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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Oxidation of Benzyl Alcohol and Benzaldehyde with Ozone in Acetic Acid

E. V. Potapenko and P. Yu. Andreev

Institute for Chemical Technology, Dal' Eastern-Ukrainian National University, Rubezhnoe, Lugansk oblast, Ukraine

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Abstract—Ozonation of benzyl alcohol and benzaldehyde in acetic acid was studied. A method for ozonation of these compounds is suggested.

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Liquid-phase oxidation of methylbenzenes with ozone has been rather long considered a promising way to obtain aromatic carboxylic acids [1]. In the course of ozonation, the primary comparatively stable products of oxidation of the methyl group are aromatic alcohols and aldehydes. Despite that their concentration in the system is rather low, these substances undoubtedly play an important role in deep conversion stages of methylbenzenes.

Apparently, to extend the concepts of processes for oxidation of methylbenzenes, it is also necessary to understand the fundamental kinetic aspects and mechanism of the reaction of ozone with aromatic alcohols and aldehydes.

In this context, it is of interest to study the fundamental aspects of ozonation of benzyl alcohol and benzaldehyde in acetic acid under the conditions characteristic of oxidation of methylbenzenes.

The interaction of benzyl alcohol with ozone in acetic acid is accompanied by preferential oxidation of the oxymethyl group (Fig. 1). Benzoic acid accumulates as the main product (83.7%), with the amount of ozonides not exceeding 15.2%. Benzaldehyde is formed in parallel with benzoic acid in minor amounts.

Introduction of cobalt(II) acetate into the oxidizing system makes it possible to raise both the yield of benzoic acid (95.4%) and the consumption rate of the alcohol (Fig. 1). It is noteworthy that benzoic acid is formed in the presence of the catalyst after a sufficient amount of benzaldehyde accumulates in the reaction mass. This is indicative of the successive nature of their formation. Already in the first minutes of ozonation, cobalt becomes trivalent and after that its concentration remains unchanged.

In contrast to benzyl alcohol, the main reaction pathway in ozonation of benzaldehyde is the destruction of the aromatic ring (52.3%), with the yield of benzoic

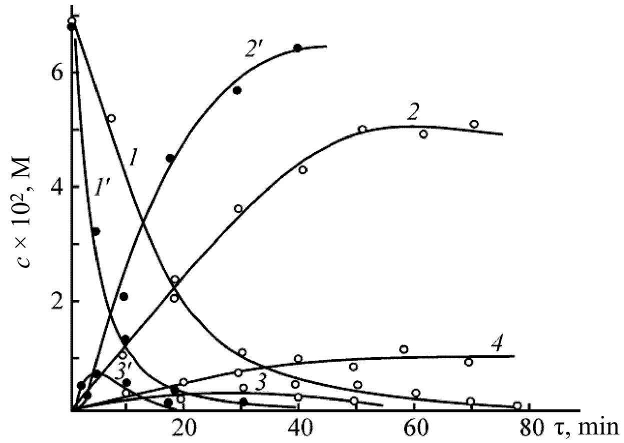

Fig. 1. Kinetic curves of (*1, 1'*) consumption of benzyl alcohol and accumulation of (*2, 2'*) benzoic acid, (*3, 3'*) benzaldehyde, and (*4*) ozonides in ozonation (*1–4*) in the absence of a catalyst and (*1'–3'*) in the presence of cobalt(II) acetate in acetic acid at 60°C. $[ArCH_2OH] = 0.069$ M, $[O_3] = 4 \times 10^{-4}$ M, $[Co(OAc)_2] = 0.08$ M. (*c*) Concentration and (τ) reaction duration; the same for Fig. 2.

