ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1079–1084. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © G.A. Bagirzade, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 896–901.

Kinetics of Oxidative Ammonolysis of 4-Bromo-*o*-xylene: IV.[1] Mechanism of Formation of the Reaction Products

G. A. Bagirzade

Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaidzhan,
pr. G. Dzhavida 29, Baku, Az1143 Azerbaidzhan
e-mail: iradam@rambler.ru

Received August 29, 2013

Abstract—Generalized kinetic data were used to analyze the mechanism of formation of the oxidative oxidative ammonolysis products 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile.

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

DOI: 10.1134/S1070363214060048

Previously [1–3] we studied kinetic regularities of vapor-phase catalytic ammonolysis of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile on a V–Sb–Bi–Zr/γ-Al_2O_3 oxide catalyst. In [3], a scheme of the oxidative ammonolysis of 4-bromo-*o*-xylene was proposed (Scheme 1).

Oxidative ammonolysis of aromatic compounds containing *ortho*-methyl groups results in formation of both nitriles and imides as major products [4, 5]. These products are used in manufacturing phthalocyanine pigments and dyes, semiconductor materials, thermally stable polymers, laser dyes, optical filters, and near-IR photosensitizers for photodynamic cancer therapy [6, 7], medicines, chemical plant protection means, indigo dye, vulcanization retarders, stabilizers and fire retardants for plastics, and lubricant additives, as well as in other fields of organic synthesis.

It is important to underlie that the oxidative ammonolysis of 4-bromo-*o*-xylene involves consecutive transformation of, first, the *para*-methyl and then meta-methyl group with respect to the bromine atom [8]. This appears to be explained by electronic factors in the 4-bromo-*o*-xylene molecule. The electronic factors are well consistent with the results of oxidative amonolysis of 4-bromo-*o*-xylene on the V–Sb–Bi–Zr/γ-Al_2O_3 oxide catalyst [2, 3].

In *o*-xylene, the order of activation of its methyl groups is of no matter because of the lack of the third substituent in the benzene ring. Therefore, the activation of one the methyl groups results in exclusive formation of *o*-tolunitrile which, in its turn, undergoes oxidative ammonolysis by the second methyl group [9, 10] to form dinitirile.

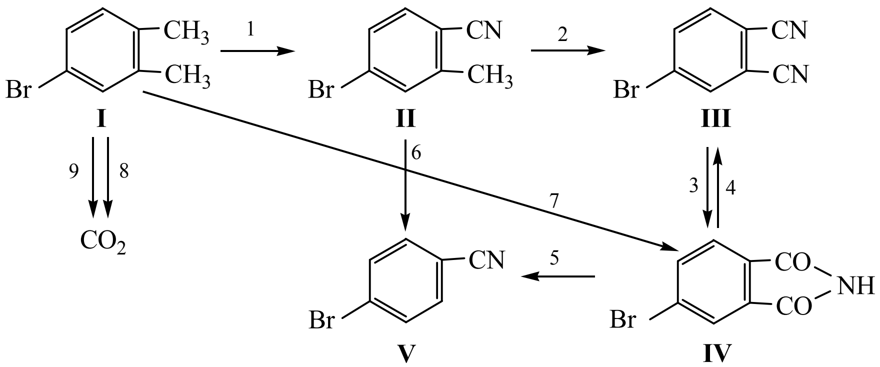
The 4-Br atom favors activation of 4-bromo-*o*-xylene on chemisorption [8]. The activation of alkylated aromatic compounds (primary interactions with metal oxide catalysts under oxidative ammonolysis conditions) is accompanied by cleavage of the side-chain C–H bond in the α position to the aromatic ring [11]. The mechanism of activation under the action of the nucleophilic oxide ion is shown in Scheme 2.

