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

X. Notes on the Reaction Mechanism

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The rates of the reactions of the urea-formaldehyde system are compared with other experimental data connected with urea and formaldehyde. The conclusions drawn from such comparisons are partly in favour of previous assumptions, partly not.

Some of the conclusions are: It is probable that a tautomer of urea may be the activated state for reactions with formaldehyde, and the tautomer may be of a zwitter ion structure. If the reactive compound would be an anion, the anion is not present in any considerable quantities prior to the reaction collisions. Only dehydrated formaldehyde or a resonance structure of dehydrated formaldehyde may react with urea or monomethylol urea. The rates of the depolymerisation, dehydration or hydration reactions of formaldehyde are of such a magnitude that they do not influence the rates of the reactions of the urea-formaldehyde system. The buffer catalysis of the urea-formaldehyde reactions is probably not simply connected with a formation of a buffer-formaldehyde complex prior to the reactions with urea or monomethylol urea.

Some of the previous theories connected with the urea-formaldehyde reaction mechanism are:

- A. An anion of urea is the reactive compound in reactions with formaldehyde¹⁻⁵.
- B. Only dehydrated formaldehyde reacts with urea or monomethylol urea^{1,2,4-6}.
- C. In concentrated solutions the slow depolymerisation of formaldehyde polymers influences the urea-formaldehyde reaction rates⁷.
- D. The main influence of the temperature on the urea-formaldehyde reactions is due to changes in the equilibrium between hydrated and dehydrated formaldehyde^{4,5}.
- E. The hydrolysis of methylol ureas catalysed by hydroxyl ions is connected with a dissociation of the OH group of the compound: $\text{—OH} + \text{OH}^- = \text{—O}^- + \text{H}_2\text{O}$. The rate of hydrolysis is proportional to the concentration of the —O^- compound⁶.

THE STATE OF UREA SOLUTIONS

I. There are several reasons to assume that urea tautomers exist. In favour of this assumption is:

X-Ray analysis shows a decrease in the bond length between carbon and nitrogen atoms. This is a typical effect of resonance hybrids⁸.

Raman- och infrared spectra of solid urea show that the force constants of the C — N and C = O bonds are 35 % above, respective 39 % below the expected figures. The occurrence of hydrogen bonds is not found to be probable⁹. The presense of such bonds was assumed by another author¹⁰, and the occurrence of tautomers representing any considerable fraction of the total amount of urea was not found to be probable. However, in this latter investigation no force constant calculations were made. The differences in opinion are also connected with differences in the interpretation of the absorption bands.

II. A urea tautomer may be of a zwitter ion structure, and the reasons for this assumption are:

The dielectric constant decreases considerably when urea is added to water, and the same effect is produced by amino acids⁸.

The melting point of urea is considerably above the figure to be expected. Amino acids show the same behaviour⁸.

III. No alkaline dissociation of urea could be detected when titrations were made with a hydrogen electrode for the pH measurements¹¹.

As mentioned in a previous paper¹², pH measurements in highly alkaline solutions by means of hydrogen electrodes require a high degree of hydrogen purity. In order to examine the investigation referred to above, the titration curves of 1.0 M urea and of distilled water at 20 °C after addition of HCl have been determined by means of the glass electrode differential method¹². Accuracy: ± 0.02 pH. The results are shown by Fig. 1. From this diagram it might be concluded that if any alkaline dissociation of urea occurs, $pK > 13$. Thus, the previous result is confirmed.

THE STATE OF FORMALDEHYDE SOLUTIONS

IV. In concentrated solutions is the formaldehyde partly present as linear polymers¹³.

V. The rate of depolymerisation of the polymers is highly dependent on pH and temperature. A rate minimum exists in the pH range 3—4. From studies below and above this range the specific catalytic constants of hydrogen and hydroxyl ions were found to be 3.7 and 3.7×10^7 liter/moles $\times$ sec, respectively, at 20 °C. The activation energy is 17.4 kcal. The reaction is mainly monomolecular, and is assumed to include the formation of a polymer zwitter ion. Correspondingly, the polymerisation reaction would involve a monomer zwitter ion¹⁴.