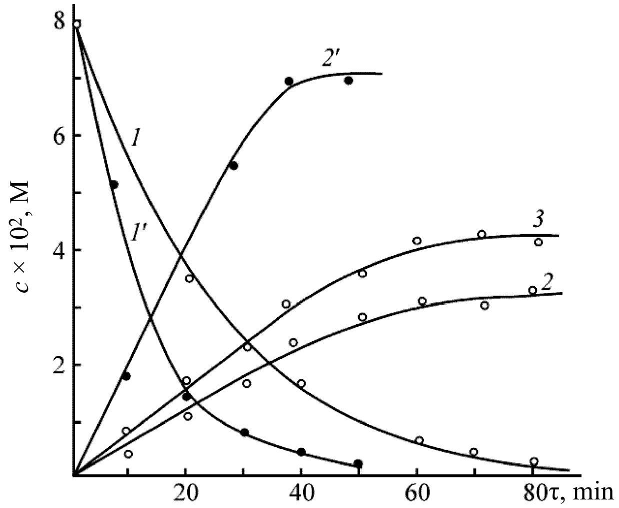

Fig. 2. Kinetic curves of (*1, 1'*) consumption of benzaldehyde and accumulation of (*2, 2'*) benzoic acid and (*3*) ozonides in ozonation (*1–3*) in the absence of a catalyst and (*1', 2'*) in the presence of cobalt(II) acetate in acetic acid at 60°C. $[ArCHO] = 0.08$ M, $[O_3] = 4 \times 10^{-4}$ M, $[Co(OAc)_2] = 0.08$ M.

acid equal to 43.2%. By using the catalyst, it is possible to change the reaction direction toward formation of aromatic acid (91.2%) (Fig. 2). As also in the case of benzyl alcohol, cobalt is present in the reaction mixture in the oxidized form.

The consumption kinetics of the alcohol and aldehyde in the reaction with ozone is described by the bimolecular law and has the first order with respect to each of the reactants (Fig. 3):

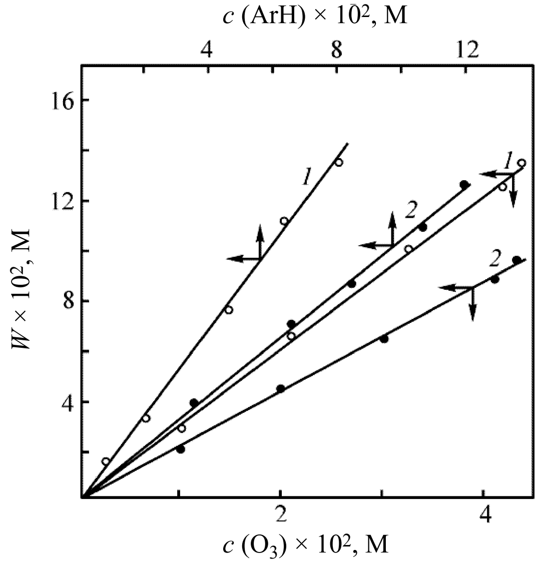

Fig. 3. Dependence of the initial rate W of consumption of (*1*) benzyl alcohol and (*2*) benzyl alcohol on the ozone concentration $c(O_3)$ at 60°C.

$$-\frac{d[ArH]}{d\tau} = k[O_3][ArH]. \quad (1)$$

A study of the effect of the concentrations of ozone, catalyst, and substrate in catalytic oxidation of benzyl alcohol demonstrated that the consumption rate of the alcohol is described by a third-order kinetic equation (Fig. 4):

$$-\frac{d[ArCH_2OH]}{d\tau} = k[ArCH_2OH][Co^{2+}][O_3]. \quad (2)$$

The dependence of the oxidation rate of benzaldehyde on the concentrations of ozone, catalyst, and substrate is more complicated, which points to a chain consumption mechanism of benzaldehyde (Fig. 5):

$$-\frac{d[ArCHO]}{d\tau} = k[ArCHO]^{1.5}[Co^{2+}]^{0.5}[O_3]^{0.5}. \quad (3)$$

On the basis of the experimental results of this study and published data, the following oxidation scheme of benzyl alcohol can be considered, and primarily just those reactions which enable understanding of the role

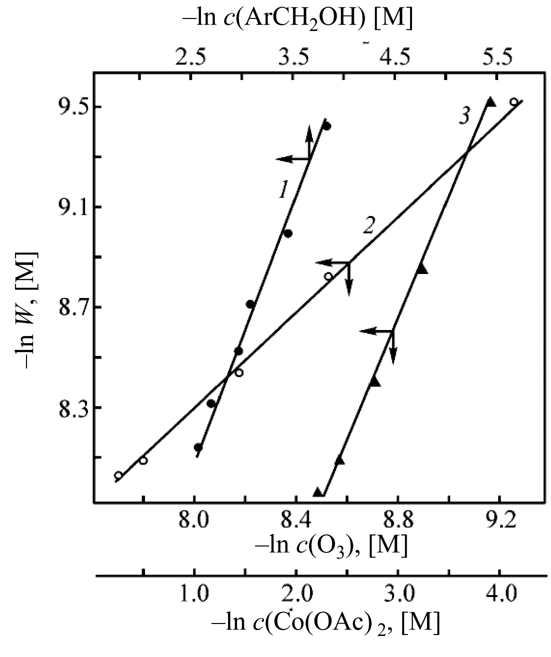

Fig. 4. Dependence of the initial rate W of oxidation of benzyl alcohol on the concentrations c of (*1*) benzyl alcohol, (*2*) ozone, and (*3*) cobalt(II) acetate at 60°C.

