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Oxidation of 4-Nitrotoluene by Ozone in Acetic Anhydride in the Presence of Manganese Sulfate

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Abstract—The reaction of 4-nitrotoluene oxidation with ozone in acetic anhydride in the presence of $MnSO_4$ and sulfuric acid was studied. The main reaction product is 4-nitrobenzyl acetate, the yield of which is 63.2%. Based on an analysis of the experimental data, a mechanism of the catalytic ozonation of 4-nitrotoluene in acetic anhydride was proposed.

INTRODUCTION

Low concentrations of aromatic alcohols and aldehydes in the products of methylbenzene oxidation with ozone in acetic acid is related to their high reactivity and the ability for further oxidation [1]. An efficient method for improving oxidation selectivity for these oxygen-containing compounds is the use of stop reagents. The introduction of these reagents into a reaction zone enables the conversion of labile intermediates into more stable species [2]. Thus, in the oxidation of 4-nitrotoluene in acetic anhydride in the presence of catalytic additives of sulfuric acid [3], the main products of oxidation of the methyl group are aromatic alcohols and aldehydes. These compounds are accumulated in oxidation products as acetates and acylals (in contrast to ozonation in acetic acid [1] when oxidation at the methyl group leads to the formation of an aromatic carboxylic acid). The formation of 4-nitrobenzoic acid was not observed under these conditions. However, in both acetic acid and acetic anhydride, ozone primarily attacks an aromatic ring, and the total yield of products with retained aromatic structures does not exceed 25%. To increase the yield of aromatic products, it seems interesting to study the oxidation of 4-nitrotoluene with ozone in acetic anhydride in the presence of a manganese sulfate catalyst and sulfuric acid.

EXPERIMENTAL

The oxidation was carried out in a glass column with a porous membrane for bubbling a gas. The reactor was loaded with 0.05 l of acetic anhydride. The calculated amounts of 4-nitrotoluene, sulfuric acid, and manganese sulfate were introduced into the reactor, and an ozone–air mixture was supplied at a flow rate of 1×10^{-2} l/s. The concentration of ozone in the gas phase at the reactor outlet was determined by spectrophotometry [4]. The current concentrations of 4-nitrotoluene and oxidation products were measured by gas–liquid chromatography [5].

The rate constants of the reactions of ozone with 4-nitrotoluene and manganese sulfate were determined according to a published procedure [4]. To determine the rate constant of the interaction of Mn(III) with 4-nitrotoluene, the rate of Mn(III) consumption was measured by iodometry in a nitrogen atmosphere. The rate constant was calculated using the equation

$$-\frac{[Mn^{3+}]}{d\tau} = k[Mn^{3+}][ArCH_3].$$

In the calculation of the rate constant, we assumed that the inhibition of the reaction by Mn(II) at the initial point in time can be neglected.

RESULTS AND DISCUSSION

The introduction of Mn(II) sulfate into the oxidation system can significantly prevent the ozonolysis of an aromatic ring and direct the reaction toward the formation of products of side-chain oxidation: 4-nitrobenzyl acetate and 4-nitrobenzylidene diacetate (Fig. 1). 4-Nitrobenzoic acid was not found among the reaction products. Figure 1 shows that 4-nitrobenzylidene diacetate appears in the system after the accumulation of a considerable amount of 4-nitrobenzyl acetate. This indicates the consecutive formation of the acetate and the acylal.

In the course of ozonation, a steady-state concentration of Mn(III) was attained in the first 50 min, which remained almost unchanged (Fig. 1, curve *4*). The inhibition of the reaction was not observed up to the complete consumption of 4-nitrotoluene. The rate of 4-nitrobenzyl acetate formation reached a maximum when the concentration of Mn(III) reached a steady-state value. If 4-nitrotoluene is introduced into a system that is ozonated to the complete conversion of Mn(II) to Mn(III), the accumulation of 4-nitrobenzyl acetate immediately starts at a maximal rate.

