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TRANSLATION

OXIDATION OF ORGANIC COMPOUNDS

By

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et. al.

FOREIGN TECHNOLOGY DIVISION

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OXIDATION OF ORGANIC COMPOUNDS

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Communication 32

Oxidizing Ammonolysis of m-Xylene

In the last few years the interest of researchers in m-xylenediamine which has been proposed for the synthesis of thermostable polyamides [1, 2] has increased, As is well known, fatty-aromatic diamines with high yield are formed on hydrogenation of phthalic acids [3, 4].

Earlier we [5, 6] and other researchers [7, 8] showed that isophthalodinitrile may be derived by the oxidizing ammonolysis of m-xylene. The aim of the work in question was the more detailed investigation of this process.

Preliminary experiments showed that when m-xylene is fed at the rate of 30-55 g, ammonia at 45-150 g, water at 200-400 g, air at 1200-3600 l per liter of catalyst per hr the basic product of the oxidizing ammonolytic reaction of m-xylene on various vanadium catalysts is the dinitrile of isophthalic acid. From the data shown in

Fig. 1 it is evident that under the indicated conditions its yield may exceed 40% of that theoretically calculated from the hydrocarbon taken. Besides isophthalodinitrile free isophthalic acid is present in the reaction products. The diamide of isophthalic acid, m-tolunitrile, and m-cyanbenzoic acid are formed in small quantities. The gaseous products of the reaction are represented by hydrocyanic acid and oxides of carbon.

Figures 2 and 3 show the results of several series of experiments on studying the influence of the contact time and volumetric velocity of hydrocarbons on the oxidizing ammonolytic reaction of m-xylene in the presence of a catalyst of stannous vanadate.

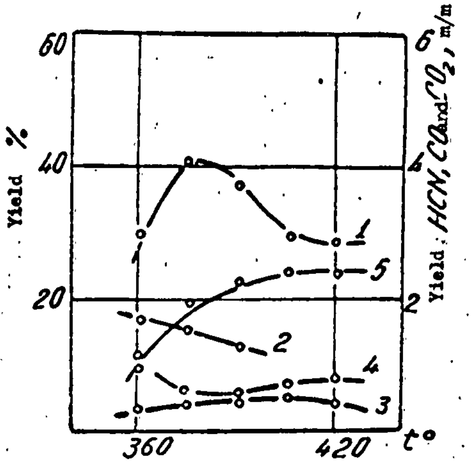

Fig. 1. Oxidizing ammonolysis of m-xylene. Rate of feed: m-xylene, 42 g; NH_3, 150 g; H_2O, 400 g; air, 2400 1 per liter of catalyst per hr; period of contact--0.6 sec. 1) Dinitrile of isophthalic acid; 2) isophthalic acid, 3) HCN, 4) CO, 5) CO_2.

The experiments studying the time of contact showed that with a feed rate of 55 g for m-xylene; for water, 450 g per liter of catalyst per hour; a 17-fold excess of water and a 9-fold excess of ammonia in comparison with the quantity theoretically necessary for the reaction $C_6H_4(CH_3)_2 + 3O_2 + 2NH_3 \rightarrow C_6H_4(CN)_2 + 6H_2O$, the largest yield of isophthalodinitrile (58%) can be obtained during a contact time of 0.4 sec (Fig. 2B). The nitrile of m-toluyl acid was discovered in these experiments in the form of traces. The yield of hydrocyanic acid, carbon monoxide, and carbon dioxide amounted to 0.6, 0.7, and 1.8 moles per mole of the original m-xylene. The following series of experiments were carried out at a contact time of 0.2 and 0.3 sec (Fig. 2A, B). Under these conditions the yield of isophthalodinitrile was depressed to 49-51%. The quantity of hydrocyanic acid and carbon monoxide also was regularly depressed. When the period of contact is increased to 0.4 sec (Fig. 2C) there is also observed a decrease in the yield of the dinitrile of isophthalic acid (to 47%); but the quantity of products of combustion considerably increased. The yield of carbon dioxide gas increased especially sharply. In experiments with a temperature of reaction of 410° its yield reached 2.8 moles per mole of the initial hydrocarbon. Thus, under these conditions even at a moderate temperature of reaction more than half of the taken m-xylene was converted into products of complete combustion.

