Kinetics of the reaction of 2-hydroxy-2-methylpropionitrile in sulfuric acid yielding methacrylamide

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The influence of temperature on acid hydrolysis of 2-hydroxy-2-methylpropionitrile is described in this paper. The rate constants were measured in the temperature interval 64.4—94.6 °C. The results were obtained by determining methacrylamide sulfate in sulfuric acid.

В работе описывается влияние температуры на кислотный гидролиз 2-гидрокси-2-метилпропионитрила. Константы скорости были измерены в интервале температур 64,4—94,6 °C. Результаты были измерены путем определения метакриламидсульфата в серной кислоте.

The synthesis of methacrylamide from 2-hydroxy-2-methylpropionitrile in the medium of concentrated sulfuric acid proceeds in two steps [1—4]. In the first step hydrogen sulfate of 2-hydroxy-2-methylpropionamide arises from nitrile and sulfuric acid. In the second step this amide is subjected to heating in sulfuric acid and transforms into methacrylamide sulfate.

Several authors [5—15] were concerned with the transformation of 2-hydroxy-2-methylpropionitrile in sulfuric acid. They investigated the influence of temperature, ratio of amounts of substance of sulfuric acid to nitrile, and concentration of sulfuric acid on the yield of methacrylamide. In all cases, the classic bromide—bromate method was used for quantitative determination of methacrylamide. This method enables us to determine all substances which contain double bonds, owing to which the yield of methacrylamide appears higher than the real content.

Experimental

Working procedure

The kinetic measurements were carried out in a four-necked flask equipped with a stirrer, reflux, thermometer, dosing funnel, and sampling orifice. The temperature in the flask was controlled by means of a thermostat and held accurate to ±1 °C. Nitrile (60 g) was added from a separatory funnel into sulfuric acid (99.8 mass %; 103 g) under intensive stirring at such rate that the temperature of mixture might not exceed 50 °C. The addition of last amounts of nitrile was so regulated that the temperature of mixture achieved the reaction temperature. The samples were taken (1 g) at certain time intervals, treated according to the described method [16] and analyzed.

Analytical methods

We developed GLC method [16] which was suited to the determination of the products of amidation. The analysis was performed with an instrument Chrom 41 with flame ionization detector. We used a column with 120 cm length and 3 mm diameter. We employed Chezasorb as a carrier and PEGA (5 mass %) as stationary phase. The granulation of packing was 0.1—0.5 mm, the temperature of column 160 °C, and the temperature of feeder 200 °C. Nitrogen of the flow rate of 30 $cm^3\ min^{-1}$ was used as a carrier gas. Under these conditions, the elution time of methacrylamide was 180 s.

The concentration of sulfuric acid was determined by titration while the concentration of nitrile was ascertained argentometrically.

Chemicals

2-Hydroxy-2-methylpropionitrile (Považské chemické závody, Žilina), n_D (20 °C) = = 1.3992; ϱ (20 °C) = 932 kg m^{-3}; melting point = 19 °C; boiling point (3.1 kPa) = 82 °C; content of HCN = 0.078 mass %; content of acetone = 0.22 mass %; total content of nitrile = 97.5 mass %.

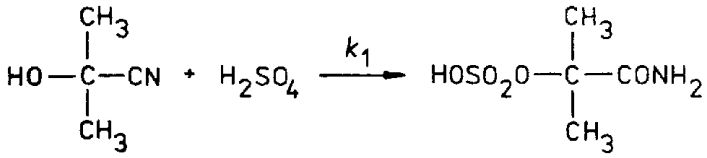
Sulfuric acid (Považské chemické závody, Žilina), ϱ (20 °C) = 1941.5 kg m^{-3}; 97.3 mass %; adjusted to convenient concentration by oleum.

Oleum (Považské chemické závody, Žilina), content of free sulfur trioxide 10.6 mass %.

Methacrylamide (Ega Chemie), 98.5 mass %, content of water 2 mass % at the maximum; melting point = 111 °C.

