

Andrey Bushuyev, Michael Keremet, Andrey Galstyan and Tatyana Galstyan

KINETICS AND PRODUCTS OF 4-AMINOTOLUENE OXIDIZATION BY OZONE IN THE LIQUID PHASE

Volodymyr Dahl East Ukrainian National University (Rubizhne city), Ukraine; bas131982@mail.ru

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Abstract. The kinetic regularities and mechanisms of oxidation reactions of 4-aminotoluene and its acylation derivatives by the gases that contain ozone in the glacial acetic acid have been studied. The process of liquid-phase catalytic oxidation of 4-acetaminotoluene by ozone in the presence of transition metal salts and their mixtures with potassium bromide to the corresponding acetaminobenzoic acid has been investigated.

Keywords: 4-acetaminotoluene, acetic acid, 4-aminotoluene, oxidization, ozone.

1. Introduction

4-Aminobenzoic acid is an important chemical product of organic synthesis used in the production of synthetic dyes, medicinal and aromatic substances, wines, pesticides, *etc.* In chemical industry, 4-aminobenzoic acid is produced by reconstitution from 4-nitrobenzoic acid, which in its turn is the product of oxidation of 4-nitrotoluene by mineral-oxidants and molecular oxygen. Oxidation by mineral oxidants is unpromising due to environmental problems that accompany this process. In contrast, oxidation by molecular oxygen eliminates environmental issues; however, this process is conducted in harsh conditions and requires sophisticated equipment. Thus, the use of ozone – a powerful oxidant – is of great interest [1]. However, literature data on the oxidation of the aromatic amines with ozone are contradictory and not sufficient for the technical implementation of this reaction [2-6]. Some authors believe that ozone mainly attacks aminotoluenes on the aromatic ring forming low molecular products [2, 3], others show preference for the oxidation of amino groups [4-6], the oxidation by methyl group in the literature being not discussed at all. In this regard, systematic studies of the reaction of ozone with 4-aminotoluene for development of the methods and technologies of synthesis of 4-aminobenzoic acid is an urgent task.

2. Experimental

Ice acetic acid of "chemically pure" qualification purified before usage by distillation under vacuum in the presence of potassium permanganate, 4-aminotoluene of "chemically pure" qualification, 4-acetaminotoluene (white crystalline powder, melting point 420 K) after repeated recrystallization from water, acetate of cobalt (II) tetrahydrate of "pure" qualification and potassium bromide of "pharmaceutical grade" qualification were used for the experiments.

The investigations were carried out in the temperature-controlled glass column ($V = 0.02$ l) with a porous barrier for dispersing gas in the kinetic regime of oxidation. The column was loaded with 0.01 l of glacial acetic acid, 0.4 mol/l of 4-acetaminotoluene (4-AAT), and cobalt(II) acetate tetrahydrate. Then the gas was fed (air, oxygen or ozone-air mixture) at the rate of 30 l/h; the concentration of ozone in the gas phase was $(1.5-6.0) \cdot 10^{-4}$ mol/l. If the catalyst is to be introduced into the system in the oxidized form, a preliminary solution of acetous acetate cobalt(II) has to be prepared. It was ozonized by passing through an ozone-air mixture until exhaustive oxidation of Co(II) to Co(III). After the cobalt oxidation, the gas flow was stopped and the column was loaded with the calculated amount of 4-AAT and renewed supplying the ozone-containing gas. At the end of the oxidation the reaction mixture was poured into the glass beaker, two-thirds filled with finely divided ice, and then diluted with cold water so that the total volume was 50 ml. After its precipitation, 4-acetaminobenzoic acid (4-AABA) was filtered and washed with cold water. Then, 10 ml of concentrated HCl, 20 ml of water, and 4 ml of alcohol were added, and the mixture was heated for one hour in a flask with reverse refrigeration with stirring. The reaction mass was then cooled and the precipitated 4-aminobenzoic acid (4-ABA) was filtered and dried.

