

# Monitoring of the carbon monoxide formation in treatment of 2-hydroxy-2-methylpropionitrile with sulfuric acid

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In reaction of 2-hydroxy-2-methylpropionitrile with an excess of sulfuric acid (100 mass %) carbon monoxide is formed and its formation depends on both temperature (measured at 90—140 °C) and water content in the starting nitrile.

В реакции 2-гидрокси-2-метилпропионитрила с избытком серной кислоты (100 % по массе) образуется окись углерода, причем ее образование зависит как от температуры, измеряемой в интервале 90—140 °C, так и от содержания воды в исходном нитриле.

Several papers [1—3] dealt with the conversion of 2-hydroxy-2-methylpropionitrile (*I*) to methacrylamide in the presence of sulfuric acid. It is known that hydrogen sulfate of 2-hydroxy-2-methylpropionamide is an intermediate of sulfuric acid treatment of *I*, which at the elevated temperature, over 120 °C, rearranges to methacrylamide sulfate. Besides the main reaction [2], sulfate of the amide of 2-hydroxy-2-methylpropanoic acid can change at the elevated temperature in a small extent also in another way. It can decompose under the formation of carbon monoxide. The influence of several reaction parameters on its formation is described in this paper.

## Experimental

2-Hydroxy-2-methylpropionitrile (acetone cyanohydrin), the total nitrile mass fraction = 97.5 %, was the product of East Bohemia Chemical Works, Pardubice; technical sulfuric acid (97.3 mass %) and technical oleum (mass fraction of free SO<sub>3</sub> = 10.6 %) were from Chemical Works, Žilina; methacrylic acid from Merck; 2-hydroxy-2-methylpropanoic acid from Fluka. The amide of 2-hydroxy-2-methylpropanoic acid was prepared from nitrile according to [4].

### Procedure

Nitrile (0.5 mol) is added under cooling to sulfuric acid (0.7 mol; 100.4 mass % prepared from the specified acid and oleum) in a four-necked 250 cm<sup>3</sup> flask with stirrer, Hg-stopper, reflux cooler, portioning funnel, and thermometer, in the inert nitrogen atmosphere, in such a way that the temperature should not exceed 60 °C. The amount of carbon monoxide formed was measured after achieving the constant temperature.

### Analytical methods

Carbon monoxide was estimated chromatographically under the following conditions: a column of 3 m length with a 3 mm diameter packed with molecular sieve „5 A“ was used; temperature 25 °C; carrier gas hydrogen. Under the given conditions, the elution times (O<sub>2</sub>, N<sub>2</sub>, CO) were 58.72 s and 470 s. The total amount of gas was estimated by measuring of the gas mixture volume formed in the reaction.

### Results and discussion

Carbon monoxide and methacrylamide sulfate are formed on treatment of nitrile *I* with sulfuric acid at the elevated temperature. This decarbonylation effect of sulfuric acid depends not only on temperature but also on the excess of the acid used, on the presence of inhibitors [5], water, etc.

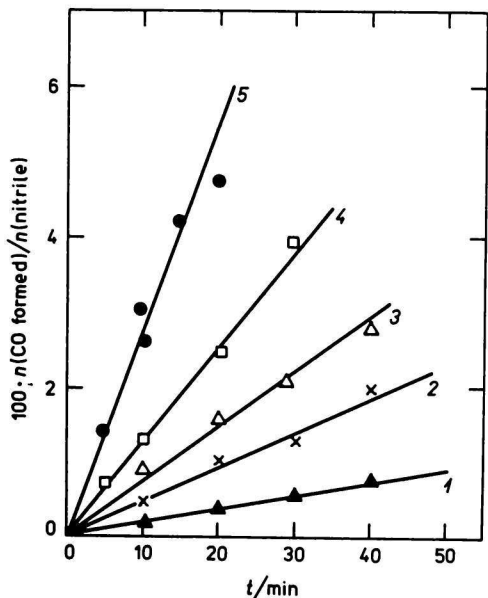


Fig. 1. Rate of the carbon monoxide formation in the nitrile conversion.

1. 100 °C; 2. 110 °C; 3. 120 °C;  
4. 130 °C; 5. 140 °C.

In the temperature range of 100–140 °C, carbon monoxide is formed under the anhydrous conditions (in the initial stage of the reaction from 20 to 40 min) following kinetics of the zero order (Fig. 1). For this reaction, Arrhenius equation is valid and the function  $\log \{k\} = f(T^{-1})$  is linear. The activation energy

$$E = (117.6 \pm 5.6) \text{ kJ mol}^{-1}$$

Anhydrous conditions are important in the conversion of nitrile *I* to methacrylamide sulfate in the presence of sulfuric acid. In the presence of water, a part of nitrile reacts by the parallel reaction to amide of 2-hydroxy-2-methylpropanoic acid, which is destroyed to acetone, carbon monoxide, and ammonia. The latter reacts in the given system to hydrogen sulfate, and acetone condenses to 2-methyl-2-pentene-4-one. 2-Hydroxy-2-methylpropanoic acid, formed from the amide by hydrolysis, gives methacrylic acid on dehydration, which decomposes

