Досліджено кінетику та механізм озонування 4-брометил-бензену в оцтовій кислоті. Визначено константи швидкості реакції озону з 4-брометилбензеном та 4-бромацетофеноном при різних температурах. Показана можливість ведення процесу не тільки за ароматичним кільцем субстрату за механізмом Кріге, але і з утворенням 4-бромацетофенону, що стане у нагоді при створенні нових методів синтезу оксигенвмісних похідних етилбензенів.

Встановлено, що окиснення 4-брометилбензену озоном в оцтовій кислоті перебігає переважно за ароматичним кільцем з утворенням озонідів – пероксидних продуктів аліфатичного характеру. Серед продуктів реакції окиснення за бічним ланцюгом ідентифіковано до 35 % 4-бромацетофенону та слідові кількості 1-(4-бромфеніл)етанолу. Реакція озону з 4-брометилбензеном в оцтовій кислоті при температурах до 30 ºС має перший порядок по вихідних компонентах, а значення константи швидкості реакції не залежить від концентрації реагентів. З підвищенням температури константа швидкості реакції починає залежати від концентрації реагентів, витрати озону при цьому суттєво зростають. Це свідчить про те, що в умовах дослідів озон витрачається одночасно на різних стадіях окиснення. Доведено, що озонування 4-брометилбензену представляє собою складний процес, в якому субстрат окиснюється за неланцюговим механізмом. Озон витрачається за двома напрямами: в реакції з субстратом за неланцюговим механізмом і за ланцюговим на стадії продовження ланцюгу в реакції з продуктами термічного розкладу озонідів. Цей факт дає підставу стверджувати, що з підвищенням температури непродуктивні витрати озону будуть швидко зростати і навпаки, в умовах запобігання озонолізу озон буде витрачатися переважно за реакцією з утворенням цільового ароматичного продукту.

Таким чином, одержані експериментальні дані є основою для розробки процесу окиснення похідних етилбензену та створення основ технології синтезу 4-бромацетофенону за допомогою озону. Це суттєво спростить апаратурне оформлення процесу, підвищить вихід цільового продукту та сприятиме подальшому удосконаленню методів окиснювальної переробки реагентів

Ключові слова: озоно-киснева суміш, 4-брометилбензен, озоноліз, 4-бромацетофенон, оцтова кислота, константа швидкості

OXIDATION OF 4-BROMETYL-BENZENE BY OZONE IN ACETIC ACID

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1. Introduction

Reactions of liquid phase oxidation of organic substances occupy an important place in modern physical and organic chemistry. Oxidation processes are frequently used by researchers as highly effective model reactive systems for studying the fundamental problems of kinetics of reactive ability, catalysis, and the structure of organic substances. The studies are also continuously stimulated by the necessity for the creation of modern low-waste energy saving methods of the synthesis of oxygen-containing derivatives of organic compounds. In view of this, the reactions of arene oxidation in liquid phase are especially interesting both theoretically and practically.

At present, a large part of oxygen containing derivatives of arene is synthesized by direct oxidation of output compounds by molecular oxygen [1, 2]. However, sometimes the use of molecular oxygen is rejected because of its relatively low redox potential and, as a consequence, due to strict conditions of conducting synthesis and a relatively low selectivity of the process. In these cases, multi-stage syntheses are applied, or expensive and deficit oxidizing agents are used to obtain oxygen-containing derivatives [3, 4]. However, it follows from the practice that most of these processes have no future due to the multi-staged, technologically sophisticated and strict conditions of processing reagents and formation of mineralized wastes that are difficult to recycle. It is natural that solving these problems is not possible without modern scientific developments aimed at the creation of new, more efficient methods of the synthesis of oxygen-containing arene derivatives.

One of the promising oxidizing agents of the future is ozone – an allotropic modification of oxygen. Ecological purity of ozone and the redox potential that is the highest (2.07 V) among the known oxidizing agents contribute to the gradual implementation of it in the experimental and

industrial practice of organic chemistry. The fundamentals of ozone synthesis of many oxygen-containing aromatic products were developed, new environmentally friendly ways of hydroxylation [5], chlorination [6], obtaining mono- and polycarboxylic acids [7, 8] were proposed, new oxidizing technologies awaiting their implementation in production were created [9].

The ozonolytic methods of arene oxidation in the liquid phase were studied in detail. However, the separate issues, such as selective oxidation of derivatives of ethylbenzenes, require additional research. In terms of the development of new methods of synthesis of corresponding phenylethanols and acetophenones, such research is relevant.