2.1. Methods of Analysis

The ozone concentration in the gas phase at the inlet and outlet of the reactor was determined by spectrophotometry. 4-AAT, the corresponding alcohol and aldehyde were analyzed by gas-liquid chromatograph with a flame ionization detector on the column of 3 m long, 4 mm in diameter, filled with a carrier "inerton AW-DMCS", coated with a stationary phase "SE-30" in the amount of 5 % by weight of the carrier under the following conditions: the temperature of the evaporator 523 K, thermostat temperature 463 K, the rate of carrier gas (nitrogen) is 1.8 l/h, hydrogen – 1.8 l/h, and air – 18 l/h. As the internal standard, 4-nitrochlorobenzene was used. The current concentration of 4-AABA was determined by titration with alkali; for this purpose 0.5 ml from the reaction mixture was sampled from which the solvent was then removed, its dry residue was then dissolved in 30 ml of a 50 % solution of ethyl alcohol, neutralized to phenolphthalein, and the obtained solution was titrated with 0.05 N of sodium hydroxide solution.

The effective reaction rate constant of ozone with 4-AAT and the quantity of ozone absorbed in the course of the reaction was determined by the procedures described in [12]. The reaction rate constants for Co(III) with 4-AAT was calculated graphically for the case of one-sided second-order reactions [21].

The structure of peroxide compounds formed during ozonation was determined by IR spectroscopy, and their concentration by iodometric titration.

3. Results and Discussion

The previous studies [7] have found out that ozone in the solution of glacial acetic acid reacts with 4-aminotoluene rapidly. The effective reaction rate constant equals to $2.66 \cdot 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Ozone attacks mainly the lone pair of electrons of the nitrogen atom mainly with formation of polymers of azo compounds, and trace amounts of 4-nitrotoluene, toluhinone, and nitroso compound. Products of oxidation on methyl group are not

formed under these conditions. Practically, the resulting composition of the products does not differ from that described in the literature and corresponds to the scheme of the transformations that P. Bailey suggested for the reaction of ozone with aromatic amines [8, 9]. His scheme presumes a fast attack by ozone of the free pair of electrons of nitrogen atom with the further development of the reaction in two directions: a) the formation of aromatic nitro products and b) the formation of ion-radical pair, which, depending on the structure of the amine, can transform into a variety of products, most of which are polymeric azocompounds.

The direction of the ozone attack can be altered and directed on the methyl group as well as aromatic ring by acylation of the amino group. In this case the amino group is largely deactivated by the conjugation of the undivided pair of nitrogen electrons to the carbonyl group of the acetyl. After the acylation of 4-aminotoluene, the effective reaction rate constant k_{ef} is reduced by three orders of magnitude (Table 1) and is close to the value of the k_{ef} of methylbenzenes (Fig. 1).

At the atmospheric pressure and the temperature of 293 K the oxidation of 4-acetaminotoluene by ozone in the glacial acetic acid proceeds without an induction period and mainly on the aromatic ring.

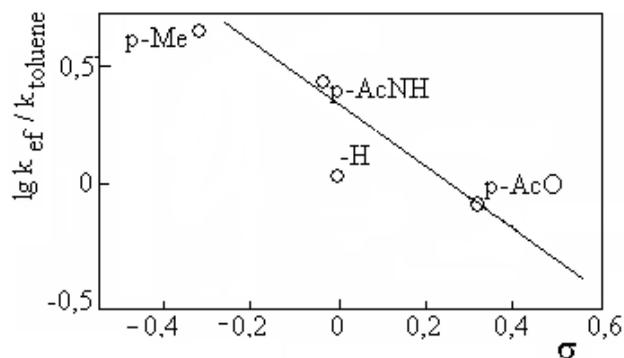


Fig. 1. Dependence of relative reaction rate constants of liquid-phase reactions of ozone with the derivatives of toluene at 288 K on the value of σ – Hammett sigma constant

Table 1

Rate constants of ozone reaction with toluene derivatives in the solution of glacial acetic acid at 293K

Substance	$[\text{O}_3]_0 \cdot 10^4, \text{ mol} \cdot \text{l}^{-1}$	$[\text{ArCH}_3]_0 \cdot 10^2, \text{ mol} \cdot \text{l}^{-1}$	$k, \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
Toluene	0.28–0.57	7.7–28.3	0.82 ± 0.08
4- Aminotoluene	0.45–0.80	2.7–18.3	$(2.66 \pm 0.20) \cdot 10^3$
4- Acetaminotoluene	0.28–0.57	10.1–27.9	2.49 ± 0.20

