

SYNTHESIS OF N-HYDROXYMETHYLACRYLAMIDE IN AN AQUEOUS SOLUTION

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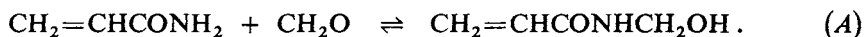
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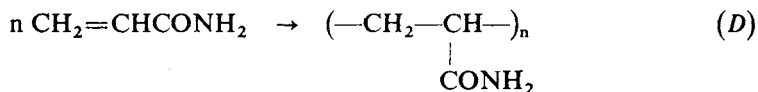
The paper deals with a reaction between acrylamide and formaldehyde leading to the synthesis of N-hydroxymethylacrylamide. The reaction was carried out in the temperature range 303.2 to 333.2 K, pH 9.2–10.35, at the methanol concentration 0–6.5239 mol l⁻¹ at the constant molar ratio of acrylamide to formaldehyde 1 : 1. The time dependence of the loss of formaldehyde in the reaction mixture was approximated by an empirical relation $(c_F)_0 - c_F = t/(A + Bt)$, which was used in the determination of the rate constants for a reaction leading to the synthesis of N-hydroxymethylacrylamide and for the reversible reaction, and of the equilibrium constant of the reaction. The measurements and calculations showed that the optimal conditions for the synthesis of N-hydroxymethylacrylamide were 313.2 K, methanol concentration 1.5 mol l⁻¹ and pH 9.8–10.1.

N-hydroxymethylacrylamide is of basic importance in the synthesis of thermoreactive polyacrylates, due to the fact that copolymers crosslinked with this monomer possess very good functional properties¹.

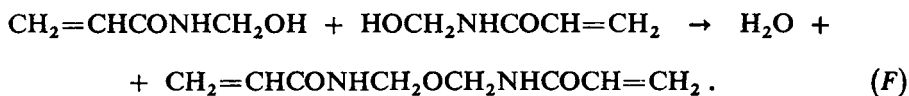
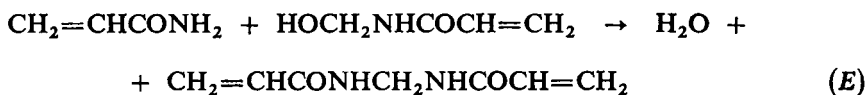
N-Hydroxymethylacrylamide can be synthesized by using a number of procedures². The procedure most commonly in use is its preparation in an aqueous solution by reacting acrylamide with aqueous formaldehyde in the presence of an alkaline catalyst:



The reactions



can be regarded as important side reactions. Some other possible reactions of the system components may also be considered, such as



We tried to determine the rate constants and the equilibrium constant for reaction (A) in order to quantify the effect of temperature, of pH of the reaction medium and of the methanol concentration in the reaction mixture, bearing in mind that under the experimental conditions used, *i.e.*, the presence of methanol in the reaction mixture, relatively low reaction temperatures, the presence of the polymerization inhibitor (NaNO_2) and at $\text{pH} > 7$ (reactions (E) and (F) were unlikely to occur) side reactions are suppressed to the highest possible extent. Our work was based on findings reported by Ugelstad and De Jonge³ for the reaction between formaldehyde and benzamide. These authors regard the reaction leading to the hydroxymethyl derivative as bimolecular and describe it in terms of relations valid for a second-order reaction; the reversible reaction is regarded as monomolecular. Reactions of a similar type may be encountered also in the reactions between urea and formaldehyde⁴, and between dicyanodiamide and formaldehyde⁵. Unlike the authors just mentioned, who determine the reaction parameters by using experimental data from the initial stage of the reaction and their graphic evaluation, we decided to use the whole conversion curve in the determination of the rate constants and of the equilibrium constant, by means of approximation by an empirical function⁶. If c_A is the concentration of acrylamide, c_F that of formaldehyde and c_p is the concentration of the product (N-hydroxymethylacrylamide), then the rate of formation of the adduct may be expressed as

