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Kinetics of Oxidative Ammonolysis of 4-Bromo-*o*-xylene: III.[1] Conversion of 4-Bromo-*o*-tolunitrile as a Substrate

G. A. Bagirzade

Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaijan
H. Javid ave. 29, Baku, Az1143 Azerbaijan
e-mail: iradam@rambler.ru

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Abstract—Kinetics of oxidative ammonolysis of 4-bromo-*o*-tolunitrile on V–Sb–Bi–Zr/γ-Al_2O_3-oxide catalyst in the temperature range 633–673 K were studied. We found that the rate of conversion of 4-bromo-*o*-tolunitrile to the target 4-bromphthalonitrile and CO_2 was described by the half-order equation with respect to the substrate concentration and was independent of the partial pressures of oxygen and ammonia. The by-products are 4-bromophthalimide formed through the hydrolysis of 4-bromophthalonitrile, CO_2 produced by oxidation of 4-bromo-*o*-tolunitrile and decarboxylation of 4-bromophthalimide, and 4-brombenzonitrile produced from 4-bromo-*o*-tolunitrile and 4-bromophthalimide.

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It is known [1] that the oxidative ammonolysis in the vapor phase of 4-bromo-*o*-xylene on V–Sb–Bi–Zr/γ-Al_2O_3-oxide catalyst results in 4-bromophthalonitrile, an important product of organic synthesis. In the study of kinetics of this reaction we have shown previously [2, 3] that 4-bromo-*o*-tolunitrile is an intermediate in the formation of the target 4-bromophthalonitrile.

It seemed appropriate to study the kinetic regularities of the transformation of 4-bromo-*o*-tolunitrile in the reaction of oxydative ammonolisys on the specified catalyst.

Kinetic measurements of the transformation of 4-bromo-*o*-tolunitrile and chromatographic separation of the reaction product components, as well as quantitative calculation of their content, were carried out in accordance with the previously developed techniques [2]. In the oxidative ammonolysis of 4-bromo-*o*-tolunitrile on V–Sb–Bi–Zr/γ-Al_2O_3-oxide catalyst the formation proceeds of 4-bromophthalonitrile, 4-bromphthalimide, 4-brombenzonitrile, and CO_2.

To clarify the nature of the oxidative ammonolysis of 4-bromo-*o*-tolunitrile reaction kinetic, we studied the effect of partial pressures of oxygen [$p(O_2)$] and ammonia [$p(NH_3)$] when the latter was somewhat larger than a certain value, designated as $[p(NH_3)]_{min}$ [3], as well as the effect of contact time τ on the process rate in the temperature range 633–673 K.

The effect of oxygen concentration on the process of oxidative ammonolysis of 4-bromo-*o*-tolunitrile was examined at the initial partial pressures p^0(bromotolunitrile) = 1.30 kPa, and $p^0(NH_3)$ = 32.19 kPa. In the studied range of $p(O_2)$ (2–19 kPa), the rate of total conversion of 4-bromo-*o*-tolunitrile *W*(bromotolunitrile), and the rate of formation of 4-bromophthalonitrile and CO_2 did not depend on the partial pressure of oxygen at τ = 0.27 s and temperature 653 and 673 K.

The study of the influence of $p(NH_3)$ at τ = 0.27 s, p^0(bromotolunitrile) = 1.30 kPa, and $p^0(O_2)$ = 8.19 kPa, at temperatures 653 and 673 K on *W*(bromotolunitrile) and the rates of individual reactions showed that the rate of overall conversion of 4-bromo-*o*-tolunitrile, as well as the rate of the formation of 4-bromophthalonitrile and CO_2 did not depend on the concentration of ammonia in the range of 19–58 kPa.

