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Kinetics and Mechanism of the Catalytic Reaction between Ozone and *para*-Cresol in Acetic Anhydride

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Abstract—The kinetics of the liquid-phase catalytic oxidation of *para*-cresol with an ozone–air mixture in the presence of manganese(II) acetate is reported. In an acetic anhydride medium, *para*-cresol reacts with ozone as *para*-cresyl acetate, which is formed at the instant the solution to be oxidized is prepared. Under these conditions, the major oxidation products are *para*-acetoxybenzyl acetate (63.5%) and *para*-acetoxybenzylidene diacetate (13.7%). The effect of the manganese(II) acetate concentration on the traction selectivity with respect to the oxidation of the methyl group of the substrate is reported. A mechanism consistent with the experimental data available on this catalytic redox reaction is suggested.

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INTRODUCTION

It was shown earlier [1] that, in an acetic anhydride medium containing sulfuric acid, *para*-cresol undergoes acylation and reacts with ozone in the form of *para*-cresyl acetate. The substrate is mainly oxidized at its aromatic ring, whereas the methyl group oxidation selectivity is rather low. *para*-Acetoxybenzyl acetate (9.5%) and *para*-acetoxybenzylidene diacetate (3.5%) were identified as the oxidation products retaining their aromatic structure intact. They result from the acylation of *para*-acetoxybenzyl alcohol and *para*-acetoxybenzaldehyde.

In the present work, we studied the kinetics of the reaction of ozone with *para*-cresyl acetate in acetic anhydride in the presence of sulfuric acid and manganese(II) acetate, which was earlier used as a catalyst for the selective oxidation of methylphenols with ozone-containing gases [1].

EXPERIMENTAL

The reaction was carried out in the kinetically controlled regime in a temperature-controlled glass column with a porous glass membrane at 5 to 20°C. The solvent (10 ml), *para*-cresyl acetate (0.4 mol/l), and a certain amount of the catalyst were loaded into the column, and an ozone–air mixture with an ozone content of 4×10^{-4} mol/l was fed at a rate of 30 l/h. The ozone concentration in the gas phase was determined spectrophotometrically as absorbance at 254–290 nm [2]. Aromatic oxidation products were identified and quantified by GLC (3 m × 4 mm column, Inerton AW-DMCS support, SE-30 stationary phase (5% of the Interton weight)). The analysis conditions were as follows: injection port temperature, 250°C; oven temperature, 190°C; carrier gas (nitrogen) flow rate, 1.8 l/h; hydrogen and air flow rates, 1.8, and 18 l/h, respectively; flame ionization detector. *para*-Nitrochlorobenzene was used as the internal standard.

The effective rate constants of the reaction of ozone with Mn(II) and the substrate were determined spectro-

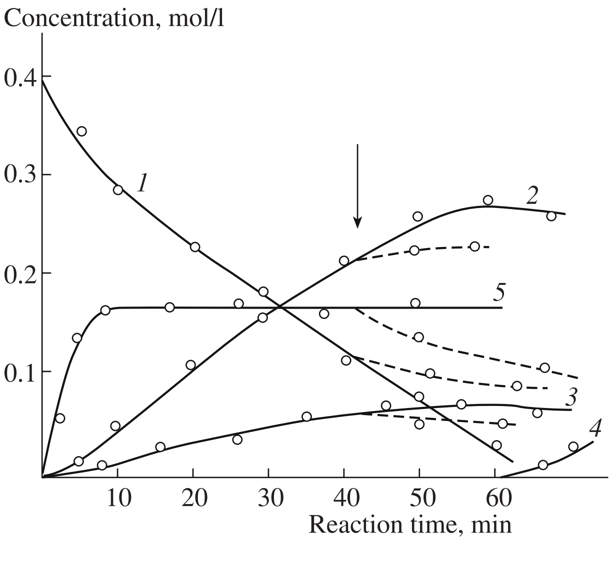

Fig. 1. Oxidation of *para*-cresyl acetate with ozone in acetic anhydride in the presence of manganese(II) acetate at 5°C: (*1*) *para*-cresyl acetate, (*2*) *para*-acetoxybenzyl acetate, (*3*) *para*-acetoxybenzylidene diacetate, (*4*) *para*-acetoxybenzoic acid, and (*5*) manganese(III) acetate. The arrow indicates the instant the ozone supply to the system is shut off. Initial concentrations: $[ArCH_3]_0 = 0.4$, $[H_2SO_4]_0 = 1.2$, and $[Mn(OAc)_2]_0 = 0.18$ mol/l. The ozone–air GHSV is $0.37\ s^{-1}$.