$$v = -\left(\frac{dc_A}{dt}\right) = -\left(\frac{dc_F}{dt}\right) = \left(\frac{dc_p}{dt}\right) = k \cdot c_A^a \cdot c_F^b, \quad (1)$$

where a, b is the reaction order with respect to the individual reaction components. Under the experimental condition $(c_A)_0 = (c_F)_0$, we have $c_A = c_F$ and

$$v = k \cdot c_F^{(a+b)}. \quad (2a)$$

With the side reactions suppressed, it may be assumed that $a + b = 2$, and thus,

$$v = k \cdot c_F^2. \quad (2b)$$

Since $c_p = (c_F)_0 - c_F$, for reaction (A) we obtain

$$\frac{d[(c_F)_0 - c_F]}{dt} = k \cdot c_F^2 - k' \cdot [(c_F)_0 - c_F], \quad (3a)$$

or

$$- \left(\frac{dc_F}{dt} \right) = k \cdot c_F^2 - k' \cdot [(c_F)_0 - c_F]. \quad (3b)$$

After separation of variables and assuming that

$$-4k \cdot k' \cdot (c_F)_0 - k'^2 < 0, \quad (4)$$

which is satisfied in our case, we obtain by integration

$$[t]_t^0 = \left[\frac{1}{\sqrt{[4kk' \cdot (c_F)_0 + k'^2]}} \ln \left| \frac{2kc_F + k' - \sqrt{[4kk' \cdot (c_F)_0 + k'^2]}}{2kc_F + k' + \sqrt{[4kk' \cdot (c_F)_0 + k'^2]}} \right| \right]_{(c_F)_0}^{c_F}. \quad (5)$$

The reaction path may be described by an empirical function

$$(c_F)_0 - c_F = \frac{t}{A + Bt}, \quad (6)$$

which can be linearized in the coordinates $y = t/[(c_F)_0 - c_F]$, $x = t$, and differentiated:

$$\frac{d[(c_F)_0 - c_F]}{dt} = \frac{1}{A + Bt} - \frac{Bt}{(A + Bt)^2}. \quad (7)$$

In this way, the reaction rate may be determined in any time point of the reaction; if, moreover, the concentrations of the reacting compounds in this point are also known, the rate constant can also be determined. For the onset of the reaction when $t \rightarrow 0$, Eq. (6) becomes

$$\frac{d[(c_F)_0 - c_F]}{dt} = \frac{1}{A}, \quad (7a)$$

hence, the rate constant is given by the relation $k = 1/A (c_F)_0^2$. For $t \rightarrow \infty$ relation (6) is reduced to

$$\lim_{t \rightarrow \infty} [(c_F)_0 - c_F] = \frac{1}{B}. \quad (7b)$$

With respect to reaction kinetics this limit is important in that we may put

$$\lim_{t \rightarrow \infty} \frac{d[(c_F)_0 - c_F]}{dt} = 0 \quad (8)$$

and, with respect to Eq. (3a) at $t \rightarrow \infty$,

$$k \cdot c_F^2 = k'[(c_F)_0 - c_F]. \quad (9)$$

In this relation the concentration c_F has the value of the equilibrium concentration $(c_F)_R$, and for the equilibrium constant (K) of reaction (A) we have, therefore,

$$K = \frac{k}{k'} = \frac{(c_F)_0 - (c_F)_R}{(c_F)_R^2}, \quad (10)$$

where $(c_F)_0 - (c_F)_R = 1/B$, as follows from relation (7b).

By comparing the results using relations (5), (6), it may be ascertained how much the theoretical course of reaction (A) differs from the real course of the reaction between acrylamide and formaldehyde.

