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Abstract

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ON THE MECHANISM OF THE OXIMATION OF CYCLOHEXANONE WITH SODIUM HYDROXYLAMINEMONOSULFONATE

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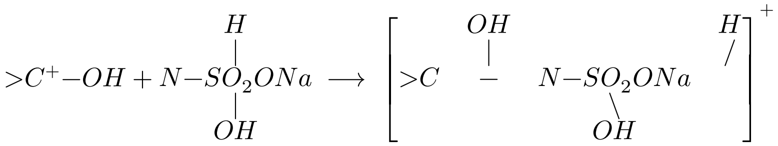
For the oximation of aldehydes and ketones it is customary to use salts of hydroxylamine. However, in industry (^{1}), for the oximation of cyclohexanone, an acidic solution of hydroxylaminemonosulfonate—the intermediate product in the synthesis of hydroxylamine sulfate by Raschig' s method (^{2})—is sometimes used instead of a hydroxylamine salt.

The mechanism of oximation by hydroxylaminemonosulfonates has not been described in the literature. The following is characteristic of the interaction of cyclohexanone with sodium hydroxylaminemonosulfonate:

1) In contrast to hydroxylamine, hydroxylaminemonosulfonate in an alkaline medium does not react with cyclohexanone.
2) Hydroxylaminemonosulfonate at room temperature in weak solutions of sulfuric acid (i.e., under the conditions in which our experiments were carried out) is practically not hydrolyzed.
3) In the simultaneous presence of cyclohexanone and acid, hydroxylaminemonosulfonate readily enters into reaction with formation of cyclohexanone oxime and also hydroxylamine.

To explain the peculiarities of the interaction of sodium hydroxylaminemonosulfonate with cyclohexanone in an acidic medium, we have proposed the following reaction scheme:

$$>C=O + H^{+} \rightleftarrows >C^{+}-OH$$



$$>C^{+}-OH + N-\underset{OH}{\overset{H}{SO_2}}ONa \longrightarrow \left[>C \quad \overset{OH}{-} \quad N-\underset{\backslash OH}{SO_2}ONa \quad \overset{H}{/} \right]^{+}$$

Figure 1: Oximation of cyclohexanone with sodium hydroxylaminemonosulfonate at 22°.

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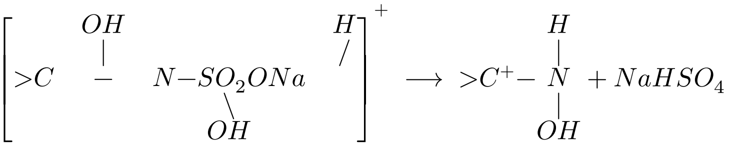
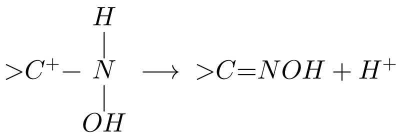


$$\left[>C\ \overset{OH}{\overset{|}{-}}\quad N{-}SO_2ONa\ \overset{H}{/}\ \underset{\setminus\ OH}{}\right]^{+} \longrightarrow >C^{+}-\overset{H}{\underset{OH}{N}} + NaHSO_4$$



$$>C^{+}-\overset{H}{\underset{OH}{N}} \longrightarrow >C{=}NOH + H^{+}$$

$$>C{=}NOH + H^{+} \rightleftarrows (>C{=}NOH)H^{+}$$

$$(>C{=}NOH)H^{+} + H_2O \rightleftarrows >C{=}O + HONH_2 + H^{+}$$

$$HONH_2 + H^{+} \rightleftarrows (HONH_2)H^{+}$$

According to the proposed mechanism, the primary product of the reaction is the carbonium ion, which then forms a coordination bond by

of the unshared electron pair of the nitrogen atom in nucleophilic hydroxylaminemonosulfonate. From the complex compound formed, a molecule of bisulfate and a proton are then split off, and an oxime is formed. In an acidic medium, equilibrium hydrolysis of the oxime is established, leading to formation of the original ketone and the hydroxylamine salt. In the scheme described, reactions (3) and (4) are the fastest. The rate of decrease in the concentration of hydroxylaminemonosulfonate (or of ketone oximation) should depend primarily on the bimolecular reactions (1) and (2), i.e., on the concentration of ketone, hydrogen ions, and hydroxylaminemonosulfonate. The presence of hydrogen ions causes hydrolysis of cyclohexanone oxime with formation of cyclohexanone and the hydroxylammonium ion

Fig. 1. Oximation of cyclohexanone with sodium hydroxylaminemonosulfonate at 22°. Initial solutions (in meq/l):

	HONHSO ONa	C H O
a	124	62
	64.8	65
	62	124
	62	31
	31	62

and therefore the secondary reactions (5)–(7) also influence the macrokinetics of the overall reaction.