VI. From diamagnetic measurements it was found that the equilibrium between polymeric and monomeric aldehyde is dependent on pH; also at pH 10 the dependency is of a considerable magnitude¹⁵.

In order to investigate this result further, cryoscopic measurements have

Fig. 1. Titration curve of 1.0 M urea (○) and of water (●) after addition of HCl to pH~3. 20°C.

been made on pure formaldehyde solutions, pH 5.5, and after addition of NaOH to pH 10. A stock solution of formaldehyde, 12.6 M, was prepared by distillation of a paraformaldehyde-water mixture, and allowed to attain equilibrium before it was used for the experiments. The stock solution was then, with and without addition of NaOH, diluted to concentrations in the range 0—6 M. Temperature 20°C. The cryoscopic measurements were made immediately after the dilution and after 24 h storage. The results obtained are shown by Table 1. As seen, there is a considerable deviation from unity in the $(t_C - t_0)_{\text{pH } 10} / (t_C - t_0)_{\text{pH } 5.5}$ ratios * when the measurements were made immediately after the dilution. However, after the storage such a devia-

Table 1. The ratios between the differences in freezing temperatures at the formaldehyde concentrations C and zero at pH 10.0 and 5.5 when the measurements are made immediately after dilution from a 12.6 M stock solution and after 24 h storage. Temperature 20°C.

$\sum_{n=1}^{\infty} nC(\text{HCHO})_n$	$(t_C - t_0)_{\text{pH } 10.0} / (t_C - t_0)_{\text{pH } 5.5}$	
	Immediate measurements	After 24 h storage
1.0	1.67	1.00
2.0	1.43	1.00
3.0	1.35	1.00
4.0	1.31	1.00
6.0	1.28	1.00

* t_C and t_0 are the freezing temperatures at the formaldehyde concentrations C and zero, respectively.

tion does not exist. This effect may be a function of differences in rate of depolymerisation: after 24 h storage the equilibrium is probably attained at both pH values. Thus, it might be concluded that the pH influence referred to above is not found when the solutions are allowed to attain equilibrium conditions.

VII. The state of monomeric formaldehyde is described as an equilibrium between methylene glycol and dehydrated formaldehyde, and this equilibrium is highly in favour of the glycol¹³. The equilibrium constant^{16,17} is $\sim 10^{-4}$. ($K = C_{\text{HCHO}} / C_{\text{HOCH}_2\text{OH}}$)

VIII. Both an acid and alkaline dissociation of formaldehyde is present^{14,18,19}. At 20 °C the dissociation constants are: $\text{p}K = 5.8$ and 13.4, respectively.

IX. The methylene glycol dehydration is catalysed by buffer substances^{17,20}. The activation energy of the dehydration reaction is 14 kcal¹⁶; the figure corresponding to the hydration reaction is close to zero¹⁷. The catalysis by buffer substances as studied in a previous paper¹⁷, is further exemplified by Table 2.

X. The composition of formaldehyde solutions can be summarized as follows²¹; the data refer to 20 °C.

ΣC_{HCHO}	% polymers	% monomer
0.67	1	99
1.67	11	89
5.00	36	64
9.33	59	41

The temperature influence on the composition of the solutions was exemplified by the fact that the amount of polymers is below 1 % in 0.7 M solutions at 45 °C and in 7.3 M solutions at 100 °C.

Table 2. Polarographically determined dehydration rate constants of methylene glycol. Temperature 20 °C.

Analytical C_{HCHO}	Buffer *	pH	C_{buffer}	$k \times 10^2 \text{ sec}^{-1}$
0.0157	KH_2PO_4	6.70	0.100	5.9
			0.050	3.4
			0.025	1.7
0.00392	borax	9.20	0.100	57
			0.050	40
			0.025	30
0.00785	Na_2CO_3	10.00	0.100	60
			0.050	49
			0.025	46

* To all solutions such amounts of the chloride of the buffer cation was added that a cationic strength corresponding to the most concentrated solution was obtained.