EXPERIMENTAL

Chemicals

Acrylamide (Am. Cyanamide Comp.), recrystallized from ethyl acetate, minimal content of the effective compound 99.5% by mass, formaldehyde (Moravian Chemical Works, Czechoslovakia), content of the effective compound 37% by mass. Methanol, sodium hydroxide and sodium nitrite were products of Lachema (Czechoslovakia); water was demineralized.

Reaction

The experiments were performed in a reactor consisting of 2 parallel cooling plates $150 \times 150 \times 10$ mm in size, made of metal sheet AKV-Extra S, 0.5 mm thick. A stirrer in the shape of a loop made of a wire AKV-Extra S, 1 mm in diameter, passing through the reactor lid, moved in the vertical direction. The lid was also provided with a Fe-constantan thermocouple covered with a teflon protective film. The reactor was placed in a thermostat, and the temperature inside the reactor was maintained with an accuracy of $\pm 0.2^\circ\text{C}$. The raw materials were introduced into the reactor by means of a syringe. At a chosen reaction time a sample of the reaction mixture was taken with a syringe, and immediately introduced into a flask cooled to 0°C . One part of the sample was used in the determination of free formaldehyde.

Analytical Methods

From the cooled sample of the reaction mixture, 0.5–2 ml (0.54–2.16 g) was pipetted into a flask cooled with ice and provided with an electromagnetic stirrer; 5 drops of thymolphthaleine and

10 ml of a similarly cooled solution of sodium sulfite (1 mol l^{-1}) were added, and the solution was immediately titrated while stirring with a solution of 1 M-HCl at the initial rate 1 ml/s until discolouration. This procedure allowed us to rule out the effect of forming hydroxide on the course of the addition, as was ascertained by a comparison with the procedure described by De Jong⁴, and later by Petersen and coworkers⁷, using a more complicated sulfite-iodometric method.

The polymerization reaction (if any) was checked by the determination of double bonds in the final sample using the bromide-bromate method⁸.

RESULTS

The reactions between acrylamide and formaldehyde were carried out each time at the initial equimolar ratio of the reaction components. The statistical characteristics of approximation of the time dependence of the reaction according to relation (6) are given in Table I. The results of the investigation of the reaction in the presence of methanol of various initial concentration, $[\text{MeOH}]_0$, and at constant temperature and pH allow it to be inferred that the approximation carried out in the particular

TABLE I

Constants used in approximation (6) of the course of formaldehyde concentration (F) in its reaction with acrylamide (A) under the condition $[\text{F}]_0 = [\text{A}]_0$. Statistical characteristics of approximation: r_{xy} correlation coefficient, s_{xy}^2 total scatter

Exp. No	Temperature, K	pH (± 0.05)	$[\text{MeOH}]_0$ mol l^{-1}	$A \cdot 10^{-1}$ mol $^{-1}$ ls	$B \cdot 10^2$ mol $^{-1}$ l	r_{xy}	$s_{xy}^2 \cdot 10^{-2}$
1	313.2	9.5	0	5.9234	19.426	0.9896	1.6987
2	313.2	9.5	1.2825	6.5505	19.241	0.9996	1.6164
3	313.2	9.5	3.1388	8.6999	19.825	0.9983	1.1116
4	313.2	9.5	4.8263	13.919	20.882	0.9895	10.943
5	313.2	9.5	6.5239	18.559	22.250	0.9893	20.703
6	303.2	9.5	1.2825	20.412	17.851	0.9997	10.564
7	313.2	9.5	1.2825	6.1866	18.871	0.9899	0.28621
8	313.2	9.5	1.2825	3.0559	19.117	0.9998	1.1536
9	313.2	9.5	1.2825	1.5467	19.311	0.9899	0.037292
10	323.2	9.5	1.2825	1.1136	20.061	0.9995	2.0875
11	333.2	9.5	1.2825	0.41552	20.408	0.9799	0.053626
12	310.2	9.2	1.6875	11.136	19.709	0.9898	5.6183
13	310.2	9.5	1.6875	10.707	19.656	0.9997	2.2655
14	310.2	9.8	1.6875	5.8487	19.241	0.9999	2.7244
15	310.2	10.1	1.6875	3.7119	19.048	0.9799	0.82294
16	310.2	10.1	1.6875	3.0593	19.241	0.9899	0.34353
17	310.2	10.2	1.6875	2.3199	19.534	0.9700	0.98168
18	310.2	10.35	1.6875	0.75243	19.780	0.9709	0.60131

