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# Urea–Formaldehyde Kinetic Studies. II. Factors Influencing Initial Reaction

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Factors influencing the initial reaction between (a) urea and formaldehyde and (b) N-methylurea and formaldehyde, have been studied. It is shown that the proportion of formaldehyde utilized during the initial rapid reaction, within the range of solution strength 8–4 *M*, does not appear to be markedly dependent on: (i) temperature, (ii) certain buffer and other additions, (iii) substitution of a methyl group in the urea molecule. At 1 *M* strength the proportion of formaldehyde used in the initial rapid reaction decreases with increasing dilution and indications are that this effect continues with dilution until no rapid reaction is observed with very dilute solutions. In connection with the effect of dilution on the initial reaction, the role of depolymerization and associated equilibria in formaldehyde solutions is discussed. The bimolecular velocity constant for the reaction between urea and formaldehyde and for the reaction between N-methylurea and formaldehyde increases with dilution and the effect of certain additions in the case of urea is shown. The reaction between N-methylurea and formaldehyde within defined conditions is shown to be mainly of the slow bimolecular type and determined values for the effective energy of activation are given.

## Introduction

In a previous paper[1] attention was drawn to the almost instantaneous utilization of a large part of the formaldehyde during the initial reaction. Further study of the factors influencing the initial reaction seemed desirable and such a study is presented here.

It is well recognized[2] that the actual structure of urea may depend greatly on environment. The familiar diamide form of urea does not play as important a part in the reaction between urea and formaldehyde as other forms.[1,3–6] In addition the state of formaldehyde in solution[1,5,6] has an important effect on reaction rate.

Urea–formaldehyde kinetic studies therefore, may well throw some light not only on the mechanism of the initial reaction between urea and formaldehyde but also on the structures of both urea and formaldehyde in aqueous solution.

This paper presents information concerning the effect of the following on the initial reaction: (i) variation in concentration of urea and formaldehyde solutions from 4 to 1 *M* and urea formaldehyde ratio 1:1; experiments M-R Table I; (ii) effect of addition of buffers and some organic compounds; 4 and 8 *M* solutions, U.F. ratio 1:1; experiments A-L Table I; (iii) substitution of one N-methyl group in the urea molecule; 4 and 8 *M* solutions, U.F. ratio 1:1; experiments S-X Table I.

In addition the order of the reaction between N-methylurea and formaldehyde has been determined and the effective energy of activation evaluated.

## Experimental

Apparatus, chemicals and general technique have been described.[1,3] Additional chemicals used were either of analytical reagent grade or specially purified. The analytical method for the estimation of formaldehyde[3] was subject to some errors when working with 1 *M* solutions. However the taking of larger samples and rapid titration obviated serious errors and the experiments P-R quoted in Table I, were the most representative of fourteen carried out under these conditions.

## Results

Table I gives relevant data for the experiments carried out. Table II compares the percentage of formaldehyde utilized in the first 300 seconds with the percentage of unhydrated formaldehyde.

## Discussion

From Table I, and as mentioned in the summary, it is seen that variation of conditions does not materially affect the percentage of formaldehyde utilized during the initial rapid reaction. From the data given in Table II it is evident that the hydration of formaldehyde in solution (forming methylene glycol), together with anion formation of urea,[1,3,5,6] are not the sole criteria of rapid reaction since there is no parallel between the amount of formaldehyde utilized and the percentage not hydrated. A proportion of the urea may possibly change with dilution to a more favorable form for reaction with the cation $HO{\cdot}CH_2^+$ formed from methylene glycol or, the question of polymeric hydrates and their depolymerization in the formaldehyde solutions might be considered.

