# A KINETIC STUDY OF THE UREA-FORMALDEHYDE REACTION

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## INTRODUCTION

The purpose of this investigation was to obtain kinetic data for the reaction between urea and formaldehyde in aqueous solution within defined conditions of hydrogen-ion concentration. An investigation of the initial reaction between equimolecular proportions of urea and formaldehyde was the primary object, subsequent polymerization being neglected.

It was early recognized (3, 4, 6, 9) that the resultant products and course of the urea-formaldehyde reaction depend on: (*a*) the hydrogen-ion concentration, (*b*) the relative proportions of reactants, (*c*) the temperature, (*d*) catalysts, if present. These criteria are critical and are responsible for the diversity of products obtained by the various investigators.

Most of the information concerning this reaction is of a qualitative nature, only a small proportion of the published data relating to physicochemical and quantitative aspects.

Walter and Gewing (10) have made an analytical study of the water and formaldehyde lost during the condensation process, and work by Dixon (2), de Chesne (1), Redfarn (8), and others has been concerned with the polymerization of the initial dimethylol- and monomethylolureas formed. The preliminary formation and rate of formation of these substituted ureas is therefore of importance with regard to subsequent polymerization and the course of the reaction.

To avoid unnecessary complications, aqueous formaldehyde solutions adjusted to pH 7.0 ± 0.05 and aqueous urea solutions (pH 8.66) were used. By employing equimolecular proportions of the reactants in aqueous solution, the reaction may be followed by estimating the decrease in concentration of formaldehyde with time. In addition, samples were taken during each reaction and the products were identified.

Owing to the critical nature of the reaction, buffering of the reaction solution was not employed, lest the buffer have some catalytic effect on the reaction. It was hoped that changes in pH during the course of the reaction might possibly be correlated with the reaction mechanism. For this reason strict control of the pH was employed and all changes were noted during each reaction.

## MATERIALS AND EXPERIMENTAL DETAILS

(*1*) *Urea:* An 8 *M* aqueous solution (480.48 g. per liter) prepared from recrystallised B.P. quality urea was used. It was checked for urea content and tested for impurities (e.g., heavy metals). The pH was 8.66.

(*2*) *Formaldehyde solution:* This was prepared by distilling paraformaldehyde with 3 *N* sulfuric acid. The aqueous distillate was diluted to the required strength with distilled water and tested for possible sulfate contamination. The acidity of the solution was determined as follows: A 100-ml. sample of the formaldehyde solution was run into a 500-ml. Erlenmeyer flask, 10 ml. of $N/2$ sodium hydroxide was added, and the excess sodium hydroxide was then back-titrated with $N/2$ sulfuric acid, using methyl red as the indicator. Then:

$$\frac{10(\text{base titer} \times \text{normality } H_2SO_4)}{\text{normality NaOH}} = \text{ml. N/2 NaOH used}$$

$$1 \text{ ml. } N/2 \text{ NaOH} \equiv 0.02302 \text{ g. HCOOH}$$

$$\therefore \text{ per cent } CH_2O \text{ by volume (g./100 ml.)} = \text{ml. } N/2 \text{ NaOH used} \times 0.02302$$

This determination of acidity (usually 0.01–0.03 per cent by volume) was necessary for adjustment of the formaldehyde solution to pH 7.0 ± 0.05. The calculated volume of $N/2$ sodium hydroxide solution was added before the formaldehyde content of the solution was determined. Final adjustments gave a formaldehyde content of 24.024 per cent by volume (8 $M$ solution) of pH 7.0 ± 0.05.

