Modern Research in Catalysis, **2014, 3, 6-11**
Published Online January 2014 (http://www.scirp.org/journal/mrc)
http://dx.doi.org/10.4236/mrc.2014.31002

Synthesis of 4-Phenylphthalonitrile by Vapor-Phase Catalytic Ammoxidation of Intermediate 4-Phenyl-*o*-Tolunitrile: Reaction Kinetics

G. A. Bagirzade[1], D. B. Tagiyev[2], M. R. Manafov[1]
[1]Institute of Chemical Problems Named after Academician M. F. Nagiyev, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan
[2]Azerbaijan Medical University, Baku, Azerbaijan
Email: mmanafov@gmail.com

Received November 11, 2013; revised December 11, 2013; accepted December 18, 2013

ABSTRACT

Kinetic regularities of 4-phenyl-*o*-tolunitrile ammoxidation on V-Sb-Bi-Zr/γ-Al_2O_3 oxide catalyst in the temperature interval 633 - 673 K have been studied. It has been established that rates of conversion of 4-phenyl-*o*-tolunitrile into the aimed 4-phenylphthalonitrile and CO_2 are described by half-order equation on concentration of substratum and to be independent of the oxygen and ammonia partial pressures. It has been revealed that formation of 4-phenylphthalimide from byproducts is due to hydrolysis of 4-phenylphthalonitrile; carbon dioxide is produced by oxidation of 4-phenyl-*o*-tolunitrile and decarboxylation of 4-phenylphthalimide, and 4-phenylbenzonitrile is produced from 4-phenyl-*o*-tolunitrile and 4-phenylphthalimide.

KEYWORDS

Catalytic Ammoxidation; Partial Pressures; 4-Phenylphthalimide; Vapor-Phase; Electron-Donorship; Kinetic Measurements

1. Introduction

The vapor-phase catalytic ammoxidation of 4-phenyl-o-xylene can give with a yield of 80% 4-phenylpthalonitrile, a feedstock for the synthesis of copper tetraphenyltetrazoporphinate (copper tetraphenyl phthalocyanine), which in turn is used for manufacturing phthalocyanine pigments and turquoise and yellow hue dyes [1]. The use of 4-phenylpthalonitrile will make it possible to replace highly chlorinated copper phthalocyanine, which is manufactured through quite a sophisticated, environmentally unfriendly process of chlorination of copper phthalocyanine in an aluminum chloride-sodium chloride melt [2]. With this purpose, we use expediently V-Sb-Bi-Zr/γ-Al_2O_3-oxide catalyst for preparation of 4-phenylphthalonitrile in the vapour-phase ammoxidation of 4-phenyl-o-xylene [1,3]. Studying the kinetic regularities of this reaction in contribution [4] is shown that 4-phenyl-*o*-tolunitrile is an intermediate at formation of the aimed 4-phenylphthalo-nitrile.

Indeed, in 4-phenyl-*o*-xylene molecule, due to electronic factor of phenyl group, para-methyl group is activated first, and as a result, an appropriate intermediate mononitrile is formed initially, which, in turn, is converted to the aimed dinitrile. Upon introducing phenyl group into 4-position of *o*-xylene aromatic ring conjugation, it does not play an appriciable role as the resonance constants of phenyl and methyl groups, located in para-positions, are distinguished insignificantly [5]. So long as phenyl group is related to substituents of III kind [6], which may show both electron-donor and electron-acceptor properties and, taking into account the absence of an appriciable role of conjugation, *i.e.* electron-donorship of phenyl group, then it is possible to make a conclusion that phenyl group in the 4-phenyl-*o*-xylene molecule shows the electron-acceptor property. Consequently, in 4-phenyl-*o*-xylene molecule on the basis of electron-acceptor property of phenyl group and, only positive inductive (+I) effect of para-methyl group, it is possible to

assert that both are directed to a side of activation of para-methyl group relative to phenyl substituents [7]. Here it should be noted that in 4-phenyl-*o*-xylene molecule phenyl group, it is known [8], to not influence on activation of meta-methyl group, which itself shows only +I effect. Regarding the mononitrile formation as an intermediate product, it is important to note that at studying kinetic regularities of ammoxidation of 4-brom-*o*-xylene on the V-Sb-Bi-Zr/γ-Al_2O_3-oxide catalyst, 4-brom-*o*-tolunitrile is the intermediate product at preparation of the aimed 4-bromphthalonitrile [9,10].

