

# Kinetics and Mechanism of 4-Nitrotoluene Oxidation with Ozone in an Acetic Acid Solution in the Presence of a Metal–Bromide Catalyst

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**Abstract**—The kinetics and mechanism of a reaction between ozone and 4-nitrotoluene in an acetic acid solution in the presence of a cobalt–bromide catalyst were studied at 100°C. Under these conditions, 4-nitrobenzoic acid was the main reaction product (96.6%). The rate of oxidation exhibited a first order with respect to the substrate, ozone, and the catalyst and a zero order with respect to oxygen. The main stages of the catalytic cycle were considered. It is believed that the selective oxidation of 4-nitrotoluene at the methyl group in the presence of a catalyst occurs as a nonchain ion–radical process, in which the role of ozone is reduced to the generation of an active catalyst species ( $\text{Co}^{3+}\text{Br}^- \longleftrightarrow \text{Co}^{2+}\text{Br}^\cdot$ ). This species involves 4-nitrotoluene in the oxidation process at a high rate.

## INTRODUCTION

Previously [1], it was found that the selective oxidation of 4-nitrotoluene with ozone without aromatic ring degradation occurs in the presence of cobalt diacetate in an acetic acid medium. Under conditions of catalysis, 4-nitrobenzoic acid is the main product of this reaction, and its yield is as high as 96.6%. This reaction becomes possible only at commensurable concentrations of the substrate and cobalt diacetate, even though the yield of the carboxylic acid is high and the reaction conditions are mild. In this context, data on the accelerating action of bromides in the oxidation of alkylaromatic compounds with molecular oxygen catalyzed by cobalt and manganese salts [2] are of particular interest.

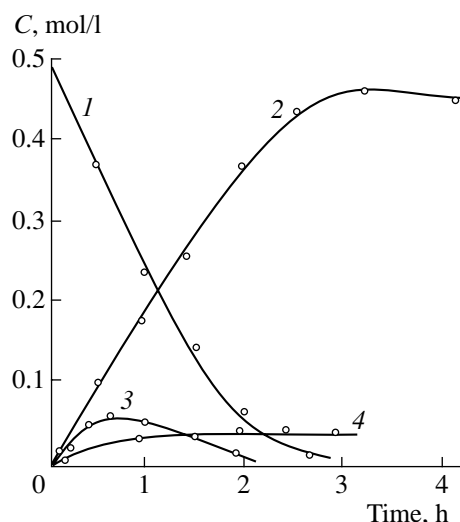
In this work, we continued a study of the reaction of 4-nitrotoluene with ozone in the presence of transition metal salts with potassium bromide additives. The experimental and analytical procedures and the preparation of reagents were described in [1].

## RESULTS AND DISCUSSION

Preliminary studies indicated that the oxidation of 4-nitrotoluene with molecular oxygen in the presence of a cobalt–bromide catalyst developed very slowly even at 110°C; only traces of aromatic carboxylic acid were detected in the reaction products after 5-h oxidation. In the presence of ozone, this catalyst exhibited a much higher activity. After the oxidation of 4-nitrotoluene for 3–7 min, the color of the solution became green, which is characteristic of  $\text{Co}^{3+}$  in the presence of bromide ions. Cobalt remained in the highest oxidation state until the completion of oxidation. The reaction products were formed without an induction period;

4-nitrobenzoic acid and 4-nitrobenzaldehyde built up in parallel reactions. Simultaneously, molecular bromine was present in exit gases, and 4-nitrobenzyl bromide and trace 4-nitrobenzyl alcohol occurred in solution (Fig. 1).

