U.D.C. 547.239 : 547.582 : 542.97

THE OXIDATIVE AMMONOLYSIS OF ORGANIC COMPOUNDS

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I. INTRODUCTION

Oxidative ammonolysis is a new catalytic process that combines the reactions of oxidation and ammonolysis. Each of these catalytic reactions has long attracted attention as very suitable for the technological design of methods of synthesising oxygen- and nitrogen-containing compounds; in these processes cheap raw materials, such as atmospheric oxygen and ammonia, may be used.

Catalytic oxidation of organic compounds was used as early as at the beginning of the twentieth century for the preparation of phthalic anhydride, anthraquinone, maleic anhydride and formaldehyde [1,2]. The replacement of expensive oxidising agents by air in the synthesis of these products was economically favourable; for this reason, a large number of papers appeared which described attempts to extent this method of synthesis to more and more organic compounds of different types. Apart from the development of new oxidative processes that found use in industry [3-10], much information was obtained on the mechanism of the reactions occurring. In particular it was shown that catalytic oxidation on oxide catalysts proceeds by a radical mechanism through a large number of intermediate stages comprising parallel and successive oxidations of the initial products and of stable and unstable intermediate products [11-15].

The catalytic ammonolysis of organic compounds has been less studied, but in this field, too, there is a fairly extensive literature [16-38]. As Andrussov showed, nitriles can be obtained directly from hydrocarbons by this reaction [39]. Catalytic ammonolysis of saturated hydrocarbons is effected in the vapour phase, as a rule, on oxide catalysts [28,29,40,41]; in contrast to the oxidation, it requires higher temperatures (500–1000°) and the yield of desired products (nitriles) generally does not exceed 20–25%. Ammonolysis of alkenes proceeds under somewhat milder conditions (400–600°) [32,42-44], but here the yield of nitriles is also low (up to 50%). The yield of nitriles is higher (up to 90%) in the ammonolysis of carboxylic acids under comparatively mild conditions [45], when the reaction may be carried out in the liquid phase in the presence of homogeneous and heterogeneous catalysts; the yield is not low even in the absence of a catalyst [45].

If ammonia is introduced into the reaction zone during the catalytic oxidation of naphthalene, phthalimide is formed in up to 50% yield instead of phthalic anhydride [47]. In the 1950's Erchak and Cosby and coworkers [48,50], and also Klimatis and Rasmussen [51,52] observed the formation of nitriles in the catalytic oxidation of alkenes, naphthene hydrocarbons, and alkylbenzenes in the presence of ammonia. Similar observations were made in the oxidation of pyridine homologues [53]. Oxides and salts of metals activated with carbon, silica gel, etc. were recommended as catalysts; the reaction could also be carried out without a catalyst. The yields of the corresponding aliphatic and aromatic nitriles never exceeded 50%, that is, they were the same as in catalytic ammonolysis.

On the other hand nitrogen-containing products were not observed when hydrocarbons, including *p*-cymene and cumene, were oxidised in the vapour phase [54,55].

Thus, up to 1950, there were only scattered observations indicating the possibility of preparing nitrogen-containing products by the catalytic oxidation of hydrocarbons in the presence of ammonia. However, there was no information in the literature on the mechanism of the reactions or on the part played by oxygen, ammonia, and catalysts in the process.

Systematic investigation of the catalytic oxidation of organic compounds of different classes in the presence of ammonia began only in the 1950's. [56-62] Experimental results showed that, when oxygen and ammonia are present simultaneously in the reaction zone, very complex parallel and successive coupled oxidations and ammonolyses of both the hydrocarbons and intermediate products occur. Oxidation takes a leading part in the process; because it proceeds by chain reactions, stable and unstable intermediates (free radicals, aldehydes, acids, etc.) that react readily with ammonia are accumulated. On the other hand, under the conditions of catalytic oxidation, ammonia too is easily converted into more active products, such as hydrazine and free radicals, which can react with hydrocarbons and intermediate products of their oxidation.

From such an interpretation of the mechanism of this complex process it received the name oxidative ammonolysis [57-59]. In recent years in non-Soviet literature the similar term "ammoxydation" has appeared [63,64] and the term "cyanodemethylation" has been used for a special case [65].

Oxidative ammonolysis is said to be used on an industrial scale for the preparation of acrylonitrile [66].

II. OXIDATIVE AMMONOLYSIS OF AROMATIC HYDROCARBONS

As mentioned above, catalytic oxidation in the presence of ammonia in the aromatic series was first carried out by Wohl [47]. Using fused vanadium(V) oxide as a catalyst, he obtained phthalimide from naphthalene in 50% yield. Later it was shown that, under conditions of oxidative ammonolysis, naphthalene can also be converted into the *o*-phthalodinitrile. According to patent information [67], phthalodinitrile is formed in 88% yield (based on starting material)

when a catalyst of vanadium(V) oxide precipitated on aluminium oxide is used together with a naphthalene : ammonia : oxygen molar ratio of 1 : (4–20) : (9–40) at a reaction temperature of ~425°. In addition to vanadium(V) oxide, the reaction is catalysed by the oxides of molybdenum, chromium, cobalt, iron, manganese, copper, tin, tungsten, thorium, aluminium, and uranium. Air may be used instead of oxygen.

A method has also been proposed for the synthesis of benzonitrile from naphthalene[68,69]. The process is effected in two stages. In the first, naphthalene is oxidised to phthalic anhydride in the absence of ammonia on a vanadium oxide catalyst promoted by potassium sulphate. Ammonia (3–5 moles per mole of naphthalene) is added to the hot gases issuing from the convertor and they are passed over porous silica gel at 390–430° in a second reactor. The yield of benzonitrile is ~70%.

Benzonitrile is more conveniently synthesised by the oxidative ammonolysis of monoalkylbenzenes.

