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Kinetics of Oxidative Ammonolysis of 4-Bromo-*o*-xylene: I. Transformations of 4-Bromo-*o*-xylene and 4-Bromo-*o*-tolunitrile

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Abstract—Kinetic laws of 4-bromo-phthalonitrile synthesis by vapor-phase oxidative ammonolisis of 4-bromo-*o*-xylene in the range of 633–69 K were studied. It was shown that formation of 4-bromophthalonitrile proceeds successively through 4-bromo-*o*-tolunitrile. Conversion rates of 4-bromo-*o*-xylene and 4-bromo-*o*-toluinitrile were found to be described by half-order equations on the corresponding components and not to depend on the oxygen and ammonia concentrations.

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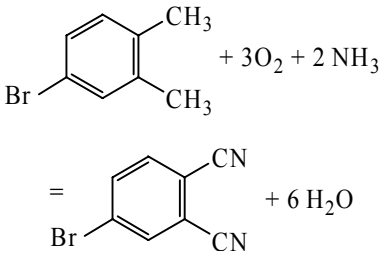
The vapor-phase catalytic oxidative ammonolysis of 4-bromo-*o*-xylene allows to obtain in good yield (up to 70–75 %) 4-bromophthalonitrile, which is used as starting material in the phthalocyanine pigments and dyes production, in the synthesis of diphthalonitrile, phthalocyanine derivatives, polyesterimides, and graft-polymers [1].



Phthalonitriles are usually used as starting materials for the synthesis of phthalocyanines of the known structure. Phthalocyanines containing alkylamino- or arylamino-groups, which are more soluble, are produced by reaction of halogen-substituted phthalocyanines with the corresponding amines at heigh temperature in the presence of copper as catalyst. In this connection, it is significant that one of the possible approaches to amino-substitited phthalonitriles is reaction of nucleophilic substitution in halogen-phthalonitriles, including 4-bromophthalonitrile [2]. Furthermore, 4-bromophthalonitrile is the starting material for the preparation of 4,4-[2,2-propylene-bis-(*p*-phenyleneoxy)]diphthalic anhydride, monomer for the synthesis of polyesteramides processed the modern methods and used in electronic industry [3].

We have studied earlier [4, 5] the kinetics of oxidative ammonolysis of *o*-xylene in the presence of the improved industrially used catalyst L-8-U. In these works equations for the rates of accumalation of phthalonitrile, *o*-tolunitrile, benzonitrile, and phthalimide were obtained. Phthalonitrile was shown to be formed only from *o*-toluntrile. Side product, phthalimide, forms directly from *o*-xylene as well as through phthalonitrile. In regard to oxidative ammonolysis of halogen-containing aromatic hydrocarbons the kinetic laws of *o*- and *p*-chlorotoluene synthesis using Sb–Bi–V/γ-Al_2O_3 catalyst were examined in the temperature range of 653–713 K [6]. Also the preparation of 4-bromophthalonitrile by oxidative ammonolysis of 4-bromo-*o*-xylene with the use of V–Ti–W catalyst in 62% yield is known [7].

This work deals with detail kinetic study of oxidative ammonolysis process of 4-bromo-*o*-xylene in the presence of V–Sb–Bi–Zr/γ-Al_2O_3 catalyst allowing avoiding 4-bromophthalimide formation under certain conditions. The formation pathways of the target and side reaction products were established. Kinetic equations of their accumulation rates were given and reaction mechanism was suggested.

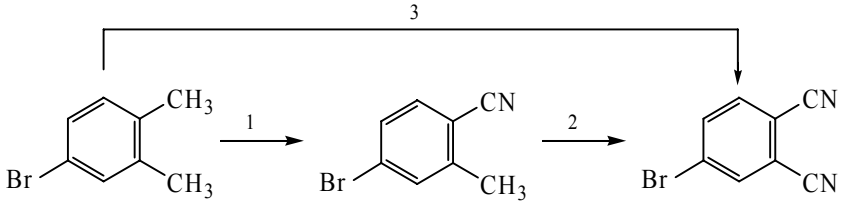
In this report the laws of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile transformation are summarized.

