Kinetics and Mechanism of Liquid-Phase Catalytic Ozonation of Nitrotoluenes

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Abstract—The kinetics of catalytic oxidation of nitrotoluenes with ozone was studied. It was shown that the introduction of transition metal salts into the system makes it possible to prevent almost completely the ozonolysis of the aromatic ring and to direct the process towards methyl-group oxidation yielding benzoic acids. A mechanism of the process that explains the experimental findings was proposed.

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Earlier it was shown [1] that toluene ozonation in acetic acid predominantly led to the ozonolysis of the aromatic ring and that the oxidation selectivity for the methyl group was 16%. The introduction of the electron-withdrawing nitro group into the toluene molecule increases the stability of the aromatic ring towards ozone electrophilic attack; however, the destructive oxidation of the compound remains the main route of the process as before, and the yield of aromatic products does not exceed 24% [2]. It is known [3] that the selectivity for side-chain oxidation in ozonation of methylbenzenes increases with an increase in temperature, as well as in the presence of oxidation catalyststransition metals—in the system. However, the mechanism of catalysis of nitrotoluene oxidation is practically unknown. In this work, the kinetics of this reaction in glacial acetic acid in the presence of transition metal salts was investigated with the aim of revealing the role of the catalyst in nitrotoluene ozonation.

EXPERIMENTAL

Glacial acetic acid (analytical grade) used in the experiments was additionally purified by vacuum distillation in the presence of potassium permanganate. Liquid 2- and 3-nitrotoluenes were purified on an aluminapacked column, and crystalline 4-nitrotoluene was purified by multiple recrystallization from water. Analytical-grade metal acetates were used without preliminary purification.

The experiments were carried out in a glass column with a porous membrane at 30–100°C. The column was loaded with 20 ml of glacial acetic acid, 0.5 mol/l of nitrotoluene, and a calculated amount of a catalyst; the column was then thermostated, and an ozone–air mixture containing 4×10^{-4} mol/l of ozone was passed through at a flow rate of 30 l/h after establishing steady-state operation of the ozonizer. The amount of ozone in the gas phase was determined spectrophotometrically

as absorption in the range 254-290 nm. Oxidation products in the solution were identified and quantified by GLC on a LKhM-80 chromatograph with a flameionization detector and a column (2 m in length and 4 mm in inner diameter) packed with Chromaton N-AW coated with the SE-30 stationary phase, using the following conditions: an evaporator temperature of 250°C; an oven temperature of 180°C; and carrier gas (nitrogen), hydrogen, and air flow rates of 1.8, 1.8, and 18 l/h, respectively. Nitrobenzene was used as an internal standard. The catalyst concentration, in particular, that of Co(III) acetate, in the reaction mixture was determined iodometrically against a blank sample lacking the aromatic products (before sampling, the reaction mixture was purged with nitrogen to remove dissolved ozone). The effective rate constants of ozone reaction with Co(II) and nitrotoluenes were determined spectrophotometrically according to the procedure described in [4].

The rate constant of Co(III) reaction with nitrotoluenes was determined graphically, assuming the case of irreversible second-order reactions [5]. Experiments in the presence of Mn, Pd, and Cr acetates were carried out in a similar manner.

RESULTS AND DISCUSSION

Data on the transition metal-catalyzed oxidation of nitrotoluene isomers with ozone in acetic acid are given in Table 1. It is seen that the presence of the catalyst prevents to a considerable extent the ozonolysis of the aromatic ring and the selective oxidation at the methyl group becomes the main reaction route. The selectivity of oxidation depends on the redox potential of an Me^{n+1}/Me^{n+} pair and reaches the maximum value in the presence of cobalt and manganese salts (Table 2). Note that the main oxidation products are the corresponding nitrobenzoic acids regardless of the metal nature. Using 4-nitrotoluene oxidation in the presence

of Co(II) acetate as an example, we observed an increase in the initial rate of substrate oxidation and in the yield of 4-nitrobenzoic acid with an increase in the catalyst concentration (Fig. 1).

