278. *The Urea–Formaldehyde Polycondensation. Part I.*
Kinetics of the Hydrolysis of Methoxymethylurea.

By A. S. Dunn.

Hydrolysis of methoxymethylurea is catalysed by acids in general and by hydroxyl ions. In alkaline solution the reaction can conveniently be followed by carrying it out in the presence of cyanide, for hydroxymethyl-urea rapidly decomposes to give formaldehyde which is removed as cyano-hydrin, residual cyanide being titrated with mercuric nitrate. In acid solution the decomposition is slower and it is not possible to remove the formaldehyde. There are then consecutive first-order reactions with a second-order reverse reaction : no exact method of treating the results is available for this case but an approximate method is described. The hydrolysis is much retarded by methanol.

EXTENSIVE studies [1] of the reactions between urea, formaldehyde, and their addition compounds, which lead to the formation of aminoplastics, have shown that the addition of formaldehyde to urea is a general acid–base catalysed reaction,[1a] whilst intermolecular condensation of amino- and hydroxyl groups to form methylene-bridged products is catalysed specifically by hydrogen ions.[1b] Rate coefficients of forward and reverse reactions, energies of activation, and equilibrium constants have been evaluated for reactions in aqueous solution. Moreover, it is known that ethers of mono- and di-(hydroxymethyl)-urea with various alcohols can be produced, not only with acid,[2] but also with alkaline catalysts.[3] However, no physicochemical study had been reported of this type of reaction
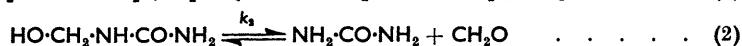
[1] *E.g.*, de Jong and de Jonge, *Rec. Trav. chim.*, (*a*) 1952, **71**, 643, 661, 890; (*b*) 1953, **72**, 139, 207, 213.

[2] (*a*) Kadowaki, *Bull. Chem. Soc. Japan*, 1936, **11**, 248; B.P. (*b*) 522,643, (*c*) 558,683.

[3] U.S.P. 2,315,745.

until the appearance of a Japanese publication [4] which does not seem very comprehensive. The present paper represents part of a programme undertaken to bring knowledge of the reactions of hydroxymethylureas to parity with that of their self-condensation. Reactions of this type are of technical importance in considering the possibility of cross-linkage of cellulose by urea–formaldehyde resins which are applied to impart crease-resistance to textiles.

Methoxymethylurea is hydrolysed to hydroxymethylurea which decomposes faster to give, ultimately, an equilibrium mixture of urea and formaldehyde.

$$CH_3 \cdot O \cdot CH_2 \cdot NH \cdot CO \cdot NH_2 + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} HO \cdot CH_2 \cdot NH \cdot CO \cdot NH_2 + CH_3 \cdot OH \quad . \quad . \quad . \quad (1)$$

$$HO \cdot CH_2 \cdot NH \cdot CO \cdot NH_2 \underset{}{\overset{k_2}{\rightleftharpoons}} NH_2 \cdot CO \cdot NH_2 + CH_2O \quad . \quad . \quad . \quad . \quad (2)$$

If cyanide is present, under alkaline conditions it reacts with the formaldehyde and practically prevents the reverse reaction (2) and, at the same time, provides a means of following the reaction :

$$CH_2O + H_2O \underset{}{\overset{k_3}{\rightleftharpoons}} CH_2(OH)_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$CH_2(OH)_2 + CN^- \rightleftharpoons HO \cdot CH_2 \cdot CN + OH^- \quad . \quad . \quad . \quad . \quad . \quad (4)$$

FIG. 1. *Decrease of rate by addition of sodium nitrate. Initial* $[OH^-] = 0.4$. *Initial* $[CN^-]$ $= 0.091$; 25°. *I, total ionic strength,* $= 1.25$ (A) *or* 2.0 (B).
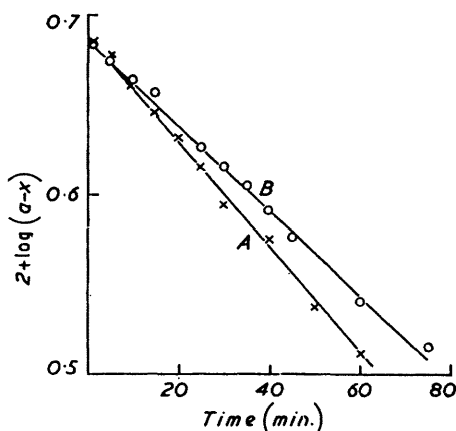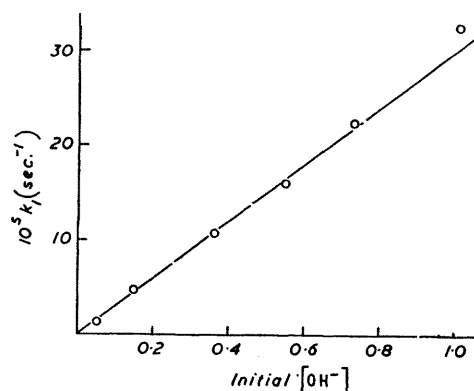

