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Kinetics of Oxidative Ammonolysis of 4-Bromo-*o*-xylene: V.[1] Synthesis of 4-Bromophthalonitrile

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Abstract—Oxidative ammonolysis of 4-bromo-*o*-xylene on a V–Sb–Bi–Zr/γ-Al_2O_3 catalyst gives 74.82 mol % of 4-bromophthalonitrile at a high conversion of the starting xylene in a one-cycle process. The process with recirculation results in decreased number of by-products and contribution of deep oxidation and increased selectivity in 4-bromophthalonitrile up to 95.42–96.58%.

Keywords: ammonolysis, nitriles, kinetics, *o*-xylene

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Previously [1–4] we studied the oxidative ammonolysis of 4-bromo-*o*-xylene (**I**) and 4-bromo-*o*-tolunitrile (**II**) on the oxide catalyst V–Sb–Bi–Zr/γ-Al_2O_3 and also considered the reaction mechanism which is consistent with the observed kinetic regularities.

Functionally substituted aromatic nitriles are applied in the synthesis of thermally stable polyimide polymers, insecticides, liquid crystals, dyes, repellents, and other valuable products [5]. 4-Bromophthalonitrile is the starting material for the synthesis of 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride), a monomer for polyetherimides which are processed by modern technologies and use in electronics [6]. Targeted synthesis of phthalocyanines with desired structure normally starts with functional derivatives of corresponding phthalic acids, prefereably phthalonitriles [2, 7, 8]. However, better soluble starting materials are phthalocyanines containing alkylamino or arylamino groups [9], which are prepared by the copper-catalyzed reaction of halogenated phthalocyanines with amines at elevated temperatures. One of the possible synthetic approaches to amino-substituted phthalonitriles involves nucleophilic substitution in halophthalonitriles, including 4-bromophthalonitrile [9]. In the latter work, 4- bromophthalonitrile was synthesized by potassium permanganate oxidation of 4-bromo-*o*-xylene to the corresponding acid followed by dehydration of the latter into anhydride by treatment with $POCl_3$. The anhydride is used to prepare first 4-bromophthalimide and then 4-bromophthalonitrile in 30% yield. 4-Bromophthalonitrile was also prepared by the ammonolysis of 4-bromophthalic anhydride on an boron phosphate catalyst. In this case, the yield of 4-bromophthalonitrile at 673 K was 50%.

4-Bromophthalonitrile can be synthesized in one stage by vapor-phase oxidative ammonolysis which combines oxidation and ammonolysis in one process and is suitable both from the financial and engineering viewpoints [7, 10, 11]. Shapovalov et al. [12] proposed a procedure for synthesis of 4-bromophthalonitrile by oxidative ammonolysis of 4-bromo-*o*-xylene [12] on fused vanadium−titanium−tungsten oxide catalyst with a 1 : 0.5 : 0.15 ratio at 643 K and the 4-bromo-*o*-xylene–atmospheric oxygen–ammonia molar ratio 1 : 67 : 15. 4-Bromophthalonitrile was prepared in yields of up to 62% at the process performance up to 86 g/L catalyst per hour.

In the present work we studied the synthesis of 4-bromophthalonitrile by vapor-phase oxidative ammonolysis of 4-bromo-*o*-xylene with high and medium conversions in a one-stage and a recirculation processes, respectively, and found an efficient catalysis

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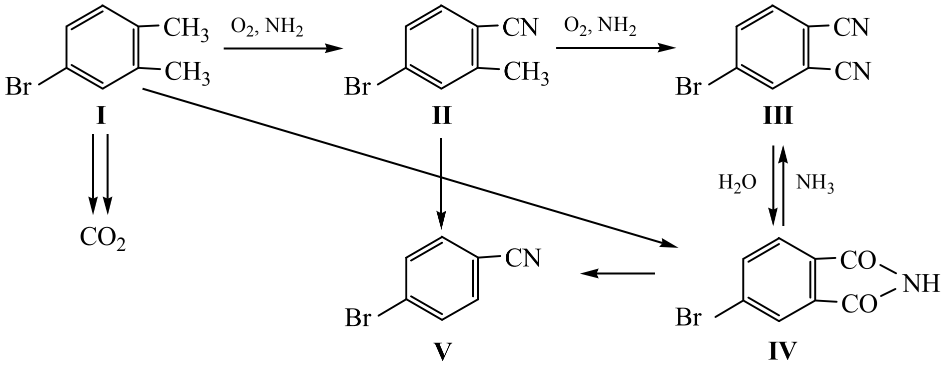
[1] For communication IV, see [1].