The objective of this work was to study kinetic regularities of 4-phenyl-*o*-tolunitrile conversion in the ammoxidation reaction on the indicated catalyst.

2. Methods and Apparatus

Kinetic measurements of 4-phenyl-*o*-tolunitrile conversion and chromatographic separation of catalyzate components, and a quantitative calculation of their content were carried out in accordance with the earlier developed methods [4]. Kinetic measurements were performed in a setup with a vibrating fluidized-bed, gradientless flow reactor of 20-cm^3 capacity made from 12Kh18N10T steel. The products absorbed by 1,4-dioxane were determined on a Chrome-5 chromatograph equipped with an FID and a column of 1.2 m length. The column packing was Chromaton N-AW (0.2 - 0.25 mm) coated with a mixed stationary phase of Apiezon L (21%) and PEG 40000 (0.5%) or with Polisorb-1 (0.25 - 0.5 mm) alone. Carbon dioxide was determined on an LKhM-8MD chromatograph with triethylene glycol butyrate supported on INZ-600 (calcined diatomaceous earth) as the stationary phase. Separation of O_2 and N_2 was carried out on the same chromatoraph using a parallel column packed with NaX.

3. Experimental

In the products of the reaction of ammoxidation of 4-phenyl-o-tolunitrile (I) on the V-Sb-Bi-Zr/γ-Al_2O_3-oxide catalyst 4-phenylphthalonitrile (II), 4-phenylpthalimide (III), 4-phenylbenzonitrile (IV), carbon dioxide, unreacted I, oxygen and the diluent gas nitrogen were determined by gas chromatography. The reaction gases were successively passed through a 1.4-dioxane-filled trap for absorption of nitriles, and III and a sulfuric acid-filled trap for absorption of ammonia. The concentration of ammonia at the reactor outlet was determined, by titration of unreacted sulfuric acid from the second trap.

4. Results and Discussion

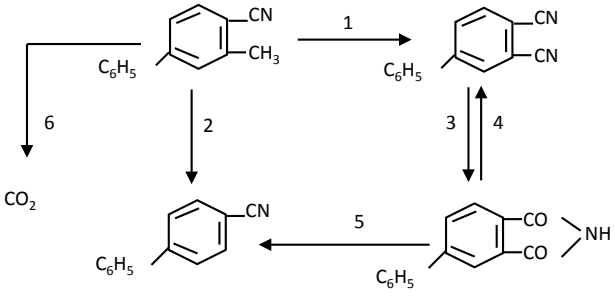
Influence of partial pressures of oxygen P_{O_2} and ammonia P_{NH_3} at values P_{NH_3}, more than a certain value, noted as $\left(P_{NH_3}\right)_{min}$ [4], and also contact time τ on the process rate in the temperature range of 633 - 673 K were studied for ascertainment of kinetic dependence character of ammoxidation reaction of 4-phenyl-*o*-tolunitrile.

Influence of oxygen concentrations on the indicators of ammoxidation process of 4-phenyl-*o*-tolunitrile was carried at initial partial pressures P_I^0 1.30 kPa and $P_{NH_3}^0$ 32.49 KPa. In the studied range of P_{O_2} (1.83 - 18.70 KPa), the rate of summary conversion of 4-phenyl-*o*-tolunitrile (W_I), and also rates of 4-phenylphthalonitrile and CO_2 formation do not depend on partial pressures of oxygen at τ 0.27s in temperatures 653 and 673 K.

Study of P_{NH_3} influence at τ 0.27 s, P_I^0 1.30 kPa and $P_{O_2}^0$ 8.19 kPa, in temperatures 653 and 673 K on W_I and rates of partial reactions was shown that the rate of 4-phenyl-*o*-tolunitrile gross-conversion, and also rates of 4-phenylphthalonitrile and CO_2 formation do not depend on ammonia concentration in range 18.83 - 57.81 kPa.

