

Kinetics of hydrolysis of methacrylamide sulfate in the medium of sulfuric acid

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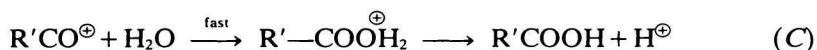
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The kinetics of hydrolysis of methacrylamide sulfate described in this paper was evaluated as a first-order reaction (with respect to methacrylamide) and this conclusion was compared with literature data concerning hydrolysis of other kinds of amides in the medium of concentrated sulfuric acid as well as with the results of numerical method of evaluation of measured data. The dependence of conversion rate on temperature and excess water was measured. The activation energy ($E = 86.2 \text{ kJ mol}^{-1}$), frequency factor ($A = 1.11 \times 10^{10} \text{ min}^{-1}$), and activation entropy were calculated. The results were confronted with literature data. It has been revealed that the value of rate constant increases with excess water (up to mole ratio acetone cyanohydrin $\text{ACH}:\text{H}_2\text{O} = 1:6$). The kinetic equation of the first order is valid up to mole ratio $\text{ACH}:\text{H}_2\text{O} = 1:4$. The reaction order changes at higher content of water.

В работе описывается кинетика реакции гидролиза метакриламидсульфата, как реакции 1 порядка (до метакриламида), и этот вывод сравнивается как с литературными данными по гидролизу других амидов в среде концентрированной серной кислоты, так и с результатами численных методов анализа полученных данных. Изучена зависимость скорости конверсии от температуры и избытка воды. Рассчитана энергия активации $E = 86,2 \text{ кДж моль}^{-1}$, частотный фактор $A = 1,11 \cdot 10^{10} \text{ мин}^{-1}$ и энтропия активации, значения которой сравнены с литературными данными. С увеличением избытка воды растет и величина константы скорости (до мольного соотношения $\text{ACH}:\text{H}_2\text{O} = 1:6$). Кинетическое уравнение для первого порядка выполняется до мольного отношения $\text{ACH}:\text{H}_2\text{O} = 1:4$. При более высоком содержании воды изменяется порядок реакции.

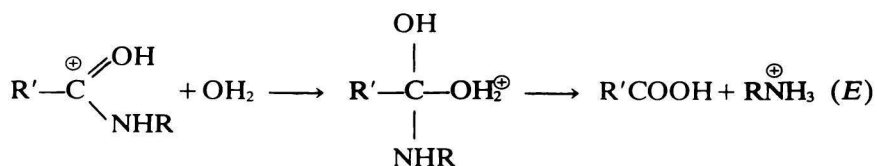
The original ideas of acid hydrolysis of amides were formulated by *Ingold* [1]. On the basis of these ideas it may be assumed that it is a bimolecular reaction where the rate-determining step is the reaction of amide of a conjugated acid with water [2], the rate of hydrolysis of individual amides increases with water content in the

system [3] and the influence of polar substituents in the acylated part of amide molecule on reaction rate is small [4]. However, the results obtained by *Duffy* and *Leisten* [2] are at variance with these assumptions. These authors investigated the course of amide hydrolysis by 95–100% sulfuric acid, *i.e.* in a medium with good ionizing properties which contains little free water and, for this reason, prefers monomolecular reaction to bimolecular reaction. These authors measured the kinetics of hydrolysis of substituted aromatic amides and evaluated the results which hinted at a first-order reaction taking place in the medium of 99.9–100% H_2SO_4 at 65–90°C. The results have shown that the rate of hydrolysis decreases with increasing amount of water in solvent and polar substituents ($-J$ and $-M$ effect) in the acyl group accelerate hydrolysis in conformity with monomolecular mechanism.



The problems concerning the influence of acid concentration on amide hydrolysis have been discussed [5]. The rate of hydrolysis increases with acid concentration, passes through a maximum and subsequently falls to very small values [6–8]. The concentration maxima for formamide, acetamide, and propionamide in H_2SO_4 are $c_{\text{max}}/\text{mol dm}^{-3}$ 4.75, 2.50, 2.40, respectively [7].

