ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 4, pp. 493–498. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.G. Galstyan, S.G. Galstyan, V.V. Lysak, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 4, pp. 504–509.

Kinetics and Products of the Reactions of Ozone with Toluene and Its Derivatives in Acetic Anhydride

A. G. Galstyan, S. G. Galstyan, and V. V. Lysak

Institute of Chemical Technologies, East-Ukrainian National University, Rubezhnoe Branch,
Rubezhnoe, Lugansk oblast, Ukraine
e-mail: ozon@megabit.com.ua

Received December 14, 2009

Abstract—The reactions of ozone with toluene and its derivatives in acetic anhydride were studied. It was found that competing parallel reactions of ozone with the aromatic ring and substituents occurred in the ozone–arene–acetic anhydride system. The ratio between these reaction paths depended on the arene structure and reaction conditions. The selectivity of the oxidation of toluene and its derivatives at the methyl group varied from 0 to 40%. The fraction of aromatic products decreased as the number of methyl groups at the ring was increased. Tri- and tetramethylbenzenes were oxidized only at the aromatic ring. The stability of an aromatic system increased upon the introduction of electron-acceptor substituents into the benzene ring. Aminotoluenes and hydroxytoluenes were oxidized with ozone mainly at the NH_2 and HO groups; however, as in the case of toluene, the aromatic ring and methyl group became the main directions upon their acylation. The oxidation of the methyl group in acetic anhydride in the presence of sulfuric acid was finished at the step of the formation of the acylated derivatives of benzyl alcohols and benzaldehydes, which are resistant to the action of ozone.

DOI: 10.1134/S0023158411040033

INTRODUCTION

It is well known [1] that, in the ozone–methylbenzene–acetic acid system, oxidation develops mainly at the aromatic ring with the formation of ozonides. The products of oxidation at the methyl group—benzoic acids—are formed to a lesser extent (0–40%). Under these conditions, the reaction of methyl group oxidation cannot be stopped at the step of the formation of aromatic alcohols because they are prone to further oxidation [2]. However, previous studies [3] demonstrated the possibility of controlling the degrees of oxidation of toluene and its derivatives with ozone by adding stop reagents to the system.

Here, we report the results of a study of the reactions of ozone with toluene and its derivatives in acetic anhydride, which is a strong acylating agent. From scientific and practical points of view, this study is important for the development of promising methods for controlling the selectivity and degree of oxidation of alkylbenzenes with ozone in a liquid phase.

EXPERIMENTAL

The oxidation of toluene and its derivatives was performed in a thermostatically controlled catalytic reactor as a long-necked flask 0.1 l in volume under conditions of the kinetic regime of oxidation, which was observed at a reactor shaking frequency higher than 7–9 s^{-1} (depending on the nature of the arene and reaction conditions) and a 0.04-m amplitude of its displacement along the horizontal axis. Acetic anhydride (chemically pure) was used as a solvent without preliminary purification. Liquid methylbenzenes (chemically pure) were purified on a column with aluminum oxide. Solid methylbenzenes were recrystallized from appropriate solvents before use. Sulfuric acid (chemically pure) was used as a mineral acid. The ozone–air mixture with an ozone concentration of 10^{-6}–10^{-4} mol/l was obtained using a laboratory ozone generator [4].

Acetic anhydride and sulfuric acid were loaded into a thermostatically controlled reactor, and the resulting mixture was saturated with ozone on shaking; thereafter, methylbenzene was introduced into the apparatus (see Table 2 for concentration). The course of the reaction was monitored based on changes in the concentration of ozone in a gas phase and the analysis of reaction products. Ozone concentrations in the gas phase at the apparatus inlet and outlet were measured automatically with the use of a spectrophotometric technique in the absorption region of 254–290 nm. An SF-26 spectrophotometer equipped with a flow cell 7 cm in length coupled to an EPN potentiometer was used for the measurements. The sensitivity to ozone was 1.8×10^{-7} mol/l. The concentration of ozone was calculated using a calibration curve constructed with the use of the equation $[O_3]_g = A/\varepsilon l$, where $[O_3]_g$ is the ozone concentration in a gas phase, mol/l; A is the absorbance of ozone-containing gas; ε is the molar absorption coefficient ($\varepsilon = 3025$ at $\lambda = 254$ nm [5]); and l is the optical path length of the cell (2–7 cm).

