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

IV. Experimental Studies of the Rates of Hydrolysis of Dimethylol Urea

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

The rate of hydrolysis of dimethylol urea at 20° C was studied. The reaction cannot be described by a simple first order reaction rate equation, but an equation deduced with regard to the reaction between monomethylol urea and formaldehyde is in agreement with experimental data.

The reaction is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution to the catalysis is not a 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 equilibrium constant of the reaction between monomethylol urea and formaldehyde at 20° C is 0.11.

The rates of the hydrolysis of dimethylol urea,

were studied by Květón and Králová¹ in 0.32 M unbuffered solutions, pH 7.0, at different temperatures. The hydroxylamine titration method used by these authors for determining the amount of "free" formaldehyde of the reaction solutions was previously discussed by Landqvist^{2,3}, and the accuracy obtained seems to be moderate. No linear relationship was found when applying a first order reaction rate equation, but from the slopes of the curves at zero reaction time, rate constants were calculated. The activation energy was found to be 16.9 kcal.

In the following paper the results of some experimental studies of the rates of dimethylol urea hydrolysis 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 dimethylol urea. A reaction rate equation will be deduced, including the regard of the reaction between the compounds liberated during the hydrolysis.

The experimental technique was the same as previously described by Landqvist². The dimethylol urea was prepared in accordance with Walter and Gewing⁴. The cryoscopic molecular weight of the product was found to be 120 ± 2 . All experiments were carried out at $20 \pm 0.1^\circ \text{C}$, and all chemicals used were of A. R. quality.

Dry dimethylol urea was added to a solution containing the buffer substances at the pH wanted. (The pH was then re-checked during the reaction and no changes found, except for a reaction in unbuffered solution at an initial pH of 6.70.) The addition of solid dimethylol urea was made in order to get a real zero reaction time, and this time was calculated from the midpoint of the time needed for dissolving the substance, and this latter time was of the order 30–60 seconds. The moderate solubility of dimethylol urea and the need of a short dissolving time gave a maximum concentration of 0.5 M, and this figure was also the upper limit used in this investigation.

When neglecting the reaction between the hydrolysis products, we obtain the following reaction rate equation:

$$\frac{dx}{dt} = k_2 \cdot (C - x) \quad t = 0, x = 0 \quad (1)$$

i. e.

$$\ln \frac{x}{C - x} = k_2 \cdot t \quad (2)$$

where x = concentration of monomethylol urea or formaldehyde, C = initial concentration of dimethylol urea, t = time of reaction and k_2 = hydrolysis reaction rate constant.

When regarding the reaction between the hydrolysis products, *i. e.* the condensation reaction between monomethylol urea and formaldehyde, but still neglecting the monomethylol urea hydrolysis, we obtain:

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

We write $k_1/k_2 = \tau$; $\tau = 1/\sigma$, where σ is the equilibrium constant, as previously used by Landqvist³.

Since at equilibrium $dx/dt = 0$, we find:

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

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

$$k_2 \cdot t = \psi = \frac{1}{\sqrt{1 + 4 \cdot \tau \cdot C}} \ln \frac{1 + 2 \cdot \tau \cdot x / (1 + \sqrt{1 + 4 \cdot \tau \cdot C})}{1 + 2 \cdot \tau \cdot x / (1 - \sqrt{1 + 4 \cdot \tau \cdot C})} \quad (5)$$

In each experiment the equilibrium constant was determined by extrapolation to infinity reaction time.

In Figs. 1–7 the function (5) is plotted from experimental data, and Fig. 6 also includes a comparison made to eqn. (2). The compositions of the reaction

Fig. 1. Hydrolysis of 0.5 M dimethylol urea at 20° C in an unbuffered solution, initial pH 6.70.

Fig. 2. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 6.70; $C_{\text{KH}_2\text{PO}_4}$: 0.1 (O), 0.05 (●) and 0.025 (+).

solutions and the experimental results are also given in Table 1. In this table the equilibrium constants, which can be calculated from the reaction rates here obtained and previously given data of the rates of the reaction between monomethylol urea and formaldehyde (Landqvist³), *i. e.* k_2/k_1 , can also be found.

In Fig. 8 the relationship between the reaction rate constants and the buffer concentrations for each buffer substance is given. This represents the results

Fig. 3. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 9.20; C_{borax} : 0.1 (O), 0.05 (●) and 0.025 (+).

Fig. 4. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 10.00; $C_{\text{Na}_2\text{CO}_3}$: 0.1 (O), 0.05 (●) and 0.025 (+).

Table 1. Experimental data of the hydrolysis of dimethylol urea in neutral and alkaline solutions at 20° C. In all cases $\sigma = 1/\tau = 0.11$.