Figure 2 presents kinetic data that have been obtained for 3-nitrotoluene oxidation with ozone in the presence of cobalt(II) acetate at 100°C. Intermediate oxidation products are 3-nitrobenzaldehyde and 3-nitrobenzyl alcohol, and the final product is 3-nitrobenzoic acid. The same kinetics was observed for the oxidation of 4-nitrotoluene. In the case of 2-nitrotoluene, the oxidation selectivity for the methyl group was lower, presumably, owing to the steric hin-drance of the substituent (Table 1).

In the presence of ozone, a steady-state concentration of Co(III) ions is established during the first 30-40 min of oxidation; this time coincides with that of the achievement of the maximum rate of nitrobenzoic acid formation. However, when nitrotoluene was introduced into a system that had been preliminarily ozonized until the complete conversion of cobalt into the trivalent state, the formation of nitrobenzoic acid began immediately at the maximum rate. The characteristic feature of catalytic oxidation is that the reaction quickly stops if ozone supply to the oxidation zone is terminated; under these conditions, the green solution takes a pink color, thus indicating the rapid reduction of Co(III) to Co(II) (Fig. 2). The consumption of ozone to yield 1 mol of 4-nitrobenzoic acid is 87% of the theoretically required amount of oxidant (Table 3). In the case of toluene oxidation, the consumption of ozone does not exceed 33% [7]. This gives grounds to believe that, upon ozonation of methylbenzenes that bear electron-withdrawing substituents on the ring, the oxidation is primarily effected by the ozone molecule itself, unlike the case of toluene, in which the oxidant is dioxygen and ozone mainly initiates the oxidation.

The initial rate of nitrotoluene oxidation in the reactions in question is first-order in substrate, Co(II) acetate, and ozone and is practically independent of dioxygen concentration (Fig. 3):

$$-\frac{d[O_2 \text{NArCH}_3]}{d\tau}$$
(1)
= $k[O_2 \text{NArCH}_3]_0[\text{Co}(\text{OAc}_2)]_0[O_3]_0.$

On the basis of the obtained experimental data and published data on the catalytic oxidation of alkylaromatic compounds [8–10], the following nitrotoluene oxidation scheme may be suggested:

$$O_2 NArCH_3 + O_3 \longrightarrow O_2 NArCH_2 + HO' + O_2, \quad (2)$$

$$O_2 \text{NArCH}_3 + O_3 \longrightarrow O_2 \text{NArCH}_2 \text{OH} + O_2, \quad (3)$$

$$O_2NArCH_3 + O_3 \longrightarrow$$
 ozonolysis products, (4)

$$O_3 + Co(II) + H^+ \longrightarrow Co(III) + HO' + O_2,$$
 (5)

$$CH_3COOH + HO' \longrightarrow CH_2COOH + H_2O,$$
 (6)

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Table 1. Oxidation of nitrotoluenes with ozone in the presence of Co(II) acetate at 100°C, $[O_2NArCH_3]_0 = 0.5$, and $[Co(OAc)_2]_0 = 0.15 \text{ mol/l}$

Compound	Initial oxidation rate, mol/(1 s)	Nitrobenzoic acid yield, wt %
2-Nitrotoluene	5.7×10^{-5}	75.2
3-Nitrotoluene	$7.2 imes 10^{-5}$	94.3
4-Nitrotoluene	7.4×10^{-5}	95.6

Table 2. Influence of catalyst nature on the selectivity of 4-nitrotoluene oxidation at 100°C; t = 4 h, $[O_2NArCH_3]_0 = 0.5$; $[M(OAc)_2]_0 = 0.15$ mol/l

