Acta Chemica Scandinavica B 38 (1984) 563–565

Effect of pH and NaOAc-buffer Concentration on the Rate of the hydrolytic decomposition of *N*,*N'*-bis(methoxymethyl)urea

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The stability of *N*,*N'*-bis(methoxymethyl)urea in aqueous 0.053 M NaOAc solution at 50 °C was studied. The rate of hydrolysis varied with the pH of the solution, the maximum stability being around pH 8. The hydrolysis reaction was found to be catalyzed not only by H^+ and ^-OH but also by the undissociated acid when NaOAc was used as buffer.

N,*N'*-bis(methoxymethyl)urea (BMMU) can be copolycondensated with monohydric alcohols to yield polymers, useful as binders in surface coatings.[1] The *N*-alkoxymethyl side groups of these polymers can decompose *via* hydrolysis, which leads to unfavourable changes in the polymers in aqueous solutions.[2] The aim of this study was to find the optimum pH value for the aqueous polymer solutions regarding the stability of their *N*-alkoxymethyl groups by investigating the hydrolytic decomposition of BMMU as a model reaction. The hydrolysis of BMMU leads at first to the formation of *N*-methoxymethyl-*N'*-hydroxymethylurea [eqn. (1)].[3] Further reactions also lead to the splitting of the second methoxymethyl group and finally, formaldehyde is liberated in the decomposition of hydroxymethyl groups. Information available on the hydrolysis of BMMU is very scarce. Petersen[4] has measured the rate constant for the reaction in eqn. (1) in the pH region below 5.5, where the decomposition of BMMU is very fast. Only one value of the rate constant for the alkaline hydrolysis of BMMU (at pH 11.9 and 35 °C) has been reported.[3] Sobue[5] *et al.* and Murakami[6] *et al.* have studied the equilibrium of the reactions of methanol and ethanol with *N*,*N'*-bis(hydroxymethyl)urea and the monoalkyl ether of this compound. Rates for these etherification reactions were not measured, however. Ugelstad and de Jonge[3] have studied the hydrolysis of monomethoxymethyl urea at pH level 11–12 (25 °C) and Nordhoy and Ugelstad[7] in acid solutions. The reaction was found to be catalyzed both by H_3O^+ and ^-OH.

RESULTS AND DISCUSSION

The hydrolytic decomposition of BMMU as described in eqn. (1) was studied at 50 °C. The pH of the reaction mixtures was varied in the range 6–9, because the maximum stability of BMMU solutions was expected to be found near neutral conditions. Sodium acetate (0.053 M) was used as buffer to avoid drift in pH of the reaction mixtures. Any contribution of the reverse reaction was minimized by using a low concentration of BMMU and by following the decomposition only to low conversion. The progress of the hydrolysis reaction was monitored by high performance liquid chromatography, which enabled the direct measurement of the unreacted BMMU.

As could be expected, both hydroxonium and hydroxide ions catalyzed the hydrolysis of BMMU (Fig. 1). The reaction was distinctly faster in acidic conditions.

$$CH_3OCH_2NHCONHCH_2OCH_3 + H_2O \xrightleftharpoons{k} CH_3OCH_2NHCONHCH_2OH + CH_3OH \qquad (1)$$

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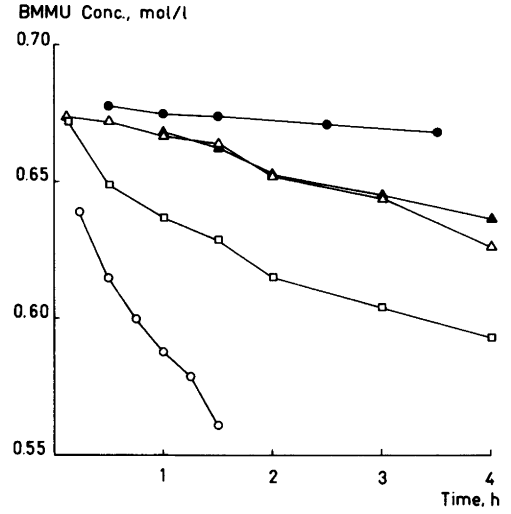

Fig. 1. Hydrolysis of BMMU at 50 °C. NaOAc (0.053 mol/l) as buffer. pH of solutions: 6.0 (○), 6.5 (□), 7.0 (△), 8.0 (●), 9.0 (▲).