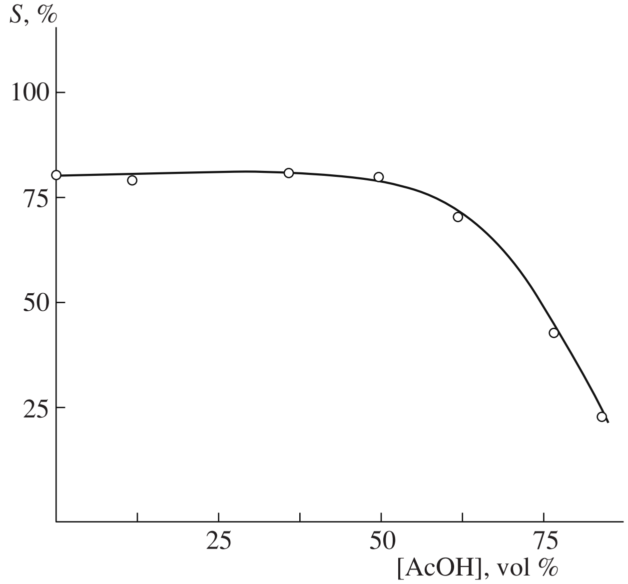

Fig. 2. Methyl group oxidation selectivity of the reaction between *para*-cresyl acetate and ozone versus the acetic acid concentration in the acetic anhydride medium at 5°C.

photometrically [2]. The rate constant of the reaction of Mn(III) with *para*-cresyl acetate was calculated graphically under the assumption that this reaction is irreversible and second-order [3].

RESULTS AND DISCUSSION

The major ozonation products of *para*-cresyl acetate in acetic anhydride in the presence of catalytic amounts of sulfuric acid and manganese(II) acetate at 5°C (Fig. 1) are *para*-acetoxybenzyl acetate (63.5%) and *para*-acetoxybenzylidene diacetate (13.7%). The reaction mixture also contains *para*-acetoxybenzyl alcohol and *para*-acetoxybenzaldehyde, whose concentrations in the solution do not exceed 10^{-4} mol/l. *para*-Acetoxybenzoic acid is accumulated in the system upon the complete oxidation of *para*-cresyl acetate. In the absence of ozone, *para*-cresyl acetate is not oxidized with dioxygen.

The methyl group oxidation selectivity of the reaction remains almost unchanged as acetic anhydride is diluted with glacial acetic acid up to a volume ratio of 1 : 1, but it decreases gradually upon further dilution (Fig. 2). High methyl group oxidation selectivities are observed only at rather high concentrations of the acylation catalyst, namely, sulfuric acid (Table 1). As the sulfuric acid content is increased, the *para*-cresyl acetate oxidation rate increases and the methyl group oxidation selectivity increases and then plateaus at an acid concentration above 1.2 mol/l. In the sulfuric acid concentration range examined, the ratio of the products resulting from the oxidation of the methyl group is nearly constant (Table 1).

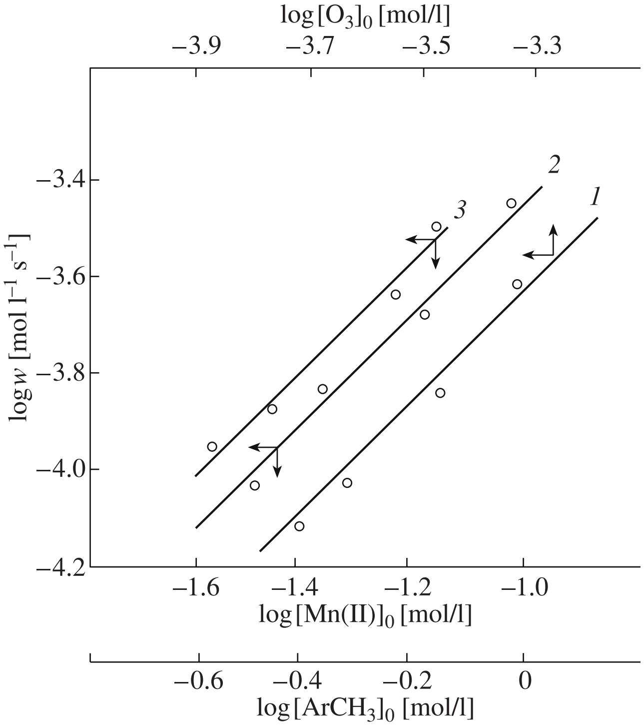

Fig. 3. *para*-Cresyl acetate oxidation rate as a function of the (*1*) ozone, (*2*) manganese(II) acetate, and (*3*) *para*-cresyl acetate concentration at 5°C.

