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Catalytic Ozonation of Alkylnaphthalenes in Acetic Acid

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Abstract—The oxidation of alkylnaphthalenes with ozone in acetic acid in the presence of cobalt(II) acetate is reported. Under the catalytic conditions, the ozonolysis of the aromatic system can be prevented to a considerable extent and the reaction can be directed toward the oxidation of the alkyl group. The kinetics of the main steps of the process is reported, and the mechanism of redox catalysis is presented.

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The low-temperature oxidation of alkylbenzenes with ozone in acetic acid in the presence of variable-valence metal salts is a promising method for the synthesis of various aromatic carboxylic acids [1]. The possibility of employing of such a catalytic system in the oxidation of alkylnaphthalenes has received little attention [2]. To gain about a deeper insight into the reactions occurring in the ozone–alkylnaphthalene–cobalt(II) acetate system, we studied the oxidation of 1-methyl-, 2-methyl-, and 2-ethylnaphthalenes with ozone in glacial acetic acid and in its mixture with trichloroacetic acid.

EXPERIMENTAL

Oxidation was carried out in a temperature-controlled glass column with a porous membrane for gas dispersion. Acetic acid (0.05 l), the appropriate amount of the substrate, and the catalyst were loaded into the column. An ozone–air mixture was fed at a rate of 1×10^{-2} l/s. The ozone concentration in the gas phase was determined spectrophotometrically as absorbance at 254–259 nm. The Co^{3+} concentration in the reaction mixture was determined photocolorimetrically by measuring absorbance with a KFK-2 instrument (315 nm, 30-mm cell). Alkylnaphthalenes and the products of their oxidation in the reaction mixture were determined via a described procedure [3].

Table 1. Oxidation of alkylnaphthalenes with ozone at 20°C ($[ArCH_2R] = 0.3$ mol/l, $[O_3] = 4 \times 10^{-4}$ mol/l)

Starting compounds	Products	Yield, %
1-Methylnaphthalene	Peroxide compounds	81.4
	1-Naphthaldehyde	traces
	1-Naphthoic acid	2.5
2-Methylnaphthalene	Peroxide compounds	84.6
	2-Naphthoic acid	1.6
	2-Methyl-1,4-naphthoquinone	traces
2-Ethylnaphthalen	Peroxide compounds	82.5
	2-Acetylnaphthalene	2.3
	2-Naphthoic acid	–

The rate constants for the reaction of ozone with alkylnaphthalenes and cobalt(II) acetate were calculated by a described procedure [4]. The kinetics of substrate oxidation with Co^{3+} was studied as a decrease in the Co^{3+} concentration. Kinetic curves were fitted to a polynomial of degree n. The first derivative of this polynomial at the $\tau = 0$ point was accepted to be the initial reaction rate.

RESULTS AND DISCUSSION

The noncatalytic reactions of alkylnaphthalenes with ozone in acetic acid mainly yield peroxide compounds, which are products of destruction of the aromatic moiety of the substrate (Table 1). Peroxides are resistant to ozone and are highly soluble in acetone. They interact with potassium iodide and hydroxide. Their reaction with potassium iodide produces molecular iodine in an amount equivalent to two peroxide groups, indicating that only one aromatic ring undergoes destruction. The corresponding naphthaldehydes and naphthoic acids were identified among the products of oxidation of the side chain of methylnaphthalenes, and 2-acetylnaphthalene was found in the case of 2-ethylnaphthalene. Quinones were detected only in the ozonation of 2-methylnaphthalene.

Use of cobalt acetate makes it possible to substantially reduce aromatic ring destruction and to increase the content of the oxidation products of the alkyl group of naphthalenes (Tables 2, 3). As the ozone–air mixture is fed into the reactor, within a few minutes the pink color of the solution characteristic of the reduced form of cobalt changes to the dark green color characteristic of the oxidized form of the metal. The steady-state concentration of Co^{3+} is established within 10–15 min at a level of 0.13 mol/l and then remains unchanged. After the ozone feed is shut off, the oxidation of alkylnaphthalenes ceases and Co^{3+} turns into Co^{2+}.

