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

I. Experimental Studies of the Rates of the Equimolecular Reaction

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Some methods for formaldehyde determinations in urea-formaldehyde reaction solutions are examined. A number of effects which have to be considered when applying polarography to this subject are analysed and a suitable supporting electrolyte composition given.

The results of reaction rate studies at 20° C of the equimolecular reaction between urea and formaldehyde at comparatively high concentrations of the reactants are given. From these studies it is found that at a urea-formaldehyde ratio of 1:1 no theoretically significant reaction order is present. The previously reported rapid initial reaction was not observed. In buffered solutions, as in unbuffered, the reaction order was approximately 1.6. In buffered solutions a reaction of second order is present if an excess of urea is used. From such reaction studies rate constants can be calculated. The reaction was found to be subject to acid-base catalysis, and different catalysts show different catalysing power. A linear relationship was found between the rate constants and the amounts of catalyst present. The hydroxyl ion catalysis is not found to be a simple function of the hydroxyl ion activity.

The rates of the reaction

were previously studied by Smythe, Crowe and Lynch, Bettelheim and Cedvall and De'Jong.

By means of a hydroxylamine titration method Smythe¹ investigated the rate of the equimolecular urea-formaldehyde reaction in concentrated, unbuffered solutions at a pH of about 7 and at different temperatures. The reaction product was found to be monomethylol urea, and no dimethylol urea was present in sufficient quantity to be detected. The reaction was of the bimolecular type, except for a rapid initial stage. An activation energy of 14.6 kcal/mole was obtained. Later on, Smythe² took a special interest in the

initial rapid reaction. It was found that influence of urea hydrolysis products could not explain this reaction, and repeated experiments, also here made by means of the hydroxylamine method, were in agreement with his earlier observations. In the temperature range 20–40° C the initial reaction during the first 300 seconds included 36–46 % of the complete condensation reaction. The mechanism of the rapid reaction was also discussed by Smythe ³, and in the same work the effect of small amounts of some compounds present in the reaction solution was also studied. (Na_2HPO_4 , $\text{H}_3\text{C}-\text{COONa}$, $\text{H}_2\text{N}-\text{CH}_2-\text{COONa}$, $\text{Na}_2\text{B}_4\text{O}_7$, CH_3OH and hydroquinone.) Smythe found that the highest rate was obtained in 1:300 Na_2HPO_4 . In this investigation, as in the previous, a change in pH during the initial reaction was observed. Finally, Smythe ⁴ studied the urea-formaldehyde reaction in dilute solutions by means of polarography. In this case no rapid initial reaction could be found. Similar studies of dilute solutions, also made by means of polarography, are due to Crowe and Lynch ^{5,6}, and the experiments included buffered, alkaline solutions. (0.1 M NaHCO_3 , pH 8.7; 0.05 M H_3BO_3 + 0.05 M LiCl + 0.045 M LiOH , pH 10.1; 0.1 M Na_2CO_3 , pH 11.2; 0.05 M LiOH , pH 12.7.) The reaction was found to be of second order, and the rate was increasing with pH and temperature. An activation energy of 15.9 kcal/mole was calculated.

Bettelheim and Cedvall ⁷ investigated the urea-formaldehyde reaction in unbuffered, concentrated solutions at 40° C in the neutral and alkaline range. The change in formaldehyde concentration of the reaction mixture was determined by means of a sodium sulfite titration method (Lemme-Doby). Also in this case a bimolecular reaction was found, but the initial reaction was more moderate, only including about 15 % of the complete reaction.

Finally, De'Jong ⁸ checked the initial rapid reaction in solutions prepared from repeatedly crystallised urea, and in this investigation no reaction of such a kind could be found. However, in the experiments an excess of urea was used. The previously observed initial reaction was assumed to be due to ammonia impurities, and these impurities would react with the formaldehyde rapidly. De'Jong did not mention what formaldehyde analysing method he used.

The purpose of the following paper is to examine the methods for formaldehyde determination in urea-formaldehyde reaction mixtures and to describe experimental studies at 20° C with special regard to the reaction order and the influence of pH and buffer substances.