Table 1. Selectivity for the oxidation of toluene and its derivatives in acetic anhydride; $[H_2SO_4]_0 = 0.08–1.2$ mol/l

Compound	*t*, °C	β, %	S_1, %	S_2, %
Toluene	5	70.0	6.0	91.3
1,4-Dimethylbenzene	5	82.0	5.0	93.1
1,3-Dimethylbenzene	5	80.0	4.8	93.2
1,2-Dimethylbenzene	5	100.0	0.0	98.3
1,3,5-Trimethylbenzene	5	100.0	0.0	98.7
1,3,4-Trimethylbenzene	5	100.0	0.0	98.5
2,3,5,6-Tetramethylbenzene	5	100.0	0.0	98.1
4-Nitrotoluene	20	28.4	32.5	62.4
4-Toluenesulfonyl chloride	20	32.0	34.1	61.0
3,4-Dinitrotoluene	30	92.2	42.2	56.1
2,4-Dinitrotoluene	30	92.0	39.8	58.4
2,6-Dinitrotoluene	30	91.0	8.2	89.6
2-Hydroxytoluene	5	100.0	0.0	94.6
3-Hydroxytoluene	5	100.0	0.0	95.1
4-Hydroxytoluene	5	100.0	0.0	96.2
2-Acetoxytoluene	5	100.0	10.9	88.2
3-Acetoxytoluene	5	100.0	19.9	79.7
4-Acetoxytoluene	5	100.0	20.5	78.0
2-Aminotoluene	5	100.0	0.0	–
3-Aminotoluene	5	100.0	0.0	–
4-Aminotoluene	5	100.0	0.0	–
2-Acetaminotoluene	5	100.0	5.6	92.0
3-Acetaminotoluene	5	100.0	13.2	83.2
4-Acetaminotoluene	5	100.0	15.6	81.6

Note: β is the conversion; S_1 is selectivity for oxidation at the methyl group; S_2 is the concentration of peroxides—benzene ring oxidation products; hydroxy- and aminotoluenes were oxidized in acetic acid.

The oxidation products of toluene and its derivatives were identified and their concentrations in solution were determined by gas–liquid chromatography on a chromatograph with a flame-ionization detector (3-m column 4 mm in diameter; solid support, Inerton AW-DMCS; stationary phase, SE-30 (5%)). The injector temperature was 250°C, and the oven temperature was programmed over a range of 100–200°C for a specified time. The carrier-gas (nitrogen), hydrogen, and air flow rates were 1.8, 1.8, and 18 l/h, respectively. 4-Nitrochlorobenzene was used as an internal standard.

The effective rate constants of the reactions of ozone with methylbenzenes and their oxidation products were determined with the use of ozone diagrams, kinetic curves, which characterize changes in ozone concentration in the gas phase at the reactor outlet in time, and the equation

$$k_{\text{eff}} = \omega([O_3]_i - [O_3]_f)/\alpha[O_3]_f^n[ArH]_0^m,$$

where ω is the gas flow rate, 1/s; α is the Henry coefficient; $[ArH]_0$ is the initial substrate concentration, mol/l; $[O_3]_i$ and $[O_3]_f$ are the concentrations of ozone in the gas phase before and after the reactor, mol/l; *n* and *m* are reaction orders with respect to reactants.

The concentration of peroxides was determined by iodometric titration.

RESULTS AND DISCUSSION

Toluene in an acetic anhydride solution was oxidized with an ozone–air mixture at 5°C mainly at the benzene ring with the formation of peroxides (91.3%), which are resistant to the action of ozone, and benzoic

Table 2. Rate constants of the reactions of ozone with toluene and its derivatives in acetic anhydride at 5°C; $[H_2SO_4]_0 = 0.08–1.2$ mol/l

