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Kinetics and Products of the Catalytic Oxidation of Acetamidotoluenes with Ozone in Acetic Acid

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Abstract—The kinetics of acetamidotoluene oxidation in glacial acetic acid in the presence of cobalt acetate is reported. At 95°C and atmospheric pressure, acetamidotoluenes are oxidized by molecular oxygen very slowly: oxidation is complete in 10–12 h, and the major reaction products are acetamidobenzoic acids (27–36% yield). The introduction of ozone into the reactive gas increases the reaction rate by one order of magnitude. The main role of ozone is to generate the active form of the catalyst.

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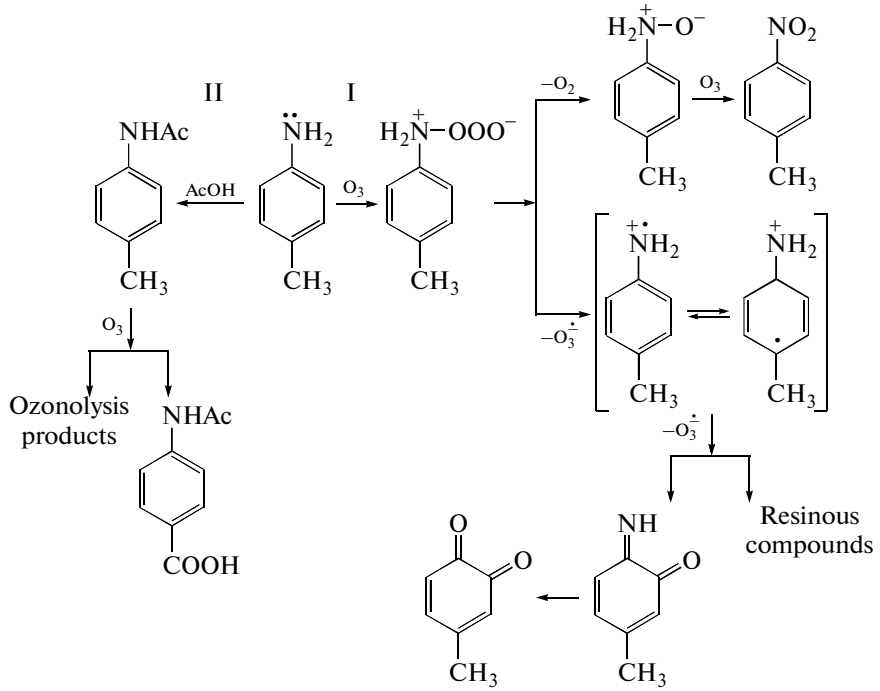
INTRODUCTION

We demonstrated in an earlier study [1] that the oxidation of 4-aminotoluene by an ozone–air mixture in glacial acetic acid proceeded according to the scheme presented below (route I) [2], mainly at the amino group, to form resinous compounds of unknown structure and small amounts of 4-nitrotoluene and toluquinone:



Scheme.

The reaction route changes after N-acylation. However, in this case, the oxidation again occurs mainly at the aromatic ring to yield the ozonolysis product (84%) and, to a considerably lesser extent, at the methyl group to form 4-acetamidobenzoic acid (14%) (scheme, route II). Our study showed that 4-acetamidotoluene (4-AAT) is oxidized via a nonchain radical mechanism and ozone is consumed in two

routes: at 20°C ozone reacts with the initial substrate via the nonchain mechanism, whereas at higher temperatures the chain reaction of ozone with the aromatic ring destruction products begins to play a noticeable role along with the nonchain route.

Here, we report the kinetics of the oxidation of isomeric acetamidotoluenes (AATs) by ozone in acetic acid in the presence of cobalt acetate, which is a conventional catalyst for the oxidation of methylbenzenes [4], and to establish the main factors determining the efficiency of oxidation at the methyl group.

EXPERIMENTAL

Experiments were carried out under kinetic control using a 20-ml temperature-controlled glass column with a porous membrane for gas dispersion. Glacial acetic acid (10 ml), AAT (0.4 mol/l), and cobalt acetate tetrahydrate were placed in the air-purged column, and a reactive gas (air, oxygen, or an ozone–air mixture) was fed at a rate of 30 l/h. The ozone concentration in the gas phase was $(1.5–6.0) \times 10^{-4}$ mol/l.

