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The nature and the velocities of the reactions occurring in concentrated solutions of urea and formaldehyde may be very similar to what is found in dilute systems.

A rapid initial reaction between urea and formaldehyde, as reported in literature, was not observed and is shown to be due to the analytical methods used,

Introduction.

Smythe[1] found the reaction between urea (U) and formaldehyde (F) in four molar solutions to show a very high initial velocity. Ignoring this stage, the further decrease in F could be described by a second order reaction equation as was affirmed by Bettelheim and Cedwall[2]. At first it occurred to the present authors that, at least partially, the rapid initial reaction might be due to a contamination of urea by ammonium salts[3]. Recently, however, Smythe[1] showed that even in the absence of ammonium salts there is a rapid reaction.

According to a previous investigation[4][5], the reaction between urea and formaldehyde in dilute aqueous solution did not show a fast initial reaction stage. This led us to the present paper dealing with some experiments with more concentrated solutions.

Again the reaction was found to be "normal" from the very beginning and therefore our analytical method was compared with those used by the other investigators.

[1] L. E. Smythe, J. Phys. Colloid Chem. 51, 369 (1947); J. Am. Chem. Soc. 73, 2735 (1951).
[2] L. Bettelheim and J. Cedwall, Svensk Kem. Tid. 60, 208 (1948).
[3] J. I. de Jong, Rec. trav. chim. 69, 1566 (1950).
[4] J. I. de Jong and J. de Jonge, Rec. trav. chim. 71, 643 (1952).
[5] J. I. de Jong and J. de Jonge, Rec. trav, chim. 71, 661 (1952),

I. **The reactions between urea and formaldehyde in concentrated solution.**

The analytical methods applied are essentially the same as previously described. Free F was estimated by the iodometric sulphite method and the sum of free F and methylol groups was determined with an alkaline iodine solution.

a) *The reaction between urea and formaldehyde.*

Urea and formaldehyde were brought together in 2 and 4 molar aqueous solution at pH = 7 and the decrease in the concentration of formaldehyde with time was followed.

Two experiments are shown graphically in fig. 1. It is clearly seen that the reaction takes a normal course from the very beginning.

The reaction constants were calculated with aid of the well-known equation for a *bimolecular* reaction.

A variation in the initial concentration of U or F appeared to have no influence on the calculated reaction constant, indicating that the rate is indeed proportional to the concentration of urea and formaldehyde (bimolecular reaction). Some experiments are summarized below:

Experiments at 35° C and pH = 7, using 0.0013 moles/litre KH_2PO_4 and 0.0009 moles/litre Na_2HPO_4 as a buffer solution:

Initial concentration in moles per litre of urea and *formaldehyde*		k_1 in litre/mole second
4.0	4.0	1.13×10^{-4}
4.0	4.0	1.08×10^{-4}
4.0	2.0	1.10×10^{-4}
4.0	2.0	1.06×10^{-4}
2.0	2.0	1.07×10^{-4}
2.0	2.0	1.09×10^{-4}

Experiments at 25° C at pH = 7 with the same buffer concentration:

Initial concentration in moles per litre of urea and *formaldehyde*		k_1 in litre/mole second
2.0	2.0	0.50×10^{-4}
2.0	4.0	0.44×10^{-4}
4.0	4.0	0.49×10^{-4}

The reaction constant at 35° C and with pH = 7 in these experiments with concentrated solutions, is found to be $k_1 = 1.1 \times 10^{-4}$
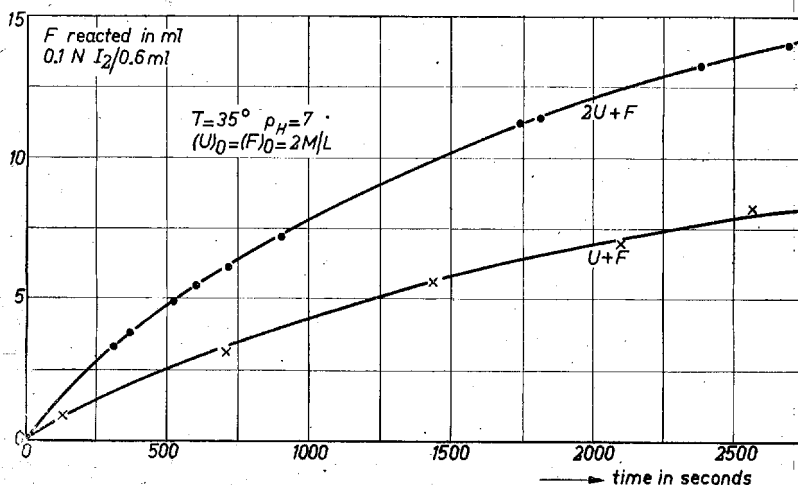
Fig. 1.