(*3*) *Estimation of formaldehyde content of solution:* The formaldehyde content of such a solution was estimated as follows: 1 ml. of the solution was run into a 100-ml. Erlenmeyer flask and approximately 10 ml. of distilled water was added. Three drops of bromophenol blue indicator were then added, followed by 10 ml. of a 10 per cent by weight aqueous hydroxylamine hydrochloride solution. The flask was then rotated to mix the contents well and allowed to stand for 20 min. The free hydrochloric acid was then estimated by titration with $N/2$ sodium hydroxide solution, the end point (purple) being determined with the aid of a standard color. The percentage by volume of formaldehyde is given by the expression:

$$\frac{3.0 \times \text{ml. titrant} \times \text{normality NaOH}}{\text{ml. of sample used}}$$

(*4*) *Estimation of free formaldehyde during the course of the reaction:* Samples of the reaction mixture were taken at intervals with the aid of a vacuum sampler and immediately cooled to 20°C. by immersion in ice water. This was carried out quickly in order to check the reaction. The requisite sample (usually 5 ml.) was then measured by a pipet into a 100-ml. Erlenmeyer flask, 10 ml. of water added, and three drops of bromophenol blue indicator, followed by 10 ml. of 10 per cent by weight hydroxylamine hydrochloride solution. From the time of adding the latter solution to the time of commencement of titration must be 30 sec., the flask being gently shaken during that time. The titration of the free hydrochloric acid with $N/2$ sodium hydroxide was immediately commenced at the end of this 30-sec. period and completed in 1–2 min. The 30-sec. period is timed from the mid point of the time taken for the pipet to deliver 10 ml. The end point (purple) was matched against a standard. The above procedure must be strictly followed, otherwise the estimation will be inaccurate, for reasons to be described. It was found that:

$$x \text{ ml. } N/2 \text{ NaOH} + 4 \text{ per cent of } x = \text{ml. } N/2 \text{ NaOH (titrant)}$$
$$\text{(to be used in the calculation below)}$$

$$\text{Per cent free } CH_2O \text{ by volume} = \frac{\text{ml. titrant} \times \text{normality NaOH} \times 3}{\text{ml. of sample used}}$$

The above method was devised after difficulty in reproducing results. Reaction samples were affected by the hydrochloric acid liberated in the reaction between hydroxylamine hydrochloride and formaldehyde. The actual figure obtained for the titrant varied very greatly, depending upon how long the sample was allowed to stand after adding the hydroxylamine hydrochloride, and before the titration was commenced. Numerous experiments were carried out concerning this variance in results; the findings are summarized in the next section.

(*5*) *Experiments relating to the method for the estimation of free formaldehyde:* Figure 1 illustrates the general findings of experiments concerning the estimation of formaldehyde (free) in: (*a*) pure formaldehyde solutions; (*b*) the urea-formaldehyde reaction mixtures; (*c*) pure formaldehyde solution containing some monomethylolurea.

Curve a: The per cent of formaldehyde by volume is plotted against the time in minutes the sample was allowed to stand before titrating and after mixing with the hydroxylamine hydrochloride solution. This curve was found to be characteristic. In this particular experiment the room temperature was 19.1°C., the strength of the pure formaldehyde solution 21.7 per cent $CH_2O$ by volume (checked by two methods), and the sample taken was 1 ml.

Curve b shows the variation in figures obtained when a 5-ml. sample of a urea-formaldehyde reaction mixture is allowed to react at varying times with the hydroxylamine hydrochloride solution. It will be seen that curve b does not flatten out as in the case of curve a. Also, the percentage of formaldehyde found varies greatly with time. The actual percentage of free formaldehyde by the method in (*4*) above is taken to be 1.08. In the experiment on which curve b is based, 1 mole of formaldehyde and 1 mole of urea, each as 12 per cent by volume concentration in the mixture, were allowed to stand for 12 hr. to allow the reaction product to be formed. The estimation was then commenced with nine 5-ml. samples. Repeat experiments showed the curve to be characteristic.

Curve c shows the variation in the estimation of the "free" formaldehyde content of a solution of pure formaldehyde containing some added monomethylolurea. Uncombined formaldehyde was 21.5 per cent by volume of the mixture, combined formaldehyde 3.9 per cent by volume of the mixture, and total formaldehyde 25.4 per cent by volume of the mixture. This curve also was characteristic of repeat experiments performed with formaldehyde solution and added monomethylolurea.

A consideration of the experiments and curves a, b, and c showed: (*1*) the method in (*4*) can be used for the estimation of free formaldehyde in urea-formaldehyde reaction mixtures. (*2*) The accuracy of the estimation, when the technique has been mastered, is the best attained to date. (*3*) The method is not recommended when the percentage of formaldehyde is less than 1.