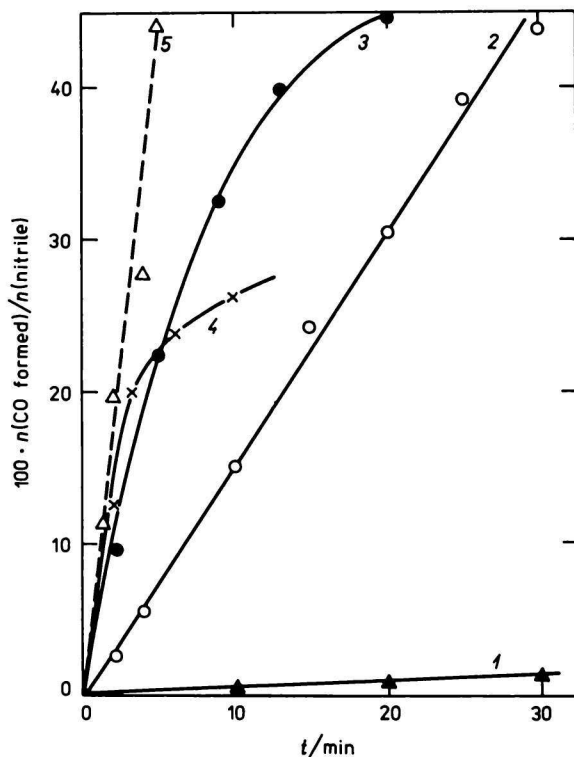


Fig. 2. Rate of decomposition of the intermediates of methacrylamide sulfate preparation to carbon monoxide.

1. Methacrylamide, 135 °C; 2. 2-hydroxy-2-methylpropaneamide, 135 °C; 3. methacrylic acid, 135 °C; 4. formic acid, 30 °C; 5. 2-hydroxy-2-methylpropanoic acid.

further to acetone and carbon monoxide. It is decomposed simultaneously to acetone and formic acid, which decomposes in turn to carbon monoxide and water.

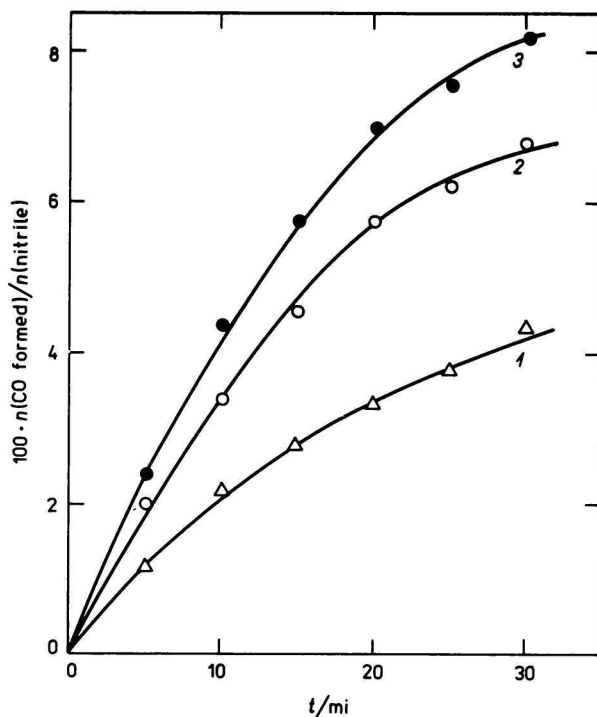


Fig. 3. Influence of the sulfuric acid concentration on the carbon monoxide formation in the nitrile conversion to methacrylamide sulfate.

1. 100.1 mass %  $\text{H}_2\text{SO}_4$ ; 2. 98.5 mass %  $\text{H}_2\text{SO}_4$ ; 3. 96.3 mass %  $\text{H}_2\text{SO}_4$ .

$n(\text{H}_2\text{SO}_4) : n(\text{nitrile}) = 1.5 : 1$ ; temperature  $135^\circ\text{C}$ .

Table 1

Influence of water content in nitrile on the carbon monoxide formation in the nitrile conversion to methacrylamide sulfate

| $w(\text{H}_2\text{O in nitrile})/\%$ | $100 \cdot (n(\text{CO formed})/n(\text{nitrile}))$ |
|---------------------------------------|---|
|                                       | %   |
| 0.7                                   | 4.4   |
| 1.0                                   | 5.6   |
| 1.3                                   | 6.5   |
| 10                                    | 19  |

This mechanism of decomposition of the individual intermediates of methacrylamide sulfate preparation from nitrile is confirmed by the respective rates of their decomposition to carbon monoxide (Fig. 2). It is evident that methacrylamide alone (in sulfuric acid as sulfate) is relatively stable. The presence of water in nitrile (Fig. 3) is mainly responsible for the carbon monoxide formation and resulting substantial decrease in the overall yield. In the reaction of nitrile with sulfuric acid ( $n(\text{H}_2\text{SO}_4):n(\text{nitrile})=1.5$ ), we found at 135 °C after 30 min the amount of carbon monoxide formed ( $100\ n(\text{CO})/n(\text{nitrile})$ ) as shown in Table 1.

It can be assumed that the unfavourable influence of water in nitrile and also in sulfuric acid may be eliminated by the addition of acid containing free sulfur trioxide (oleum). Previous results [6] showed, however, in this case a decrease of the yields of methacrylamide sulfate. It is, therefore, suitable to minimize the water content in nitrile and to use 100 % sulfuric acid in the reaction of nitrile *I* with sulfuric acid in its excess in the methacrylamide sulfate preparation. Under the conditions of optimalization of further reaction parameters [7], a high yield of methacrylamide sulfate can be achieved.

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