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

V. Experimental Studies of the Order of the "Equimolecular" Reaction between Urea and Formaldehyde at Equal Concentrations of the Reactants

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Experimental results obtained on the reaction between urea and formaldehyde at equal concentrations are analysed mathematically under the assumption that only the formation of mono- and dimethylol urea is of importance, and that the amount of dimethylol urea produced is small. A linear relationship between the reaction rate function deduced and the reaction time is present during the first 85% of the complete reaction when previously obtained reaction rate constants are used for the calculations. From the slopes of the lines reaction rate constants are determined, and found to be in agreement with the corresponding figures obtained from reactions in solutions containing an excess of urea.

Two numerical solutions of a system of differential equations, representing the generalized reaction rate problem, are obtained by means of the modified Euler method. The "free" formaldehyde-reaction time relationship calculated from these solutions is found to be in a good agreement with the experimental results.

Finally, an empirical equation is given, suitable for practical purposes.

In a previous paper Landqvist\textsuperscript{1} found that the equimolecular reaction at equal concentrations of urea and formaldehyde cannot be described by a second order reaction rate equation. However, if the reaction was carried out in an excess of urea, linear relationships could be obtained and reaction rate constants calculated. (The use of an excess of urea suppresses the influence of side reactions, such as dimethylol urea formation.)

In other papers by the same author the rate constants of the formation of dimethylol urea from monomethylol urea and formaldehyde\textsuperscript{2}, the hydrolysis of monomethylol urea\textsuperscript{3} and the hydrolysis of dimethylol urea\textsuperscript{4} were given. All reactions were found to be acid-base catalysed.

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The purpose of this paper is to describe further investigations of the reaction between urea and formaldehyde at equal concentrations and to compare the experimental results with a reaction rate equation which considers the formation of mono- and dimethylol urea, but neglects the hydrolysis of these compounds; the amount of dimethylol urea produced is assumed to be small. Numerical solutions of the system of differential equations which represents the generalized reaction rate problem in this case, will be compared with the corresponding experimental results. Finally, a search for an empirical reaction rate relationship, suitable for practical purposes, will be made.

All the experiments were carried out as previously described \(^1\).

If we only consider the formation of mono- and dimethylol urea, and assume that the amount of dimethylol urea produced is small, we get the following equation:

\[
- \frac{dF}{dt} = k \left( F^2 + k_1 (C_0 - F) \right) F \quad t = 0, \quad F = C_0
\]  

(1)

or, when introducing \(k_1/k = \beta\):

\[
- \frac{dF}{dt} = k \left( \beta C_0 F - (1 - \beta) F^2 \right)
\]  

(2)

where \(F\) = concentration of "free" formaldehyde of the reaction solution, \(t\) = time of reaction, \(C_0\) = initial concentration of urea and formaldehyde, \(k\) = rate constant of the reaction between urea and formaldehyde producing monomethylol urea and \(k_1\) = rate constant of the reaction between monomethylol urea and formaldehyde producing dimethylol urea.

When regarding the initial conditions, we obtain the following solution to eqn. (2):

\[
\varphi = \frac{1}{\beta C_0} \ln \left( 1 - \beta + \frac{\beta C_0}{F} \right) = kt
\]  

(3)

If the experimental data are plotted in accordance with the equation of a second order reaction, and the slopes at zero reaction time are determined, these data can be used for rate constant calculations. By means of a method previously described \(^3\), a better accuracy can be obtained. In the present case it is found that

\[
V \sqrt{d \left[ \frac{C_0 - F}{C_0 F} \right]} \, dt = f (t)
\]  

(4)

is a suitable function for linear extrapolations. By means of this the reaction rate constants were determined, and from comparisons made with the previously obtained data \(^2\) of dimethylol urea formation, the \(\beta\)-values were calculated. For each buffer and pH group the average \(\beta\) values were used for calculations from eqn. (3), including the determination of the rate constants of the reaction producing monomethylol urea.

In Table 1 the compositions of the reaction solutions and the experimental results are given. The table also includes the data obtained from reactions in
solutions containing an excess of urea, and the results are in comparatively good agreement with the present data.

In the Figs. 1—4 the plots of the $\psi$-function are given, and it is seen that a good linearity is present during the main part of the reaction. During the last 15% of the reactions deviations appear, which is exemplified by Fig. 1.

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In the same figure an example is given of the results of the use of a simple second order equation, i.e. no linearity is obtained.

The deviations mentioned are, of course, due to the approximations introduced in eqn. (1), i.e. the hydrolysis of the reaction products cannot be neglected, and further, the amount of dimethylol urea produced cannot be regarded as small.

During the reaction between urea and formaldehyde at equal concentrations, the following reactions are possible:

$$\begin{align*}
\text{H}_2\text{N}-\text{CO}-\text{NH}_2 + \text{HCHO} &= \text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CH}_2\text{OH} \\
\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CH}_2\text{OH} + \text{HCHO} &= \text{HOCH}_2-\text{NH}-\text{CO}-\text{NH}-\text{CH}_4\text{OH} \\
\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CH}_2\text{OH} &= \text{H}_2\text{N}-\text{CO}-\text{NH}_2 + \text{HCHO} \\
\text{HOCH}_2-\text{NH}-\text{CO}-\text{NH}-\text{CH}_4\text{OH} &= \text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CH}_4\text{OH} + \text{HCHO}
\end{align*}$$

When considering all of these reactions we have:

$$\begin{align*}
\frac{\partial M}{\partial t} &= k_1 U F - k_1 M F - k_M M + k_D D \\
\frac{\partial D}{\partial t} &= k_2 D
\end{align*}$$

Initial conditions: $t = 0$, $U = C_0$, $F = C_0$, $M = 0$ and $D = 0$.

