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

VIII. Studies of the Reactions and Equilibria at Formaldehyde-Urea Molecular Ratios in the Range 1.4—2.0

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Reactions and equilibria at formaldehyde-urea ratios in the range 1.4—2.0 were investigated experimentally at 20 °C.

The general reaction rate equation was solved by means of an electronic differential analyser, using rate constants previously determined for the different reactions involved. The equilibrium concentrations were calculated, and both the course of reaction and equilibrium show a good agreement between experimental and theoretically determined data.

An empirical relationship between free formaldehyde and reaction time is also given.

For several practical purposes, *e. g.* the use of methylol ureas for textile finishing purposes, the reaction between formaldehyde and urea at molecular ratios within the range 1.4—2.0 is of a great interest. The purpose of the following paper is to describe studies of the kinetics of such reactions at 20 °C and to give the results of investigations on the equilibrium state of said reactions.

The experiments were carried out by means of the chemicals and the technique previously described ^{1,9}.

We introduce the following symbols:

Concentrations: U = urea; U_0 = urea, initial; F = formaldehyde; F_0 = formaldehyde, initial; M = monomethylol urea; D = dimethylol urea.

Reaction rate constants: monomethylol urea: k = formation, k' = hydrolysis; dimethylol urea: k_1 = formation, k_2 = hydrolysis.

Reaction time: t .

If mono- and dimethylol urea are assumed to be the reaction products, see *e. g.* de Jong and de Jonge ²⁻⁴, the general reaction rate equations can be written:

$$\left. \begin{aligned} \frac{dM}{dt} &= k \cdot U \cdot F - k' \cdot M - k_1 \cdot M \cdot F + k_2 \cdot D \\ \frac{dD}{dt} &= k_1 \cdot M \cdot F - k_2 \cdot D \\ U &= U_0 - M - D; F = F_0 - M - 2 D \\ t = 0: U &= U_0; F = F_0; M = D = 0 \\ t \rightarrow \infty \quad \frac{dM}{dt} &= \frac{dD}{dt} = 0 \end{aligned} \right\} \quad (1)$$

If we write: $\tau = k \cdot t$; $k'/k = \alpha$; $k_1/k = \beta$; $k_2/k = \gamma$; we have:

$$\left. \begin{aligned} \frac{dM}{d\tau} &= U_0 \cdot F_0 - [U_0 + (1 + \beta) \cdot F_0 + \alpha] \cdot M + (1 + \beta) \cdot M^2 + \\ &\quad (3 + 2 \beta) \cdot M \cdot D - (2 U_0 + F_0 - \gamma) \cdot D + 2 D^2 \\ \frac{dD}{d\tau} &= \beta \cdot F_0 \cdot M - \beta \cdot M^2 - 2 \beta \cdot M \cdot D - \gamma \cdot D \\ \tau = 0: M &= D = 0; \tau \rightarrow \infty : \frac{dM}{d\tau} = \frac{dD}{d\tau} = 0 \end{aligned} \right\} \quad (2)$$

Since a simple solution to the system of differential equations given above cannot easily be found, numerical solutions were obtained by means of an electronic differential analyser, the EIDA of Chalmers University of Technology, Gothenburg.

The accuracy of the solutions are, as calculated on the initial formaldehyde concentrations, of the order 3 %. Thus, the figures related to high τ values, $\tau > 4$, are moderately accurate. However, the equilibrium concentrations can be calculated exactly, as will be shown later on.

Numerical solutions given as $F = f(\tau)$ curves in Figs. 1—3 refer to 1 M urea and formaldehyde-urea ratios 1.4, 1.6 and 2.0. The buffer concentration was 0.050 M and the temperature 20 °C. The buffers were KH_2PO_4 , pH = 6.70; borax, pH = 9.20; Na_2CO_3 , pH = 10.00 at cationic strengths as in previous studies ^{1,5-7}. The reaction rate constants were taken from these studies. As can be seen, experimental data agree closely with the calculated curves. From this it might be concluded that the reaction rate constants, as previously determined under specialized conditions, are applicable to the more general case.

An example of the concentration-reaction time relationships of the reactants and the reaction products is given in Fig. 4, as calculated by means of the electronic differential analyser for 1.0 M urea + 1.7 M formaldehyde, 0.050 M Na_2CO_3 , pH 10.00, 20 °C. The concentrations of urea, mono- and dimethylol urea were determined in accordance with Landqvist ⁹. As seen from Fig. 4, experimental data and calculated curves are in a close agreement.