Checking of the fulfillment of conditions of non-gradient temperature and concentration and also of the absence of influence of the reactor material, mass transfer process, and homogeneous stages on the observed rates W_i preceded the kinetic measurements.

Kinetic laws were examined in the range of 633–693 K. The contact time τ was varied from 0.09 to 1.87 s and was varied with catalyst charge quantity as well as with the change in the volume rate. We found that the variation of $P(O_2)$ at $P(NH_3)$ = 33.20 kPa causes no changes in the observed conversion rates of 4-bromo-*o*-xylene and accumulation of the reaction products. The variation of $P(NH_3)$ showed that the conversion rate of 4-bromo-*o*-xylene $W_{Bo\text{-}Xy}$ and 4-bromo-*o*-tolunitrile $W_{Bo\text{-}TN}$ do not practically depend on this parameter.

Variation of $P_{Bo\text{-}Xy}$ was made both by changing its concentration at the reactor input $P^0_{Bo\text{-}Xy}$ at τ = 0.27 s and also by varying τ at $P^0_{Bo\text{-}Xy}$ 1.24 kPa. The results obtained at 633, 673, 693 K are given in Tables 1–3. Similar laws were observed at intermediate temperature 653 K.

It follows from these results that the observed order of $W_{Bo\text{-}Xy}$ with respect to $P^0_{Bo\text{-}Xy}$ is < 1. Fractional order was known to result from certain stage in the reaction mechanism or to be an approximation of fractional rational type equation [8]. If the latter is realized, it is naturally to assume that $W_{Bo\text{-}TN}$ is described by kinetic equation of the same type as $W_{Bo\text{-}Xy}$ with similar denominator $W_i = k_j P^n_i f(P_i)$, where $f(P_i)$ is a function of the partial pressures of the reaction mixture components and temperature. The choice of kinetic equation type was made on the basis of analysis of dependence of selectivity of 4-bromo-*o*-tolunitrile formation $S_{Bo\text{-}TN}$ from $P_{Bo\text{-}Xy}$ and $P_{Bo\text{-}TN}$. For parallel consecutive scheme of 4-bromophthalonitrile formation the selection of value n was made graphically.



$$S_{Bo-TN} = (W_1 - W_{Bo-TN})/W_{Bo-Xy} = a - (k_2/k_1)(P_{Bo-TN}/P_{Bo-Xy})^n. \quad (1)$$

Table 1. Dependence of accumulation rate (mmol g^{-1} h^{-1}) of 4-bromo-*o*-tolunitrile and of conversion rate of 4-bromo-*o*-xylene on τ and $P^0_{Bo\text{-}Xy}$ [633 K; $P^0(O_2)$ = 7.80–8.37 kPa, $P^0(NH_3)$ = 33.20–61.91 kPa]

τ, s	$P^0_{Bo\text{-}Xy}$, kPa	P_i, kPa		$W_{Bo\text{-}Xy}$		$r_{Bo\text{-}TN}$	
		Bo-Xy	Bo-TN	experiment	calculation	experiment	calculation
1.87	1.24	0.329	0.269	0.31	0.32	0.092	0.088
1.55	1.24	0.402	0.269	0.34	0.35	0.110	0.120
1.23	1.24	0.505	0.292	0.38	0.39	0.152	0.152
0.91	1.24	0.624	0.285	0.43	0.43	0.200	0.197
0.75	1.24	0.709	0.267	0.45	0.46	0.229	0.232
0.59	1.24	0.794	0.243	0.48	0.49	0.264	0.269
0.43	1.24	0.891	0.206	0.51	0.52	0.310	0.310
0.27	1.24	1.005	0.153	0.55	0.55	0.370	0.370
0.20	1.24	1.059	0.122	0.56	0.57	0.390	0.400
0.13	1.24	1.114	0.091	0.58	0.58	0.440	0.440
0.27	0.31	0.210	0.056	0.24	0.25	0.134	0.145
0.27	0.60	0.450	0.094	0.36	0.37	0.220	0.230
0.27	1.33	1.090	0.164	0.57	0.57	0.390	0.390
0.27	2.18	1.860	0.224	0.75	0.75	0.532	0.530
0.27	3.11	2.720	0.283	0.91	0.91	0.667	0.658
0.27	3.96	3.520	0.327	1.04	1.03	0.775	0.762

