ISSN 0965-5441, Petroleum Chemistry, 2008, Vol. 48, No. 2, pp. 118–122. © Pleiades Publishing, Ltd., 2008.
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Reactions of *o*-Cresol with Ozone in Acetic Anhydride

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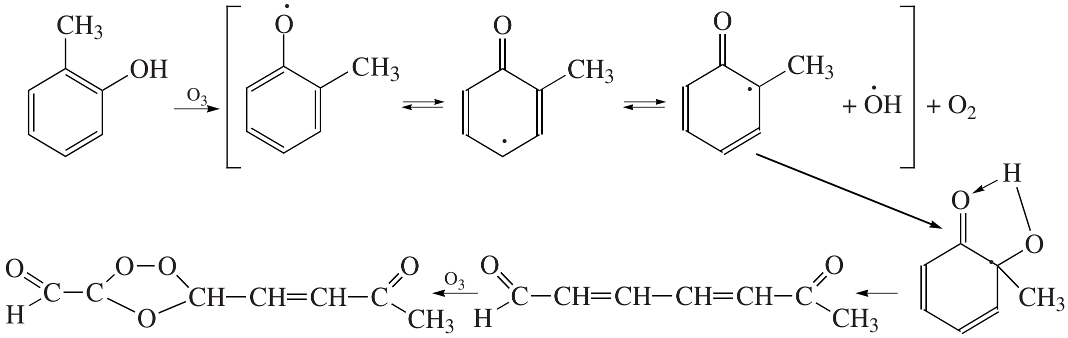
Received December 3, 2006

Abstract—The kinetics of *o*-cresol oxidation with ozone in acetic anhydride was studied. It was shown that *o*-cresol was acylated in acetic anhydride to give *o*-cresyl acetate. Ozone attacks the C=C bonds of the aromatic ring of *o*-cresyl acetate to give unsaturated peroxide compounds. The composition of the oxidation products alters when the ozonation is carried out in the presence of catalytic amounts of sulfuric acid. Along with the products of the destructive oxidation of the aromatic ring, the methyl group oxidation products appeared as the acyl derivatives *o*-acetoxybenzyl alcohol and *o*-acetoxybenzaldehyde, a form that is more stable toward the action of ozone (10%). The addition of manganese(II) acetate to the reaction mixture increases the methyl group oxidation selectivity to 75%. The mechanism of the ozone reaction with *o*-cresol in acetic anhydride that explains the obtained results is discussed.

DOI: 10.1134/S0965544108020072

It is known that ozone first attacks *o*-cresol in a CCl_4 solution at the H atom of the hydroxyl group yielding phenoxyl radicals with the subsequent addition of the hydroxyl radical, aromatic-cycle opening, and the formation of carbonyl compounds and ozonides, according to the scheme [1]



According to Razumovskii et al. [2], this mechanism provides for a substantial gain in the reaction rate ($k = 9.8 \times 10^2$ l mol^{-1} s, $T = 20°C$), because the first step of the reaction, the complex formation, requires a low energy, and the second step, the ozone addition to the C=C bond, occurs as a unimolecular reaction with a high preexponential factor. The products of methyl group oxidation with conservation of the aromatic structure were not found under these conditions.

In this work, we examined the possibility of ozone oxidation of methylphenols at the methyl group to corresponding aromatic products using, as an example, the ozone reaction with *o*-cresol in acetic anhydride.

EXPERIMENTAL

Acetic anhydride and manganese(II) acetate (analytical grade) were used without additional purification. Chromatographically pure *o*-cresol was obtained by multiple recrystallization from water.

The reaction was carried out in a glass column with a porous membrane at temperatures of 5–60°C. Acetic anhydride (10 ml), *o*-cresol (0.4 mol l^{-1}), and the catalyst were loaded into the column and air was supplied to agitate the reaction mixture. Over 20 min, the column was thermostated, and an ozone–air mixture with an ozone concentration of 4×10^{-4} mol l^{-1} was bubbled at a flow rate of 30 l/h. The ozone concentration in the gas phase was determined spectrophotometrically by measuring absorbance at 254–290 nm. The aromatic oxidation products were identified and determined in the solution by means of GLC (an LKhM-80 chromatograph with a flame-ionization detector, a 3 m × 4 mm column packed with Inerton AW-DMCS coated with the SE-30 (5% of support mass) stationary phase) at an evaporator temperature of 250°C; a column temperature of 190°C; and carrier gas (nitrogen), hydrogen, and air flow rates of 1.8, 1.8, and 18 l/h, respectively. *p*-Nitrochlorobenzene was the internal standard. The concentration of the peroxide products was determined by iodometric titration. The effective rate constants for the reaction of ozone with *o*-cresol and its oxidation products were determined spectrophotometrically according to the procedure described in [3].