The efficiency of heterolytic dissociation of the methyl C–H bond is provided first of all by the reaction of the O^{2-} nucleophile with the outgoing proton. Heterolytic dissociation of C–H bonds also occurs on activation of the second methyl group in 4-bromo-*o*-xylene, as judged from the formation of 4-bromophthalonitrile 4-bromo-*o*-tolunitrile on the V–Sb–Bi–Zr/γ-Al_2O_3 catalyst. Thus, the primary interaction of 4-bromo-*o*-xylene with contact surface occurs as an acid–base interaction, i.e. stage 1 (Scheme 2) involves no change of the oxidation state of M^{n+} and is accompanied by proton abstraction from the substrate molecule (CH acid) on the nucleophilic center of the catalyst to form a surface anion compound [8, 11]. In the case of oxidation reactions whose mechanism includes acid–base stages, more fruitful is the concept

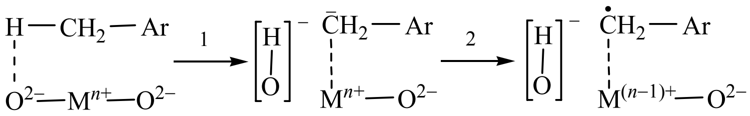
---

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

Scheme 1.



Scheme 2.



of a combined effect of the redox and acid–base characteristics of the surface on the catalytic properties of substances [12]. Oxidative ammonolysis of toluene and its homologs just relates to the mentioned reactions, because the primary interaction of these compounds with the oxide catalyst can be acid−base in nature [11].

The aim of the present work was to discuss the mechanism of oxidative ammonolysis of 4-bromo-*o*-xylene. The mechanaism, i.e. the sequence of transformations leading to formation of the target reaction product and by-products, is still unclear even for the simplest and sufficiently well-studied oxidative ammonolysis reactions. As already mentioned, the mechanisms of oxidative ammonolysis reactions forming not only one but also two cyano groups, as well as imido group are even more difficult to study.

The previously discussed mechanism of oxidative ammonolysis of *o*-xylene and *p*-xylene [13], which is consistent with the kinetic regularities observed in each case, showed that the consumption rate of arenes suggested their dissociative adsorption.

According to Scheme 1, the vapor-phase oxidative ammonolysis of 4-bromo-*o*-xylene (**I**) gives rise to 4-bromo-*o*-tolunitrile (**II**), 4-bromophthalonitrile (**III**), 4-bromophthalimide (**IV**), 4-bromobenzonitrile (**V**), and CO_2. As follows from the experimental data, the rates of formation and consumption of the key components of the oxidative ammonolysis of 4-bromo-*o*-xylene on the V–Sb–Bi–Zr/γ-Al_2O_3 oxide catalyst at oxygen and ammonia partial pressures above their minimal values are described by Eqs. (1)–(7).

$$w_1 = k'_1\sqrt{P_\mathrm{I}}, \tag{1}$$

$$w_2 = k'_2\sqrt{P_\mathrm{II}}, \tag{2}$$

$$w_3 = k'_3P_\mathrm{III}P(H_2O)/P(NH_3), \tag{3}$$

$$w_4 = k'_4P_\mathrm{IV}/P(H_2O), \tag{4}$$

$$w_5 = k'_5, \tag{5}$$

$$w_6 = k'_6P_\mathrm{II}/1 + aP_\mathrm{I}, \tag{6}$$

$$w_9 = k'_9\sqrt{P_\mathrm{I}}. \tag{7}$$

Here k'_i is the rate constant of the reaction sequence (Scheme 1).

In view of the observed dependence of product distribution on the O_2 and NH_3 concentration ratio at $P(NH_3)$ lower than a certain value denoted as $P(NH_3)$ min [3], the rates of the transformation of 4-bromo-*o*-xylene into 4-bromo-*o*-tolunitrile and of 4-bromo-*o*-tolunitrile into 4-bromophthalonitrile will take Eqs. (8) and (9), respectively.

$$w_1 = k'_1\sqrt{P_\mathrm{I}}P(NH_3)/P(NH_3) + bP(O_2), \tag{8}$$

$$w_2 = k'_2\sqrt{P_\mathrm{II}}P(NH_3)/P(NH_3) + bP(O_2). \tag{9}$$

In the above range of ammonia concentrations, routes 7 and 8 (Scheme 1) appear. Their rates are given by Eqs. (10) and (11).