The maximum alkyl group oxidation selectivity is observed at 90°C and an alkylnaphthalene : cobalt ratio of about 2 : 1 (the reaction mixture is resinified at a higher catalyst content). Under these conditions, 1- and 2-methylnaphthalenes are oxidized to naphthoic acids in 66.4 and 45.4% yields, respectively (Table 2). Naphthaldehyde forms in a considerably smaller amount, and its concentration passes through a maximum (Fig. 1). The catalytic ozonation of 2-ethylnaphthalene is accompanied by the formation of 2-acetylnaphthalene and 2-naphthoic acid. A The main product of alkyl group oxidation at 20°C is a ketone, and the 2-naphthoic acid content of the reaction products increases with increasing temperature (Table 3).

It was shown earlier for toluene [5] that the catalytic activity of cobalt increases to a considerable extent if ozonation is carried out in the presence of strong organic acids. Use of trichloroacetic acid in the catalytic oxidation of alkylnaphthalenes makes it possible to carry out the reaction with high selectivity at 60°C (Tables 2, 3). As in the case of ozonation in the absence of a strong acid, Co^{3+} accumulates in the system, and its steady-state concentration is 0.12 mol/l. Once the ozone feed is shut off, the oxidation of alkylnaphthalenes ceases.

These results suggest the following scheme of alkylnaphthalene oxidation:

$$ArCH_2R + O_3 \rightarrow \text{peroxides}, \qquad \text{(I)}$$

$$Co^{2+} + O_3 \xrightarrow{H^+} Co^{3+} + HO^{\bullet} + O_2, \qquad \text{(II)}$$

$$ArCH_2R + Co^{3+} \rightarrow ArCHR^{\bullet} + Co^{2+} + H^+, \qquad \text{(III)}$$

where $R = H$ or CH_3.

Therefore, selective oxidation is ensured when $W_{III} > W_I$ provided that $W_{II} > W_I$.

To estimate the contribution from the reactions occurring in the $ArCH_2R$–O_3–cobalt(II) acetate system, we studied the kinetics of the reactions of ozone with alkylnaphthalenes and the catalyst and of Co^{3+} with alkylnaphthalenes.

The rate of the reaction of ozone with alkylnaphthalenes and cobalt(II) acetate obeys the bimolecular law (Eqs. (1), (2)) and depends linearly on the concentrations of the reactants (Fig. 2). Addition of trichloroacetic acid exerts no effect on the order of the reactions but decreases the rate constant (Table 4).

$$-\frac{d[O_3]}{d\tau} = k[O_3][ArCH_2R], \qquad (1)$$

Table 2. Yield of naphthoic acid for the exhaustive oxidation of methylnaphthalenes with ozone in the presence of cobalt(II) acetate ($[ArCH_2R] = 0.3$ mol/l, $[O_3] = 4 \times 10^{-4}$ mol/l)

Temperature, °C	$[Co^{2+}]$, mol/l	$[CCl_3COOH]$, mol/l	Yield, %
1-Methylnaphthalene			
20	–	–	12.3
50	0.14	–	26.1
70	0.14	–	45.8
90	0.14	–	66.4
100	0.14	–	60.8
90	0.06	–	35.4
90	0.10	–	52.7
20	0.14	1.5	52.3
40	0.14	1.5	63.2
60	0.14	1.5	71.8
80	0.14	1.5	63.3
2-Methylnaphthalene			
40	0.14	–	13.5
70	0.14	–	23.8
90	0.14	–	45.4
20	0.14	1.5	36.1
40	0.14	1.5	42.6
60	0.14	1.5	51.2

Table 3. Yield of products of the total oxidation of 2-ethylnaphthalene with ozone in the presence of cobalt(II) acetate ($[ArCH_2R] = 0.3$ mol/l, $[O_3] = 4 \times 10^{-4}$ mol/l)