In order to study the effect of pH on the hydrolysis rate in detail, the data in Fig. 1 were analyzed further by assuming irreversible second order kinetics [eqn. (2)] for the decomposition

$$-\frac{d[\mathrm{BMMU}]}{dt} = k[\mathrm{BMMU}][\mathrm{H_2O}] \qquad (2)$$

reaction [eqn. (1)]. The aim of this treatment was not to verify any suggestions about the reaction mechanism but to create a model that could be used in searching for the maximum stability of BMMU in aqueous solutions. By denoting the ratio of the initial concentrations of H_2O and BMMU (Bo, mol/l) by M and the conversion of BMMU by X, the integration of eqn. (2) yields

$$\frac{1}{B_0}\left(\frac{1}{M-1}\right)\ln\left(\frac{M-X}{M(1-X)}\right) = kt \qquad (3)$$

eqn. (3). The rate constants were obtained by fitting the experimental results to eqn. (3) by the method of least squares (Table 1). The fit of the data with the rate equation can be considered quite good in most of the experiments (Fig. 2). The optimum conditions regarding the hydrolytic stability of BMMU at 50 °C was found to be in the alkaline region around pH 8 (Fig. 3).

The mechanism involving a general acid catalysis has been observed in hydrolysis of methoxymethyl derivatives of cyclic substituted ureas.[8] Also Nordhoy and Ugelstad[7] regard this mechanism most probable in the hydrolytic decomposition of monomethoxymethyl urea in the presence of NaOAc, although they could not observe it in their studies in the pH range 4–5. The effect of buffer on the reactivity of BMMU was tested by carrying out the hydrolysis experiments at the constant pH value of 7 in the presence of various concentrations of sodium acetate (NaOAc). The results (Fig. 4) show the catalytic effect of NaOAc revealing the evidence for the general acid and base catalysis in the hydrolysis of BMMU.

Table 1. Reaction rate constants.[a]

pH	k (l/mol min	R^b
6.0	3.18×10^{-5}	0.994
6.5	0.990×10^{-5}	0.964
7.0	0.626×10^{-5}	0.986
8.0	0.137×10^{-5}	0.978
9.0	0.537×10^{-5}	0.989

[a] At 50 °C, in presence of NaOAc 0.053 mol/l.
[b] Correlation coefficient.

EXPERIMENTAL

Hydrolysis experiments. BMMU (10 g, 0.067 mol) was weighed into a 100 ml measuring flask

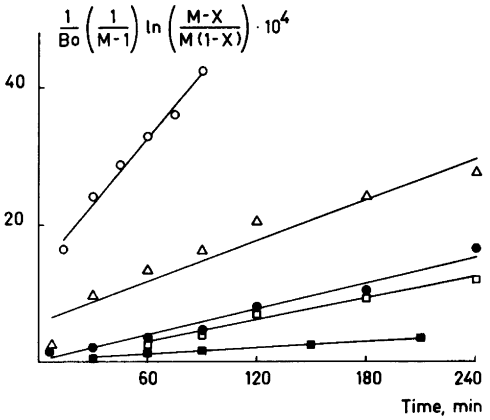

Fig. 2. Fit of the experimental results with the used rate equation. Points: ○ (pH=6), △ (pH=6.5), ● (pH=7), ■ (pH=8), □ (pH=9). Solid lines represent calculated values.