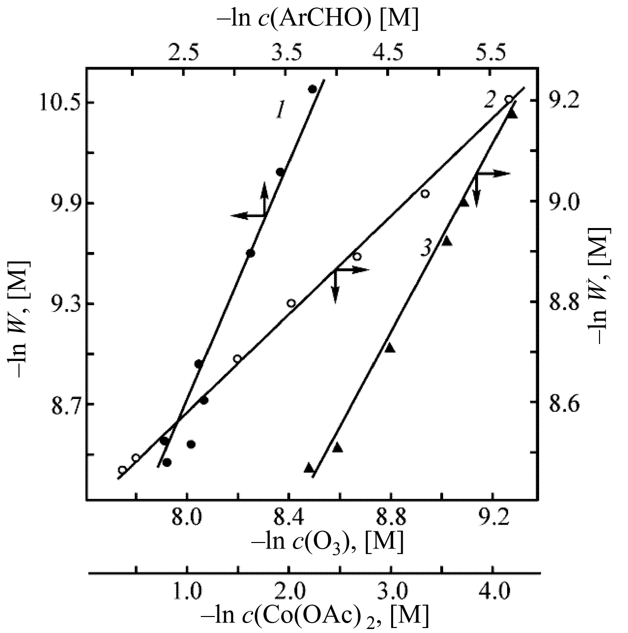

Fig. 5. Dependence of the initial rate W of oxidation of benzaldehyde on the concentrations c of (*1*) benzaldehyde, (*2*) ozone, and (*3*) cobalt(II) acetate at 60°C.

played by each of the reactants:

$$(\mathrm{ArCH_2OH + O_3 \rightarrow [ArCH_2OH{\cdot}O_3]}, \tag{4}$$

$$\mathrm{[ArCH_2OH{\cdot}O_3] \rightarrow ArCH(OH)OOOH}, \tag{5}$$

$$\mathrm{[ArCH_2OH{\cdot}O_3]} \rightarrow \text{products of disintegration of the aromatic ring}, \tag{6}$$

$$\mathrm{ArCH(OH)OOOH \rightarrow ArCOOH + H_2O_2}, \tag{7}$$

$$\mathrm{ArCH(OH)OOOH \rightarrow ArCHO + H_2O + O_2}, \tag{8}$$

$$\mathrm{ArCH(OH)OOOH \rightarrow ArC^{\cdot}HOH + HO^{\cdot} + O_2}, \tag{9}$$

$$\mathrm{Co^{2+} + O_3 + H^+ \rightarrow Co^{3+} + HO^{\cdot} + O_2}, \tag{10}$$

$$\mathrm{ArCH_2OH + Co^{3+} \rightarrow ArC^{\cdot}HOH + Co^{2+} + H^+}, \tag{11}$$

$$\mathrm{ArC^{\cdot}HOH + O_2 \rightarrow ArCH(OH)OO^{\cdot}}, \tag{12}$$

$$\mathrm{ArCH(OH)OO^{\cdot} \rightarrow ArCHO + HOO^{\cdot}}, \tag{13}$$

$$\mathrm{ArCH(OH)OO^{\cdot} + HOO^{\cdot}} \rightarrow \text{molecular products}, \tag{14}$$

$$\mathrm{2ArCH(OH)OO^{\cdot}} \rightarrow \text{molecular products}. \tag{15}$$

In the case of a noncatalytic oxidation, ozone react with the alcohol to give a π-complex [reaction (4)], whose further transformation yields either hydrotrioxide [reaction (5)] or destruction products of the aromatic ring [reaction (6)]. Hydrotrioxide can be consumed by reactions (7)–(9) [2, 3]. If the fact that the yield of the acid does not exceed 43% in oxidation of the aldehyde (Fig. 2) and is 83.7% in oxidation of the alcohol is taken into account, then the most probable pathway for formation of benzoic acid is reaction (7).

