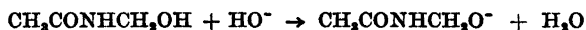


Kinetics of the Base-catalysed Reaction between Acetamide and Formaldehyde and the Ionization Constants of Formaldehyde and Hydroxymethylacetamide

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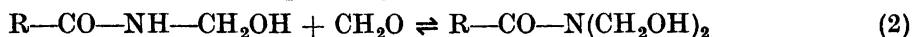
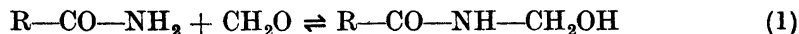
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The rate of formation of hydroxymethylacetamide from acetamide and formaldehyde has been measured in aqueous solution at different sodium hydroxide concentrations. The second-order rate constant approaches a limiting value as the concentration of sodium hydroxide is increased. At a constant alkali concentration, the second-order rate constant decreases as the formaldehyde concentration is increased, but a change in the acetamide concentration does not alter the rate constant. The same applies to the reverse reaction. From these results it has been deduced that only the hydroxymethylacetamide and formaldehyde hydrate anions formed in the alkaline solution react. The ionization constants of hydroxymethylacetamide ($K_a = 6.0 \times 10^{-14}$) formaldehyde ($K_a = 8.5 \times 10^{-14}$), both at 20°, have been calculated from the kinetic data. The second-order rate constant of the reaction between acetamide and formaldehyde anion, $k_2 = 0.085 \text{ l mole}^{-1}\text{sec}^{-1}$, and the first-order rate constant of the opposing reaction of hydroxymethylacetamide anion, $k_1 = 3.72 \times 10^{-3} \text{ sec}^{-1}$ were obtained by an extrapolation method. From measurements made at different temperatures, the heat of the reaction



has been found to be about 1.1 kcal. The parameters of the Arrhenius equation for the formation of acetamide and formaldehyde from the hydroxymethylacetamide anion are $E = 21.8 \text{ kcal.}$ and $\log A = 13.8$.

Two different hydroxymethylamides are formed in the reaction between formaldehyde and an acid amide:



Both reactions proceed until an equilibrium state is reached and are catalysed by various acids and bases ¹⁻³. The reaction between acetamide and formaldehyde was studied kinetically by Grove and Lynch ⁴. From polarographic

studies they deduced that formaldehyde, which in neutral and dilute aqueous solution is known to be almost completely in the form of a hydrate (99.99 %) ⁵, is dehydrated in the presence of alkali, and concluded that formaldehyde reacts with acetamide only in the dehydrated form. Their value for the heat of dehydration (4 kcal.) differs considerably from the value (14.6 kcal.) obtained by Bieber ⁵.

The similar reaction between urea and formaldehyde has been studied by several authors. de Jong and de Jonge ³ found that the reaction rate is proportional to the hydroxyl and hydrogen ion concentrations of the medium. They believed that in alkaline solution urea forms an anion $\text{NH}_2\text{—CO—NH}^-$ which reacts with formaldehyde to form the hydroxymethylurea anion. A similar mechanism has been proposed by Okano and Ogata ⁶ who studied the reaction between melamine and formaldehyde, whereas Grove and Lynch ⁴ concluded that the amide anion is unable to react with formaldehyde. Iliceto ² determined the equilibrium constants of the reactions 1 and 2 for various acid amides. At 20° the values for acetamide were found to be 28.2 and 0.117, respectively, and the equilibrium constant remained unchanged over a wide range of pH (7—13.5) and concentration (0.05—6 M). In dilute solutions of formaldehyde and acetamide, the formation of bishydroxymethylacetamide can be neglected. In order to study the role of alkali as catalyst in the reaction between acetamide and formaldehyde, the present author has carried out further kinetic measurements of the reaction.

EXPERIMENTAL

Materials. Acetamide (Merck, purum grade) was purified by crystallization from hot ethanol. Aqueous solutions of formaldehyde were prepared by dissolving paraformaldehyde (Merck, purum grade) in boiling water and filtering after cooling the solution. Hydroxymethylacetamide was prepared according to Einhorn ¹ from acetamide and formaldehyde. The product (m. p. 51°) contained 0.98 mole of methylol and 0.01 mole of free formaldehyde per 89 g (the molecular weight) of hydroxymethylacetamide when analysed by the hypiodite and sulphite methods. The sodium hydroxide solutions were prepared by dilution from a carbonate-free 1:1 mixture with water.

