Investigation of oxidation process of 3-aminotoluene with ozone in presence of manganese bromide catalyst

A. Galstyan, G. Galstyan, L. Timoshyna

Volodymyr Dahl East-Ukrainian national university, e-mail: gaalst@mail.ru

Summary. The possibility of producing 3-aminobenzyl alcohol and 3-aminobenzaldehyde by oxidation of 3-aminotoluene with ozone in the solution of acetic anhydrite in the presence of manganese (II) acetate, potassium bromide and sulfuric acid has been shown.

The catalytic systems for regulating selectivity and depth of substrate oxidation has been developed. The catalytic system $Mn(OAc)_2 - Ac_2O - H_2SO_4$ promotes the formation of alcohol (65.5%) and 3-acetylaminobenzylidendiacetate (20.1%) with the system $Mn(OAc)_2 - KBr - Ac_2O - H_2SO_4$ increases oxidation selectivity on the methyl group to 90.8% producing mainly aldehyde (80.8%)

The optimum temperature of selective oxidation of 3 – aminotoluene with the ozone – air mixture (30°C) which is much lower than that of oxidation by the known methods (120°-240°C) and the optimum rations of the reagents concentrations: for alcohol synthesis – $[ArCH_3]$: $[Mn(OAc)_2]$: $[H_2SO_4]$ =1 : 0.2 : 2.5; for aldehyde synthesis –$[ArCH_3]$: $[Mn(OAc)_2]$: $[KBr]$ aldehyde synthesis – $[ArCH_3]$: $[Mn(OAc)_2]$: $[KBr]$: $[H_2SO_4]$ = 1:0.2:2.5 have been determined.

Key words: oxidation, 3-acetylaminotoluene, ozone, sulfuric acid, selectivity, potassium bromide.

INTRODUCTION

The product of incomplete oxidation of 3-aminotoluene, 3-aminobenzaldehyde, is an important product of organic synthesis. It is used as an intermediate product in the synthesis of drugs [1].

In practice 3-aminobenzaldehyde is synthesized using oxidation – reduction methods [2]. However, most of these methods are not perspective because of their environmental polluting effect, hard synthesis conditions and low coefficients of processing feedstock.

It is quite natural that the problems mentioned above can be solved only in the process of searching for more perfect, improved methods of synthesizing oxygen – containing derivatives of methyl benzenes. Practice of investigations shows that one of the most promising methods of their production is oxidation process of methyl benzenes with ozone [3-7]. However, the known ozonolysis methods of oxidation of methyl benzenes in the liquid phase are mainly used for producing benzoic acids. Under these conditions it is impossible to produce aromatic aldehydes including 3-aminobenzaldehyde as objective products due to their high reactivity in reactions with ozone. It is known [8] that the primary reaction of aminotoluenes with ozone occurs on the lone pair of electrons of nitrogen atom of NH_2 – group followed by the subsequent formation of resin–like products of unknown structure and small amounts of nitrotoluenes and toluquinones. Methyl group oxidation of substrate molecule is not discussed.

THE ANALYSIS OF RECENT RESEARCHES AND PUBLICATIONS

For the first time the published data concerning reactions of ozone with aromatic amines were systematized and described in Bailey's monograph [8], where in the process of ozonation of methyl anilines he noted the formation of resin-like compounds, some amounts of 1,4–benzoquinone and azobenzene.

Further the publications revealed some contradictions. Some researchers believe that ozone mainly attacks aminotoluenes on the aromatic ring forming low-molecular products [9], others underline preferential oxidation of the methyl group [10]. Only one fact unites these authors – the methyl group in the molecule of aminotoluene is not almost oxidized. The reaction provides a quick attack of ozone on the free pair of electrons of nitrogen atom forming ion – radical pair, which depending on amine structure changes into a variety of products, most of them being resin – like polymers of unknown structure[8]. The exceptions are the latest publications [11, 12], which show the possibility of aminotoluene ozonation on the methyl group. These authors have found out that previous acetylating the substrate results in the typical reaction of ozone with amines on NH_2 – group becoming secondary, and ozone preferably reacts with the binary bonds of the aromatic ring forming aliphatic products of peroxidation character (83.5 – 92.9 %) and, to a lesser extent, on the methyl group, forming acetamidobenzoic acids (5.1 – 14.2 %). The usage of cobalt (II) acetate as a catalyst in the conditions of oxidation with ozone-air gases in acetic acid increases selectivity of oxidation of acetamidotoluene on the methyl group up to 27 – 40 %. The ozonation carried out in the presence of cobalt bromide catalyst reduces the optimum concentration of cobalt (II) acetate in the system by 28.5 %. Further increasing selectivity of oxidation on the methyl group up to 70 – 90 % is achieved in the conditions of oxidation in the ozone-air mixture. As the researchers have noted under these conditions it is not yet possible to stop the

reaction at the stage of forming intermediate products in order to isolate them subsequently.