Tests results on τ variation at P_I^0 1.52 kPa, $P_{O_2}^0$ 9.55 kPa and $P_{NH_3}^0$ 53.03 kPa are presented in **Table 1**. As seen, an increase of τ leads to growth of 4-phenyl-*o*-tolunitrile conversion degree (α) and decrease of W_I. Upon increasing τ selectivity of 4-phenyl-*o*-tolunitrile conversion to 4-phenylphthalonitrile decreases but selectivity of 4-phenylphthalimide and 4-phenylbenzonitrile formation increases. The dependence of selectivity of CO_2 formation on τ is expressed weaker. This implies that CO_2 as opposed to 4-phenylphthalimide and 4-phenylbenzonitrile, generally, is formed immediately from 4-phenyl-*o*-tolunitrile. Formation of 4-phenylphthalimide and 4-phenylbenzonitrile occurs by a consecutive route. The absence of 4-phenylphthalimide and 4-phenylbenzonitrile in the reaction products at short time of contact and preparation of 4-phenyl-*o*-tolunitrile at relatively high conversion indicates to the consecutive character of their formation, as well. Thus, an analysis of changing of formation selectivity of the reaction products (S_i) in dependence on α gives a possibility to assume that 4-phenylphthalonitrile is subjected to the secondary conversions in the ammoxidation reaction of 4-phenyl-*o*-tolunitrile under an action of H_2O, being a product of concomitant reactions [3,11] of ammoxidation-oxidative dehydrogenation and deep substratum oxidation. In compliance with above-mentioned data 4-phenylphthalo-nitrile, appears, to hydrolyse to 4-phenylphthalimide, which in turn is decarboxylated to 4-phenylbenzonitrile. Furthermore, apparently, the additional route of 4-phenylbenzonitrile formation exists by oxidative destruction immediately from 4-phenyl-*o*-tolunitrile, that it is shown more clearly with increasing temperature and contact time. This result is conformed to data [4] at studying kinetics of 4-phenyl-*o*-xylene ammoxidation, because of in the latter case 4-phenyl-*o*-tolunitrile is produced as an intermediate product and subjected to the further conversion.

On the basis of carried out investigations a scheme of reaction flowing of 4-phenyl-*o*-tolunitrile ammoxidation can be presented as:



Therefore, kinetics of 4-phenyl-*o*-tolunitrile summary conversion is described by Equation (1):

$$W_1 = kP_1^n \quad (1)$$

where *k*—apparent constant of the rate of summary conversion of the substratum (I).

Experimental data processing in the coordinates $\lg W_I = kP_I$ (**Figure 1**) at 673 K shows that reaction order, describing by Equation (1) is equal to 0.5. The analogous dependences were observed at 633 and 653 K. Taking into account aforesaid, Equation (1) is written as:

$$W_1 = kP_1^{0.5} \quad (2)$$

Consistency of constant values at changing of contact time testifies about Equation implementation (2).

Apparent activation energy of 4-phenyl-*o*-tolunitrile conversion reaction, determined graphically from Arrhenius curve is found 116.53 kJ/mole (**Figure 2**). Therefore, a numerical value of the constant of 4-phenyl-*o*-tolunitrile conversion rate is expressed by the Equation (3):

$$k = k_0 \exp\left(116530/RT\right) \quad (3)$$

Taking into account above stated, the rates on separate routes in the range of oxygen and ammonia partial pressures, is higher their minimal values, may be described by the following Equations (4)-(9), that is conformed with data [4].

$$W_1 = k_1 P_1^{0.5} \quad (4)$$

$$W_2 = k_2 P_1 \quad (5)$$

$$W_3 = k_3 \left(P_{II} P_{H_2O} / P_{NH_3}\right) \quad (6)$$

$$W_4 = k_4 \left(P_{III} / P_{H_2O}\right) \quad (7)$$

$$W_5 = k_5 \quad (8)$$

$$W_6 = k_6 P_1^{0.5} \quad (9)$$

Constants of Equations (4)-(9) were selected at condition of minimization of squares sum of relative errors between experimental and calculated buildup rates of all reaction products.

$$k_1 = 10^{9.48} \exp\left(-118047.4/RT\right)$$

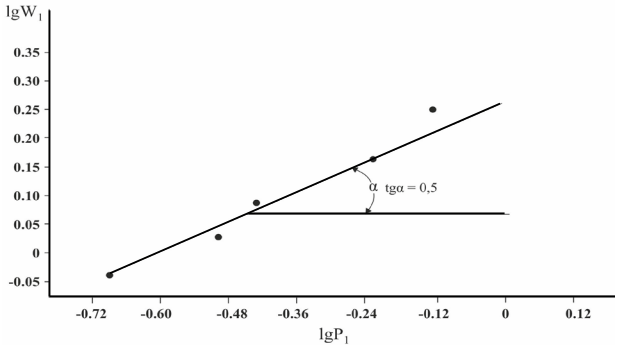


Figure 1. Dependence of $\lg W_I$ on $\lg P_I$ in the ammoxidation reaction of 4-phenyl-*o*-tolunitrile at T = 673 K.

