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

IX. The Influence of Methanol on the Rates of Reaction

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The effects of methanol on the rates of the urea-formaldehyde reactions were studied. Decreased rates were observed at increasing amounts of methanol in the case of urea or monomethylol urea and formaldehyde reactions. No influence on the hydrolysis reactions was found.

The formation of a hemiacetal between methanol and formaldehyde was studied cryoscopically as regards the rate constants and the equilibrium. On the basis of the theory that the hemiacetal does not take part in the reactions mentioned above some rate and equilibrium relationships were derived and found to be in agreement with experimental data.

It has been observed by, *e. g.*, Smythe¹ that the presence of methanol in urea-formaldehyde reaction mixtures decreases the rate of reaction. Since commercially available formaldehyde solutions very often contain methanol, added in order to prevent polymer precipitation, the effect mentioned is of some technical importance. The scope of the following paper is to describe some investigations carried out in order to study the influence of methanol on the rates of the different urea-formaldehyde reactions.

It is known that methanol and formaldehyde form a hemiacetal as follows:

The role of such a compound in water-methanol solutions containing different amounts of formaldehyde was investigated cryoscopically.

Chemicals: Formaldehyde stock solutions prepared by means of distillation of A. R. paraformaldehyde solutions.

Procedure: All experiments refer to 20 °C. Formaldehyde solutions were prepared by dilution of stock solutions at least 24 h before the addition of the methanol; this was made in order to allow any depolymerisation reactions to be completed. The alcohol was then stirred into these solutions and samples were taken and investigated cryoscopically until a constant value was obtained. This means that from time to time samples at 20 °C

were cooled quickly and the freezing temperature determined; the total change in this temperature was calculated as the difference between the temperatures at extrapolated zero and infinite reaction time. The figure corresponding to zero reaction time was always in good agreement with calculated data.

The equilibrium constants of reaction (A) were calculated from:

$$\frac{C_{\text{CH}_3\text{OCH}_2\text{OH}}}{C_{\text{HCHO}} \cdot C_{\text{CH}_3\text{OH}}} = K \quad (1)$$

The reaction solution composition and the results obtained can be found in Table 1.

Table 1. Equilibrium constants of the hemiacetal formation between methyl alcohol and formaldehyde. 20 °C.

$C_{\text{CH}_3\text{OH}}$	C_{HCHO}	K liter / moles
0.100	0.100	0.67
0.100	0.274	0.63
0.250	0.264	0.63
0.500	0.264	0.64
1.018	0.274	0.66
0.250	0.537	0.63
1.018	0.537	0.68
0.500	1.048	0.64
		Av. 0.65

As seen from this table, the K values are acceptably constant, thus reaction (A) may be the most important one under the conditions here studied.

The reaction rate equation can be written:

$$\frac{dy}{dt} = k_1 (C_M - y) \cdot (C_F - y) - k_2 \cdot y \quad (2)$$

where

- y = concentration of the hemiacetal.
- C_M = initial concentration of methanol.
- C_F = initial concentration of formaldehyde.
- k_1 = formation rate constant.
- k_2 = dissociation rate constant.
- t = time of reaction.

Initial conditions: $t = 0$, $y = 0$.

The solution to eqn. (2) can be written:

$$\varphi = k_1 \cdot t = \frac{1}{\sqrt{b^2 - 4a}} \cdot \ln \frac{(2y + b - \sqrt{b^2 - 4a}) \cdot (b + \sqrt{b^2 - 4a})}{(2y + b + \sqrt{b^2 - 4a}) \cdot (b - \sqrt{b^2 - 4a})} \quad (3)$$

where $a = C_M \cdot C_F$; $b = -(C_M + C_F + \frac{1}{K})$; $K = \frac{k_1}{k_2}$.