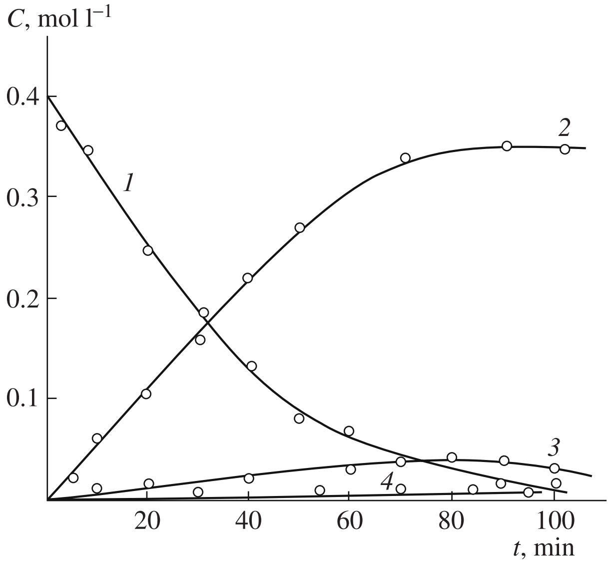
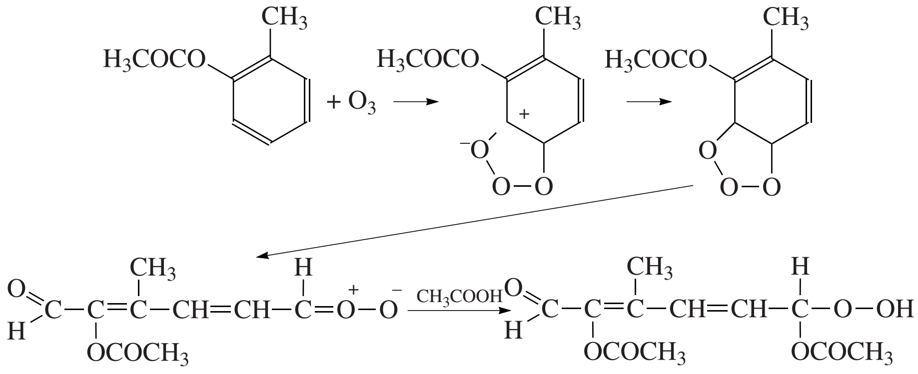


Fig. 1. The kinetics of *o*-cresyl acetate oxidation with ozone in acetic anhydride in the presence of sulfuric acid at 20°C. $[ArCH_3]_0 = 0.4$; $[H_2SO_4]_0 = 1.2$ mol l^{-1}, and an ozone–air mixture space velocity of 0.37 s^{-1}: (*1*) *o*-cresyl acetate, (*2*) peroxides, (*3*) *o*-acetoxybenzyl acetate, and (*4*) *o*-acetoxybenzylidene diacetate.

RESULTS AND DISCUSSION

We found, in this study, that *o*-cresol is acylated in acetic anhydride to give *o*-cresyl acetate and the direction of the primary attack of ozone is different in this medium. Ozone interacts predominantly with the C=C bonds of the aromatic ring to give ozonides and, then, unsaturated peroxide compounds. The change in the mechanism of ozonation manifests itself in a decrease in the reaction rate constant by three orders of magnitude ($k = 0.58$ l mol^{-1}s^{-1}, 20°C).

The peroxides isolated after solvent removal by distillation in a vacuum (5 mm Hg) are an oily, viscous, light yellow liquid, which dissolves well in acetic acid and acetic anhydride, but is sparingly soluble in CCl_4. The ozone resistance of the peroxides and the stoichiometric coefficient found for the reaction ($n = 1.1$) suggest that they are the products of the destructive ozonolysis of the aromatic ring and, structurally, are linear monomers [4], whose formation is described by the following scheme:



The monomeric structure of the peroxides is confirmed by their reaction with potassium iodide: the reaction takes an hour to be completed, with molecular iodine being evolved in the amount equivalent to one peroxide group. This result does not contradict the literature data [5], according to which it is the hydroperoxide groups that readily react with KI.