Provided the mass fraction of H_2SO_4 drops under 78%, the rate of hydrolysis starts to increase with decreasing concentration of acid [9, 10]. That is characteristic of the bimolecular A-2 mechanism according to which the rate of hydrolysis increases with concentration of free water



The reaction rate of hydrolysis starts to increase from mass fraction of H_2SO_4 of 78% with decreasing content of water (first-order reaction) as well as with increasing concentration of water (A-2 reaction).

All these data were a clue for studying the hydrolysis of methacrylamide sulfate (MAAS) though the discussed papers are concerned with substituted aromatic amides (anilides). In our case, the situation is more explicit because methacrylamide (MAA) is protonated as early as it arises in the form of MAAS. The protonated amide enters into hydrolysis. The conditions of this hydrolysis were investigated by *Ambrós* [11] who recommended the optimum mole ratios, *i.e.* $\text{ACH}:\text{H}_2\text{SO}_4 = 1:1.5-1.7$ and $\text{ACH}:\text{H}_2\text{O} = 1:4.5$, and the optimum reaction temperature of 127–132°C.

Experimental

Chemicals

MAAS was prepared from ACH (VChZ, Pardubice) and 100% H_2SO_4 according to the procedure described in [12, 13]. In addition, the following chemicals were used: γ -butyrolactone, anal. grade (Fluka), DTBC (ChZJD, Bratislava), hydroquinone (Lachema, Brno), MAA (Ega Chemie), MAC (Merck).

Methods

The kinetic measurements were carried out in a jacketed glass reactor equipped with a temperature sensor, stirrer, and sampling cock at the bottom. The number of stirrer revolutions was constant for all kinetic measurements. The temperature was held constant within accuracy $\pm 1.5^\circ\text{C}$ by means of a ultrathermostat. The starting MAAS was synthesized according to [12, 13] and contained 32.2 mass % of MAA. The quantities of 232 g of MAAS (mole ratio $\text{ACH}:\text{H}_2\text{SO}_4 = 1:1.5$), 55 g of γ -butyrolactone serving as homogenizing agent, 1 g of hydroquinone, and 1 g of DTBC were put into the thermostated reactor. On thermostating this mixture, the calculated amount of water (referred to ACH) was added. Then the time started to be measured. The samples were taken in programmed time intervals and analyzed by the methods of gas chromatography [14, 15] for MAC and MAA.

Results and discussion

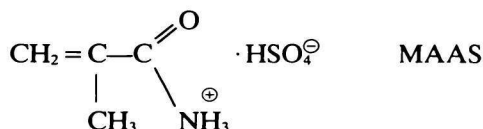
The dependence of the degree of MAAS hydrolysis on excess water was measured for reaction time $t = 150$ min and mole ratios $\text{ACH}:\text{H}_2\text{O} = 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:8, \text{ and } 1:10$ at $90 \pm 1.5^\circ\text{C}$. The decrease in MAA and increase in MAC in the reaction mixture was estimated. All evaluations were referred to the decrease in MAA. In spite of careful stabilization, MAC polymerized, especially at temperatures above 100°C . 2-Hydroxy-2-methylpropionic acid which could theoretically arise by addition of water to MAC was not found in any analytically provable quantity.

In the introduction the influence of H_2SO_4 concentration on hydrolysis mechanism was mentioned. At high concentrations of H_2SO_4 the hydrolysis follows the monomolecular mechanism. The high concentration of H_2SO_4 is operative in the protonation of amide and favours decomposition of the ammonium salt according to the scheme

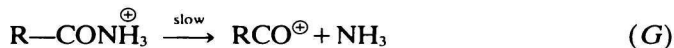


as well as liberation of the acyl cation for the reaction with water. At low concentrations of H_2SO_4 , the addition of water to carboxyl group (A-2 mechanism) is preferred.