Toluene can be converted into benzonitrile by the action of air and ammonia over a wide range of conditions and on a variety of catalysts. At 480–550° the reaction goes even on silicon oxide and aluminium oxide or on activated carbon, but the yield of benzonitrile is then low[51,52]. Catalysts consisting of oxides of metals of variable valency are much more active. Moreover, they enable the reaction to be carried out at lower optimal temperatures, and, as a result, the proportion of pyrolysis by-products is reduced. For example, on a catalyst of oxides of vanadium, molybdenum, and phosphorus in the proportions 11.4 : 3.9 : 0.034 and with a feed of 2 moles of ammonia and 75 moles of air per mole of toluene and a temperature range of 430–450°, benzonitrile was obtained in 75 mole % yield; the total conversion of starting material was 95%.[50] Satisfactory results were also obtained with vanadium(V) oxide precipitated on alumina[70] or on aluminium oxide that had been heated to 1250°.[60,61] However, the best catalysts appear to be tin and titanium vanadates, on which the yield of benzonitrile reaches 89–90% of the theoretical based on toluene taken[71,73]. It is recommended that 6–10 moles of ammonia and 50–60 moles of oxygen (as air) should be used per mole of hydrocarbon.

The introduction of chlorine atoms into the aromatic nucleus appears to complicate the conversion of the methyl group into a nitrile group; according to Koopman[74,75], 2,6-dichlorotoluene gives the dichlorobenzonitrile in only 45–50% yield.

Tin and titanium vanadates may also be recommended for the preparation of benzonitrile from other monoalkylbenzenes. On a vanadium oxide catalyst ethylbenzene is converted into benzonitrile in only 53% yield[60,61], but on tin vanadate the reaction goes practically completely (93–96%)[71,73]. Cumene behaves in the same way; the yield of benzonitrile from it reaches 98%.[71,73] When n-propyl- and n-butyl-benzenes are used, the yield of benzonitrile is somewhat lower; phthalimide[73] in 15% yield is one of the products of oxidative ammonolysis of these hydrocarbons. Commercial mixtures of monoalkylbenzenes containing ethyl-, propyl-, and butyl-benzenes, which are difficult to separate, are also used for the preparation of benzonitrile. As a result of the oxidative ammonolysis of these so-called "polyalkyls", which are by-products of ethylbenzene and cumene production, benzonitrile is formed at the rate of 700–750 g per kilogramme of starting material[71,73]. It should be mentioned that, with other optimal conditions, the concentration of oxygen in the reaction gases has the greatest effect on the yield of benzonitrile from monoalkylbenzenes (Fig. 1)[73].

Great attention has been paid to the oxidative ammonolysis of *p*- and *m*-xylenes. Hydrogenation of the terephthalodinitrile and isophthalodinitrile formed gives *p*- and *m*-xylylenediamine[76–79], which are used as raw materials in the preparation of a variety of polyamides with melting points up to 300° and higher[80–83], and this has attracted the attention of research workers. Moreover, these aromatic dinitriles may be hydrolysed to free terephthalic and isophthalic acids or to various intermediate products with mixed functions[84,85].

A patent of Cosby and Erchak[50] shows that a mixed catalyst of oxides of vanadium, molybdenum, and phosphorus does not make the process selective enough; as a result oxidative ammonolysis of *p*-xylene on this catalyst gives *p*-toluonitrile and terephthalodinitrile at the same time, each in yield of not more than 25–26%.

By analogy with the monoalkylbenzenes the oxidative ammonolysis of *p*-xylene proceeds smoothly on fused tin vanadate[86]. It is characteristic that on this catalyst the degree of conversion of *p*-xylene can be controlled by changing the ratio of the components of the initial reaction mixture, the contact time and the reaction temperature. For example, at 330–350° with comparatively small feeds of air and ammonia the predominating reaction products are *p*-toluamide and *p*-toluonitrile, formed in yields of 15% and 55% respectively[87]. Under more drastic conditions terephthalodinitrile is obtained in 70–75% yield as the main product[56]. Still greater selectivity is shown by fused titanium vanadate and coprecipitated aluminovanadium catalyst, the use of which gives terephthalodinitrile practically free from *p*-toluonitrile and amide impurities[86]. Tin and titanium vanadates may be used not only in the fused state but also deposited on aluminium oxide[88,89].

The oxidative ammonolysis of *p*-xylene depends not only on the composition of the active phase of the catalyst, but also on the nature and method of preparation of the carrier. Hadley and coworkers, who studied the oxidative ammonolysis of alkylbenzenes on a catalyst of vanadium(V) oxide precipitated on aluminium oxide, found that the temperature used in the preliminary heating of the Al_2O_3 has a great effect on the yield of nitriles[61,64,90–92]. As Table 1 shows, the most satisfactory results were obtained with a catalyst the carrier of which had been roasted at 1250–1300°. Several catalysts based on aluminium oxide prepared in this way were obtained and by means of them

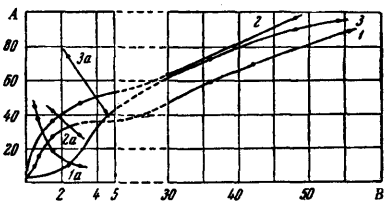


Fig. 1. Dependence of the yield of benzonitrile on the quantity of air in the oxidative ammonolysis of toluene (1), ethylbenzene (2), and cumene (3) on titanium vanadate[73]; 1*a*), 2*a*), and 3*a*) unreacted hydrocarbon. *A*) Yield of reaction products in %; *B*) quantity of oxygen (as air) in moles per mole of hydrocarbon.

TABLE. Effect of roasting temperature of aluminium oxide on the oxidative ammonolysis of *p*-xylene with a vanadium oxide catalyst[61]. Roasting time of carrier 22 h. $V_2O_5 : Al_2O_3$ = = 10 : 90 (wt.%), contact time 6 s. Xylene : ammonia : air = 1.5 : 6 : 92.5 (vol.%).

Roasting temperature of carrier, °C	Reaction temperature, °C	Yield, %		
		p-toluonitrile	terephthalodinitrile	CO_2
1050	360	1	66	18
1050	380	1	53	28
1250	370	1	77	12
1250	395	1	47	38
1300	355	15	61	5
1300	375	1	74	14
1300	395	1	30	53
1325	370	1	70	19
1325	395	1	52	33
1400	355	29	37	6
1400	395	0	73	20

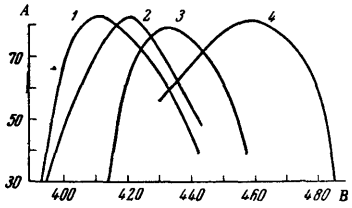


Fig. 2. Effect of thermal treatment of catalyst on the yield of terephthalodinitrile in the oxidative ammonolysis of *p*-xylene with a catalyst of vanadium oxides on aluminium oxide[94]. *p*-Xylene : NH_3 : O_2 = 1 : 4 : 13, contact time 3 s. *A*) Yield of reaction products, %; *B*) reaction temperature, °C. Roasting temperature of catalyst: 1) without roasting; 2) 500°; 3) 600°; 4) 700°.

terephthalodinitrile could be prepared in yields of 80% and more[88,93,94]. These workers also note that the thermal treatment of the finished catalyst is of great importance[94]. For example, increasing the roasting temperature of the catalyst does not affect the yield of terephthalodinitrile, but it extends the limits of the optimum temperature range of the reaction and moves it into a region of higher temperatures (Fig. 2).