Fig.	Conc. of dimethylol urea	Buffer substance	C_{buffer}	pH	$k_2 \times 10^5$	σ ; from reaction rate data
1	0.50	—	—	6.70 *	0.10	0.16
2	0.50	KH ₂ PO ₄	0.100	6.70	0.98	0.12
2	0.50	KH ₂ PO ₄	0.050	6.70	0.53	0.14
2	0.50	KH ₂ PO ₄	0.025	6.70	0.33	0.14
2	0.50	KH ₂ PO ₄	0.00 **	6.70	0.12	0.12
3	0.50	borax	0.100	9.20	0.42	0.12
3	0.50	borax	0.050	9.20	0.30	0.12
3	0.50	borax	0.025	9.20	0.23	0.12
3	0.50	borax	0.00 **	9.20	0.17	0.11
4	0.50	Na ₂ CO ₃	0.100	10.00	1.45	0.11
4	0.50	Na ₂ CO ₃	0.050	10.00	1.10	0.11
4	0.50	Na ₂ CO ₃	0.025	10.00	0.90	0.11
4	0.50	Na ₂ CO ₃	0.00 **	10.00	0.74	0.09
5	0.50	Na ₂ CO ₃	0.100	11.50	11.0	0.11
5	0.50	Na ₂ CO ₃	0.050	11.50	9.3	0.11
5	0.50	Na ₂ CO ₃	0.025	11.50	8.3	0.10
5	0.50	Na ₂ CO ₃	0.00 **	11.50	7.4	0.10
6	0.50	Na ₂ PO ₄	0.100	12.40	54	0.11
6	0.50	Na ₂ PO ₄	0.050	12.40	54	—
6	0.50	Na ₂ PO ₄	0.025	12.40	54	—
7	0.50	Na ₂ CO ₃	0.100	10.00	1.5	
7	0.30	Na ₂ CO ₃	0.100	10.00		
7	0.10	Na ₂ CO ₃	0.100	10.00		
Average						0.12

* Initial pH; final pH was 7.50.

** Extrapolated data.

obtained at constant cationic strength, since to each solution so much of a chloride of the buffer cation was added as corresponds to the difference between actual cationic strength and that of the most concentrated solution. If the curves of Fig. 8 are extrapolated to zero buffer concentration, we get the sum of the "zero reaction rate" and the hydroxyl ion contribution: k_2° . The relation between the logarithm of k_2° and pH is shown by Fig. 9.

As regards the equilibrium constant data, such determined by extrapolation to infinity reaction time are all 0.11. The figures calculated from reaction rate data are somewhat scattered, but the over all agreement must be regarded as good. Since the two reactions starts from two entirely different states of the reaction solutions, differences in the activity of both the reactants and the catalysts may be present.

Fig. 5. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 11.50; $C_{\text{Na}_2\text{CO}_3}$: 0.1 (○), 0.05 (●) and 0.025 (+).

Fig. 6. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 12.40; $C_{\text{Na}_3\text{PO}_4}$: 0.1 (○), 0.05 (●) and 0.025 (+). (Φ) $C_{\text{Na}_3\text{PO}_4}$: 0.1.

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

Fig. 7. Hydrolysis of dimethylol urea at the concentrations 0.5 (○), 0.3 (●) and 0.1 (+). At 20° C, pH 10.00 and $C_{\text{Na}_2\text{CO}_3}$: 0.1.

Fig. 8. Relationship between the hydrolysis rate constant of 0.5 M dimethylol urea at 20° C and the buffer substance concentrations; KH_2PO_4 , pH 6.70 (×); borax, pH 9.20 (○); 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 hydrolysis of dimethylol urea at 20° C.

1. No linear relationship can be found when applying a simple first order reaction rate equation (Fig. 6).
2. When applying a reaction rate equation which includes the regard of the condensation reaction between monomethylol urea and formaldehyde, but still neglecting monomethylol urea hydrolysis, a good linearity is obtained (Figs. 1—7).
3. The concentration of the reactants does not affect the reaction rate constants to any considerable extent (Fig. 7).
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. 8).
5. A very low catalytic effect is present in the case of borate buffers (Fig. 3).
6. No simple relationship exists between the catalytic contribution of the hydroxyl ions and their activity (Fig. 9).
7. The equilibrium constant of the reaction between monomethylol urea and formaldehyde is at 20° C 0.11. (Table 1 of this paper and Table 1 in Landqvist³.) The equilibrium constant is, within the range studied, not dependent on the pH of the reaction solutions.

The author wishes to thank the board of *Rydboholms A. B.* for permission to publish this paper, and is also indebted to Mr. G. Johansson for his valuable assistance in the experimental work.

REFERENCES

1. Květoň, R. and Králová, M. *Chem. Listy* **46** (1952) 403.
2. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
3. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
4. Walter, G. and Gewing, M. *Kolloid-Beihfte* **34** (1934) 163.

Received June 30, 1955.