Fig. 1. Relationship between unreacted formaldehyde and the τ -value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M KH_2PO_4 , pH 6.70. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

Fig. 2. Relationship between unreacted formaldehyde and the τ -value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M borax, pH 9.20. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

In a previous paper⁸, an empirical equation for the relationship between free formaldehyde and the reaction time was given:

$$\log \log \frac{F_0}{F} = A \cdot \log \log t + B \quad (3)$$

This equation was found to be approximately valid in the case of equal con-

Fig. 3. Relationship between unreacted formaldehyde and the τ -value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M Na_2CO_3 , pH 10.00. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

Fig. 4. Relationship between the reaction solution composition and the τ -value; 1.0 M urea and 1.7 M formaldehyde. 0.050 M Na_2CO_3 , pH 10.00, 20 °C. (—) formaldehyde, (---) urea, (....) monomethylol urea and (-.-.-) dimethylol urea. The curves: theoretical solutions, (●): experimental data.

Fig. 5. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M KH_2PO_4 , pH 6.70, 20 °C.

Fig. 6. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M borax, pH 9.20, 20 °C.

centrations of the reactants. The same equation applied to the solutions mentioned above is shown by the plots of Figs. 5—7. Curves of this kind may be of value when applied to practical work.

From the previous equations we find the equilibrium conditions:

$$t \rightarrow \infty : \frac{dM}{dt} = \frac{dD}{dt} = 0$$

$$M = \frac{k}{k'} \cdot U \cdot F = K_1 \cdot U \cdot F; D = \frac{k_1}{k_2} \cdot M \cdot F = \frac{k \cdot k_1}{k' \cdot k_2} \cdot U \cdot F^2 = K_2 \cdot U \cdot F^2$$

$$U_0 = U (1 + K_1 \cdot F + K_2 \cdot F^2); F_0 = F + U (K_1 \cdot F + 2 \cdot K_2 \cdot F^2)$$

and

$$\frac{F_0 - F}{U_0} = \frac{K_1 \cdot F + 2 K_2 \cdot F^2}{1 + K_1 \cdot F + K_2 \cdot F^2} \quad (4)$$

Fig. 7. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M Na_2CO_3 , pH 10.00, 20 °C.

This equation can be solved straightforwardly, or by means of step by step approximation, starting from $F_0 - F \sim F_0$. Thus U , M and D can be calculated. The amounts of unreacted formaldehyde of the reaction solutions previously discussed in this paper were determined up to very long reaction times, ~ 100 h. From plots of the formaldehyde concentrations *versus* the inverse of the reaction time, the figures corresponding to infinite reaction time were found by extrapolation to zero. Further, these reaction solutions were diluted, and then subject to the same procedure. Finally, for some of the solutions the amounts of urea, mono- and dimethylol urea were determined in accordance with Landqvist⁹. The results can be found in Table 1, and we find that calculated equilibrium data agree with the observed values.

Table 1. Equilibrium data of reactions between formaldehyde and urea at the molecular ratios 1.4, 1.7 and 2.0. Temperature 20 °C. Buffer concentrations: 0.050 M.

Urea concentration U_0	Molecular ratio	Buffer	Calculated data				Observed data			
			U	M	D	F	U	M	D	F
1.0	1.4	KH_2PO_4 pH 6.70	0.13	0.47	0.41	0.13	0.13	0.46	0.41	0.12
	1.7		0.06	0.38	0.56	0.21	0.07	0.36	0.57	0.21
	2.0		0.03	0.28	0.69	0.34	0.03	0.27	0.70	0.33
	1.4	Borax pH 9.20	0.14	0.43	0.43	0.11	0.15	0.43	0.42	0.11
	1.7		0.07	0.36	0.57	0.19	0.07	0.34	0.59	0.18
	2.0		0.03	0.26	0.71	0.32	0.02	0.28	0.70	0.32
	1.4	Na_2CO_3 pH 10.00	0.15	0.40	0.45	0.10	0.16	0.43	0.41	0.10
	1.7		0.07	0.33	0.60	0.17	0.08	0.32	0.60	0.18
	2.0		0.03	0.23	0.74	0.30	0.03	0.24	0.73	0.29
0.50	1.4	KH_2PO_4 pH 6.70				0.10				0.10
	1.7					0.16				0.16
	2.0					0.23				0.22
	1.4	Borax pH 9.20				0.09				0.09
	1.7					0.15				0.15
	2.0					0.20				0.20
	1.4	Na_2CO_3 pH 10.00				0.10				0.09
	1.7					0.13				0.13
	2.0					0.20				0.20
0.33	1.4	KH_2PO_4 pH 6.70				0.09				0.09
	1.7					0.13				0.14
	2.0					0.18				0.18
	1.4	Borax pH 9.20				0.08				0.07
	1.7					0.12				0.12
	2.0					0.16				0.16
	1.4	Na_2CO_3 pH 10.00				0.09				0.08
	1.7					0.11				0.11
	2.0					0.16				0.15

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