The table summarizes the results obtained in the studies of 4-nitrotoluene oxidation in the presence of various catalysts. It can be seen that the aromatic acid was formed in almost 100% yield with the initiation of



**Fig. 1.** Oxidation of 4-nitrotoluene with an ozone–air mixture in the presence of a cobalt–bromide catalyst at 100°C ( $[\text{ArCH}_3] = 0.5 \text{ mol/l}$ ;  $[\text{Co}(\text{OAc})_2] = 1.9 \times 10^{-2} \text{ mol/l}$ ;  $[\text{KBr}] = 8.4 \times 10^{-2} \text{ mol/l}$ ;  $[\text{O}_3] = 4.5 \times 10^{-4} \text{ mol/l}$ ): (1) 4-nitrotoluene, (2) 4-nitrobenzoic acid, (3) 4-nitrobenzaldehyde, and (4) 4-nitrobenzyl bromide.

Oxidation of 4-nitrotoluene with an ozone–air mixture in the presence of metal–bromide catalysts at  $[KBr] = 0.105 \text{ mol/l}$  and  $100^\circ\text{C}$

Experiment no.	Catalyst concentration, $[Cat] \times 10^2, \text{ mol/l}$				Yield of 4-nitrobenzoic acid, wt %
	cobalt acetate	manganese acetate	chromium acetate	palladium acetate	
1	1.95*	—	—	—	58.5
2	14.60*	—	—	—	96.6
3	1.95	—	—	—	96.2
4	0.95	1.03	—	—	53.2
5	0.95	—	0.85	—	24.1
6	0.95	—	1.50	—	27.6
7	—	8.24	—	—	48.5
8	—	—	13.52	—	54.2
9	—	—	—	12.16	54.6

\* Experiments were performed without KBr.

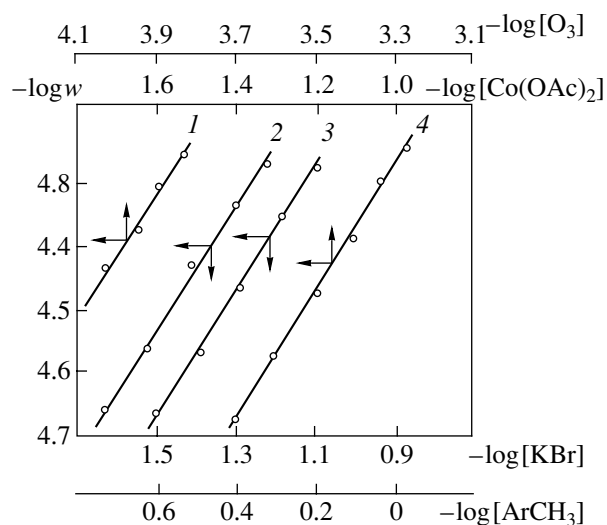
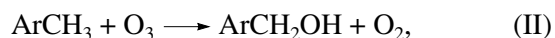
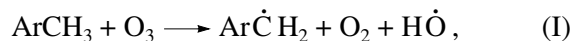
selective oxidation at the methyl group by cobalt diacetate in the absence of potassium bromide with a sufficiently high concentration of a cobalt salt. Bromide additives, which increase the yield of selective oxidation, decreased the optimum concentration of cobalt acetate by a factor of 7 (see table, experiment nos. 2 and 3). The partial or complete replacement of cobalt acetate with manganese, chromium, or palladium acetate considerably decreased the rate of reaction and the yield of the aromatic acid. In the order Mn–Cr–Pd, the yield of the acid depends only slightly on the nature of the metal and slowly increases with metal concentration in solution. Hence, it follows that the catalytic effect was completely achieved only in the case of the combined use of cobalt diacetate and potassium bromide taken in a ratio of 1 : 5.

A study of the reaction kinetics of 4-nitrotoluene oxidation with ozone demonstrated that the initial rate of oxidation is independent of molecular oxygen concentration (over the range of oxygen concentrations in the gas mixture  $[O_2]_g = 20.15\text{--}99.20 \text{ vol \%}$ ;  $w_{ArH} = (5.5 \pm 0.2) \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ ;  $100^\circ\text{C}$ ), and the reaction is of first order with respect to the other reactants (Fig. 2). On this basis, an empirical expression for the rate of 4-nitrotoluene oxidation has the form