experiments fits very well, judging by high values of the correlation coefficients. The reliability of determination decreases with increasing methanol content in the reaction mixture, due to the increasing total scatter. Even so, however, the value of the variation coefficient for the mean value of the reaction times does not exceed 1% under the condition of the highest chosen value of $[\text{MeOH}]_0$, when there is the highest total experimental scatter. The dependences of the rate constants (k for addition, k' for the splitting-off of formaldehyde) and of the equilibrium constant (K) of reaction (A) allow us to deduce (Fig. 1) that the best conditions for addition lie in the range about $[\text{MeOH}]_0$ 1.5 mol l^{-1} , when the K value reaches its maximum and the rate constant k' reaches the minimum.

At a constant starting methanol content in the reaction mixture ($1.2825 \text{ mol l}^{-1}$) and pH 9.5 the dependence of the logarithm of the rate constant on the reciprocal temperature value for the addition reaction (Fig. 2a) may be approximated by a straight line, the slope of which gives us the apparent activation energy of the reaction, $104.3 \text{ kJ mol}^{-1}$. The equilibrium constant increases with decreasing temperature (Fig. 2b), while the rate constant of the reversible reaction decreases with decreasing temperature (Fig. 2a). The synthesis of N-hydroxymethylacrylamide should take place at temperatures up to 310 K at most.

During the investigation of the effect of pH on the reaction course at 310.2 K and at the starting methanol concentration in the reaction mixture $1.6875 \text{ mol l}^{-1}$,

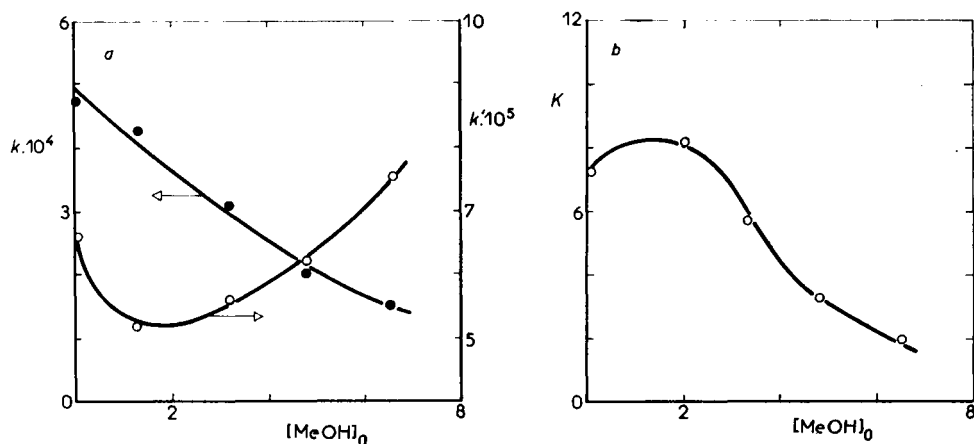


FIG. 1

Dependence (a) of the rate constant of addition (k) and splitting-off (k') of formaldehyde and (b) of the equilibrium constant (K) of the reaction between acrylamide and formaldehyde on methanol concentration in the reaction system (313.2 K, pH 9.5)

the pH value of the reaction mixture was measured at the beginning of the experiment and after its completion; the difference between these two measurements was not larger than 0.1 pH. As can be seen in the values in Table I, the approximations of the course of the individual experiments by means of relation (6) are satisfactory from the statistical standpoint; the maximal value of the variation coefficient at pH 9.2 is 2.5% for the reaction time 1 000 s. The rate constants k , k' steeply rise