Oxidation in the Presence of Co(III) and Co(II)

The solution of cobalt(II) acetate in acetic acid was ozonated for 40 min. After the complete oxidation of Co(II) to Co(III), the gas flow was shut off, the solution was purged with nitrogen for 3 min, an appropriate amount of AAT was added, and feeding of the ozone-containing gas or dioxygen was resumed. After the completion of oxidation, the reaction mixture was poured into a glass beaker two-thirds full of finely crushed ice and was diluted with cold water to a total volume of 50 ml. The acetamidobenzoic acid (AABA) precipitate was filtered off, washed with cold water, and diluted with a mixture consisting of concentrated HCl (10 ml), water (20 ml), and alcohol (4 ml). The solution was held under stirring for 1 h at 60°C in a flask with a reflux condenser. The reaction mixture was then cooled, and the resulting aminobenzoic acid was filtered and dried.

Oxidation in the presence of Co(II) was carried out similarly, but without Co(II) preconversion into Co(III).

Analysis of the Reaction Products and Reactants

The ozone concentration in the gas phase at the inlet and outlet of the reactor was determined by spectrophotometry [2].

Acetamidotoluenes and the corresponding alcohols and aldehydes were analyzed chromatographically (flame ionization detector, column 3 m in length and 4 mm in diameter, Inerton AW-DMCS support, SE-30 (5%) stationary phase). The chromatographic conditions were as follows: evaporator temperature of 250°C; oven temperature of 190°C; carrier gas (nitrogen), hydrogen, and air flow rates of 1.8, 1.8, and 18 l/h, respectively. 4-Nitrochlorobenzene was used as the internal standard. The current concentration of 4-AABA was determined by alkaline titration: a sample (0.5 ml) was taken from the reaction mixture, the solvent was distilled out from the sample, the dry residue was dissolved in 50% ethanol (30 ml) brought to neutrality to phenolphthalein, and the solution was titrated with 0.05 N NaOH.

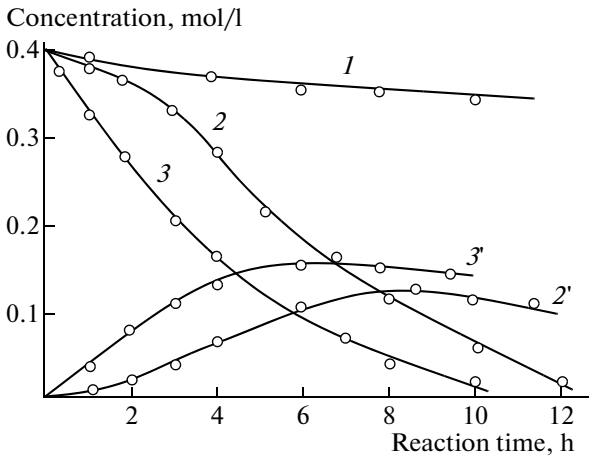


Fig. 1. Oxidation of 4-AAT by oxygen in acetic acid at 95°C and initial concentrations of $[AAT]_0 = 0.4$ mol/l and $[Co(OAc)_2]_0 = 0.14$ mol/l, a feed rate of 30 l/h, and a solution volume 0.01 l: (*1–3*) 4-AAT consumption in oxidation with (*1*) air and (*2*) dioxygen in the presence of Co(II) and with (*3*) dioxygen in the presence of Co(III); (*2'*, *3'*) 4-AABA buildup in experiments *2* and *3*, respectively.

Determination of Rate Constants

The apparent rate constants of the reaction of ozone with AAT and the ozone uptake during the reaction were calculated using standard procedures [2]. The rate constants of the reaction of Co(III) with AAT were determined graphically under the assumption that this process is a second-order irreversible reaction [3].