DETERMINATION OF FORMALDEHYDE IN UREA-FORMALDEHYDE REACTION SOLUTIONS

The use of *polarography* for determination of formaldehyde in urea-formaldehyde reaction solutions was primarily introduced by Crowe and Lynch ^{5,6}. From formaldehyde limiting current measurements in solutions containing the same amount of buffer substances and of the same pH as the reaction mixtures, the formaldehyde was determined directly in these mixtures. Smythe ⁴ used a somewhat different method: Samples from the reaction solutions were analysed on formaldehyde polarographically at 25° C; the supporting electrolyte was 0.095 M Na_2HPO_4 + 0.022 M KH_2PO_4 , pH 7.15. Calibration curves gave a linear relationship between limiting current and formaldehyde concentration, except for small deviations at low formaldehyde concentrations. These deviations are probably due to difficulties when evaluating the polarograms; this seems to be probable since Na^+ and K^+ are the cations of the supporting electrolyte and the waves of these ions interfere with the formaldehyde wave. The evaluation difficulties are also increased because the formaldehyde current-voltage curve shows a maximum at high concentrations (Smythe ⁴, p. 575, Fig. 2). Smythe mentions that methylol urea acts as a maximum suppressor,

Fig. 1. Formaldehyde polarograms of a urea-formaldehyde reaction solution, $C_{Na^+} = 0.2$; obtained by means of Smythe's method (A) and the method described in this paper (B).

Fig. 2. The maximum suppression effect of gelatin at different formaldehyde concentrations: 0.150 (○), 0.100 (●), 0.060 (+), 0.025 (×) and 0.010 (■) at 25° C. Supporting electrolyte: 0.10 M Li_2CO_3 , pH 9.50.

but this effect is of course not present at the beginning of the urea-formaldehyde reaction. Within the limits of the experimental conditions used by Smythe, the method seems to be applicable. However, the determination becomes more complicated if the reaction mixtures contain a considerable amount of Na^+ due to buffer substances present. When the sodium and formaldehyde waves interfere, the accuracy is often low. An example is given in Fig. 1, polarogram A, representing a 15 % urea-formaldehyde reaction mixture, the molar ratio of urea to formaldehyde is 1:1.5 and 6 % formaldehyde is still unreacted. The Na^+ concentration is 0.2 M, and the polarogram was recorded at 25° C with a supporting electrolyte according to Smythe and by means of a LKB type 3 266 polarograph. The dilution ratio was 1:20. Air oxygen was present and no maximum suppressor used. The drop time of the mercury electrode was 3.5 sec. From the diagram it is found that we have reasons to look for a supporting electrolyte which is more generally applicable.

Since the cation of the supporting electrolyte ought to have as negative half wave potential as possible, in order to reduce the interference, $(CH_3)_4N^+$ would be suitable. However, this ion might cause some uncontrolled reactions in solutions containing methylol urea and formaldehyde, and therefore it might be better to use Li^+ . The half wave potential of Li^+ is more negative than that of Na^+ , the difference being 0.16 V, and this would decrease the difficulties mentioned above, especially if a suitable pH of the supporting electrolyte is chosen. As shown by Bieber and Trümpler⁹, the half wave

potential of formaldehyde is dependent on pH; increasing pH gives a more negative half wave potential. This effect, which is undesirable from the point of view of interference, is compensated by the increasing rate of methylene glycol dehydration, *i. e.* the ratio between limiting current and formaldehyde concentration increases with increasing pH; Bieber and Trümpler⁹. A number of preliminary experiments carried out by the present author, gave the result that the higher the pH, the easier the evaluation of the polarograms.

Methylol urea is hydrolysed in alkaline solutions, which was shown by Crowe and Lynch⁵, and this effect has to be regarded. The results of another set of preliminary experiments made by the present author were that the rate of hydrolysis is dependent on:

1. pH; the rate of hydrolysis increasing with increasing pH.
2. Temperature; the rate of hydrolysis increasing with increasing temperature.
3. Dilution of the reaction mixture with supporting electrolyte; the rate of hydrolysis increasing with increasing dilution.

(Some of these results were previously known from Crowe and Lynch⁵)

Of course, the reaction between urea and formaldehyde can also continue in the polarographic solution, and further preliminary experiments gave the results that the rate of this reaction is dependent on 1 and 2 in the same way as the hydrolysis. The opposite effect is present in the case 3, decreasing reaction rates were found when the dilution was increased.