Temperature, °C	$[Co^{2+}]$, mol/l	$[CCl_3COOH]$, mol/l	Yield, %	
			2-acetylnaphthalene	2-naphthoic acid
20	0.14	–	18.4	2.3
50	0.14	–	34.4	16.4
70	0.14	–	29.2	32.6
90	0.14	–	24.5	46.6
100	0.14	–	18.7	47.4
90	0.06	–	12.5	29.8
90	0.10	–	18.3	42.1
20	0.14	1.5	52.8	4.6
40	0.14	1.5	46.3	19.4
60	0.14	1.5	41.1	34.3
80	0.14	1.5	23.8	42.1

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

The oxidation of 1-methyl- and 2-ethylnaphthalenes with Co^{3+} in nitrogen yields 1-methylmethylol and 1-(2-naphthyl)ethanol acetates, and the corresponding alcohols, aldehyde, and ketone form in smaller amounts. The reaction of trivalent cobalt with 2-methylnaphthalene affords 1-acetoxy-2-methylnaphthalene along with the products of methyl group oxidation (Table 5). This accounts for the lower yield of 2-naphthoic acid in catalytic ozonation.

Investigation of the kinetics of the reactions of alkylnaphthalenes with trivalent cobalt showed that, in the absence of trichloroacetic acid, as in alkylbenzene oxidation [6], the reactions are inhibited (Fig. 3, curve *1*) due to the accumulation of Co^{2+}. The rate of Co^{3+} reduction is directly proportional to the concentrations of Co^{3+} and $ArCH_2R$ and is inversely proportional to the Co^{2+} concentration (Eq. (3)) (Fig. 4a). It was assumed in the calculation of rate constants that the inhibition of the reaction of the reduced form of cobalt at the initial moment can be neglected.

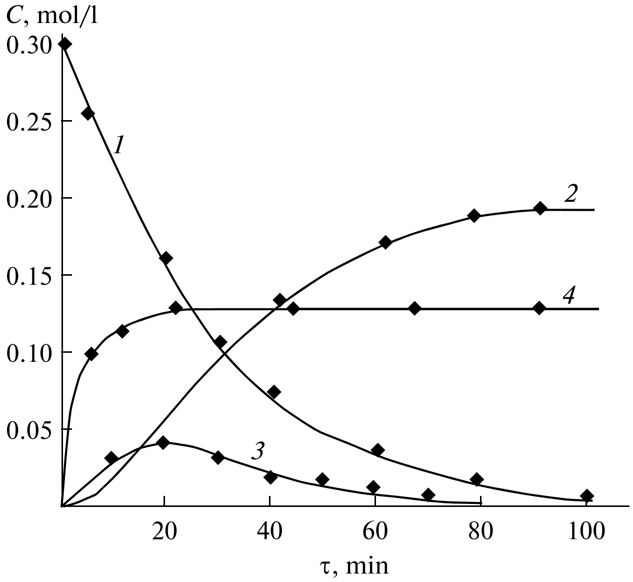

Fig. 1. Oxidation of 1-methylnaphthalene with ozone in the presence of Co^{2+} acetate at 90°C: (*1*) 1-methylnaphthalene, (*2*) 1-naphthoic acid, (*3*) 1-naphthaldehyde, and (*4*) Co^{3+} ($[ArCH_2R] = 0.3$ mol/l, $[O_3] = 4 \times 10^{-4}$ mol/l, $[Co^{2+}] = 0.1$ mol/l.