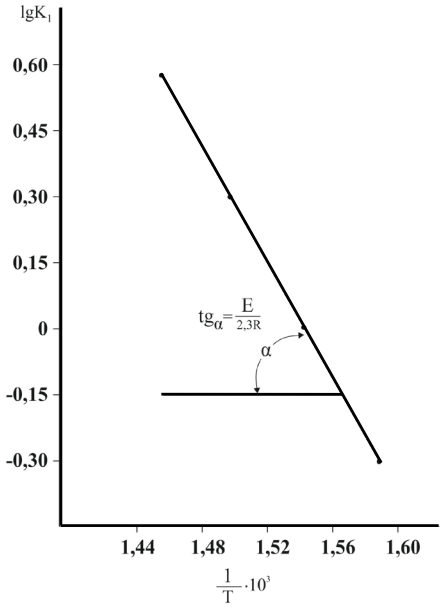


Figure 2. Dependence of logarithm of 4-phenyl-*o*-tolunitrile gross-conversion constant on reverse temperature.

$$k_2 = 10^{9.95} \exp\left(-148560.9/RT\right)$$

$$k_3 = 10^{-12.51} \exp\left(154970.3/RT\right)$$

$$k_4 = 10^{-3.90} \exp\left(51394.2/RT\right)$$

$$k_5 = 10^{5.29} \exp\left(-91939.5/RT\right)$$

$$k_6 = 10^{11.39} \exp\left(-162127.5/RT\right)$$

Activation energy is given in J/mole.

Table 2 presents the values for the product buildup rates and the 4-phenyl-*o*-tolunitrile consumption rate calculated by Equations (4)-(9) with the use of the constants found for these equations. The difference between experimental and calculated values does not exceed the experiment accuracy. It is also seen from **Table 2** that at 653 K analogous regularities are observed as at 633 and 673 K in dependence on τ (**Table 1**).

Table 1. **Influence of contact time on kinetics of 4-phenyl-*o*-tolunitrile ammoxidation.**

(a)

τ, s	α, %	W_{tot}, mmol/g·h	S_i, %			
			II	III	IV	CO_2
			633 K			
0.14	9.23	0.65	98.22	-	-	1.78
0.27	16.67	0.60	98.21	-	-	1.79
0.43	25.34	0.57	96.93	1.26	-	1.81
0.59	32.67	0.54	94.89	1.61	1.67	1.83
0.75	39.73	0.51	93.85	2.60	1.71	1.84
0.91	45.50	0.48	92.81	3.47	1.86	1.86
			673 K			
0.14	30.53	2.15	97.11	-	-	2.89
0.27	50.60	1.82	97.10	-	-	2.90
0.43	66.35	1.49	97.09	-	-	2.91
0.59	76.46	1.26	94.58	0.67	1.83	2.92
0.75	82.23	1.07	93.87	1.01	2.19	2.94
0.91	87.18	0.93	93.49	1.31	2.25	2.95

(b)

τ, s	α, %	W_{tot}, mmol/g·h	P_i, kPa				
			I	II	III	NH_3	H_2O
			633 K				
0.14	9.23	0.65	1.375	0.14	-	52.89	0.43
0.27	16.67	0.60	1.263	0.25	-	52.78	0.77
0.43	25.34	0.57	1.131	0.37	0.0048	52.66	1.16
0.59	32.67	0.54	1.020	0.47	0.0080	52.56	1.48
0.75	39.73	0.51	0.913	0.56	0.0157	52.47	1.78
0.91	45.50	0.48	0.826	0.64	0.0239	52.39	2.03
			673 K				
0.14	30.53	2.15	1.053	0.45	-	52.58	1.42
0.27	50.60	1.82	0.748	0.74	-	52.29	2.36
0.43	66.35	1.49	0.510	0.98	-	52.05	3.09
0.59	76.46	1.26	0.357	1.10	0.0080	51.93	3.50
0.75	82.23	1.07	0.269	1.17	0.0130	51.86	3.75
0.91	87.18	0.93	0.194	1.23	0.0170	51.80	3.97

Table 2. Dependence of buildup rates of reaction products and 4-phenyl-*o*-tolunitrile conversion on contact time (653 K, P_I^0 1.52 kPa, $P_{O_2}^0$ 9.55 kPa, $P_{NH_3}^0$ 53.03 kPa).