(*6*) *Apparatus and working details:* The reaction was studied at 10°C. intervals from 30° to 60 C. A glass electrode pH meter was used for pH determinations, and the accuracy of the determinations was ±0.05 pH. The reactions were carried out in a 1-liter three-necked flask and maintained at the required temperature ±0.1°C. by an electric immersion heater in an oil bath and governed by a toluene regulator. The bath consisted of light paraffin, and efficient stirring for the bath and reaction vessel was provided by an electric motor driving glass stirrers. A standard mercury-in-glass solid-stem thermometer was used, and the necessary corrections were applied. The reaction vessel was fitted with stirrer, thermometer, vacuum sampler, cooling or heating coil, and condenser.

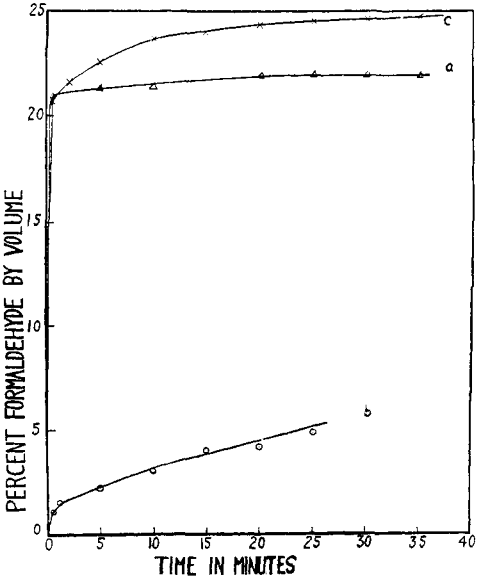


FIG. 1. Factors influencing the estimation of free formaldehyde in reaction mixtures

The measured volume of formaldehyde solution was introduced into the flask and allowed to reach the required temperature. When the temperature was steady the measured volume of urea solution, previously adjusted to the required temperature, was quickly added with the aid of reduced pressure. The time of mixture of the urea and formaldehyde solutions was taken as the mid point of the time required to add the urea solution. The slightly exothermic reaction necessitated temperature control with the aid of the cooling coil within the reaction vessel.

## RESULTS OF THIS INVESTIGATION

*Experiments at 30°C.:* The reaction was between 250 ml. of formaldehyde solution and 250 ml. of urea solution. The initial concentration of formaldehyde in the mixture was 12.01 per cent by volume. Experiment No. 17 is typical (see table 1).

In this experiment $a = 2.52$ from * in table 1, and $t$ = the figure in the column (seconds) minus 300. It was found that the initial reaction upon mixing the solutions was of greater rapidity than the subsequent reaction. A further noticeable feature was the drop in pH to 4.95 immediately upon mixing the solutions. It was found that no constant applicable to any reaction order could be derived unless the initial reaction (first 300 sec.) were disregarded. Even if the temperature were lowered or the reaction conducted using more dilute solutions, this initial reaction could not be followed. It appears that the reaction for the first 5 min. is approximately fourteen times faster than for the second 5 min. The change in pH during these two periods is in each case of the order of 0.05 pH. The change in velocity therefore must be attributed to the instantaneous change in pH upon mixing the solutions. The initial stage in such reactions, in order to be followed, would require an accurate method for the estimation of free formaldehyde in very dilute solutions.

TABLE 1

*Results of experiment No. 17*

$t = 30°C.$; $k$ (observed) at 30°C. $= 5.5 \times 10^{-5}$ liters/gram-mole second