litre/moles second, while with about 0.1 molar solution, using the same buffer concentration, a value of 0.9×10^{-4} was obtained (see fig. 4 in [4]). The value for the rate constant at 25° C, obtained in concentrated solutions, viz. $k_1 = 0.5 \times 10^{-4}$, is also very close to the result $k_1 = 0.6 \times 10^{-4}$ recently found in dilute solution under similar conditions of pH and buffer concentration.

b) *The reaction between monomethylolurea and formaldehyde* was studied in a solution containing 2 moles/litre UF and 2 moles/litre F. At 35° C and pH = 7, using 0.0026 moles/litre KH_2PO_4 and 0.0018 moles/litre Na_2HPO_4, the reaction rate constant appeared to be 0.35×10^{-4} litre/moles second, while in about 0.1 molar solution a value of 0.37×10^{-4} litre/moles second was found.
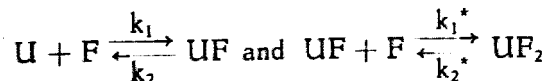
c) *The measurement of the decomposition of UF* in concentrated solution appeared to be rather difficult as the forward bimolecular reaction between U and F prevails already at a very low decomposition (see below). Though the result may not be expected to be very reliable a run was made with initial concentrations of UF of 1.28 and 2.56 moles/litre (T = 35° C, pH = 7, the solution contained 0.0013 moles/litre KH_2PO_4 and 0.0009 moles/litre Na_2HPO_4). From the initial slope of the decompositon curve (F — t plot) was found: $k_2 = 2.7 \times 10^{-6}$ sec $^{-1}$ and 2.6×10^{-6} sec^{-1}. Recently with a diluted solution and under similar conditions the value was found to be $k_2 = 2.5 \times 10^{-6}$ sec^{-1}.

d) *Reversibility.* When studying the reaction between U and F in concentrated solutions the reverse reaction may be ignored up to a considerable conversion, as the following calculation shows:

When in a solution originally containing 2 moles/litre U and 2 moles/litre F, 0.7 moles/litre UF is formed the velocity of the UF formation is roughly: $1.1 \times 10^{-4} \times 1.3 \times 1.3 \approx 2 \times 10^{-4}$ moles/litre second and the velocity of the reverse reaction is: $2.7 \times 10^{-6} \times 0.7 \approx 2 \times 10^{-6}$ moles/litre second, where 1.1×10^{-4} and 2.7×10^{-6} are the values for k_1 and k_2 respectively at 35° C, in dilute phosphate buffers at pH = 7.

Thus the decomposition velocity at 35 % conversion is only 1 % of the UF formation velocity. This explains why previous investigators did not find indications for the reversibility of the reaction in concentrated solution.

e) *Equilibria.* From the foregoing experiments it is reasonable to assume that the rate constants at 35° C and pH = 7 in dilute and concentrated solutions will have the same value. Consequently the equilibrium constants $K = k_2/k_1$ and $K^* = k_2^*/k_1^*$ for the equilibria

$$U + F \underset{k_2}{\overset{k_1}{\rightleftarrows}} UF \quad \text{and} \quad UF + F \underset{k_2^*}{\overset{k_1^*}{\rightleftarrows}} UF_2$$

as calculated from the rate constants in dilute systems, will also hold in concentrated solutions.