The influence of the buffer concentration of the supporting electrolyte on the reactions mentioned above was not studied, because the concentration is limited by the solubility of the Li⁺ salts, and because a concentration close to this limit has to be used. This is necessary since otherwise the hydroxyl ions produced at the electrode surface during the reduction of formaldehyde

will change the acid-base catalysis of the electrode reaction, *i. e.* will reduce the linear interval of the current concentration curve, as can be concluded from Landqvist¹⁰. (For further informations concerning the theory of formaldehyde polarography, reference is given to that paper.)

When considering the interference, the hydrolysis and the continuing reaction mentioned above, 0.1 M Li₂CO₃, pH 9.5 might be a suitable supporting electrolyte. The solubility of Li₂CO₃ does not permit a higher concentration than 0.1 M, and no other suitable buffer substance for the pH range in question could be found. The *pK'* of the carbonate at the ionic strength here present is of the order 9.8, and this means that a slight influence of hydroxyl ions at moderate and high limiting currents may be expected.

As regards the temperature of the polarographic solutions, an increased temperature is likely to cause an increased limiting current-formaldehyde concentration ratio, *i. e.* gives a favourable effect. However, at the same time the increased rate of the reactions previously mentioned is unfavourable. Because the temperature coefficient of the limiting current is high (Crowe and Lynch⁶, Fig. 1), it is necessary to maintain a good temperature constancy. From the point of view of thermostating a temperature a little above the room temperature is useful, *i. e.* 25°C is in most cases to be preferred.

As mentioned before, the polarographic current-voltage curve of formaldehyde shows a maximum. In very dilute solutions this effect is not present, but increasing concentration will cause more pronounced maxima. Some preliminary experiments made by the present author gave the information that maxima are pH-dependent, at pH 6.9 and 25° C no maxima were present when $C_{(\text{HCHO})_a}$, *i. e.* the analytical formaldehyde concentration, was below 0.05 M. However, at pH 9.50 and the same concentration and temperature, this effect cannot be neglected. The increased tendency to maxima could be regarded as a function of the magnitude of the limiting current, but in still more alkaline solutions the effect decreases. In 0.05 M LiOH, for instance, no maxima can be found at the concentration and temperature mentioned above.

Since from other points of view a supporting electrolyte pH of 9.5 is desirable, we need to reduce the tendency to form maxima, *i. e.* to find a maximum suppressor. The only one of the generally known suppressors which gives a sufficient effect even at low concentrations of the substance, seems to be gelatin. Unfortunately gelatin is not a chemically defined product, and it is probably wise to be careful when changing from one gelatin to another. When expecting a large "consumption" of the substance, *e. g.* for a research project or for industrial control purposes, a comparatively large amount can be kept in stock, so that the same product is available for the whole investigation. The gelatin is preferably dried and grinded dry. After grinding the gelatin is thoroughly mixed. Before using a batch it might be tested to find the appropriate concentration at the highest amounts of formaldehyde expected.

In the following an investigation is described the purpose of which was to study the relationship between maximum suppression and formaldehyde and gelatin concentrations. The experiments were made in an open cell, *i. e.* dissolved oxygen was present, and at 25° C. The drop time of the mercury electrode was 3.4 sec. and the mercury flow 1.57 mg/sec. The supporting electrolyte was 0.10 M Li_2CO_3 , pH 9.50. The investigation included 5 formaldehyde concentrations, covering the range 0.00–0.15 M. All chemicals were of A. R. quality, except for formaldehyde, which was a Merck product of high purity, only containing traces of methyl alcohol and formic acid.* The reference electrode was of the saturated calomel type.

In Fig. 2 the function $I_{\text{max}}/C_{(\text{HCHO})_a}$, where I_{max} = maximum current and $C_{(\text{HCHO})_a}$ = analytical formaldehyde concentration, is plotted as a function of the gelatin concentration in g/l. From this study we find the following:

1. Maxima are dependent on the formaldehyde concentration; increasing concentrations give rise to increased maxima.
2. A limiting gelatin concentration is present, *i. e.* at a concentration above this limit no maxima occur.
3. The limiting concentration is dependent on the amount of formaldehyde present, but to a comparatively low degree.

The findings 2 and 3 are in accordance with the idea that one kind of polarographic maximum suppression mechanism includes the adsorption of the maximum suppressor at the electrode surface (Heyrovsky¹¹).

* $< 2 \cdot 10^{-4}$ M at 380 g/l formaldehyde.