Analytical. Free formaldehyde was determined using the sulphite method ³ and the amount of free and bound (as methylol) formaldehyde with the hypiodite method ³.

A volume of aqueous sodium sulphite solution which contained about twice the amount of sulphite corresponding to the amount of formaldehyde in the sample was added to the latter. The solution of sulphite also contained the calculated amount of sulphuric acid required to reduce the pH of the final mixture to about 6. After standing for about 30 minutes, the solution was acidified to pH 4 by introducing 3 ml of 1 M acetic acid, and the excess of sulphite titrated with 0.1 N iodine solution. Ten ml of 1 M sodium carbonate were then added and the liberated sulphite was titrated with the same iodine solution using starch as indicator. This latter titration gives the amount of free formaldehyde present in the sample. The method was checked with the aid of hydroxymethylacetamide which was not found to decompose to any appreciable extent in the sulphite solution during periods varying from 30 to 120 minutes. Determinations made on formaldehyde solutions in the concentration range involved in the experiments showed that a standing period of about 30 minutes is sufficient for the formaldehyde-sulphite reaction to go to completion.

In the hypiodite method 4 ml of 2.5 N sodium hydroxide and 15 ml of 0.1 N iodine solution were added to a sample of 10 ml. After a period of about 15 minutes, the mixture was acidified by adding 10 ml of 1.1 N sulphuric acid, and the excess of iodine was titrated with 0.025 N thiosulphate. The consumption of iodine corresponds to the free

formaldehyde and the methylol groups present. From the data obtained with both methods, the concentration of hydroxymethylacetamide can be calculated. When the hypiodite method was checked with hydroxymethylacetamide, uniform results were obtained with different standing periods varying from 10 to 60 minutes. Methylenebisacetamide underwent no detectable decomposition in the hypiodite solution during periods up to 30 minutes, and only some 0.5% formaldehyde was formed after 60 minutes. Thus if condensation of methylol and acetamide to methylenebisacetamide occurs, it would be detected as a decrease in the hypiodite titration value. No such decrease was observed when samples were titrated after a reaction period about 20–40 times the half-life.

When a solution of formaldehyde was analysed using both methods, the hypiodite method gave somewhat higher results (about 1.5%) than the sulphite method. As no reason could be found for the different results, the same solution was also analysed using the cyanide method of Pfeil and Schroth⁷. The results obtained were similar to those obtained by the sulphite method (about 0.5% lower), which is therefore believed to give the best values. The effect of the error in the analytical method is negligible when calculating rate constants but the values obtained for equilibrium constants are probably some 5% too high.

As the hypiodite titration value is not altered during the experiment, the slow Cannizzaro reaction of formaldehyde in alkaline solution can be neglected⁸. Other reactions such as the hydrolysis of acetamide and hydroxymethylacetamide probably occur to some extent during the experiment. The amount of ammonia and acetic acid liberated in a reaction mixture containing initially 0.01 mole of hydroxymethylacetamide and 0.01 mole of sodium hydroxide per litre was about 4% during 1 000 minutes (20 times the half-life of the reaction studied) at 20° as determined by potentiometric titration. During the main part of the reaction, the hydrolysis could thus be neglected, but in the determination of the equilibrium constant, a small error results.

Calculations. The kinetic experiments were performed in reaction vessels described by Tommila and Lindholm⁹. The temperatures of the thermostats were electrically controlled to about 0.02°. The reaction was arrested by introducing rapidly a calculated amount of sulphuric acid in order to reduce the pH to about 6 and sulphite to react with the formaldehyde in the mixture. As the reaction did not go to completion in any of the experiments, the equilibrium mixture was analysed after a reaction time of about 20 times the half-life.



$$-\frac{dM}{dt} = k_1M - k_2FA \quad (4)$$

$$k_1 = \frac{2.303}{t} \cdot \frac{M_0 - M_{eq}}{M_0 + M_{eq}} \log \frac{M_0^2 - MM_{eq}}{(M - M_{eq})M_0} \quad (5)$$

Starting from hydroxymethylacetamide (M), the first-order rate constant k_1 can be calculated¹⁰ using eqn. 5. M_0 denotes the initial methylol (hydroxymethylacetamide) concentration, M_{eq} the methylol concentration at equilibrium and M its concentration at time t ; F and A denote formaldehyde and acetamide, respectively.