THE UREA OR MONOMETHYLOL UREA AND FORMALDEHYDE REACTIONS

When the collision theory of reaction will be used here for discussions, this does not mean that the theory is generally accepted. However, the frequency factors calculated can be used as a base for probability discussions: from a distribution curve, made from a great number of experimental data ²², it can be seen that 8 % of the frequency factors exceed 10^{13} , and only 4 % exceed 10^{14} .

In the following the calculations refer to data given in a series of previous papers ²³⁻²⁶. The activation energy to be used is 15.4 kcal ²⁷, equal for both the reactions.

The rate constants of the reactions between urea or monomethylol urea and formaldehyde are, within the range studied, 2×10^{-5} — 2×10^{-3} liter/moles $\times$ sec. 20 °C, pH 6.70—11.50. Not only the formation reaction, but also the hydrolysis is catalysed by buffer substances ^{1,5,23-26}. The rate constants mentioned correspond to the frequency factors 5×10^8 — 5×10^8 , i.e. the values are considerably below the figure to be expected from the collision theory, $\sim 3 \times 10^{11}$.

However, if we apply the assumption (B, see above) that only dehydrated formaldehyde reacts, and use the equilibrium constant 10^{-4} for the methylene glycol—formaldehyde equilibrium (VII), the "corrected" rate constants corresponding to this would be 0.2—20 liter/moles. sec., and the frequency factors 5×10^{10} — 5×10^{12} . When we compare these figures with the probability of different frequency factors as mentioned above, we find that if the dehydrated aldehyde is the formaldehyde reactant, the reactive structure of urea probably ought to be at least 1 % of the total amount. As previously mentioned (A,B), several reaction mechanism theories include the assumption that an anion of urea reacts with dehydrated formaldehyde. Since $pK > 13$ (III) for the formation of such an anion, it is not very probable that a reaction mechanism of this kind would be of any considerable importance in neutral and moderately alkaline solutions, if the anion is assumed to exist prior to the reaction stage. The complex relationships between pH and the logarithm of the reaction rate constants extrapolated to zero buffer concentration ^{23,24}, show that the reaction mechanism is not solely including the presence of an anion of urea, as regards the effect of pH on the rates. Further, the catalytic effect of buffers cannot simply be explained by assumptions on the formation of the anion prior to the reaction stage.

The order of the dissociation constants of formaldehyde (VIII) shows that it is not very probable that formaldehyde ions would be of importance for the reactions in neutral and moderately alkaline solutions.

At this stage of the discussion some of the previous experimental results ought to be examined. From one of the papers ²³ (Fig. 9 of Ref. ²³) it is seen that the rate relationship curves of the equimolecular urea—formaldehyde reactions are practically independent of the reactant concentrations in the interval studied, 0.5—4 M, 20 °C. As regards the monomethylol urea—formaldehyde reactions, the same behaviour was observed ²⁴ in the studied range, 0.25—1 M, 20 °C. From above (X) it is known that at the upper concentrations of the ranges mentioned, the fraction of formaldehyde polymers is not

negligible. This would mean that the monomer fraction decreases when the concentration increases, and the fraction of the dehydrated formaldehyde too. A consequence of this would be a decrease in the rate constants.

This decrease in the concentration of the dehydrated aldehyde is exemplified by some data previously given ²⁸. When repeating the experiments on which these data are based, a fairly good agreement with the 60 °C figures was obtained. At 30 °C the very low absorption did not permit any accurate calculations.

An explanation to the non—influence of the presence of a considerable fraction of polymeric formaldehyde may be that collisions involving polymers also are active for producing a state of the aldehyde which is able to react with urea. The number of collisions is, from the theoretical point of view, more dependent on the number of HCHO groups than on their state: polymers or monomers.

This is seen from the well-known expression

$$Z = \sigma_{1,2}^2 n_1 n_2 \sqrt{8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$$

Z = number of collisions pr ml and sec between the molecules 1 and 2. $\sigma_{1,2}$ = sum of molecular radii, n_1 and n_2 = number of molecules pr ml. M_1 and M_2 = molecular weights. When the number, n , of one of the molecules decreases by polymer formation, σ increases since polymerisation means an increase in molecular dimensions.