In this connection, the comprehensive investigation of reactions of ozone with 3-aminotoluene in order to accumulate the data necessary for determining the basic regularities of the process and for developing fundamentals of production technology of 3-aminobenzaldehyde is an urgent problem.

OBJECTIVE

The studies carried out aimed to explore the kinetic features of the catalytic reaction of ozone with 3-acetylaminotoluene in acetic anhydride in the presence of sulfuric acid and manganese bromide catalyst for developing the promising method for synthesis of 3-aminobenzaldehyde.

To achieve this objective the following tasks were put forward:

– to examine the process of liquid – phase catalytic oxidation of 3-aminotoluene with ozone to 3-aminobenzaldehyde in the presence of the mixture of manganese (II) acetate and potassium bromide;

– to investigate the impact of technological parameters (catalyst composition, reagents and temperature concentration) on rate, selectivity, depth of oxidation and yield of the products involved.

THE MAIN RESULTS OF THE RESEARCH

The interaction of 3-aminotoluene with ozone in acetic anhydride was investigated by the method described in [13]. The concentration of 3-acetylaminotoluene and products of its subsequent transformation in the solution was determined by the method of gas – liquid chromatography and chromatography of flame ionization detector on the column of 3 meter length and 4 millimeter diameter, filled with the carrier "Inerton AWDMCS", processed with the solution of NaOH (10%) and the applied stationary phase "Apieson L" in the amount of 10 % of the carrier weight under the following conditions: thermostat temperature – according to the program – is 100 – 240 ºC for 15 minutes; rate of gas carrier (nitrogen) – 1.8, hydrogen – 1.8; air – 18 l/h. The concentration of oxidized form of catalyst was determined by the method of iodometric titration. The effective constants of reaction rate of ozone with catalyst and substrate were determined by the method of spectrometry according to the procedure described in [3] and those of 3–acetylaminotoluene with Mn^{3+} and $Mn^{2+}Br$ were determined for the case of unilateral reactions of the secondary order.

3-Aminotoluene in acetic anhydride is quickly acylated already in the process of preparation of the solution for oxidation and, therefore, reacts with ozone as 3-acetylaminotoluene (scheme 1). At the temperature of 20°C molecular oxygen oxidizes 3-acetylamino-toluene in acetic anhydride very slowly: after 6 hours of the reaction the substrate concentration decreases only by 5%, oxidation products occurring in trace amounts. But in the conditions of investigations 3-acetylamino-

Scheme 1
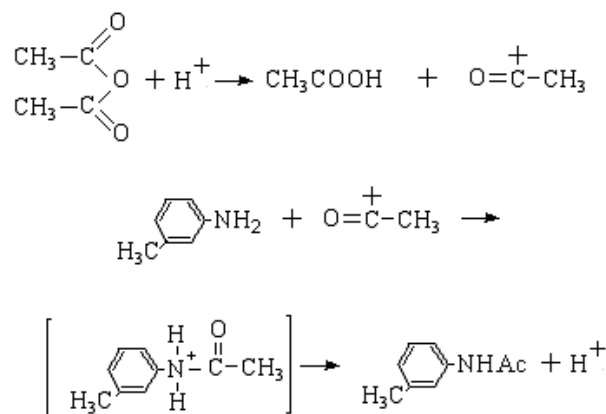
toluene is rapidly oxidized with the ozone – air mixture: at 20°C mainly the peroxide compounds (70.0%) resistant to ozone effect, and the oxidation products on the methyl group, the composition of which changes depending in the presence of sulfuric acid, an acylation catalyst, are produced (scheme 2). In the absence of mineral acids mainly 3-acetylaminobenzylacetate (3.5%), 3-acetyl-aminobenzylidendiacetate (10.5%) and 3-acetyl-aminobenzoic acid (14.3) are produced, these being produced subsequent lye. In the presence of catalytic additives of sulfuric acid 3-acetylamino-benzylacetate (3.5%) and 3-acetylaminobenzyliden-diacetate (25.5%) are accumulated in the system after the complete substrate oxidation (scheme 3).