Compound	Concentration, mol/l		k_{eff}, l mol^{-1} s^{-1}	$n^* = \Delta[O_3]/\Delta[ArH]$
	$[ArH]_0 \times 10^2$	$[O_3]_0 \times 10^4$		
Toluene	1.0–10.20	0.1–1.20	0.56 ± 0.05	3.17
1,4-Dimethylbenzene	0.20–1.40	0.2–1.20	3.02 ± 0.28	2.81
1,3-Dimethylbenzene	0.20–1.26	0.21–1.15	2.81 ± 0.26	–
1,3,5-Trimethylbenzene	0.04–0.28	0.31–2.00	32.00 ± 2.95	3.06
1,3,4-Trimethylbenzene	0.05–0.40	0.32–2.10	17.83 ± 1.62	–
1,3,5,6-Tetramethylbenzene	0.02–0.23	0.20–1.31	56.84 ± 1.21	–
4-Nitrotoluene	2.1–20.82	0.11–2.56	0.04 ± 0.003	2.10
3,4-Dinitrotoluene	9.11–22.6	0.18–3.38	0.01 ± 0.001	1.02
2,4-Dinitrotoluene	9.11–22.6	0.18–3.30	0.01 ± 0.001	1.09
2,6-Dinitrotoluene	9.11–22.6	0.18–3.32	0.008 ± 0.001	1.11
2-Hydroxytoluene	9.7–38.3	0.35–0.90	$(0.96 \pm 0.08) \times 10^3$	–
4-Hydroxytoluene	9.9–31.9	0.35–0.90	$(2.26 \pm 0.20) \times 10^3$	–
2-Acetoxytoluene	20.1–38.9	0.29–0.57	0.47 ± 0.04	1.12
3-Acetoxytoluene	15.1–35.9	0.28–0.57	0.56 ± 0.05	1.09
4-Acetoxytoluene	15.1–35.9	0.28–0.57	0.59 ± 0.05	1.07
2-Aminotoluene	2.7–18.3	0.45–0.80	$(2.46 \pm 0.20) \times 10^3$	–
3-Aminotoluene	2.7–18.3	0.45–0.89	$(2.15 \pm 0.20) \times 10^3$	–
4-Aminotoluene	2.7–18.3	0.45–0.80	$(2.66 \pm 0.20) \times 10^3$	–
2-Acetaminotoluene	10.1–29.7	0.28–0.57	1.45 ± 0.19	1.25
3-Acetaminotoluene	15.1–29.7	0.28–0.57	0.56 ± 0.04	1.30
4-Acetaminotoluene	10.1–29.7	0.28–0.57	1.53 ± 0.12	1.35

Note: k_{eff} was calculated on condition that the reaction of ozone with methylbenzenes is of first order with respect to reactants (as determined experimentally); * stoichiometric coefficient for ozone.

acid (the product of oxidation at the methyl group) in considerably smaller amounts (5.8%). Benzyl alcohol, benzaldehyde, and their acylated derivatives (benzyl acetate and benzylidene diacetate, the total amount of which was no higher than 10^{-4} mol/l) appeared at the early stages.

In the presence of the catalytic additives of sulfuric acid (0.8 mol/l), benzyl acetate (3.8%), benzylidene diacetate (2.2%), and benzaldehyde, whose concentration in solution was no higher than 4×10^{-4} mol/l, were detected among the products of oxidation at the methyl group. Benzoic acid was not detected under these conditions (Table 1).

The stability of an aromatic system in the reaction with ozone increased upon the introduction of electron-acceptor substituents into the aromatic ring (Table 1). Upon the oxidation of 4-nitrotoluene in an acetic anhydride solution in the presence of sulfuric acid at a temperature of 20°C, the selectivity of the process for the methyl group increased to 32.5%: 4-nitrobenzyl acetate (7.9%), 4-nitrobenzylidene diacetate (24.6%), and trace amounts of 4-nitrobenzaldehyde were detected among the oxidation products. The introduction of the second nitro group into the benzene ring led to a further increase in the fraction of selective oxidation: 3,4-dinitrotoluene was oxidized with the formation of 3,4-dinitrobenzyl acetate (10.2%), 3,4-dinitrobenzylidene diacetate (32.0%), and trace amounts of 3,4-dinitrobenzyl alcohol and 3,4-dinitrobenzaldehyde. Analogous results were obtained upon the oxidation of 4-toluenesulfonyl chloride and 2,4-dinitrotoluene. The selectivity of the oxidation of *ortho* isomers was lower because of steric hindrances.