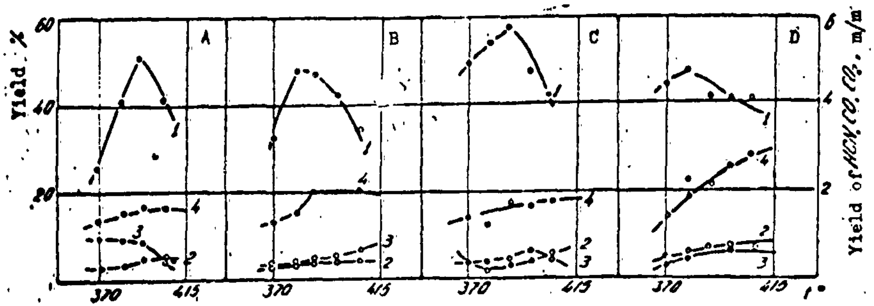

Fig. 2. Effect of time of contact on reaction of oxidizing ammonolysis of m-xylene. Rate of feeding: m-xylene, 55g; NH_3, 160 g; H_2O, 450 g; air, 5400 l (A), 4045 l (B), 4000 l (C), 2700 l (D). 1) Dinitrile of isophthalic acid, 2) HCN, 3) CO, 4) CO_2.

The experimental data obtained indicate that the change in the period of contact exerts a noticeable influence on the process of the oxidizing ammonolytic reaction of m-xylene. With a short period of contact, part of the original hydrocarbon manages to pass through the reaction zone in an unchanged state. When the time is increased the reaction conditions become so stable that the formed reaction products, among them isophthalodinitrile, undergo more profound transformations right up to oxidizing into carbon monoxide and water.

Figure 3 shows the results of the series of experiments with identical period of contact, but with varying rate of feeding the m-xylene into the reaction chamber. A change in the feed of hydrocarbon within the limits studied exerted no essential influence on the yield of dinitrile of isophthalic acid. The optimum reaction temperature, and yield of gaseous products, however, changed somewhat. Thus, with a small rate of feeding m-xylene, the maximum quantity of isophthalonitrile was obtained at 380-390°; and the yield of combustion products reached rather large values. When the rate of feeding hydrocarbon increased, the yield of gaseous products of reaction decreased and the maximum of the yield curve of isophthalodinitrile shifted into the higher temperature region. The productivity of the process also increased, i.e., the take-off of the whole product per volumetric unit of catalyst.

In the described experiments the ratio of the original components also changed simultaneously along with the alteration in the period of contact and the volumetric rate. Since the water and ammonia were introduced, however, into the reaction chamber in great excess, these fluctuations were insignificant and reflected themselves slightly in the yield of the basic reaction products.

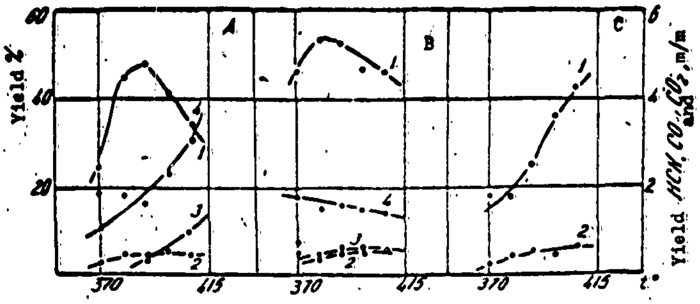

Fig. 3. Effect of volumetric rate on reaction of oxidizing ammonolysis of m-xylene. Rate of feed: NH_3, 160 g; H_2O; 450 g; air, 4050 l; m-xylene, 40 g (A), 77 g (B), 93 g (C) per liter of catalyst per hr. Period of contact, 0.3 sec. 1) Dinitrile of isophthalic acid, 2) HCN, 3) CO, 4) CO_2.

A comparison of the data cited above with the results from oxidizing ammonolysis of n-xylene [9] shows that the m-isomer is more capable of reaction. This is indicated by the fact that the optimum conditions for the formation of isophthalodinitrile are situated in a lower temperature region than occurred for dinitrile of terephthalic acid. In comparison with n-xylene the total yield of reaction products of C_8 composition was somewhat less, in the case of the m-isomer, and the gaseous products were obtained to considerably greater quantities.