(a)

τ, s	P_i, kPa				
	I	II	III	NH_3	H_2O
0.14	1.249	0.26	-	52.77	0.81
0.27	1.031	0.47	-	52.56	1.48
0.43	0.828	0.66	0.009	52.37	2.08
0.59	0.672	0.80	0.013	52.23	2.52
0.75	0.557	0.90	0.021	52.13	2.86
0.91	0.449	0.99	0.031	52.04	3.16

(b)

τ, s	W_i, mmol/g·h									
	I		II		III		IV		CO_2	
	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
0.14	1.24	1.22	1.21	1.19	-	-	-	-	0.028	0.028
0.27	1.15	1.11	1.12	1.08	-	-	-	-	0.026	0.026
0.43	1.02	0.99	0.98	0.95	0.013	0.014	-	-	0.023	0.024
0.59	0.92	0.90	0.87	0.85	0.014	0.014	0.016	0.016	0.021	0.021

5. Conclusions

1) Kinetic regularities of I ammoxidation on V-Sb-Bi-Zr/γ-Al_2O_3 oxide catalyst in the temperature interval 633 - 673 K have been studied.

2) Rates of conversion of substratum into the aimed II and CO_2 are described by half-order equation on concentration of I and to be independent of the oxygen and ammonia partial pressures.

3) It has been revealed that formation of III occurs due to hydrolysis of II; carbon dioxide is produced by oxidation of I and decarboxylation of III, and IV is produced from I and III.

REFERENCES

[1] G. A. Bagirzade, "Innovative Chemical Technologies and Biotechnologies of Materials and Products," Abstracts of Papers of II International Conference of the Mendeleev Russian Chemical Society, RKhTU im. D. I. Mendeleeva, Moscow City, 2010, p. 197. (in Russian)

[2] R. G. Rizaev, V. E. Sheinin, G. A. Bagirzade and M. M. Mirataev, "Abstracts of Papers of the First Baku International Conference on Petroleum Chemistry," Baku, 1994, p. 34. (in Russian)

[3] G. A. Bagirzade, "Resource-Saving and Power-Efficient Technologies in Chemical and Petrochemical Industries," In: *Abstracts of Papers of III International Conference of the Mendeleev Russian Chemical Society* (RKhTU im. D. I. Mendeleeva, Moscow, 2011), p. 133. (in Russian)

[4] G. A. Bagirzade, "Preparation of 4-Phenylphthalonitrile by Vapor-Phase Ammoxidation of 4-Phenyl-*o*-Xylene: Reaction Kinetics," *Neftekhimiya*, Vol. 52, No. 2, 2012, pp. 105-112.

[5] G. A. Bagirzade, "On the Reactivity of O-Xylene and It 4-Substituted at the Heterogeneous Catalytis Oxidative Ammonolysis," *Izvestia Vysshykh Uchebnykh Zavedeniy Khimia I Khimicheskay Tekhnologia*, Vol. 52, No. 12, 2009, pp. 47-49.

[6] V. V. Plemenkov, "Electronic and Steric Structure of Monofunctional Cyclopropanes," *Russian Journal of Organic Chemistry*, Vol. 33, No. 6, 1997, pp. 849-859.

[7] G. A. Bagirzade, "On Sequence of Activation of Methyl Groups of 4-Phenyl- and 4-Brom-o-Xylenes at the Heterogeneous Catalytic Oxidative Ammonolysis," *Izvestia Vysshykh Uchebnykh Zavedeniy Khimia I Khimicheskay Tekhnologia*, Vol. 55, No. 5, 2012, pp. 23-27.

[8] A. A. Ravdel and A. M. Ponomarevf, "Short Handbook of Chemical-Physical Parameters," Khimiya, Leningrad, 1983. (in Russian)

[9] G. A. Bagirzade, "Kinetics of Oxidative Ammonolysis of

4-Brom-o-Xylene I. Transformation of 4-Brom-o-Xylene and 4-Brom-o-Tolunitrile," *Russian Journal of General Chemistry*, Vol. 80, No. 8, 2010, pp. 1360-1364.

[10] G. A. Bagirzade, "Kinetics of Oxidative Ammonolysis of 4-Brom-o-Xylene II. Formation of By-Products," *Russian Journal of General Chemistry*, Vol. 80, No. 9, 2010, pp. 1460-1466.

[11] G. A. Bagirzade, V. Y. Sheinin, Z. Y. Magerramova and R. G. Rizaev, "Towards the Issue on Separation of Crystalline Mixture of the Main Products of Vapor Phase Ammoxidation of O-Xylene and Ist 4-Substitutives," *Azerbaijan Chemical Journal*, Vol. 1, 2000, pp. 60-63.