Catalyst	$E_{eq}^{298} M^n/M^{n+1}$ [6]	Maximum yield of 4-nitrobenzoic acid, wt %
Co(II)	1.810	95.6
Mn(II)	1.510	36.4
Pd(II)	0.987	31.2
Cr(II)	0.740	27.9

$$O_2NArCH_3 + Co(III) \longrightarrow O_2NArCH_2 + Co(II) + H^+, (7)$$

$$O_2 \text{NAr}\dot{C}H_2 + O_2 \longrightarrow O_2 \text{NAr}CH_2O_2, \qquad (8)$$
$$O_2 \text{NAr}CH_2O_2H + \text{Co}(\text{II})$$

$$\rightarrow O_2 \text{NArCH}_2 \text{O'} + \text{Co(III)} + \text{HO}^-,$$
 (9)



Fig. 1. Dependence of the 4-nitrotoluene oxidation rate and the 4-nitrobenzoic acid yield on the concentration of Co(II) acetate at 100°C, $[Co(OAc)_2]_0 = 0.15 \text{ mol/l}$, $[O_2NArCH_3]_0 = 0.5 \text{ mol/l}$, and a space velocity of ozone-air mixture of 0.37 s⁻¹.



Fig. 2. Kinetics of 3-nitrotoluene oxidation with ozone in acetic acid in the presence of cobalt(II) acetate at 100°C, $[Co(OAc)_{2}]_0 = 0.15 \text{ mol/l}$, $[O_2NArCH_3]_0 = 0.5 \text{ mol/l}$, and an ozone–air mixture space velocity of 0.37 s^{-1} : (1) 3-nitrotolune, (2) 3-nitrobenzoic acid, (3) 3-nitrobenzaldehyde, (4) 3-nitrobenzyl alcohol, and (5) Co(III) acetate. (The arrow indicates the time of cessation of ozone supply to the system; the dashed lines represent oxidation kinetic curves as measured 2 h after stopping the ozone supply.)

$$O_2 \text{NArCH}_2 O_2 + O_2 \text{NArCH}_3$$

$$\longrightarrow O_2 \text{NArCH}_2 O_2 \text{H} + O_2 \text{NArCH}_2, \qquad (10)$$

 $O_2 NAr CH_2 O_2^{\bullet} + Co(II) + H^+$ (11)

 \rightarrow O₂NArCH₂O₂H + Co(III),

 $2O_2NArCH_2O_2^{\bullet} \longrightarrow \text{ products.}$ (12)

Under noncatalytic oxidation conditions, nitrotoluenes are mainly consumed via reactions (2)–(4). In the presence of Co(II) acetate, the two-stage oxidation by ozone begins to play a determining role; in this process, ozone predominantly reacts with the reduced form of metal (reaction (5)) and the oxidized form of metal is reduced in reaction (7) with the substrate. An analysis of the obtained experimental data leads to the conclusion that the selective oxidation of nitrotoluenes at the

 Table 3. Ozone consumption in oxidation of nitrotoluenes

 with an ozone-air mixture (see Table 2 for conditions)

Compound	Ozone uptake per mole of nitrotoluene		
Compound	mole	% of theoretical amount	
2-Nitrotoluene	4.88	130.2	
3-Nitrotoluene	3.33	89.3	
4-Nitrotoluene	3.27	87.1	



Fig. 3. Dependence of the 2-nitrotoluene oxidation rate on the concentration of (1) cobalt(II) acetate, (2) ozone, and (3) 2-nitrotoluene at 100°C, $[Co(OAc)_2]_0 = 0.15 \text{ mol/l}, [O_2NArCH_3]_0 = 0.5 \text{ mol/l}.$

methyl group depends on the ratio of the rates of reactions (4), (5), and (7). The data presented in Table 4 show that the rate constant of ozonolysis reaction (4) of nitrotoluenes exceeds by many times the rate constant of reaction (7) of their oxidation with Co(III). Hence, in the presence of cobalt(II) acetate, which is rapidly converted into the oxidized form in reaction (5) with ozone, the oxidation of nitrotoluene isomers without destruction of the aromatic system is possible only at commensurable concentrations of the metal salt and the substrate, which is in fact the case observed experimentally (Fig. 2).