Kinetic parameters of elementary reactions in catalytic oxidation of benzyl alcohol and benzaldehyde with ozone in acetic acid at 25°C

Reaction	k	A	E, J mol^{-1}
	M^{-1} s^{-1}		
(4)	3.7	2.0×10^5	27000
(10)	9.6×10^2	2.6×10^8	31000
(11)	5.3×10^{-2}	2.3×10^8	55000
(16)	2.7	1.1×10^6	32000
(21)	3.1×10^{-2}	2.3×10^9	62000

In the presence of cobalt(II) acetate, ozone primarily reacts with the reduced form of the metal [reaction (10)]; $W_{10} > W_4$ (see table).

Direct oxidation of benzyl alcohol occurs by reaction (11) with cobalt(III) acetate. The increase in the alcohol consumption rate and oxidation selectivity in the presence of the catalyst is accounted for by the fact that $W_{11} > W_4$ (see table). Further, oxyalkyl radicals interact with oxygen by reaction (12) and oxyperoxide radicals formed in this case are consumed in accordance with reactions (13)–(15) [4].

The hydroxy radicals formed in the system by reactions (9) and (10) are mostly consumed in the reaction with acetic acid [5].

Benzaldehyde is consumed in accordance with the scheme [4, 6], which is in rather good agreement with the experimental data obtained:

$$\mathrm{ArCHO + O_3 \rightarrow [ArCHO{\cdot}O_3]}, \tag{16}$$

$$\mathrm{[ArCHO{\cdot}O_3] \rightarrow ArC(O)OOOH}, \tag{17}$$

$$\mathrm{[ArCHO{\cdot}O_3]} \rightarrow \text{disintegration products of the aromatic ring}, \tag{18}$$

$$\mathrm{ArC(O)OOOH \rightarrow ArCOOH + O_2}, \tag{19}$$

$$\mathrm{ArC(O)OOOH \rightarrow ArC^{\cdot}O + HO^{\cdot} + O_2}, \tag{20}$$

$$\mathrm{ArCHO + Co^{3+} \rightarrow ArC^{\cdot}O + Co^{2+} + H^+}, \tag{21}$$

$$\mathrm{ArC^{\cdot}O + O_2 \rightarrow ArC(O)OO^{\cdot}}, \quad (22)$$

$$\mathrm{ArC(O)OO^{\cdot} + ArCHO \rightarrow ArC(O)OOH + ArC^{\cdot}O}, \quad (23)$$

$$\mathrm{ArC(O)OOH + Co^{2+} \rightarrow ArC(O)O^{\cdot} + Co^{3+} + OH^{-}}, \quad (24)$$

$$\mathrm{ArC(O)OOH + Co^{3+} \rightarrow ArC(O)OO^{\cdot} + Co^{2+} + H^{+}}, \quad (25)$$

$$\mathrm{2ArC(O)OO^{\cdot} \rightarrow} \text{ molecular products.} \quad (26)$$

In the absence of a catalyst, benzaldehyde is mostly oxidized with disintegration of the aromatic ring by reaction (18). Benzoic acid can be formed directly from hydrotrioxide [reaction (19)] or via reactions (20), (22), and (26). Even if the benzoyl peroxide radical interacts with the aldehyde in this process [reaction (23)], it has no effect on the kinetics because benzaldehyde is consumed in noncatalytic ozonation by the nonchain pathway [Eq. (1)].

In the presence of the catalyst, the chain oxidation is initiated by the interaction of benzaldehyde with trivalent cobalt ($W_{21} > W_{16}$) (see table). Further transformation of the benzoyl radical occurs in accordance with the commonly accepted mechanism [reactions (22)–(26)]. With the fact that $[\mathrm{Co^{3+}}] >> [\mathrm{Co^{2+}}]$ under the experimental conditions taken into account, reaction (25) may play a noticeable role in the catalytic decomposition of perbenzoic acid.