Using kinetic data on the reaction of oximation of cyclohexanone with sodium hydroxylaminemonosulfonate, the reaction mechanism given above has been confirmed. From Fig. 1 it is seen that, with an increase in the initial concentration of cyclohexanone, other conditions being equal, the rate of oximation increases. The effect of the concentration of hydroxylaminemonosulfonate on the reaction rate follows the same regularity. In all experiments shown in Fig. 1, in the initial period of interaction between the starting substances the reaction accelerates itself. In addition, from the slopes of the curves in these same figures it follows that the greater the concentration of ketone or hydroxylaminemonosulfonate, the faster the reaction rate increases.

This leads one to suppose that the autocatalytic character of the process is due to the growth in concentration of one of the products of the interaction of hydroxylaminemonosulfonate and cyclohexanone. Experiments show that in the course of the reaction the acidity of the system increases.

However, part of the protons formed must interact with the oxime and hydroxylamine, owing to which only free hydrogen ions can influence the rate of oximation, i.e., the reaction studied apparently represents a case of specific acid catalysis.

For additional confirmation of the mechanism we proposed for the interaction of cyclohexanone with hydroxylaminemonosulfonate in an acidic medium, experiments were carried out to determine the order of the reaction. In calculating the rate constant from the concentration of hydroxylaminemonosulfonate (C_1)

Fig. 2. Oximation of cyclohexanone (I—95.6, II—62 meq/l) by sodium hydroxylaminemonosulfonate (I—96, II—62 meq/l). a –total acidity, b –concentration of hydrogen ions

and the rate of oximation was judged from the increase in the total acidity of the system. The content of cyclohexanone (C_2) in the reaction mixture at the beginning of the experiment (i.e., with a large excess of cyclohexanone relative to cyclohexanone oxime, when hydrolysis of the oxime may be neglected) was calculated from the increase in total acidity, analogously to the concentration of hydroxylaminemonosulfonate. In subsequent determinations, the amount of cyclohexanone formed during hydrolysis of the oxime was also taken into account. For this purpose the equilibrium constants (3) of reaction (6) were used, with the conditional assumption that in this reaction the equilibrium state had been reached. The concentration of hydrogen ions (C_3) was calculated from the pH of the medium. The experimental data (total acidity and hydrogen-ion concentration) are given in Fig. 2.

Table 1

Calculation of the rate constant for the oximation of cyclohexanone by sodium hydroxylaminemonosulfonate at 22°

Time, min	Total acidity, meq/l	C_1, meq/l	C_2, meq/l	C_3, meq/l	Rate, meq/(l · h)	Rate constant, $k \cdot 10^4$
4						
24	0.88	94.6	94.2	1.02	1.61	1.77
44						
67	1.95	92.8	92.4	2.40	3.23	1.55
91						
141	4.48	86.1	87.2	5.37	6.54	1.63
191	15.4					
217		76.9	80.0	7.6	8.5	1.83
243	22.8					
293		66.8	75.1	8.5	7.6	1.77
343	35.5					
					Average ...	**1.71**

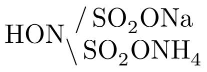
On the basis of the data in Fig. 2, the rate constant was calculated (Table 1) from the equation for third-order reactions

$$V = kC_1C_2C_3,$$

and it is, on average, equal to $1.7 \cdot 10^{-4}$ $l^2/h \cdot meq^2$. Without assuming the participation of hydrogen ions in the reaction, it was not possible to obtain any convergent results for the rate constant. Thus, the rate of oximation varies proportionally to the concentration of sodium hydroxylaminemonosulfonate, cyclohexanone, and hydrogen ions, which is consistent with the reaction mechanism proposed in the present article.

Experimental Part

For the synthesis of sodium hydroxylaminemonosulfonate, 500 ml of a technical solution of hydroxylaminedisulfonate



$$\mathrm{HON}\begin{matrix}/\,\mathrm{SO_2ONa}\\ \backslash\,\mathrm{SO_2ONH_4}\end{matrix}$$

with a concentration of 396 g/l, obtained from sodium nitrite, ammonium bisulfite, and sulfur dioxide, was taken; 61 ml of 40% NaOH was added to it to remove ammonia, and then 250 ml of methanol was added to precipitate sodium hydroxylaminedisulfonate. The resulting precipitate was reprecipitated twice with methanol from a 9% NaOH solution. Subsequent treatment of sodium hydroxylaminedisulfonate was carried out according to the procedure of Nast and co-workers[4] to obtain potassium hydroxylaminemonosulfonate. The yield of sodium hydroxylaminemonosulfonate (with a content of the principal substance of 98–100%) was 10–20 g.

Commercial cyclohexanone was purified through the bisulfite compound; the product obtained had $d_4^{20}0.9454$, $n_D^{20}1.4495$.

The experiments were carried out at $22\pm0.05^\circ$. The initial acidity of the reaction mixtures corresponded to pH 3.6–3.2. To determine the total acidity, periodically withdrawn samples were titrated with 0.01 *N* NaOH using phenolphthalein. The pH was determined with an LP-5 vacuum-tube potentiometer with a glass electrode.

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Note: Figure translations are in progress. See original paper for figures.