| TIME | pH | PER CENT $CH_2O$ BY VOLUME | $x$ | $a - x$ | $k \times 10^5$ |
|---|---|---|---|---|---|
| *sec.* | | | | | |
| 0 | 4.95 | 12.01 | | | |
| 300 | 5.10 | 7.57* | | | |
| 600 | 5.18 | 7.26 | 0.10 | 2.42 | 5.46 |
| 1200 | 5.31 | 6.72 | 0.28 | 2.24 | 5.51 |
| 1800 | 5.45 | 6.24 | 0.44 | 2.08 | 5.59 |
| 3600 | 5.60 | 5.19 | 0.79 | 1.73 | 5.48 |
| 5400 | 5.76 | 4.44 | 1.04 | 1.48 | 5.47 |
| 7200 | 5.87 | 3.87 | 1.23 | 1.29 | 5.48 |
| 9000 | 5.98 | 3.42 | 1.38 | 1.14 | 5.52 |
| 10800 | 6.03 | 3.06 | 1.50 | 1.02 | 5.56 |
| 12600 | 6.09 | 2.79 | 1.59 | 0.93 | 5.51 |
| 14400 | 6.15 | 2.55 | 1.67 | 0.85 | 5.53 |

$$k = \frac{1}{ta} \cdot \frac{x}{a - x}.$$

$a$ = initial concentration of formaldehyde in gram-moles per liter.
$a - x$ = free formaldehyde in gram-moles per liter.
$t$ = time in seconds.

The product isolated at 14,400 sec. was identified as monomethylolurea (mp. 111°C., corrected) obtained in 95 per cent yield. No dimethylolurea was

TABLE 2

*Results of experiments 33a and 33b*

$t = 30°C.$

| $a$ | $t_{\frac{1}{2}}$ | $k = \frac{1}{t_{\frac{1}{2}}a}$ |
|---|---|---|
| *gram-moles/liter* | *sec.* | *$10^4$ liters/gram-mole second* |
| (a) 4 | 1920 | 1.30 |
| (b) 2 | 3900 | 1.28 |

TABLE 3

*Results of experiment No. 23*

$t = 40°C.$; $k$ (observed) at 40°C. = $11.8 \times 10^{-6}$ liters/gram-mole second

| TIME | pH | PER CENT $CH_2O$ BY VOLUME | $x$ | $a - x$ | $k \times 10^6$ |
|---|---|---|---|---|---|
| *sec.* | | | | | |
| 0 | 4.95 | 12.01 | | | |
| 300 | 5.30 | 7.02* | | | |
| 600 | 5.47 | 6.48 | 0.18 | 2.16 | 11.87 |
| 900 | 5.60 | 6.03 | 0.33 | 2.01 | 11.69 |
| 1800 | 5.80 | 4.98 | 0.68 | 1.66 | 11.66 |
| 3600 | 6.05 | 3.66 | 1.12 | 1.22 | 11.88 |
| 5400 | 6.17 | 2.91 | 1.37 | 0.97 | 11.83 |
| 7200 | 6.28 | 2.43 | 1.53 | 0.81 | 11.71 |
| 9000 | 6.38 | 2.07 | 1.65 | 0.69 | 11.74 |
| 10800 | 6.45 | 1.83 | 1.73 | 0.61 | 11.77 |
| 12600 | 6.50 | 1.59 | 1.81 | 0.53 | 11.87 |

* $a = 2.34$.

TABLE 4

*Results of experiment No. 29*

$t = 50°C.$; $k$ (observed) at 50°C. = $24.5 \times 10^{-5}$ liters/gram-mole second

| TIME | pH | PER CENT $CH_2O$ BY VOLUME | $x$ | $a - x$ | $k \times 10^5$ |
|---|---|---|---|---|---|
| *sec.* | | | | | |
| 0 | 4.95 | 12.01 | | | |
| 300 | 4.40 | 6.22* | | | |
| 600 | 5.57 | 5.40 | 0.27 | 1.80 | 24.15 |
| 1200 | 5.95 | 4.26 | 0.65 | 1.42 | 24.55 |
| 1800 | 6.28 | 3.51 | 0.90 | 1.17 | 24.78 |
| 3600 | 6.42 | 2.21 | 1.30 | 0.77 | 24.70 |
| 5400 | 6.52 | 1.74 | 1.49 | 0.58 | 24.35 |
| 7200 | 6.60 | 1.38 | 1.61 | 0.46 | 24.50 |
| 9000 | 6.67 | 1.14 | 1.69 | 0.38 | 24.68 |

* $a = 2.07$.

present in sufficient quantity to be detected. The observed figure for the bimolecular constant, given above table 1, is the average of four independent experiments; this also applies to the constants for 40°, 50°, and 60°C.