In that case it is possible to calculate the amount of U, F, UF and UF_2 present at equilibrium conditions in a solution with given initial concentrations of U and F. In equilibrium the following relations hold:

$$\frac{[U]_{eq}\,[F]_{eq}}{[UF]_{eq}} = K \quad \text{and} \quad \frac{[UF]_{eq}\,[F]_{eq}}{[UF_2]_{eq}} = K^*$$

with K = 0.036 moles/litre and $K^* = 0.22$ moles/litre at 35° C. The result of the calculations is as follows:

Initial concentrations of U and F in moles/litre	Calc. equilibrium conc. in moles/litre of				Conc. of F in moles/litre found exp.
	U	F	UF	UF₂	
0.4	0.12	0.06	0.22	0.06	0.060
1.0	0.26	0.08	0.56	0.18	0.080
2.0	0.49	0.09	1.11	C.40	0.085

The calculated equilibrium concentrations of free F have been checked experimentally in solutions of U and F left standing for 2—3 days, after which time the concentrations of F were constant. The agreement with the calculated values is excellent, as is shown in the table above, from which it may also be seen that a five-fold dilution of a solution containing initially 2 moles U and F per litre has only a slight influence on the equilibrium concentration of F.

In conclusion it may be said that the reactions between U and F in dilute and in concentrated solutions will be very similar at 35° C and pH = 7, and that the reaction rate constants will have nearly the same value.

Experimental details.

The reaction vessel consisted of a platinum crucible, kept in a water bath of constant temperature (within 0.1° C). Evaporation of water from the reaction mixture was negligible during the short reaction periods. The formole was previously neutralized with dilute sodium hydroxide solution.

Solutions containing U and F were adjusted to the reaction temperature chosen and then added to the reaction vessel from a burette; the platinum allowed of the temperature being well regulated.

In all experiments the temperature was 35° or 25° C and the pH was adjusted to pH = 7 using 0.0013 moles/litre KH_2PO_4 and 0.0009 moles/litre Na_2HPO_4.

The total reaction volume was 25 ml. Samples of 1 or 2 ml were taken and run into 6 ml ice water, the resulting solution then being diluted to 10.0 ml with ice water. From this solution 3 ml samples were analyzed.

Example of an experiment:

Initial concentrations of U and F: 2 moles/litre. Temperature 35° C, pH = 7. 2 ml samples were taken and diluted to exactly 10.0 ml. From the diluted solution 3 ml samples were taken for analysis on formaldehyde using the method previously described [4]. The results are collected in the next table.

time in seconds	ml. 0.1 N I_2	consumed F in moles/litre	k_1 in litre/mole sec
0	24.00	0	
720	20.85	0.26	1.05×10^{-4}
1440	18.25	0.48	1.09×10^{-4}
1980	16.90	0.59	1.06×10^{-4}
2460	15.68	0.68	1.08×10^{-4}
2880	19.85	0.76	1.07×10^{-4}

The concentration of F at zero time was known from the amount of formaldehyde added to the reaction mixture. Moreover F was estimated in the reaction mixture by analyzing, according to the alkaline-iodine method, a sample a short time after mixing. Even if some methylolurea should already be formed this method would still give an accurate result since with this method both free formaldehyde and methylol groups are determined. The difference between the added amount and estimated amount of formaldehyde in the reaction mixture never exceeded 1 %.

In the experiment mentioned above 40.10 ml 0.0996 N I_2 was added to a 3 ml sample. After reaction the amount of I_2 not consumed appeared to be equivalent to 16.15 ml 0.0993 ml thiosulphate. Consequently the sample had consumed 24.0 ml 0.0996 N I_2; calculated from the added amount of formaldehyde 24.0 ml 0.0996 N I_2.

II. Comparison of analytical methods for the urea-formaldehyde solutions.

As the high initial reaction rate between urea and formaldehyde

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as reported in literature[1][4] was not found in the foregoing investigation the present authors were led to suppose that the method of analysis might be the cause of the differences in the results.

This was indeed found to be the case. The hydroxylamine method as used by *Smythe*[1] the acidimetric sulphite method of *Bettelheim* and *Cedwall*[2] and the iodometric sulphite method as used by the present authors were applied simultaneously in the same run (the directions given by the various authors were followed as closely as possible).

Initial concentration of urea and formaldehyde 4 moles/litre; temperature 30° C, pH = 7. The reaction mixture contained 0.0013 moles/litre K_2HPO_4 and 0.0009 moles/litre Na_2HPO_4.