Tables 1, 2 show the results of experiments on the variation of τ at p^0(bromotolunitrile) = 1.52 kPa, $p(O_2)$ = 9.55 kPa, and $p^0(NH_3)$ = 53.03 kPa. It is evident that the increase in the τ results in the increase in the degree of conversion of 4-bromo-*o*-tolunitrile (α) and

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

Table 1. Effect of the contact time on the selectivity of the oxidative ammonolysis of 4-bromo-*o*-tolunitrile

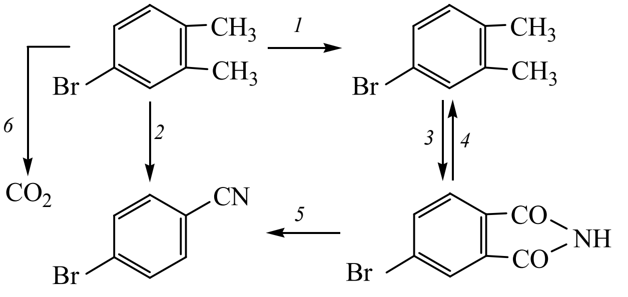
τ, s	α, %	W_{sum}, mmol g^{-1} h^{-1}	S_i, %			
			II	**III**	**IV**	**CO_2**
633 K						
0.14	7.45	0.52	97.41	–	–	2.59
0.27	13.79	0.50	97.40	–	–	2.60
0.43	21.09	0.47	95.13	–	2.26	2.61
0.59	26.99	0.45	94.25	0.77	2.35	2.63
0.75	33.53	0.43	93.50	1.40	2.45	2.65
0.91	38.89	0.41	92.74	2.07	2.52	2.67
673 K						
0.14	24.31	1.71	95.70	–	–	4.30
0.27	41.71	1.50	95.69	–	–	4.31
0.43	58.29	1.31	93.24	–	2.44	4.32
0.59	68.43	1.13	92.70	0.47	2.50	4.33
0.75	75.70	0.98	92.21	0.86	2.58	4.35
0.91	81.72	0.87	91.74	1.25	2.64	4.37

Table 2. Effect of the contact time on the kinetics of the oxidative ammonolysis of 4-bromo-*o*-tolunitrile

τ, s	α, %	W_{sum}, mmol g^{-1} h^{-1}	P_i, kPa				
			I	**II**	**III**	NH_3	H_2O
633 K							
0.14	7.45	0.52	1.402	0.11	–	52.92	0.34
0.27	13.79	0.50	1.306	0.20	–	52.83	0.62
0.43	21.09	0.47	1.196	0.30	–	52.73	0.94
0.59	26.99	0.45	1.106	0.39	0.0031	52.64	1.20
0.75	33.53	0.43	1.007	0.48	0.0071	52.56	1.48
0.91	38.89	0.41	0.926	0.55	0.0122	52.48	1.71
673 K							
0.14	24.31	1.71	1.147	0.35	–	52.68	1.10
0.27	41.71	1.50	0.883	0.60	–	52.43	1.88
0.43	58.29	1.31	0.632	0.82	–	52.21	2.59
0.59	68.43	1.13	0.478	0.96	0.0049	52.07	3.03
0.75	75.70	0.98	0.368	1.06	0.0100	51.97	3.34
0.91	81.72	0.87	0.277	1.14	0.0150	51.89	3.59

in a decrease in *W*(bromotolunitrile). With the increase in τ the selectivity of conversion of 4-bromo-*o*-4-tolunitrile into bromophthalonitrile diminishes, and the selectivity of formation of 4-bromophthalimide and 4-bromobenzonitrile grows. The dependence of the selectivity of the CO_2 formation on τ is less pronounced. This indicates that the CO_2, in contrast to 4-bromophthalimide and 4-bromobenzonitrile formed mainly from 4-bromo-*o*-tolunitrile directly, while 4-bromophthalimide and 4-bromobenzonitrile are formed in a consecutive way. Also, the absence of 4-bromophthalimide and bromobenzonitrile in the reaction products at low contact time and the appearance of 4-bromo-*o*-tolunitrile at a relatively high degree of transformation points to the consecutive nature of their formation. Thus, analysis of variation of the selectivity of the reaction products (S_i) as a dependence on the α suggests that 4-bromophthalonitrile is subjected to secondary transformations in the oxidative ammonolysis of 4-bromo-*o*-tolunitrile under the influence of H_2O, which is the product of accompanying reactions [4, 5] of oxidative ammonolysis, namely, the oxidative dehydrogenation and deep oxidation of the substrate. In accordance with the above data, 4-bromophthalonitrile is apparently hydrolyzed to 4-bromophthalimide, which in turn is decarboxylated to 4-bromobenzonitrile. Also, apparently there is an additional pathway of 4-bromobenzonitrile formation directly from 4-bromo-*o*-tolunitrile through oxidative decomposition, which is more clearly seen at increasing temperature and contact time. This result is consistent with the data of [3] on the study of the kinetics of oxidative ammonolysis of 4-bromo-*o*-xylene, because in this case the 4-bromo-*o*-tolunitrile is formed as an intermediate [2] and is subjected to further transformation.