For formaldehyde solutions of higher concentration (*e.g.*, 8 *M*) the equilibria would be between

$$\underbrace{\begin{array}{c}\text{I}\\ \mathrm{CH_2O}\\ \text{unhydrated}\end{array}}_{49\%} \rightleftarrows \underbrace{\begin{array}{c}\text{II}\\ \mathrm{CH_2(OH)_2}\\ \text{methylene}\\ \text{glycol}\end{array} \rightleftarrows \begin{array}{c}\text{III}\\ \mathrm{HO{\cdot}CH_2OCH_2OH}\\ \text{dioxymethylene}\\ \text{glycol}\end{array} \rightleftarrows \begin{array}{c}\text{IV}\\ \mathrm{HO{\cdot}CH_2OCH_2O{\cdot}CH_2OH}\\ \text{trioxymethylene}\\ \text{glycol}\end{array}}_{51\%}$$

For lower concentrations of formaldehyde (*e.g.*, 0.5 *M* solutions) the proportions of III and IV would decrease, I would decrease and II increase

$$\begin{array}{ccl}\text{I} & & \text{II}\\ \mathrm{CH_2O} & \rightleftarrows & \mathrm{CH_2(OH)_2}\\ 2\% & & 98\%\ \text{including only a little of}\\ & & \text{III and IV)}\end{array}$$

Depolymerization of III and IV in the case of solutions of high concentrations would be more important than in the case of dilute solutions and may not occur at all for solutions below about 0.1 *M*.

It is possible that in the more concentrated solutions there is a depolymerization of the hydrated polymers which is rather slow and equilibria of the type

$$\text{Solns. of } pH > 5\quad \mathrm{HO{\cdot}CH_2O{\cdot}CH_2O{\cdot}CH_2OH} \rightleftarrows \mathrm{HO{\cdot}CH_2O{\cdot}CH_2O{\cdot}CH_2^+} + \mathrm{OH^-}$$

$$\mathrm{HO{\cdot}CH_2O{\cdot}CH_2OH} \rightleftarrows \mathrm{HO{\cdot}CH_2O{\cdot}CH_2^+} + \mathrm{OH^-}$$

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[1] L. E. Smythe. THIS JOURNAL, **73**, 2735 (1951).

[2] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 285.

[3] L. E. Smythe. *J. Phys. Colloid Chem.*, **51**, 369 (1947).

[4] G. A. Crowe and C. C. Lynch, THIS JOURNAL, **70**, 3795 (1948).

[5] G. A. Crowe and C. C. Lynch, *ibid.*, **71**, 3731 (1949).

[6] G. A. Crowe and C. C. Lynch, *ibid.*, **72**, 3622 (1950).