Recently several publications have appeared on the oxidative ammonolysis of *p*-xylene with the use of dust catalysts[95,96]. This variation does not materially change other parameters of the process and has little effect on the yield of reaction products, although in one of the patents it is pointed out that the use of a fluid process makes it possible to reduce the consumption of ammonia to 3 moles per mole of xylene[95].

It has been proposed that water vapour should be introduced into the reaction zone with the object of increasing the yield of terephthalodinitrile, extending the optimum temperature range, and suppressing deep oxidation processes[56,86]. The effect of changes in the water feed on the enumerated characteristics of the process is shown in Fig. 3.

In addition to *p*-xylene, other *p*-dialkylbenzenes may be used as raw materials in the synthesis of terephthalodinitrile. Investigation of the oxidative ammonolysis

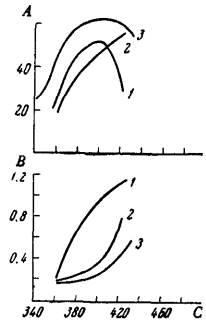


Fig. 3. Effect of quantity of water on the oxidative ammonolysis of *p*-xylene on tin vanadate[98]. $V_{hydrocarbon}$ = 50–52 g; V_{air} = 2400 litres; V_{NH_3} = 150–180 g per litre of catalyst per hour; contact time 0.4–0.6 s. *A*) Yield of terephthalodinitrile, %; *B*) yield of CO_2 in moles per mole of xylene; *C*) reaction temperature, °C. H_2O (g): 1) 35; 2) 400; 3) 800 per × × litre of catalyst per hour.

of *p*-cymene[56,89], and of diethyl- and diisopropyl-benzene[59,94,97] has shown that the dinitrile may be obtained from them in 45 to 60% yield and only traces of the nitriles of the corresponding alkylbenzoic acids are formed.

In oxidative ammonolysis *m*-xylene behaves in the same way as *p*-xylene[64,98–101]. The process is usually carried out under analogous conditions with the same catalysts. The only difference is that the yield of isophthalodinitrile, and particularly of *m*-toluonitrile, is somewhat lower than in the case of the *p*-isomers. Attempts to increase the yield of these nitriles by varying the reaction conditions, or by using new types of catalysts and carriers, for example, platinum on oxides of the heavy metals and vanadium(V) oxide on silicon carbide, did not lead to the desired results[102].

The difference in the behaviour of the *p*- and *m*-isomers of xylene is explained by structural features of the *m*-xylene and of the products into which it is converted[99]. The relatively low yield of the monofunctional nitrogen derivatives of *m*-xylene is connected with the adsorption of the *m*-xylene on the catalyst by means of the two side groups, as a result of which the groups react at the same time. In contrast to *p*-xylene, the *m*-isomer is unsymmetrical and it is assumed that because of the joint orienting effect of the side groups the C–H bond at the carbon atom of the ring situated between the groups is weakened and is therefore susceptible to the action of oxygen to a greater degree than the other C–H bonds. With a high concentration of oxygen, this means destruction of the ring and the formation of aliphatic oxygen- and nitrogen-containing compounds, and combustion products.

Since the separation of *p*- and *m*-xylenes is difficult it has been proposed that commercial and other mixtures of these isomers should be used in oxidative ammonolysis with subsequent separation of the dinitriles with the aid of selective solvents. On a stationary or moving catalyst of vanadium oxides precipitated on aluminium oxide the composition of the mixture of xylenes taken does not appear to

affect the conversion of each of the components; the proportion of isomers in the starting material is the same as that in the dinitriles obtained[103,104]. The total yield of terephthalo- and isophthalo-dinitriles reaches 75% of the theoretical. On fused tin vanadate the behaviour of the isomers depends on the proportion of isomers in the starting material and the general picture of the process assumes a different character[105]. Fig. 4, which is given as an example, shows that, when the quantity of isomer in the mixture decreases, its degree of conversion increases. This applies to a great degree to *m*-xylene; in the pure state this is converted into isophthalodinitrile in 20–40% yield, but in a mixture with 9 parts of *p*-xylene the conversion of *m*-xylene is practically complete. It is noteworthy that in experiments with equimolar, or close to equimolar, mixtures deep oxidation is considerable and the yield of carbon oxides increases.

The oxidative ammonolysis of *o*-xylene proceeds in a peculiar manner. Because of the proximity of the methyl groups, the main products are usually phthalic anhydride and phthalimide, irrespective of the nature of the catalyst. With a molar ratio of ammonia : hydrocarbon of 2 : 1 and above, phthalimide begins to predominate. Under optimal conditions its yield may reach 65–70%[50,61] and even 75%,[106] based on the throughput of hydrocarbon. As a rule, only traces of *o*-toluonitrile and *o*-phthalodinitrile are formed. The formation of phthalodinitrile is promoted by a high concentration of ammonia and by the introduction of water vapour into the reaction zone[107]. With the ratio *o*-xylene: : NH_3 : H_2O equal to 1 : (20–30) : (25–30) and an adequate supply of air, it may be obtained on tin vanadate in yields up to 45–50%. Only one worker has succeeded in obtaining phthalonitrile in a yield up to 60 wt.% with a feed containing less than 15 moles of ammonia per mole of *o*-xylene[100].

As a rule, oxidative ammonolysis of polyalkylbenzenes with three or more alkyl groups gives a mixture of aromatic nitriles. In particular, mesitylene on vanadium oxides or tin vanadates forms a mixture of mesitylenonitrile, uvitodinitrile, and trimesotrinitrile, the yields of which vary in the range 10–15, 20–25, and 20–25% respectively[60,101,108]. On dust vanadium oxide catalysts about 60% of mesitylene is converted into trimesotrinitrile[100].