2. Literature review and problem statement

The reactions of oxidation of ethylbenzene and its derivatives by different oxidizing agents were researched in detail. In paper [10], it was shown that the reaction of ethylbenzene with the cobalt-bromide complex takes place at elevated temperatures and has the induction period; hydroperoxide was identified as the intermediate product. Acetophenone and benzoic acid were detected among the end products. Authors of paper [11] found that ethylbenzene oxidation in the presence of copper and nickel oxides flows by the chain-radical mechanism. Initiation of radicals occurs on the surface of catalysts by decomposition of hydroperoxide by molecular oxygen. The reaction flows at $60-90$ °C with the prevailing formation of acetophenone. Zirconium oxides were used in paper [12] as ethylbenzene oxidation catalysts. Zirconium catalyst, modified with chromium, was active for ethylbenzene conversion (65%) with 77 % selectivity towards acetophenone at the temperature of 60 °C. Another ferrum-based catalyst, mounted on substrate of SiO_2/Al_2O_3 was used in article [13] for ethylbenzene oxidation by molecular oxygen to corresponding acetophenone. Ethylbenzene oxidation [14] was conducted over silicates TS-1, VS-1 and SN-silicalite-1 (MFI structure) at the temperature of $60-80$ °C. The main products of the reaction were 1-phenylethanol and acetophenone. Hydroxylation of the aromatic ring led to the formation of 4-hydroxyethylbenzene. The catalytic effect of a small amount of water (~10^{-3} mol/l), added to the reaction of oxidation of ethylbenzene by molecular oxygen, which is catalyzed by the system {Fe (III) (acac) 3+18-crown-6 (18C6)}, was revealed in paper [15]. An increase in the rate of the reaction and a change in the direction of oxidation were observed. At the existence of the catalytic system (Fe (III) (acac) 3 (5.0×10^{-3} mol/l)+18C6 × ×(5.0×10^{-3} mol/l) + H_2O (3.7×10^{-3} mol /l), the main product at the early stages of ethylbenzene oxidation is acetophenone, but not α-phenylethylhydroperoxide, obtained in case of catalysis by the system {Fe (III) (acac) 3 (5.0×10^{-3} mol/l)+ +18C6 5.0×10^{-3} mol/l)) (in the absence of water additives). Ethylbenzene oxidation in the solution of acetic acid at high concentrations of cobalt (III) (from 0.01 to 0.2 mol/l) was studied at $60-90$ °C with the help of gasometrical absorption of O_2, spectrophotometric accumulation of Co (III) [16]. It was shown that the oxidation rate increases due to reaction $RO_2\cdot+Co(II)+H^+\rightarrow ROOH+Co(III)$, whereas the inhibition effect is caused by decomposition of $RO_2\cdot$ radical with two atoms of cobalt (II): $RO_2\cdot+2\ Co(II)\rightarrow R'CO+Co(III)$. The detailed scheme (through the formation of $RO_2\cdot Co(II)$) complex, which describes the flow of these reactions, was proposed.

An analysis of the literature data reveals that reactions of ethylbenzene oxidation flow by complex mechanisms and require elevated temperatures and a variety of catalysts to increase the rate and selectivity for target products. Obviously, to simplify the conditions of the reaction and to improve selectivity of oxidation of ethylbenzene derivatives, it is necessary to use more effective oxidizing agents, such as ozone [5, 6]. However, there are almost no literary data on ozone oxidation of ethylbenzene derivatives. Only papers [17, 18] showed the possibility of ethylbenzene ozonation with formation of 35 % of acetophenone and 65 % of the products of destruction of aromatic ring. Along with acetophenone, we identified 1-phenylethanol that acted as an intermediate product of the reaction at the initial stage of the reaction.

Thus, it seems interesting to obtain the experimental data that can spread the theoretical ideas when it comes to the influence of the kind of a substitute on the rate and selectivity of ethylbenzenes oxidation by ozone in acetic acid. From the practical point of view, such data can appear useful when creating new environmentally friendly methods of synthesis of oxygen-containing ethylbenzene derivatives.

3. The aim and objectives of the study

The aim of this research is to obtain new kinetic data on the liquid phase reaction of 4-bromidemethylbenzene with ozone.