The composition of the ozonation products of *o*-cresyl acetate changes when oxidation is carried out in the presence of sulfuric acid. In addition to the products of the aromatic ring degradation, small amounts (10%) of the products of the incomplete oxidation of the substrate methyl group are accumulated in the form of acylated derivatives: *o*-acetoxybenzyl acetate and *o*-acetoxybenzylidene diacetate (Fig. 1). A comparison of the values found for the effective rate constants of the ozone reaction with *o*-cresyl acetate and its oxidation products (Table 1) leads to the conclusion that *o*-acetoxybenzyl alcohol and *o*-acetoxybenzaldehyde formed in the presence of sulfuric acid are subjected to

Table 1. Rate constants of ozone reactions with *o*-cresyl acetate and its oxidation products in acetic anhydride at 20°C, $[O_3]^{gas} = 2.4 \times 10^{-5}$ mol l^{-1}

Compound	$[ArH] \times 10^2$, mol l^{-1}	$k \pm 10\%$, l mol^{-1} s^{-1}
o-Cresyl acetate	2.2–4.1	0.58
o-Acetoxybenzyl alcohol	1.1–1.5	20.16
o-Acetoxybenzaldehyde	1.1–1.5	22.50
o-Acetoxybenzyl acetate	0.8–0.9	0.25
o-Acetoxybenzylidene diacetate	0.5–0.8	0.33

Table 2. Rate orders of the reaction of ozone with *o*-cresyl acetate in reactants at different temperatures

T, °C	Reaction order	
	in ozone	in *o*-cresyl acetate
10	0.99	1.01
20	1.02	1.00
30	1.11	0.88
40	1.33	0.72
60	1.47	0.56

acylation [6] yielding *o*-acetoxybenzyl acetate and *o*-acetoxybenzylidene diacetate, compounds that are more stable to ozone oxidation.

Thus, the experimental data demonstrate that there are two routes of ozone consumption during the ozonation of *o*-cresyl acetate in acetic anhydride: by the aromatic ring (reaction (1)) and by the methyl group (reaction (2)):

$$\mathrm{AcOArCH_3} + \mathrm{O_3} \longrightarrow \text{Ozonolysis products}, \quad (1)$$

$$\mathrm{AcOArCH_3} + \mathrm{O_3} \longrightarrow \mathrm{AcOAr\dot{C}H_2} + \mathrm{HO^\bullet} + \mathrm{O_2}, \quad (2)$$

with the oxidative degradation of the aromatic ring (reaction (1)) being the predominant reaction. The overall selectivity of the methyl group oxidation does not exceed 10% (Fig. 1).

To obtain more complete information about the mechanism of the ozone consumption in its reaction with *o*-cresyl acetate, the kinetics of the reaction was examined.

The reaction of *o*-cresyl acetate with ozone has the first order with respect to each reactant (Table 2) at temperatures below 20°C, and the rate equation for the reaction has the form

$$w_{\mathrm{O_3}} = k_{\mathrm{eff}}[\mathrm{O_3}]_0[\mathrm{ArCH_3}]_0. \quad (3)$$

At a temperature above 20°C, the first order in the reactants does not hold (Table 2) and the effective rate constant for the ozone consumption in the reaction with *o*-cresyl acetate depends on their initial concentration ratio (Fig. 2)

$$k_{\mathrm{eff}} = k' + k''\left(\sqrt{[\mathrm{O_3}]_0/[\mathrm{ArCH_3}]_0}\right), \quad (4)$$

where k' and k'' are the experimental parameters depending on the temperature.

The ozone uptake rate under these conditions is described by the equation

$$w_{\mathrm{O_3}} = k'[\mathrm{O_3}]_0[\mathrm{ArCH_3}]_0 + k''[\mathrm{O_3}]_0^{1.5}[\mathrm{ArCH_3}]_0^{0.5}. \quad (5)$$

The first term in Eq. (5) describes the ozone consumption according to the radical–ion nonchain mechanism in the primary reaction with *o*-cresyl acetate ($w'_{\mathrm{O_3}} = k'[\mathrm{O_3}]_0[\mathrm{ArCH_3}]_0$) (reactions (1) and (2)), and the second term describes the ozone consumption via the chain mechanism ($w''_{\mathrm{O_3}} = k''[\mathrm{O_3}]_0^{1.5}[\mathrm{ArCH_3}]_0^{0.5}$ [7]). This means that the deviation from the first order at temperatures above 20°C can be due to the appearance of the chain route of the ozone consumption.