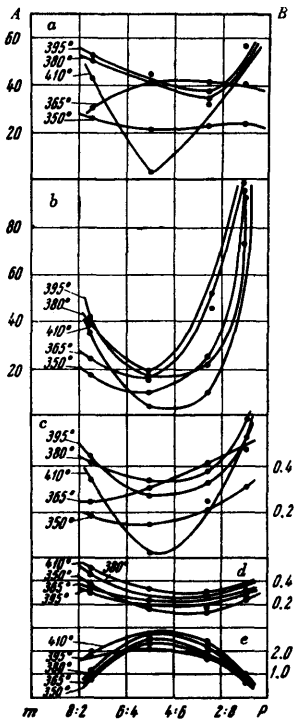


Fig. 4. Dependence of the yield of reaction products of oxidative ammonolysis on tin vanadate[105] on a mixture of *p*- and *m*-xylenes on the proportions of isomers in the mixture.
V_{mixt} = 45–50 g, V_{NH_3} = 130 g, V_{H_2O} = 350–400 g, V_{air} = 2350 litres per litre of catalyst per hour; contact time 0.5 s. *A*) Yield %; *B*) yield of HCN and CO_2 in moles per mole of xylene; *C*) composition of mixture of *p*- and *m*-xylenes.
a) Terephthalodinitrile; *b*) isophthalodinitrile; *c*) total yield of dinitriles; *d*) hydrocyanic acid; *e*) CO_2.

III. OXIDATIVE AMMONOLYSIS OF CYCLOALKANES AND CYCLOALKENES

Alkyl-substituted cycloalkanes and cycloalkenes are dehydrogenated under the conditions of oxidative ammonolysis on oxide catalysts to aromatic hydrocarbons, which are then converted into the corresponding nitriles. Only nitriles of aromatic acids are found in the catalysates, which indicates that the reaction proceeds in two stages. Thus, benzonitrile was obtained from methylcyclohexane[49] and the terephthalodinitrile from dimethylcyclohexane[109]. The oxidative ammonolysis of various terpene hydrocarbons has been studied on various catalysts[110–112]. In all cases the main product was terephthalodinitrile. The yield was 48–50% from α-pinene, dipentene, and *d*-limonene, and 15–30% from menthol, borneol, terpin hydrate, [*p*-menthane-1,8-diol (Ed. of Translation)], α-terpinolene, terpinen-4-ol, and isopulegol.

IV. OXIDATIVE AMMONOLYSIS OF ALKENES

The oxidative hydrolysis of alkenes to the nitriles of unsaturated acids is of exceptional importance. It is considered[66] that on the basis of this one of the most economic methods can be developed for the synthesis of vinyl cyanides, in particular acrylonitrile, the monomer for high-quality chemical fibres, synthetic rubber, and other polymers. Intensive work on the oxidative ammonolysis of propene is being carried on in the Soviet Union[113], the United States[66,114,115], Great Britain[64], and other countries. Several variants of the oxidative ammonolysis of propene to acrylonitrile have been described; these have been developed in the search for a more economic process and they differ mainly in the proportion of propene to ammonia. Acrylonitrile can be obtained in 65% yield, based on hydrocarbon used, or 72% based on hydrocarbon consumed, with a feed of 3 or more molecules of ammonia per mole of propene and a large excess of oxygen on cobalt, tin or antimony oxide catalysts, and also on mixed catalysts of molybdenum, tellurium, bismuth and phosphorus oxides[116–121]. Water vapour is an essential component of the reaction mixture; it is used in a molar ratio to propene of 0.25 to 10.[116] In all papers it is noted that the yield of acrylonitrile increases with increasing concentration of ammonia.

When a high concentration of ammonia is used, a considerable part of it passes through the convertor without change, and it may interact in the scrubbers with acrylonitrile to form various amino-derivatives. Cyanethylation of water also occurs in the scrubber system with the formation of hydracrylonitrile and 2,2'-oxydiacetonitrile; other secondary processes, due to the presence of unreacted ammonia, lead to the undesirable consumption of acrylonitrile. To avoid this, the ammonia coming from the reactor is preferably neutralised with sulphuric acid.

In another variant, an equimolar mixture of propene, ammonia and oxygen are passed over the catalyst, or the reaction is carried out with insufficient ammonia and air [116,120,122,123]. The conversion of ammonia is relatively high, side reactions are at a minimum, and unreacted propene is returned to the reaction. The yield of acrylonitrile, based on hydrocarbon consumed, varies between 60 and 75%. Methods of synthesising acrylonitrile from allyl chloride have also been described [124,125]; in a two-stage method propene is first oxidised in the gaseous phase by air to acrolein, after which ammonia is added to the reaction gases and they are passed over a catalyst (oxides of molybdenum, phosphorus, or other elements of variable valency) at 350–400°. [126]

V. OXIDATIVE AMMONOLYSIS OF ALKYLPYRIDINES

In recent years a considerable amount of work has been done on the oxidative ammonolysis of alkyl derivatives of pyridine. The reaction is of interest because the cyanopyridines formed can be rapidly hydrolysed to give a good yield of free pyridinecarboxylic acids or their amides [127,128], many of which are widely used in the pharmaceutical industry [129]. According to published information the reaction conditions for 3- and 4-picolines differ little from the conditions for the oxidative ammonolysis of the alkylbenzenes. The reaction goes well with 1–3% of picoline and 3–10 vol.% of ammonia in the air feed, a contact time of 0.5–3 s, and a temperature of 350–420°. Vanadium(V) oxide [53,130–133], titanium and tin vanadates [134–137], iron [138,139], silver [138], a mixture of vanadium oxides with oxides of molybdenum and phosphorus [53,140] or with potassium sulphate [139], iron niobates [138], etc. may be used as catalyst. The catalyst may be fused or precipitated on a carrier and used as 3–5 mm granules or as a dust. As a rule, nicotinic acid and isonicotinic acid nitriles are obtained in a stable yield of 60 to 85% based on the weight of picoline taken, or 75 to 95% based on the picoline consumed. Some amides of pyridinecarboxylic acids, hydrogen cyanide, and carbon oxides are also formed. The oxidative ammonolysis of 3- and 4-ethylpyridines proceeds in the same way, although the yield of nitriles is somewhat lower (30–50%) [53]. The nitrile of picolinic acid has been obtained from 2-picoline in the same yield [132,138,141]. The presence of pyridine in the reaction products indicates that, under the given conditions, the side group in the α-position can be eliminated and replaced by a hydrogen atom [141].