This second-order reaction was also confirmed by determining how the time of half-completion of the reaction varied with concentration of initial reactants. Experiments No. 33a and 33b at 30°C. illustrate this (see table 2).

*Experiments at 40°C.:* What has been said with regard to the experiments at 30°C. applies also at this temperature. Monomethylolurea was again the exclusive product at 12,600 sec. A greater increase in pH toward the bottom of the table is noticeable. Experiment No. 23 is illustrated in table 3.

*Experiments at 50°C.:* As at 30°C. and 40°C., monomethylolurea was obtained in almost theoretical yield from sample No. 8. Experiment No. 29 is illustrated in table 4.

TABLE 5

*Results of experiment No. 38*

$t$ = 60°C.; $k$ (observed) at 60°C. = $50.1 \times 10^{-5}$ liters/gram-mole second

| TIME | pH | PER CENT $CH_2O$ BY VOLUME | $x$ | $a - x$ | $k \times 10^5$ |
|---|---|---|---|---|---|
| *sec.* | | | | | |
| 0 | 4.96 | 12.01 | | | |
| 300 | 5.90 | 5.65* | | | |
| 600 | 6.10 | 4.83 | 0.46 | 1.61 | 50.6 |
| 1200 | 6.40 | 3.03 | 0.87 | 1.01 | 50.8 |
| 1800 | 6.50 | 2.24 | 1.10 | 0.78 | 50.0 |
| 3600 | 6.60 | 1.38 | 1.42 | 0.46 | 49.8 |
| 5400 | 6.65 | 0.96 | 1.56 | 0.32 | 50.8 |

* $a$ = 1.88.

*Experiments at 60°C.:* As at the other temperatures studied, monomethylolurea was obtained in almost theoretical yield from sample No. 6. Experiment No. 38 is illustrated in table 5.

## DISCUSSION OF RESULTS

Considering the general bimolecular course of the reaction, no relation was found connecting the velocity constant with the change in hydrogen-ion concentration. It will be seen in tables 1 to 5 that the constants are steady over a change in pH of 1.

The variation with temperature of the velocity constant for a thermal reaction occurring in solution is expressed by:

$$k = Ze^{-E/RT}$$

or

$$\ln k = Z - \frac{E}{RT}$$

Plotting $\ln k$ against $1/T$ (see figure 2), the Arrhenius equation takes the form:

$$\ln k = 14.61 - \frac{14{,}700}{RT}$$

when $E$ = 14,700 cal. and the collision number $Z$ = approximately $2.2 \times 10^6$.

The low values of $E$ and $Z$ are interesting in the light of current theories regarding bimolecular reactions in solution. The deviation of the reaction from the ideal behavior of the simple collision theory introduces the probability factor $P$ and

$$k = PZe^{-E/RT}$$

$P$ in the case of the reaction studied is approximately $2 \times 10^{-6}$. The $P$ factor may be interpreted in terms of vibrational and rotational partition functions and according to the statistical theory in the case of two non-linear polyatomic molecules.

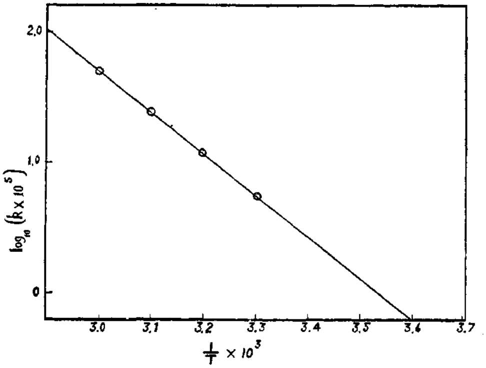


FIG. 2. Plot of ln $k$ against $1/T$

$$P \approx \left(\frac{f_V}{f_R}\right)^5$$

If the reactant molecules have to be placed together in a particular way before reaction, the probability of the formation of the activated complex will be less, and when a linear complex is formed the rate should be less by a factor of $f_V/f_R$ than for a non-linear complex, assuming that the activation energy is the same in each case. The formation of the activated complex from two polyatomic molecules is accompanied by the formation of five new vibrational degrees of freedom and a translational degree of freedom along the reaction coordinate, this of course being accompanied by the disappearance of three translational and three rotational degrees of freedom (5).