Scheme 2
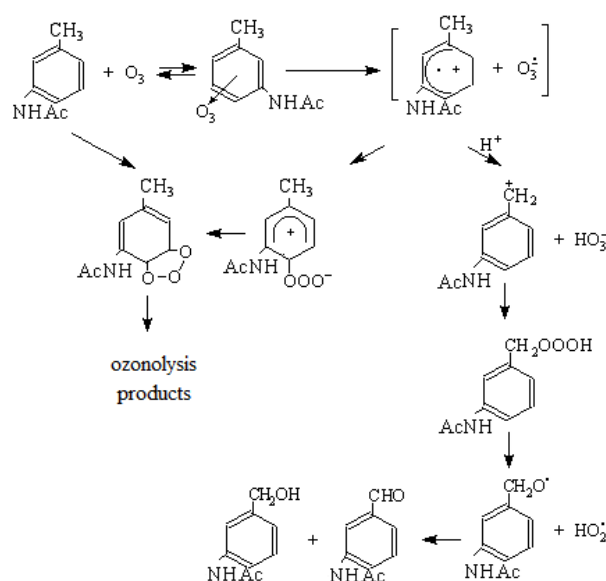
Scheme 3
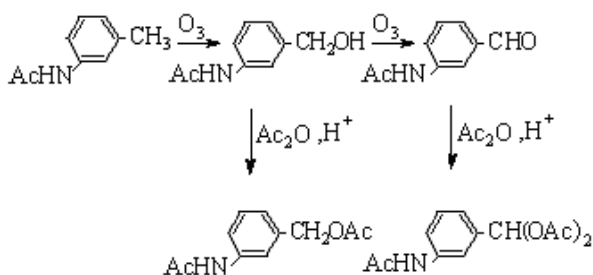
The peroxy compounds, formed in the system, have sufficiently high stability to ozone effect that contributes to their accumulation with high yield. They are readily soluble in acetic acid and acetic anhydride, and with high rate react with potassium jodide, during 1 hour and during 24 hours the same quantity of molecular jodine, which corresponds to one hydroperoxide group, being produced. This fact and as well as the stechiometric coefficient according to ozone (at 20°C n = ΔO_3 / $\Delta ArCH_3 \approx 1$) allow to suppose that the final product of 3-acetylaminotoluene oxidation on the aromatic ring contains one hydroperoxide group.

At the catalysis with manganese (II) acetate of the reaction of oxidation of 3-acetylaminotoluene in acetic anhydride in the presence of sulfuric acid the main reaction products are corresponding aromatic alcohol and aldehyde in the form of corresponding di-and triacetates(Figure 1). The important feature of the catalysis in this case is the creation of the condition when mainly aromatic alcohol (65.5 %) is produced, the content of 3-acetylaminobenzylidendiacetate in the reaction mixture being not more that 20% (Fig. 1).
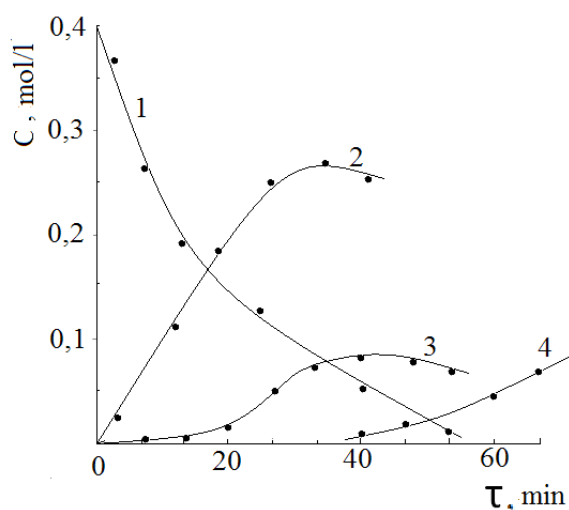

Fig.1. Kinetics of oxidation of 3-acetylaminotoluence in acetic anhydride at 20° C in the presence of sulfuric acid manganese (II) acetate: 1- 3-acetylaminotoluence; 2- 3-acetylaminobenzylacetate; 3- 3-acetylaminobenzylideiacetat; 4 - 3-acetylaminobenzoic acid; $[ArCH_3]_0 = 0.4$; $[Mn(OAc)_2]_0 = 0.08$; $[H_2SO_4]_0 = 1.0$; $[O_3]_0 = 4.0 \cdot 10^{-4}$ mol/l; $Vp = 0.01$ l

The selective oxidation of substrate with ozone in the conditions of catalysis becomes possible due to the process of the rapid reaction (3) (Table 1):

$$Mn^{2+}+O_3+H^+\rightarrow Mn^{3+}+O_2+HO^{\cdot} \qquad (1)$$
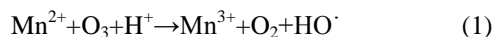
Oxidation selectivity on the methyl group depends on the relationship of the rates of reactions (2) and (3). As one can see from Table 1, the constant of the rate is much (by an order) higher than that of substrate oxidation Mn^{3+}. Therefore, selective oxidation on the methyl group is possible only at the higher concentration of Mn^{3+} and this is observed in practice (Table 2).