Table 2

Oxidation of 4-acetaminotoluene by ozone in glacial acetic acid
 at 293 K $[O_3]_0 = 4.7 \cdot 10^{-4}$; $[AcNHArCH_3]_0 = 0.4 \text{ mol} \cdot \text{l}^{-1}$; $V_r = 0.01 \text{ l}$

Selectivity, %		
On the methyl group	On the aromatic ring	Unidentified products
14.2	83.5	2.3

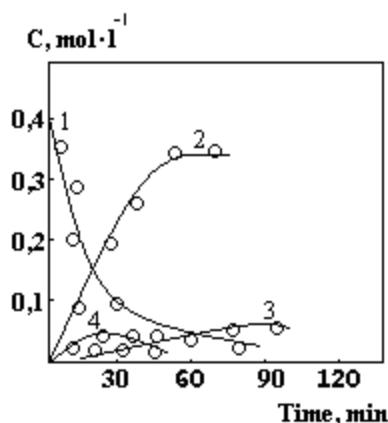


Fig. 2. Kinetics of oxidation of 4-acetaminotoluene by ozone in acetic acid; $T = 293 \text{ K}$; $[O_3]_0 = 4.7 \cdot 10^{-4}$; $[AcNHArCH_3]_0 = 0.4 \text{ mol} \cdot \text{l}^{-1}$; $V_r = 0.01 \text{ l}$; gas flow speed is $5.6 \cdot 10^{-4} \text{ l} \cdot \text{s}^{-1}$. Change of concentrations: 4-acetaminotoluene (1); peroxides (2); 4-acetaminobenzoic acid (3) and 4-acetaminobenzaldehyde (4)

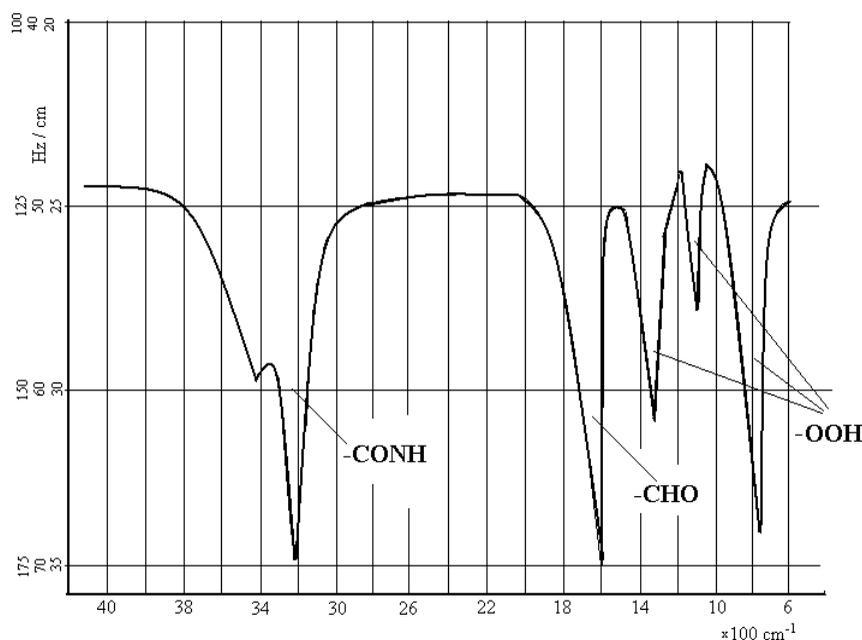


Fig. 3. IR spectrum of absorption of aliphatic peroxides produced by oxidation of 4-acetaminotoluene

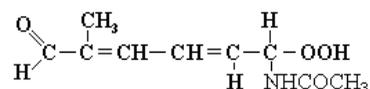
The total yield of the products of oxidation of the methyl group of 4-acetaminotoluene is 14.2 %, the yield of the products from ozonolysis on the aromatic ring (aliphatic peroxidic compounds) is 83.5 %, the yield of the unidentified products is 2.3 % (Table 2).

Among the products of oxidation of the methyl group identified at the early stages are 4-acetaminobenzaldehyde (13.1 %) and 4-acetaminobenzyl alcohol ($\approx 10^{-4} \text{ mol} \cdot \text{l}^{-1}$). At the later stages of oxidation, the main product with the aromatic structure kept is 4-acetaminobenzoic acid (14.2 %) (Fig. 2).