TABLE I

DATA FOR THE UREA–FORMALDEHYDE AND N-METHYLUREA–FORMALDEHYDE REACTIONS

| Expt. No. | Temp., °C. | Molar strength solns.[a] and U:F ratio 1:1[b] | $k \times 10^5$ to ( )sec.[c] | | Addition w./w. | $CH_2O$, % utilized 1st. 300 sec. | Yield, % reaction product[f] | Initial $p$H[g] | Final $p$H[h] | Sec. | $\Delta E_a$, calories |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 20 | 8 | 6.5 | (7,200) | 1 in 600 $Na_2HPO_4$ | 41 | 90 | 7.90 | 7.46 | (21,600) | |
| B | 30 | 8 | 13.4 | (12,000) | 1 in 600 $Na_2HPO_4$ | 43 | 92 | 7.92 | 7.36 | (18,000) | |
| C | 20 | 8 | 11.0 | (7,000) | 1 in 300 $Na_2HPO_4$ | 41 | 93 | 8.50 | 8.00 | (14,000) | |
| D | 30 | 8 | 22.8 | (8,400) | 1 in 300 $Na_2HPO_4$ | 43 | 93 | 8.50 | 7.85 | (12,000) | |
| E | 20 | 4 | 44.0 | (9,600) | 1 in 300 $Na_2HPO_4$ | 36 | 85 | 8.60 | 8.10 | (14,400) | |
| F | 30 | 4 | 91.4 | (7,200) | 1 in 300 $Na_2HPO_4$ | 38 | 85 | 8.60 | 8.00 | (15,600) | |
| G | 20 | 8 | 5.1 | (7,200) | 1 in 300 $CH_3COONa$ | 48 | 95 | 7.47 | 7.13 | (14,400) | |
| H | 20 | 8 | 6.0 | (19,800) | 1 in 300 hydroquinone | 48 | 95 | 7.00 | 6.12 | (19,800) | |
| I | 20 | 8 | 4.5 | (9,900) | 1 in 300 $NH_2CH_2COOH$ | 47 | 90 | 4.90 | 4.70 | (13,500) | |
| J | 20 | 8 | 4.8 | (9,600) | 1 in 300 $Na_2B_4O_7$ | 39 | 90 | 8.80 | 9.02 | (10,800) | |
| K | 20 | 8 | 3.0 | (9,600) | 5% $CH_3OH$ | 38 | 85 | 7.50 | 6.15 | (11,700) | |
| L | 20 | 8 | 2.5 | (9,600) | 15% $CH_3OH$ | 38 | 85 | 7.24 | 6.80 | (13,500) | |
| M | 20 | 4 | 21.2 | (9,600) | ........ | 39 | 85 | 6.50 | 6.20 | (12,000) | |
| N | 30 | 4 | 44.4 | (7,200) | ........ | 40 | 85 | 6.80 | 6.10 | (12,000) | |
| O | 40 | 4 | 93.9 | (7,200) | ........ | 43 | 85 | 7.00 | 6.00 | (12,000) | |
| P | 20 | 1 | 32.5[d] | (12,600) | ........ | 23 | 50 | 7.00 | 6.40 | (12,600) | |
| Q | 30 | 1 | 68.2[d] | (12,600) | ........ | 25 | 50 | 7.00 | 6.30 | (12,600) | |
| R | 40 | 1 | 14.2[e] | (12,600) | ........ | 26 | 50 | 7.00 | 6.30 | (12,600) | |
| S | 20 | 8 | 0.75 | (12,600) | ........ | 41 | .. | 6.90 | 6.10 | (12,600) | |
| T | 30 | 8 | 1.80 | (14,400) | ........ | 43 | .. | 6.85 | 5.80 | (14,400) | 15,400[i] |
| U | 40 | 8 | 4.2 | (10,800) | ........ | 43 | .. | 6.85 | 5.70 | (12,600) | |
| V | 20 | 4 | 3.0 | (9,600) | ........ | 38 | .. | 6.80 | 6.10 | (12,600) | |
| W | 30 | 4 | 7.2 | (9,600) | ........ | 39 | .. | 6.80 | 5.90 | (12,600) | 15,600[j] |
| X | 40 | 4 | 17.2 | (9,600) | ........ | 41 | .. | 6.75 | 5.58 | (12,600) | |

[a] Strength of solutions before mixing. [b] Urea–formaldehyde and N-methylurea–formaldehyde mole ratios. [c] $k$ in liters/gram-mole second; evaluated for reaction time given in parentheses. [d] Value here $k \times 10^4$. [e] Value $k \times 10^3$. [f] Refers to monomethylolurea isolated after 8-hour reaction period. [g] Initial $p$H on mixing reactants. [h] Final $p$H after reaction time (given in parentheses). [i] Evaluated from rate constants in experiment numbers S, T and U. [j] Evaluated from rate constants in experiment numbers V, W and X.

TABLE II

| Molar strength $CH_2O$ soln. | $CH_2O$ not hydrated,[a] % | Molar strength U. and F. in react. mixture[b] | $CH_2O$ utilized 1st. 300 sec., % |
|---|---|---|---|
| 8 | 49 | 6 | 46 |
| 4 | 30 | 4 | 40 |
| 2 | 13 | 2 | 40 |
| 0.5 | 2 | 0.5 | 23 |

[a] Data from F. Auerbach, "Formaldehyde," A.C.S. Monograph 98, 1944, p. 33. [b] Effective molar strengths after mixing reactants.

for the trimer and dimer, respectively. It is not likely that these cations would react during the short period considered and prior to depolymerization. In this case the reaction would be between urea in a suitable form[1,3,5] and the unhydrated formaldehyde.

In the case of dilute solutions, depolymerization would be negligible and the equilibrium would be essentially

$$\text{Solns. of } pH > 5 \quad \underset{\text{(methylene glycol)}}{HO\cdot CH_2\cdot OH} \rightleftharpoons HO\cdot CH_2^+ + OH^-$$

The cation in this case would be produced more rapidly.

In the case of 0.5 $M$ solutions (Table II) only 2% of the formaldehyde is available in the unhydrated form but 23% is utilized in the first 300 seconds of the reaction. The extra formaldehyde utilized over and above the 2% might be accounted for by the reaction of urea with the cation $HO\cdot CH_2^+$ produced.

