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Abstract

Full Text

CHEMISTRY

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SYNTHESIS OF NITRILES FROM ALCOHOLS AND AMMONIA ON OXIDE CATALYSTS

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In recent years an ever greater number of previously difficult-to-obtain substances have become products of large-scale production. This applies fully to nitriles as well. Such nitriles as acrylonitrile and adipic acid dinitrile already find broad industrial application. Acetonitrile and other nitriles of fatty acids are finding increasing use. The preparation of nitriles by direct interaction of ammonia with organic compounds has attracted the attention of numerous researchers both in our country and abroad. This interest is caused by the desire to find a method which, using relatively inexpensive raw materials, would make it possible to obtain acetonitrile and other nitriles in large quantities. Such inexpensive raw materials are gaseous hydrocarbons from the thermal and catalytic cracking of petroleum, as well as low-molecular paraffin hydrocarbons. Recently the preparation of nitriles from olefins and ammonia has been covered rather extensively in the literature; several articles have also been devoted to reactions of paraffin hydrocarbons with ammonia. In many works the interaction of alcohols with ammonia is considered, although mainly from the standpoint of obtaining amines.

The preparation of nitriles from alcohols and ammonia is also reported in several patents. Thus, a British patent ⁽¹⁾ describes the preparation of butyronitrile in 45% yield from butyl alcohol and ammonia in the vapor phase over a reduced nickel catalyst at 159° and with a 2-5.5-fold excess of ammonia. Other researchers also established the formation of nitriles as intermediate products in the production of amines ⁽²⁾. *n*-Butyronitrile and benzonitrile were obtained by Denton and Bishop, respectively, from *n*-butyl and benzyl alcohols in the presence of an alumomolybdenum catalyst at a temperature of 438° and a twofold excess of ammonia ⁽³⁾. A British patent ⁽⁴⁾ describes the preparation of nitriles from primary alcohols and ammonia in the vapor phase in the presence of catalysts containing oxides of vanadium, molybdenum, tungsten, and salts of molybdenum and nickel. A Danish patent ⁽⁵⁾ likewise indicates the possibility of obtaining nitriles from the corresponding alcohols and ammonia over a Zn catalyst at 350-475°. Thus, from *n*-heptyl alcohol at 440° the nitrile C₆H₁₃CN was obtained in 60% yield. Ethyl alcohol with ammonia over reduced copper at 301-344° gives acetonitrile in 40% yield ^(6,7).

We investigated the reaction of ethyl and isoamyl alcohols with ammonia in the presence of an oxide alumomolybdenum catalyst (10% MoO₃, 90% Al₂O₃).

The alcohol was fed at a space velocity of 0.13 l/l of catalyst per hour, set by means of a clock mechanism, into a reactor with the catalyst placed in a catalytic furnace with a thermoregulator. Ammonia from a cylinder, after drying over solid caustic potash, was introduced there as well at the required rate,

set according to the rheometer. The reaction products were first condensed in a receiver fitted with a reflux condenser, and then in traps cooled with dry ice in isopropyl alcohol. The exit gases, freed of ammonia by passage over the surface of water and through a tube with solid ammonium thiocyanate, were measured with a gas meter and collected in a gas holder for analysis. Gas analysis was carried out on a VTI apparatus.

The experiments were carried out for three hours. The catalyst was regenerated by blowing air through it until the coke formed during the reaction had been completely burned off. After removal of the ammonia and ammonium cyanide dissolved in it, the catalyzate was distilled from a Favorskii flask by boiling on a water bath with a reflux condenser. A broad fraction with b.p. up to 98° was collected; the residue was water. The broad fraction was then redistilled and the 74–77° fraction was collected, representing the azeotrope of acetonitrile with water. Anhydrous acetonitrile was obtained by drying the azeotrope over solid potassium hydroxide, followed by distillation over P₂O₅. Identification of acetonitrile was carried out by a series of qualitative reactions, by physicochemical constants, and by obtaining the condensation product with phloroglucinol (Table 1).