Table 1. Reaction rate constants of the catalytic cycle of the oxidation of 3-acetylaminotoluene with ozone in the presence of sulfuric acid and manganese (II) acetate at 30 ºC. $[ArCH_3]_0 = 0.4$; $[O_3]_0 = 4.0 \cdot 10^{-4}$; $[Mn(OAc)_2]_0 = 0.08$; $[H_2SO_4]_0 = 1.0$ mol/l^{-1}

Reaction	k_{eff}, l·(mol·s)$^{-1}$	$r \cdot 10^{-4}$ mol·l^{-1}·s^{-1}	E, kJ·mol^{-1}
$O_3 + ArCH_3 \rightarrow$	0,85	1,4	16,9±2,0
$O_3 + ArCH_2OAc \rightarrow$	0,48	1,2	18,7±2,0
$O_3 + ArCH(OAc)_2 \rightarrow$	0,36	0,9	20,9±2,0
$O_3 + Mn^{2+} \rightarrow$	38,22	12,2	24,1±2,4
$Mn^{3+} + ArCH_3 \rightarrow$	0,048	15,4	22,1±2,2
$Mn^{3+} + ArCH_2OAc \rightarrow$	0,031	9,9	31,6±3,1
$Mn^{3+} + ArCH(OAc)_2 \rightarrow$	0,014	4,5	33,5±3,5

Table 2. Effect of manganese (II) acetate concentration on the oxidation selectivity of 3-acetylaminotoluene on the methyl group at 30 ºC. $[ArCH_3]_0 = 0.4$; $[O_3]_0 = 4.0 \cdot 10^{-4}$; $[H_2SO_4]_0 = 1.0$ mol·l^{-1}; $Vr = 8.3 \cdot 10^{-3}$ l·s^{-1}

$[Mn(OAc)_2]$ mol·l^{-1}	Reaction Product Output,%		Oxidation selectivity on the methyl group,%
	alcohol	aldehyde	
0,02	44,5	7,9	52,4
0,04	52,8	12,2	65,0
0,06	57,0	16,9	76,9
0,08	65,5	20,0	85,5
0,12	64,7	20,5	85,2

The results of kinetic investigations (Table1) explain the reasons of ceasing oxidation of 3-acetylaminotoluene at the stage of forming corresponding benzylacetate or benzylidendiacetate since the rate of substrate oxidation with the oxidized form of metal and with ozone in the series: substrate>alcohol>aldehyde.

The rate and the selectivity of oxidation of 3-acetylaminotoluene with ozone in acetic anhydride in

A. Galstyan, G. Galstyan, L. Timoshyna

the presence of sulfuric acid and manganese (II) acetate depend on temperature. With its rise the total rate of oxidation increases and oxidation selectivity on the objective products decreases (Table 3).

At the first sight, the dependency found out contradicts the experimental data, according to which, at the general tendency to increasing, the rate of substrate (1) oxidation selectivity increases more rapidly than that of ozonolysis (E_1=22.1; $E_{ozonolysis}$ =16.9 kJ·mol^{-1}; Table 1).

Table 3. Effect of temperature on rate and selectivity of oxidation of 3-acetylaminotoluene on the methyl group. $[ArCH_3]_0$ = 0.4; $[O_3]_0$ = 4.0·10^{-4}; $[Mn(OAc)_2]_0$ =0 .08; $[H_2SO_4]_0$ =1.0 mol·l^1

T°C	Corresponding reaction products,%			Selectivity of oxidation on the methyl group,%
	alcohol	aldehyde	acid	
10	65,0	18,8	-	83,8
20	65,5	20,0	-	85,5
30	57,5	17,5	12,0	87,0
40	52,4	12,6	26,8	91,8

However, the study of ozone reaction with reaction products has shown that regularities obtained do occur since the rates of ozone reactions with intermediate products with temperature rise increase more rapidly than the rate of the reaction (1) (Table 3).

The decrease of the selectivity of alcohol and aldehyde is followed by forming 3-acetylaminobenzoic acid (Table 3).

The total selectivity of oxidation on the side chain amounts to 85.5 %. At the complete substrate oxidation 3-acetylaminobenzoic acid is accumulated in the solution (Fig., curve 4). As one can see from the figure the reaction products are produced subsequently. Alcohol is formed at once at maximum rate (Curve 2) and at Curve 3 during 20 minutes the inductive period is being observed and only after reaching the certain concentration of alcohol (Curve 2) aldehyde is produced in the system at maximum rate. The maximum of its accumulation (Curve 3) coincides with the beginning of the consumptions of acylated alcohol.