In the presence of ozone at 5°C, divalent manganese in the mixed solvent medium passes into the trivalent state in the first 10 min. Later, the Mn(III) concentration remains unchanged (Fig. 1). No retardation of the reaction is observed until the complete consumption of the substrate. At the very beginning of the process, the accumulation rate of *para*-acetoxybenzyl acetate and *para*-acetoxybenzylidene diacetate is lower than its maximum value (Fig. 1, curves *2*, *3*). The maximum formation rate of these products is achieved after the

Table 1. Effect of the sulfuric acid concentration on the oxidation rate of *para*-cresyl acetate and the methyl group oxidation selectivity at 5°C

$[H_2SO_4]_0$, mol/l	Product concentrations, mol/l		Methyl group oxidation selectivity, %
	para-acetoxybenzyl acetate	*para*-acetoxybenzylidene diacetate	
0.0	0.039	0.012	13.0
0.4	0.105	0.021	31.5
0.8	0.181	0.033	53.5
1.2	0.253	0.056	77.2
1.6	0.258	0.054	78.0

Note: The initial concentrations are $[ArCH_3]_0$ = 0.40, $[Mn(OAc)_2]_0$ = 0.18, and $[O_3]_0 = 4 \times 10^{-4}$ mol/l. The volume of the liquid phase is 0.01 l. The reaction time is 1 h.

Table 2. Rate constants of the reactions of the catalytic cycle of *para*-cresyl acetate oxidation in acetic anhydride in the presence of manganese(II) acetate

Reaction	k, l mol^{-1} s^{-1}		E, kJ/mol
	5°C	20°C	
para-Cresol + O_3	1.2×10^3	2.2×10^3	–
para-Cresyl acetate + O_3^*	0.44	0.63	26.0 ± 4.0
para-Acetoxybenzyl acetate + O_3	0.27	0.41	–
Mn(II) + O_3	10.20	47.60	–
para-Cresyl acetate + Mn(II)	2.11×10^{-3}	3.26×10^{-3}	33.0 ± 4.0

* This reaction includes the interaction of ozone both with the aromatic ring and with the methyl group of *para*-cresyl acetate.

conversion of Mn(II) into Mn(III). If manganese in the system is initially in the oxidized state (Mn(III)), the reaction products will immediately form at the highest rate. Ozone should be supplied continuously; once ozone is shut off, the process begins to decay: *para*-cresyl acetate oxidation and product accumulation soon stop, and trivalent manganese returns to the divalent state (Fig. 1). In our experiments, the ozone consumption was 1.15 mol per mole of the substrate.

All these data suggest that the main role of ozone in catalytic *para*-cresyl acetate oxidation is to generate active Mn(III) species. Showing high substrate selectivity in the oxidation of the methyl groups of methylarenes [4], these species favor the selective oxidation of the substrate examined.

The initial rate of the reaction depends linearly on the reactant concentrations and is first-order with respect to the catalyst, substrate, and ozone (Fig. 3). It is independent of the dioxygen concentration.

From the experimental results obtained and data available from the literature [4–6], under the assumption that *para*-cresyl acetate is oxidized via a radical–ion nonchain mechanism, we suggest the following reaction network:

$$\mathrm{ArCH_3 + O_3 \longrightarrow Ar\dot{C}H_2 + HO^{\bullet} + O_2}, \quad \text{(I)}$$

$$\mathrm{ArCH_3 + O_3 \longrightarrow ArCH_2OH + O_2}, \quad \text{(II)}$$

$$\mathrm{ArCH_3 + O_3 \longrightarrow \text{ozonolysis products}}, \quad \text{(III)}$$

$$\mathrm{Mn^{2+} + O_3 + H^+ \longrightarrow Mn^{3+} + HO^{\bullet} + O_2}, \quad \text{(IV)}$$

$$\mathrm{ArCH_3 + Mn^{3+} \longrightarrow Ar\dot{C}H_2 + Mn^{2+} + H^+}, \quad \text{(V)}$$

$$\mathrm{Ar\dot{C}H_2 + O_2 \longrightarrow ArCH_2O_2^{\bullet}}, \quad \text{(VI)}$$

$$\mathrm{2ArCH_2O_2^{\bullet} \longrightarrow 2ArCH_2O^{\bullet} + O_2}, \quad \text{(VII)}$$

$$\mathrm{ArCH_2O^{\bullet} + Mn^{2+} \longrightarrow ArCH_2O^- + Mn^{3+}}, \quad \text{(VIII)}$$