To attain the set aim, the following tasks were set:
– to examine the composition of the products of reactions of ozone with 4-bromethylbenzene and 4-bromacetophenone in acetic acid at different temperatures;
– to determine the constants of the rate of reactions of ozone with 4-bromethylbenzene and 4-bromacetophenone in acetic acid at different temperatures;
– to study the kinetic patterns and the mechanism of the reaction of oxidation of 4-bromethylbenzen by ozone in acetic acid.

4. Procedure of ozonation of 4-bromethylbenzene and analysis of reactive mass

Ice acetic acid of pure chemical brand without prior purification, chromatographic pure 4-bromethylbenzen and 4-bromacetophenone were used in the experiments. Ozone was synthesized from the air in the barrier discharge [19].

The studies were carried out in thermostatic reactor of the "catalytic duck" type with a volume of 0.2 l. Concentration of 4-bromethylbenzene and the products of its further transformation in the solution were determined by the method of gas-liquid chromatography on the chromatograph with the flame-ionization detector on the column of the length of 3 m and the diameter of 4 mm, filled with the medium "Inerton super" with the applied stationary phase "FFAP" in the amount of 5 % of the weight of the medium under the following conditions: the temperature of the thermostat by the program was $100-160$ °C in 10 min; the carrier gas (nitrogen) flow was 1.8; hydrogen – 1.8; the air – 18 l/h. Nitrobenzene was used as the internal standard. The products of peroxide character were determined by the iodometric method. Determination of constants of the rate of reaction of ozone with 4-bromethylbenzene was carried out using the methods described in paper [19]. The amount of absorbed

ozone was determined by the spectrophotometric method [19]. Stoichiometric coefficient for ozone was found from the formula: $n=n=\Delta O_3/\Delta ArH$, where ΔArH is the costs of the reagent that correspond to the amount on absorbed oxygen (ΔO_3) in moles.

5. Results of research into ozonolysis of 4-bromethylbenzene

5. Results of kinetic studies of the reaction of 4-bromethylbenzene with ozone

Fig. 1 shows the results of the study of the reaction of ozone with 4-bromethylbenzene in the medium of acetic acid at the temperature of 20 °C. At atmospheric pressure, oxidation of 4-bromethylbenzene by ozone flows without the induction period and, mainly, on the aromatic ring with the formation of ozonides – peroxides of aliphatic character – 65 % (Fig. 1). The trace amounts of 1-(4-bromphenyl)ethanol, and in the end – 4-bromacetophenone (35 %) were identified among the products of oxidation of ethylic group in the initial period of the reaction (Fig. 1).

The ozonides, separated after driving off the solvent under vacuum (5 mm of mercury column), are an oily viscous liquid of light-yellow color; they are easily dissolved in acetic acid, acetic anhydrite, but are difficultly soluble in tetrachloromethane, actively react with potassium iodide and sodium hydroxide. Ozonides react with potassium iodide within one hour to produce molecular iodine in the amount equivalent to one peroxide group (Table 1). The nature of the interaction with potassium iodide [20] and stoichiometric factor of the reaction for ozone, which is close to unity, make it possible to imagine the structure of ozonides with one hydroperoxide group (Fig. 2).
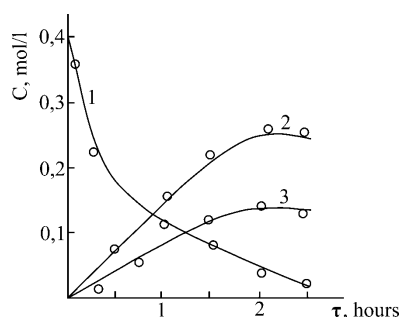

Fig. 1. Kinetics of oxidation of 4-bromethylbenzene by ozone in acetic acid at 20 ºC: 1 — flow rate of 4-bromethylbenzene, 2 — accumulation of ozonides; 3 — accumulation of 4-bromacetophenone. [ArC$_2$H$_5$]=0.4; [O$_3$]=10^{-3} mol·l^{-1}; ω=0.18 s^{-1}

Thus, the experimental data show that in the reaction with 4-ethylbenzen, ozone attacks by the side chain and by aromatic ring. Regardless of the conditions of the reaction, ozonolysis of the aromatic ring prevails (Fig. 2) [21].