In this case, the low probability factor that is found may be due to restrictions on the molecule, making the energy transitions necessary for the formation of the activated complex. The initial rapid reaction rate appears to be intimately related to this subsequent slow bimolecular reaction and involves a consideration of the changes in hydrogen-ion concentration noted.

Possibly the rate of reaction is dependent on the ionization of the urea, in turn dependent upon the hydrogen-ion concentration. Initially, therefore, the reaction in the first instance may be a normal one where

$$\text{Ion}^{\pm} + \text{molecule}^{0} = \text{normal rate}$$

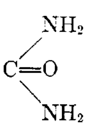
$$E \approx 22{,}000 \text{ cal.}$$

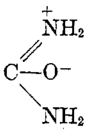
$$Z \approx 2.8 \times 10^{11}$$

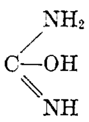
Consideration of tables 1 to 5 shows that the hydrogen-ion concentration is increased by $10^2$ initially. Thereafter increases are of a smaller order.

As the main reaction is of the slow bimolecular type the course would appear to be *via* neutral molecules, one of them, urea, necessarily assuming the suitable reacting condition prior to the formation of the activated complex. This condition of urea appears to be the rate-determining factor.

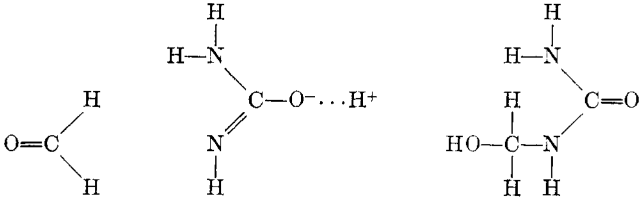
Urea in solution may be regarded as an equilibrium mixture of the forms:







The normal rate of reaction may depend on the migration of hydrogen ion from the hydroxyl group of the tautomeric form of urea, leading to an activated complex and subsequent rearrangement to monomethylolurea:



Monomethylolurea

According to Lecher (7), migration of the hydrogen ion from the hydroxyl group to the imino group is more likely than migration to the amino group. The fact that monomethylolurea is the exclusive product under the conditions studied suggests that two identical amino groups are not involved in the reaction. The rate of reaction then appears to be closely associated with the condition of the urea molecule, which is in turn influenced by hydrogen-ion concentration.

## SUMMARY

1. The reaction between urea and formaldehyde in aqueous solution within defined conditions has been shown to be mainly of the slow bimolecular variety.
2. Determined values for $E$, $Z$, and $P$ are given and discussed in the light of present knowledge regarding bimolecular reactions in solution.

3. A method for estimating the free formaldehyde during the course of a urea–formaldehyde reaction is presented.

In conclusion I wish to express my thanks to Dr. T. Iredale for valuable advice and discussion.

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# ANILINE FORMATE AND ITS CHANGES ON KEEPING

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A study of the system aniline–formic acid–water was made in 1934 by A. M. Wilson and the present writer (1). The conditions under which crystals of aniline formate were obtainable at room temperatures were indicated, and also the changing of these crystals into formanilide and water. There are two equilibria involved:

$$\text{Aniline} + \text{formic acid} \overset{(1)}{\rightleftharpoons} \text{aniline formate} \overset{(2)}{\rightleftharpoons} \text{formanilide} + \text{water}$$

These affect both the liquid mixtures and the solid crystals of aniline formate.

### I. CHANGES IN THE CRYSTALS ON KEEPING

The original colorless crystals of aniline formate become in a few days sticky, then they often completely liquefy, then crystals of formanilide separate, and finally the whole re-solidifies. These changes generally are retarded in the presence of a drying agent. After twelve years four sealed samples of such crystals were re-investigated. There were determined (*a*) the "free formic acid" (by direct titration with alkali), (*b*) the "combined formic acid" (by boiling with excess alkali and back-titration by acid), and (*c*) the total aniline (by the bromate method). (*b*) indicates the formanilide content, and (*a*) the aniline formate