As one can see from Table 4, the addition of potassium bromide to the catalytic system at the temperature of 30 ºC practically does not effect on the oxidation selectivity for the methyl group, but greatly increases the oxidation depth mainly with the formation of 3-aminobenzaldehyde, the content of which in the reaction products increases with rising the concentration of potassium bromide and reaches a maximum value at $[KBr]_0$ = 0.08 mol/l. According to the ratio of $[ArCH_3]:[Mn(OA)_2]:[KBr]$=5:1:1, 3-aminobenzaldehy-de of 80.8 % in the form of 3-acetylaminobenzyliden-diacetate and 3-acetylaminobenzylacetate of 11 % are formed in the system at the total selectivity of 91.8 % (Fig. 2).
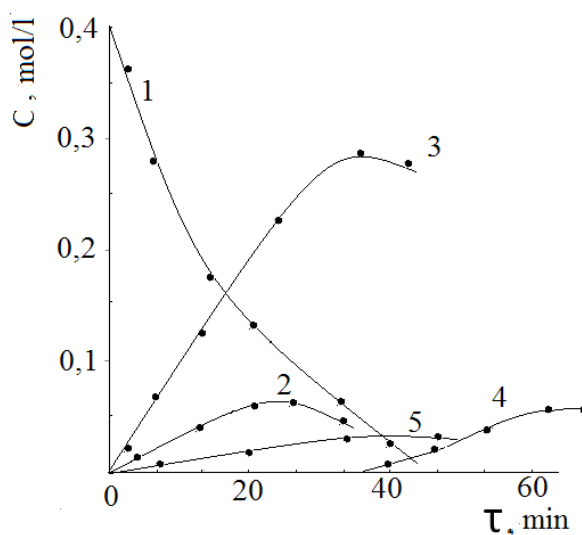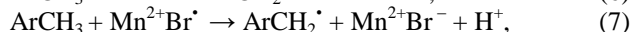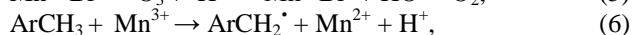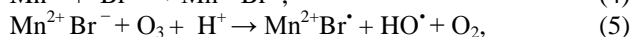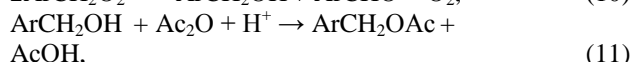

Fig. 2. Kinetics of oxidation of 3-acetylaminotoluence in acetic anhydride at 20° C in the presence of sulfuric acid manganese (II) acetate and potassium bromide: 1- 3-acetylaminotoluence; 2- 3-acetylaminobenzylacetate; 3- 3-acetylaminobenzylideiacetat; 4 - 3-acetylaminobenzoic acid; 5 - 3-acetylaminobenzyl bromide. $[ArCH_3]_0$ = 0.4; $[Mn(OAc)_2]_0$ = 0.08; $[KBr]_0$ = 0.08; $[H_2SO_4]_0$ = 1.0; $[O_3]_0$ = 4.0·10^{-4} mol/l; Vp = 0.01 l

Table 4. Effect of reagent concentration on the composition of oxidation products of 3-acetylaminotoluene with ozone in acetic anhydride at 30 ºC $[ArCH_3]_0$ = 0.4; $[H_2SO_4]_0$ = 1.0 mol/l

Reagent Concentration mol/l			Product Reaction Concentration mol/l; (%)		Total selec-tivity, %
$[Mn^{2+}]$	[KBr]	$[O_3]_0$ ·10^{-4}	3-acetyl-aminobenzyl-acetate	3-acetylamino-benzyliden-diacetate	
0,080	0,08	0,50	traces	0,106(27,0)	27,0
0,080	0,08	1,00	0,020(5,5)	0,216(54,0)	59,5
0,080	0,08	2,00	0,025(6,4)	0,292(73,5)	79,9
0,080	0,08	4,00	0,038(11,0)	0,329(80,8)	90,8
0,040	0,08	4,00	0,024(6,1)	0,305(76,5)	82,6
0,020	0,08	4,00	0,024(6,1)	0,239(59,0)	65,1
0,005	0,08	4,00	0,017(4,5)	0,179(44,3)	48,8
0,080	0,10	4,00	0,039(10,0)	0,328(80,5)	90,5
0,080	0,04	4,00	0,073(18,2)	0,280(70,0)	88,2
0,080	0,01	4,00	0,106(26,1)	0,203(52,5)	78,6