RESULTS AND DISCUSSION

Acetamidotoluenes were oxidized at 95°C and atmospheric pressure in glacial acetic acid. The initial concentrations of the reaction components were as follows: $[AAT]_0 = 0.4$ mol/l, $[Co(OAc)_2]_0 = 0.14$ mol/l, and $[O_3]_0 = (1.5–6.0) \times 10^{-4}$ mol/l. The oxidation of 4-AAT by atmospheric oxygen in the presence of cobalt(II) acetate occurs very slowly (Fig. 1, curve *1*): in 12 h, the substrate conversion does not exceed 10% and 4-AABA is observed in the reacting solution, whose yield is 31% in terms of the reacted 4-AAT.

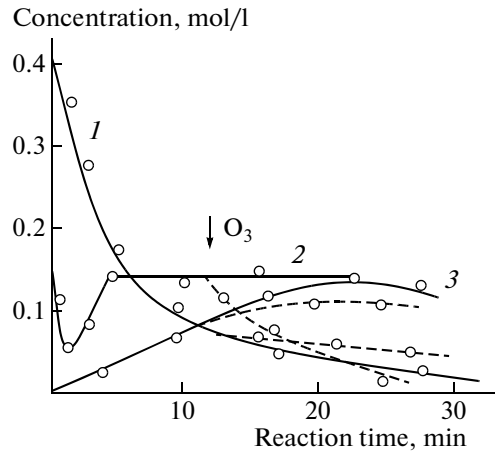


Fig. 2. Oxidation of 3-AAT with the ozone–air mixture in acetic acid at 95°C in the presence of cobalt(II) acetate at initial concentrations of $[Co(OAc)_2]_0 = 0.14$, $[3\text{-AAT}]_0 = 0.4$, and $[O_3]_0 = 4.5 \times 10^{-4}$ mol/l (reacting gas flow rate of 30 l/h, solution volume of 0.01 l): (*1*) 3-AAT, (*2*) [Co(III)], and (*3*) 3-AABA. The dashed lines show how curves *1*–*3* change after the ozone feed is shut off.

The 4-AAT oxidation rate increases with an increasing concentration of dioxygen in the system. Oxidation with pure oxygen in the presence of cobalt(II) acetate is complete within 12 h (Fig. 1, curve *2*). In this case, the Co(III)/Co(II) = 0.14 ratio is established in the system within the first 2 h and remains unchanged to the end of the experiment. At the early stages of oxidation (2 h), the kinetic curve indicates an induction period, whose end point coincides in time with the appearance of Co(III) in the system. The reaction products include 4-AABA (30.6% yield), and traces of 4-acetamidobenzaldehyde were detected in the time interval from 2 to 4 h.

Table 1. Effect of the ozone concentration in the ozone–air mixture on the rate and selectivity of AAT oxidation

Compound	$[O_3]_0 \times 10^4$, mol/l	$w \times 10^4$, mol l^{-1} s^{-1}	Yield of AABA, %
2-AAT	1.5	1.1	20.0
	3.0	1.8	23.0
	4.5	2.1	25.0
3-AAT	1.5	1.2	25.0
	3.0	1.8	27.0
	4.5	2.2	34.0
4-AAT	1.5	1.3	28.1
	3.0	3.7	32.5
	4.5	7.4	35.5

Note: For the reaction conditions, see the caption to Fig. 2.

A different situation is observed when trivalent cobalt is introduced into the system (Fig. 1, curve *3*). Oxidation develops without an induction period and is complete within 10 h. Throughout the reaction time, cobalt is predominantly in the trivalent state, 4-AABA forms in 36% yield, and traces of 4-acetamidobenzaldehyde are observed.

Similar results were obtained for the catalytic oxidation, with oxygen, of 3-AAT (oxidation time of ~10 h, 3-AABA yield of 35%) and 2-AAT (oxidation time of ~11 h, 2-AABA yield of 27%).

The experimental data obtained in the presence of Co(II) acetate are quite consistent with the view that radicals form at the early stages of the reaction via the interaction of divalent cobalt with oxygen and AAT [4]:

$$Co^{2+} + O_2 \longrightarrow Co^{2+}...O_2, \qquad \text{(I)}$$

$$Co^{2+}...O_2 + AcHNArCH_3 \longrightarrow Co^{3+} + AcHNArCH_2O^{\cdot} + HO^{-}. \qquad \text{(II)}$$

The induction period due to the slow formation of Co(III) and radicals via reaction (II) is observed in kinetic curve *2* (Fig. 1).