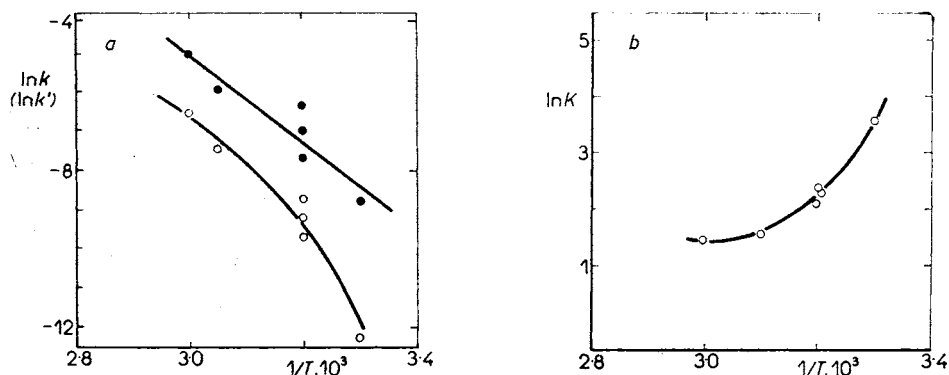


FIG. 2

Dependence (a) of the rate constant of addition (k) (points denoted with ●) and splitting-off (k') (points denoted with ○) of formaldehyde and (b) of the equilibrium constant (K) on temperature (pH 9.5, $[\text{MeOH}]_0 = 1.2825 \text{ mol l}^{-1}$).

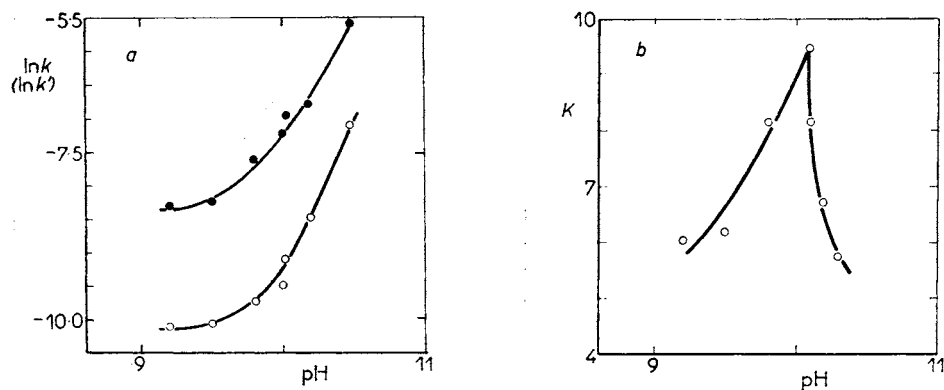


FIG. 3

Dependence (a) of the rate constant of addition (k) (points denoted with ●) and splitting-off (k') (points denoted with ○) of formaldehyde and (b) of the equilibrium constant (K) on pH (310.2 K, $[\text{MeOH}]_0 = 1.6875 \text{ mol l}^{-1}$).

starting from pH 9.8 (Fig. 3a). The equilibrium constant has a certain maximum in the pH range (9.8, 10.1) (Fig. 3b). From these data it may be deduced that the best pH range for the addition of formaldehyde is (9.8, 10.1).