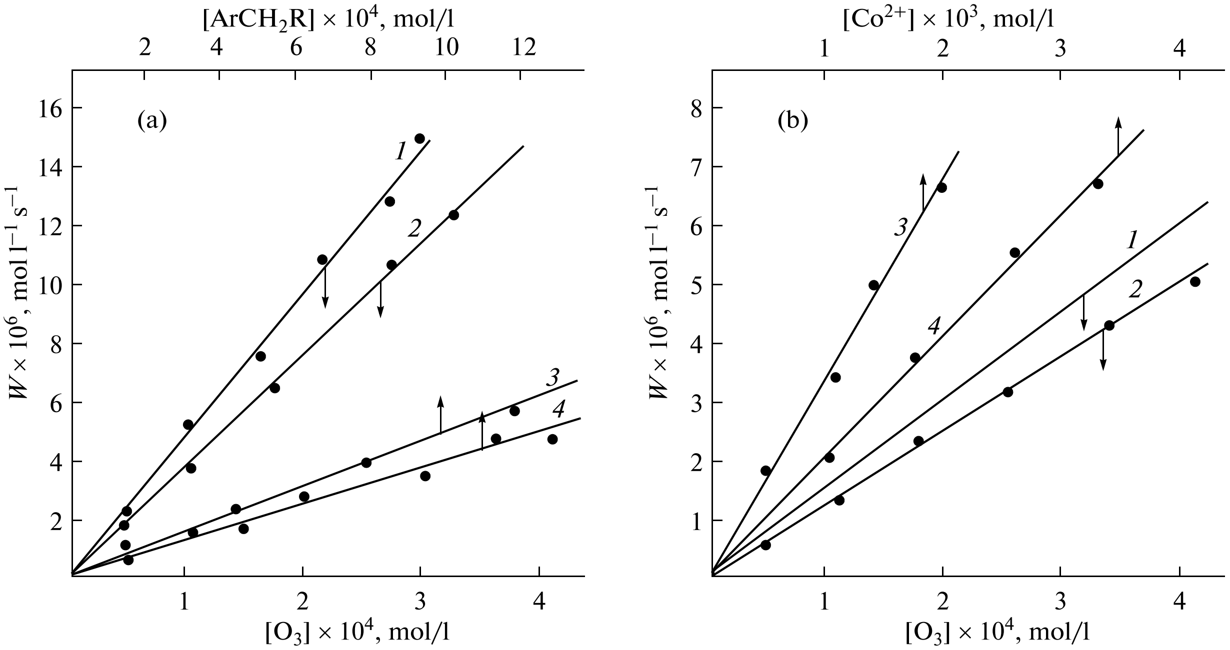

Fig. 2. Dependences of the initial rate of oxygen disappearance (a) in the reaction with 1-methylnaphthalene on $[O_3]$ at $[ArCH_2R] = 6 \times 10^{-4}$ mol/l (*1*) in the absence and (*2*) in the presence of CCl_3COOH and on $[ArCH_2R]$ at $[O_3] = 4 \times 10^{-4}$ mol/l (*3*) in the absence and (*4*) in the presence of CCl_3COOH; (b) in the reaction with Co^{2+} on $[O_3]$ at $[Co^{2+}] = 3 \times 10^{-3}$ mol/l (*1*) in the absence and (*2*) in the presence of CCl_3COOH and on $[Co^{2+}]$ at $[O_3] = 4 \times 10^{-4}$ mol/l (*3*) in the absence and (*4*) in the presence of CCl_3COOH.

$$-\frac{d[Co^{3+}]}{d\tau} = k[ArCH_2R][Co^{3+}][Co^{2+}]^{-1}. \qquad (3)$$

The reduction of Co^{3+} in the presence of CCl_3COOH revealed of the following regularities. Firstly, there is no pronounced inhibition of the process (Fig. 3, curves *2–4*). Secondly, the rate of Co^{3+} disappearance depends on the concentration of the strong acid and, when the acid concentration is high, the activity of Co^{3+} increases in such a way that the

Table 4. Kinetic parameters for the reactions of ozone with alkylnaphthalenes in the presence of cobalt(II) acetate and for the reactions of Co^{3+} with alkylnaphthalenes at 20°C

Reaction	$[CCl_3COOH]$, mol/l	k, L mol^{-1} s^{-1}	E, kJ/mol
1-Methylnaphthalene + O_3	– 1.5	79.6 64.3	21.5 22.3
2-Methylnaphthalene + O_3	– 1.5	98.1 72.3	22.7 22.9
2-Ethylnaphthalene + O_3	– 1.5	93.4 81.1	22.1 22.8
$Co^{2+} + O_3$	– 1.5	9.3×10^2 5.2×10^2	34.9 26.7
1-Methylnaphthalene + Co^{3+}	– 1.5	3.1×10^{-2} 0.23	56.1 39.6
2-Methylnaphthalene + Co^{3+}	– 1.5	2.4×10^{-2} 0.17	52.1 36.5
2-Ethylnaphthalene + Co^{3+}	– 1.5	4.6×10^{-2} 0.31	57.2 42.3