The growth of the catalytic activity of manganese (II) acetate in the presence of alkali metal bromide is due to the formation of highly active manganese bromide ion – radical $Mn^{2+}Br \cdot$ (4,5) [14-18] with is able to involve CH molecule in the selective oxidation with a higher speed than Mn^{3+}(6)(K_6 = 3.5 · 10^{-2} l/mol · sec.; K_7 = 9.3 · 10^{-2} l/mol · sec.; t= 30 ºC).

$$Mn^{2+} + Br^- \rightarrow Mn^{2+}Br^-, \tag{4}$$

$$Mn^{2+}Br^- + O_3 + H^+ \rightarrow Mn^{2+}Br^{\bullet} + HO^{\bullet} + O_2, \tag{5}$$

$$ArCH_3 + Mn^{3+} \rightarrow ArCH_2^{\bullet} + Mn^{2+} + H^+, \tag{6}$$

$$ArCH_3 + Mn^{2+}Br^{\bullet} \rightarrow ArCH_2^{\bullet} + Mn^{2+}Br^- + H^+, \tag{7}$$

$$ArCH_2OAc + Mn^{2+}Br^{\bullet} \rightarrow ArCH^{\bullet}OAc + Mn^{2+}Br^-$$
$$+ H^+, \tag{8}$$

$$ArCH_2^{\bullet} + O_2 \rightarrow ArCH_2O_2, \tag{9}$$

$$2ArCH_2O_2^{\bullet} \rightarrow ArCH_2OH + ArCHO + O_2, \tag{10}$$

$$ArCH_2OH + Ac_2O + H^+ \rightarrow ArCH_2OAc +$$
$$AcOH, \tag{11}$$

$$ArCHO + Ac_2O \rightarrow ArCH(OAc)_2. \tag{12}$$

Alcohol of 3-acetylaminobenzyl and 3-acetylaminobenzaldehyde at the moment of their formation transforms into acetate and acetal (11, 12) respectively which are resistant to ozone attack.

Oxidation of 3-acetylaminotoluene with ozone in acetic anhydride in the presence of sulfuric acid and manganese bromide catalyst runs with the predominant formation of 3-acetylaminobenzylidendiacetate (Table4) and oxidation selectivity depends on ozone concentration in the ozone – air mixture: its decreasing from $4,0 \cdot 10^{-4}$ to $0,5 \cdot 10^{-4}$ mol/l leads to total selectivity reduction by almost 68% (Table 4, Experiment 1 – 4).

The analysis of data received showed that the dependence obtained is observed only in the presence of sulfuric acid and it occurs as a result of the ratio changes $r_2 : r_5 : r_7$. If ozonation runs without sulfuric acid, the change in ozone concentration in the investigated interval does not practically effect on the selectivity of oxidation since r_4 is always much higher than r_7 ($r_5 : r_7 = 21 \div 65$) and manganese (II) acetate in the solution is mainly in the oxidized form and this contributes to 3-acetylaminotoluene oxidation on the methyl group (at $[O_3]_0 = 4.0 \cdot 10^{-4}$; $[ArCH_3]_0 = 0.4$; $[Mn(OAc)_2]_0 = 0.08$; $[KBr]_0 = 0.08$ mol/l; $K_5 = 2.0 \cdot 10^{-3}$; $K_7 = 9.3 \cdot 10^{-2}$ l/mol · sec.; $r_5 = 4.8 \cdot 10^{-2}$, and $r_7 = 2.1 \cdot 10^{-3}$ mol/l · sec., that is $r_5 : r_7 = 23$. At $[O_3]_0 = 1.25 \cdot 10^{-4}$ mol/l $r_5 : r_7 = 7$).

In the presence of sulfuric acid K_5 is reduced to 40.3 l/mol · sec. (t = 30 ºC) which greatly slows the reaction (5). In these conditions $r_5 : r_7 = 0.46$, i.e. the rate of manganese reduction by the reaction (7) is much higher than that of its oxidation by the reaction (5). It is known that in the system where both forms of manganese – oxidized and reduced – occur, binuclear complexes with highly underestimated oxidation – reduction potential and with much lower catalytic activity than that of Mn^{3+}[19, 20] are formed. Thus, as ozone concentration in the ozone – air mixture [21, 22] decreases, the reaction (7) slows and the ratio $r_3 : r_7$ (in the presence of sulfuric acid K_2 does not practically change and equals 2.08 l/mol · sec.) increases and this leads to selectivity reduction and oxidation on the methyl group.

The rate and selectivity of substrate oxidation in the conditions of investigation depend on the reaction temperature. The optimum temperature for producing 3-acetylaminobenzylindendiacetate with maximum output is 30 ºC (Table 5). At lower temperatures the total selectivity of substrate oxidation for the methyl group practically does not change but the portion of 3-acetylaminobenzylacetate increases. Increase in temperature leads to increase in oxidation rate and oxidation depth: 3-acetylaminobenzylidendiacetate becomes an intermediate product with transformation in the corresponding benzoic acid (Table 5).