A comparison between experimental data and those calculated using the theoretical relation (5) is shown in Fig. 4 as a correlation between calculated and determined reaction times, in those points where the same concentrations of the reactants were

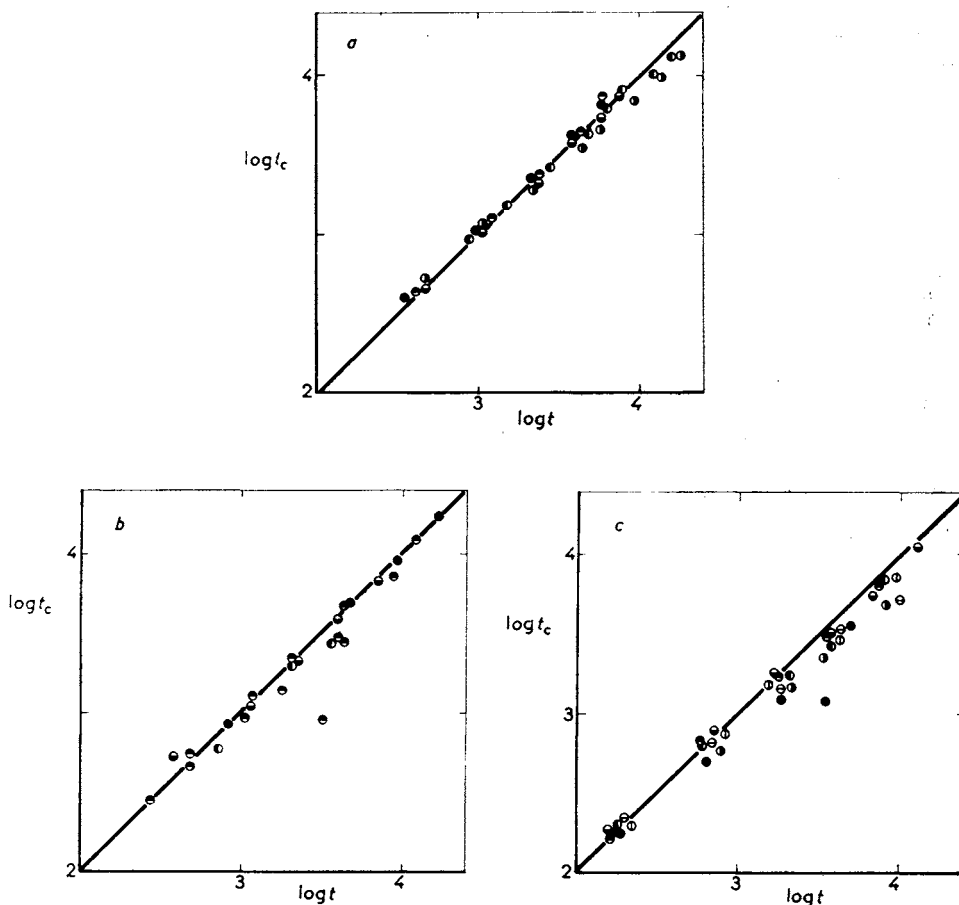


FIG. 4

Correlation of the reaction time measured ($\log t$) and calculated ($\log t_c$) according to Eq. (5) for experiments carried out at different (a) $[\text{MeOH}]_0$ (313.2 K, pH 9.5), (b) temperatures (pH 9.5, $[\text{MeOH}]_0 = 1.2825 \text{ mol l}^{-1}$), (c) pH (310.2 K, $[\text{MeOH}]_0 = 1.6875 \text{ mol l}^{-1}$). Assignment of points to experiments (No) in Table I: a) ● 1, ○ 2, ⊖ 3, ⊕ 4, ⊙ 5; b) ● 6, ⊖ 7 - 9, ⊖ 10, ⊙ 11; c) ● 12, ⊖ 13, ⊖ 14, ⊙ 15, ⊙ 16, ⊖ 17, ⊙ 18

reached in the reaction system. It may be concluded, from the distribution of experimental points about the diagonal, that the theoretical calculation relation (5) adequately describes the process of formation of N-hydroxymethylacrylamide at constant temperature and pH at various starting methanol concentrations in the reaction mixture (Fig. 4a) and at constant pH and $[\text{MeOH}]_0$ at different reaction temperatures (Fig. 4b). A somewhat poorer agreement between the correlated data is obtained in experiments at different pH values, where the difference may be as high as 12% (Fig. 4c).

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