FIG. 2. *Dependence of rate on hydroxyl-ion concentration at 25°. Initial ether concn.* $= 0.05$M. *Initial* $[CN^-] = 0.10$N.

RESULTS

Order of Reaction.—The reaction is of the first order. Plots of the logarithm of the ether concentration against time are linear (Fig. 1). First-order rate constants calculated from experiments at different initial ether concentrations are in satisfactory agreement (Table 1).

TABLE 1.

Temp. 25°. Initial $[CN^-] = 0.10$M. Initial $[OH^-] = 0.55$M.

Initial ether concn. (M)	0.0985	0.0849	0.0479	0.0481	0.0240
$10^5 k_1$ (sec.$^{-1}$)	16.1	16.0	15.5	15.6	15.5

Catalytic Coefficient of Hydroxyl Ions.—The rate increases linearly with hydroxyl-ion concentration (Fig. 2). The rate constant may be written $k_1 = k_0 + k_{OH}$-$[OH^-]$. The catalytic coefficient for hydroxyl ions at 25° is $k_{OH^-} = 3.00 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. Hydrolysis of the potassium cyanide does not sensibly increase the hydroxyl concentration even at the lowest hydroxide concentration used.

As will appear below, k_{CN}-$[CN^-] \sim 10^{-8}$ sec.$^{-1}$, so that the contribution of the cyanide ion to the catalysis is negligible. k_0 is too small to be determined from Fig. 2.

[4] Muraksmi, Sakaguchi, and Akiba, *Bull. Text. Res. Inst. (Japan)*, 1955, No. 32, 77, 86.

Energy of Activation.—A plot of log k_1 against $1/T$ is linear. The energy of activation is evaluated as 19·3 kcal./mole. Thus

$$k_{\mathrm{OH}^-} = 9 \cdot 46 \times 10^9 \exp\left(-19{,}300/\boldsymbol{R}T\right)$$

Effect of Ionic Strength.—Since the rate-determining process in the alkaline hydrolysis of methoxymethylurea is probably a bimolecular reaction between a neutral molecule (the ether)

TABLE 2.

Initial ether concn. 0·05M.	Initial [OH⁻] 0·35N.		Initial [CN⁻] 0·10M.	
Temp.	13°	25°	37°	50°
$10^3/T$	3·50	3·36	3·23	3·10
$10^5 k_1$ (sec.⁻¹)	4·00	10·6	41·2	106

TABLE 3.

		Temp. 25°.	Ionic strength ~1·1.	Initial [CN⁻] 0·1M.		
$x = $[HA]/[A]	[HA]	$10k^6$ (sec.⁻¹)	pH	10^3[OH]	$10^6(k_{\mathrm{HA}} + k_{\mathrm{A}}/x)$	
1·0	0	(0·45)	—			
	0·2	1·50	11·19⎫			
	0·5	2·16	11·14⎬	1·5	2·99	
	1·0	3·84	11·20⎭			
2·0	0	(0·12)	—			
	0·3	1·12	10·67⎫			
	0·75	2·57	10·61⎬	0·4	2·95	
	1·5	5·02	10·60⎭			

and an ion (hydroxyl), no large primary kinetic salt effect is expected. The ionic strength in these experiments is high (often I 0·65) : in the experiments of Fig. 2 the ionic strength varies between 0·15 and 1·10. Fig. 1 shows that the rate of reaction is decreased as the ionic strength is increased by addition of sodium nitrate. In subsequent experiments sodium nitrate was added to maintain the ionic strength constant.