1 ml samples were analyzed. The results are given below:

time in seconds	concentration of free F in moles litre using the method of S. B. and C.		de J. and de J.	reaction rate constant k in litre/mole sec.
0	4.0	4.0	4.0	0.7×10^{-4}
300	2.43	3.00	3.70	0.7×10^{-4}
720	2.05	2.86	3.30	0.7×10^{-4}
1620	1.76	2.36	2.75	0.7×10^{-4}

It may be seen that the hydroxylamine method and the acidimetric sulphite method indeed suggest a rapid initial reaction with a consumption of about 40 % and 25 % respectively, of the initial amount of F, within the first five minutes. The iodometric sulphite method appears to lead to a normal bimolecular reaction from the very beginning.

As all these methods are known to give reliable results in the determination of F in aqueous solution the reason for the differences in the results must originate from the proporties of the U–F system investigated.

From previous studies of the U–F system[4][5] it may be taken that the velocities of formation and dissociation of UF and UF_2 are subject to catalysis by hydrogen and by hydroxyl ions. Fig. 2 gives the influence of pH on the rate constant of the reaction between U and F at 35° C, clearly illustrating that at a pH higher than 9 and lower than 4, the reaction becomes very rapid[4]. It follows that during the analytical procedure a high alkalinity or acidity must be avoided in order to exclude the possibility that *during the analysis* of a sample of F the amount of free F will decrease or increase owing to formation or dissociation of UF. It was found that the iodometric
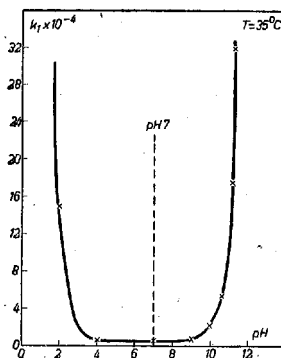
Fig. 2.

sulphite method as applied by the present authors gave good results for F in the presence of U or UF (see below).

Following the acidimetric sulphite method to determine formaldehyde an excess of sulphite is added to the sample and after one minute the alkali liberated is titrated with HCl. A rough calculation (see below) shows that the high alkalinity during one minute may result in a considerable decrease in free F due to reaction with U. (The reason that *Bettelheim* and *Cedwall* obtained rather reproducible results may be due to a careful standardisaton of the procedure.)

A similar complicaton is encountered when using the hydroxylamine method. During the analysis the solution becomes strongly acid through HCl liberated from $NH_2OH . HCl$ by reaction with F. This acidity appears to be sufficient to explain the disappearance of a considerable portion of free F during the analysis.

Some more details as to the analytical methods and the calculations are given below.

Comparison of the analytical methods.

a. The iodometric sulphite method.

A 1 ml or 2 ml sample from the reaction vessel is diluted to 10 ml with ice water. 3 ml of the diluted solution, containing about 1.2 mmoles F, is made alkaline with a few drops of 1 M Na_2CO_3 (pH = 10, blue colour of thymolphthalein) and then mixed with 2—3 ml sulphite and 5—10 ice water: Indicator: three drops of a 0.1 % alcoholic thymolphthalein solution. *Immediately* the resulting deep blue colour is reduced to a faint blue with 0.5 N HCl (pH 8.5). After being left for 7 minutes the solution is acidified to about pH = 4 with 5 ml molar AcOH and the excess of sulphite is exactly removed with iodine solution using starch as an indicator. The formaldehyde bisulphite addition compound is decomposed with about 25 ml $2 N . Na_2CO_3$ (pH 9—10) and the liberated sulphite is titrated with 0.1 N I_2 till the blue colour of starch is persistent. Only the normality of the iodine solution has to be known. When during the 7 minutes waiting the faint blue colour intensifies again (through the formation of alkali) the pH has to be readjusted with HCl.

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The critical point in this analysis is the moment when the solution becomes strongly alkaline through the formation of alkali by the reaction between F and sulphite:

$$CH_2O + Na_2SO_3 + H_2O \rightleftharpoons CH_2OH . SO_3Na + NaOH.$$
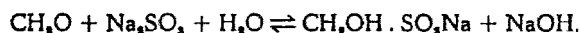
In strongly alkaline solution the UF formaton (k_1) and decomposition (k_2) become rapid, as is clear from the following equations[4]) holding at 35° C:

$$k_1 = 0.56 \times 10^{-4} + 0.14\ [H^+] + 1.7\ [OH']\ \text{and}\ k_2 = 0.036\ k_1.$$

However, by analyzing free F only in diluted samples and immediately removing excess alkali, an accurate determination of F in the presence of U and UF appears to be possible, as is shown by the following experiments.