$$w_7 = k'_1\sqrt{P_\mathrm{I}}bP(O_2)\beta/P(NH_3) + bP(O_2), \tag{10}$$

$$w_8 = k'_1\sqrt{P_\mathrm{I}}bP(O_2)(1 - \beta)/P(NH_3) + bP(O_2). \tag{11}$$

Here β is the fraction of 4-bromo-*o*-xylene, which transforms into 4-bromophthalimide at low ammonia concentrations and *b* is a constant which reflects the ratio of the absorption equilibrium constants of O_2 and NH_3.

$$w_{tot} = w_1 + w_7 + w_8 + w_9 = (k'_1 + k'_9)\sqrt{P_I}.$$

In agreement with Scheme 1, w_{tot} is independent on the concentration of NH_3 and described by a half-order equation in 4-bromo-*o*-xylene. Such dependence suggests dissociative adsorption of 4-bromo-*o*-xylene on centers that are completely coated by oxygen at $P(O_2) > P(O_2)_{min}$. The adsorbed fragment of 4-bromo-*o*-xylene is oxidized to CO_2 and H_2O by route 9 with the probability $k_9/(k_1 + k_9)$, forms 4-bromo-*o*-tolunitrile with the probability $k_1/(k_1 + k_9)$, and also forms 4-bromophthalimide, CO_2, and H_2O at low $P(NH_3)$ values. The relative rates of 4-bromo-*o*-tolunitrile formation by route 1 (w_1) and other reaction products by routes 7 and 8 ($w_7 + w_8$) depends on the $P(NH_3)/P(O_2)$ ratio. This fact, as well as the independence of the rate of 4-bromo-*o*-xylene transformation of $P(NH_3)$ gives us grounds to suggest that NH_3 and 4-bromo-*o*-xylene are adsorbed on different centers, and, therewith, NH_3 competes for its absorption centers with O_2 and completely expels the latter at high $P(NH_3)$ values. Obviously, these centers (Z) have a lower oxygen adsorption heat that the adsorption centers of 4-bromo-*o*-xylene (Y).

The above sequence of stages leading to adsorption of 4-bromo-*o*-xylene and its complete oxidation by route 9 can be presented as follows.

$$(1)\ 2YO + CH_3BrC_6H_3CH_3 \rightleftarrows YOCHBrC_6H_3CH_3 + YOH_2,$$

$$(2)\ YOCHBrC_6H_3CH_3 + YO \rightarrow YO_2CHBrC_6H_3CH_3 + Y,$$

$$(3)\ YOCHBrC_6H_3CH_3 + 2YO \rightarrow YOCHBrC_6H_3CHOY + YOH_2,$$

$$(4')\ YOCHBrC_6H_3CHOY + 8O_2 \rightarrow 8CO_2 + 2H_2O + HBr + 2Y,$$

$$(5)\ YOH_2 \rightarrow Y + H_2O,$$

$$(6')\ 2Y + O_2 \rightarrow 2YO.$$

Here (1) is an equilibrium stage, primed numbers relate to momentary stages [14], and all other stages are slow.

Oxygen and ammonia equilibrially adsorbed on centers Z completely coat the latter.

$$(7)\ Z + O_2 \rightleftarrows ZO_2,$$

$$(8)\ Z + NH_3 \rightleftarrows ZNH_3.$$

From this $[ZO_2] + [ZNH_3] = 1$.

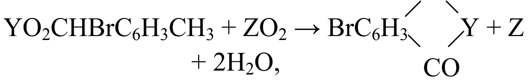
Then the O_2 and NH_3 coatings can be estimated as follows.