The induction period ends once a certain amount of trivalent cobalt is accumulated in the system (for the oxidation of 4-AAT, $[Co^{3+}] \approx 1.7 \times 10^{-2}$ mol/l) and the radicals begin to form via reaction (III). The absence of an induction period in the case of trivalent cobalt confirms this assumption and proves that the oxidation of AAT occurs at the methyl group:

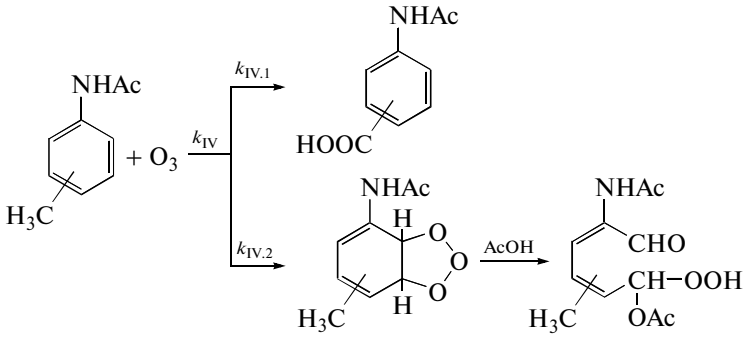
$$Co^{3+} + AcHNArCH_3 \longrightarrow Co^{2+} + AcHNArCH_2^{\cdot} + H^{+}. \qquad \text{(III)}$$

Thus, to accelerate the process, a sufficiently high Co(III) formation rate should be ensured in the initial period, which would be favorable for the acceleration of reaction (III) and for the rapid oxidation of AAT at the methyl group. This problem can be successfully solved by using ozone as the oxidizer, passing it together with air or dioxygen through an acetic acid solution of AAT and cobalt(III) acetate. Cobalt(III) acetate is obtained by the complete ozonation of cobalt(II) acetate in an acetic acid solution.

Figure 2 shows that, as an ozone–air mixture is passed through the 3-AAT–$Co(OAc)_3$–AcOH system, oxidation occurs at a high rate and the oxidation time shortens from 10 to 0.3 h (compare Figs. 1 and 2). Ozone should be fed continuously, otherwise the process is terminated (Fig. 2). The AAT oxidation rate (w) increases with an increasing ozone concentration, whereas the yield of the corresponding AABA changes insignificantly, ranging from 20.0 to 35.5% (Table 1). The AAT consumption rate depends linearly on the initial ozone concentration in the ozone–air mixture. The order of the 4-AAT oxidation reaction with

respect to ozone is 1.5, whereas the order of the reaction with respect to the substrate and cobalt acetate is unity (Fig. 3). From one to two moles of ozone is consumed in the oxidation of 1 mol of AAT (Table 2).

The low selectivity of oxidation at the methyl group is a consequence of the high rate of the noncatalytic reaction between ozone and AAT, which results mainly in the opening of the aromatic ring [1, 2]:



(IV)

For instance, for 4-AAT oxidation (Fig. 2) at 95°C $k_{III} = 0.074$ and $k_{IV} = 70.8$ l mol^{-1} s^{-1}. The data on the selectivity of 4-AAT oxidation by ozone at the methyl group and aromatic ring (14.2 and 85.8%, respectively [1]) were used to estimate $k_{IV.1}$ and $k_{IV.2}$ since it can be assumed in the first approximation that the $k_{IV.1}$ and $k_{IV.2}$ values and the selectivity in this direction are mutually proportional. Therefore, $k_{IV.1} = 70.8 \times 0.142 = 10.1$ l mol^{-1} s^{-1} and $k_{IV.2} = 70.8 \times 0.858 = 60.7$ l mol^{-1} s^{-1}. Under the assumption that the selectivity of oxidation at the methyl group (in percent) is determined by the ratio of the sum of the oxidation rates at the methyl group in reactions (III) and (IV.1) to the total AAT oxidation rate in reactions (III) and (IV), the selectivity can be calculated as

$$S = \frac{k_{IV.1}[O_3]_0 + k_{III}[Co(OAc)_2]_0}{k_{IV}[O_3]_0 + k_{III}[Co(OAc)_2]_0} \times 100.$$