Table 5. Effect of temperature on the composition of product oxidation of 3-acetylaminotoluene with ozone in acetic anhydride in the presence of sulfuric acid and manganese bromide catalyst: $[ArCH_3]_0 = 0.4$; $[Mn(OAc)_2]_0 = 0.08$; $[KBr]_0 = 0.08$; $[O_3]_0 = 4.0 \cdot 10^{-4}$; $[H_2SO_4]_0 = 1.0$ mol/l. Oxidation period is 15 minutes

T, ºC	Product Composition of Reaction, %		
	3-acetylamino-benzylacetate	3-acetylamino-benzylidendi-acetate	3-acetyl-aminobenzoic acid
10	29,7	65,1	-
20	18,5	76,3	-
30	11,0	80,8	-
40	8,4	78,2	4,1
50	5,3	77,5	6,0
60	4,5	75,2	11,0
70	3,4	70,0	17,3

It should be noted, that the reaction products received – acetylated alcohol and aldehyde – can be readily, if necessary, hydrolyzed to the corresponding 3-aminobenzylic alcohol and 3-aminobenzaldehyde nearly with quantitative yield.

CONCLUSIONS

As a result of the investigation it has been:

1. – studied the process of liquid phase catalyst oxidation of 3-aminotoluene with ozone in acetic anhydride. It has been showed that in the presence of manganese bromide catalyst oxidation can be stopped at the stage of forming the corresponding benzaldehyde in the acetylated form.

– developed a new catalytic system Mn(II)-KBr-H_2SO_4-Ac_2O to produce 3-aminobenzaldehyde with ozonation of 3-aminotoluene. The presence of potassium bromide significantly improves the depth, rate and selectivity of substrate oxidation, the main reaction product being 3-aminobenzaldehyde in the acetylated form with the yield of 80.8 %.

The active particle which is responsible for involving substrate into oxidation on the methyl group in the presence of manganese (II) acetate and potassium bromide is manganese bromide ion – radical (Mn(II)Br) which is more active than Mn(II) and, therefore, initiates oxidation on the methyl group with higher rate.

– offered the mechanism of the process when the oxidation of 3-aminotoluene is carried out according to ion – radical non – chain mechanism, where manganese bromide radical is generated in the reaction with ozone.

2. Investigated the effect of catalyst composition, reagent concentration and temperature on the rate, selectivity and depth of oxidation and the yield of reaction products. The optimum ratio of the reagents is $[ArCH_3] : [Mn(II)OAc] : [KBr] : [H_2SO_4] = 1 : 0.15 : 0.15 : 2$, the optimum temperate of the process being 30ºC.