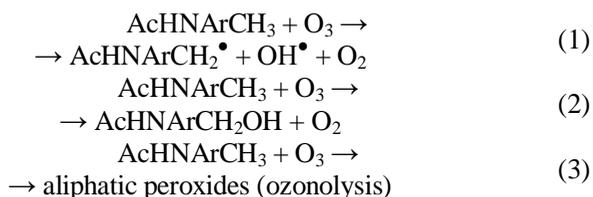
Peroxide compounds formed in the process of ozonation are quite stable at 293 K and inert to the further action of ozone. To identify their chemical nature the solvent was distilled under vacuum of 6.5 kPa. The peroxides were isolated as an oily viscous liquid of light-yellow color. The liquid is difficult to dissolve in acetic acid. It reacts with alkali and potassium iodide. The reaction ends in about 1 h when molecular iodide is released in a quantity equivalent to one peroxide group. These findings do not contradict the literature, according

to which hydroperoxide groups easily react with potassium iodide (the recovery of dialkyl-peroxide groups ends in $\approx 20\text{--}24 \text{ h}$). IR spectrum analysis showed the absence of aromatic structures in the peroxides produced. The absorption bands of IR spectra in the area of 760, 1050 and 1300 cm^{-1} are related to the oscillation of hydroperoxide groups, while the band in the area of 1620 cm^{-1} to that of carbonyl groups, and the bands in the area 3200 cm^{-1} to that of $-\text{CONH}$ groups (Fig. 3).

These facts, as well as the found stoichiometric coefficients of the reaction with ozone at 288 K ($n \approx 1$), presume that the oxidation of the aromatic ring produces aliphatic compounds, which are formed by the scheme of Krihe [10, 11] and have the following structure :



Thus, ozone reacts with 4-acetaminotoluene in two directions: on the methyl group and the aromatic ring. According to [12], oxidation proceeds as follows:



Thus, the dominant reaction is the ozonolysis of aromatic ring (3). In order to obtain the necessary information to produce selective syntheses of aminobenzoic acids we further studied kinetic characteristics and mechanism of reaction of ozone with acetaminotoluenes in the presence of salts of transition metals (STM) that were found to be electron donors during ozonation [13–15].

We studied the acetates of Co(II), Mn(II), Cr(III) and Ni(II) as the potential catalysts for selective oxidation of 4-acetaminotoluene by ozone in the presence of glacial acetic acid. It was found that the selectivity for the oxidation of methyl group depends on the magnitude of oxidation-reduction potential of the couples M/M^+ of the studied catalysts. The selectivity also depends on the velocity of interaction between renewable forms of metal and ozone, as well as on oxidized forms of metal in the original substrate. Kinetically acetate Co(II) was found to be the most effective catalyst (Table 3) but the output of

acetaminobenzoic acid in the given conditions is quite low – for 4-acetaminobenzoic acid it reaches only 35.5 %, because the predominant direction of reaction remains ozonolysis of aromatic ring.

Following these results, the further studies of oxidative catalysis of alkylbenzenes were conducted in the presence of alkali metal bromides, which increase selectivity and reaction rate [16, 17]. We found out that the use of our catalytic system (ozone–4-acetaminotoluene–Co(III)–glacial acetic acid–potassium bromide) significantly increases the reaction rate and the selectivity of substrate oxidation of methyl groups (Fig. 4). The main product of oxidation of 4-acetaminotoluene becomes 4-acetaminobenzoic acid (73.5 %), but we also identified small amounts of 4-acetaminobenzylbromide (4.5 %) and traces of 4-acetaminobenzaldehyde.

The maximal selectivity of oxidation of 4-acetaminotoluene was achieved at the molar ratio of 1:1 ($[\text{Co}(\text{OAc})_2]_0 : [\text{KBr}]_0$). The further increase in the concentration of potassium bromide does not affect the selectivity of oxidation (Table 4). This is a kinetic evidence of 4-acetaminobenzyl radical formation as a result of inner electron transfer from the π -electron system of the substrate to the cobalt-bromide radical to form the aromatic cation-radical (5-9) [18, 19].