When gelatin is used in solutions containing formaldehyde, the possibility of reactions between these two components cannot be neglected. In order to find if a reaction occur when applying the conditions mentioned above, $I_{\max}/C_{(\text{HCHO})_a}$ was measured in the supporting electrolyte in question and at a gelatin concentration of 0.20 g/l and a formaldehyde concentration of 0.15 M. The temperature was 25° C as before. During the 60 minutes studied no time dependence could be observed, *i. e.* no gelatin-formaldehyde reaction was found. It is probably necessary to apply the same test to every new batch of gelatin, since it cannot *a priori* be postulated that the results here obtained are valid for any type of gelatin.

From Fig. 2 it is seen that the limiting concentration of gelatin is of such an order that 0.12 g/l is sufficient in the here actual concentration range.

Smythe ⁴ reports that methylol urea acts as a maximum suppressor, however, preliminary experiments made by the present author gave the result that the limiting concentration of this suppressor was comparatively high: 2—3 g/l. Such a high concentration will decrease the accuracy at low formaldehyde concentration determinations too much, since the equilibrium formaldehyde concentration of methylol urea in such a case can exceed the amount to be determined. Thus, the use of monomethylol urea as a maximum suppressor cannot be recommended.

In Fig. 1, polarogram B is obtained by means of a supporting electrolyte comprising 0.10 M Li_2CO_3 , pH 9.50, 0.12 g/l gelatin; the temperature was 25° C. The reaction mixture investigated was the same as that of curve A of the same figure. The result will clearly explain that the method is suitable also in more difficult cases.

Fig. 3 shows a calibration curve, *i. e.* the limiting current — formaldehyde concentration relationship; supporting electrolyte as above, drop time 3.4 sec. and flow of mercury 1.62 mg/sec. At high aldehyde concentrations the hydroxyl ion effect is present and the linearity lost. However, the linearity is good up to 0.06 M formaldehyde, but attention must be drawn to the fact that this concentration is not of a general significance, as it relates to the conditions of the capillary here used. This since the "diffusion layer" of hydroxyl ion neutralisation by the supporting electrolyte buffer substances and the corresponding layer of methylene glycol dehydration and formaldehyde reduction are entirely different. Thus, for each capillary the corresponding calibration curve has to be obtained experimentally. Theoretical calculations in this field seem to be very complicated.

For some of the formaldehyde concentrations in Fig. 3, four polarograms were recorded, 3, 6, 12 and 18 minutes from the moment when a 1.0 M formaldehyde stock solution and the supporting electrolyte were mixed. No influence of time could be found, *i. e.* the rate of depolymerisation of any formaldehyde polymers present was in this case sufficiently high to prevent any disturbances.

In order to investigate the role of continuing reaction and hydrolysis in the polarographic solution when the here studied supporting electrolyte is used, the following reactions were investigated by means of polarography: 4.0 M urea + 4.0 M formaldehyde, and 4.0 M urea + 8.0 M formaldehyde. The solutions were 0.1 M with respect to Na_2CO_3 and had a pH of 9.80. The

Fig. 3. A limiting current — formaldehyde concentration curve at 25° C. Supporting electrolyte: 0.10 M Li_2CO_3 + 0.12 g/l gelatin, pH 9.50.

Fig. 4. Continuing reaction and hydrolysis effects in 0.10 M Li_2CO_3 + 0.12 g/l gelatin, pH 9.50. The temperature was 25° C and the dilution 1:100. Reaction solution: 4.0 M $\text{CO}(\text{NH}_2)_2$ + 4.0 M HCHO in 0.10 M Na_2CO_3 , pH 9.80 and at 20° C. The curves are related to the following degree of reaction: 1 % (Δ), 26 % ($\square$), 33 % ($\blacksquare$), 52 % ($\times$), 78 % (+), 86 % ($\bullet$) and 94 % ($\circ$).

reaction temperature was 20° C. The polarography was carried out at 25° C and the dilution ratio was 1:100. These conditions seem to be "unfavourable" as regards the effects to be studied. The results obtained can be found in Figs. 4 and 5, where the ratio between the actual limiting current and the current extrapolated to zero time is plotted against the time from mixing the sample and the supporting electrolyte. For both reactions we find that in the beginning of the urea-formaldehyde reaction this reaction continues in the polarographic solution. However, during the later parts of the reaction, hydrolysis is the most important effect. The curves of the functions are approximately straight lines, and for accurate determinations the zero time extrapolation mentioned above can easily be applied. If the accuracy need is moderate — of the order 3 % — it is sufficient to record the polarograms within 5 minutes from mixing. It was further observed that within the limits of the linear part of the current-concentration curve, no influence of the dilution ratio (1:5—1:100) on the polarographic result was found. However, it must always be regarded that the dilution does not change the buffer concentration of the polarographic solution so much that the calibration curve becomes invalid. The effects here mentioned were also found when a supporting electrolyte in accordance with Smythe was used.