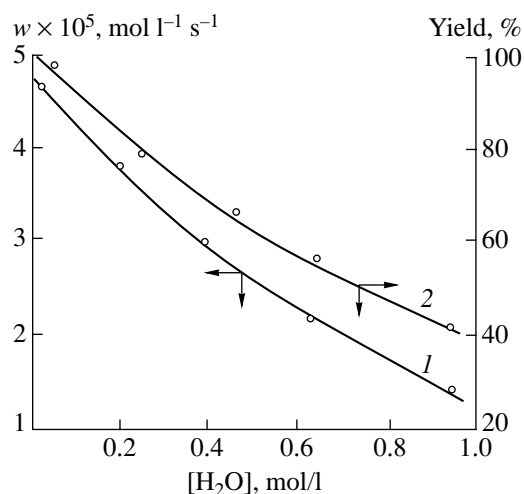
$$-d[ArCH_3]/d\tau = k_a[ArCH_3]_0[O_3]_0[Br^-]_0[Co^{2+}]_0.$$

A negative effect of water on the oxidation process was found. As can be seen in Fig. 3, the selectivity and rate of oxidation decreased to the levels of an uncatalyzed reaction even when the water concentration in the system was equal to 1 mol/l. The negative effect of water can be explained by catalyst deactivation, as evidenced by the color change in the solution and by the formation of a precipitate.

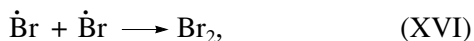
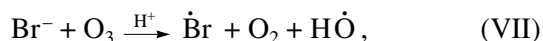
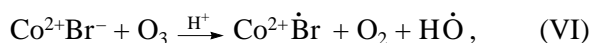
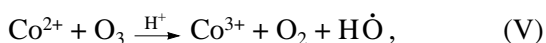
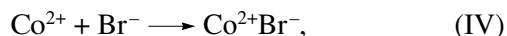
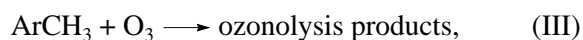
In accordance with general considerations of the reaction of ozone with alkylaromatic compounds [3, 4] and on the mechanism of alkylbenzene oxidation in the presence of metal–bromide catalysts [4–7], we consider the following reaction scheme, which explains the experimental results:



**Fig. 2.** Rate of 4-nitrotoluene oxidation as a function of the concentration of (1)  $Co(OAc)_2$ , (2) 4-nitrotoluene, (3) KBr, or (4)  $O_3$  at  $100^\circ\text{C}$ .  $[ArCH_3] = 0.5 \text{ mol/l}$ ;  $[Co(OAc)_2] = 1.9 \times 10^{-2} \text{ mol/l}$ ;  $[KBr] = 8.4 \times 10^{-2} \text{ mol/l}$ ;  $[O_3] = 4.5 \times 10^{-4} \text{ mol/l}$ .



**Fig. 3.** Effects of water additives on (1) the rate of accumulation and (2) the yield of 4-nitrobenzoic acid.  $[\text{ArCH}_3] = 0.5 \text{ mol/l}$ ;  $[\text{Co}(\text{OAc})_2] = 1.9 \times 10^{-2} \text{ mol/l}$ ;  $[\text{KBr}] = 8.4 \times 10^{-2} \text{ mol/l}$ ;  $[\text{O}_3] = 4.5 \times 10^{-4} \text{ mol/l}$  at temperatures lower than  $100^\circ\text{C}$ .



In the absence of a catalyst, ozonolysis products (reaction (III)) and small amounts of methyl group oxidation products (reactions (I), (II), (XI), and (XVII)) were formed. In the presence of a catalyst and a strong oxidizing agent (ozone), fast reactions (V)–(VII) occurred even at the initial instant of time. As a result

of this, the active species  $\text{Co}^{3+}$ ,  $\text{Co}^{2+}\dot{\text{Br}}$ , and  $\dot{\text{Br}}$ , which involved 4-nitrotoluene in the process of oxidation (reactions (VIII)–(X)), appeared in the system. Simultaneously, molecular bromine was formed in reaction (XVI); most of the bromine was irretrievably lost by being carried away with the exit gases. A portion of molecular bromine reacted with the benzyl radical (reaction (XV)) to form 4-nitrobenzyl bromide (Fig. 1, curve 4).