Another explanation could be that a concentration effect connected with the formaldehyde is compensated by an opposite effect connected with the urea. When examining the results of the previous paper ²³ (Table 1 and Figs. 15 and 16 of Ref.²³), we find that such an assumption is improbable.

As mentioned previously, (V), the specific catalytic constant of hydroxyl ions for the formaldehyde polymer depolymerisation is 3.7×10^7 liter/moles $\times$ sec at 20 °C. If we compare this figure with the data of Table 2, we find that the rates of depolymerisation considerably exceed the rates of methylene glycol dehydration. Thus, when dehydrated formaldehyde is liberated in solutions containing polymers, the rate of methylene glycol dehydration might be the rate determining step.

It may also be of some interest to compare the catalytic effect of some buffer substances at a constant cationic strength on the dehydration rate constants of methylene glycol, as given in Table 2, with the catalytic effect of the same buffers on the reactions of the urea—formaldehyde system ^{23–26}. Such a comparison is given in Table 3, where the constants of the equation describing the rate constant — buffer concentration relationship

$$k = k_0 + a \cdot C_{\text{buffer}} \quad (1)$$

can be found. k = rate constant at the buffer concentration C_{buffer} , k_0 = rate constant at the extrapolated zero buffer concentration.

If we examine the data of Table 3, we find that the rates of methylene glycol dehydration is considerably greater than the figures related to the urea—formaldehyde system. Thus, the dehydration rates have no influence on the rates of the urea—formaldehyde forward reactions. Since the hydration

Table 3. The constants of eqn. (1) of the methylene glycol dehydration and of the urea-formaldehyde reactions. Temperature 20 °C. Dehydration and hydrolysis reactions: k_0 sec⁻¹; a liter/moles · sec, Formation reactions: k_0 liter/moles · sec, a liter²/moles² · sec.

Reactioo	Buffers						$a_{\text{KH}_2\text{PO}_4} :$ $a_{\text{borax}} :$ $a_{\text{Na}_2\text{CO}_3}$
	KH_2PO_4 , pH 6.70		borax, pH 9.20		Na_2CO_3 , pH 10.00		
	$k_0 \times 10^5$	$a \times 10^5$	$k_0 \times 10^5$	$a \times 10^5$	$k_0 \times 10^5$	$a \times 10^5$	
Methylene glycol dehydra- tion	1 200	45 000	23 000	34 0000	41 000	18 0000	1 : 7.6 : 4.0
$\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH}_2 + \text{HCHO}$	3.4	126	4.3	37	6.7	133	1 : 0.29 : 1.1
$\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH} +$ HCHO	0.9	60	1.5	20	8.1	71	1 : 0.33 : 1.2
$\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{OH}$ hydrolysis	0.09	5.1	0.15	1.5	0.21	5.5	1 : 0.29 : 1.1
$\text{HOCH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot$ CHOH_2 hydrolysis	0.11	8.7	0.18	2.4	0.72	7.3	1 : 0.28 : 0.8

reaction rates are 10⁴ times greater than the dehydration rates, the same conclusion can be drawn regarding the hydrolysis reactions of the methyol ureas.

Another conclusion which might be drawn from Table 3 is that the mechanisms of methylene glycol dehydration and of the urea-formaldehyde reactions are probably not identical. This since the catalytic effect of the different buffers on the different reactions deviates considerably, as seen from the $a_{\text{KH}_2\text{PO}_4} : a_{\text{borax}} : a_{\text{Na}_2\text{CO}_3}$ ratios. The ratios connected with the urea-formaldehyde reactions are practically identical for all of these latter reactions. Thus, the catalysis of the rate determining step of the urea-formaldehyde reactions is probably not simply connected with the formation of an activated buffer-formaldehyde complex during the dehydration reaction, a complex which would represent an activated state for reactions with urea or mono-methyol urea. However, the catalysts, *i.e.* buffers, H₂O and OH⁻, increase the prior formaldehyde depolymerisation and dehydration reactions to such an extent that these reactions do not influence the rates of the urea-formaldehyde reactions.