The second-order rate constant k_2 for the reaction between acetamide and formaldehyde can be calculated using eqn. 6

$$k_2 = \frac{2.303}{t} \cdot \frac{M_{eq}}{F_0A_0 - M_{eq}^2} \log \frac{F_0A_0M_{eq} - M_0M_{eq}^2}{F_0A_0M_{eq} - F_0A_0M} \quad (6)$$

At equilibrium

$$K = \frac{k_2}{k_1} = \frac{M_{\text{eq}}}{F_{\text{eq}}A_{\text{eq}}} \quad (7)$$

and thus k_1 or k_2 can be calculated easily from the latter equation if one of them is known. Tables 1 and 2 contain two examples of the measurements. Usually a good constancy of the specific rate was obtained over a wide range of the reaction (10–90 %). The rate and equilibrium constants obtained are collected in Tables 3–5.

DISCUSSION

From Tables 3 and 4 it will be seen that the first- and second-order rate constants increase with increasing sodium hydroxide concentration, but no direct proportionality is observed. At high alkali concentrations, the constants

Table 1. The conversion of hydroxymethylacetamide (0.00976 M) into acetamide and formaldehyde in the presence of sodium hydroxide (0.0198 M) at 20°. 10-ml samples.

Time min	0.0125 M I ₂ ml	%	10 ⁴ k ₁ sec. ⁻¹
5	0.87	13.9	4.04
8	1.35	21.6	3.79
12	1.90	30.4	3.97
15	2.29	36.7	3.94
19.5	2.94	47.0	4.17
25	3.37	53.5	3.94
35	4.10	65.5	3.84
42.5	4.62	74.0	3.99
48	4.88	78.1	3.92
65	5.44	87.0	3.81
360	6.25	100	mean 3.95

Table 2. The reaction between acetamide (0.500 M) and formaldehyde (0.0507 M) in the presence of sodium hydroxide (0.0503 M) at 20°. 10-ml samples.

Time min	0.0500 M I ₂ ml	%	10 ⁴ k ₂ l mole ⁻¹ sec. ⁻¹
0	10.07	0	
0.25	8.57	16.2	217
0.50	7.18	32.2	219
0.75	6.16	42.1	215
1.00	5.24	52.1	219
1.25	4.63	58.5	212
1.50	4.04	65.0	211
2.0	3.04	75.8	215
3.0	1.94	87.7	215
30	0.80	100	mean 216

Table 3. The equilibrium constants $K = M/FA$, first-order rate constants and activation energies for the reaction: hydroxymethylacetamide \rightarrow acetamide + formaldehyde. The second-order rate constants for the reverse reaction have been calculated from $k_2 = k_1K$.

t°	Concentrations mole/litre				K l/mole	$10^4 k_1$ sec. ⁻¹		$10^3 k_2$ litres mole ⁻¹ sec. ⁻¹ .	E kcal
	initial		at equilibrium			found	calc.		
	NaOH	Methylol	Methylol	CH ₂ O and Acet- amide					
20°	0.00487	0.00501	0.00057	0.00444	29.0	0.952	1.07	0.635 0.635 0.493 2.49 5.30 5.19	
	0.0101	0.00986	0.00191	0.00795	30.2	2.10	2.09		
	0.0101	0.0486	0.0214	0.0272	28.9	1.71	1.73		
	0.0198	0.00976	0.00190	0.00787	30.6	3.95	3.90		
	0.0499	0.00980	0.00185	0.00795	29.2	8.55	8.50		
	0.0497	0.0491	0.0220	0.0271	29.9	7.87	7.40		
	0.197	0.00970	0.00168	0.00802	26.1	20.3	20.2		
	0.197	0.0479	0.00203	0.00276	26.6	19.5	19.3		
	0.579	0.00981	0.00154	0.00827	22.5	27.9	29.2		
	1.075	0.00983	0.00150	0.00833	21.6	31.5	32.2		
∞						37.2			
0°	0.0100	0.00500	0.00110	0.00390	72.4	0.175	0.166		
	0.0099	0.00985	0.00293	0.00692	61.2	0.162	0.160		
	0.0099	0.0485	0.0263	0.0222	53.4	0.140	0.132		
	0.0501	0.0100	0.00275	0.00725	52.4	0.669	0.686		
	0.0503	0.0483	0.0265	0.0217	56.2	0.554	0.569		
	0.202	0.00961	0.00232	0.00729	43.7	1.54	1.53		
	∞						2.64		
40°	0.0099	0.00985	0.00160	0.00825	23.5	20.0	20.2	20.5 20.9 21.2 21.8	
	0.0502	0.0100	0.00155	0.00845	21.7	88.2	87.9		
	0.202	0.00961	0.00126	0.00835	18.1	223	222		
	∞						441		
	∞								