The introduction of the second, third, and fourth methyl groups into the aromatic ring of toluene led to a decrease in the selectivity of oxidation (Table 1). Upon the oxidation of 1,4-dimethylbenzene, 4-methylbenzylidene diacetate (4.6%) and 4-methylbenzyl acetate (0.4%) were identified among the oxidation products of the methyl group. 1,2-Dimethylbenzene

Table 3. Oxidation of acetoxy- and acetaminotoluenes with ozone in acetic anhydride at 5°C. $[ArCH_3]_0 = 0.4$; $[O_3]_0 = 4 \times 10^{-4}$ mol/l

Compound	$[H_2SO_4]_0$, mol/l	Yield of oxidation products, %			
		peroxides	benzyl acetates	benzylidene diacetates	benzoic acids
2-Acetoxytoluene	–	87.7	4.3	1.9	4.6
	1.2	88.2	7.4	3.5	–
3-Acetoxytoluene	–	79.7	7.5	3.2	8.6
	1.2	79.1	12.6	7.3	–
4-Acetoxytoluene	–	78.6	7.8	3.4	9.2
	1.2	78.0	13.0	7.5	–
2-Acetaminotoluene	–	92.4	2.0	1.2	2.3
	1.1	92.0	3.2	2.4	–
3-Acetaminotoluene	–	83.9	4.1	3.1	5.8
	1.1	83.2	8.0	5.2	–
4-Acetaminotoluene	–	82.1	5.2	4.1	6.3
	1.1	81.6	9.3	6.5	–

was almost completely converted into benzene ring oxidation products. Tri- and tetramethylbenzenes also reacted with ozone only at the aromatic ring (Table 1).

The reaction of ozone with toluene derivatives having HO– and NH_2– groups at the benzene ring occurs in a different way. At the initial moment of time, hydroxytoluenes in a tetrachloromethane solution react with ozone at the H–O bond of the hydroxyl group with the formation of phenoxyl radical with the subsequent addition of a hydroxyl radical, benzene ring opening, and formation of ozonides—the products of the addition of ozone molecules at double bonds [1]. The rate of a primary attack by ozone is so high (Table 2) that the reactions of ozone at the double bonds of an aromatic ring and the methyl group can be ignored (Table 1).

In an acetic anhydride solution, the reaction mechanism changes because hydroxytoluenes are rapidly acylated under the experimental conditions (the acylation it complete at the stage of reagent preparation). In this case, the O–C bond, which is stronger than H–O, is formed [6] and the direction of reaction changes and becomes typical of ozone reactions with alkylbenzenes—at the double bonds of an aromatic ring and at the methyl group [1]. The found reactivity of hydroxytoluenes and acetoxytoluenes confirms this conclusion: after the acylation of hydroxytoluenes, it decreases by three orders of magnitude and approaches the reactivity of methylbenzenes (Table 2). In this case, oxidation is mainly developed at the benzene ring and the methyl group (Table 3). In the absence of a mineral acid at a temperature of 5°C, the main reaction products are peroxides—benzene ring oxidation products (78.6–87.7%)—and, to a lesser degree, the products of oxidation at the methyl group—acetoxybenzyl acetates (4.3–7.8%), acetoxybenzylidene diacetates (1.9–3.4%), and acetoxybenzoic acids (4.6–9.2%).

In the presence of acid acylation catalysts, for example, sulfuric acid, the total selectivity of oxidation remains almost unchanged, but the oxidation of methyl group completes at the stage of formation of acetoxybenzyl acetates and acetoxybenzylidene diacetates (Table 3).