The composition of the products of oxidation of ethylbenzene of aromatic nature corresponds to the following diagram (Fig. 3) of conversion of ethyl group, in which ethylbenzene peroxide recombines with the formation of alcohol and aldehyde [22] with subsequent conversion into the products of oxidative decarboxylation:

Table 1

Influence of duration of keeping the mix of the solution of 4-bromethylbenzen peroxides with potassium iodide on results of analysis at 20 ºC ([ArC$_2$H$_5$]=0.4, [O$_3$]=1.7·10^{-3} mol·l^{-1})

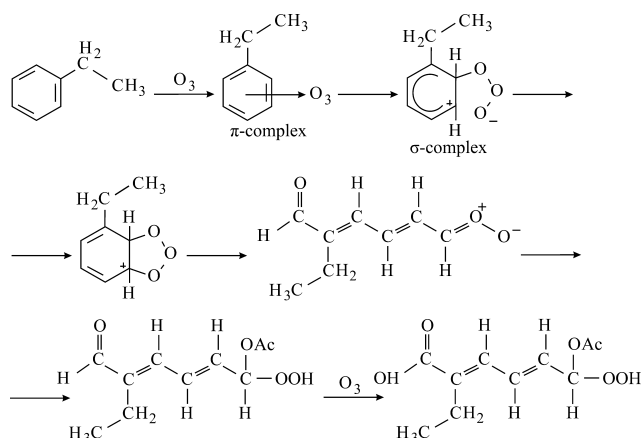| Oxidation time, min.	Concentration of ozonides, mol·l^{-1}·10^2	
	after an hour of keeping	after 24 hours of keeping
20	5.3	5.4
40	9.3	9.3
60	13.5	13.7
100	21.6	21.5
120	26.2	26.5
150	25.8	25.9

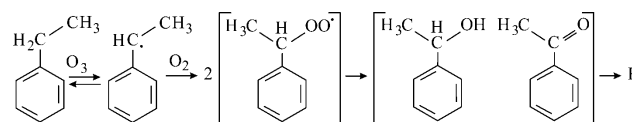Fig. 2. Diagram of ozonolysis of 4-bromethylbenzene by the Krige mechanism

Fig. 3. Diagram of ozonation of 4-bromethylbenzen by side chain. P — products of oxidation and oxidative decarboxylation of carboxylic acids

A more detailed mechanism of the oxidation of 4-bromethylbenzene by ozone at the initial stages of the reaction may be close to that described for isopropyl benzene [23, 24] (Fig. 4).

According to Fig. 4, π-complex (I) is the first to appear, then there is the electron transportation stage with the formation of aromatic cation-radical ArH$^{\bullet+}$ and anion- radical O$_3^{\bullet-}$ (II), that are transformed in two directions: direction A is in line with the Krige diagram (Fig. 4), and in direction B, ion couple (III) is the first to be formed, followed by the formation of hydrotrioxide (IV) at low temperatures (approximately of 170 K). At normal temperatures, hydrotrioxide is barely identified by modern methods of analysis due to its instability. It is assumed that it instantly turns into a radical couple and then – into the appropriate methyl phenylcarbinol and acetophenone. The mechanism of ozonation of 4-bromacetophenone has not been studied up to now and, as it will be shown further, is quite complicated and substantially different from the mechanism of oxidation by molecular oxygen.
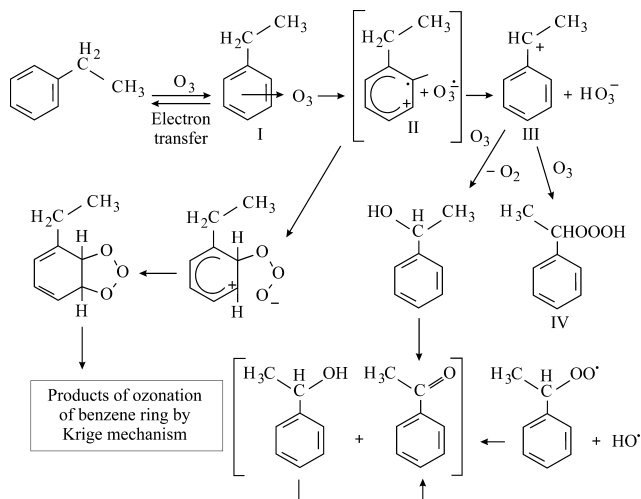
Fig. 4. General schematic of ozonation of 4-bromethylbenzene

The reaction of ozone with 4-bromethylbenzene in acetic acid at temperatures of up to 30 °C has the first order for the original components (1), and the value of constant of reaction rate does not depend on the concentration of reactants (Fig. 5).

