1. Introduction

In the acetic acid the toluene react with ozone mostly for double bonds of the aromatic ring to form ozonides. The output of the oxidation products of the methyl group in these conditions does not exceed 16 % [1]. Investigation of the influence of electron donor and acceptor substituents on the oxidation of the methylbenzenes and their derivatives by ozone in acetic acid were carried out in [2, 3]. It is shown that in the presence of electron donor (\(-\text{CH}_3, \text{-OH}\)) substituents direction of attack by ozone of the methyl group is virtually absent, but the presence of electron acceptor (\(-\text{NO}_2\)) substituents increases selectivity of the methyl group to 36 % [3]. The data of the oxidation of aminotoluenes by ozone in the acetic acid in the literature are mostly absent. Therefore, the study of the reaction of ozone with 2- and 3-aminotoluene in acetic acid to further clarify the nature of the substituent influence on the selectivity and composition of the oxidation products of methylbenzenes are actual.

2. Analysis of literature data

Isomeric aminobenzoic acid is an important chemical product of organic synthesis used in the production of synthetic dyes, medicinal and aromatic substances, wines, pesticides, etc [4, 5]. In chemical industry, 2-aminobenzoic acid (2-ABA) is produced from phthalimide [6], 3-aminobenzoic acid (3-ABA) is produced by reconstitution from 3-nitrobenzoic acid [7], which in its turn is the product of oxidation of 3-nitrotoluene by mineral-oxidants and molecular oxygen. Oxidation by mineral oxidants is unpromising from the point in view of the environmental problems that thereby occur. In contrast, oxidation by molecular oxygen eliminates environmental issues, but this process is conducted in harsh conditions and requires sophisticated equipment. Thus, the purpose of this work was to investigation the reaction of the oxidization of 2- and 3-aminotoluene by gases containing ozone in the liquid phase with the purpose of reception of the corresponding 2- and 3-aminobenzoic acid under mild conditions and in high yield.

3. The methodology of the experiment

Ice acetic acid of the qualification “chemically pure” was used for the experiments and before usage it had been purified by distillation under vacuum in the presence of potassium permanganate; 2-, 3-aminotoluene (3-AT) of the qualification “chemically pure”, 2-, 3-acetamidotoluene (3-AAT) (white crystalline powder, the melting point is 147 °C) after repeated recrystallization from water. The acetate of cobalt (II) of the qualification “pure” and bromide of potassium of the “pharmaceutical grade” were used.

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 liter of glacial acetic acid, 0.4 mol/L of 3-acetamidotoluene (3-AAT) (white crystalline powder, the melting point is 147 °C) after repeated recrystallization from water. The acetate of cobalt (II) tetrahydrate of the qualification “pure” and bromide of potassium of the “pharmaceutical grade” were used.

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SELECTIVE OXIDIZATION OF 2- AND 3-AMINOTOLUENE BY OZONE IN THE GLACIAL ACETIC ACID TO THE CORRESPONDING AMINOBENZOIC ACIDS

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catalyst is to be introduced into the system in the oxidized form, a preliminary solution of acetic acid cobalt (II) had to be prepared, it was ozonized by passing through an ozone-air mixture until exhaust 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 3-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, 3-acetamidobenzoic acid (3-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 heated for one hour in a flask with a reverse refrigeration with stirring. The reaction mass was then cooled, and the precipitated 3-ABA was filtered and dried.

4. The methods of analysis

The ozone concentration in the gas phase at the inlet and outlet of the reactor was determined by spectrophotometry. 2- and 3-AAT, the corresponding alcohol and aldehyde were analyzed by gas-liquid chromatography 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 amount of 5 % by weight of the carrier under the following conditions: the temperature of the evaporator 250 ºC, thermostat temperature 190 ºC, 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 2- and 3-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 2- and 3-AAT and the quantity of ozone absorbed in the course of the reaction was determined by the procedures described in [8]. The reaction rate constants for Co (III) with 2- and 3-AAT was calculated graphically for the case of one-sided second-order reactions.

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

5. Research results oxidation of aminotoluenes by ozone and discussion of this data

The previous studies [9] have found out that ozone in the solution of glacial acetic acid reacts with 2- and 3-AT rapidly. The effective reaction rate constant equals to 2.46·10³ l·mol⁻¹·sec⁻¹ for 2-AT and 2.15·10³ l·mol⁻¹·sec⁻¹ for 3-AT respectively. Ozone attacks mainly the lone pair of electrons of the nitrogen atom with formation, mainly, of polymers of azo compounds, and trace amounts of nitrotoluene, toluidine and nitroso compound. The products oxidation on methyl group are not formed in 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. S. Bailey suggested for the reaction of ozone with aromatic amines. 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 azo compounds.