We found experimentally that at least the following two conditions should be fulfilled for the accumulation of benzyl acetates and benzylidene diacetates in the system:

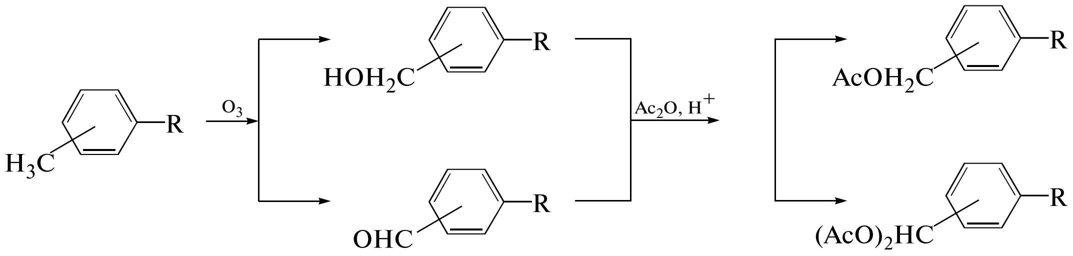
(1) The rate of acylation of alcohols and aldehydes formed upon oxidation should be considerably higher than the rate of their ozonation.

(2) The rate of ozonation of the resulting benzyl acetates and benzylidene diacetates should be no higher than the rate of ozonation of the corresponding toluenes.

For the quantitative assessment of the first condition, the rates of ozonation and acylation of benzyl alcohol were determined. The rate of acylation of benzyl alcohol was found considerably higher than the rate of its ozonation (3.3×10^{-2} and 2.3×10^{-4} mol l^{-1} s^{-1}, respectively; $T = 20$°C); that is, the first condition is satisfied.

The second condition is also satisfied: the effective reaction rate constant of ozone with benzyl acetate does not exceed the rate constant of ozonation of toluene ($k_{eff} = 0.56$ and 0.87 l mol^{-1} s^{-1}, respectively).

Thus, the formation of the products of the partial oxidation of toluene and its derivatives at the methyl group in an acetic anhydride solution is caused by the fast acylation reactions of benzyl alcohols and benzaldehydes at the moment of their appearance in the system with the formation of corresponding benzyl acetates and benzylidene diacetates:



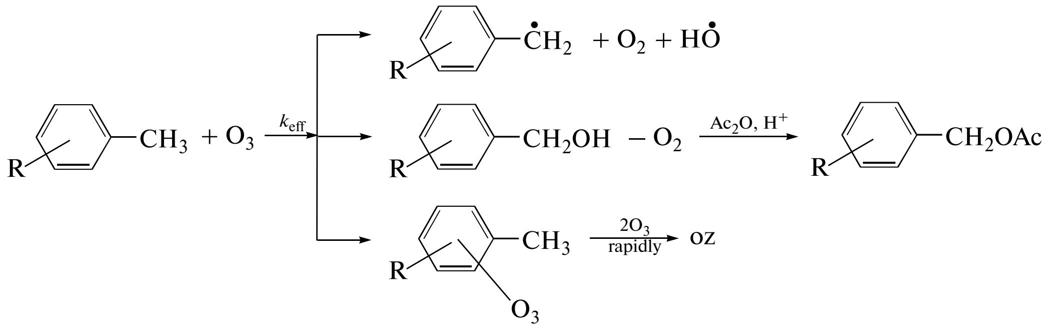
where R = $-H$, $-CH_3$, $-NO_2$, $-SO_2Cl$, $-OAc$, or $-NHAc$.

Aminotoluenes react with ozone more rapidly than hydroxytoluenes (Table 2). The reaction mainly occurs at the lone electron pair of the nitrogen atom with the predominant formation of tar products (it is assumed that these are polymeric azo compounds [7]), nitrotoluenes (to 14%), and trace toluquinones. The products of oxidation at the methyl group are not formed at 5–15°C under conditions of the experiments. After the acylation of the amino group, as in the case the ozonation of hydroxytoluenes, oxidation at the aromatic ring (81.6–92.0%) and the methyl group (5.6–15.6%) become the main reaction paths (Table 1). In this case, the amino group is deactivated to a considerable degree as a result of the formation of the –N–C bond, which is stronger than N–H, and the participation of the lone electron pair of the nitrogen atom in conjugation with the carbonyl group of acetyl [6].

After acylation, the effective rate constant of ozone interaction with aminotoluenes (k_{eff}) decreases by three orders of magnitude and approaches the values of k_{eff} characteristic of methylbenzenes (Table 2). Acetaminobenzyl acetates (2.0–5.2%), acetaminobenzylidene diacetates (1.2–4.1%), acetaminobenzoic acids (2.3–6.3%), and trace acetaminobenzaldehyde were detected among the products of oxidation at the methyl group in the absence of a catalyst for acylation reaction (sulfuric acid) at 5°C (Table 3). Under the conditions of sulfuric acid catalysis at the same selectivity of oxidation, the main reaction products are acylated alcohols and aldehydes (Table 3).