As for hydrolysis of MAAS, the protonation step can be omitted because MAA enters into reaction in protonated form, *i.e.* in the form of sulfate which arises in the reaction of ACH with 100% H_2SO_4



The whole mechanism of MAAS hydrolysis can be written in accordance with literature [9] as follows



where R stands for $\text{CH}_2 = \text{C}-$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_3$



The temporal dependence of conversion was linearized by means of kinetic equation of the first order (Fig. 1)

$$\ln \frac{a}{a-x} = k_1 t \quad (1)$$

where a is initial MAA concentration (mol dm^{-3}), x is conversion of MAA after time t (mol dm^{-3}), k_1 rate constant of the first-order reaction with respect to MAA (min^{-1}), and t time (min).

On the basis of this linearization we could discern at which excess of water the reaction still obeys the monomolecular mechanism. All evaluations and results were referred to MAA. The results are given in Table 1 while the linearization is represented in Fig. 1.

The relationships for mole ratios ACH:H₂O = 1:2, 1:3, 1:4 can be conveniently linearized according to eqn (1) to give straight lines passing through the origin. The good linearization is reflected in low values of standard deviations S_y and S_k (Table 1). If the excess of water is higher, the temporal course of conversion does not fulfil eqn (1). The rate constant regularly increases till the mole ratio ACH:H₂O = 1:6 is attained. If the content of water exceeds this limit, the rate of conversion does not significantly change. We may state that a monomolecular reaction which may be described by mechanism (G—I) proceeds provided the

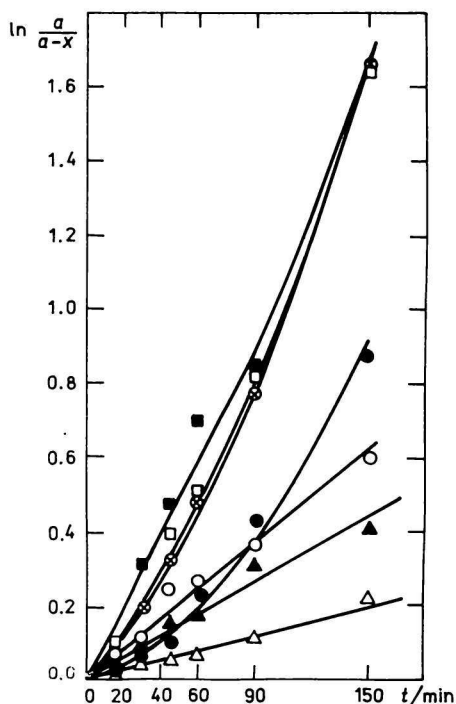


Fig. 1. Linearization of the temporal dependence of MAA concentration according to eqn (1) for different mole ratios ACH:H₂O.

△ 1:2; ▲ 1:3; ○ 1:4; ● 1:5; □ 1:6; ■ 1:8;
⊗ 1:10.

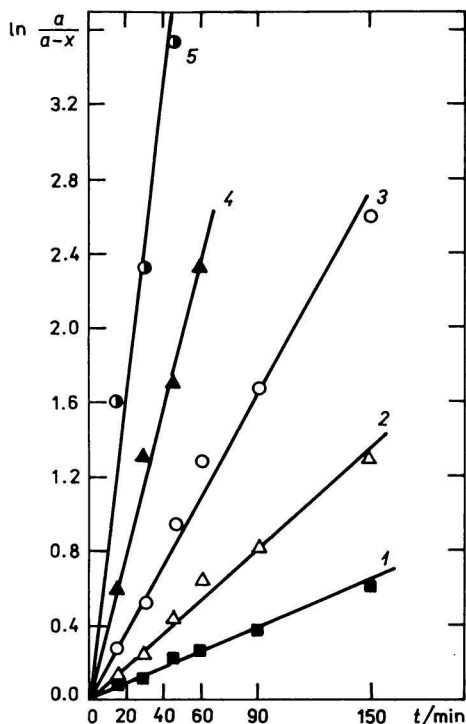


Fig. 2. Linearization of the temporal dependence of MAA concentration according to eqn (1) for different temperatures.