The rate of chain initiation is, naturally, determined by the limiting stage, i.e., the reaction of trivalent cobalt with the aldehyde [reaction (21)]. In the steady reaction mode, the rates of chain initiation and termination are equal:

$$2k_{21}[\mathrm{Co^{3+}}][\mathrm{ArCHO}] = k_{26}[\mathrm{ArC(O)OO^{\cdot}}]^2, \quad (27)$$

$$[\mathrm{ArC(O)OO^{\cdot}}] = (2k_{21}[\mathrm{Co^{3+}}][\mathrm{ArCHO}]/k_{26})^{0.5}. \quad (28)$$

Consequently, the expression for the benzaldehyde consumption rate has the form

$$W = k_{23}[\mathrm{ArCHO}][\mathrm{ArC(O)OO^{\cdot}}] = k_{23}\left(\frac{2k_{21}}{k_{26}}\right)^{0.5}[\mathrm{ArCHO}]^{1.5}[\mathrm{Co^{3+}}]^{0.5}. \quad (29)$$

Because the concentration of trivalent cobalt is proportional to the rate of interaction between ozone and divalent cobalt at a current instant of time ($[\mathrm{Co^{3+}}] \sim k[\mathrm{Co^{2+}}][\mathrm{O_3}]$) [6], it can be concluded that Eq. (29) is in good agreement with the experimental data [Eq. (1)].

EXPERIMENTAL

The oxidation was performed in a thermostated glass column with a porous partition for gas dispersion. The reactor was charged with 0.05 l of acetic acid and calculated amounts of the substrate and catalyst, and the ozone–air mixture was delivered at a rate of 1×10^{-2} l s^{-1}. The ozone concentration in the gas phase was found spectrophotometrically from the absorption at 254–259 nm. The starting substances and oxidation products were determined by gas-liquid chromatography [7].

The rate constants of the interaction between ozone and cobalt(II) acetate were determined by the procedure described in [8]. To find the rate constants of interaction of $\mathrm{Co^{3+}}$ with benzyl alcohol and benzaldehyde, the $\mathrm{Co^{3+}}$ consumption rate was measured. The $\mathrm{Co^{3+}}$ concentration in the reaction mixture was found using the photometric method by measuring the optical density with a KFK-2 instrument (λ = 315 nm, 30-mm cuvette). The rate constants were calculated by the equation

$$-\frac{d[\mathrm{Co^{3+}}]}{d\tau} = k[\mathrm{Co^{3+}}][\mathrm{ArH}].$$

It was assumed in the calculations that the reaction hindrance by divalent cobalt can be neglected at the initial instant of time.

CONCLUSIONS

(1) The yield of benzoic acid is 83.7% in ozonation of benzyl alcohol and 43.2% in ozonation of benzaldehyde.

(2) Comparison of the oxidation products of benzyl alcohol and benzaldehyde shows that benzoic acid accumulates directly in the interaction of the alcohol with ozone, rather than via intermediate formation of the aldehyde.

(3) Use of Co(II) acetate as a catalyst makes it possible to raise the consumption rates of benzyl alcohol and benzaldehyde. The yield of benzoic acid increases to 95.4% in oxidation of the alcohol and to 91.2% in oxidation of the aldehyde.

(4) Results of a study of the oxidation kinetics demonstrate that benzyl alcohol is only consumed by the nonchain mechanism. Benzaldehyde is consumed by the nonchain mechanism in the reaction with ozone, and by the chain mechanism in catalytic ozonation.

REFERENCES

1. Galstyan, G.A., Galstyan, T.M., and Sokolova, S.M., *Kinet. Kataliz*, 1992, vol. 35, no. 4, pp. 779–787.
2. Nangia, P.S. and Benson, S.W., *J. Am. Chem. Soc.*, 1980, vol. 102, no. 9, pp. 3105–3115.
3. Murray, R.W. and Kapton, M.L., *J. Am. Chem. Soc.*, 1976, vol. 91, no. 10, pp. 5358–5367.
4. Denisov, E.T., Mitskevich, N.I., and Agabekov, V.E., *Mekhanizm zhidkofaznogo okisleniya kislorodsoderzhashchikh soedinenii* (Mechanism of Liquid-Phase Oxidation of Oxygen-containing Compounds), Minsk: Nauka i tekhnika, 1975.
5. Galstyan, G.A., Galstyan, T.M., and Mikulenko, L.I., *Kinet. Kataliz*, 1994, vol. 35, no. 2, pp. 255–260.
6. Galstyan, G.A., *Reactions of Alkylbenzenes and Their Oxygen Derivatives with Ozone,* Doctoral Dissertation, 1992.
7. Galstyan, G.A., Potapenko, E.V., Pluzhnik, I.M., et al., *Regional Conf. on Ozone Generation and Application to Water and Waster Treatment*, Moscow, 1998, pp. 667–694.
8. Razumovskii, S.D. and Zaikov, G.E., *Ozon i ego reaktsii s organicheskimi soedineniyami* (Ozone and Its Reactions with Organic Compounds), Moscow: Nauka, 1974.