From this it is seen that the use of polarography in studies of the urea-formaldehyde reaction rates requires the consideration of a number of effects.

Fig. 5. Continuing reaction and hydrolysis effects in 0.10 M Li_2CO_3 + 0.12 g/l gelatin, pH 9.50. The temperature was 25° C and the dilution 1:100. Reaction solution: 4.0 M $\text{CO}(\text{NH}_2)_2$ + 8.0 M HCHO in 0.10 M Na_2CO_3 , pH 9.80 and at 20° C. The curves are related to the following degree of reaction: 10 % ($\square$), 39 % ($\blacksquare$), 70 % ($\times$), 82 % (+) and 86 % ($\circ$).

Fig. 6. Reaction between 3.92 M $\text{CO}(\text{NH}_2)_2$ + 3.92 M HCHO at 20° C in an unbuffered solution with the initial pH 8.0. Per cent "free" formaldehyde of the reaction solution was determined by means of: polarography ($\bullet$), the sulfite method ($\circ$) and the hydroxylamine method ($\times$).

However, when such a consideration is given, the polarographic method offers several advantages, *e. g.* reliability, speed and accuracy.

In order to examine the titration methods previously applied (Smythe, Bettelheim and Cedvall) two experiments were carried out, involving the reaction between 3.92 M $\text{CO}(\text{NH}_2)_2$ + 3.92 M HCHO and 1.96 M $\text{CO}(\text{NH}_2)_2$ + 3.92 M HCHO at 20° C in unbuffered solutions with an initial pH of 8.0. These reactions were studied by means of: a) the polarographic method described in this paper, b) the hydroxylamine titration method, and c) the sulfite titration method.

The hydroxylamine titration method was applied as follows:

2 ml of the reaction mixture were measured by a pipet into a 100 ml Erlenmeyer flask, 10 ml distilled water added, 10 drops of bromophenol blue indicator, followed by 20 ml 10 % by weight hydroxylamine hydrochloride solution. (This represents 79 % hydroxylamine hydrochloride excess at the highest formaldehyde concentration.) Exactly 30 seconds from the midpoint of the time taken for the pipet to deliver 20 ml solution, the titration of the liberated hydrochloric acid with 0.5 M NaOH begun and was completed within 1–2 minutes. The endpoint was matched against a standard. (Smythe¹.)

The sulfite method was handled in accordance with the following description:

2 ml of the reaction mixture were measured by a pipet into a 100 ml Erlenmeyer flask, 10 ml distilled water and 5 drops of thymolphthalein indicator added, followed by 25 ml 15 % by weight (anhydrous) sodium sulfite solution. (This amount of sodium sulfite

Fig. 7. Reaction between 1.96 M $\text{CO}(\text{NH}_2)_2$ + 3.92 M HCHO at 20°C in an unbuffered solution with the initial pH 8.0. Per cent "free" formaldehyde of the reaction solution was determined by means of: polarography (●), the sulfite method (○) and the hydroxylamine method (×).

Fig. 8. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 4.0 M HCHO at 20°C in: an unbuffered solution, initial pH 6.70 (×); 0.10 M KH_2PO_4 , pH 6.70 (●); 0.10 M borax, pH 9.20 (×) and 0.10 M Na_2CO_3 , pH 9.80 (○).

represents 87% excess at the highest formaldehyde concentration.) The sulfite solution was neutralised against an indicator standard (pale blue), which also was used for the titration with 0.5 M HCl. The titration begun exactly 1 minute from the midpoint of the sulfite delivery.