$$\mathrm{ArCH_2O^- + CH_3{-}\overset{+}{C}{=}O \longrightarrow ArCH_2OCOCH_3}, \quad \text{(IX)}$$

$$\mathrm{ArCH_2OCOCH_3 + Mn^{3+} \longrightarrow Ar\dot{C}HOCOCH_3 + Mn^{2+} + H^+}, \quad \text{(X)}$$

$$\mathrm{2ArCH_2O_2^{\bullet} \longrightarrow ArCH_2OH + ArCHO + O_2}, \quad \text{(XI)}$$

$$\mathrm{(CH_3CO)_2O + H^+ \longrightarrow CH_3{-}\overset{+}{C}{=}O + CH_3COOH}, \quad \text{(XII)}$$

where $ArCH_3$ is *para*-cresyl acetate and $ArCH_2OCOCH_3$ is *para*-acetoxybenzyl acetate.

Table 3. Effect of the initial concentration of manganese(II) acetate on the formation of the oxidation products of *para*-cresyl acetate and the methyl group oxidation selectivity at 5°C

$[Mn(OAc)_2]_0$, mol/l	Product contents, mol/l		Methyl group oxidation selectivity, %
	para-acetoxybenzyl acetate	para-acetoxybenzylidene diacetate	
0.04	0.124	0.024	37.00
0.08	0.197	0.038	58.75
0.14	0.223	0.048	67.75
0.18	0.253	0.056	77.25
0.20	0.251	0.055	76.50

Note: The initial concentrations are $[ArCH_3]_0 = 0.4$, $[H_2SO_4]_0 = 1.2$, and $[O_3]_0 = 4 \times 10^{-4}$ mol/l. The volume of the liquid phase is 0.01 l. The reaction time is 1 h.

At 5°C in the absence of the manganese salt, the main route of the process is ozonolysis (III). In the presence of manganese(II) acetate, ozone is consumed in reaction (IV) to form Mn(III) (at the initial concentrations $[ArCH_3]_0$, $[Mn(OAc)_2]_0$, and $[O_3]_0$ equal to 0.4, 0.18, and 4×10^{-4} mol/l, respectively, $k_{III} = 0.35$ l mol^{-1} s^{-1}, $k_{IV} = 10.2$ l mol^{-1} s^{-1}, and the ratio of the rates of reactions (IV) and (III) is $w_{IV}/w_{III} = 13 : 1$). Manganese(III), exhibiting high selectivity in the oxidation of the methyl group of methylbenzenes, causes the oxidation of *para*-cresyl acetate according to reaction (V) to yield the benzyl radical. Under our experimental conditions, at $[O_2] \gg [O_3]$, reaction (VI) yields the peroxy radical, which then probably recombines

Table 4. Kinetic parameters of the reactions of manganese(II) acetate with *para*-cresyl acetate and *para*-acetoxybenzyl acetate at different temperatures

T, °C	*para*-Cresyl acetate			*para*-Acetoxybenzyl acetate		
	$k \times 10^3$, l mol^{-1} s^{-1}	$w \times 10^4$, mol l^{-1} s^{-1}	E, kJ/mol	$k \times 10^4$, l mol^{-1} s^{-1}	$w \times 10^4$, mol l^{-1} s^{-1}	E, kJ/mol
5	2.11	6.26	33.0 ± 3.0	1.94	2.94	42.0 ± 4.0
20	3.26	10.41		3.84	4.76	
30	4.15	13.89		5.51	8.33	

Note: $[\mathrm{ArH}]_0 = 0.4$ mol/l and $[\mathrm{Mn(III)}] = 0.1$ mol/l.

via reaction (VII) to give alkoxy radicals [5]. Since the alkoxy radicals are strong oxidants [6], it is natural to expect that they will react in the liquid phase with reduced manganese (Mn(II)), as do peroxy radicals [5], to form an anion (reaction (VIII)). The reaction between this anion and the acylium cation (reaction (IX)) yields *para*-acetoxybenzyl acetate, which is rather stable in the presence of ozone (Table 2). The contribution from reaction (XI) to the overall oxidation process is likely insignificant because this reaction simultaneously yields *para*-acetoxybenzyl alcohol and *para*-acetoxybenzaldehyde, whereas, according to experimental data, the major product in the presence of manganese acetate is *para*-acetoxybenzyl acetate (Fig. 1). It is likely that *para*-acetoxybenzylidene diacetate results from the oxidation of the acylated alcohol via reaction (X) followed by reactions analogous to reactions (VII)–(IX).