In oxidation with an ozone–air mixture, the concentration of dioxygen in the gas mixture is an order of magnitude above that of ozone; therefore, the benzyl radical formed via reaction (7) in the system reacts predominantly with an oxygen molecule (reaction (8)), yielding arylperoxide radicals which further recombine according to Eq. (12). The participation of arylperoxide radicals in propagation reactions (10) and (11) under the reaction conditions is negligible, as $w_{12} : w_{11} : w_{10} \approx 2 \times 10^3 : 20 : 1$ (according to published data [11], $w_{12} = 1.5 \times 10^{-2}$, $w_{11} = 9 \times 10^{-4}$, and $w_{10} = 8 \times 10^{-6}$ mol/(1 s) for toluene at 70°C, $k_{10} = 1.6$, $k_{11} = 6.1 \times 10^2$, $k_{12} = 1.5 \times 10^8$ l/(mol s), [O₂NArCH₃]₀ = 0.5, [Co(OAc₂)]₀ = 0.15, and [O₂NArCH₂O₂] $\approx 10^{-5}$ mol/1).

These calculations, and the experimental fact that the selective oxidation is accomplishable only under commensurable catalyst and substrate concentrations, as well as the determining role of ozone in the reaction,

Reaction no.	Reaction	k _{eff} , l/(mol s)	Initial reaction rates, mol/(1 s)
4	O_3 + 2-nitrotoluene	0.38	0.7×10^{-4}
4	+ 3-nitrotoluene	0.45	$0.9 imes 10^{-4}$
4	+ 4-nitrotoluene	0.46	$0.9 imes 10^{-4}$
5	$Co^{2+} + O_3$	9.3×10^{2}	5.8×10^{-2}
7	$Co^{3+} + 2$ -nitrotoluene	0.0041	3.0×10^{-4}
7	+ 3-nitrotoluene	0.0108	$7.9 imes 10^{-4}$
7	+ 4-nitrotoluene	0.0130	9.5×10^{-4}

Table 4. Reaction rate constants for the catalytic cycle of oxidation of nitrotoluenes with ozone at 100° C [Co(OAc)₂]₀ = 0.15 mol/l; [O₂NArCH₃]₀ = 0.5 mol/l

testify that the process follows the radical ion mechanism. According to this mechanism, arylperoxide radicals recombine, yielding oxidation products and retaining the aromatic structure (reaction (12)).

The above assumption that Co(III) regeneration mainly occurs via reaction (5) of Co(II) with ozone is entirely consistent with the calculated kinetic data. Under experimental conditions at $k_5 = 9.3 \times 10^2$ l/(mol s) (Table 4), [Co(OAc₂)]₀ = 0.15, and [O₃]₀^{gas} = 4 × 10⁻⁴ mol/l, w_5 is 5.8 × 10⁻² mol/(l s) and the value of w_{11} calculated above is 9 × 10⁻⁴ mol/(l s). It is logical that the cessation of ozone supply to the system at w_5/w_{11} = 65 stops the process.

All these results suggest that the reaction of ozone with nitrotoluenes in the presence of cobalt(II) acetate follows the (5)-(7)-(8)-(12) route.

Note that manganese(II) acetate exhibits the same catalytic activity at 30°C as cobalt(II) acetate; oxidation of nitrotoluenes in its presence follows a similar scheme. However, the activity of manganese gradually declines with an increase in temperature, so that the yield of 4-nitrobenzoic acid falls down to 36% at 100°C (Table 5), which is almost 3 times lower than in the presence of cobalt(II) acetate and only 12% higher than in the case of noncatalytic oxidation.