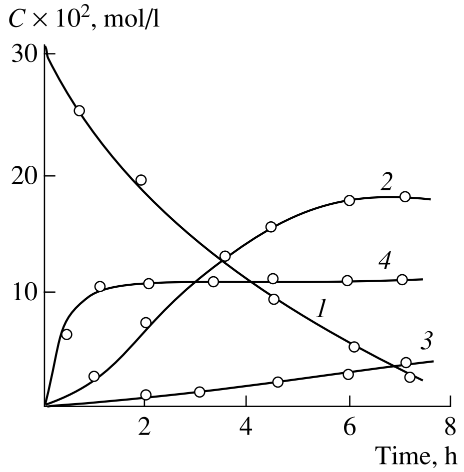

Fig. 1. Concentrations of reaction components as functions of time in the oxidation of 4-nitrotoluene with an ozone–air mixture in acetic anhydride in the presence of $MnSO_4$ at 20°C; $[ArCH_3] = 0.3$ mol/l; $[MnSO_4] = 0.14$ mol/l; $[O_3] = 4 \times 10^{-4}$ mol/l; $[H_2SO_4] = 1.27$ mol/l; gas flow rate of 1×10^{-2} l/s; (*1*) 4-nitrotoluene, (*2*) 4-nitrobenzyl acetate, (*3*) 4-nitrobenzylidene diacetate, and (*4*) Mn^{3+}.

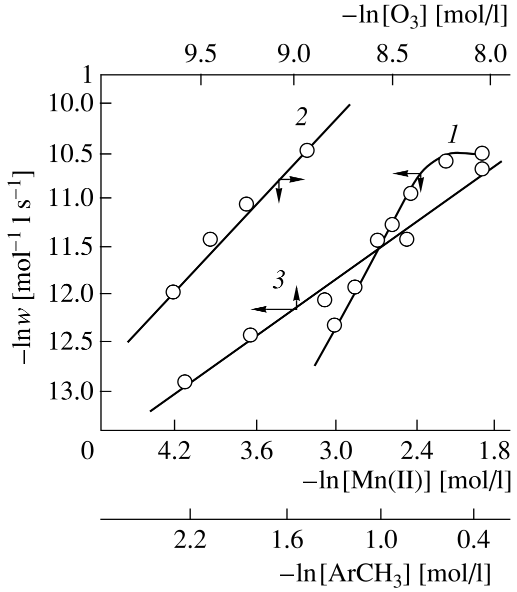

Fig. 2. Rate of 4-nitrotoluene oxidation as a function of the concentration of (*1*) manganese sulfate, (*2*) 4-nitrotoluene, or (*3*) ozone at 20°C.

The study of the influence of ozone, catalyst, and 4-nitrotoluene concentrations on ozonation showed that the rate of substrate consumption is described by the equation (Fig. 2)

$$-\frac{d[\mathrm{ArCH_3}]}{d\tau} = k[\mathrm{ArCH_3}][\mathrm{Mn}^{2+}][\mathrm{O_3}]. \qquad (1)$$

Thus, a change in the reaction path in the presence of Mn(II) is due to the fact that ozone primarily reacts with the catalyst (Table 1) under the experimental conditions. As a result, the fraction of ozone participating in the reaction with 4-nitrotoluene decreases:

$$\mathrm{Mn}^{2+} + \mathrm{O_3} \xrightarrow{\mathrm{H^+}} \mathrm{Mn}^{3+} + \mathrm{HO}^{\bullet} + \mathrm{O_2}, \qquad (\mathrm{I})$$

$$\mathrm{ArCH_3} + \mathrm{O_3} \begin{array}{l} \nearrow \text{products of methyl group oxidation} \\ \searrow \text{products of aromatic ring degradation} \end{array} \qquad (\mathrm{II})$$

The Mn(III) formed in reaction (I) initiates the oxidation of 4-nitrotoluene at the methyl group [6]:

$$\mathrm{ArCH_3} + \mathrm{Mn}^{3+} \longrightarrow \mathrm{ArCH}_2^{\bullet} + \mathrm{Mn}^{2+} + \mathrm{H}^{+}. \qquad (\mathrm{III})$$

The rate of 4-nitrotoluene ozonolysis is higher by almost two orders of magnitude than the rate of its oxidation by Mn(III) (Table 1). Therefore, the maximal rate and selectivity (80.3%) of the catalytic oxidation of 4-nitrotoluene were reached under the experimental conditions only at comparable concentrations of Mn(II) and 4-nitrotoluene (Table 2). A further increase in manganese sulfate concentration in the reaction mixture does not affect the oxidation rate (Fig. 2). This fact can also be the kinetic evidence of the formation of free radicals in the interaction of Mn(III) with 4-nitrotoluene [6].