According to the above scheme, the methyl group oxidation selectivity (in percent) is determined by the reaction rate ratio

$$S = \frac{((k_{\mathrm{I+II}} + k_{\mathrm{III}})[\mathrm{O_3}]_0[\mathrm{ArCH_3}]_0)a + k_{\mathrm{V}}[\mathrm{Mn(OAc)_2}]_0[\mathrm{ArCH_3}]_0}{(k_{\mathrm{I+II}} + k_{\mathrm{III}})[\mathrm{O_3}]_0[\mathrm{ArCH_3}] + k_{\mathrm{V}}[\mathrm{Mn(OAc)_2}]_0[\mathrm{ArCH_3}]_0} \times 100, \quad (1)$$

where a is the noncatalytic methyl group oxidation selectivity. At 5°C, $a = 0.13$, $k_{\mathrm{I+II+III}} = 0.44$ l mol^{-1} s^{-1}, $k_{\mathrm{V}} = 10^{-3}$ l mol^{-1} s^{-1}, $[\mathrm{ArCH_3}]_0 = 0.4$ mol/l, $[\mathrm{Mn(OAc)_2}]_0 = 0.18$ mol/l, and $[\mathrm{O_3}]_0 = 4 \times 10^{-4}$ mol/l.

According to our calculations, the methyl group oxidation selectivity is 80%, which is close to the experimental data (Table 1).

The rate constant of ozonolysis via reaction (III) is many times higher than the rate constant of *para*-cresyl acetate oxidation with manganese (III) via reaction (V) (Table 2). This fact and relationship (1) suggest that, in the presence of Mn(II), the selective oxidation of *para*-cresyl acetate can take place only when the metal salt and substrate concentrations are comparable, which was the case in our experiments (Table 3). Thus, it is clear why the maximum *para*-cresyl acetate oxidation rate and the minimum *para*-acetoxybenzyl acetate formation rate are observed at the initial moment of the reaction, when the Mn(III) concentration in the solution is low (Figs. 1, 4): under these conditions, most of the *para*-cresyl acetate is oxidized with ozone to yield products of aromatic ring destruction [1].

The rate and selectivity of *para*-cresyl acetate oxidation are temperature-dependent. As the temperature increases, the total oxidation rate increases and the methyl group oxidation selectivity decreases (Fig. 4). At first glance, the latter finding is in conflict with experimental data indicating that the rate of selective oxidation via reaction (V) increases more rapidly than the rate of ozonolysis via reaction (III) (as can be seen

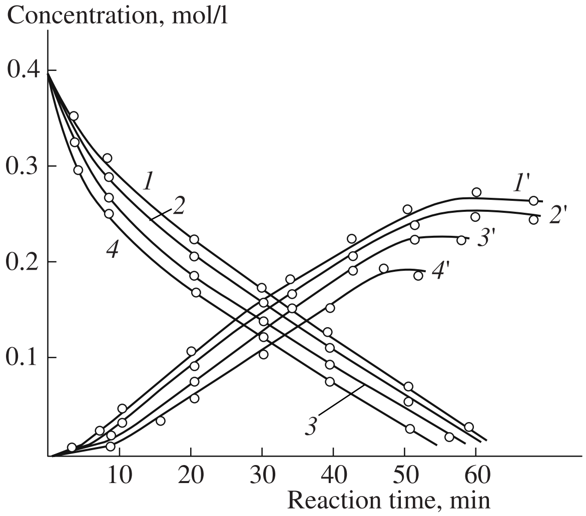

Fig. 4. Temperature effect on the kinetics of *para*-cresyl acetate oxidation with ozone in acetic anhydride in the presence of manganese(II) acetate: T = (*1*) 5, (*2*) 10, (*3*) 15, and (*4*) 20°C (curves *1*–*4* show the consumption of *para*-cresyl acetate, and curves *1'*–*4'* show the accumulation of *para*-acetoxybenzyl acetate). For the reaction conditions, see Fig. 1.

from the data presented in Table 2, E_V = 33 kJ/mol and E_{III} = 26 kJ/mol). Actually, this finding is explained by the fact that, as was demonstrated by our kinetic measurements, the rate of reaction (X) increases with temperature more rapidly than the rate of reaction (V) (Table 4).

Thus, the catalytic oxidation of *para*-cresyl acetate with an ozone–air mixture in acetic anhydride is a radical–ion chain process. This is indicated by the following observations: (1) the methyl group oxidation selectivity is the highest at comparable substrate and catalyst concentrations; (2) 1.15 mol of ozone is consumed per mole of *para*-cresyl acetate; and (3) once the ozone supply is shut off, the process is completely terminated and Mn(III) turns into Mn(II). The major oxidation product is *para*-acetoxybenzyl acetate, which results from reactions (V)–(IX).

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