An analysis of the possible routes of the ozone reactions via the chain mechanism show that, as in the case of toluene ozonation [8], the chain consumption of ozone in the reaction with the products of the thermal decomposition of peroxides, e.g., aliphatic aldehydes [9], is the most likely process:

$$\mathrm{Oz} \xrightarrow{t} \mathrm{RCHO} \quad (6)$$

$$\mathrm{RCHO} + \mathrm{O_3} \longrightarrow \mathrm{R\dot{C}(O)} + \mathrm{HO^\bullet} + \mathrm{O_2}, \quad (7)$$

$$\mathrm{R\dot{C}(O)} + \mathrm{O_2} \longrightarrow \mathrm{RC(O)\dot{O}_2} \quad (8)$$

$$\mathrm{R_1^\bullet} + \mathrm{O_2} \longrightarrow \mathrm{R_1O_2^\bullet} \quad (9)$$

$$\mathrm{RC(O)O_2^\bullet} + \mathrm{O_3} \longrightarrow \mathrm{R_1^\bullet} + \mathrm{CO_2} + 2\mathrm{O_2} \quad (10)$$

$$\mathrm{R_1O_2^\bullet} + \mathrm{O_3} \longrightarrow \mathrm{R_1O^\bullet} + 2\mathrm{O_2} \quad (11)$$

$$\mathrm{R_1O^\bullet} + \mathrm{O_3} \longrightarrow \mathrm{R_1O_2^\bullet} + \mathrm{O_2} \quad (12)$$

$$2\mathrm{R_1O_2^\bullet} \longrightarrow \text{Products}. \quad (13)$$

According to the given scheme, the chain consumption of ozone proceeds via the alternation of reactions (11) and (12), which are, in essence, chain propagation reactions. This scheme is supported by the finding that the temperature at which the chain consumption of ozone becomes noticeable coincides with the onset temperature of the thermal degradation of peroxides (20°C) (Fig. 3).

The ozone oxidation selectivity for the methyl group increases significantly (75%) when *o*-cresyl acetate is ozonated in acetic anhydride in the presence of sulfuric acid and manganese(II) acetate (Fig. 4). The presence

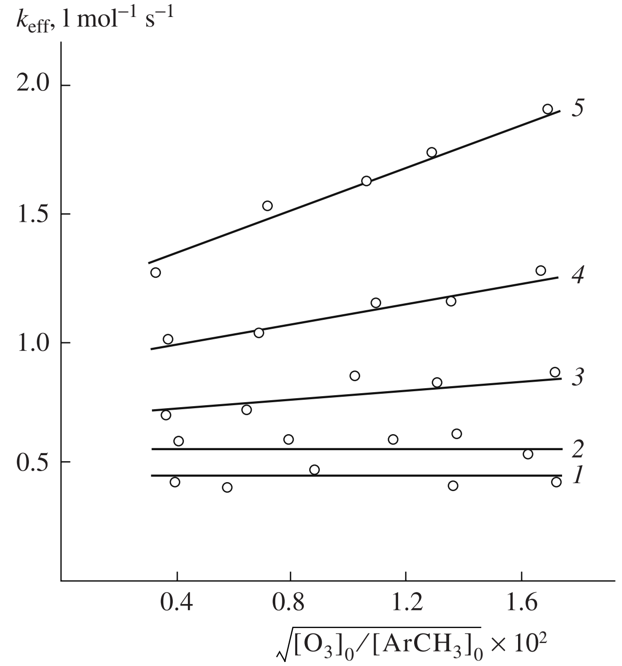


Fig. 2. Dependence of the effective rate constant for *o*-cresyl acetate oxidation with ozone on the concentration of the reactants at temperatures of (*1*) 10, (*2*) 20, (3) 30, (*4*) 40, and (5) 60°C.

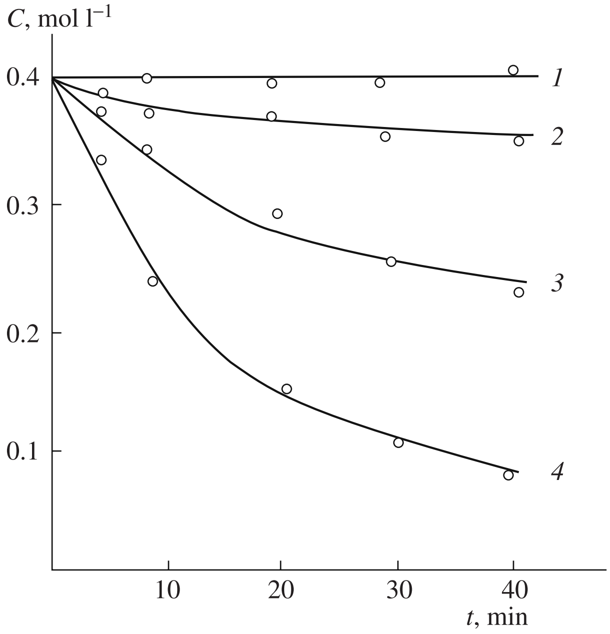


Fig. 3. Rate curves for the thermal degradation of *o*-cresyl acetate peroxides at temperatures of (*1*) 20, (*2*) 30, (*3*) 40, and (*4*) 60°C.