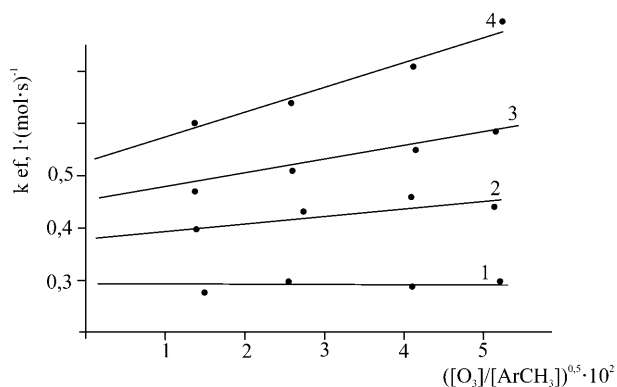$$r_{ef} = k_{ef}[ArC_2H_5][O_3]. \tag{1}$$

Fig. 5. Dependence of effective constant of the rate of oxidation of 4-bromethylbenzene on the initial concentration of ozone and substrate at temperatures of 20 (1), 30 (2), 40 (3), 50 °C (4)

At temperatures above 30 °C, effective constant of ozone flow rate under conditions of the experiments linearly depends on the concentration of reactants. According to data in Fig. 5

$$k_{ef} = k' + k''([O_3]/[ArC_2H_5])^{0,5}, \tag{2}$$

$$r_{ef} = k'[ArC_2H_5][O_3] + k''[ArC_2H_5]^{1,5}[O_3]^{0,5}, \tag{3}$$

where k' and k'' are the experimental parameters, dependent on temperature.

The components of expression (3) for ozone flow rate suggests that in terms of experiments, ozone is consumed by the same non-chain ion-radical and radical-chain mechanisms [25]. The expression (3) is typical for reagent flow rate, in this case – ozone, which takes part in the limiting

stage of chain continuation and the stages of its quadratic failure [25] ($r_{o3} = k''[O_3]r_i^{0,5}$, where $r_i \sim [ArC_2H_5][O_3]$ is the rate of process initiation).

It is characteristic that under conditions of the chain mechanism of ozone consumption, 4-bromethylbenzen is oxidized by in the non-chain way. This is proved by several facts: experimental expression for the rate of substrate oxidation ($r = k_{ef}[ArC_2H_5][O_3]$); constant of the rate of 4-bromethylbenzene oxidation in the studied temperature range (15–25 °C) does not depend on the concentration of reactants (at 30 °C and $[ArC_2H_5] = 0.1–0.4$; $[O_3] = (0.07–5.70) \cdot 10^{-5}$ mol/l; $k_{ArC2H5} = 0.39$ l/mol·s; at 50 °C k $_{ArC2H5} = 0.53$ l/mol·s).

Non-chain oxidation of 4-bromethylbenzene indicates that ozone is consumed by the chain mechanism in the reaction not with the substrate, but with other compounds, most probably – with the products of the thermal decomposition of ozonides. In this connection, the fact that the temperature the chain ozone consumption starts from coincides with the beginning of thermal destruction of ozonides (Fig. 6).
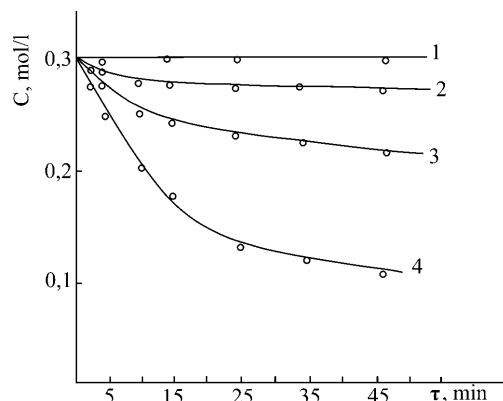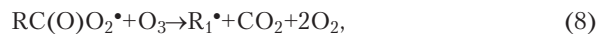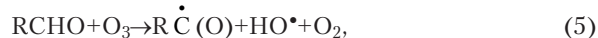

Fig. 6. Kinetic curves of thermal decomposition of ozonides of 4-bromethylbenzene at 20 (1); 30 (2); 40 (3); 50 ° C (4)

This may indicate that the chain ozone consumption is the result of its reaction with low molecular compounds – the products of thermal decomposition of ozonides, such as aliphatic aldehydes, which, as a rule, are oxidized by the chain mechanism (reactions 4–11) [25].