On oxidative ammonolysis the dialkyl pyridines only give the nitriles of the alkylpyridine acids and nitriloamides in small quantities. Thus, 2,6-dimethylpyridine (lutidine) gives 6-methylpyridine-2-nitrile and 2-cyanopyridine-6-carboxamide; 5-ethyl-2-methylpyridine (collidine) gives 5-methylpyridine-2-nitrile and 2-cyanopyridine-5-carboxamide [53,138,142]. By analogy with 2-picoline, in oxidative ammonolysis of 5-ethyl-2-methylpyridine a side group is eliminated from the α-position and as a result nicotinonitrile appears amongst the reaction products. When a catalyst consisting of vanadium oxides precipitated on aluminium oxide is used, the yield of nicotinonitrile is 37%, based on the 5-ethyl-2-methylpyridine passed through [53].

Because of the difficulty of separating 3- and 4-picolines from the corresponding coal-tar fractions, attempts have been made to subject various commercial mixtures to oxidative ammonolysis. From the 3-picoline fraction, which contains ~30% of other alkylpyridines, nicotinonitrile was obtained on a dust-like vanadium-oxide catalyst in 83% yield, based on the pure isomer [143]. Commercial 4-picoline, containing ~8% of impurities, is converted into isonicotinonitrile in almost 88% yield. From a mixture of 3- and 4-picolines in close to equimolecular proportions, nitriles were obtained in practically the same ratio; the yield varied between 55 and 85%, depending on the conditions of the reaction [144,145]. Oxidative ammonolysis of a commercial product consisting of 3-picoline (33.8%), 4-picoline (35.7%), and lutidine (27.4%) gave a mixture of nitriles in 59.9% yield; the mixture consisted of 31% of nicotinonitrile, 51% of isonicitinonitrile, 11% of 6-methylpyridine-2-nitrile, and 7% of picolinonitrile [143].

VI. SOME QUESTIONS CONNECTED WITH THE MECHANISM OF OXIDATIVE AMMONOLYSIS OF ORGANIC COMPOUNDS

A number of workers quite rightly consider that amino-compounds are the primary products of the reaction of hydrocarbons and ammonia [33,146]; these products are then dehydrogenated to nitriles:

$$R{-}CH_3 + NH_3 \rightarrow R{-}CH_2NH_2 \rightarrow R{-}CN,$$
$$R{-}CH_2{-}R' + NH_3 \rightarrow R{-}CHNH_2{-}R' \rightarrow R{-}CN.$$

With alkenes the first stages of the process are connected with the addition of ammonia to the double bond:

$$R{-}CH{=}CH{-}R' + NH_3 \rightarrow R{-}CHNH_2{-}CH_2{-}R' \rightarrow R{-}CN.$$

The orientation of the NH_2-group may differ according to the nature of the radicals R and R'. This question has been extensively considered in the literature, but is still not finally elucidated [26,32,33]. Moreover, in α-alkenes the amino-group often combines, according to Markovnikov's rule, with the carbon atom attached to other carbon atoms [44,147–150]:

$$R{-}CH{=}CH_2 + NH_3 \rightarrow R{-}CHNH_2{-}CH_3 \rightarrow R{-}CN.$$

Nitriles with an unchanged carbon skeleton are formed from α-alkenes in very small quantities; as a rule, they require special conditions, for example, high pressure [150–153]:

$$R{-}CH{=}CH_2 + NH_3 \rightarrow R{-}CH_2{-}CH_2NH_2 \rightarrow R{-}CH_2{-}CN.$$

Amino-compounds appear in fact to be the intermediate products of ammonolysis of hydrocarbons, as they have been separated in very small quantities and identified by a number of workers [16,151–154].

It is thought by some that a similar reaction also occurs in the oxidative ammonolysis of hydrocarbons [57,59,58,155]. Although the direct ammonolysis proceeds under very drastic conditions (at 500–600°) with a very small yield of nitriles, in the presence of oxygen the optimal temperature is sharply reduced and the conversion of starting material increases.

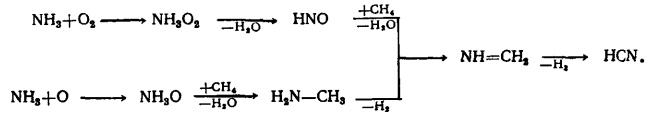
Paushkin and Osipova regard ammonolysis as a free--radical process in which both hydrocarbon and NH_2 radicals take part[32]. This point of view is in agreement with other results on ammonolysis, in particular those dealing with the thermal synthesis of aniline from benzene and ammonia[156], or the ammonlysis of benzene in the silent electric discharge[157], that is, in conditions under which the reactions proceed through free radicals.

In the presence of oxygen the rate of generation of hydrocarbon radicals by a catalyst surface increases[158]. The rate of formation of NH_2 radicals also increases[159-161]. The rate of formation of the latter may be so high that hydrazine appears in the reaction products[162]. In the presence of silver oxide at 300–400°, hydrazine can be obtained by the oxidation of ammonia in up to 20% yield[163,164]. This obviously leads to an increase in the rate of formation of amino-compounds.

Moreover, as has been noted above, amino-compounds are present in small quantities in the products of the reaction of hydrocarbons with ammonia. This is explained by the fact that at high temperature in the presence of metallic or oxide catalysts they are rapidly dehydrogenated to nitriles. Experiments on the dehydrogenation of benzylamine on a nickel catalyst have been described[165,166]. On tin and titanium vanadates, benzylamine is converted into benzonitrile in 45–50% yield[167]. The nitriles of aliphatic acids are obtained in still higher yields from various aliphatic amines on nickel, palladium, platinum[168-171], molybdenum oxide[172] chromium oxide[173], and aluminium oxide[174,175]. Oxygen to a still higher degree promotes the further conversion of amino-compounds, in particular the dehydrogenation of these compounds to nitriles. Even aniline under the action of air on thallium oxides is subjected to oxidative dehydrocondensation to azobenzene and phenazine[176]. Methallylamine with air in the presence of a silver catalyst gives 76 mole % of acrylonitrile[177,178], and on titanium vanadate, with an equimolecular quantity of oxygen and 8–10 moles of ammonia, benzylamine is converted almost quantitatively into benzonitrile[167].