Table 5. Oxidation of alkylnaphthalenes with Co^{3+} in nitrogen at 20°C ($[ArCH_2R] = 0.1$ mol/l, $[Co^{3+}] = 0.25$ mol/l)

Compound	$[CCl_3COOH]$, mol/l	Conversion, %	Yield of products (based on reacted alkylnaphthalene), %			
			I	II	III	IV
1-Methylnaphthalene	– 1.5	15 64	– –	74.2 80.4	12.3 10.2	4.8 2.3
2-Methylnaphthalene	– 1.5	12 53	19.4 21.2	58.3 61.8	10.5 5.3	3.7 3.1
2-Ethylnaphthalene	– 1.5	18 71	– –	76.2 81.3	12.2 7.2	3.5 2.1

Note: I are ring acylation products, II is alcohol acetate, III is alcohol, and IV is aldehyde or ketone.

oxidation of the solvent becomes a competing process (Fig. 3, curve *5*). The increase in the reactivity of the oxidized form of cobalt can be due to the destruction of the $[Co_3O(OAc)_6(AcOH)_3]OAc$ cluster complexes, the formation of monomeric species, and the enhancement of the electrophilicity of the metal atom [7]. The rate of Co^{3+} disappearance is described by a second-order kinetic equation (Eq. (4)) (Fig. 4b):

$$-\frac{d[Co^{3+}]}{d\tau} = k[ArCH_2R][Co^{3+}]. \qquad (4)$$

An analysis of the results obtained (Table 4) shows that, in the reaction mixture containing alkylnaphthalene and cobalt(II) acetate, regardless of the presence of an acidic activator, ozone reacts primarily with the catalyst (reaction (II)) and thus decreases the probability of the direct attack of ozone on the hydrocarbon (reaction (I)) and the substrate is oxidized via its reaction with Co^{3+}. For example, for 2-ethylnaphthalene in the presence of trichloroacetic acid (1.5 mol/l) at 60°C $W_{II}/W_I = 3.6$ ($k_I = 249.6$ L mol^{-1} s^{-1}, $k_{II} = 19.4 \times 10^2$ L mol^{-1} s^{-1}, $[Co^{2+}] = 0.14$ mol/l, $[ArCH_2R] = 0.3$ mol/l) and $W_{III}/W_I = 3.0$ ($k_{III} = 2.5$, $[Co^{3+}] = 0.12$ mol/l, $[O_3] = 4 \times 10^{-4}$ mol/l).

Thus, our studies demonstrate that the oxidation of the side chain is the main pathway of the ozonation of alkylnaphthalenes in acetic acid in the presence of Co^{2+} acetate. The role of ozone is to generate the oxi-

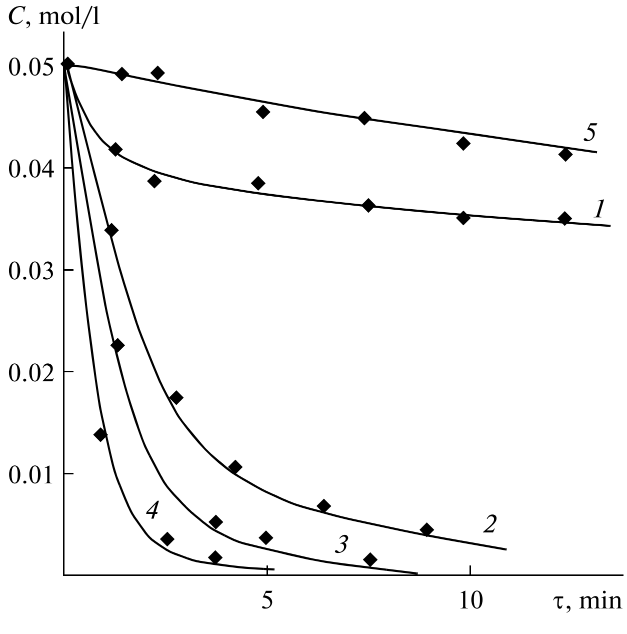

Fig. 3. Kinetics of Co^{3+} disappearance in the reaction with 2-ethylnaphthalene in nitrogen at various concentrations of CCl_3COOH, mol/l: (*1*) 0, (*2*) 1.0; (*3*) 1.5, (*4*) 2.5, and (*5*) 2.5 (in the absence of 2-ethylnaphthalene). Temperature 20°C, $[ArCH_2R] = 0.1$ mol/l.