Further transformations of the benzyl radical into benzyl acetate can be presented by the following reactions [5, 7, 8]:

$$\mathrm{ArCH}_2^{\bullet} + \mathrm{Mn}^{3+} \longrightarrow \mathrm{ArCH}_2^{+} + \mathrm{Mn}^{2+}, \qquad (\mathrm{IV})$$

$$\mathrm{ArCH}_2^{+} \xrightarrow{\mathrm{Ac_2O}} \mathrm{ArCH_2OAc} + \mathrm{Ac}^{+}, \qquad (\mathrm{V})$$

$$\mathrm{ArCH}_2^{\bullet} + \mathrm{O_2} \longrightarrow \mathrm{ArCH_2O}_2^{\bullet}, \qquad (\mathrm{VI})$$

Table 1. Rate constants of the reactions of ozone with 4-nitrotoluene and manganese sulfate and of the reaction of the oxidized form of the metal with 4-nitrotoluene in acetic anhydride at 20°C in the presence of sulfuric acid. $[H_2SO_4] =$ 1.27 mol/l

Reaction	k, l mol^{-1} s^{-1}
O_3 + 4-nitrotoluene	8.3×10^{-2}
O_3 + Mn(II)	15.2
Mn(III) + 4-nitrotoluene	1.1×10^{-3}

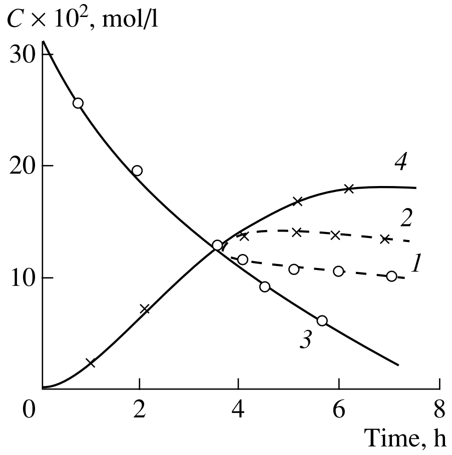

Fig. 3. Changes in the concentrations of (*1*) 4-nitrotoluene and (*2*) 4-nitrobenzyl acetate upon the termination of ozone supply after oxidation for several hours and with a continuous supply of ozone (*3* and *4*, respectively) at 20°C. $[\mathrm{ArCH_3}]$ = 0.3 mol/l; $[\mathrm{MnSO_4}]$ = 0.14 mol/l; $[\mathrm{O_3}] = 4 \times 10^{-4}$ mol/l; $[\mathrm{H_2SO_4}]$ = 1.27 mol/l; gas flow rate of 1×10^{-2} l/s.

$$\mathrm{ArCH_2^{\bullet} + O_3 \longrightarrow ArCH_2O^{\bullet} + O_2}, \qquad \text{(VII)}$$

$$\mathrm{ArCH_2O_2^{\bullet} + O_3 \longrightarrow ArCH_2O^{\bullet} + 2O_2}, \qquad \text{(VIII)}$$

$$\mathrm{ArCH_2O_2^{\bullet} + Mn^{2+} \xrightarrow{H^+} ArCH_2O_2H + Mn^{3+}}, \qquad \text{(IX)}$$

$$\mathrm{ArCH_2O_2^{\bullet} + ArCH_3 \longrightarrow ArCH_2O_2H + ArCH_2^{\bullet}}, \qquad \text{(X)}$$

$$\mathrm{ArCH_2O_2H + Mn^{2+} \longrightarrow ArCH_2O^{\bullet} + Mn^{3+} + HO^{-}}, \qquad \text{(XI)}$$

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

$$\mathrm{ArCH_2O^{-} + Ac_2O \xrightarrow{H^+} ArCH_2OAc + AcOH}, \qquad \text{(XIII)}$$

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

$$\mathrm{ArCH_2OH,\ ArCHO \xrightarrow{Ac_2O,\ H^+} ArCH_2OAc,\ ArCH(OAc)_2}. \qquad \text{(XV)}$$

Let us analyze this scheme for the determination of reactions that primarily contribute to the formation of 4-nitrobenzyl acetate.