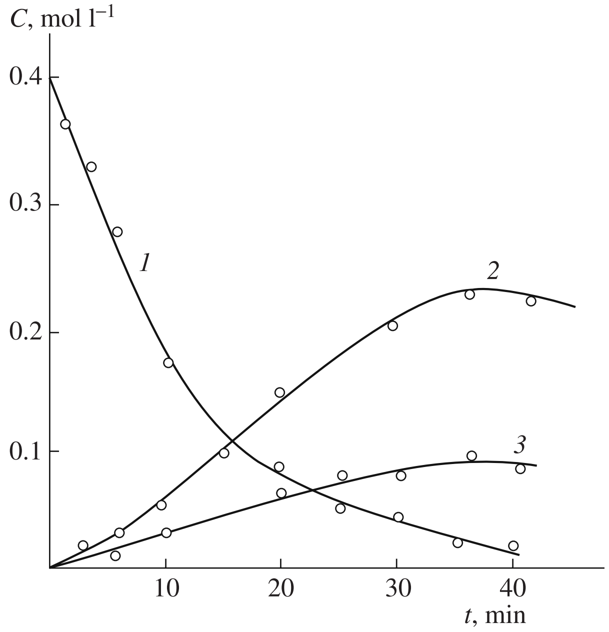
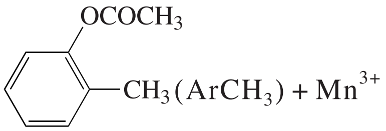


Fig. 4. The kinetics of *o*-cresyl acetate oxidation with ozone in acetic anhydride in the presence of manganese(II) acetate at 5°C. $[ArCH_3]_0 = 0.4$; $[H_2SO_4]_0 = 1.2$; $[Mn(OAc)_2]_0 = 0.14$ mol l^{-1}; and an ozone–air mixture space velocity of 0.37 s^{-1}: (*1*) *o*-cresyl acetate, (*2*) *o*-acetoxybenzyl acetate, and (*3*) *o*-acetoxybenzylidene diacetate.

of Mn(II) results in the fact that ozone interacts mainly with Mn^{2+} to give active species Mn^{3+} (reaction (14), $k \approx 5 \times 10^3$ l mol^{-1} s^{-1} [10]), rather than with the substrate (reactions (1) and (2)):

$$Mn^{2+} + O_3 + H^+ \longrightarrow Mn^{3+} + O_2 + HO^-. \qquad (14)$$

These active species possess a higher substrate selectivity for methyl group oxidation (reactions (15)–(19)) than ozone [7]:



$$o\text{-}(CH_3COO)C_6H_4\text{—}CH_3\,(ArCH_3) + Mn^{3+} \qquad (15)$$

$$\longrightarrow Ar\dot{C}H_2 + Mn^{2+} + H^+$$

$$Ar\dot{C}H_2 + O_2 \longrightarrow ArCH_2O_2^{\bullet} \qquad (16)$$

$$2ArCH_2O_2^{\bullet} + Mn^{2+} + H^+ \longrightarrow ArCH_2O_2H + Mn^{3+} \qquad (17)$$

$$ArCH_2O_2H + Mn^{2+} \longrightarrow ArCH_2O^- + Mn^{3+} + HO^{\bullet} \qquad (18)$$

$$ArCH_2O^- + CH_3\overset{+}{C}{=}O \longrightarrow ArCH_2OCOCH_3 \qquad (19)$$

The mechanism of formation of the acylium cation is considered in [6].

Thus, it was shown that *o*-cresol in acetic anhydride is acylated to give *o*-cresol acetate. Ozone attacks the C=C bonds of the *o*-cresyl acetate aromatic ring to give unsaturated peroxide compounds. The product composition changes when ozonation is run in the presence of sulfuric acid in catalytic amounts. In addition to the products of the destructive oxidation of the aromatic ring, the products of oxidation at the methyl group were identified in the acylated form as *o*-acetoxybenzyl alcohol and *o*-acetoxybenzaldehyde (10%), which are more stable to ozonation. The introduction of manganese(II) acetate into the reaction zone enhances the oxidation selectivity for the methyl group (75%). The oxidation mechanism explaining the results is considered.

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