REFERENCES

1. **Dayson G., Mey P. 1964.** Chemistry of synthetic drugs. Moscow.: Mir, 128-140. (in Russia).
2. **1953.** Synthesis of organic products. - M .: Foreign Literature. V. 4, 30. (in Russia).
3. **Razumovsky S.D., Zaikov G.E. 1974**. Ozone and its reaction with organic compounds. Moscow: Nauka, 322. (in Russia).
4. **Nakagawa T. W., , Andrews L. J., Keefer R. M. 1960.** The Kinetics of Ozonization of Polyalkylbenzenes. J. Amer. Chem. Soc. V.82, 269-276.
5. **Sherhovtsov Y., Zaigrayev L. 2013.** Feature comparison regeneration particulate filter withe the catalytic coating end the use of oxidation catalyst. Teka Com. Mot. end Energ. in Agric. V. 13. (4), 240-249.
6. **Holoptsev A., Bolshikh A., Bekirova V., Nikiforova M. 2014**. Assessment of monthly mean total ozone distribution changes with regard to Atlantic ocean surface temperatures variations. Teka Com. Mot. end Energ. in Agric. V. 14. (4), 31-36.
7. **7. Wibaut J. P. 1956.** Ozonation and ozonolysis of aromatic and heterocyclic compounds in the determination of structure of molecules. J. Chim. Phis. Chim. ibid. V. 53, 111.
8. **Bailey P. S. 1982.** Ozonation in organic chemistry. Nonolefinic Compounds. N-Y. L. Academic Press. V. 2, 497.
9. **Hon Y. S., Wong Y. C. 2005.** Synthetic applications of the amine-base treatment in the ozonolysis of substituted-allyl silyl ethers or -allyl esters via a novel enediol type rearrangement. Tetrahedron. V.46. (8), 1365-1368.
10. **Hon Y. S. Wu K. C. 2003.** Polymer-supported tertiary amine in organic synthesis: a useful reagent in the conversion of alkenes to carbonyl compounds via the corresponding ozonides. Tetrahedron. V.59, 493-498.
11. **Galstyan A., Bushuev A., Solomyany R., Galstyan G. 2008.** Kinetics oxidation of 4-aminotoluene ozone in liquid phase. Ukr. him. Zh. V. 74, (7), 57-61. (in Ukrainian).
12. **Galstyan A., Bushuev A., Solomyany R. 2008.** Oxidation of 4-aminotoluene ozone in acetic acid. Russian journal of applied chemistry. V 81, (7), 1120 - 1123. (in Russia).
13. **Galstyan, G., Tyupalo N., Galstyan A. 2009.** Liquid-phase catalytic oxidation of aromatic compounds with ozone. Lugansk: VNU by Dal, 415. (in Ukrainian).
14. **Zakharov I. Galetey Y. 1978.** Mechanism and parameters of the oxidation of alkylaromatic hydrocarbons in the presence of cobalt ions and bromine. Petrochemicals. V.18 (4), 615-621. (in Russia).
15. **Buharkina T., Gavrilenko N, Digurov N., Knyazev N. 1978.** The kinetics of the oxidation of toluene in acetic acid salts Co (III) and Mn (III) in the presence of potassium bromide. Kinetics and Catalysis. V.19, (2), 506-510. (in Russia).
16. **Galstyan G., Galstyan T., Mikulenko L. 1994.** Kinetics and mechanism of the catalytic reaction of ozone with methylbenzene acetic acid. Kinetics and Catalysis. V. 35 (№ 2), 255-260. (in Russia).
17. **Jacobi V.A. 1978.** Ozonization aromatics compounds. MCTI: Moscow. 66-92. (in Russia).
18. **Pluzhnik I., Galstyan G. 1999.** Kinetics and mechanism of the catalytic reaction of ozone with toluene in acetic acid. Petrochemicals. V. 39 (№ 2), 120-123. (in Russia).
19. **Litvinova I., Galstyan G. 2000.** Ozone oxidation of toluene with a mixture of acetic acid in the presence of a catalyst kobaltbromid. Russian journal of applied chemistry. V. 73 (11), 1914-1915. (in Russia).
20. **Heiba E. I., Dessau R. M., Koehl W. I. 1969.** Oxidation by metal salts. V. Cobaltic acetate oxidation of alkylbenzenes. J. Amer. Chem. Soc. V.91, (24), 6830-6837.
21. **Haaijman P. W., Wibaut J. P. 1941.** Quantitative investigation of the ozonization of o-xylene and 1,2,4-trimethylbenzene. A chemical proof of the equivalence of the six C-C bons in the benzene ring. Real.Trav. Chim. Pays-Bas. V. 60, 842-847.
22. **Wibaut J. P. 1950.** The application of ozonolysis to the study of the structure of aromatic compounds. Bull. Soc. Chim. Fr., 998-1005.

ИССЛЕДОВАНИЕ ПРОЦЕССА ОКИСЛЕНИЯ 3-АМИНО-ТОЛУОЛА ОЗОНОМ В ПРИСУТСТВИИ МАРГАНЕЦ-БРОМИДНОГО КАТАЛИЗАТОРА

Галстян А.Г., Галстян Г.А., Тимошина Л.В.

Аннотация. Показана возможность синтеза 3-аминобензи-лового спирта и 3-аминобензальдегида окислением 3-аминотолуола озоном в растворе уксусного ангидрида в присутствии марганца(II) ацетата, калий бромида и серной кислоты.

Разработаны каталитические системы для регулирования селективности и глубины окисления субстрата. Каталитическая система $Mn(OAc)_2$ - Ac_2O - H_2SO_4 способствует образованию спирта (65,5%) и альдегида (20,1%) с суммарной селективностью 85,6%; катализ системой $Mn(OAc)_2$ - KBr - Ac_2O - H_2SO_4 повышает селективность окисления по метильной группой до 90,8% с преимущественным образованием альдегида (80,8%).

Определена оптимальная температура селективного окисления 3-аминотолуола озоновоздушной смесью (30°С), которая значи-тельно ниже температуры окисления известными методами (120-240°С) и оптимальные соотношения концентраций реагентов: для синтеза спирта - $[ArCH_3] : [Mn(OAc)_2] : [H_2SO_4] = 1 : 0,2 : 2,5$; для синтеза альдегида - $[ArCH_3] : [Mn(OAc)_2] : [KBr]: [H_2SO_4] = 1 : 0,2 : 0,2 : 2,5$.

Ключевые слова: окисление, 3-ацетиламинотолуол, озон, серная кислота, селективность, калий бромид.