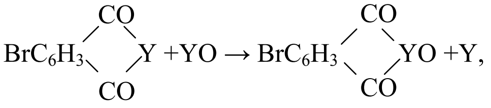
$$[ZO_2] = K_7P(O_2)/K_8P(NH_3) + K_7P(O_2) = K_7/K_8P(O_2)/P(NH_3) + K_7/K_8P(O_2),$$

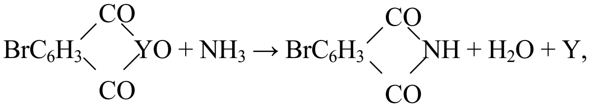
$$[ZNH_3] = K_8P(NH_3)/K_8P(NH_3) + K_7P(O_2) = P(NH_3)/P(NH_3) + K_7/K_8P(O_2).$$

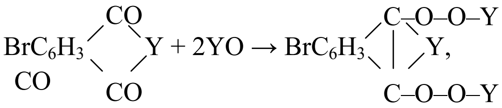
The reaction of $YO_2CHBrC_6H_3CH_3$ with ZNH_3 forms 4-bromo-*o*-tolunitrile, whereas the reaction of $YO_2CHBrC_6H_3CH_3$ with ZO_2 forms either 4-bromophthalimide or CO_2 and H_2O by routes 7 and 8 (Scheme 1).

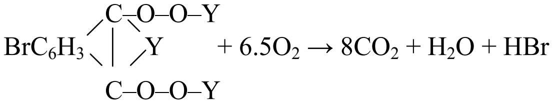
$$(9')\ YO_2CHBrC_6H_3CH_3 + ZNH_3 \rightarrow CH_3C_6H_3BrCN + Y + Z + 2H_2O,$$

(10')

$$YO_2CHBrC_6H_3CH_3 + ZO_2 \rightarrow BrC_6H_3(CO)_2Y + Z + 2H_2O,$$

(11')

$$BrC_6H_3(CO)_2Y + YO \rightarrow BrC_6H_3(CO)_2YO + Y,$$

(12')

$$BrC_6H_3(CO)_2YO + NH_3 \rightarrow BrC_6H_3(CO)_2NH + H_2O + Y,$$

(13')

$$BrC_6H_3(CO)_2Y + 2YO \rightarrow BrC_6H_3(C{-}O{-}O{-}Y)_2Y,$$

(14')

$$BrC_6H_3(C{-}O{-}O{-}Y)_2Y + 6.5O_2 \rightarrow 8CO_2 + H_2O + HBr + 3Y.$$

Centers Y are only slightly coated by organic fragments.

If the rate of $YOCHBrC_6H_3CH_3$ consumption at stages (2) and (3) is roughly equal to the rate of YOH_2 consumption at stage (5), the concentrations of these compounds are also equal to each other: $[YOCHBrC_6H_3CH_3] \approx [YOH_2]$.

Then from the equilibrium (1) and under the assumption that centers Y are completely coated by oxygen ($[YO] \approx 1$) we obtain Eqs. (12) and (13).

$$K_1 = [YOCHBrC_6H_3CH_3]^2/P_I, \qquad (12)$$

$$[YOCHBrC_6H_3CH_3] = \sqrt{K_1P_I}. \qquad (13)$$

The rate of 4-bromo-*o*-xylene consumption by route 9 at $[YO] \approx 1$ and with account for the slow stage (3), which is rate-limiting at this route, can be found by Eq. (14), and that by routes 1, 7, and 8 at [YO] ≈ 1 and with account for the slow stage (2), can be found by Eq. (15).

$$w_9 = k_3[YOCHBrC_6H_3CH_3] = k_3\sqrt{K_1}P_{I}, \quad (14)$$

$$w_1 + w_7 + w_8 = k_2[YOCHBrC_6H_3CH_3] = k_2\sqrt{K_1}P_{I}, \quad (15)$$

$$k'_1 = k_2\sqrt{K_1},\ k'_9 = k_3\sqrt{K_1}.$$

Here k_i is the rate constant of the reaction stage.