Based on published data [4] and the experimental results, we can make the following conclusions:

(1) The general reaction scheme of the oxidation of toluene and its derivatives in acetic anhydride in the presence of sulfuric acid has the form



(I)

(II)

(III)

where R = $-H$, $-CH_3$, $-NO_2$, $-SO_2Cl$, $-OAc$, or $-NHAc$; oz refers to ozonides.

In this case, reaction path (3) is predominant.

(2) The amount of aromatic products decreases with the number of methyl groups at the benzene ring.

(3) The stability of the benzene ring in the reaction with ozone increases upon the introduction of electron-acceptor substituents into the ring.

(4) Hydroxy- and aminotoluenes react with ozone mainly at the hydroxy and amino groups; reaction paths (I)–(III) become possible after the preliminary acylation of the hydroxy and amino groups.

Benzyl radicals formed in reaction (I) are oxidized in accordance with the following reaction scheme of chain oxidation [8]:

$$\text{R–ArC}\dot{\text{H}}_2 + \text{O}_2 \longrightarrow \text{R–ArCH}_2\dot{\text{O}}_2 \qquad \text{(IV)}$$

$$\begin{gathered}\text{R–ArCH}_2\dot{\text{O}}_2 + \text{ArCH}_3 \\ \rightarrow \text{R–ArCH}_2\text{O}_2\text{H} + \text{ArC}\dot{\text{H}}_2,\end{gathered} \qquad \text{(V)}$$

$$\text{R–ArCH}_2\text{O}_2\text{H} \longrightarrow \text{R–ArCH}_2\text{O}^\bullet + \text{HO}^\bullet \qquad \text{(VI)}$$

$$2\text{R–ArCH}_2\text{O}_2^{\bullet} \rightarrow \text{R–ArCH}_2\text{OH} + \text{ArCHO}. \qquad \text{(VII)}$$

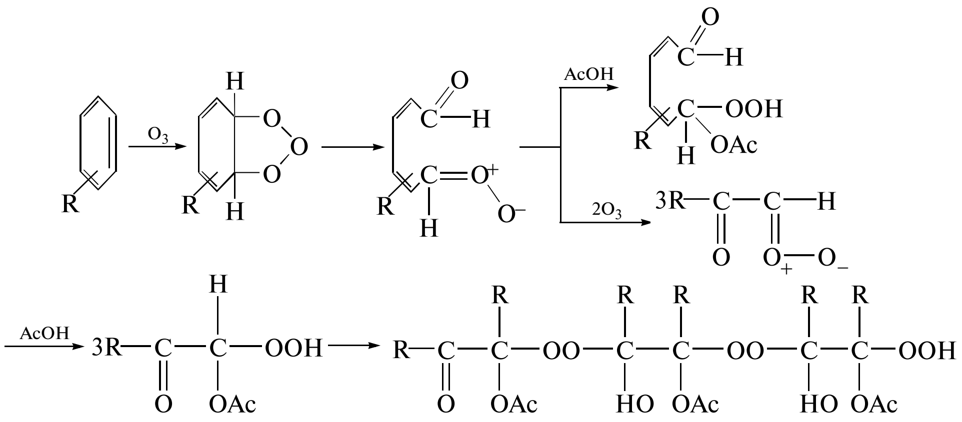
Rough estimates show that the chain length for toluene is $v = \omega_\text{V}/\omega_\text{I} \approx 27$ ($\omega_\text{I} = k_\text{eff}[\text{O}_3]_0[\text{ArH}]_0 \cdot S' = 0.87 \times 1.2 \times 10^{-4} \times 0.1 \times 0.06 = 4.0 \times 10^{-7}$ mol l^{-1} s^{-1}, $\omega_\text{V} = k_\text{V}[\text{ArCH}_2\text{O}_2^{\bullet}][\text{ArH}]_0 = 1.0 \times 1.1 \times 10^{-4} \times 0.1 = 1.1 \times 10^{-5}$ mol l^{-1} s^{-1}, where S' is the selectivity of oxidation at the methyl group (Table 1, 6.0%); $\left[\text{ArCH}_2\text{O}_2^{\bullet}\right] \approx 1.1 \times 10^{-4}$ mol/l was found from steady-state concentration conditions at $k_\text{V} = 1.0$ [11]; $k_\text{VII} = 10^8$ l mol^{-1} s^{-1} [11]; $k_\text{eff} = 0.56$ l mol^{-1} s^{-1} (Table 2)).