The results of these comparative investigations are given in Figs. 6 and 7, where the amount of "free" formaldehyde of the reaction solution is plotted against the logarithm of the reaction time in minutes, as determined by means of the different analytical methods. From the results it is found that the agreement between the polarographic and the sulfite method is good. The hydroxylamine method, however, gives different results. The values obtained were generally too low; in the beginning of the reaction a figure about 35 % below the theoretical value was obtained. The influence of the time used for completing the titration, *i. e.* the time from the start of a titration 30 seconds after mixing and to a completed titration, is elucidated by the following experiment. A reaction sample containing 4.20 % "free" formaldehyde (polarography and sulfite method) was analysed by means of the hydroxylamine method as described above, 10 ml sample used, and the titration was completed at different time delays. The results were:

Titration time min.	% «free» formaldehyde obtained
0.5	3.49
1.0	4.12
1.5	4.50
2.0	4.74

Fig. 9. The reaction in 0.05 M Li_2CO_3 , pH 9.50 at 20° C between: 4.0 M $\text{CO}(\text{NH}_2)_2$ + 4.0 M HCHO (○), 2.0 M $\text{CO}(\text{NH}_2)_2$ + 2.0 M HCHO (●), 1.0 M $\text{CO}(\text{NH}_2)_2$ + 1.0 M HCHO (×) and 0.5 M $\text{CO}(\text{NH}_2)_2$ + 0.5 M HCHO (+).

Fig. 10. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C, pH 6.70 and $C_{\text{KH}_2\text{PO}_4}$: 0.1 (○), 0.05 (●) and 0.025 (×).

From this it might be concluded that the time interval "1—2 minutes" is not defined sufficiently sharply when a high accuracy is needed.

The influence of the amount of reaction mixture sample used for the titrations can be found from the following data, obtained by analysing a reaction

Fig. 11. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C, pH 9.20 and C_{borax} : 0.1 (○), 0.05 (●) and 0.025 (×).

Fig. 12. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C, pH 10.00 and $C_{\text{Na}_2\text{CO}_3}$: 0.2 (○), 0.1 (●), 0.05 (×) and 0.025 (+).

Fig. 13. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C, pH 11.5 and CNa_2CO_3 : 0.2 (○), 0.1 (●) and 0.05 (×).

Fig. 14. The reaction between 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C and: 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$, pH 8.50 (○); 0.1 M Na_2PO_4 , pH 11.50 (●) and 0.1 M Na_2PO_4 , pH 12.40 (×).

solution containing 4.30 % "free" formaldehyde by means of the hydroxylamine method, titration time 1.5 minutes: 2 ml sample: 1.65 %, 5 ml sample: 2.97 % and 10 ml sample: 4.27 % "free" formaldehyde.

A similar experiment made by means of the sulfite method gave the results: 2 ml sample: 4.27 % and 5 ml sample: 4.33 % "free" formaldehyde. Within the practical limits of titration times no influence similar to that described for the hydroxylamine method could be found in this case.

Fig. 15. The reaction in 0.05 M Li_2CO_3 , pH 9.50 at 20° C. CHCHO = 0.10 and $\text{CCO}(\text{NH}_2)_2$: 4.0 (○), 2.0 (●), 1.0 (×) and 0.5 (+).

Fig. 16. The reaction in 0.05 M Li_2CO_3 , pH 9.50 at 20° C. $\text{CCO}(\text{NH}_2)_2$ = 4.0 and CHCHO : 0.50 (○), 0.25 (●), 0.10 (×) and 0.05 (+).

It seems to be probable that a highly standardized hydroxylamine method will give a better accuracy than that here obtained. However, in the beginning of the urea-formaldehyde reaction the method might give results which are below the real values also in such a case. From this we find that the hydroxylamine method cannot be recommended.

The sulfite method seems to be more satisfactory; however, both of the titration methods include some disadvantages: After adding the reaction sample the pH of the titration solution will change anomalously, and in some cases this will cause a continuing reaction or hydrolysis before the titration is completed. Of course, this effect can be partly reduced if a buffer substance is added to the solution, *e. g.* a formic acid buffer in the case of the hydroxylamine method and a carbonate buffer in the case of the sulfite method. (These buffers must be preneutralised and the titration stopped at the same pH as used for the preneutralisation.) A more serious disadvantage is that the methods fail when applied to reaction solutions containing buffer substances which have their buffering intervals in a pH range where the titration must be completed. A simple oxidation method, applicable to the sulfite titration method, cannot easily be found, otherwise such a method would solve the problems in question. Another possibility would be the use of ion exchange resins for removing the buffer substances; such a method, however, seems to be comparatively slow.

Thus, when considering a general applicability, the polarographic method might be preferred.