We found experimentally that, in the oxidation of 4-nitrotoluene by Mn(III) in acetic anhydride in the presence of sulfuric acid in a nitrogen atmosphere, 4-nitrobenzyl acetate is the main reaction product. In an oxygen atmosphere, in addition to 4-nitrobenzyl acetate, 4-nitrobenzylidene acetate is formed in the ratio $[\mathrm{ArCH_2OAc}]/[\mathrm{ArCH(OAc)_2}] = 1.1$. Therefore, reactions (IV) and (V) take place in the oxidation in a nitrogen atmosphere. In an oxygen atmosphere, the benzyl radical is primarily transformed according to reactions (VI), (XIV), and (XV).

Under conditions of the catalytic oxidation of 4-nitrotoluene at $[\mathrm{O_2}]/[\mathrm{O_3}] > 20$, it is likely that the benzyl radical is also consumed in reaction (VI). Reaction (VII) does not play an important role under these conditions.

Comparative analysis of the rate constants of reactions (I), (VIII), (XI), and (XIV) shows that the peroxide radical formed in reaction (VI) under catalytic conditions is consumed mainly according to the scheme (VIII)–(XII)–(XIII), and reactions (IX), (XI), and (XIV) represent a secondary path ($w_1/w_9 \approx 6 \times 10^2$ at $k_9 \approx 10^3$ l mol^{-1} s^{-1} [10]; $k_1 = 15.2$ l mol^{-1} s^{-1}; $[\mathrm{ArCH_2O_2^{\bullet}}] \approx 10^{-8}$ mol/l [11]; $[\mathrm{O_3}] = 4 \times 10^{-4}$ mol/l. $w_8/w_{14} \approx 16.5$ at $k_8 = 6.2 \times 10^4$ l mol^{-1} s^{-1} [12]; $k_{14} = 1.5 \times 10^8$ l mol^{-1} s^{-1} [13]; $[\mathrm{O_3}] = 4 \times 10^{-4}$ mol/l; $[\mathrm{ArCH_2O_2^{\bullet}}] \approx 10^{-8}$ mol/l [11]). The complete termination of oxidation after the stopping of ozone supply into the well-developed process (Fig. 3) and the ratio between 4-nitrobenzyl acetate and 4-nitrobenzylidene diacetate (Table 2) formed in the course of oxidation are evidence for this suggestion. The formation of a hydroperoxide in reaction (X) is almost improbable because 4-nitrotoluene is consumed by a nonchain mechanism (Eq. (1)).

Table 2. Effect of Mn(II) concentration on selectivity and yields of products of 4-nitrotoluene oxidation at 20°C; $[\mathrm{ArCH_3}]$ = 0.3 mol/l; $[\mathrm{H_2SO_4}]$ = 1.27 mol/l; $[\mathrm{O_3}] = 4 \times 10^{-4}$ mol/l; gas flow rate of 1×10^{-2} l/s; τ = 7 h

[Mn(II)], mol/l	Composition of the mixture of oxidation products, mol/l			Selectivity of oxidation*, %
	4-nitrotoluene	4-nitrobenzyl acetate	4-nitrobenzylidene diacetate	
0.140	0.015	0.108	0.046	80.3
0.095	0.026	0.148	0.030	68.0
0.071	0.035	0.130	0.023	62.7
0.049	0.044	0.105	0.011	53.3

* The selectivity of oxidation was determined as a ratio of the total quantity of reaction products with retained aromatic structures to the quantity of reacted nitrotoluene.

CONCLUSION

Thus, the investigations showed that the predominant reaction path in the ozonation of 4-nitrotoluene in acetic anhydride in the presence of sulfuric acid and manganese(II) sulfate is the oxidation of the methyl group with the formation of 4-nitrobenzyl acetate as a main product. The role of the catalyst is reduced to the generation of trivalent manganese in the reaction with ozone. This trivalent species can initiate the selective oxidation of the methyl group. The experimental results and published data permitted us to suggest a mechanism of the process and to explain the predominating formation of an aromatic alcohol.

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