General Acid–Base Catalysis.—Piperidine and piperidinium ion. The catalytic coefficients of the acidic (HA) and basic (A) components of a buffer may be separately evaluated by carrying out experiments at several buffer ratios and concentrations. It can be shown that $k = k_x + $ HA$(k_{\mathrm{HA}} + k_{\mathrm{A}}/x)$. In Table 3, k_x, the rate in absence of buffer, has been obtained from the measured pH and the catalytic coefficient for hydroxyl ions determined above. Then $(k_{\mathrm{HA}} + k_{\mathrm{A}}/x)$ has been obtained from a graph of k against [HA]. Solution of simultaneous equations then gives the catalytic coefficient for piperidinium ion $k_{\mathrm{HA}} = 2 \cdot 91 \times 10^{-6}$ l. mole⁻¹ sec.⁻¹, for piperidine $k_{\mathrm{A}} = 0 \cdot 08 \times 10^{-6}$ l. mole⁻¹ sec.⁻¹. Table 3 clearly demonstrates catalysis by piperidinium ion, but the graphs of k against [HA] at the two buffer ratios are nearly parallel and it is not possible to say that k_{A} differs significantly from zero. It seems that it may not be possible to detect catalysis by bases weaker than hydroxyl ion. This was confirmed by experiments in which trisodium phosphate was added : no catalytic effect attributable to the phosphate ions could be detected. Thus it is clear that the cyanide ions present in all experiments under alkaline conditions will not exert any catalytic effect.

Hydrolysis in Methanol–Water Mixtures.—The effect of change of solvent on the rate of hydrolysis is illustrated by Fig. 3. There is a marked reduction in the rate of reaction with increasing methanol concentration. The concentration of hydroxyl ions is reduced by addition of methanol because of the equilibrium OH⁻ + MeOH ⟶ MeO⁻ + H₂O. The equilibrium constant for this reaction [5] has a value of about 1. If it is supposed that methoxide ions would not cause hydrolysis, reduction in the hydroxide-ion concentration could account for a reduction in the rate of 13% at most. The major part of the reduction in rate probably arises from change in the polarity of the solvent and, in fact, the results are consistent with a linear relationship between log k_{OH^-} and the reciprocal of the dielectric constant of the solvent, as shown in the inset to Fig. 3.

Hydrolysis in Acid Solution.—Fig. 4 shows catalysis by hydrogen ions. However, neither reaction (4) with cyanide nor any similar reaction by which the formaldehyde formed could be removed occurs in acid solution. Reaction (2) therefore proceeds to equilibrium. Comparison of the rate constants k_1 derived from a first-order plot below 40—50% reaction of the data in

⁵ Unmack, *Z. phys. Chem.*, 1928, **133**, 45.

Fig. 4 with those (k_2) calculated from de Jong and de Jonge's values [1a] for the decomposition of hydroxymethylurea give ratios of k_2/k_1 of 1·39 in 0·2N- and 1·54 in 1N-nitric acid. This indicates that consecutive-reaction treatment should be applied. Rate constants derived by calculation

FIG. 3. *Relation between hydrolysis rate constant k_1 and solvent composition at 25°. Initial* $[CN^-] = 0·10N$. *Initial ether concn.* $= 0·05M$. $[OH^-] + [OMe^-] = 0·50N$.

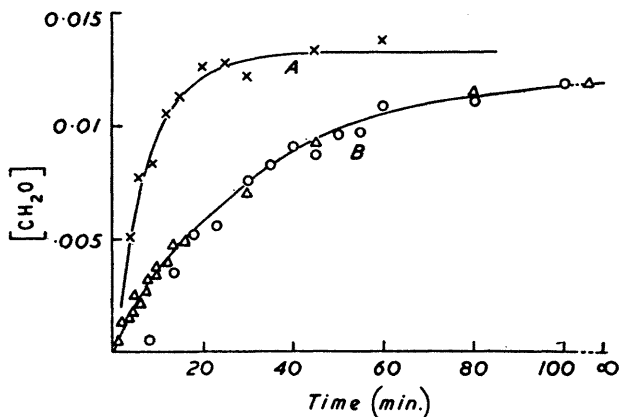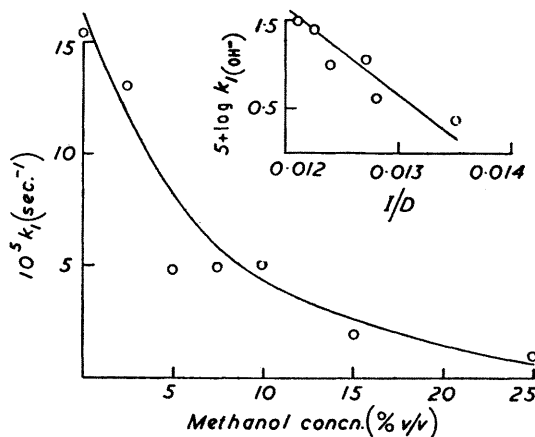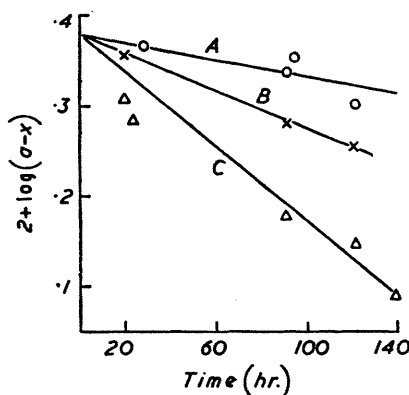*Inset: Linear relation of k_{OH^-} and reciprocal of dielectric constant (D).*