Boundary conditions: $t \to \infty$, $\partial M/\partial t = \partial D/\partial t = 0$.

were $C_0 = \text{initial concentrations of urea and formaldehyde}$, $U = \text{concentration of urea}$, $F = \text{concentration of formaldehyde}$, $M = \text{concentration of monomethylol urea}$, $D = \text{concentration of dimethylol urea}$, $t = \text{time of reaction}$, $k = \text{rate constant of reaction (A)}$, $k_1 = \text{rate constant of reaction (B)}$, $k' = \text{rate constant of reaction (C)}$ and $k_2 = \text{rate constant of reaction (D)}$.

Since

$$U = C_0 - M - D \quad \text{and} \quad F = C_0 - M - 2D$$

and when introducing $k \ t = \tau$

we get:

\[
\begin{align*}
\frac{\partial M}{\partial \tau} &= a + b \ M + c \ M^2 + d \ M \ D + e \ D + f \ D^2 \\
\frac{\partial D}{\partial \tau} &= g \ M + h \ M^2 + i \ M \ D + j \ D \\
F &= C_0 - M - 2D
\end{align*}
\]

(6)

When considering the initial conditions, we find the following constants:

\[
\begin{align*}
a &= C_0^2, \ b = -(2 + \beta) \ C_0 + a, \ c = 1 + \beta, \ d = 3 + 2 \beta, \ e = -(3 \ C_0 - \gamma), \\
f = 2, \ g = \beta \ C_0, \ h = -\beta, \ i = -2 \ \beta, \ \text{and} \ j = -\gamma;
\end{align*}
\]

where $\alpha = k'/k$, $\beta = k_1/k$ and $\gamma = k_2/k$.

Fig. 7. The empirical expression (7) applied to the reaction between 1 M urea and 1 M formaldehyde at 20°C, pH 6.70. $C_{KH_2PO_4}$: 0.100 (×), 0.050 (○) and 0.025 (●). (†) refers to eq. (8), the equilibrium concentration of formaldehyde is taken from experimental data.

Fig. 8. The empirical expression (7) applied to the reaction between 1 M urea and 1 M formaldehyde at 20°C, pH 9.20. $C_{Na_2CO_3}$: 0.100 (×), 0.050 (●) and 0.025 (○).

Numerical solutions to this system of differential equations can be obtained by means of the modified Euler method (See e.g. Margenau and Murphy 5). The $F$-reaction time relationship was calculated for the cases 1.0 M urea + 1.0 M formaldehyde in $KH_2PO_4$, pH 6.70 (Fig. 5) and in $Na_2CO_3$, pH 10.00 (Fig. 6).

Fig. 9. The empirical expression (7) applied to the reaction between 1 M urea and 1 M formaldehyde at 20°C, pH 10.00. $C_{Na_2CO_3}$: 0.100 (×), 0.050 (●) and 0.025 (○).

Fig. 10. The empirical expression (7) applied to the reaction between 1 M urea and 1 M formaldehyde at 20°C, pH 11.50. $C_{Na_2CO_3}$: 0.100 (×), 0.050 (●) and 0.025 (○).

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using previously obtained data\textsuperscript{1–4} of $k$, $k_1$, $k'$ and $k_2$. In the diagrams 5 and 6 experimental data are also plotted, and it is seen that a very good agreement is present. Thus, the generalized solution to the rate problem describes the reactions with a high degree of accuracy. It can also be mentioned that experimentally determined formaldehyde concentrations at equilibrium are the same as obtained from 1.0 M monomethylol urea hydrolysis experiments\textsuperscript{3}.

However, for practical purposes an empirical equation which describes the amount of "free" formaldehyde of the reaction mixtures as functions of the reaction times would be of a great value. From logarithmical plots it is found that such a relationship is given by:

$$\log \log \left( \frac{F}{F_0} \right) = A \log \log t + B$$  \hspace{1cm} (7)

Here $A$ and $B$ are empirical constants. $F_0$ is the initial formaldehyde concentration.

This equation can be further refined if we introduce the equilibrium concentration of formaldehyde, $F_\infty$, which refers to infinite reaction time. Then we have:

$$\log \log \left( \frac{F}{F_\infty} \right) = A \log \log t + B$$  \hspace{1cm} (8)

I Figs. 7—10 the plots of the eqn. (7) are given, and it is seen that a good linearity is obtained. In Fig. 7 an example is given, which shows that the expression (7) is also valid close to equilibrium, and that the range of validity is further extended if eqn. (8) is applied.

The practical value of an empirical expression of this kind is not only the characterization of the reactions, but also the possibility of linear extrapolations during the run of a technical reaction.

Finally, the difference between actual and eqn. (8) behaviour can be used for determination of the equilibrium formaldehyde concentrations, since the value of $F_\infty$ necessary for a linear relationship can easily be determined.

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REFERENCES


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