On this basis the reaction between urea and formaldehyde in dilute solutions[4–6] would be mainly of uniform velocity and markedly dependent on the dehydration of methylene glycol involving the cation $HO\cdot CH_2^+$ and this is found to be the case by Crowe and Lynch.

The addition of compounds listed in Table I, column 4, resulted in a slight decrease in reaction rate in the case of glycine and sodium tetraborate and a slight increase in the case of hydroquinone, sodium acetate and disodium hydrogen phosphate. The reaction rate in the above cases was compared with that for urea and formaldehyde alone and given previously.[3] Under conditions of $p$H favoring the formation of methylol compounds, a concentration of 1 in 300 disodium hydrogen phosphate resulted in the highest rate. The presence of methanol resulted in a marked decrease in reaction rate. No special significance can yet be attached to the results observed from these additions except that it is shown that the initial rapid reaction with depolymerization and associated ionic phenomena, is not affected to any great extent by the addition of the majority of compounds, including methanol which lowers the ionic product of water. Wadano and coworkers,[7] have shown that methanol lowers the rate of depolymerization but it is not likely that such additions would influence the initial reaction if this is between the urea and the formaldehyde already existing in a dehydrated form.

Data are also given (Table I) for the reaction between N-methylurea and formaldehyde under specified conditions. As in the case of urea[1,3-5] the reaction is shown to be mainly of the slow bimolecular type. The value for the energy of activation $\Delta E_a$ is higher than the value for the urea–formaldehyde reaction previously given[1] but is very close to that given by Crowe and Lynch for the reaction between urea and formaldehyde in dilute solution.[5] In addition the value for the bimolecular velocity constant is much reduced by the substitution of one N-methyl group in the urea molecule. Of interest is the fact that no simple methylol compound could be identified in the reaction product after 8–24 hours. Only after allowing the reaction mixture to stand at 20° for one week was methylene bis (methyl urea)[8] m.p. 184° identified in small yield.

Further work with dilute solutions of N-methylurea and other substituted ureas is being carried out and discussion of the reaction between N-methylurea and formaldehyde will be continued in a later paper.

[7] M. Wadano, C. Trogus and K. Hess, *Ber.*, **67**, 174 (1934).

[8] H. Kadowaki, *Bull. Chem. Soc. Japan*, **11**, 248 (1936).

TASMANIA, AUSTRALIA RECEIVED SEPTEMBER 25, 1951

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[CONTRIBUTION NO. 189 FROM THE GOODYEAR TIRE AND RUBBER CO. RESEARCH LABORATORY]

# Polyelectrolyte Behavior of Polyamides. II. Viscosities of Solutions of Linear and Multichain Polyamides in Formic Acid[1]

BY JOHN R. SCHAEFGEN[2] AND CHARLES F. TRIVISONNO

RECEIVED NOVEMBER 2, 1951

It is shown that dilute solutions of linear, tetrachain, or octachain poly-$\epsilon$-caproamides in anhydrous formic acid exhibit the steep rise in reduced viscosity as the polymer concentration approaches zero characteristic of polyelectrolyte solutions. The data for reduced viscosity as a function of concentration fit the equation $\eta_{sp}/c = A/(1 + Bc) + D$ where $A$, $B$ and $D$ are constants for a given polymer. The constant $D$ may be identified with the intrinsic viscosity of the uncharged coiled polymer molecule while $A + D$ may be thought of as the intrinsic viscosity of the polyion. Graphs of log $(A + D)$ vs. log $\bar{M}_n$ are linear for each series of polymers, and the observed slopes are 1.41, 1.45 and 1.59, respectively, for linear, tetrachain and octachain polymers. Graphs of log $(A + D)$ vs. log $\bar{M}_v$ are also linear and show that at the same molecular weight branching decreases the intrinsic viscosity of the polyion, presumably by forming a more compact structure in solution.