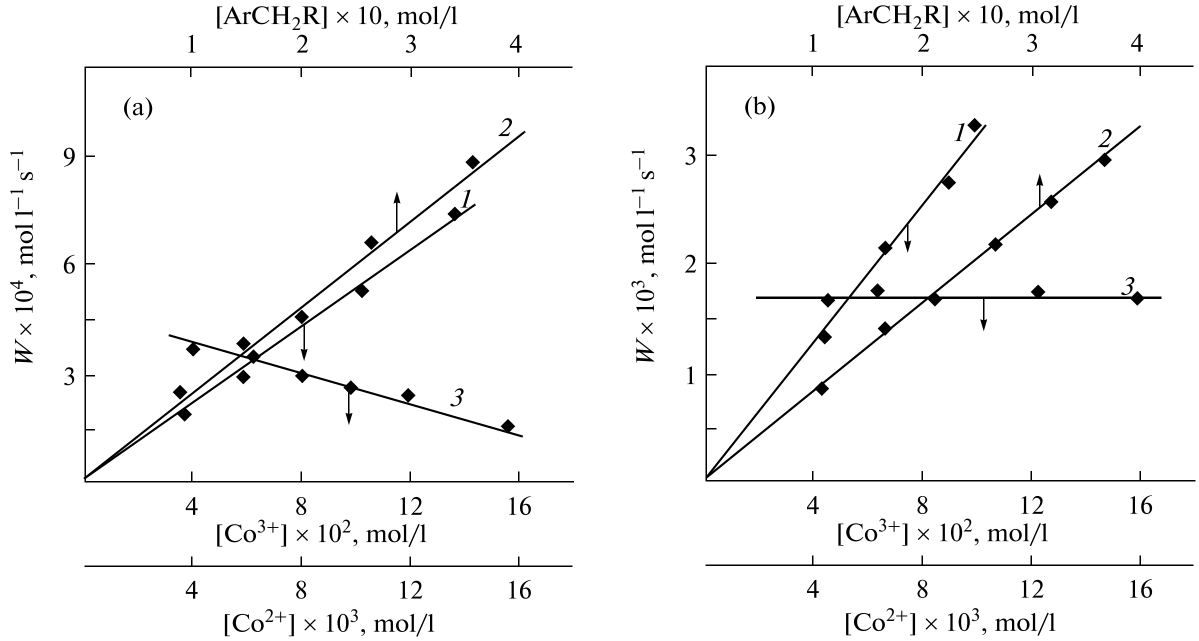

Fig. 4. Dependences of the initial rate of Co^{3+} disappearance in the reaction with 2-methylnaphthalene at 20°C: (a) in the absence of CCl_3COOH on (*1*) [Co^{3+}] at [$ArCH_2R$] = 0.2 mol/l, (*2*) on [$ArCH_2R$] at [Co^{3+}] = 0.1 mol/l, and (*3*) om [Co^{2+}] at [$ArCH_2R$] = 0.2 mol/l and [Co^{3+}] = 0.1 mol/l; (b) in the presence of CCl_3COOH (1.5 mol/l) (*1*) on [Co^{3+}] at [$ArCH_2R$] = 0.2 mol/l, (*2*) on [$ArCH_2R$] at [Co^{3+}] = 0.05 mol/l, and (*3*) on [Co^{2+}] at [$ArCH_2R$] = 0.2 mol/l and [Co^{3+}] = 0.05 mol/l.

dized form of cobalt capable of initiating the selective oxidation of the alkyl group. Addition of trichloroacetic acid enhances the catalytic activity of cobalt.

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