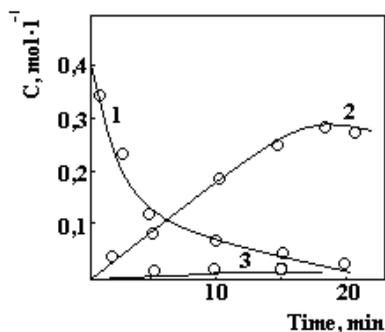
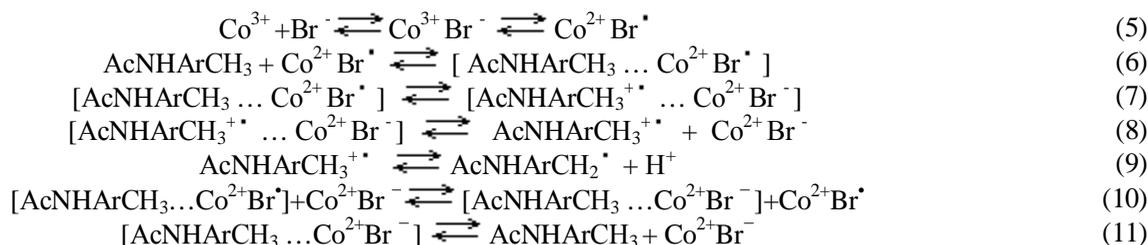


Fig. 4. Changes in the concentration of components of the reaction mixture during the oxidation of 4-acetaminotoluene by ozone–air mixture in the presence of cobalt bromide catalyst at 368 K: 4-acetaminotoluene (1); 4-acetaminobenzoic acid (2) and 4-acetaminobenzyl bromide (3). $[\text{AcNHArCH}_3]_0 = 0.4$, $[\text{Co}(\text{OAc})_2]_0 = 0.1$, $[\text{KBr}]_0 = 0.1$, $[\text{O}_3]_0 = 4.5 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$

Table 3

Influence of catalyst nature on the selectivity of oxidation of 4-acetaminotoluene in glacial acetic acid at 368 K.
 $[\text{M}(\text{OAc})_n]_0 = 0.14$; $[\text{ArCH}_3]_0 = 0.4$; $[\text{O}_3]_0 = 4.5 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $V_r = 0.01 \text{ l}$; speed of adding ozone – air mixture = $0.5 \text{ l} \cdot \text{s}^{-1}$

Catalyst	$E_p^{298} \text{ M/M}^+$	$k_{\text{M}+\text{O}_3}^{295} \text{ l} \cdot (\text{mol} \cdot \text{s})^{-1}$	$k_{\text{M}+\text{ArCH}_3}^{295} \text{ l} \cdot (\text{mol} \cdot \text{s})^{-1}$	Yield of the 4- amino-benzoic acid, %
Co(OAc) ₂	1.810	$9.8 \cdot 10^2$	0.0015	35.5
Mn(OAc) ₂	1.510	$4.5 \cdot 10^3$	0.0008	20.2
Cr(OAc) ₃	0.740	44	0.0004	17.5
Ni(OAc) ₂	0.407	14	0.0002	15.0

Table 4

**Oxidation of 4-acetaminotoluene at the presence of cobalt-bromide catalyst
of different composition (see Fig. 4 for conditions)**

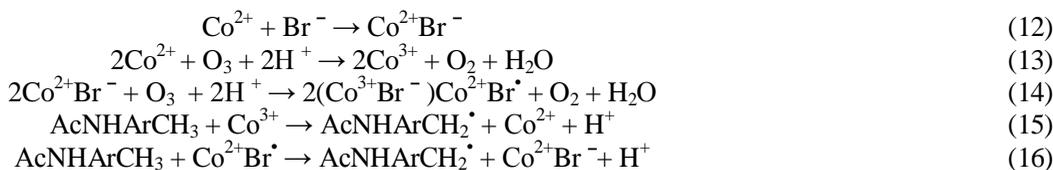
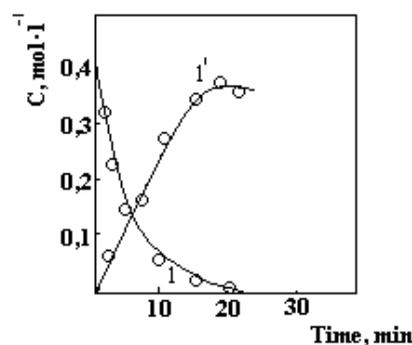
[Co(OAc) ₂] ₀ , mol·l ⁻¹	[KBr] ₀ , mol·l ⁻¹	Yield of the aminobenzoic acid, %
0.14	–	35.5
0.10	0.025	46.3
0.10	0.050	52.6
0.10	0.075	60.8
0.10	0.100	73.5
0.10	0.120	73.2