Scheme 1.



system for oxidative ammonolysis of 4-bromo-*o*-xylene. It was established that the V–Sb–Bi/γ-Al_2O_3 catalyst modified with zirconium oxide is a good contact catalyst for this reaction.

For the carrier we chose a microspherical alumina which possesses a high mechanical strength. The particle size of Al_2O_3 allows the process to be performed in a fluidized catalyst bed. The carries was subjected to special thermal pretreatment, and catalysts samples were prepared by impregnating the carrier with metal salts which enter in the composition of the active mass [13].

The choice of catalyst and conditions for selective conversion of 4-bromo-*o*-xylene into dinitrile is complicated by the fact that *ortho*-substituents in aromatic compounds hinder formation of nitriles but facilitate formation of imides [7, 14, 15]. Therefore, the major products of the oxidative ammonolysis of *o*-xylene, as well as 4-bromo- and 4-phenyl-*o*-xylene are the corresponding dinitriles and imides of *o*-phthalic acid, which form a hardly separable crystal mixture [16, 17].

It is important to note that the possibility of intramolecular interaction at intermediate stages [11] creates prerequisites for specific kinetic regularities [2, 3], and this circumstance makes selectivity difficult to control by varying process conditions.

According to the Scheme 1, 4-bromophtalonitrile (**III**) is formed via 4-bromo-*o*-tolunitrile, and 4-bromophthalimide (**IV**) is formed both by hydrolysis of 4-bromophthalonitrile and directly from 4-bromo-*o*-xylene; 4-bromobrnzonitrile (**V**) is formed from 4-bromophthalimide and 4-bromo-*o*-tolunitrile (**II**).

To find optimal conditions for the recirculation process, we first had to focus on the one-stage process. The study was performed in a gradientless reactor with a vibratory fluidized bed by varying process parameters over a wide range [2–4].

Table 1 lists the experimental data obtained at varied molar ratios of 4-bromo-*o*-xylene and oxygen in the starting mixture. When the oxygen fraction in the mixture is increased above some certain minimal value [$P(O_2)_{min}$], the conversion of the starting material and the selectivity of its conversion into 4-bromophthalonitrile sharply increase, and the quantity of the 4-bromo-*o*-tolunitrile intermediate therewith decreases. Further variation of the molar ratio of the starting compounds no longer affects the selectivity of the process (S_i) and the conversion of 4-bromo-*o*-xylene (α). As seen from Table 1, as the temperature is elevated to 693 K, 4-bromobenzonitrile starts to form. Decrease of the oxygen fraction in the mixture below [$P(O_2)_{min}$] decreases the conversion, yields of 4-bromophthalonitrile and CO_2, and increases the yield of the 4-bromo-*o*-tolunitrile intermediate. These findings are likely to be explained by decreased degree of oxygen contact with catalyst surface, which, however, does not change the relative quantities of specific oxygen species responsible for partial and complete oxidation. Analogous reasoning can be found in [18].

The composition of the reaction products is much affected by the fraction of ammonia in the starting mixture. At a fairly low molar ratio of NH_3 and 4-bromo-*o*-xylene, the preferential reaction pathway is deep oxidation of the starting compound, and the yield of 4-bromophthalimide is fairly high even at quite a short contact time (Table 2). As the NH_3 : 4-bromo-*o*-xylene molar ratio is increased, the yield of 4-bromophthalonitrile increases but the conversion of 4-bromo-*o*-xylene on the V–Sb–Bi–Zr/γ-Al_2O_3 oxide catalyst is independent on the partial pressure of

Table 1. Effect of oxygen concentration of oxidative ammonolysis of 4-bromo-*o*-xylene[a]

I : NH_3 : O_2 : N_2 molar ratio	α, %	S_i, %			
		III	**II**	**V**	CO_2
653 K					
1 : 25 : 1.5 : 47.8	13.70	21.92	75.58	–	2.50
1 : 25 : 3.0 : 46.3	29.50	38.30	57.70	–	4.00
1 : 25 : 4.0 : 45.3	29.60	38.52	57.50	–	3.98
1 : 25 : 6.3 : 43.0	29.69	38.66	57.38	–	3.96
1 : 25 : 8.0 : 41.3	29.80	39.06	57.00	–	3.94
1 : 25 : 12.0 : 37.3	29.90	39.28	56.80	–	3.92
1 : 25 : 15.0 : 34.3	30.00	39.48	56.62	–	3.90
693 K					
1 : 25 : 2.0 : 47.3	27.00	49.30	45.90	–	4.80
1 : 25 : 4.0 : 45.3	62.20	58.19	31.70	1.69	8.42
1 : 25 : 6.3 : 43.0	62.30	58.53	31.40	1.67	8.40
1 : 25 : 8.0 : 41.3	62.40	58.29	31.65	1.68	8.38
1 : 25 : 12.0 : 37.3	62.50	58.13	31.82	1.69	8.36
1 : 25 : 15.0 : 34.3	62.60	57.96	32.00	1.70	8.34

[a] Contact time 0.27 s.