The w_1 and $[w_7 + w_8]$ values, taking into account the NH_3 and O_2 coatings which control routes 1, 7, and 8, are given by Eqs. (16) and (17).

$$w_1 = k_2\sqrt{K_1P_{I}}\, P(NH_3)/P(NH_3) + K_7/K_8P(O_2), \quad (16)$$

$$w_7 + w_8 = k_2\sqrt{K_1P_{I}}\, K_7/K_8P(O_2)/P(NH_3) + K_7/K_8P(O_2), \quad (17)$$

$$b = K_7/K_8.$$

In turn, the rate ratio for routes 7 and 8 are determined by the rate constant ratio for stages (11') and (13').

$$w_7/w_8 = \beta/(1 - \beta) = k_{11'}/k_{13'},$$

$$\beta = k_{11'}/k_{11'} + k_{13'}.$$

4-Bromo-*o*-tolunitrile, like 4-bromo-*o*-xylene, is dissociatively adsorbed on centers Y.

(15) $2YO + CH_3BrC_6H_3CN \rightleftarrows YOCHBrC_6H_3CN + YOH_2$,

(16) $YOCHBrC_6H_3CN + YO \rightarrow YO_2CHBrC_6H_3CN + Y$,

(17′) $YO_2CHBrC_6H_3CN + ZNH_3 \rightarrow BrC_6H_3(CN)_2 + Y + Z$.

As the rates of $YOCHBrC_6H_3CN$ and YOH_2 formation at stage (15) are equal to each other, then $[YOCHBrC_6H_3CN] = [YOH_2]$.

Therefore, from the equilibrium (15) and under the assumption that centers Y are completely associated with oxygen ([YO] ≈ 1), we have $K_{15} = [YOCHBr\cdot C_6H_3CN]^2/P_{II}$, from which $[YOCHBrC_6H_3CN] = \sqrt{K_{15}P_{II}}$.

Then the rate of 4-bromo-*o*-tolunitrile transformation by route 2 at [YO] ≈ 1 and with account for the slow stage (16), which is rate-limiting at this route, can be found by Eq. (18).

$$w_2 = k_{16}[YOCHBrC_6H_3CN] = k_{16}\sqrt{K_{15}P_{II}}. \quad (18)$$

Taking into account the NH coating which controls route 2, the reaction rate can be found by Eq. (19).

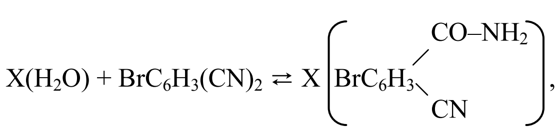
$$w_2 = k_{16}\sqrt{K_{15}P_{II}}\, P(NH_3)/P(NH_3) + bP(O_2), \quad (19)$$

$$k'_2 = k_{16}\sqrt{K_{15}}.$$

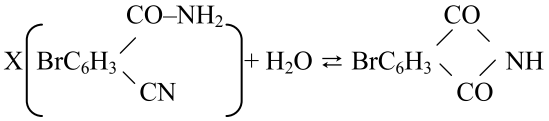
Analysis of the dependences of the kinetics of 4-bromophthalonitrile hydrolysis and the reverse reaction of 4-bromopthalimide ammonolysis on water and ammonia concentrations shows that these reactions occur at the catalytic centers of a different nature. Ammonia competes with water on these centers, and, moreover, ammonium is adsorbed to a much higher degree than water (the NH_3 coating degree is close to 1).

(18) $X + H_2O \rightleftarrows (H_2O)$,

(19) $X + NH_3 \rightleftarrows X(NH_3)$,

(20)


$$X(H_2O) + BrC_6H_3(CN)_2 \rightleftarrows X\left[BrC_6H_3\begin{matrix}CO\text{–}NH_2\\ CN\end{matrix}\right],$$

(21)


$$X\left[BrC_6H_3\begin{matrix}CO\text{–}NH_2\\ CN\end{matrix}\right] + H_2O \rightleftarrows BrC_6H_3\begin{matrix}CO\\ CO\end{matrix}NH$$

$+ X(NH_3)$.

Here stages (18), (19), and (21) are equilibrium stages, and stage (20) is reversible but not equilibrium.

The water coating is gived by Eq. (20).