Based on our studies, we write the reaction scheme of the oxidative ammonolysis of 4-bromo-*o*-tolunitrile as follows:



Thus, the overall kinetics of 4-bromo-*o*-tolunitrile transformation is described by the equation

$$W_{\text{I}} = kp_{\text{I}}^{n}, \tag{1}$$

where *k* is the apparent rate constant of the total transformation of 4-bromo-*o*-tolunitrile.

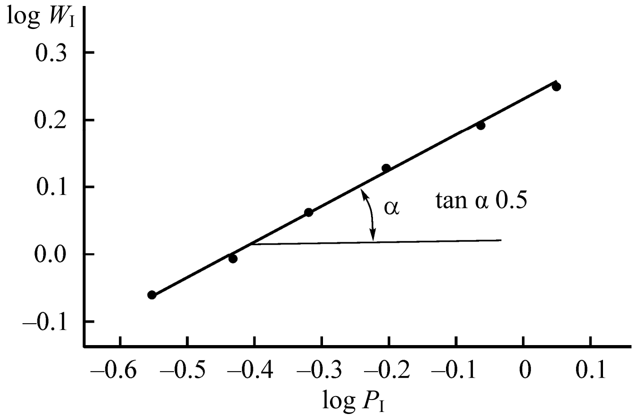


Fig. 1. The dependence of log W_I on log P_I in the oxidative ammonolysis of 4-bromo-*o*-tolunitrile at $T = 673$ K.

The experimental data in coordinates log *W*(bromotolunitrile) = *kp*(bromotolunitrile) (Fig. 1) at 673 K showed that the order of the reaction described by Eq. (1) is equal to 0.5. Similar dependences were observed at 633 and 653 K. Taking this into account, the Eq. (1) can be written as

$$W_I = kp_I^{0.5}, \tag{2}$$

The constancy of the constants at varying the contact time evidences the fulfillment of Eq. (2).

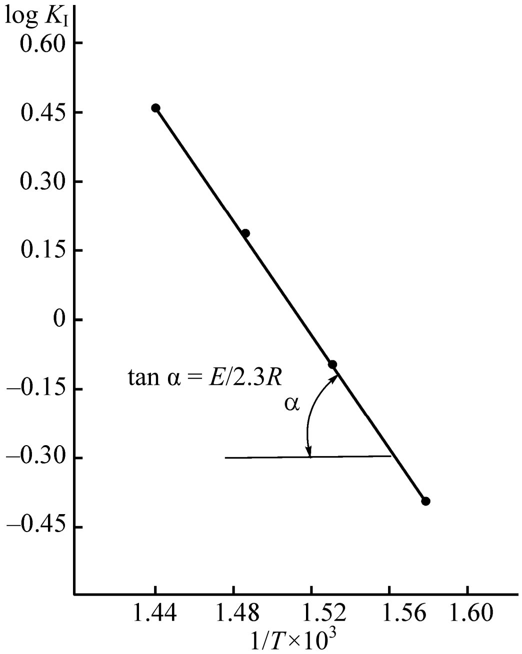


Fig. 2. The dependence of the logarithm of the constant of the overall conversion of 4-bromo-*o*-tolunitrile on the reciprocal temperature.