Table 1
Physicochemical properties of acetonitrile

<i>CH</i> ₃ <i>CN</i>	B.p., °C and pres- sure, mm Hg	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Mol. wt.	<i>MR</i>	M.p.	Elementary	Elementary
						of acetonitrile- phloroglucinol, °C	com- posi- tion, % H	com- posi- tion, % C
Synthesis	80.0- 81.5/730	1.3432	0.7819	42	11.04*	216- 218	58.73	7.45

Literature data (⁸) and theo- reti- cal	81.6/760	1.3442	0.7828	41.1	11.13	218.5 (⁹)	58.52	7.36
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* MR , theoretically calculated on the basis of atomic refractions, is 11.25.

In experiments with ethyl alcohol, the influence of temperature on the yield of acetonitrile was studied.

Below we present the data obtained, from which it is evident that formation of acetonitrile begins at temperatures above 350°, and with further increase in temperature the yield rises to a certain maximum, after which it begins to fall as a result of an increase in the rate of side reactions involving decomposition of ammonia and of the acetonitrile formed (space velocity of alcohol = 0.13 hr⁻¹; $C_2H_5OH : NH_3 = 1 : 2$):

	350	415	466	487	510	538
Temperature, °C						
Yield of ace- toni- trile, mol. %: based on NH_3	—	6.6	7.8	12.6	10.4	4.2
Yield of ace- toni- trile, mol. %: based on C_2H_5OH	—	12.2	14.4	22.9	19.5	11.8

	350	415	466	487	510	538
Yield of NH_4CN per alcohol passed, mol. %	—	1.2	2.5	2.7	4.8	10.2

When working with ethyl alcohol at temperatures below 400° , traces of pyridine were detected. All fractions had an elevated refractive index and the characteristic odor of pyridine. The presence of pyridine was established by a qualitative reaction with nickel thiocyanate and copper sulfate ⁽¹⁰⁾. In addition, a small upper layer had a refractive index of 1.5057, close to that given in the literature for pure pyridine (1.5092).

The reaction of isoamyl alcohol with ammonia was also studied. The experiments were carried out in an analogous manner. After removal of ammonia and ammonium cyanide, which formed in small amounts, the catalyzate separated into two layers. By a qualitative reaction with $FeCl_3$, acetonitrile in the aqueous layer ...

was not detected. After drying over solid KOH, the upper layer was distilled from a Claisen flask, with collection of the fraction $28-70^\circ$ ($n_D^{20} = 1.3778$) and the broad fraction $70-128^\circ$. In order to verify the absence of isoamyl alcohol in the broad fraction, its hydroxyl number was determined by the method of Tsereteli–Chugaev. The percentage of OH was found to be 1.17, which is within the experimental error; thus, isoamyl alcohol is absent from the $70-128^\circ$ fraction. The yield and physicochemical properties of the $70-128^\circ$ fraction are given in Table 2.

Table 2

Yield and physicochemical properties of the $70-128^\circ$ fraction

(space velocity of alcohol = 0.13 h^{-1} ; $i-C_5H_{11}OH : NH_3 = 1 : 3$)

Temperature, $^\circ\text{C}$	Yield of the $70-128^\circ$ fraction from the starting alcohol, wt. %	Mol. wt.	d_4^{20}	n_D^{20}
319	33	83	0,7990	1,3981
356	27	81	0,7972	1,3959

Temperature, °C	Yield of the 70-128° fraction from the starting alcohol, wt. %	Mol. wt.	d_4^{20}	n_D^{20}
418	21	74	0,7924	1,3949
458	21	71	0,7932	1,3918
487	27	59	0,7944	1,3783
510	23	60	0,7927	1,3741

As is seen from Table 2, with an increase in the reaction temperature the molecular weight, specific gravity, and refractive index of the product decrease, i.e., the yield of low-molecular nitriles increases. Distillation of the 70-128° fraction on a column showed that at low experimental temperatures the principal mass boils at 125-128° and amounts to as much as 60% by weight ($t = 319^\circ$). At a temperature of 510° this fraction amounts to only 10%. Correspondingly, the yield of light fractions increases. For the 125-128° fraction, the physicochemical constants and elemental composition were determined (Table 3).