FIG. 4. *Catalysis by hydrogen ions, at 25°.* (A) N-HNO$_3$; (B) 0·2N-HNO$_3$. $\bigcirc$, $\triangle$ *Duplicate experiments.*

FIG. 5. *Catalysis by acetic acid–acetate buffer, at 25°. Ionic strength 0·10; pH 4·65. A, Unbuffered (pH 4·6); B, 0·02N-acetic acid; C, 0·06N-acetic acid.*

allowing for the reverse reaction as above do not differ significantly from those derived by simple first-order treatment of the early part of the curve. The approximate value of k_{H^+} is 1×10^{-3} l. mole^{-1} sec.$^{-1}$.

Catalysis by Acetic Acid.—The results in Fig. 5 show catalysis by acetic acid–sodium acetate buffer solutions. In view of the value derived for the catalytic coefficient for piperidine,

catalysis by acetate ions which are much more weakly basic may be presumed negligible. An approximate value of $k_1^{HAc} = 2 \cdot 2 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ was derived. From a similar series of experiments on the decomposition of hydroxymethylurea in acetate buffers a value for the catalytic coefficient for acetic acid $k_2^{HAc} = 4 \cdot 3 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ was derived though it is not certain that the effect of the acetate ions is negligible in this case. Thus $k_1^{HAc}/k_2^{HAc} \sim 2$: it appears that consecutive-reaction treatment would be required under all conditions of reaction in acid solution.

DISCUSSION

In alkaline solution, in the presence of cyanide, the reverse reaction (2) can be neglected; the concentration of hydroxymethylurea is at all times small and the reverse reaction (1) is also negligible. The system then comprises only consecutive, irreversible, first-order reactions.

For such a system, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where $k_2 = \alpha k_1$, it can be shown that

$$[C]_t = [A]_0 \left\{ 1 + \frac{1}{1-\alpha} (\alpha e^{-k_1 t} - e^{-\alpha k_1 t}) \right\}$$

It was found that when $\alpha = 3$, a plot of log $(1 - [C]_t)$ against t is concave to the t axis. At $\alpha = 11$, the curvature persists but is so slight that it would be imperceptible experimentally. In the present case, in the conditions in which the overall rate constant is calculated in Table 1 to be $1 \cdot 57 \times 10^{-4}$ sec.$^{-1}$, the rate constant of reaction (2) is calculated from the results of de Jong and de Jonge [1a] to be $1 \cdot 02 \times 10^{-2}$ sec.$^{-1}$: hence $\alpha = 65$. Reactions (3) and (4) are even faster. From the results of Brdička [6] on the rate of dehydration of formaldehyde, together with the value for the equilibrium constant for reaction (3) determined by Biebler and Trümpler,[7] it appears that the catalytic coefficient for the hydration of formaldehyde at 20°, k_{OH^-}, is $5 \cdot 8 \times 10^7$ l. mole^{-1} sec.$^{-1}$: hence $k_3 = ca.\ 3 \times 10^7$ sec.$^{-1}$. No quantitative information is available about the rate of reaction (4) but it is certainly faster than reaction (2), for it is complete within a minute under analytical conditions whilst 15 min. is necessary for the complete decomposition of hydroxymethylurea under similar conditions. Thus reaction (1) is the rate-determining reaction.