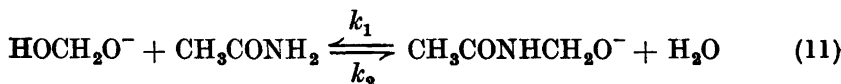
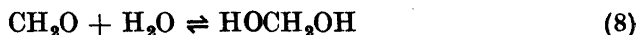
Table 4. The equilibrium constants K and second-order rate constants k_2 for the reaction: acetamide + formaldehyde \rightarrow hydroxymethylacetamide at 20°.

Concentrations mole/litre						K l/mole	$10^3 k_2$ litres mole ⁻¹ sec. ⁻¹ .	
initial		at equilibrium					found	calc.
NaOH	CH ₂ O	Acet- amide	Acet- amide	CH ₂ O	Methylol			
0.00985	0.00902	0.0500	0.0444	0.00443	0.00556	28.3	0.601	0.616
0.0502	0.0102	0.200	0.191	0.00166	0.00855	26.9	2.46	2.53
0.0501	0.0516	0.0500	0.0273	0.0289	0.0277	28.8	2.17	2.06
0.0503	0.0511	0.200	0.159	0.0100	0.0411	25.9	2.13	2.06
0.0502	0.0505	0.500	0.455	0.00407	0.0454	25.1	2.16	2.06
0.201	0.00947	0.200	0.192	0.00166	0.00834	26.2	5.44	5.31
0.201	0.0505	0.0500	0.0283	0.0287	0.0217	26.7	5.04	5.04
1.46	0.0505	0.0500	0.0294	0.0299	0.0206	23.4		
2.91	0.0505	0.0500	0.0307	0.0312	0.0193	20.1		
∞								8.50

Table 5. The mean values of the equilibrium constants K given in Tables 3 and 4, and the values of K' calculated from eqn. 21.

cNaOH mole/l	K obtained in experiments starting from				K' calculated 20°	ΔH kcal
	methylol			formaldehyde- acetamide 20°		
	0°	20°	40°			
0.01	57.3	29.6	20.8	28.3	21.0	4.24
0.05	54.7	29.6	19.2	26.6	20.5	4.47
0.1		28.3			23.2	
0.2	43.7	26.3	18.1	26.7	23.0	3.72
0.58		22.5			21.0	
1.08		21.6		23.4	21.6	
2.9				20.1	19.8	
					mean 21.4	mean 4.14

seem to approach a limiting value. At constant alkali concentration, an increase in the methylol or formaldehyde concentration decreases the rate constant k_1 or k_2 , respectively, but when the acetamide concentration is changed, the second-order rate constant remains unaffected. In order to explain these results, the following equilibria may be considered:



As already mentioned, in dilute aqueous solutions formaldehyde is almost completely in the hydrated form⁵. In strongly alkaline solutions a considerable proportion of the formaldehyde is present in the anion form¹¹. If only the anion form of formaldehyde or methylol reacts, a limiting rate constant should be obtained in concentrated alkali solutions. At different alkali concentrations, the rate should be proportional to the concentration of the anion in the solution.

$$K_1 = \frac{[\text{CH}_3\text{CONHCH}_2\text{OH}] \cdot [\text{HO}^-]}{[\text{CH}_3\text{CONHCH}_2\text{O}^-]} = \frac{(M-x)(B-x)}{x} \quad (12)$$

$$\text{If } B \gg x, \text{ then } B-x \simeq B \quad \text{and} \quad x = \frac{M \cdot B}{K_1 + B} \quad (13)$$

$$-\frac{dM}{dt} = k_1 x = k_1 \cdot \frac{B}{K_1 + B} \cdot M = k_{\text{exp}} \cdot M \quad (14)$$