Table 5

**Consumption of ozone for oxidation of 4·10⁻³ mol of 4-acetaminotoluene
by mixture of ozone-air/ozone-oxygen (see Fig. 4 for conditions)**

Ozone let through, mol·10 ³	Ozone unreacted, mol·10 ³	Ozone absorbed, mol·10 ³	Consumption of ozone per 1 mol of substrate		
			practically, mol	theoretically, mol	in % of theory
5.95/3.66	0.95/0.66	5.00/3.00	1.25/0.75	1.53/1.68	81.7/44.6

Fig. 5. Change in the components concentration of the reaction mixture during the oxidation of 4-acetaminotoluene, using ozone-oxygen mixture at 368 K (see Fig. 4 for the terms and conditions). Line 1' represents concentration of the corresponding 4-acetamidobenzoic acid



The higher rate and selectivity of the oxidation in the presence of potassium bromide (KBr) is tributary to the higher rate of initiation of selective oxidation of the substrate, which is higher by an order of the magnitude for $\text{Co}^{2+}\text{Br}^-$ (16) compared to cobalt acetate (Fig. 5, Table 6).

Achieving high selectivity of oxidation in the presence of KBr is accompanied by a decrease in the optimal concentration of cobalt by 30 %. The further increase in selectivity for the oxidation on methyl group is achieved by increasing the concentration of molecular oxygen in the gas containing ozone. Replacing ozone-air mixture with the ozone-oxygen mixture leads to higher yield of 4-acetaminobenzoic acid (90.0 %) (Fig. 5), while the consumption of ozone

is reduced by about 40 %, in the case of oxidation of the 4-acetaminotoluene giving 44.6 % of the theoretically required amount (Table 5).

According to classical concepts when $[\text{O}_2] \gg [\text{O}_3]$, an acetaminobenzyl radical becomes an acetaminoperoxidic radical (17), which can recombine by the reaction (21) with the formation of aromatic products. However, the concentration of molecular oxygen in the ozone containing gas affects the selectivity of oxidation and our experiments show that a part of radicals can recombine according to the reactions (21a) and (21b), thus forming oxidations products (e.g. diphenylethane with the boiling point of 560 K), not identified for the purposes of this analysis.

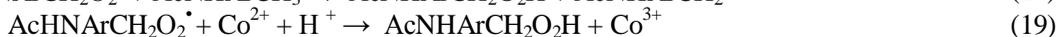


Table 6

Kinetic parameters of the reactions in the catalytic cycle
[4-AcNHArCH₃(4-AT)]₀ = 0.4; [O₃]₀ = 4.5·10⁻⁴; [Me(OAc)₂]₀ = 0.1; [Co²⁺Br⁻]₀ = 0.1 mol l⁻¹

Reaction	<i>k</i> , l·(mol·s) ⁻¹ *				<i>E</i> , kJ·mol ⁻¹	<i>I</i> ³⁶⁸ , mol·(l·s) ⁻¹
	293 K	313 K	343 K	368 K		
O ₃ + Co(II)	0.98·10 ³	2.10·10 ³	4.40·10 ³	12.40·10 ³	30.9±3.0	0.56
4-AT + O ₃	3.36	8.11	25.10	56.20	34.8±3.4	0.0101
4-AT + Co(III)	0.0015	0.005	0.0200	0.070	46.7±4.6	0.0028
4-AT + Mn(IV)	0.0008	0.0016	0.0038	0.0070	27.9±2.7	0.0014
4-AT+Co(II)Br [•]	0.0071	0.027	0.149	0.520	50.87±5.0	0.021