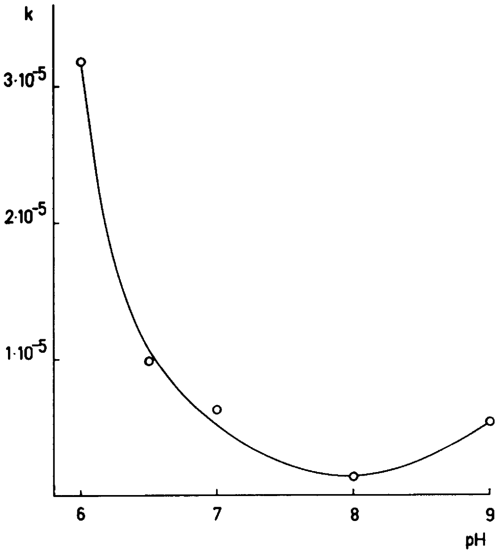

Fig. 3. Effect of pH on the rate constant of the hydrolysis of BMMU at 50 °C. NaOAc 0.053 mol/l as buffer.

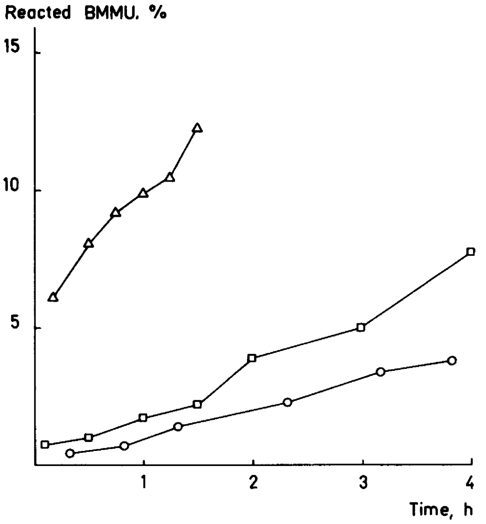

Fig. 4. Effect of buffer concentration on hydrolysis of BMMU at 50 °C and at constant pH of 7.0. Buffers: none (○), NaOAc 0.053 mol/l (□), NaOAc 0.54 mol/l (△).

and immersed in a water bath at 50 °C. The weighed amount of sodium acetate in 40 ml of 50 °C water was added and after the complete dissolution and adjustment of the pH by dilute NaOH- or HCl-solutions, the flask was topped up with water, weighed and the mixture transferred into a 3-necked flask provided with a magnetic stirrer and a pH-electrode. The transfer of the reaction mixture was taken as the zero time for the kinetic measurements.

Analysis. 0.5 ml samples were weighed and diluted with water in 50 ml measuring flasks. Equal volumes of the solution and the internal standard (0.2 mg/ml phenol in water) were mixed and analyzed by liquid chromatography.

Chromatography. A Varian 5020 liquid chromatograph, (Varian Aerograph, Walnut Creek, CA, U.S.A.) equipped with a Perkin-Elmer LC-75 variable wavelength UV–VIS detector (Perkin–Elmer Oak Brook, IL, U.S.A.) set at 200 nm, a Valco loop injector (15 μl) and a self-packed Spherisorb 10 ODS (Phase Separations, Deeside Industrial Estate, CLWYD, GB) 250×I.D. 4.6 nm column was used for the chromatographic separation and detection of the compounds. The samples were eluted with pH 7 buffered acetonitrile-water (5:95 v/v) mixture at 2 ml/min at ambient conditions. BMMU eluted at *ca.* 2 and phenol at 6 min. Quantitative results were obtained by manual peak height measurements using the internal standard method. Standard deviation was <1 %.

Reagents. BMMU was synthesized as described elsewhere.[1] The compound was purified by repeated crystallization until the chromatographic analysis yielded only a single peak. The product melting at 100.5–101 °C was used in experiments. Other chemicals were of *pro analysi* grade and used as such.

Acknowledgement. We thank Arja Kerttula for technical assistance and extraordinary patience during the work.

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Received September 8, 1983.