It has been shown[3] that linear poly-$\epsilon$-caproamides when dissolved in anhydrous formic acid ionize to produce positively charged substituted ammonium ions along the chains which cause uncoiling of the polymer molecules in dilute solution, thereby resulting in a steep rise in reduced viscosity as the polymer concentration approaches zero. While linear molecules may approach a rod-like structure due to repulsion between ions on the chain in the limit of zero concentration, tetrachain and octachain molecules[4] approach cross-shaped and eight-armed structures, respectively. Solutions containing these latter molecules therefore should exhibit lower viscosities than solutions of the linear molecules because of the restraints placed on expansion of the molecules by the central multifunctional unit. Conversely, the intrinsic viscosity of the polyion should provide a sensitive test for branching in polymer molecules.

## Experimental

Polymers (see Table I) were prepared by the method described previously.[3,4] Number average molecular weights were calculated from carboxyl and amine end-group titers,[5] or alternatively, from the intrinsic viscosity in concentrated sulfuric acid.[4] In the case of the multichain polymers the proportion of linear polymer was small (see $w_L$, Table I). Before use, each polymer was heated at 184° and 1 mm. pressure for four hours to free it of monomeric $\epsilon$-caprolactam.

TABLE I

POLY-$\epsilon$-CAPROAMIDES: VISCOSITIES AND MOLECULAR WEIGHTS

| Polymer | $[\eta]$, $H_2SO_4$ 30° | $D$ | $A$ | $(A + D)$ | $B$ | $w_L \times 10^2$ | $\bar{M}_n$ | $\bar{M}_v$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Linear | | | | |
| L I | 0.338 | 0.313 | 0.700 | 1.013 | 9.1 | 0.71 | 4320 | 6900 |
| L II | .560 | .535 | 2.19 | 2.73 | 10.1 | 1.5 | 8490 | 13500 |
| L III | .772 | .760 | 4.18 | 4.94 | 11.5 | 2.3 | 12900 | 20500 |
| L IV | 1.060 | 1.08 | 7.48 | 8.56 | 12.7 | 5.5 | 19200[a] | 30200 |
| L V | 1.357 | 1.47 | 11.43 | 12.9 | 13.0 | 7.8 | 26000 | 40600 |
| | | | | Tetrachain | | | | |
| T II | 0.421 | 0.404 | 1.27 | 1.67 | 12.0 | 1.04 | 8080 | 11200 |
| T III | .495 | .490 | 1.92 | 2.41 | 10.9 | 1.26 | 10100 | 14000 |
| T IV | .722 | .69 | 3.26 | 3.95 | 8.6 | 1.56 | 15700 | 21800 |
| T V | .970 | .99 | 6.72 | 7.71 | 10.9 | 3.5 | 23700[a] | 32500 |
| T VI | 1.130 | 1.25 | 10.44 | 11.7 | 13.8 | 6.4 | 29700 | 40000 |
| | | | | Octachain | | | | |
| O I | 0.286 | 0.275 | 0.520 | 0.759 | 7.1 | 0.43 | 7500 | 9190 |
| O II | .406 | .420 | 1.35 | 1.77 | 7.8 | .24 | 12500 | 15400 |
| O III | .580 | .60 | 2.58 | 3.18 | 6.8 | 2.0 | 18400 | 22300 |
| O IV | .687 | .74 | 4.27 | 5.01 | 10.3 | 0.54 | 24000 | 29400 |
| O V | 1.032 | 1.20 | 8.18 | 9.38 | 9.0 | 3.7 | 37000 | 44200 |
| O VI | 1.547 | 1.75 | 13.1 | 14.9 | 8.1 | 5.2 | 48500 | 57200 |

[a] Estimated from intrinsic viscosity.

**Formic acid** analyzing 100% by titration and having a freezing point of at least 8.05° was prepared by repeated distillation at reduced pressure of 97–98% by weight formic acid from concentrated sulfuric acid (5 cc. of sulfuric acid to 100 cc. of formic acid). Two successive distillations in which the fraction boiling from 33–34° at 60 mm. was re-

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[1] Presented in the "Symposium on Polyelectrolytes," Division of Polymer Chemistry at the New York Meeting of the American Chemical Society, September, 1951.

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[3] J. R. Schaefgen and C. F. Trivisonno, THIS JOURNAL, **73**, 4580 (1951).

[4] J. R. Schaefgen and P. J. Flory, *ibid.*, **70**, 2709 (1948).

[5] J. R. Schaefgen and P. J. Flory, *ibid.*, **72**, 689 (1950).