$$ROOH \rightarrow RCHO, \tag{4}$$

$$RCHO + O_3 \rightarrow R\overset{\bullet}{C}(O) + HO^\bullet + O_2, \tag{5}$$

$$R\overset{\bullet}{C}(O) + O_2 \rightarrow RC(O)\overset{\bullet}{O}_2, \tag{6}$$

$$R_1^\bullet + O_2 \rightarrow R_1O_2^\bullet, \tag{7}$$

$$RC(O)O_2^\bullet + O_3 \rightarrow R_1^\bullet + CO_2 + 2O_2, \tag{8}$$

$$R_1O_2^\bullet + O_3 \rightarrow R_1O^\bullet + 2O_2, \tag{9}$$

$$R_1O^\bullet + O_3 \rightarrow R_1O_2^\bullet + O_2, \tag{10}$$

$$2R_1O_2^\bullet \rightarrow products. \tag{11}$$

Because according to [25], initiation of a chain process of ozone consumption occurs by the reaction with aliphatic aldehyde at the rate $r_i \sim [RCHO][O_3]$, we obtain $r_{O_3}'' = k''[RCHO]^{0,5}[O_3]^{1,5}$ or $r_{O_3}'' \sim [O_3]\sqrt{r_i} \cdot [O3]$. This form of dependence of the rate of the chain reaction on r_i and $[O_3]$ indicates the possi-

ble involvement of ozone in the limiting stage of the chain extension (9) and (10) and quadratic failure of the chain (11). The course of reaction (8) is proved by the qualitative registration of CO_2 in flue gases.

5. 1. Results of kinetic studies of the reaction of 4-bromacetophenone with ozone

4-Bromacetphenon compared with bromethylbenzene is rather resistant to the action of ozone (Table 2). At 4-bromethylbenzene ozonation (Fig. 1), it is formed from methylphenylcarbinole and is the major product of the reaction with preserved aromatic structure. Maximum of its accumulation (35 %) is at the time of the conversion of the substrate (≈120 min), after which it is slowly consumed.

Table 2

Constants of the rate of reaction of 4-bromacetophenone with ozone in acetic acid at different temperatures

T, °C	Henry coefficient (α)	$([O_3]/[ArH])^{1/2} \cdot 10^2$	k, l/mol·s
20	1.70	2.5	0.030
		3.4	0.029
		5.0	0.030
		6.2	0.031
30	1.55	2.5	0.036
		3.4	0.038
		5.0	0.040
		6.2	0.043
40	1.14	2.5	0.042
		3.4	0.049
		5.0	0.050
		6.2	0.054
50	1.23	2.5	0.053
		3.4	0.059
		5.0	0.065
		6.2	0.071

To determine the role of 4-bromacetophenone in the process of oxidation of 4-bromethylbenzene, the kinetics of ozonolysis of 4-bromacetophenone was studied (Fig. 7, 8).

The conducted studies showed that under conditions of the experiments at the temperature of 15 °C, molecular oxygen does not oxidize 4-bromacetophenone. Ozone as an oxidizing agent with increased redox potential oxidizes acetophenone, although rather slowly. The reaction flows at a constant rate for a long time and finishes after 13.5 hours under conditions of the exhaustive oxidation of the substrate.
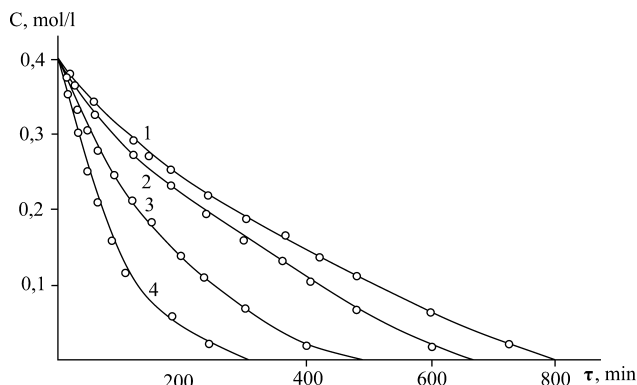
Fig. 7. Influence of temperature on kinetics of oxidation of 4-bromacetophenone by ozone mixture in acetic acid. $[O_3]=1.2\cdot10^{-3}$, $[ArC(O)CH_3]=0.4$ mol·l^{-1}, $\omega=30$ l·h^{-1}, $V_p=10$ ml. Temperature: 15 (1), 20 (2), 30 (3), 40 °C (4)
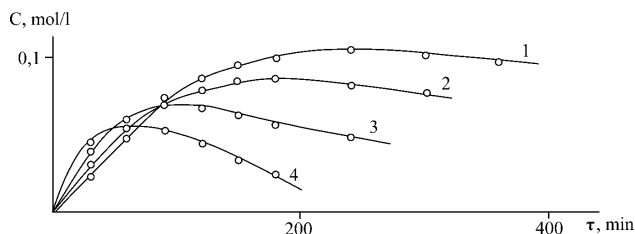
Fig. 8. Influence of temperature on kinetics of 4-bromacetophenone ozonides accumulation. $[O_3]_o=1,2\cdot10^{-3}$, $[ArC(O)CH_3]_o=0.4$ mol·l^{-1}, $\omega=30$ l·h^{-1}, $V_p=10$ ml. Temperature: 15 (1), 20 (2), 30 (3), 40 °C (4)