Table2. Dependence of accumulation rate (mmol g^{-1} h^{-1}) of 4-bromo-*o*-tolunitrile and of conversion rate of 4-bromo-*o*-xylene on τ and $P^0_{Bo\text{-}Xy}$ [633 K; $P^0(O_2)$ = 7.80–8.37 kPa, $P^0(NH_3)$ = 33.20–61.91 kPa]

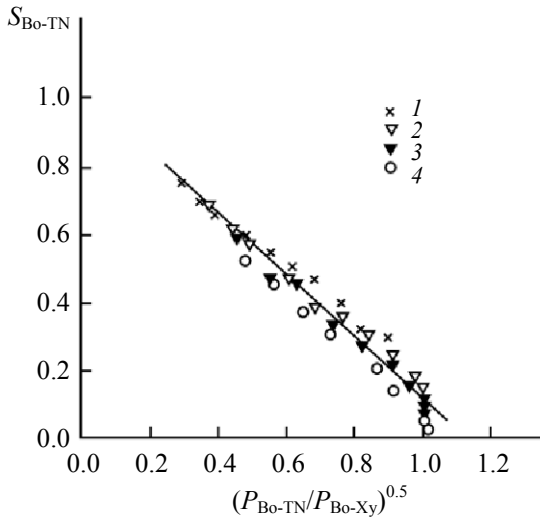
τ, s	$P^0_{Bo\text{-}Xy}$, kPa	P_i, kPa		$W_{Bo\text{-}Xy}$		$r_{Bo\text{-}TN}$	
		Bo-Xy	Bo-TN	experiment	calculation	experiment	calculation
1.87	1.24	0.059	0.069	0.40	0.40	0.023	0.023
1.55	1.24	0.078	0.087	0.48	0.46	0.036	0.037
1.23	1.24	0.122	0.127	0.58	0.58	0.066	0.065
0.91	1.24	0.195	0.178	0.73	0.73	0.125	0.122
0.75	1.24	0.253	0.210	0.84	0.83	0.180	0.170
0.59	1.24	0.344	0.229	0.97	0.97	0.250	0.270
0.43	1.24	0.467	0.254	1.15	1.13	0.380	0.400
0.27	1.24	0.659	0.258	1.38	1.35	0.620	0.590
0.20	1.24	0.781	0.234	1.45	1.46	0.750	0.740
0.13	1.24	0.905	0.192	1.58	1.58	0.920	0.900
0.27	0.31	0.100	0.063	0.50	0.52	0.149	0.159
0.27	0.60	0.250	0.128	0.82	0.83	0.305	0.304
0.27	1.33	0.730	0.271	1.42	1.42	0.640	0.640
0.27	2.18	1.360	0.411	1.95	1.93	0.973	0.967
0.27	3.11	2.090	0.541	2.42	2.40	1.280	1.277
0.27	3.96	2.780	0.651	2.79	2.76	1.545	1.528

Table 3. dependence of accumulation rate (mmol g^{-1} h^{-1}) of 4-bromo-*o*-tolunitrile and of conversion rate of 4-bromo-*o*-xylene on τ and $P^0_{Bo\text{-}Xy}$ [633 K; $P^0(O_2)$ = 7.80–8.37 kPa, $P^0(NH_3)$ = 33.20–61.91 kPa]

τ, s	$P^0_{Bo\text{-}Xy}$, kPa	P_i, kPa		$W_{Bo\text{-}Xy}$		$r_{Bo\text{-}TN}$	
		Bo-Xy	Bo-TN	experiment	calculation	experiment	calculation
1.87	1.24	0.022	0.0235	0.42	0.41	0.008	0.008
1.55	1.24	0.029	0.0310	0.50	0.47	0.013	0.012
1.23	1.24	0.051	0.0530	0.62	0.63	0.028	0.031
0.91	1.24	0.086	0.0860	0.81	0.81	0.061	0.062
0.59	1.24	0.179	0.1520	1.15	1.17	0.166	0.178
0.43	1.24	0.267	0.2000	1.45	1.43	0.300	0.290
0.27	1.24	0.458	0.2420	1.86	1.88	0.580	0.600
0.20	1.24	0.575	0.2450	2.11	2.11	0.780	0.810
0.13	1.24	0.730	0.2300	2.42	2.37	1.100	1.100
0.09	1.24	0.859	0.1960	2.57	2.57	1.340	1.360
0.27	0.31	0.050	0.0400	0.61	0.62	0.094	0.100
0.27	0.60	0.150	0.1040	1.06	1.08	0.246	0.243
0.27	1.33	0.500	0.2600	1.96	1.96	0.620	0.640
0.27	2.18	1.000	0.4380	2.79	2.78	1.036	1.046
0.27	3.11	1.610	0.6170	3.54	3.52	1.461	1.453
0.27	3.96	2.210	0.7530	4.15	4.13	1.784	1.824