If the possibility of dehydrogenating amines is excluded, they may accumulate in the reaction products. An example of this is the formation of aniline on the ammonolysis of benzene in the presence of iron, nickel, or copper catalysts[179], and cobalt or iron oxides[180].

Andrussov[181-184], Wendlandt[185], and other workers[186] have come to the conclusion that intermediate amino-compounds may also be formed in the catalytic synthesis of hydrogen cyanide from methane and ammonia in the presence of oxygen. Since the process starts with the oxidation of ammonia, they suggest that methylamine and methylenimine stages precede the formation of nitroxyl [sic (Ed. of Translation)]:



The synthesis of hydrocyanic acid is carried out at a temperature of ~1000° on metallic catalysts (platinum and alloys of platinum with rhodium, iridium, ruthenium, etc.) under specific conditions that differ substantially from oxidative ammonolysis. It may be thought that for this reason the hypothetical scheme given with the participation of nitroxyl cannot be considered as applying to the mechanism of oxidative ammonolysis of hydrocarbons.

Under conditions of oxidative ammonolysis ammonia may be oxidised to nitrogen oxides[187-190], and these could react with hydrocarbons to give carboxylic acid nitriles. Toluene and the xylenes readily react with oxides of nitrogen at 400–700° in the presence of dehydrogenating catalysts (for example, silver), to give the corresponding aromatic nitriles[191]. Isonicotinonitrile is formed from 3-picoline. There are reports of the construction of an industrial plant for the preparation of acrylonitrile from propene and nitrogen monoxide[192]. Nitro-compounds appear to be intermediate products in this reaction. In this connection, it should be noted that Wohl[47], Green[193], and also Zal'kind and Kesarev[194] observed the formation of phthalimide in the vapour-phase oxidation of nitronaphthelenes on various oxide catalysts in the absence of ammonia. The routes considered above with participation of amines and nitro-compounds are not the only ones in oxidative ammonolysis. It has been shown that with a sufficient concentration of oxygen in the presence of oxide catalysts the initial hydrocarbon may be subjected to oxidation to oxygen--containing compounds, which then participate in the formation of nitriles[57-59,72,73,86,98,99,107,155]. Later this point of view was confirmed by many workers[64,120].

It is well known that the catalytic vapour-phase oxidation of hydrocarbons leads to the formation of peroxide compounds, aldehydes, ketones, alcohols, acids, anhydrides, lactones, and other oxygen-containing products[1,11,12,15]; the products depend on the structure of the initial compound. Many of these compounds have also been found in the oxidative ammonolysis of hydrocarbons. The yield of these compounds depends on temperature, ammonia concentration, time of contact, and other parameters, but under certain conditions they may accumulate in considerable amounts (see Figs. 5-8).

At a high temperature in the presence of catalysts nearly all the oxidation products of hydrocarbons mentioned are capable of reacting at some rate or other with ammonia, giving amines, imines, amides, and acid nitriles.

The simplest route is that through an acid stage:

$$R{-}COOH \longrightarrow R{-}COONH_4 \longrightarrow R{-}CONH_2 \longrightarrow R{-}CN.$$

An extensive literature is devoted to the vapour-phase ammonolysis of acids and this method has long been considered very convenient for the synthesis of nitriles of the most varied structure. Methods of preparing nitriles from aromatic[196-199], aliphatic[200-205], and heterocyclic[206-208] acids have been described, as well as methods of preparing dinitriles from acid anhydrides[209-211] and imides[212-214], also imides from anhydrides[210], methods of dehydrating amides[200,208,215,216], etc. Ammonolysis is carried out on oxide catalysts, preferably catalysts with dehydrating activity at ~500°, and, as a rule, a large excess of ammonia is used.

On catalysts of metals of variable valency at 350–450° in the presence of air, that is, under oxidative ammonolysis conditions, the degree of conversion of acids into nitriles is low. The cause of this is connected not with the amide dehydration stage, the rate of which is sufficiently high, but with the formation of the amide group from the carboxyl[195,217,218]. The fact is that under the given conditions the acids not only react with ammonia to form amides, but they are also decarboxylated. Dilution of the reaction mixture with air, which finally leads to a reduced concentration of acid and ammonia in the reacting gases, promotes this side reaction.

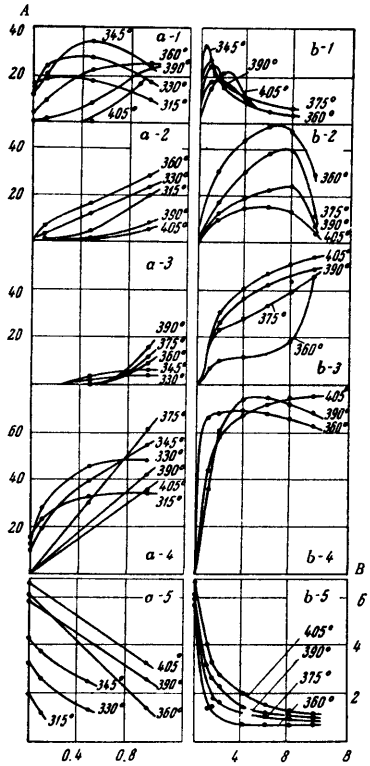


Fig. 5. The effect of ammonia additions on the yields of products of oxidative ammonolysis of *p*-xylene on tin vanadate[86].
$V_{hydrocarbon}$ = 50–52 g, V_{air} = 2400 litres, V_{H_2O} = 350–400 g per litre of catalyst per hour. Contact time = = 0.4–0.6 s. *A*) Yield %; *B*) yield of CH_2O, HCN, CO, and CO_2 in moles per mole of xylene; *C*) moles NH_3 per mole of xylene. *a*) Up to 1 mole of NH_3; *b*) up to 10 moles of NH_3 per mole of xylene. 1) Terephthalic acid; 2) *p*-toluonitrile; 3) terephthalodinitrile; 4) total yield of C_8 products; 5) total yield of gaseous products.