Among the products of the reaction, ozonides – the products of benzene ring destruction (Fig. 8) and the traces of the amount of benzaldehyde and benzoic acid – were identified. Significant quantities of CO_2 were found in flue gases.

4-bromacetophenone hydroperoxide was not detected under conditions of the experiment.

The rate of acetophenone oxidation significantly depends on the temperature (Fig. 7). With an increase from 15 to 40 °C, the rate increases by 4 times. It is characteristic that the temperature almost does not affect the release of CO_2. In the studied temperature range, the amount of the formed CO_2 increases from 1.92 mol to 2.19 mol per a mole of the substrate that reacted, that is, only by 14 %.

The absence of aromatic carboxylic acids in the products of the reaction is a bit of a surprise, since it is known that benzoic acid is the main product of the reaction during oxidation of acetophenone by molecular oxygen.

However, the analysis of data in literature [26, 27] showed that oxidation of acetophenone by oxygen, as in our case, flows very slowly. In paper [26], it was noted that at the temperature of 120 °C, acetophenone is not oxidized at all. The salts of cobalt or mangane, or their mixture, are used to stimulate this reaction, that is, only catalytic oxidation of acetophenone by oxygen in severe conditions leads to the formation of benzoic acid. This is explained by the low rate of formation of free radicals in the oxidation of ketones. Thus, for methylethylketone, $k_i=3\cdot10^9\cdot\exp(-30000/RT)$ l·(mol·s)$^{-1}$ [26]. That is at 20 °C, radicals are formed more slowly $k_i=1.2\cdot10^{-13}$ l·(mol·s)$^{-1}$, than at acetophine oxidation by ozone $k_i=4\cdot10^{-2}$ l·(mol·s)$^{-1}$.

The specific feature of the reaction of ozonation of 4-bromacetophenone, as shown above, is the absence of 4-bromacetophenone hydroperoxide in the products of the reaction. This is proved by approximate kinetic calculations under conditions of stationarity of the concentration of the formed radicals by the classical scheme [22]:
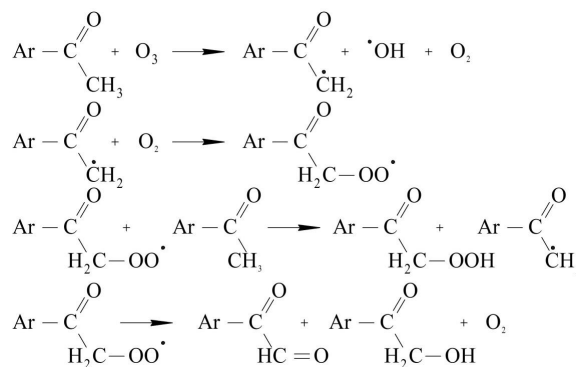
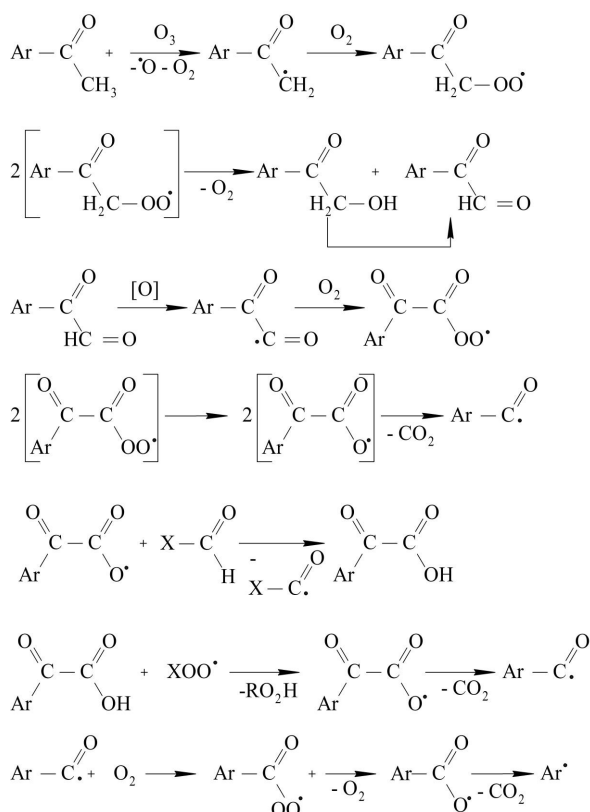Fig. 9. Diagram of ozonation of 4-bromacetophenone