We found that n value in Eq. (1) is close to 0.5 (see the figure). As follows from data given on the figure, parallel way of 4-bromophthalonitrile formation is not realized. Small divergence of $S_{Bo\text{-}TN}$ from 1 at ($P_{Bo\text{-}TN}/P_{Bo\text{-}Xy}$) = 0 is connected with 4-bromo-*o*-xylene oxidation into CO_2, which was neglected in this report since the value $S(CO_2)$ even at 693 K did not exceed 0.086. The analysis of the ratio $W_{Bo\text{-}Xy}/P^n_{Bo\text{-}Xy}$ showed that $f(P_i) \equiv 1$ at all the temperatures. Therefore, the reaction rates of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile conversion are described by the half-order equations with respect to the corresponding components. We found that $k_1=10^{7.55}$ exp (–94680.8/*RT*); $k_2 = 10^{8.01}$exp(–101492.4/*RT*). The activation energy is given in J mol^{-1}.

Rate values are given it Tables 1–3 calculated using the found constants. The divergence between experimental and calculated values does not exceed experiment accuracy.



Dependence of selectivity of 4-bromo-*o*-tolunitrile formation on the partial pressures of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile in coordinates of Eq. (1) at different temperatures, K: (*1*) 633, (*2*) 653, (*3*) 673, and (*4*) 693.

EXPERIMENTAL

Kinetic measurements were performed on an installation equipped with flowing non-gradient reactor (20 cm^3) made of "12X18H10T" steel with vibro-liquified catalyst layer. The part of the installation was maintained at 500–520 K to avoid the condensation of high-boiling products. Oxygen and nitrogen were purified from traces of organic compounds and dried before use. Ammonia was passed through an oil filter. 4-Bromo-*o*-xylene of chemically pure grade was used. 4-Bromophthalonitrile, 4-bromophthalimide, 4-bromo-*o*-tolunitrile, and 4-bromobenzonitrile were isolated from the products of 4-bromo-*o*-xylene oxidative ammonolysis and purified by distillation.

4-Bromophthalonitrile, 4-bromo-*o*-tolunitrile, 4-bromophthalimide, 4-bromobenzonitrile, carbon dioxide, and unreacted 4-bromo-*o*-xylene, oxygen and gas-diluent nitrogen were chromatographically identified in the reaction products. Chromatographic analysis was performed by the following scheme. Reaction gases were sequentially passed through a trap with 1,4-dioxane to absorb nitriles, 4-bromophthalimide and 4-bromo-*o*-xylene and with sulfuric acid to absorb ammonia. The analysis of carbon dioxide was performed on a LKhM-8MD chromatograph. TEGNM on INZ-600 was used as stationary phase. Separation of O_2 and N_2 was made on this chromatograph using parallel column filled with NaX. Ammonia concentration at the reactor output was determined by titration results of the unreacted sulfuric acid in the second trap. The analysis of the products absorbed with 1,4-dioxane was carried out on a Khrom-5 chromatograph with flame-ionization detector. A mixture of Apiezon L (21%) and PEG-40000 (0.5%) on Chromaton N-AW (0.2–0.25 mm) or only polysorb-1 (0.25–0.5 mm) were used as stationary phase, by which column (1200′4 mm) was filled. Carrier gas nitrogen, flow-rate 80 ml min^{-1}. Temperature of the tests inlet is 353 K; rate of the programmed temperature rise 20 deg min^{-1}.

The calculation of the chromatograms was made by the internal reference method (relative to tetradecane).

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