$$\frac{1}{k_{\text{exp}}} = \frac{K_1}{k_1 B} + \frac{1}{k_1} \quad (15)$$

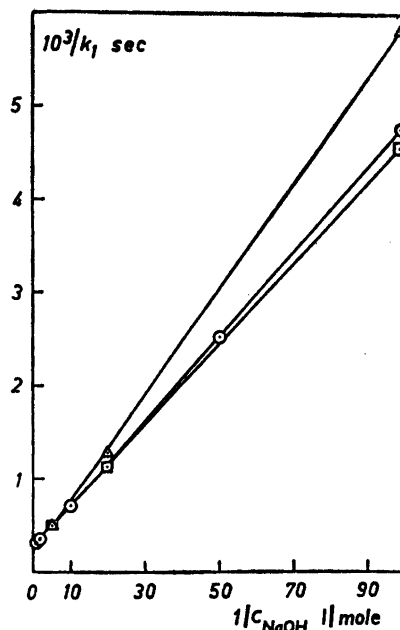


Fig. 1. Plot of the reciprocal of the first-order rate constant k_{exp} for the reaction: hydroxymethylacetamide \rightarrow acetamide + formaldehyde at 20° versus the reciprocal of the sodium hydroxide concentration (Equation 15). Δ $c_{methylol} = 0.05$ mole/l, \circ $c_{methylol} = 0.01$ mole/l, and \square rate constant values (k_{exp}) relating to zero methylol concentration.

where B and M denote the total concentrations of base and methylol and x the concentration of methylol anion, k_{exp} is the experimentally measured first-order rate constant and k_1 the first-order rate constant for the reaction 11. As the sodium hydroxide was used in excess, $B > M$ and K_1 is large, and hence the assumption made in calculating the amount of unionized methylol (eqn. 13) is justified. In Fig. 1, $1/k_{exp}$ is plotted against $1/B$. It will be seen that the curve approaches a straight line at high sodium hydroxide concentrations (Fig. 1, $\circ \Delta$). If the rate constants obtained at constant alkali concentrations are extrapolated to zero methylol concentration, all the points obtained lie on a straight line (Fig. 1, \square). This is what is expected because the assumption $B - x \simeq B$ is valid for the extrapolated values.

The first-order rate constant of the methylol anion k_1 and the equilibrium constant K_1 (of reaction 10) can be computed from the intercept and the slope of the line (Table 6). The ionization constant is easily obtained since $K_a = K_1 / K_w$. With aid of the value obtained for the equilibrium constant

Table 6. The equilibrium constants K_1 and K_2 of reactions 9 and 10 and the rate constants k_1 and k_2 of the reaction 11 calculated using eqn. 15.

$10^4 k_1 \text{ sec}^{-1}$			E kcal	$\log A$	$k_2 \text{ l mole}^{-1} \text{ sec}^{-1}$ 20°	$K_1 \text{ l/mole}$			ΔH kcal	K_2 l/mole 20°
0°	20°	40°				0°	20°	40°		
2.64	37.2	441	21.8	13.8	0.085	0.142	0.165	0.194	1.3	0.117

K_1 , the amount of methylol anion in any mixture of methylol and sodium hydroxide can be calculated. The corresponding rate constant is $k_1x/M = k_{\text{exp}}$ (eqn. 14). These calculated rate constants are given in Tables 3 and 4 and are found to be fairly close to the experimental values over more than a 200-fold range of sodium hydroxide concentration. A similar treatment of the second-order rate constant of the reverse reaction gives a limiting rate k_2 and equilibrium constant $K_2 = 0.117$ at 20° (Table 6). From a graph given by Martin¹¹ which contains values of K_2 obtained by different authors, a mean value $K_2 = 0.111$ is obtained which is fairly close to the above value.

No value was found in the literature for the acid ionization constant of acetamide. When the alkali concentration is held constant, the second-order rate constant remains unaffected when the concentration of acetamide is changed. Thus it is improbable that any detectable amounts of acetamide anion are formed in the reaction mixtures used and that this ion is involved in the reaction mechanism as stated by some authors^{3,6}.

$$K = \frac{[\text{CH}_3\text{CONHCH}_2\text{OH} + \text{CH}_3\text{CONHCH}_2\text{O}^-]}{[\text{CH}_3\text{CONH}_2][\text{HOCH}_2\text{OH} + \text{HOCH}_2\text{O}^-]} \quad (16)$$

$$K' = \frac{[\text{CH}_3\text{CONHCH}_2\text{O}^-]}{[\text{CH}_3\text{CONH}_2] \cdot [\text{HOCH}_2\text{O}^-]} \quad (17)$$

The equilibrium constant K calculated using the total methylol and formaldehyde concentrations without taking into account the ionization of these compounds decreases as the alkali concentration is increased (Tables 3–5).