1. 90°C; 2. 100°C; 3. 110°C; 4. 120°C; 5. 130°C.

Table 1

Dependence of the course of MAAS hydrolysis on excess water ($\Theta = 90^\circ\text{C}$)

	Mole ratio ACH:H ₂ O						
	1:2	1:3	1:4	1:5	1:6	1:8	1:10
$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	1.38	2.99	4.18				
$\frac{S_y}{\text{mol dm}^{-3}}$	± 0.12	± 0.031	± 0.030	It is not linearized according to eqn (1)			
$\frac{S_{k_1}}{\text{min}^{-1}}$	$\pm 6.2 \times 10^{-5}$	$\pm 1.6 \times 10^{-4}$	$\pm 1.5 \times 10^{-4}$				

excess of water does not surpass the value corresponding to mole ratio ACH:H₂O = 1:4. If the content of water exceeds this limit, the reaction order changes.

The temperature dependence was measured for the above-mentioned mole ratio and temperatures $\Theta/^\circ\text{C}$ 70, 90, 100, 110, 120, and 130. The linearized relationships according to eqn (1) are represented in Fig. 2. At the temperature of 70°C the reaction was so slow that it could not be evaluated with sufficient precision. The rate constants were evaluated with respect to concentration decrease of MAA (Table 2).

Table 2

Temperature dependence of the course of MAAS hydrolysis for mole ratio ACH:H₂O = 1:4

	Temperature $\Theta/^\circ\text{C}$				
	90	100	110	120	130
$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	4.18	9.07	18.3	39.2	81.0
$\frac{S_y}{\text{mol dm}^{-3}}$	± 0.030	± 0.067	± 0.124	± 0.087	± 0.294
$\frac{S_{k_1} \cdot 10^4}{\text{min}^{-1}}$	± 1.54 ($\pm 3.7\%$)	± 3.44 ($\pm 3.8\%$)	± 6.44 ($\pm 3.5\%$)	± 10.6 ($\pm 2.7\%$)	± 52.5 ($\pm 6.5\%$)

The variation of logarithm of the numerical value of rate constant with reciprocal numerical value of absolute temperature is drawn in Fig. 3. The straight line the equation of which has the form

$$\ln \{k_1\} = \ln \{k_0\} + \frac{10^3}{T} \left[\frac{-E}{R} \right] \quad (2)$$

was drawn through experimental points by linear regression. It resulted from this equation $\ln \{k_0\} = 23.13 \pm 1.09$, the deviation being $\pm 4.7\%$ and $-E/R \text{ K} = -10.36 \pm 0.39$, the deviation being $\pm 3.8\%$. The symbol k_0 stands for frequency factor and E is activation energy.

The Arrhenius equation expressing the dependence of rate constant on temperature has the form

$$k_1 = 1.11 \times 10^{10} \exp \left[\frac{-(86.2 \pm 3.2) \text{ kJ mol}^{-1}}{RT} \right] \quad (3)$$

The activation entropy ΔS^* was calculated according to literature [16]

$$\Delta S_{298}^* = [19.159 \log(k_0) - 253.43] \text{ J K}^{-1} \text{ mol}^{-1} \quad (4)$$

The calculated value of activation entropy is

$$\Delta S_{298}^* = -95.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

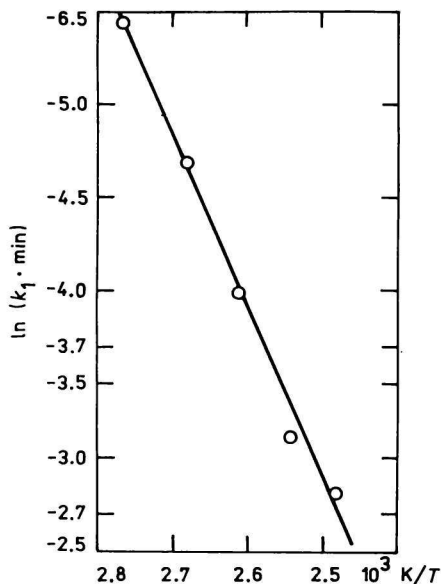


Fig. 3. Variation of rate constant k_1 with temperature.