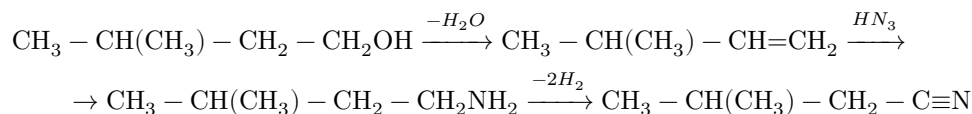
Table 3
Physicochemical constants of isovaleronitrile

Isovaleronitrile Synthesized 125- 128/730	B.p., °C and pres- sure, mm Hg	Mol. wt.	d_4^{20}	n_D^{20}	M.p. of con- densa- tion prod- uct with phloroglu- cinol	Elementa	Elementa	Elemental
						com- posi- tion, % H	com- posi- tion, % C	com- posi- tion, % N
		82	0,7951	1,3955	206°	72,21	10,91	16,62

Isovaleronitrile	B.p., °C and pres- sure, mm Hg	Mol. wt.	d_4^{20}	n_D^{20}	M.p.	Elementa	Elementa	Elemental
					of con- densa- tion prod- uct with phloroglu- cinol			
According to liter- a- ture data (8) and theo- reti- cal	129,5/764	83,1	0,7884*	0,8061**	—	72,24	10,91	16,85

* d_{20}^{20} . ** d_0^{20} . *** For *n*-valeronitrile.

Since the initial isoamyl alcohol contains an admixture of other isomeric alcohols, the 125–128° fraction may also contain methylethylacetone, whose properties (b.p. 125°/760, $d_0^{20} = 0.8061$) are similar to those of isovaleronitrile. The mechanism of formation of nitriles from alcohols has not been studied, but, using the scheme proposed by Denton and Bishop ⁽⁷⁾ for obtaining acetonitrile from propylene and ammonia, the following mechanism may be assumed:



However, this scheme requires verification, since the work of A. F. Plate and M. E. Vol'pin ¹¹ has shown that, in the case of propylene, addition of ammonia proceeds according to Markovnikov's rule.

It is of interest to compare the data obtained in the present work with the data obtained by the authors for the synthesis of acetonitrile directly from *n*-pentane and NH_3 (Table 4).

Table 4

Preparation of nitriles from *n*-pentane, ethyl alcohol, and isoamyl alcohol

Starting substance	Optimal temperature, °C	Molar ratio of starting substances to		Yield of nitrile per converted hydrocarbon, wt. %
		NH ₃	Nitrile	
CH ₃ -CH(CH ₃)-CH ₂ -CH ₂ -OH	487	1 : 3	CH ₃ -CH(CH ₃)-CH ₂ -CN	18
CH ₃ -(CH ₂) ₃ -CH ₃	510	1 : 2	CH ₃ CN	28
C ₂ H ₅ OH	487	1 : 1.87	CH ₃ CN	20.4

From pentane, as well as from ethyl alcohol and ammonia, acetonitrile is obtained, for the most part. In the case of pentane, the reaction does not proceed below 450°. By contrast, the preparation of valeronitrile from isoamyl alcohol and ammonia proceeds at low temperatures. Moreover, this indicates a different mechanism for these reactions.

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CITED LITERATURE

1. I. F. Olin, I. F. McKenna, U.S. Pat. 2,365,721, XII, 1944; Chem. Abstr., **39**, 4619 (1945).
2. British Pat. 586470, III, 1947; Chem. Abstr., **41**, 6894 (1947).
3. R. B. Bishop, W. I. Denton, U.S. Pat. 2,487,299, XI, 1949; Chem. Abstr., **44**, 2545 (1950).
4. British Pat. 664832, January, 1952; Chem. Abstr., **46**, 10203 (1952).
5. Danish Pat. 70867, X, 1952; Chem. Abstr., **48**, 1416 (1954).
6. Hara Tohoru, Komatsu Shigeru, Met. Coll. Sci. Kyoto Imp. Univ., **8A**, 241 (1925).
7. W. I. Denton, R. B. Bishop, Ind. and Eng. Chem., **45**, No. 2, 282 (1953).
8. Beilsteins Handb. d. org. Chemie, 4 Aufl., **2**, 183 (1920); **2**, 315 (1920).
9. H. P. Howells, I. G. Little, J. Am. Chem. Soc., **54**, 2451 (1932).
10. G. Meyer, *Analysis and Determination of the Structure of Organic Compounds*, L., 1937, p. 398.

11. A. F. Plate, M. E. Vol' pin, DAN, **89**, No. 3, 491 (1953).

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