Since polarographic investigation on formaldehyde in connection with the urea-formaldehyde reactions have previously⁴ been used for discussions (A, B, D) regarding these reactions, some of the interpretations given will be examined.

The extent of formaldehyde dehydration was estimated from the ratios between actual "formaldehyde wave height" and the "total dehydrated wave height". The "total dehydrated wave height" was assumed to refer to a less steep slope appearing at increased temperatures when a $\log i = f(1/T)$ curve is plotted from experimental data obtained on formaldehyde solutions containing buffer substances; (i = polarographic limiting current, T = temperature in °K). As easily seen from a previous paper²¹, the change in slope mentioned does not mean that the formaldehyde is completely dehydrated; the less steep

slope appears when the rate of methylene glycol dehydration exceeds the rate of diffusion of this substance to such an extent that the latter rate controls the polarographic electrode process.

It was further found that the following expression, derived from the Arrhenius equation:

$$\log \frac{k_2}{k_1} = \frac{\Delta E_a}{\Delta E_{aa}} \cdot \log \frac{i_2}{i_1} \quad (2)$$

is in a good agreement with experimental data. k_2 and k_1 = rate constants of the urea-formaldehyde reactions at two different temperatures but at the same buffer composition. i_2 and i_1 = the corresponding polarographic limiting currents of formaldehyde under the same conditions. ΔE_a and ΔE_{aa} = the "activation energies" of the urea-formaldehyde reaction, respectively the polarographic limiting current of formaldehyde. It is easily seen that eqn. (2) is self-consistent:

$$\log \frac{k_2}{k_1} = \log Z_k - \log Z_k - \frac{\Delta E_a}{M \cdot R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{i_2}{i_1} = \log Z_i - \log Z_i - \frac{\Delta E_{aa}}{M \cdot R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(M = \ln 10)$$

and thus eqn. (2) is obtained from these expressions. Any pair of reactions will give the coincidence observed, provided they obey the Arrhenius equation.

Finally, a relationship between urea-formaldehyde reaction rate constants and the polarographic limiting currents of formaldehyde at different pH values was given. However, this relationship is purely empirical²⁰.

It has previously been stated that the influence of the temperature on the urea-formaldehyde forward reaction rates is mainly due to changes in the equilibrium between hydrated and dehydrated formaldehyde (D); this assumption is also verified by comparisons between the activation energies referred to in this paper. Thus, the formation of an active state of urea would not be connected with any considerable change in energy.

Since our present knowledge of the state of urea in water solutions is highly limited, it is difficult to give any statement regarding the activated form of urea. However, it seems to be probable that urea tautomers exist, and that they may represent a considerable fraction of the total amount (I). Further, a zwitter ion structure of a tautomer is not improbable (II).

It has previously been assumed³ that the urea structures

would be of importance for the urea-formaldehyde reactions. (The anion assumed to be necessary for the reactions would be obtained mainly through

ionization to $\text{HN} = \overset{\text{OH}}{\underset{|}{\text{C}}} - \bar{\text{N}}\text{H}$. The low probability of the formation of such an ion prior to the reaction with formaldehyde as a part of the reaction mechanism has been discussed above.)

The structures shown above may be in agreement with the requirements which follow from the experimental results regarding the state of urea previously mentioned in this paper. Further, a nitrogen atom is activated as a nucleophilic center.

In the polymerisation reactions of formaldehyde, a zwitter ion was assumed to be of importance (V), and the structure of the zwitter ion would be:

This structure may simply be regarded as a symbol for a resonance state of the dehydrated formaldehyde molecule, where the carbon atom is activated as an electrophilic center. With reference to the previous discussions regarding the formaldehyde polymers, and if we assume that the formaldehyde zwitter ion is in an activated state for both the hydration—dehydration reaction and for the reactions with urea or monomethylol urea, we get, *e.g.*, the following example of a possible reaction mechanism:

The proton exchange may be catalysed by proton donors and proton acceptors, *i.e.* buffer substances, and may represent the rate determining steps of the reactions.

