 M $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH}$ + 1.0 M HCHO at 20° C in an unbuffered solution, initial pH 6.70.

Fig. 2. Reaction between 1.0 M $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH}$ + 1.0 M HCHO at 20° C and pH 6.70 [at CKH_2PO_4 : 0.1 (○), 0.05 (●) and 0.025 (+)].

Fig. 3. Reaction between $1.0 \text{ M H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH} + 1.0 \text{ M HCHO}$ at 20°C and $\text{pH } 9.20$ at $C_{\text{borax}} : 0.1$ (○), 0.05 (●) and 0.025 (+).

Fig. 4. Reaction between $1.0 \text{ M H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH} + 1.0 \text{ M HCHO}$ at 20°C and $\text{pH } 10.00$ at $C_{\text{Na}_2\text{CO}_3} : 0.1$ (○), 0.05 (●) and 0.025 (+).

In Figs. 1—7 the function (5) is plotted from experimental data, and in the case of Fig. 6 a comparison is also made to eqn. (2). In this investigation the reactions were continued much longer than was made by Květoň and Králová, since the later part of the reaction is of great practical interest. The composi-

Fig. 5. Reaction between $1.0 \text{ M H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH} + 1.0 \text{ M HCHO}$ at 20°C and $\text{pH } 11.40$ at $C_{\text{Na}_2\text{CO}_3} : 0.1$ (○), 0.05 (●) and 0.025 (+).

Fig. 6. Reaction between $1.0 \text{ M H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH} + 1.0 \text{ M HCHO}$ at 20°C and $\text{pH } 12.40$ and $C_{\text{Na}_2\text{PO}_4} : 0.1$.

Fig. 7. Reaction at 20° C, pH 10.00 and $C_{Na_2CO_3}$ 0.1 between $H_2N \cdot CO \cdot NH \cdot CH_2OH$ and $HCHO$ at the concentrations: 1.0 (O), 0.5 (●) and 0.25 (+).

Fig. 8. Relationship between the reaction rate constant of 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M $HCHO$ at 20° C and the buffer substance concentrations: KH_2PO_4 , pH 6.70 (x); borax, pH 9.20 (O); Na_2CO_3 , pH 10.00 (●); Na_2CO_3 , pH 11.50 (+).

Fig. 9. Relationship between the logarithm of the reaction rate constant extrapolated to zero buffer concentration and pH for the reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M $HCHO$ at 20° C. (+) refers to 0.1 M Na_2PO_4 pH 12.40.

Table 1. Experimental data of the equimolecular reaction between monomethylol urea and formaldehyde in neutral and alkaline solutions at 20° C. In all cases $\sigma = 0.11$.

Fig.	Concentration of the reactants	Buffer substance	C_{buffer}	pH	$k_1 \times 10^4$
1	1.00	—	—	6.70 *	0.064
2	1.00	KH ₂ PO ₄	0.100	6.70	0.79
2	1.00	KH ₂ PO ₄	0.050	6.70	0.38
2	1.00	KH ₂ PO ₄	0.025	6.70	0.24
3	1.00	borax	0.100	9.20	0.35
3	1.00	borax	0.050	9.20	0.26
3	1.00	borax	0.025	9.20	0.20
4	1.00	Na ₂ CO ₃	0.100	10.00	1.52
4	1.00	Na ₂ CO ₃	0.050	10.00	1.16
4	1.00	Na ₂ CO ₃	0.025	10.00	0.99
5	1.00	Na ₂ CO ₃	0.100	11.50	10.2
5	1.00	Na ₂ CO ₃	0.050	11.50	8.7
5	1.00	Na ₂ CO ₃	0.025	11.50	8.0
6	1.00	Na ₂ PO ₄	0.100	12.40	48
7	1.00	Na ₂ CO ₃	0.100	10.00	} 1.5
7	0.50	Na ₂ CO ₃	0.100	10.00	
7	0.25	Na ₂ CO ₃	0.100	10.00	

* Initial pH; final pH was 7.20.

tions of the reaction solutions and the experimental results are given in Table 1. (The cationic strength of the solutions was kept constant by adding an amount of the chloride of the buffer cation, corresponding to the difference between actual cationic strength and that of the most concentrated solution.)

When plotting the rate constants obtained at different buffer concentrations as functions of these concentrations, a relationship in accordance with Fig. 8 is found. If the curves are extrapolated to zero buffer concentration we get the sum of the "zero reaction rate" and the hydroxyl ion catalytic contribution: k_1^0 . The relation between the logarithm of k_1^0 and pH is shown by Fig. 9.

From these experiments the following conclusions might be drawn, as regards the temperature and concentration range studied:

1. No linear relationship can be found when applying the simple second order reaction rate equation (Fig. 6).
2. When applying a reaction rate equation, including the regard of dimethylol urea hydrolysis, but still neglecting that of monomethylol urea, a good linearity is obtained (Figs. 1—7).
3. No rapid initial reaction can be found (Figs. 1—7).
4. The concentration of the reactants do not affect the reaction rate constants to any considerable extent (Fig. 7).

5. 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. 8).
6. A very low catalytic effect is present in the case of borate buffers (Fig. 3).
7. No simple relationship exists between the catalytic contribution of the hydroxyl ions and their activity (Fig. 9).

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