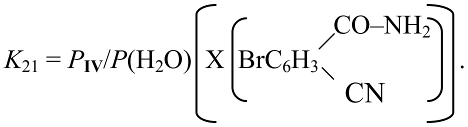
$$[X(H_2O)] = K_{18}P(H_2O)/K_{19}P(NH_3). \quad (20)$$

Then the rate of the forward reaction by route 3, with account for the rate-limiting stage (20), is calculated by Eq. (21).

$$w_3 = k_{20}P_{III}[X(H_2O)] = k_{20}P_{III}K_{18}P(H_2O)/K_{19}P(NH_3), \quad (21)$$

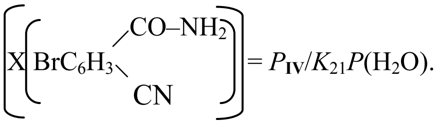
$$k'_3 = k_{20}K_{18}/K_{19}.$$

The equilibrium constant of stage (21), under the assumption $[X(NH_3)] \approx 1$, can be found by Eq. (22).



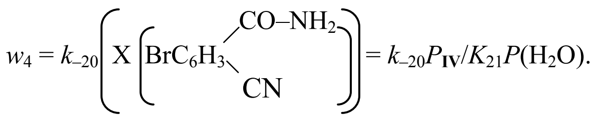
$$K_{21} = P_{IV}/P(H_2O)\left[X\left[BrC_6H_3\begin{matrix}CO\text{–}NH_2\\ CN\end{matrix}\right]\right]. \quad (22)$$

From this the degree of coating with the intermediate compound is found by Eq. (23).



$$\left[X\left[BrC_6H_3\begin{matrix}CO\text{–}NH_2\\ CN\end{matrix}\right]\right] = P_{IV}/K_{21}P(H_2O). \quad (23)$$

Then the rate of the reverse reaction by route 4 (ammonolysis of 4-bromophthalimide), with account for the rate-limiting stage (20), can be found by Eq. (24).

 (24)

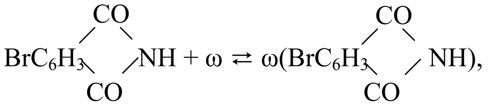
$$w_4 = k_{-20}\left(X\left[BrC_6H_3\begin{matrix}\diagup CO\text{–}NH_2\\ \diagdown CN\end{matrix}\right]\right) = k_{-20}P_{IV}/K_{21}P(H_2O). \quad (24)$$

Consequently, $k'_4 = k_{-20}/K_{21}$. In equilibrium, $w_3 = w_4$.

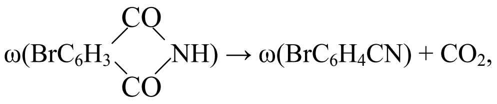
Then $k_{20}K_{18}P_{III}P(H_2O)/K_{19}P(NH_3) = k_{-20}P_{IV}/K_{21}P(H_2O)$, and the equilibrium constant of 4-bromophthalonitrile hydrolysis can be described by Eq. (25).

$$k_{20}K_{18}K_{21}/K_{19}k_{-20} = P_{IV}P(NH_3)/P_{III}P^2(H_2O)$$
$$= K_e = K_3/K_4. \quad (25)$$

Judging from the observed kinetic regularities [1, 3], the formation of 4-bromobenzonitrile both from 4-bromophthalimide and from 4-bromo-*o*-tolunitrile occurs on different centers than oxidative ammonolysis. Such centers may well exist on the surface of a multicomponent catalyst. The character of the kinetic curves for 4-bromophthalimide decarboxylation suggests that this reaction occrs on catalytic centers (ω) coated with imide.

(22) 

$$BrC_6H_3\begin{matrix}CO\\ \diagdown\ \diagup\\ CO\end{matrix}NH + \omega \rightleftarrows \omega(BrC_6H_3\begin{matrix}CO\\ \diagdown\ \diagup\\ CO\end{matrix}NH),$$

(23) 

$$\omega(BrC_6H_3\begin{matrix}CO\\ \diagdown\ \diagup\\ CO\end{matrix}NH) \rightarrow \omega(BrC_6H_4CN) + CO_2,$$

(24') $\omega(BrC_6H_4CN) \rightarrow BrC_6H_4CN + \omega$.