1. Determination of F in the presence of U:

a) 28 mmoles F and 83 mmoles U were mixed at pH = 7 in 500 ml water at 25° C. A 20 ml sample containing about 1.1 mmoles F was taken two minutes after mixing.

The sample consumed 21.34 ml 0.1044 N I_2. Calculated: 21.4 ml.
Checked with an alkaline iodine solution: 21.40 ml 0.1044 N I_2.

b) 20 mmoles U and 2.26 mmoles F and 5 ml molair sulphite were mixed with 20 ml ice water and immediately neutralized on thymolphthalein with HCl, and so on.

Found: 45.33 ml 0.0996 N I_2.
Calculated and experimentally checked, using an alkaline iodine solution: 45.37 ml 0.0996 N I_2.

However, when waiting five minutes before neutralisation we found: 43.40 ml 0.0996 N I_2! This clearly indicates the critical point of the method.

2) Determination of F in the presence of UF:

1 mmol UF, 1.13 mmoles F, 1 mmole U and 3 ml molair sulphite were dissolved in 10 ml ice water and analysed for free F.

Found: 22.50 ml 0.1000 N I_2.
Calc.: 22.60 ml 0.1000 N I_2.

b. The acidimetric sulphite method.

An excess of sulphite solution is added, to the sample to be analyzed (containing U, F and UF). After one minute the alkali liberated is titrated with HCl.

The alkali liberated, when adding sulphite, increases the reaction velocity between U and F enormously, as is shown by the following rough calculation:

To 1 ml solution, originally containing 4 m moles U and 4 mmoles F, 8 ml molair sulphite is added. In the resulting solution the U and F concentrations are about 0.4 molar. When half of the F has reacted with sulphite the OH^- concentration has risen to 0.2 N. At that moment k_1 (at 35° C) becomes: 1.7×0.2 litre/moles sec. At room temperature (20° C) k_1 will be roughly 0.7×0.2.

Consequently per second $0.7 \times 0.2 \times 0.2 \times 0.4 = 0.01$ moles/litre F will be converted into UF! This explains the deviating results obtained by this method.

c. The hydroxylamine method.

During this analysis the solution becomes strongly acid through HCl liberated by F from $NH_2OH . HCl$. This acidity is sufficient to explain the disappearance of a considerable portion of the free F through reaction with U during the analysis, as is shown by the following experiment.

To 23 mmoles U dissolved in 20 ml 10% $NH_2OH . HCl$ solution, 23 mmoles F

(2 ml) were added. After 30 seconds the solution was titrated rapidly (in 1—2 minutes) with 1.23 N NaOH, using bromo-phenol blue as an indicator till the colour of the solution became purple. For a set of titrations the results were: 11.7, 11.9, 11.2 and 11.7 ml NaOH. Calculated 18.7 ml NaOH.

The latter value was found experimentally for a solution of F *without* U titrated with NaOH 20 minutes after the addition of $NH_2OH.HCl$. When the solution was titrated 30 seconds after the addition of $NH_2OH.HCl$ the values were 3 % too low.

Consequently the presence of urea leads to erroneous results when applying the hydroxylamine method for the determination of formaldehyde. In that case the reproducibility is rather bad too.

The following rough calculation illustrates how the method is influenced by the high acidity and high concentrations: When half of the F has reacted with $NH_2OH.HCl$ in the experiment just given the H^+-ion concentration has increased to 0.5 N. At 35° k_1 can be calculated to be $0.14 \times 0.5 = 0.07$ litre/moles second. At 20° k_1 will be about 0.03 litre/moles second.

The result will be that then per second $0.03 \times 1 \times 0.5 = 0.015$ moles/litre F will be converted into UF.

It will be clear that this velocity is sufficient to make the reaction between U and F fast enough to compete successfully with the analogous reaction between F and NH_2OH. Moreover, in strongly acid solutions the latter reaction is retarded.

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