The kinetic evaluation of the measured results was also carried out numerically by multiple linear regression (LMREG) for general equation $\{r\} = \{k_0\} \{c\}^n \exp(-E/RT)$ in the linearized form

$$\ln \{r\} = \ln \{k_0\} + n \ln \{c\} - \frac{E}{RT} \quad (5)$$

where r , n , c are conversion rate, reaction order, and concentration of reactant (MAA).

For calculating by means of LMREG, it was necessary to obtain the values of conversion rate as well as the concentrations of methacrylamide (MAA) (mol l^{-1}) in each experimental point at all particular temperatures. The reaction rate was obtained by describing each concentration dependence by a hyperbola equation

$$c = \frac{t}{(a_0 + a_1 t)}$$

The constants a_0 and a_1 were obtained for each curve by linear regression. Then the reaction rate may be calculated as the first derivation of this function with respect to time $r = dc/dt = a_0/(a_0 + a_1 t)^2$, where c is the concentration of MAA after time t . Subsequently, the values of conversion rate r were calculated for the programmed moments of time. The following regression coefficients of eqn (5) were obtained by calculation $k_0 = 1.74 \times 10^{11} \text{ min}^{-1}$, $E = 94.8 \text{ kJ mol}^{-1}$, $n = 1.14 \doteq 1.0$.

The value of activation entropy obtained from the thus calculated frequency factor is $\Delta S_{298}^* = -38.1 \text{ J K}^{-1} \text{ mol}^{-1}$.

Owing to classical evaluation, the values of k_0 and E obtained by LMREG are somewhat higher. However, the value of the parameter n ($n \doteq 1$) which characterizes the reaction order with respect to MAA shows that the preceding assumption of monomolecular reaction was correct.

The value of activation entropy is a datum which is regarded by some authors as a criterion of certain mechanism of hydrolysis. Other authors studied the hydrolysis of many amides catalyzed by acid catalysts and compiled tabular relations between the values of activation entropy and the type of reaction [17, 18]. Biggs and coworkers [17] allege the values of activation entropy ΔS^* to be in the interval between -29.3 and $+3.3 \text{ J K}^{-1} \text{ mol}^{-1}$ for the monomolecular A-1 mechanism and in the interval between -71.2 and $+125.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for the bimolecular A-2 mechanism. The Japanese authors [18] found the values of activation entropy in the interval between -40.2 and $+33.1 \text{ J K}^{-1} \text{ mol}^{-1}$ for the A-1 mechanism and in the interval between -87.5 and $-103.0 \text{ J K}^{-1} \text{ mol}^{-1}$ for the A-2 mechanism.

The values of activation entropy calculated by us for the hydrolysis of MAAS are $\Delta S_{298}^* = -95.0 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_{298}^* = -38.1 \text{ J K}^{-1} \text{ mol}^{-1}$. The second value was calculated by the numerical LMREG method which enabled us to place this reaction under above-mentioned conditions among the reactions obeying the

monomolecular A-1 mechanism [18]. Nevertheless, the values obtained by classical method are not in agreement with the values presented in papers [17, 18].

Symbols

MAAS	methacrylamide sulfate
MAA	methacrylamide
MAC	methacrylic acid
MMA	methyl methacrylate
MeOH	methanol
ACH	acetone cyanohydrin
DTBC	2,6-di- <i>tert</i> -butyl-4-methyl-1-hydroxybenzene

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