The rate of 4-bromophthalimide consumption by route 5 (w_5), with account for the rate-limiting stage (23) and an imide coating close to 1, is equal to k_{23}. Consequently, $k'_5 = k_{23}$.

The formation of 4-bromobenzene by oxidative destruction (demethylation) of 4-bromo-*o*-tolunitrile is retarded by 4-bromo-*o*-xylene, and, therefore, centers λ are fully coated by 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile adsorbed uder equilibrium conditions.

(25) $\lambda + CH_3BrC_6H_3CH_3 \rightleftarrows \lambda(CH_3BrC_6H_3CH_3)$,

(26) $\lambda + CH_3BrC_6H_3CN \rightleftarrows \lambda(CH_3BrC_6H_3CN)$.

Then the 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile coatings can be found by Eqs. (26) and (27).

$$[\lambda(CH_3BrC_6H_3CH_3)] = K_{25}P_I/K_{25}P_I + K_{26}P_{II}$$
$$+ K_{25}/K_{26}P_I/K_{25}/K_{26}P_I + P_{II}, \quad (26)$$

$$[\lambda(CH_3BrC_6H_3CN)] = K_{26}P_{II}/K_{26}P_{II} + K_{25}P_I$$
$$= P_{II}/P_{II} + K_{25}/K_{26}P_I. \quad (27)$$

The oxidative destruction of 4-bromo-*o*-tolunitrile by route 6 can be desribed by the following reaction sequence.

(27) $3\lambda + 1.5O_2 \rightarrow 3\lambda O$,

(28) $\lambda(CH_3BrC_6H_3CN) + 2\lambda O \rightarrow \lambda(HOCBrC_6H_3CN)$
$+ \lambda OH_2 + \lambda$,

(29') $\lambda(HOCBrC_6H_3CN) + \lambda O \rightarrow \lambda(HOOCBrC_6H_3CN) + \lambda$,

(30') $\lambda(HOOCBrC_6H_3CN) \rightarrow \lambda(BrC_6H_4CN) + CO_2$,

(31') $\lambda(BrC_6H_4CN) \rightarrow BrC_6H_4CN + \lambda$,

(32) $\lambda OH_2 \rightarrow \lambda + H_2O$,

$[\lambda\ (CH_3BrC_6H_3CH_3)] + [\lambda(CH_3BrC_6H_3CN)] \approx 1$.

In view of the aforesaid and the fairly low yields of 4-bromobenzonitrile even by routes 5 and 6 (Scheme 1), we can suggest that centers λ are only slightly coated by inorganic fragments [Eq. (28)].

$$[\lambda(CH_3BrC_6H_3CH_3)] + [\lambda(CH_3BrC_6H_3CN)] >> [\lambda O]. \quad (28)$$

From stage (26) for $[\lambda(CH_3BrC_6H_3CN)]$, equating the total numer of centers to 1, we obtain Eqs. (29) and (30).

$$K_{26} = [\lambda(CH_3BrC_6H_3CN)]/P_{II}, \quad (29)$$

$$[\lambda(CH_3BrC_6H_3CN)] = K_{26}P_{II}. \quad (30)$$

Then the rate of consumption of adsorbed 4-bromo-*o*-tolunitrile $[\lambda(CH_3BrC_6H_3CN)]$ for the formation of BrC_6H_4CN at the slow stage 28) is given by Eq. (31).

$$w_6 = k_{28}[\lambda(CH_3BrC_6H_3CN)] = k_{28}K_{26}P_{II}, \quad (31)$$

$$w_6 = k_{28}K_{26}P_{II}/1 + K_{25}/K_{26}P_I,$$

$$k'_6 = k_{28}K_{26},\ a = K_{25}/K_{26}.$$

Here a is a constant which reflects the ratio of the adsorption equilibrium constants of 4-bromo-*o*-xylene and 4-bromo-*o*-tolunitrile.