Considering the two equilibria (eqns. 9 and 10)

$$K_1 = \frac{[\text{CH}_3\text{CONHCH}_2\text{OH}][\text{HO}^-]}{[\text{CH}_3\text{CONHCH}_2\text{O}^-]} = \frac{(M-x)(B-x-y)}{x} \quad (18)$$

$$K_2 = \frac{[\text{HOCH}_2\text{OH}][\text{HO}^-]}{[\text{HOCHO}^-]} = \frac{(F-y)(B-x-y)}{y} \quad (19)$$

it can again be assumed that $B-x-y \simeq B$. Then

$$x = \frac{MB}{K_1 + B} \quad \text{and} \quad y = \frac{FB}{K_2 + B} \quad (20)$$

$$K' = \frac{x}{Ay} = \frac{M}{F \cdot A} \cdot \frac{K_2 + B}{K_1 + B} = K \frac{K_2 + B}{K_1 + B} \quad (21)$$

where M , F , A and B denote the total concentrations of methylol, formaldehyde, acetamide and sodium hydroxide. According to eqn. 21, K' can be calculated for different sodium hydroxide concentrations from the experimental values of K obtained using total formaldehyde and methylol concentrations by substituting for K_1 and K_2 the values 0.165 and 0.117 obtained from the kinetic measurements at 20° (Table 6). These calculated K' values which are given in Table 5 are fairly constant (mean value $K' = 21.4$) although the K values change considerably when the alkali concentration is altered. The value $K = 22.8$ is obtained from the extrapolated rate constants: $k_2/k_1 =$

$8.5 \times 10^{-2}/3.72 \times 10^{-3}$ (Table 6). This is a further proof that the values of the ionization constants obtained for formaldehyde and methylenebisacetamide from kinetic experiments are of correct order of magnitude. At low alkali concentrations (below 0.05 mole/l) K would be expected to remain fairly constant, as has been found to be the case by several authors *e. g.* Ref.³

From the values for different temperatures it will be seen that the unionized form of hydroxymethylacetamide is favoured at higher temperatures, a value of about 1.3 kcal being obtained for the heat of the ionization reaction. Because of this pre-equilibrium (eqn. 10), the activation energy calculated for the reaction 11 does not remain constant when the concentration of alkali is changed (Table 3). The difference between the apparent activation energy obtained for the reaction at low alkali concentrations and the value obtained using the k_1 values for the reaction of the methylol ion (about 1.3 kcal) should be close to the heat of reaction 10 (1.3 kcal).

The energy of activation for the reaction, calculated using the k_1 values given in Table 6, is 21.80 kcal and the frequency factor $A = 7 \times 10^{13}$ which is close to the predicted value for unimolecular reactions¹⁰. In order to estimate the value of activation energy for the reverse reaction of methylol formation from acetamide and formaldehyde, the heats of the reactions should be of the same order of magnitude. From the value $K_2 = 0.134$ at 40° given by Martin¹¹ and the above value $K_2 = 0.117$ at 20°, the value $\Delta H_2 = 1.2$ kcal is obtained which is close to value $\Delta H_1 = 1.3$ kcal (Table 6). Thus using the mean value obtained for the heat of reaction 11, $\Delta H = 4.14$ (Table 5), it is found that $E_2 = E_1 - \Delta H = 17.7$ kcal and $A = 1.6 \times 10^{12}$.

All the results obtained show clearly that the reaction between formaldehyde and acetamide occurs in alkaline solution between the anion of formaldehyde hydrate and acetamide (eqn. 11). Similarly, in the reverse reaction, it is the methylol anion that undergoes change. In order to determine whether any reaction occurs between the uncharged molecules, an aqueous solution of hydroxymethylacetamide was kept for several weeks at 20°, but no formaldehyde was found to be liberated. The reaction of the methylol anion is thus at least 10^6 times faster than the reaction of unionized methylol.

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