The calculated selectivity checks well with the experimental data (Table 3). It can be seen from the data in Table 3 that, in the presence of cobalt acetate, the oxidation of AAT without aromatic ring breaking is possible only at moderate catalyst concentrations (0.14 mol/l). It is impossible to increase the selectivity

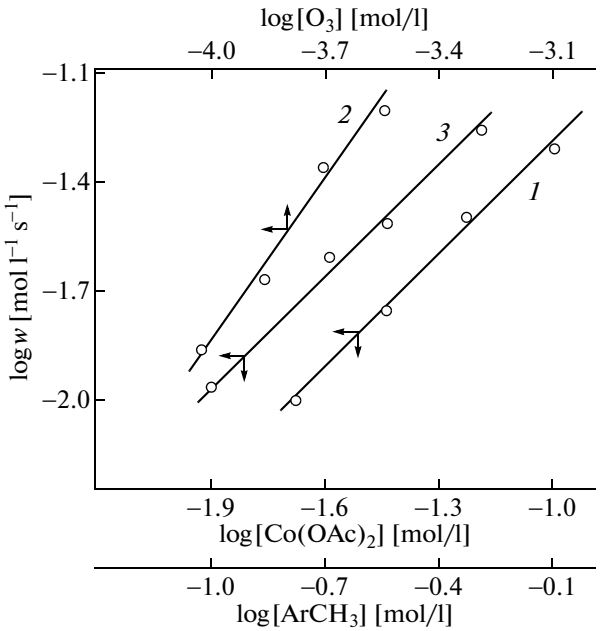


Fig. 3. 4-AAT oxidation rate versus the concentration of (*1*) cobalt acetate, (*2*) ozone, and (*3*) substrate.

Table 2. Ozone uptake per mole of AAT at 95°C

Compound	Oxidation time, min	Amount of ozone passed, mol × 10^{-3}	Ozone uptake, mol × 10^{-3}	Ozone uptake per mole of AAT
2-AAT	40	11.0	8.0	2.0
3-AAT	30	8.3	6.3	1.6
4-AAT	20	5.5	4.2	1.1

Note: $[AAT]_0 = 0.4$, $[Co(OAc)_2]_0 = 0.14$, $[O_3]_0 = 5.5 \times 10^{-4}$ mol/l, gas flow rate of 30 l/h, solution volume of 0.01 l.

Table 3. Effect of the cobalt(II) acetate concentration on the AAT oxidation rate and selectivity

Compound	$[Co(OAc)_2]_0$, mol/l	$w \times 10^4$, mol l^{-1} s^{-1}	Yield of acetamidobenzoic acids, %	
			calculated	observed
2-AAT	0.05	1.2	13.4	19.0
	0.10	1.5	20.3	22.5
	0.14	2.1	24.7	25.0
	0.20	3.7	30.8	27.5
3-AAT	0.05	1.3	21.1	21.8
	0.10	1.6	29.0	28.1
	0.14	2.2	33.1	34.0
	0.20	3.9	40.6	34.4
4-AAT	0.05	1.8	23.2	22.6
	0.10	3.7	29.9	31.2
	0.14	7.4	35.1	35.5
	0.20	10.2	41.3	35.5

Note: For the reaction conditions, see the caption to Fig. 2.

by further raising the catalyst concentration, because of the increasing viscosity of the solution, which decreases the rate of ozone dissolution in the liquid phase.

Thus, in the present work we studied, for the first time, the oxidation of isomeric acetamidotoluenes by an ozone-containing gas in glacial acetic acid in the presence of cobalt(II) acetate as the catalyst. Under the catalytic conditions, the selectivity achieved for the oxidation at the methyl group is not higher than 27–36%, which is a consequence of the high ozonolysis rate ($k_{IV.1} \gg k_{III}$).

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