EXPERIMENTAL STUDIES OF THE EQUIMOLECULAR UREA-FORMALDEHYDE REACTION IN NEUTRAL AND ALKALINE SOLUTIONS

The experiments were carried out in a closed flask or an open beaker at 20° C. At this temperature no difference could be found between the results obtained by means of a closed or an open vessel. The reaction mixture was kept at a constant temperature as follows: The vessel was immersed into a water thermostat, kept at $25 \pm 0.1^\circ \text{C}$, and in the vessel a cooling coil was fitted. Through the coil water at 10°C was circulated by a pump. The water circulation was on-off regulated by a contact thermometer in the reaction solution, and this solution was kept in motion by a stirrer. This device gave a temperature constancy within $\pm 0.1^\circ \text{C}$.

The solutions, containing the amount of buffer substances to be used, were made up to twice the reaction concentration of urea and formaldehyde. All the chemicals were of A. R. quality, except for the formaldehyde, which was a Merck product of high purity, only containing traces of methyl alcohol and formic acid.* The pH of the solutions was then adjusted by hydrochloric acid or the hydroxide of the buffer cation; for the pH measurements the glass electrode technique was used, and at high pH values the differential method in accordance with Landqvist¹² was applied. The accuracy was ± 0.02 pH. The "buffer substances" mentioned above also included a chloride of the cation, added in such an amount that the cationic strength in all cases was the same as at the highest buffer concentration. This was made in order to keep the concentration-activity ratio for the buffer anions at different amounts of buffer as constant as possible. The reaction solutions were comparatively concentrated as regards the reactants, since such solutions are of greatest practical interest. In each experiment samples were taken from the reaction mixture at different time delays from the mixing of the reactant solutions, the pH constancy checked (no differences found) and the "free" formaldehyde content determined polarographically by means of the method previously described.

* $< 2.10^{-4} \text{ M}$ at 350 g/l formaldehyde.

One set of experiments was made with solutions containing urea and formaldehyde in the molecular ratio 1:1. In this case we have the following reaction rate equation, if we assume that monomethylol urea is the reaction product and neglect the hydrolysis reaction:

$$\frac{dx}{dt} = k (C-x)^2 \quad t = 0, x = 0$$

and

$$\frac{x}{C(C-x)} = k \cdot t \quad (1)$$

where x = monomethylol urea concentration, C = initial urea and formaldehyde concentration, k = reaction rate constant and t = time of reaction.

Another set of experiments were carried out on solutions containing an excess of urea, and in this case we have:

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

where C_U = initial urea concentration and C_F = initial formaldehyde concentration.

From this we obtain:

$$\frac{1}{C_U - C_F} \cdot \ln \frac{C_F (C_U - x)}{C_U (C_F - x)} = k \cdot t \quad (2)$$

or, when $C_F \ll C_U$:

$$\frac{1}{C_U} \cdot \ln \frac{C_F}{C_F - x} = k \cdot t \quad (2a)$$

The experimental conditions and results can be found in Figs. 8—16, and they are summarized in Table 1.

In all experiments a small volume contraction occurred, of the order 1 %, and correction has been applied for this effect.

In the unbuffered solution at pH 6.70 a small change in pH occurred during the reaction. However, the same curve was obtained when the pH was kept constant by adding NaOH.

From the second order reaction relationship found in solutions containing an excess of urea, reaction rate constants can be calculated. If we plot these constants for each buffer substance at a constant pH as functions of the buffer concentrations, we get a relationship as shown by Fig. 17. The linearity of the curves is good, i. e. the concentration-activity ratio is fairly constant, as can be expected from the constant cationic strength of the solutions. The different catalytic properties of the different buffer substances clearly appear from the diagram. If the curves of Fig. 17 are extrapolated to zero buffer concentration, the sum of the "zero reaction rate" and the hydroxyl ion catalytic contribution, k_0 , can be calculated. The relation between the logarithm of k_0 and pH is shown in Fig. 18.

Table 1. Experimental data of the equimolecular urea-formaldehyde reaction in neutral and alkaline solutions at 20° C.