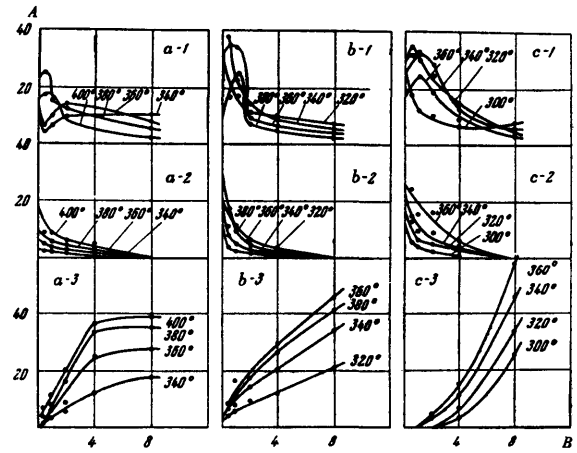


Fig. 6. Effect of ammonia additions on the yield of products of the oxidative ammonolysis of toluene (*a*), ethylbenzene (*b*), and cumene (*c*) on tin vanadate[73].
$V_{hydrocarbon}$ = 30 g, V_{air} = 2200 litres, V_{H_2O} = 250 g per litre of catalyst per hour. *A*) Yield %; *B*) moles of NH_3 per mole of hydrocarbon. 1) Benzoic acid; 2) maleic anhydride; 3) benzonitrile.

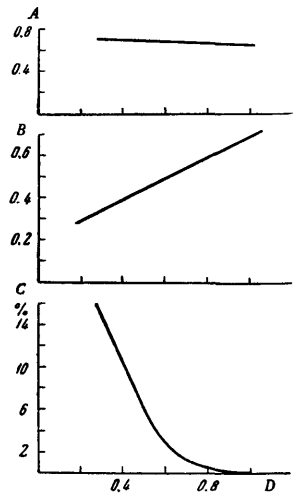


Fig. 7. The effect of the quantity of ammonia on the oxidative ammonolysis of propene in the presence of oxide catalyst[120], $C_3H_6 : O_2 : H_2O$ = = 1 : 1.5 : 1. Contact time = 2 s, t = 450°. *A*) Total degree of propene conversion; *B*) degree of propene conversion into acrylonitrile; *C*) yield of aldehydes, %; *D*) moles of NH_3 per mole of propene.

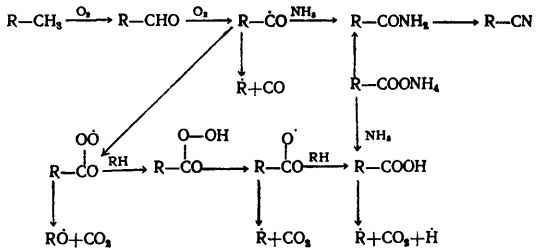
This special feature in the ammonolysis of acids has been used to prepare benzonitrile from phthalic anhydride and phthalimide; when these, mixed with ammonia and air, are passed over oxide catalysts they undergo decomposition with opening of the five-membered ring and elimination of one of the side groups[219–221]. The two-stage synthesis of benzonitrile from naphthalene described above is based on the same principle[68–69].

In the gas phase, aldehydes react with ammonia in two main directions. One of them, which was already studied by Chichibabin, is cyclisation with the formation of pyridine derivatives at a temperature of ~500°, often without a catalyst or with catalysts of the aluminium-oxide or silica type[222–227].

Ammonolysis of aldehydes on oxides of metals of variable valency gives acid nitriles. Thus benzonitrile is obtained in 40% yield from benzaldehyde and ammonia on thorium oxides[228,229]. On a copper catalyst the yield of benzonitrile was 46%,[230] and on titanium and tin vanadates nearly 90%.[231,232] On chromium and cobalt catalysts propionaldehyde is converted into propionitrile in 50–70% yield[233,235]. The preparation of methacrylonitrile[230], heptanenitrile (oenanthonitrile), 3,3,5-trimethylcapronitrile[236], acrylonitrile[237], and nitriles of a number of other carboxylic acids[238,239] by the direct ammonolysis of aldehydes on vanadium and molybdenum oxides, etc. has also been reported.

In contrast to the ammonolysis of acids, when aldehydes react with ammonia the addition of oxygen or air not only accelerates the process but also suppresses many side reactions. In the presence of air, benzonitrile, for example, is formed from benzaldehyde in 93.6% yield [62,72] and acrolein is converted into acrylonitrile (50–70% yield) on nearly all types of oxidative catalysts, including vanadium [237,240], molybdenum [241-243], chromium, manganese [126], and various mixed catalysts [244-246].

In this connection, the authors of this review concluded that when the methyl group is subjected to oxidative ammonolysis, the nitriles are formed through an amide stage, usually not from acids but from aldehydes [57-59,72,247]:



Similar interpretations on the role of aldehydes, in particular the role of acrolein in the oxidative ammonolysis of propene to acrylonitrile have been put forward by Hadley [64]. However, he considers that ammonia reacts with the carbonyl group by an aldimine mechanism:

$$R{-}CHO + NH_3 \longrightarrow R{-}CH{=}NH \longrightarrow R{-}CN.$$

Ketones as well as aldehydes may be intermediates in the oxidative ammonolysis of hydrocarbons with a side-chain having two or more carbon atoms [248-250]. The vapour-phase reaction of ketones with ammonia has been little studied. In one of the earlier papers it is reported that the ammonolysis of acetophenone and propionphenone on thorium oxide gives small amounts of the corresponding ketimines, which were isolated only as hydrochlorides [251]. On tin and titanium vanadate catalysts, acetophenone reacts with ammonia by a Chichibabin-type reaction, giving 2,4,6-triphenylpyridine in 35% yield based on ketone taken or 98% on ketone consumed [252]. Oxidative ammonolysis, even with very small air feeds, of acetophenone gives benzonitrile as the only product; the yield exceeds 70%. [72]

Therefore in oxidative ammonolysis of hydrocarbons the sequence for the conversion of the alkyl group into the nitrile group depends on the process conditions (hydrocarbon : NH_3 : O_2 ratio) and on the structure of the initial compounds. On the basis of data from the literature and experimental results, the authors of the present review have proposed a scheme of the basic probable stages in the oxidative ammonolysis of toluene, ethylbenzene, and cumene [72] (See Fig. 9).

Alcohols may also be intermediates in the catalytic vapour-phase oxidation of hydrocarbons. Ammonolysis of alcohols leads to the formation of amines or nitriles according to the conditions.