Table 2. Effect of ammonia concentration on oxidative ammonolysis of 4-bromo-*o*-xylene[a]

I : NH_3 : O_2 : N_2 molar ratio	α, %	S_i,%				
		III	**II**	**IV**	**V**	CO_2
653 K						
1 : 1.5 : 6.3 : 66.5	29.50	25.57	48.79	9.78	–	15.86
1 : 3.0 : 6.3 : 65.0	29.40	32.37	52.35	5.34	–	9.94
1 : 7.0 : 6.3 : 61.0	29.60	37.59	53.65	2.43	–	6.33
1 : 12.0 : 6.3 : 56.0	29.75	37.90	55.46	1.38	–	5.26
1 : 15.0 : 6.3 : 53.0	30.00	39.48	56.62	–	–	3.90
1 : 25.0 : 6.3 : 43.0	29.69	38.66	57.38	–	–	3.96
1 : 35.0 : 6.3 : 33.0	29.80	39.06	57.00	–	–	3.94
1 : 45.0 : 6.3 : 23.0	29.90	39.28	56.80	–	–	3.92
693 K						
1 : 1.5 : 6.3 : 66.5	61.90	28.35	24.00	16.16	1.49	30.00
1 : 3.0 : 6.3 : 65.0	62.00	39.46	28.20	8.74	1.60	22.00
1 : 7.0 : 6.3 : 61.0	62.10	50.22	30.10	3.69	1.64	14.35
1 : 12.0 : 6.3 : 56.0	62.40	54.16	30.61	2.00	1.65	11.58
1 : 15.0 : 6.3 : 53.0	62.60	57.96	32.00	–	1.70	8.34
1 : 25.0 : 6.3 : 43.0	62.30	58.53	31.40	–	1.67	8.40
1 : 35.0 : 6.3 : 33.0	62.20	58.19	31.70	–	1.69	8.42
1 : 45.0 : 6.3 : 23.0	62.50	58.13	31.82	–	1.69	8.36

[a] Contact time 0.27 s.

ammonia in the reaction mixture. In the presence of large quantities of ammonia, the yield of 4-bromobenzonitrile changes only slightly, whereas at minimal concentrations of ammonia, i.e. at $[P(NH_3)] > [P(NH_3)_{min}]$, a zero reaction order in ammonia is realized. Deacrese off the fraction of ammonia in the reaction mixture to $[P(NH_3)] < [P(NH_3)_{min}]$ results in intensification of deep oxidation of 4-bromo-*o*-xylene to CO_2 and 4-bromophthalimide. Probably, ammonia functions here not only as a reagent, but also as a modifier of catalyst surface and blocks deep oxidation centers of 4-bromo-*o*-xylene and affects the nature of catalytic centers, thus favoring more selective formation of 4-bromophthalonitrile.

Figure 1 shows the dependences of the conversion of 4-bromo-*o*-xylene and reaction selectivity on contact time (τ). As τ increases, the yield of 4-bromophthalonitrile increases, and the yield of 4-bromo-*o*-tolunitrile decreases. However, at high τ values, formation of 4-bromophthalimide and 4-benzene is observed, and their yield increases with contact time.

Figure 2 shows the temperature dependences of treaction selectivity. As the temperature is elevated to 693 K, the selectivity of 4-bromo-*o*-xylene conversion into 4- bromophthalonitrile increases, and the yields of 4-bromo-*o*-tolunitrile and 4-bromophthalimide decrease. High temperatures favor more rapid formation of 4-bromobenzonitrile and CO_2: Their show increased yields at high temperatures.

The resulting kinetic regularities allowed us to determine optimal conditions for the one-stage process: 673 K, τ 1.55–1.60 s, **I** : NH_3 : air molar ratio 1 : 15 : 30.