Applied to the reactions studied, eqn. (3) gives relationships as exemplified by Fig. 1, when the equilibrium constant mentioned previously is introduced into the equation. Since the rate of reaction is high as compared with the experimental technique — *i. e.* the cryoscopic measurements — figures corresponding to the initial part of the reaction could not be obtained. Despite of this lack of accuracy, we may accept

$$k_1 = 0.65 \times 10^{-3} \text{ liter/moles} \cdot \text{sec.}$$

$$k_2 = 1.0 \times 10^{-3} \text{ sec}^{-1}.$$

These figures are related to unbuffered solutions. Since addition of buffer substances considerably increases the reaction rates, no accurate measurements could be made on solutions containing such substances.

The reaction between urea or monomethylol urea and formaldehyde and the hydrolysis of mono- and dimethylol urea were investigated as previously described ²⁻⁵. The solutions were the same as the 0.050 M KH_2PO_4 , pH 6.70, series of the previous papers, but they also contained methanol.

The experimental results can be found in Table 2.

Table 2. Reaction rate constants of the reactions between urea or monomethylol urea and formaldehyde and of the hydrolysis of mono- and dimethylol urea in the presence of methanol; 0.050 M KH_2PO_4 , pH 6.70, 20 °C.

C_{methanol}	C_{urea}	$C_{\text{monomethylol urea}}$	$C_{\text{dimethylol urea}}$	$C_{\text{formaldehyde}}$	$k \cdot 10^5 *$	$k_0 \cdot 10^5 *$ calculated
0.000	4.0			0.40	10	10
0.094	4.0			0.40	10	11
0.72	4.0			0.40	8.3	10
1.34	4.0			0.40	6.4	10
0.000	2.0			0.20	10	10
0.063	2.0			0.20	10	11
0.69	2.0			0.20	8.2	11
1.31	2.0			0.20	6.2	10
0.72	2.0			0.80	8.0	11
0.00		1.0		1.0	3.8	3.8
0.22		1.0		1.0	3.5	3.8
0.85		1.0		1.0	2.6	3.6
1.47		1.0		1.0	2.1	3.6
0.00		1.0			0.35	
0.63		1.0			0.35	
1.25		1.0			0.34	
0.00			1.0		0.53	
0.63			1.0		0.52	
1.25			1.0		0.53	

* The rate constants of the formation reactions: liter / moles · sec.; the hydrolysis reactions: sec⁻¹.

Fig. 1. Relationship in accordance with eqn. (3) of 0.500 M CH_3OH + 0.264 M HCHO (+) and 0.500 M CH_3OH + 1.048 M HCHO (●). 20 °C.

Fig. 2. Relationship in accordance with eqn. (6) for 4.0 M urea + 0.4 M formaldehyde; 0.050 M KH_2PO_4 , pH 6.70, 20 °C; 1.34 M methanol.

If we compare the rate constant of hemiacetal hydrolysis and the rate constants of the urea — formaldehyde reaction systems, and remember that the hemiacetal hydrolysis appears to be catalysed by buffer substances, we may assume that the equilibrium in accordance with eqn. (1) is maintained throughout the urea or monomethylol urea and formaldehyde reactions. Assuming that the change in rates of the last mentioned reactions is dependent on the formation of a hemiacetal between methanol and formaldehyde⁶, and further that this hemiacetal does not take part in the reactions with urea or monomethylol urea, we find that the rate constants at zero reaction time of the urea or monomethylol urea and formaldehyde reactions would be related as follows:

$$\frac{k_0}{k_{C_M}} = \frac{C_F}{C_F - y} \quad (4)$$

where

k_0 = reaction rate constant at zero methanol concentration.

k_{C_M} = reaction rate constant at C_M methanol concentration.

C_{C_F} = initial formaldehyde concentration.

y = initial hemiacetal concentration.

y as calculated from eqn. (2): $y^2 - (C_M + C_F + \frac{1}{K}) \cdot y + C_M \cdot C_F = 0$; symbols defined as previously.

The results, as found in Table 2, can be summarized: Within the range studied, 0—1.3 M methanol,

- A. a considerable influence of methanol on the reaction rates of the urea or monomethylol urea and formaldehyde reactions is found;
- B. the k_0 -figures calculated by means of eqn. (4) are in agreement with the figures related to zero methanol concentration;
- C. no effect of methanol on the rates of hydrolysis of mono- and dimethylol urea could be detected.