As has been seen above, the rates of reactions (1) and (2) are similar under acid conditions. The case of two consecutive first-order reactions with a second-order reverse reaction does not appear to have been treated in the literature.

The differential equation for the concentration, y, of formaldehyde is of the form

$$dy/dt + f(t)y + ay^2 + g(t) = 0$$

where $f(t)$ and $g(t)$ are functions of t and a is constant. This is a form of Ricatti's equation which can be integrated. However, no rigorous method of evaluating k_1 from the data has been found.

It has been conclusively shown that the hydrolysis of methoxymethylurea is subject to general acid–base catalysis; in this respect the reaction resembles the decomposition of hydroxymethylurea but differs from the condensations between amino- and hydroxymethyl groups which are catalysed specifically by hydrogen ions.[1b] This observation of course implies that the etherification of hydroxymethylurea will be subject to general acid–base catalysis.

EXPERIMENTAL

Hydroxymethylurea was prepared by Walter and Gewing's method [8] except that it was advisable to reduce the amount of potassium hydroxide and to dry the material in a vacuum-desiccator over silica gel. The hydroxymethylurea was recrystallised by dissolution in methanol at $\not> 40°$, followed by cooling in solid carbon dioxide–methanol. The recrystallised material melted sharply at 110° [Found : $CH_2 \cdot OH$ (hypoiodite method [9]), 35·8; N, 30·2. Calc.

[6] Brdička, *Coll. Czech. Chem. Comm.*, 1955, **20**, 387.
[7] Biebler and Trümpler, *Helv. Chim. Acta*, 1947, **30**, 1860.
[8] Walter and Gewing, *Kolloid-Beih.*, 1931, **34**, 163.
[9] Walker, " Formaldehyde," Reinhold, New York, 2nd. Edn., 1953, p. 385.

for $C_3H_6O_2N_2$: CH_2·OH, 34·4; N, 31·1%]. Fresh preparations dissolved rapidly in methanol and in water, but the solid deteriorated on storage, becoming partially insoluble in methanol and dissolving only slowly in water.

Methoxymethylurea.—Of the suggested methods [2] of preparation that preferred [2b] uses oxalic acid as catalyst which is neutralised by barium hydroxide after dissolution of the hydroxymethylurea. The ether separates on cooling in solid carbon dioxide–methanol and may be recrystallised after dissolution in methanol at room temperature. It then has m. p. 90° (Found : N, 27·25. Calc. for $C_3H_8O_2N_2$: 26·9%). Solid methoxymethylurea was also liable to deteriorate.

Determination of Free Formaldehyde.—The mercuric cyanide method [10] was used to determine free formaldehyde which could usually be equated to hydroxymethylurea under the conditions of the experiments. An indicator consisting of 0·5 g. of diphenylcarbazone per 100 ml., screened with 0·12 g. of Kiton Pure Blue V (C.I. 672) per 100 ml., in 95% ethanol was used.

To 0·1N-potassium cyanide (10 ml.), a sample containing formaldehyde (*ca.* 0·5 mmole) is added, followed by the indicator (8 drops) (brown colour). The solution is acidified to pH about 2 by 2N-nitric acid (apple-green colour : blue-green shade indicates insufficient acid; yellow, excess). The solution is *immediately* titrated with 0·025N-mercuric nitrate. As the end-point is approached the solution is decolorised and, at the end-point, a violet colour is produced which is permanent for at least 3 min. A small blank is required. Mercuric nitrate is standardised against sodium chloride, and potassium cyanide against the mercuric nitrate. Red rubber tubing is not suitable for use with apparatus containing mercuric nitrate solutions but polyvinyl chloride may be used.

Kinetic Experiments.—A solution containing the requisite quantities of methoxymethylurea and potassium cyanide was allowed to attain the working temperature. Experiments were started by running in the requisite amount of sodium hydroxide solution. No free formaldehyde could be titrated in neutral solutions of methoxymethylurea until 2 days after their preparation. Samples were withdrawn at suitable intervals by a pipette fitted with a detachable pipette pump, run into a flask containing the indicator, and acidified immediately.

First-order rate constants were read as the gradients of plots of log $(a - x)$ against t, where a is the initial ether concentration and x the decrease in cyanide concentration.

Mr. K. Anderson assisted with the experimental work.

[10] *Op. cit,* p. 388.