The alcohols and aldehydes formed in the system are converted into acetates and acetals, which are resistant to the action of ozone, in an acetic anhydride solution [9, 10]:

$$\text{R–ArCH}_2\text{OH} + \text{AC}_2\text{O} \rightarrow \text{R–ArCH}_2\text{OAc} + \text{AcOH}, \qquad \text{(VIII)}$$

$$\text{R–ArCHO} + \text{Ac}_2\text{O} \longrightarrow \text{R–ArCH(OAc)}_2. \qquad \text{(IX)}$$

The properties of the resulting peroxides are almost the same as the properties of peroxides obtained upon the oxidation of methylbenzenes in an acetic acid solution [4]: they are resistant to the action of ozone; they are accumulated upon oxidation at a high rate in a high yield (Table 1); they are light yellow viscous liquid readily soluble in acetic acid and acetic anhydride. The stoichiometric coefficient of the reaction $\Delta[\text{O}_3]_0/\Delta[\text{ArCH}_3]_0$ found some toluene derivatives is 1–3 (Table 2). According to published data [4, 7], the above facts suggest that peroxides are monomers, trimers, or their mixtures with a linear structure depending on the structure of the arene; the preparation of them can be described in accordance with the Kriege mechanism:



(X)

Thus, we found that ozone reacts with toluene and its derivatives in acetic anhydride predominantly at the benzene ring. The amount of the products of oxidation at the methyl group decreases with the number of methyl groups at the benzene ring, whereas it increases in the presence of electron-acceptor substituents. Amino- and hydroxytoluenes in acetic acid react with ozone mainly at the amino and hydroxy groups, but the benzene ring and the methyl group become the main directions of reaction after their acylation. The oxidation of the methyl group in acetic anhydride and in the presence of sulfuric acid becomes complete at the stage of the formation of acylated benzyl alcohol and benzaldehyde derivatives, which are resistant to the action of ozone.

REFERENCES

1. Galstyan, G.A., Tyupalo, N.F., and Razumovskii, S.D., *Ozon i ego reaktsii s aromaticheskimi soedineniyami v zhidkoi faze* (Ozone and Its Liquid-Phase Reactions with Aromatic Compounds), Lugansk: VUNU, 2004.
2. Galstyan, G.A. and Galstyan, T.M., *Neftekhimiya*, 1994, vol. 30, p. 829.
3. Galstyan, G.A., Matsegora, L.A., and Rister, O.I., *Zh. Prikl. Khim.*, 1982, vol. 55, p. 2547.
4. Razumovskii, S.D. and Zaikov, G.E., *Ozon i ego reaktsii s organicheskimi soedineniyami* (Ozone and Its Reactions with Organic Compounds), Moscow: Nauka, 1974.
5. Calvert, J.G. and Pitts, J.N., *Photochemistry*, New York: Wiley, 1965.
6. Gurvich, L.V., Karachintsev, G.B., and Kondrat'ev, V.N., *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Bond Dissociation Energies, Ionization Potentials, and Electron Affinity), Moscow: Nauka, 1974.
7. Bailey, P.S., *Ozonation in Organic Chemistry: Nonolefinic Compaunds*, New York: Academic, 1982, vol. 2.
8. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase), Moscow: Nauka, 1965.
9. Traffers, H.P. and Hammett, L.P., *J. Am. Chem. Soc.*, 1937, vol. 59, p. 1708.
10. Gillespie, R.J., *J. Am. Chem. Soc.*, 1950, vol. 39, p. 2997.
11. Denisov, E.T., *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* (Rate Constants of Homolytic Liquid-Phase Reactions), Moscow: Nauka, 1971.