To explain these peculiarities, we studied the behavior of manganese acetate under the conditions of 4-nitrotoluene oxidation with ozone at different temperatures (Fig. 4). Preliminary experiments showed that Mn(II) in acetic acid is oxidized by ozone to Mn(IV) (similar results were reported by other researchers [12, 13]). At 30°C, Mn(II) transforms into Mn(IV) within 10 min, and the system reaches an equilibrium at which manganese occurs predominantly in the oxidized form Mn(IV) for the entire length of the experimental run. An increase in temperature decreases the equilibrium Mn(IV) concentration—the higher the temperature, the stronger the concentration fall.

As the equilibrium Mn(IV) concentration decreases in the system, a dark brown solid precipitates, which is insoluble in water or glacial acetic acid, is slightly soluble in sulfuric acid, and dissolves well in hydrochloric acid. The absorption spectrum of the dissolved precipitate corresponds to MnO_2 .

Thus, the decrease in the selectivity of oxidation of nitrotoluenes in the presence of manganese(II) acetate with an increase in temperature is explained by a decrease in the equilibrium concentration of Mn(IV) ions as a result of the formation of manganese dioxide, which is insoluble under the reaction conditions.

In agreement with the experimental and published data [14, 15], it may be assumed that MnO_2 formation in the catalyzed reaction of ozone with nitrotoluenes is due to the accumulation of reaction water according to the scheme

 $Mn(II) + O_3 + 2H^+ \longrightarrow Mn(III) + O_2 + H_2O, \quad (13)$

$$Mn(IV) + Mn(II) \longrightarrow 2Mn(III),$$
 (14)

$$Mn(III) + O_3 + 2H^+ \longrightarrow Mn(IV) + O_2 + H_2O, \quad (15)$$

$$O_2 \text{NArCH}_3 + \text{Mn}(\text{IV}) \longrightarrow O_2 \text{NArCH}_2 + \text{Mn}(\text{III}) + \text{H}^+, \qquad (16)$$

 $O_2NArCH_3 + Mn(III)$

$$\rightarrow$$
 O₂NArĊH₂ + Mn(II) + H⁺, (17)

$$Mn(II) + H_2O \longrightarrow MnOH^+ + H^+, \qquad (18)$$

$$MnOH^+ + O_3 \longrightarrow MnO_2 + O_2.$$
(19)

In summary, the selectivity of oxidation of nitrotoluenes by ozone at the methyl group yielding nitrobenzoic acids increases in the presence of transition metal com-

Table 5. Temperature dependence of 4-nitrobenzoic acid yield in the presence of transition metals; $[O_2NArCH_3]_0 = 0.5 \text{ mol/l};$ $[M(OAc)_2]_0 = 0.15 \text{ mol/l}$

T °C	Yield of 4-nitrobenzoic acid, wt %		
<i>I</i> , C	Co(II) acetate	Mn(II) acetate	
30	56.8	53.4	
50	62.7	44.9	
70	79.5	39.6	
100	95.6	36.7	



Fig. 4. Influence of temperature on the concentration of Mn(IV) ions in solution upon oxidation of 4-nitrotoluene with ozone at T = (I) 30, (2) 50, (3) 70, and (4) 100°C; $[O_2NArCH_3]_0 = 0.5 \text{ mol/l}; [Mn(OAc)_2]_0 = 0.15 \text{ mol/l}; and <math>[O_3]_0^{\text{gas}} = 4 \times 10^{-4} \text{ mol/l}.$

pounds, especially, cobalt(II) acetate. The role of the catalyst consists in the appearance of the metal in the higher oxidation state after the reaction with ozone, and it this form that involves the substrate molecule in the selective oxidation at the methyl group. Exhibiting the same catalytic activity as cobalt(II) acetate at low temperatures, manganese(II) acetate gradually loses its activity with an increase in temperature, since the active manganese form Mn(IV) transforms into an inactive MnO₂ precipitate.

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