Thus, the kinetic data obtsined in [1–3] allow us to discuss only certain characterstic features of the mechanism and to make suggestions concerning surface stages.

REFERENCES

1. Bagirzade, G.A., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 3, p. 492.
2. Bagirzade, G.A., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 8, p. 1672.
3. Bagirzade, G.A., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 9, p. 1779.

4. Bagirzade, G.A., Sheynin, V.E., and Magerramova, Z.Yu., Abstracts of Papers, *I Mezhdunar. konf. RHO im. D.I. Mendeleeva "Resurso- i energosberegayushchie tekhnologii v khimicheskoi i neftekhimicheskoi promyshlennosti"* (I Int. Conf. of the Mendeleev Russian Chemical Society "Resource- and Energy-Saving Technologies in Chemical and Petrochemical Industries"), Moscow: RKhTU im. D.I. Mendeleeva, 2009, p. 94.
5. Bagirzade, G.A., Abstarcts of Papers, *II Mezhdunar. konf. RKhO im. D.I. Mendeleeva "Innovatsionnye khimicheskie tekhnologii i biotekhnologii materialov i produktov"* (II Int. Conf. of Mendeleev Russ. Chem. Soc. "Innovative Chemical Technolofies and Biotechnologies of Materials and Products"), Moscow: RKhTU im. D.I. Mendeleeva, 2010, p. 197.
6. Bagirzade, G.A, Abstracts of Papers, *III Mezhdunar. konf. RHO im. D.I. Mendeleeva "Resurso- i energosberegayushchie tekhnologii v khimicheskoi i neftekhimicheskoi promyshlennosti"* (III Int. Conf. of the Mendeleev Russian Chemical Society "Resource- and Energy-Saving Technologies in Chemical and Petrochemical Industries"), Moscow: RKhTU im. D.I. Mendeleeva, 2011, p. 133.
7. Bagirzade, G.A. and Tagiev, D.B., Abstracts of Papers, *IV Mezhdunar. konf. RHO im. D.I. Mendeleeva "Khimicheskaya tekhnologiya i biotekhnologiya novykh materialov i produktov"* (IV Int. Conf. of the Mendeleev Russian Chemical Society "Chemical Technology and Biotechnology of New Materials and Products"), Moscow: RKhTU im. D.I. Mendeleeva, 2012, vol. 1, p. 9.
8. Bagirzade, G.A., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 2012, vol. 55, no. 5, p. 23.
9. Rizaev R.G., Sheynin, V.E., Allakhkulu A.ogly, and Avetisov, A.K., *Kinet. Katal.*, 1985, vol. 26, no. 2, p. 345.
10. Rizaev, R.G., Sheynin, V.E., Allakhkulu A. ogly, and Avetisov, A.K., *Kinet. Katal.*, 1986, vol. 27, no. 2, p. 339.
11. Rizaev, R.G., Mamedov, E.A., Sheynin, V.E., and Vislovskii, V.P., *Geterogennyi kataliz v proizvodstve aromaticheskikh nitrilov* (Heterogeneous Catalysis in the Production of Aromatic Nitriles), Baku: Elm, 1992.
12. Golodets, G.I., *Partsial'noe okislenie organicheskikh soedinenii* (Partial Oxidation of Organic Compounds), Moscow: Nauka, 1985, vol. 19, p. 28.
13. Rizaev, R.G., Sheynin, V.E., and Bagirzade, G.A., *Mater. IV Vsesoyuzn. konf. po kinetike geterogenno-kataliticheskikh reaktsii "Kinetika-4"* (Proc. IV All-Union Conf. on Kinetics of Heterogeneous Catalytic Reactions "Kinetics-4"), Moscow: Nauka, 1988, p. 212.
14. Kiperman, S.L., *Osnovy khimicheskoi kinetiki v geterogennom katalize* (Fundamnetals of Chemical Kinetcs in Heterogeneous Catalysis), Moscow: Khimiya, 1979.