In the case of the urea-formaldehyde reactions, carried out with an excess of urea present (hydrolysis reactions negligible), we write:

$$\frac{dx}{dt} = k \cdot (C_U - x) \cdot (C_F - x - y) \quad (5)$$

$$\frac{y}{(C_M - y) \cdot (C_F - x - y)} = K = \frac{1}{\alpha}$$

$t = 0, x = 0$;

Here is C_U = initial urea concentration; x = monomethylol urea concentration; k = rate constant and t = time of reaction. Other symbols as previously defined. If $y \ll C_M + C_F + \alpha - x$, we obtain the following solution to eqn. (5):

$$\psi = k \cdot t = \frac{\alpha + C_M + C_F - C_U}{(C_U - C_F) \cdot (C_U - C_F - \alpha)} \cdot \ln \frac{C_U}{C_U - x} + \frac{\alpha + C_M}{\alpha \cdot (C_U - C_F)} \cdot \ln \frac{C_F}{C_F - x} - \frac{C_M}{\alpha \cdot (C_U - C_F - \alpha)} \cdot \ln \frac{C_F + \alpha}{C_F + \alpha - x} \quad (6)$$

An example of the relationships according to this equation, plotted from experimental data, $C_M = 1.34$, $C_U = 4.0$, $C_F = 0.40$, is shown by Fig. 2. As seen a good linearity and agreement with the corresponding rate constant from Table 2 is present.

As a result of the fact that only the forward reaction rates are influenced, by the presence of methanol, the equilibrium formaldehyde concentration, as determined analytically, may also be dependent on the amount of alcohol in the reaction mixtures.

Under the conditions used for the polarographic analysis of the amount of equilibrium formaldehyde of the reaction mixtures, all hemiacetal is completely hydrolysed. (The figures obtained on formaldehyde solutions with and without methanol present are the same, when samples of the solutions are added to the supporting electrolyte in accordance with the previous paper².) Thus, the analytically determined "equilibrium" formaldehyde concentration $C_{F\infty}$ is related to the concentration of "free" formaldehyde $C_{F\infty}^0$, *i. e.* the amount in actual equilibrium with urea, mono- and dimethylol urea, as follows: $C_{F\infty} = C_{F\infty}^0 + y$; y is the concentration of the hemiacetal.

Eqn. (1) can be written

$$\frac{y}{(C_M - y) \cdot C_{F\infty}^0} = K \quad (7)$$

Symbols defined as previously. If we combine this expression with $C_{F\infty} = C_{F\infty}^{\circ} + y$, we obtain:

$$C_{F\infty} = C_{F\infty}^{\circ} + \frac{C_M}{1 + \frac{1}{K \cdot C_{F\infty}^{\circ}}} \quad (8)$$

From above we see that $C_{F\infty}^{\circ}$ is independent of the presence of methanol and can be found from a determination of the analytical amount of formaldehyde in the urea-formaldehyde reaction mixtures at zero alcohol concentration. The validity of eqn. (8) is exemplified by the experimental data, extrapolated to infinite reaction time, obtained for the reactions between monomethylol urea and formaldehyde in accordance with the experiments of Table 2. The results are as follows:

C_{methanol}	$C_{F\infty}$	
	measured	calculated
0.00	0.22 *	—
0.22	0.25	0.25
0.85	0.33	0.33
1.47	0.40	0.39

* Thus, $C_{F\infty}^{\circ} = 0.22$.

The principle introduced is, of course, generally applicable to these problems.

The influence of methanol on the reaction rates may also be attributed to influences on the ion activities of the catalysts. However, the behaviour of the mono- and dimethylol urea hydrolysis reactions, as seen from Table 2, shows that such effects may be negligible.

The conclusions to be drawn from the investigations described in this paper may be: The reduction in reaction rates of the urea or monomethylol urea and formaldehyde reactions caused by methanol depends mainly on the formation of a hemiacetal between methanol and formaldehyde. The hemiacetal does not take part in the reactions, and the equilibrium conditions of the hemiacetal are maintained throughout the reactions between the ureas and the formaldehyde.

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