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Abstract

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STUDY OF THE REACTION OF OXIDATIVE AMMONOLYSIS OF METHYL VINYL KETONE

The reaction of oxidative ammonolysis of organic compounds is becoming increasingly important as a convenient method for the synthesis of nitriles of carboxylic acids. Along with aromatic hydrocarbons ([1]–[3]) and alkylpyridines ([4], [5]), unsaturated compounds ([6]) are also beginning to be used as starting materials. Reports have appeared on the industrial application of the reaction under consideration for the synthesis of acrylonitrile from propylene ([7]). At the same time, the oxidative ammonolysis of this important group of substances has still been studied quite insufficiently. Particularly little has been investigated concerning the behavior of oxygen-containing unsaturated compounds, although some of them are of considerable importance as raw materials for obtaining unsaturated nitriles ([3], [8]) and are of great theoretical interest for understanding the mechanism of oxidative ammonolysis as a whole. Of definite interest in this respect is methyl vinyl ketone (MVK), in the oxidative ammonolysis of which one might expect the formation of acrylonitrile, analogous to the conversion of acetophenone into benzonitrile ([1]).

The studies were carried out in a continuous-flow apparatus with a single-tube reactor and a scrubber system for trapping the reaction products. The reaction tube, made of stainless steel, had a diameter of 20 mm and a length of 750 mm. The catalyst was a coprecipitated alumovanadium contact of composition: V_2O_5 36%, Al_2O_3 64%. Methyl vinyl ketone, obtained by the Mannich reaction ([9]), had b.p. 72°/690 mm and $n_D^{20} = 1.408$.

Analysis of all reaction products was carried out by a chromatographic method; in the separation of the liquid components of the catalyzate, polyethylene glycol adipate deposited on Inza brick of grade N3-600 was used as the liquid phase. In parallel with this, in most experiments the amount of unreacted MVK and of reaction products of composition C_3 was determined polarographically ([10]).

Oxidative ammonolysis of organic compounds is a very complex multistage reaction, in which oxidation processes play an important role both at the initial stages and in the subsequent steps. In this connection, it seemed necessary first to study the catalytic oxidation of MVK in the absence of ammonia. At a feed rate of 206 g of MVK and 3600 l of air per 1 l of catalyst per hour, a contact time

of 0.3 sec, and 340°, the principal reaction products were acrolein and acetaldehyde, which were obtained in yields of 16 and 21% of the theoretically possible amount calculated for the starting material taken, as well as carbon oxides. In addition, acrylic and acetic acids, formaldehyde, and hydrogen were detected in small amounts. Changing the ratio of MVK to oxygen in the range 1 : 5–1 : 10 (in moles), as is evident from Fig. 1, had a substantial effect only on the completeness of conversion of MVK and on the yield of acetaldehyde and carbon oxides, whereas the yield of acrolein changed little. The simultaneous presence of acrolein and acetaldehyde among the reaction products indicates that, in the MVK molecule, not only the methyl group but also, to a considerable extent, the double bond is attacked by oxygen:

$$CH_2 = CH - CO - CH_3 \xrightarrow{O_2} \begin{cases} CH_2 = CHCHO & (I) \\ CH_3CHO & (II) \end{cases}$$

With a decrease in the oxygen concentration to 1 : 5, the share of the second of the indicated reaction pathways decreased and, although the overall conversion of MVK fell slightly, the overall selectivity of the process, from the standpoint of acrolein formation, increased as a whole.

The introduction of ammonia into the reaction zone sharply changed the character of the process. Even with the addition of 1-2 mol of NH_3 per 1 mol of MVK, a significant increase in the yield of CO_2 and CH_3CHO was noted (Fig. 2), which indicates an intensification of reactions proceeding with participation of the double bond of the MVK molecule. On the other hand, nitrogen-containing compounds appeared in substantial amounts in the catalyzate—acrylonitrile, ammonium cyanide, and, in trace amounts, acetonitrile. Raising the NH_3 concentration to 5-6 mol per 1 mol of MVK was accompanied by an increase in the yield of acrylonitrile (up to 48%), with a simultaneous increase in the amount of hydrogen formed to 1 mol per 1 mol of MVK taken.