A similar reaction scheme can also be applied to the monomethylol urea—formaldehyde system.

It will here be stressed that this scheme ought to be regarded as an example of a *possible* and not of a highly probable reaction mechanism description. Our present knowledge does not allow any conclusive statements.

THE HYDROLYSIS REACTIONS

A hydrolysis reaction mechanism previously assumed (E) may be within the scope of the scheme given above.

The shape of the rate constant— C_{OH^-} curve was shown to be in favour of the assumption that the anion of the methylol compound can be regarded as the activated complex for the hydrolysis reaction ⁶.

However, it is interesting to note that an assumption that the ionic form does *not* react, *i.e.* solely the -OH compound would be reactive and subject to a hydroxyl ion catalysis, is "verified" by the same experimental results.

This is found from the following:

$$\frac{C_{R \cdot CH_2O^-}}{C_{R \cdot CH_2OH} \cdot C_{OH^-}} = K$$

$$C_{R \cdot CH_2OH} + C_{R \cdot CH_2O^-} = C_{total}$$

and

$$\frac{C_{total}}{C_{R \cdot CH_2OH}} - 1 = K \cdot C_{OH^-}$$

If only $R \cdot CH_2OH$ reacts and under the influence of hydroxyl ion catalysis, this means that the actual hydrolysis rate constant k is related to a rate constant k_0 at the same hydroxyl ion concentration and extrapolated from the slope of the $k = f(C_{OH^-})$ curve at $C_{OH^-} = 0$ as follows:

$$\frac{k_0}{k} = \frac{C_{total}}{C_{R \cdot CH_2OH}}$$

($C_{total} \ll C_{NaOH}$ in the experiments, thus $C_{OH^-} \sim C_{NaOH}$)
and thus:

$$K = \frac{1}{C_{OH^-}} \cdot \left(\frac{k_0}{k} - 1 \right)$$

If we apply this expression to the figures taken from the experimental curves ⁴ related to monomethylol urea, MU, and also include the data for methylol benzamine, MB, methylol propioamide, MP and methylol chloroacetamide, MCh, we get the following K values:

C_{OH^-}	K_{MU}	K_{MB}	K_{MP}	K_{MCh}
0.2	1.7	6.9	5.6	16.0
0.3	2.0	6.7	5.7	15.3
0.4	2.1	6.8	6.0	15.1
0.6	2.1	7.0	6.0	14.6
1.0	2.1	7.1	6.2	14.7

When regarding the experimental accuracy to be expected, these results mean that no distinction between the two opposite reaction mechanism theories can be made.

However, the assumption (E) seems not to be unreasonable, even when there is a lack of significance in the experiments referred above. The initial stage of the hydrolysis reaction would, *e.g.*, be an ionization of the -OH group, followed by a proton transfer in accordance with the scheme above.

Table 4. The k_0 and a ratio between formation and hydrolysis reactions of the urea-formaldehyde system. k_0 and a formation, k_0' and a' hydrolysis. Temperature 20 °C.

Buffer	pH	Monomethylol urea		Dimethylol urea	
		k_0/k_0'	a/a'	k_0/k_0'	a/a'
KH ₂ PO ₄	6.70	38	25	8.2	6.9
Borax	9.20	29	25	8.3	8.3
Na ₂ CO ₃	10.00	32	24	11.3	9.7

It may be of some interest to compare the formation—hydrolysis k_0 and a ratios, respectively, at different buffer solution compositions calculated from the figures of Table 3. These ratios can be found in Table 4. As seen, the ratios of the urea or monomethylol urea and formaldehyde reaction systems are of the same order, and as regards the urea—formaldehyde reaction the a ratios are practically constant. This may be in favour of an assumption that the buffer catalysis mechanism of both the formation and the hydrolysis are identical. However, the variations in the other ratios do not exclude such an identity even in these cases; the ionization state of the reactants may influence the activities of the different buffer ions in different ways when these ions are approaching in order to promote a proton transfer.

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