The optimal conditions were chosen on a laboratory installation with a fluidized-bed reactor 40 mm in

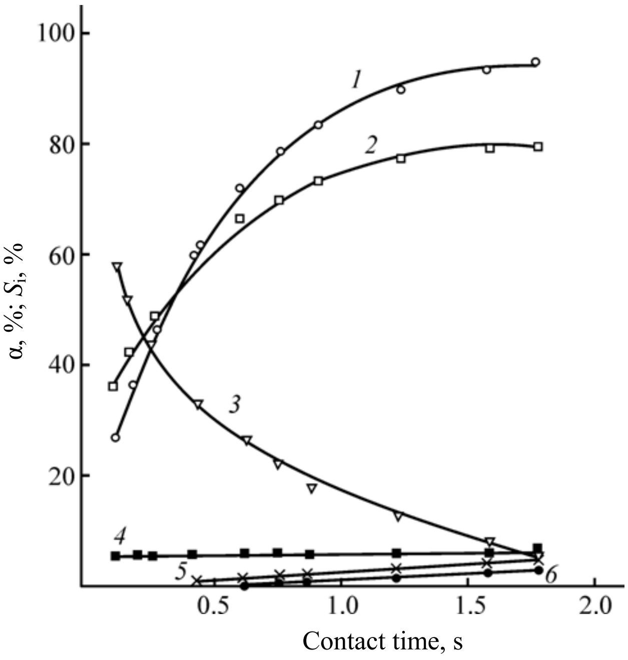


Fig. 1. Dependence of the results of oxidative ammonolysis of 4-bromo-*o*-xylene (**I**) on contact time at 673 K and **I** : NH_2 : O_2 molar ratio 1:15:6.3. (*1*) Conversion of compound **I** (α) and (*2–6*) selectivity of formation (S_i) of compounds **III, II**, CO_2, **V**, and **IV**, respectively.

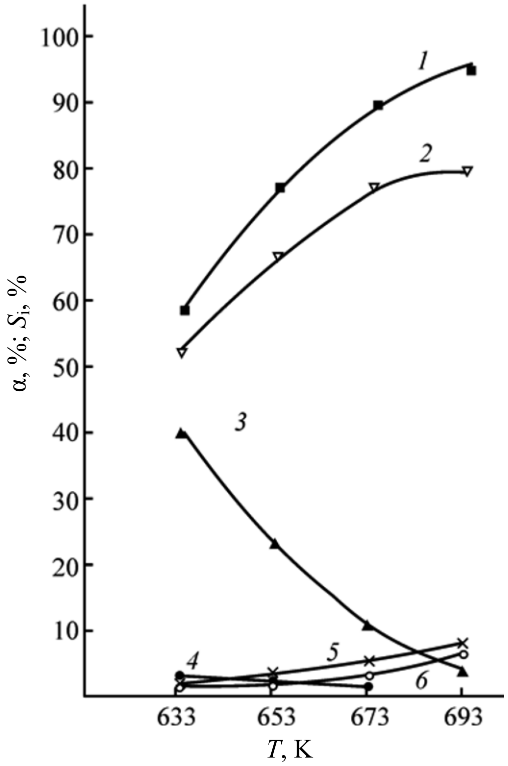


Fig. 2. Dependence of the results of oxidative ammonolysis of 4-bromo-*o*-xylene (**I**) on temperature at the contact time 1.23 s and **I** : NH_2 : O_2 molar ratio 1:15:6.3. (*1*) Conversion of compound **I** (α) and (*2–6*) selectivity of formation (S_i) of compounds **III, II, IV**, CO_2, and **V**, respectively.

diameter. The parameters of the process and its results are listed below.

Temperature, K	663–673
Contact time, s	1.55
I : NH_3 : air molar ratio	1 : 15 : 30
Conversion of compound **I**, %	93.70
Selectivity of formation, % :	
III	79.85
II	7.50
IV	2.85
V	3.96
CO_2	5.84

As seen from these data, the yield of 4-bromophthalonitrile on the V–Sb–Bi–Zr/γ-Al_2O_3 oxide catalyst is 74.82 mol % per 4-bromo-*o*-xylene. Taking into account that 4-bromophthalonitrile is quite difficult to purify from 4-bromo-*o*-tolunitrile, 4-bromobenzonitrile, and 4-bromophthalimide, especially from 4-bromophthalimide crystals, while the requirements to 4-bromophthalonitrile as the starting material for preparing phthalocyanine dyes are quite severe [16], we considered it more reasonable to turn to the process scheme which provides a medium conversion of 4-bromo-*o*-xylene with recirculation.