The apparent activation energy for the conversion of 4-bromo-*o*-tolunitrile, determined graphically from the Arrhenius plot, was found equal to 119 kJ mol^{-1}

Table 3. Dependence of the rate of accumulation of the reaction products of 4-bromo-*o*-tolunitrile on the contact time[a]

τ, s	p_i, kPa				
	I	**II**	**III**	NH_3	H_2O
0.14	1.314	0.19	–	52.84	0.60
0.27	1.149	0.35	–	52.68	1.09
0.43	0.965	0.53	–	52.50	1.64
0.59	0.815	0.65	0.005	52.38	2.04
0.75	0.695	0.76	0.011	52.27	2.38
0.91	0.589	0.85	0.019	52.18	2.68

[a] 653 K, p_I^0 1.52 kPa, $p^0(O_2)$ 9.55 kPa, $p^0(NH_3)$ 53.03 kPa.

Table 4. Dependence of the rate of consumption of 4-bromo-*o*-tolunitrile on the contact time[a]

τ, s	W_i, mmol g^{-1} h^{-1}									
	I		**II**		**III**		**IV**		CO_2	
	experiment	calculation	experiment	calculation	experiment	calculation	experiment	calculation	experiment	calculation
0.14	0.94	0.95	0.91	0.91	–	–	–	–	0.033	0.033
0.27	0.87	0.88	0.84	0.85	–	–	–	–	0.031	0.031
0.43	0.83	0.82	0.78	0.78	–	–	0.020	0.021	0.029	0.029
0.59	0.76	0.75	0.71	0.70	0.006	0.006	0.019	0.020	0.027	0.026
0.75	0.70	0.70	0.65	0.64	0.009	0.010	0.018	0.018	0.025	0.024
0.91	0.65	0.64	0.60	0.59	0.013	0.013	0.017	0.017	0.023	0.022

[a] 653 K, p_I^0 1.52 kPa, $p^0(O_2)$ 9.55 kPa, $p^0(NH_3)$ 53.03 kPa.

(Fig. 2). Consequently, the numerical value of the rate constant of conversion of 4-bromo-*o*-tolunitrile is expressed as:

$$k = k_0\exp\,(119000/RT). \tag{3}$$

Given the above, the rates of the certain pathways (see the scheme) in the region where the partial pressure of oxygen and ammonia is above their minimum value, can be described by the following equations, which are consistent with the data of [3].

$$W_1 = k_1p_{\mathrm{I}}^{0.5}, \tag{4}$$

$$W_2 = k_2p_{\mathrm{I}}, \tag{5}$$

$$W_3 = k_3[p_{\mathrm{II}}p(\mathrm{H_2O})/p(\mathrm{NH_3})], \tag{6}$$

$$W_4 = k_4[p_{\mathrm{III}}/p(\mathrm{H_2O})], \tag{7}$$

$$W_5 = k_5, \tag{8}$$

$$W_6 = k_6p_{\mathrm{I}}^{0.5}. \tag{9}$$

The constants in the Eqs. (4)–(9) were selected to fulfill the condition of minimizing the sum of the squares of relative errors between the experimental and calculated rates of accumulation of all the reaction products.

$$k_1 = 10^{9.60}\exp(-121117.7/RT),$$

$$k_2 = 10^{9.61}\exp(-143865.7/RT),$$

$$k_3 = 10^{-9.62}\exp(118685.2/RT),$$

$$k_4 = 10^{-2.87}\exp(38249.9/RT),$$

$$k_5 = 10^{4.72}\exp(-84218/RT),$$

$$k_6 = 10^{11.44}\exp(-162013.4/RT).$$

The activation energy is given in J mol^{-1}.

Tables 3, 4 show the rates of accumulation of the reaction products and consumption of 4-bromo-*o*-tolunitrile calculated using Eqs. (4)–(9) and the constants selected for them. The deviations between the experimental and calculated values do not exceed the experimental accuracy. Also, from Tables 3, 4 it is clearly seen that the regularities of dependence on τ at 653 K are similar to those at temperatures 633 and 673 K (see Tables 1, 2).

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