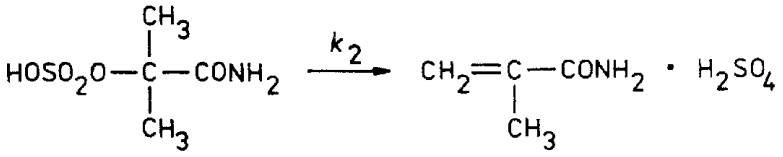
Results and discussion

The synthesis of methacrylamide from 2-hydroxy-2-methylpropionitrile and sulfuric acid proceeds in two steps. In the first step hydrogen sulfate of 2-hydroxy-2-methylpropionamide immediately arises by mixing sulfuric acid with nitrile



(A)

This substance transforms by heating into methacrylamide sulfate



(B)

The limiting step of the overall rate is thus the rate of reaction (*B*). This reaction obeys the kinetic equation of the zero order. The rate constant of the reaction was calculated from the following kinetic equation

$$k = \frac{1}{t} \cdot x \qquad (1)$$

k = rate constant (mol dm^{-3} s^{-1})
x = consumed amount of substance (mol dm^{-3})
t = time (s)

By using the corresponding concentrations c_t and c_0 (concentrations of methacrylamide in the time moments t and 0) in the calculation of rate constants, eqn (*1*) assumed the form

$$k = \frac{1}{t} \cdot (c_t - c_0) \qquad (2)$$

The measurements were performed at constant ratio of amounts of substance of acid to nitrile (1.5 : 1) and at temperature 64—95 °C. The dependence of concentration on time confirms that the transformation of nitrile into methacrylamide obeys under given reaction conditions (Fig. 1) the kinetic equation of the zero order. The measured values of rate constants are given in Table 1. The Arrhenius equation is fulfilled and the apparent activation energy is $E = (58.3 \pm 3.0)$ kJ mol^{-1}.

By using eqn (*2*) and the Arrhenius equation we obtain

$$k = (1.1 \times 10^6 \pm 2.7) \text{ mol dm}^{-3} \text{ s}^{-1} \exp \frac{-(58.3 \pm 3.0)}{RT} \text{ kJ mol}^{-1} \qquad (3)$$

This equation enables us to calculate the optimum time for the reaction of nitrile giving rise to amide even for temperatures outside the measured region. The calculated datum may be verified experimentally. For instance, the maximum yield calculated for 134 °C was obtained in 26 min. The maximum yield found experi-

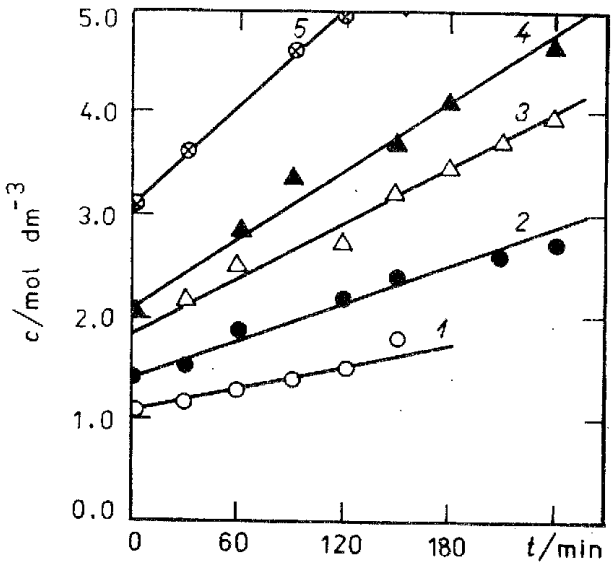


Fig. 1. Variation of concentration with time for temperatures 64—95 °C.
1. 64 °C; *2.* 74 °C; *3.* 81 °C; *4.* 89 °C; *5.* 95 °C.

Table 1

Rate constants for the transformation of nitrile into amide

θ/°C	$k \cdot 10^4$/mol dm^{-3} s^{-1}
64	0.59
74	1.00
81	1.58
89	2.55
94	3.13

mentally was 94.4 mass % and was reached in 31 min. The extrapolation of these relationships makes possible to use the measured data for obtaining information about the course of reactions at higher temperatures where precise measurements are unreliable.

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