Fig. 10. Diagram of ozonation of 4-bromacetophenone in acetic acid

To understand the absence of benzoic acid and significant release of carbon (IV) oxide in the process of ozonation of acetophenone, the hypothetical ozonation scheme (Fig. 10), which was recorded with respect to the expert and theoretical data for its individual stages, was proposed [22, 26].

According to Fig. 10, the formed peroxides are recombined. Phenylglyoxal, like a typical aldehyde, must be quickly oxidized and then subsequently transformed in directions: to be recombined with sequential formation of oxo carbonyl and phenyl carbonyl radicals and the release of CO_2, or to take part in reactions via phenyl carboxylic acid, which also ends in the formation of phenyl carbonyl radical and the release of CO_2. Then phenyl carbonyl radical reacts by similar schemes with the formation of CO_2 and phenyl radicals with subsequent condensation to Ar–Ar.

6. Discussion of results of research into kinetics and the mechanism of reaction of ozone with 4-bromethylbenzene in acetic acid

According to the results of research into kinetics and the mechanism of reaction of ozone with 4-bromethylbenzene in acetic acid, it was shown that oxidation flows predominantly by the aromatic ring of the substrate with the formation of peroxides of aromatic character. Among the products of ozonation by the ethylic group, the trace amounts of 1-(4-bromphenyl) ethanol and 4-bromacetophenone were identified. With an increase in temperature, unproductive consumption of ozone quickly grows and vice versa, under conditions of prevention of ozonolysis, ozone will be also consumed in the reaction with the formation of the target aromatic product. It should be noted that regardless of the conditions of the reaction, the ozonolysis of aromatic rings always dominates. It is not possible to obtain 4-bromacetophenone with a great release under these conditions.

However, the possibility of direct ozonation of 4-bromethylbenzene by the side chain was shown. This will be useful in further studying of the reaction in the presence of catalytic impurities, which will contribute to the growth of selectivity of oxidation by the ethylic group of the substrate. The experimental data is the first step to create the basics of the technology of 4-bromethylbenzene synthesis with the help of ozone. This will significantly simplify the apparatus design of the process, increase the output of the target product and contribute to subsequent improvement of the methods of oxidizing processing of reagents.

7. Conclusions

1. The composition of the products of reactions of ozone with 4-bromethylbenzene and 4-bromacetophenone in acetic acid was studied. It was established that oxidation of 4-bromethylbenzene by ozone in acetic acid flows predominantly by the aromatic ring with the formation of ozonides – peroxide products of aliphatic character. Up to 35 % 4-bromacetophenone and trace amounts of 1-(4-bromphenyl) ethanol were identified among the products of the oxidation reaction by the side chain. Ozonides – the products of destruction of the aromatic ring and trace amounts of benzaldehyde and benzoic acid – were identified among the products of oxidation of 4-bromacetophenone.

2. The determined constants of the rates of the reaction of ozone with 4-bromethylbenzene and 4-bromacetophenone in acetic acid at different temperatures were determined. The reaction at temperatures of up to 30 °C has the first order by the initial components and the value of constants of reaction rate does not depend on the concentration of reactants. With an increase in temperature, constant of reaction rate begins to depend on the concentration of reagents; in this case, the ozone consumptions significantly increase.

3. The kinetic patterns and the mechanism of the reaction of oxidation of 4-bromethylbenzene by ozone in acetic acid were studied. It was proved that ozonation of 4-bromethylbenzene is a complicated process, in which the substrate is oxidized by the non-chain mechanism, and ozone is consumed in two directions: in the reaction with the substrate by the non-chain mechanism and by the chain mechanism at the stage of the chain continuation of the reaction with the products of the thermal decomposition of ozonides.

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