Comparison of the data presented above shows that if, under the conditions of oxidation and oxidative ammonolysis of MVK with a small feed of ammonia, the fraction of participation of the methyl group and of the double bond of the starting substance is, on the whole, of the same order, then at an elevated NH_3 concentration the direction of the process shifts noticeably toward acrolein formation (reaction I), which under oxidative ammonolysis conditions readily passes into acrylonitrile ([8]):

$$CH_2 = CHCHO \xrightarrow{O_2+NH_3} CH_2 = CHCN.$$

The increase in the relative importance of the latter reaction contributes to a decrease in the rate of deep oxidation processes, which is associated with the high resistance of acrylonitrile to oxidation in comparison with the other reac-

Fig. 2.

Figure 1: Fig. 2.

Fig. 3.

Figure 2: Fig. 3.

tion products. Special experiments showed that under oxidative ammonolysis conditions no more than 15-20% of the acrylonitrile undergoes decomposition.

Fig. 1. Dependence of the yield of MVK oxidation products on the concentration of oxygen in the reaction mixture (contact time 0.3 sec). **A**—yield in percent of theory based on MVK taken; **B**—yield in moles per 1 mol of MVK; **V**—oxygen in moles per 1 mol of MVK. **I**—unreacted MVK; **II**—acrolein; **III**—acetaldehyde, in %; **IV**—CO_2; **V**—CO in moles per 1 mol of MVK. 1—320°, 2—340°, 3—360°, 4—380°.

In all the experiments described above, one of the reaction products was molecular hydrogen. Previously, its presence had been noted only in homogeneous gas-phase oxidation of hydrocarbons ([11]). The results of the present work show that hydrogen can also be formed in heterogeneous oxidative ammonolysis of organic compounds.

It should be noted that, in the oxidation of MVK in the absence of ammonia, the yield of hydrogen was low even in experiments with a low oxygen concentration and rarely exceeded 0.05-0.1 mol per 1 mol of the starting substance. In the presence of ammonia, however, its yield reached 2 mol per 1 mol, which often even exceeded the difference between its content in the starting substance fed and in the oxidation products detected. This shows that under oxidative ammonolysis conditions the source of molecular hydrogen is not

Fig. 2

Fig. 3

not only organic substances but, to an even greater extent, ammonia, as occurs in the vapor-phase oxidation of ammonia on oxide contacts ([12]).

It is seen from Fig. 2 that, as the ammonia feed is changed, the amount of unreacted ketone passes through a minimum, which corresponds to an MVK : NH_3 ratio of 1 : 1—2. The reason for this phenomenon may be connected with the fact that, as the amount of ammonia increases, the consumption of oxygen for its oxidation increases, which leads to a decrease in the oxygen concentration in the reaction mixture and, correspondingly, to a lowering of the oxidation rate of MVK. Experiments studying the influence of oxygen concentration on the oxidative ammonolysis of MVK confirmed this assumption. As is seen from Fig. 3, with an increase in the oxygen concentration from 5 to 7 moles per 1 mole of MVK, the amount of unreacted starting material at 340° decreases

from 40 to 30%, while the amounts of acrolein, acetaldehyde, and especially acrylonitrile formed increase over the entire temperature range studied. The yield of acrylonitrile in this case is about 50% based on the amount taken and 68.5% based on the MVK that entered into the reaction.

Under the indicated conditions, 85-90% of the MVK that entered into the reaction was converted into oxygen- and nitrogen-containing products of composition $C_2 + C_3$. The reactions of deep oxidation in this case had a comparatively small share—the amount of carbon oxides and hydrogen cyanide formed did not exceed 10-12% of the theoretically calculated amount.

The ratio of the yields of the reaction products of composition C_2 and C_3 shows that acrolein and acrylonitrile account for 90-95% of the total amount of products of incomplete oxidation.

Thus, the data obtained indicate that the direction of the oxidative ammonolysis reaction of MVK depends to a large extent on the concentration of oxygen and, especially, ammonia in the reaction mixture. By varying the reaction conditions, it is possible to select an optimal regime for the preferential oxidation of the methyl group with preservation of the double bond.

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Fig. 2. Influence of the amount of ammonia on the oxidative ammonolysis reaction of MVK. Molar ratio MVK : O_2 = 1 : 7.5, contact time 0.3 sec. $A, B, I, II, III, IV, 1, 2, 3, 4$–as in Fig. 1. B–ammonia in moles per 1 mole of MVK, VI–acrylonitrile, VII–HCN, $VIII$–H_2 in moles per 1 mole of MVK, 5–400°.

Fig. 3. Influence of the amount of oxygen on the oxidative ammonolysis reaction of MVK. Molar ratio MVK : NH_3 = 1 : 5.5, contact time 0.3 sec. VI–acrylonitrile, VII–HCN, $VIII$–H_2. A–B, I–V, 1–5–as in Fig. 1.

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