The indicated differences in the behavior of the xylene isomers may be explained by the structural peculiarities of m-xylene and its products of successive conversions. From the literature it is known that in reactions with radical substitution in aromatic cycles the o- and n-positions are the most vulnerable, independent of the nature of the attacking substitute [10]. In this connection, in contrast to the n-isomer in the molecule of m-xylene (and its derivatives) the C-H bond in the carbon atom situated between them is weakened because of the joint orienting effect of the side groups, and therefore to a greater degree is subjected to the action of oxygen than the other C-H bonds in the nucleus. With large oxygen concentration this entails the destruction of the cycle with formation of aliphatic oxygen-containing compounds giving products of combustion in the last analysis.

The structural features determine also the capability of the m-isomer to be adsorbed on the contact surface by both side groups, by virtue of which they may enter into reaction simultaneously. This is confirmed by the fact that in oxidizing ammonolysis of m-xylene its monofunctional derivatives, in particular m-tolunitrile, were obtained as a rule with low yield.

Experimental Section

The "pure" make of m-xylene was dried over calcined calcium chloride and was twice distilled over metallic sodium in a rod-and-disk type fractionating column 40 cm long. The thus cleaned hydrocarbon had the following indices: b.p. 136°/682 mm; d_4^{20}, 0.866; and n_D^{20}, 1.4969.

The ammonia was used in an aqueous solution.

Air entered the reactor from the compressor without previous cleaning and drying.

All the experiments to study the reaction of oxidizing ammonolysis of m-xylene were conducted in a flow-through type of installation with a reaction column of stainless steel 1100 mm in length and 21 mm in diameter. The device used to feed the raw material into the reaction chamber and the spiral coil system for trapping the products of reaction have been described earlier [11].

As a catalyst stannous vanadate was used, made by fusing the pentoxide of vanadium with stannic oxide and used in the form of pieces 3-5 mm in cross-section.

Analysis of the products of reaction was conducted as follows. The contents of the collecting system together with the wash water was treated with petroleum ether. The undissolved precipitate was filtered out and dried at 100-110°. The white solid obtained had m.p. 160-161° and in mixture with the pure isophthalodinitrile melted without lowering. For additional intensification 1 g of the substance was saponified by two hours of boiling with 50 ml of a 60% solution of sulfuric acid in water. There was obtained 0.9 g of isophthalic acid with m.p. 348° (in a sealed capillary) and equivalent neutralization of 82.8.

Analysis of the obtained isophthalodinitrile for its nitrogen content gave the following results:

0.004371 g subst.: 0.872 ml N_2 (20°, 693 mm)
0.003401 g subst.: 0.671 ml N_2 (20°, 699 mm)

Percentage found: N 21.10; 21.01. $C_8H_4N_2$. Calculated %: N 21.86.

The ether extract was separated from the aqueous layer, dried over calcined sodium sulfate, and distilled. The fraction with b.p. 90-93°/14 mm had $n_D^{20} = 1.5270$, which corresponded to the indices of the m-tolunitrile. When this substance was saponified, m-toluyl acid was obtained with m.p. 110° and equivalent neutralization 136.

Isophthalic acid with m.p. 350° and coefficient of neutralization 83.1 was separated from the aqueous solution by evaporation and acidification with hydrochloric acid; in some experiments, m-cyanbenzoic acid melting at 217° and with coefficient of neutralization of 147.9.

The analysis of the gaseous reaction products was conducted in accordance with the methods described earlier [12].

Conclusions

1. The reaction of oxidizing ammonolysis of m-xylene with a catalyst of stannous vanadate was studied.

2. It has been shown that the basic product of the process is isophthalodinitrile. With a hydrocarbon:air:ammonia ratio of 1:80:3, contact period of 0.4 sec, and reaction temperature of 390° its yield reached 60% of that theoretically calculated for the substance taken.

3. The reaction studied may be recommended as a method of synthesizing the dinitrile of isophthalic acid.

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