*Experiment error is 8 %

Under the experimental conditions the continuation of the chain reactions (18-20) is insignificant because their reaction rate is at least three times lower than the rate of the recombination of acetaminoperoxide radicals (according to [20] for toluene at 368 K [AcNHArCH₃]₀ = 0.4; [Co²⁺Br⁻]₀ = 0.1; [AcNHArCH₂O₂·] = 1.0·10⁻⁵ l·(mol·s)⁻¹; *k*₁₄ = 12.5·10³; *k*₁₆ = 0.52; *k*₁₈ = 2.0; *k*₁₉ = 1.6·10³; *k*₂₀ = 6.6·10³; *k*₂₁ = 2.0·10⁸ l·(mol·s)⁻¹, values of reaction rates are: *I*₁₄ = 0.5; *I*₁₆ = 2.1·10⁻²; *I*₁₈ ≈ 2·10⁻⁶; *I*₁₉ ≈ 4.5·10⁻⁴; *I*₂₀ ≈ 0.66·10⁻²; *I*₂₁ ≈ 1.0·10⁻² mol·(l·s)⁻¹, and *v* = *I*₂₀/*I*₁₆ ≈ 0.33).

It follows that the oxidation on methyl group occurs mainly by ion-radical non-chain mechanism.

The cessation of ozone input into the system leads to the results that confirm this conclusion: the rate of oxidation is constantly decreasing, Co³⁺ is reduced to Co²⁺, and the process goes to oxidation by molecular oxygen. Taking into consideration that appearance of the reactive species (Co³⁺ and Co²⁺Br[•]) promoting the oxidation of 4-acetaminotoluene is determined mainly by the passage of reactions (13), (14), (19), and (20) slowing of this process in the absence of ozone is possible only when the chain extension reactions (19) and (20) play a secondary role. Our calculations show that the rate of reaction (20) is really significantly lower than the rate of reaction (14) (*I*₁₄/*I*₂₀ = 0.50/0.66·10⁻² ≈ 76).

Reduction of the optimal concentration of cobalt acetate and the increase of the rate and selectivity of

catalytic oxidation with cobalt-bromide catalyst is due to its higher catalytic activity with 4-acetaminotoluene and 4-acetaminobenzyl radical (Table 6).

Increase in selectivity during the oxidation process with ozone-oxygen mixture is probably a consequence of increased part of acetaminobenzoic radicals used in the reactions (17, 20 and 21) to form the corresponding 4-acetaminobenzoic acid. Increasing the rate of the formation of Co²⁺Br[•] by the reaction (20), obviously leads to further reduction of ozone consumption during the oxidation of 4-acetaminotoluene (Table 6).

4. Conclusions

It has been shown that the reaction of ozone with 4-aminotoluene in glacial acetic acid proceeds with high speed and preferably with the free electron pair of heteroatom with the formation of polymeric azocompounds. In these conditions, the products of oxidation on methyl group of substrate are not formed. By the acylation of amino group, the direction of ozone attack changes towards methyl groups and aromatic ring. 4-Acetaminotoluene are oxidized to form the products of destructive oxidation (ozonolysis) of aromatic ring – aliphatic peroxides (83.5 %) as well as the products of oxidation of methyl group – 4-acetaminobenzaldehyde and 4-acetaminobenzoic acid (14.2 %).

We have found that the usage of cobalt-bromide catalyst in oxidation gases containing ozone increases the rate and selectivity of the oxidation of 4-acetaminotoluene to 73 %. The increase of oxidation rate on methyl group in the presence of catalytic system with supplements of bromides of alkali metals is associated with the formation of highly reactive cobalt-bromide complex, which quickly attracts the substrate in the process of selective oxidation to form 4-acetaminobenzoic acid.

It has also been found out that further increase in selectivity of the oxidation of methyl group to 90 % and the consumption reduction of ozone by 40 % is achieved in the conditions of oxidation with ozone-oxygen mixture.

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КІНЕТИКА І ПРОДУКТИ ОКИСНЕННЯ 4-АМІНОТОЛУЕНУ ОЗОНОМ У РІДКІЙ ФАЗІ

Анотація. Встановлені кінетичні закономірності та запропонований механізм реакції окиснення 4-амінотолуену і його ацильованої похідної у крижаній оцтовій кислоті. Вивчено процес каталітичного рідиннофазного окиснення 4-ацетамінотолуену озоном у присутності солей перехідних металів та їх сумішей з калій бромідом.

Ключові слова: 4-ацетамінотолуен, оцтова кислота, 4-амінотолуен, окиснення, озон.