The direction of the ozone’s attack can be altered and directed on the methyl group, as well as by an 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’s electrons to the carbonyl group of the acetyl. After the acylation of 2- and 3-AT, the effective reaction rate constant k_o2 is reduced by three orders of magnitude (Table 1) and is close to the value of the k_o of methylbenzenes (Fig. 1).

At the atmospheric pressure and the temperature of 293 K, the oxidation of 2-AAT or 3-AAT by ozone in the glacial acetic acid proceeds without an induction period and mainly on the aromatic ring.

Fig. 1. 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

The total yield of the products of oxidation of the methyl group of 2- and 3-AAT is 5.1 and 12.4 % respectively, the yield of the products from ozonolysis on the aromatic ring (aliphatic peroxidic compounds) is 92.9 and 84.7 %, the yield of the unidentified products is 2.0, 2.9 % (Table 2).

Table 1

| Substance | [O₃]₁₀⁵ mol⁻¹ | [ArCH₃]₁₀⁵ mol⁻¹ | kₒ mol⁻¹·sec⁻¹ |
|-----------|---------------|-----------------|----------------|
| Toluene   | 0.28±0.57     | 7.7±28.3        | 0.82±0.08      |
| 2-AT      | 0.45±0.10     | 2.7±18.3        | (2.46±0.20)·10³|
| 3-AT      | 0.45±0.80     | 2.7±18.3        | (2.15±0.20)·10³|
| 2-AAT     | 0.28±0.57     | 10.1±27.9       | 2.17±0.20      |
| 3-AAT     | 0.28±0.57     | 10.1±27.9       | 1.26±0.15      |

Among the products of oxidation of the methyl group identified at the early stages are 3-acetaminobenzaldehyde (13.1 %) and 3-acetaminobenzyl alcohol (≈10⁻⁴ mol·L⁻¹). At the later stages of oxidation, the main product with the aromatic structure kept is 3-AABA (14.2 %) (Fig. 2).
On the methyl group, the aromatic ring (Fig. 3). In order to obtain the necessary information for producing selective syntheses of aminobenzoic acids, we further studied kinetic characteristics and mechanism of reaction of ozone with aminotoluenes in the presence of salts of transition metals (STM) that were found to be electron donors during ozonation [11].

We studied the acetates of Co (II), Mn (II), Cr (III) and Ni (II) as the potential catalysts for selective oxidation of 2- and 3-AAT 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. In this study, kinetically, acetate Co (II) was found to be the most effective catalyst, but the output of 2- and 3-AABA in given conditions is quite low – for 2-AABA it reaches only 25.0 and for 3-AABA 31.2 %, because the predominant direction of reaction remains the 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 [12]. We found out that the use of our catalytic system (ozone – aminotoluene – Co (III) – glacial acetic acid – potassium bromide) significantly increases the reaction rate and the selectivity of substrate oxidation of methyl groups. The main product of oxidation of 2-AAT becomes 2-AABA 55.0 % (Fig. 4). The main product of oxidation of 3-AAT becomes 3-AABA 71.2 % (Fig. 5), but we also identified small amounts of 3-acetaminobenzylbromide (4.5 %) and traces of 3-acetaminobenzaldehyde.

The maximal selectivity of oxidation of 2- and 3-AAT was achieved at the molar ratio of 1:1 ([Co(OAc)₂]₂[KBBr₃]). The further increase in the concentration of potassium bromide does not affect the selectivity of oxidation. This is a kinetic evidence of 4-acetaminobenzyl radical formation as a result of inner electron transfer from the π-electron system of the studied catalysts.
of the substrate to the cobalt-bromide radical to form the aromatic cation-radical. 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 to the cobalt-bromide radical to form the aromatic cation-radical. The higher rate and selectivity of the oxidation of the substrate to the cobalt-bromide radical to form the aromatic cation-radical 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 2-AABA (70,0 %) and 3-AABA (86,0 %).

5. Conclusion

It has been found that the reaction of ozone with 2- and 3-AT in glacial acetic acid proceeds with high speed and preferably with the free electron pair of heteroatom with the formation of polymeric azo compounds. 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's attack changes and is directed by methyl groups and aromatic ring. Acetaminotoluene are oxidized to form the products of destructive oxidation (ozonolysis) of aromatic ring – aliphatic peroxides (84,7 and 92,9 % respectively for 2- and 3-AT) as well as the products of oxidation of methyl group – 2- and 3-AABA (5,1 and 12,4 %).

We've found that the usage of cobalt-bromide catalyst in oxidation gases containing oxygen increases the rate and selectivity of the oxidation of acetaminotoluene to 55,0 % for 2-AT and output of 3-ABA for the corresponding 3-AT is 71,2 %. 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 corresponding acetaminobenzolic acid.

It has also been found out, that a further increase in selectivity of the oxidation of methyl group to 70,0 and 86,0 % (2- and 3-AABA) and the consumption reduction of ozone by 40 % is achieved in the conditions of oxidation with ozone-oxygen mixture.

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