Sabatier and Mailhe were amongst the first to show the possibility of forming alkylamines by the ammonolysis of alcohols [253,254]. In the 1930's a series of papers of Shuikin and coworkers [255-257] on the study of the reaction of alcohols with ammonia in the presence of mixed oxide dehydration catalysts, began to appear. In these papers it was shown, in particular, that butylamine could be obtained in 35–40%

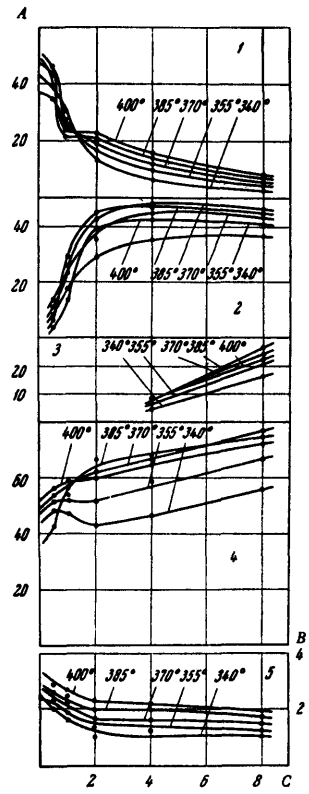


Fig. 8. Dependence of the yield of products of the oxidative ammonolysis of *o*-xylene on the reaction temperature and quantity of ammonia on a tin vanadate catalyst [107]. V_{xylene} = 55–60 g, V_{air} = 2500 litres, V_{H_2O} = = 40 g per litre of catalyst per hour. Contact time = 0.6 s. *A*) Yield %; *B*) yield in moles per mole of xylene; *C*) moles NH_3 per mole of xylene. 1) Phthalic anhydride; 2) phthalimide; 3) *o*-phthalodinitrile; 4) total yield of C_8 reaction products, %; 5) total yield of gaseous products in moles per mole of xylene.

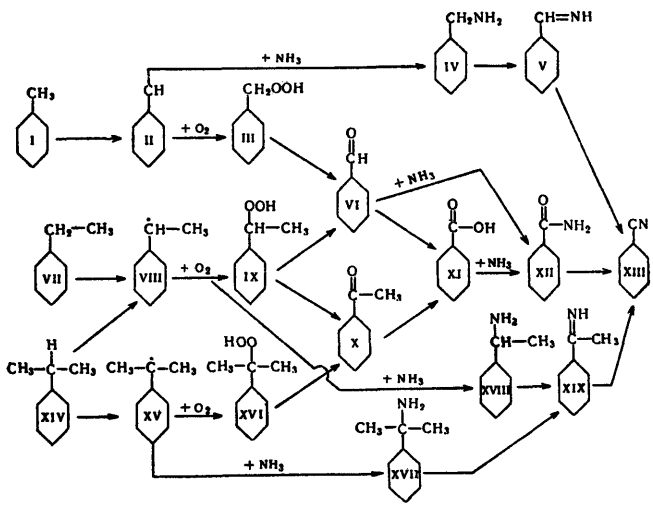


Fig. 9. Reaction scheme for the oxidative ammonolysis of monoalkylbenzenes [72].

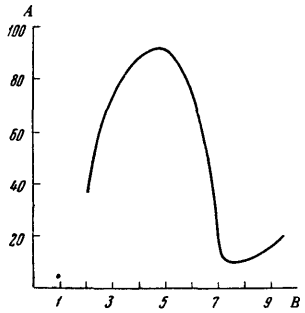


Fig. 10. Dependence of nitrile content of catalysate on the number of carbon atoms in the alcohol molecule[261]. Catalyst Ni/Al_2O_3, Ni content = 7.5%. *A*) Nitrile content of catalysate, %; *B*) number of carbon atoms in alcohol molecule.

yield from butanol at 380–420° on aluminium oxide. This reaction goes quite satisfactorily on catalysts of such natural materials as alumina and bauxite[258].

The position of the hydroxyl group has a great effect on the ammonolysis of alcohols[259]. Thus, in the butyl alcohol series the primary alcohol reacts fastest and the tertiary alcohol gives amines in only negligible amounts.

The use of dehydrogenating catalysts changes the direction of the reaction and nitriles become the main products of the ammonolysis of alcohols. Popov showed that, when butyl alcohols react with ammonia in the presence of platinised silica gel, butyronitrile is formed in yield up to 27%.[259] On a nickel catalyst, ethanol, propanol, butanol, and benzyl alcohol give the corresponding nitriles in 50 to 90% yield[260-262]. Similar activity is shown by copper and silver catalysts[263,264]; the sulphides of zinc, tungsten, nickel, titanium, and chromium[265]; aluminomolybdenum oxide catalyst[266]; and oxygen-free zinc salts[267].

In a study of the ammonolysis of various aliphatic alcohols Popov and Shuikin[261] found that on a nickel catalyst the greatest amount of nitrile is obtained from alcohols with four or five carbon atoms (Fig. 10).

According to available patent information[246,268], in the presence of dehydrogenating and oxidative catalysts, especially when oxygen is present in the reaction zone, the formation of nitrile from alcohol and ammonia should proceed through the intermediate aldehyde:

$$R{-}CH_2OH \xrightarrow[-H_2]{} R{-}CHO \xrightarrow{+NH_3} R{-}CONH_2 \xrightarrow[-H_2O]{} R{-}CN$$

It has been noted above that in the oxidative ammonolysis of hydrocarbons the addition of water vapour has a favourable effect on the yield of nitriles[50,86,116,242].

The introduction of water vapour into the reaction zone also promotes the formation of carbonyl and carboxylic derivatives in the vapour-phase catalytic oxidation of hydrocarbons with atmospheric oxygen[250,269-271]. It has been shown by direct experiments that toluene, benzil, and benzaldehyde on oxides of vanadium at 350–420° in the absence of air react with water to form benzoic acid and other oxygen compounds[272]. In this connection it has been suggested that the favourable action of water on the oxidative ammonolysis of hydrocarbons is also connected with the participation of water in the formation of intermediate oxygen-containing compounds[247].

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U. D. C. 547.362.1/3

REACTION OF ACETYLENE AND ALKYNYL COMPOUNDS WITH AMINES AND AMMONIA

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