Fig.	$C_{\text{CO}(\text{NH}_2)_2}$	C_{HCHO}	Buffer substance	C_{buffer}	pH	Reaction order	$k \cdot 10^3$
8	4.00	4.00	—	—	6.70 *	—	—
8	4.00	4.00	KH_2PO_4	0.100	6.70	—	—
8	4.00	4.00	borax	0.100	9.20	—	—
8	4.00	4.00	Na_2CO_3	0.100	9.80	—	—
9	4.00	4.00	Li_2CO_3	0.050	9.50	—	—
9	2.00	2.00	Li_2CO_3	0.050	9.50	—	—
9	1.00	1.00	Li_2CO_3	0.050	9.50	—	—
9	0.50	0.50	Li_2CO_3	0.050	9.50	—	—
10	4.00	0.40	KH_2PO_4	0.100	6.70	2	0.16
10	4.00	0.40	KH_2PO_4	0.050	6.70	2	0.10
10	4.00	0.40	KH_2PO_4	0.025	6.70	2	0.065
11	4.00	0.40	borax	0.100	9.20	2	0.080
11	4.00	0.40	borax	0.050	9.20	2	0.060
11	4.00	0.40	borax	0.025	9.20	2	0.052
12	4.00	0.40	Na_2CO_3	0.200	10.00	2	0.34
12	4.00	0.40	Na_2CO_3	0.100	10.00	2	0.20
12	4.00	0.40	Na_2CO_3	0.050	10.00	2	0.12
12	4.00	0.40	Na_2CO_3	0.025	10.00	2	0.10
13	4.00	0.40	Na_2CO_3	0.200	11.50	2	1.9
13	4.00	0.40	Na_2CO_3	0.100	11.50	2	1.6
13	4.00	0.40	Na_2CO_3	0.050	11.50	2	1.4
14	4.00	0.40	$\text{Na}_4\text{P}_2\text{O}_7$	0.100	8.50	2	0.13
14	4.00	0.40	Na_2PO_4	0.100	11.50	2	1.6
14	4.00	0.40	Na_2PO_4	0.100	12.40	2	7.5
15	4.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	2.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	1.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	0.50	0.10	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.50	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.25	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.05	Li_2CO_3	0.050	9.50	2	0.091

* initial pH; final pH was 6.50.

From these experiments the following conclusions might be drawn:

1. The polarographic and the sulfite method for formaldehyde determinations in urea-formaldehyde reaction solutions give similar results (Figs. 6 and 7).

2. The hydroxylamine method gives, especially in the beginning of the urea-formaldehyde reaction, too low formaldehyde concentration values (Figs. 6 and 7).

3. The accuracy of the hydroxylamine method seems to be moderate (Figs. 6 and 7).

Fig. 17. Relationship between the reaction rate constant of 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C and the buffer substance concentrations: Na_2CO_3 , pH 11.5 (○), Na_2CO_3 , pH 10.0 (●), borax, pH 9.2 (+) and KH_2PO_4 , pH 6.7 (×).

Fig. 18. Relationship between the logarithm of the reaction rate constant at zero buffer concentration and pH for the reaction 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO at 20° C.

4. When applying the polarographic method, continuing reaction and hydrolysis effects in the polarographic solution must be considered (Figs. 4 and 5).

5. In an unbuffered solution, 4.0 M $\text{CO}(\text{NH}_2)_2$ + 4.0 M HCHO, initial pH 6.70 and at 20° C, no rapid initial reaction can be found. No theoretically significant reaction order is present; the order is approximately 1.6. (A number of repeated experiments of this kind, at different concentrations of the reactants and different initial pH, and also such carried out with the pH of the reaction solution kept constant, gave the same result.) (Fig. 8).

6. In buffered solutions and a urea-formaldehyde ratio of 1:1 at 20° C no theoretically significant reaction order is present and no initial reaction observed. The reaction order is approximately 1.6 (Fig. 8).

7. At the urea-formaldehyde ratio 1:1, in buffered solutions at 20° C, no obvious concentration dependence of the reaction rate can be seen (Fig. 9).

8. In buffered solutions containing 4.0 M $\text{CO}(\text{NH}_2)_2$ + 0.4 M HCHO a second order reaction occurs (Figs. 10–14).

9. The rate of the second order reaction in solutions containing an excess of urea is not obviously dependent on this excess or the concentration of the reactants. (At a low urea-formaldehyde ratio, 5:1, small deviations from linearity are present, showing a tendency to a non-linear relationship.) (Figs. 15 and 16).

10. The urea-formaldehyde reaction at 20° C in solutions containing an excess of urea is subject to an *acid-base catalysis*. Different acid and base ions show different catalysing power. An extremely small effect is present in the

case of borate ions (Fig. 17). The same effects were observed at a urea-formaldehyde ratio of 1:1.

11. The hydroxyl ion catalytic effect is not a simple function of the activity of this ion (Fig. 18).

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