Analysis of the kinetic data (Table 2) shows that 4-bromophthalimide (**IV**) is formed at high ammonia concentrations (beginning with 15 mol NH_3/mole substrate) by hydrolysis of 4-bromophthalonitrile with water (see scheme) which results from side reactions [16, 19], specifically, oxidative dehydrogenation and deep oxidation of 4-bromo-*o*-xylene. In the medium conversion range of 4-bromo-*o*-xylene, at a short contact time the target dinitrile does not have enough time to undergo the secondary conversion into imide.

Table 3 lists the results of oxidative ammonolysis of mixtures of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile. As seen, an almost quantitative yield of 4-bromophthalonitrile per reacted 4-bromo-*o*-xylene can be provided.

Unlike what is observed with the one-stage process, when the process on the V–Sb–Bi–Zr/γ-Al_2O_3 oxide

Table 3. Oxidative ammonolysis of mixtures of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile[a]

T, K	Compounds in the system	Fed to the reactor, mmol/h	Obtained, mmol/h	α,[b] %	Yield,[c] mol %	
					III	CO_2
633	**I**	14.05	11.46	18.4	97.3	2.7
	II	4.69	4.69			
	III		2.52			
	CO_2		0.07			
653	**I**	14.05	9.91	29.5	94.4	4.0
	II	4.69	4.75			
	III		3.91			
	CO_2		0.17			
673	**I**	14.05	7.54	46.3	92.3	5.8
	II	4.69	4.81			
	III		6.01			
	CO_2		0.38			

[a] Contact time 0.27 s, (**I** + **II**) : O_2 : NH_3 molar ratio 1 : 6.3 : 15. [b] Coversion of compound **I**. [c] Per reacted 4-bromo-*o*-xylene (**I**).

catalyst is performed at a short contact time at 638–653 K and the **I** : air : NH_3 molar ratio of 1 : 30 : 15 with 50–60% conversion and recirculation of unreacted 4-bromo-*o*-xylene and intermediate 4-bromo-*o*-toludinitrile, the selectivity in 4-bromophthalonitrile results increases to 95.42–96.58%, and the yield of by-products (4-bromophthalimide and 4-bromobenzonitrile) and the contribution of the deep oxidation to CO_2 decrease. Therewith, the recirculation product is ~1.7–2.0. Consequently, the process with recirculation excludes the stage of purification of the target product and is continuous, highly selective, and efficient. Taking into account that decrease of the conversion depth in the one-stage process decreases the reaction volume and, consequently, reactor efficiency [20], increase of selectivity in 4-bromophthalonitrile on recirculation ensures a high-efficiency process. The catalyst efficiency on recirculation is ~3 times higher than in the one-stage process, which at a high conversion of 4-bromo-*o*-xylene makes ~175 g/L catalyst per hour [19]. Moreover, because of the higher conversion of 4-bromo-*o*-xylene in the one-stage process, the yield of CO_2, a product of the highly exothermal complete oxidation reaction, increases, which, in its turn, prevents efficient heat abstraction and reactor control [19, 21]. Since the selectivity problem is one of the central problems in the theory of catalysis [22], of primary importance is the selectivity of the catalyst, i.e. efficient contact preferably drives only one of the multitude of thermodynamically possible oxidative transformations of the substrate.

In the case of recirculation, 4-bromophthalonitrile and CO_2 are the only reaction products. The contact gases contain O_2, NH_3, N_2, CO_2, HBr, 4-bromo-*o*-xylene, 4-bromo-*o*-tolunitrile, and 4-bromophthalonitrile. The unreacted 4-bromo-*o*-xylene and intermediate 4-bromo-*o*-tolunitrile, separated from 4-bromophthalonitrile, are returned into the reactor. Therefore, the engineering design of the process should envision separation and entrapping of solid and liquid reaction products contained in contact gases, isolation of 4-bromophthalonitrile from the product mixture, return of unreacted 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile into the reactor, and regeneration of excess ammonia and its recirculation.

The quality characteristics of 4-bromophthalonitrile prepared by recirculation of 4-bromo-*o*-xylene are listed below:

Main substance content, wt %	99.62–99.80
Melting point, K	393.0–393.5
Calcination residue, wt %	0.03–0.05
Moisture content, wt %	0.17–0.33

No 4-bromophthalimide admixture was detected

Thus, the proposed procedure (recirculation) makes it possible to develop an efficient one-stage technology for the production of 4-bromophthalonitrile by oxidative ammonolysis of 4-bromo-*o*-xylene.

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