The cobalt bromide radical is more active in the reaction with 4-nitrotoluene (for toluene,  $k(\text{ArCH}_3 + \text{Co}^{2+}\dot{\text{Br}})/k(\text{ArCH}_3 + \text{Co}^{3+}) = 12$ ;  $t = 100^\circ\text{C}$  [9]). Therefore, in the absence of potassium bromide from the system, oxidation is initiated by reaction (IX) of 4-nitrotoluene with  $\text{Co}^{3+}$ . As the concentration of KBr in the system is increased, the concentration of free  $\text{Co}^{2+}$  decreases and 4-nitrotoluene is involved in the process of oxidation, primarily, by reaction (VIII).

Under experimental conditions when  $[\text{O}_2]/[\text{O}_3] \approx 10^2$ , the benzyl radical is primarily converted into a peroxide radical (reaction (XI)), which subsequently recombines in reaction (XVII). As will be demonstrated below, the participation of the peroxide radical in chain propagation reactions (XII)–(XIV) can be ignored.

The nonchain path of 4-nitrotoluene oxidation results from the following considerations:

(1) According to published data [8], for toluene at  $70^\circ\text{C}$   $w_{12} \approx 0.8 \times 10^{-6}$ ;  $w_{13} \approx 1.2 \times 10^{-5}$ ;  $w_{14} \approx 4 \times 10^{-5}$ , and  $w_{17} \approx 1.5 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$  ( $[\text{ArCH}_3] = 0.5$  and  $[\text{Co}(\text{OAc})_2] = 1.9 \times 10^{-2} \text{ mol/l}$ ;  $k_{12} = 1.6$ ,  $k_{13} = 6.1 \times 10^2$ , and  $k_{14} = 2.1 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$  [6]). Hence, it follows that at temperatures of up to  $100^\circ\text{C}$  the rate of recombination of peroxide radicals ( $w_{17}$ ) is higher than the rates of chain propagation reactions ( $w_{12}$ ,  $w_{13}$ , and  $w_{14}$ ), on average, by one order of magnitude.

(2) The termination of ozone supply to the system completely stopped the process; in this case,  $\text{Co}^{3+}$  was converted into  $\text{Co}^{2+}$ . Taking into account that the appearance of the active species  $\text{Co}^{3+}$  and  $\text{Co}^{2+}\dot{\text{Br}}$ , which involve 4-nitrotoluene in oxidation, in the system depends on the occurrence of reactions (V), (VI), (XIII), and (XIV), the process can be stopped in the absence of ozone only in the case when chain propagation reactions (XIII) and (XIV) play a secondary role. Indeed, we calculated that the rate of reaction (XIV) is lower than that of reaction (VI) by three orders of magnitude ( $w_6 = 1 \times 10^{-2}$  and  $w_{14} = 4 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$  at  $k_6 = 1.1 \times 10^3 \text{ l}^{-1} \text{ mol}^{-1} \text{ s}^{-1}$  [9],  $[\text{O}_3] = 4.5 \times 10^{-4}$ , and  $[\text{Co}^{2+}\dot{\text{Br}}] = 1.9 \times 10^{-2} \text{ mol/l}$ ).

(3) According to kinetic data, the rates of consumption of ozone and 4-nitrotoluene are similar; the reaction of 4-nitrotoluene oxidation is of zero order with respect to oxygen and of first order with respect to the substrate, the catalyst, and ozone; the ozone consump-

tion per mole of the substrate is close to the theoretical amount of the oxidant (96%) required for the conversion of 4-nitrotoluene into 4-nitrobenzoic acid. These data correspond to the scheme of reactions (VI), (VIII), (XI), and (XVII).

(4) The selectivity of oxidation at the methyl group essentially depends on catalyst concentration, and it reaches high values at commensurable 4-nitrotoluene and catalyst concentrations when  $w_8/w_3 \geq 10$  ( $w_3 = 0.41 \times 10^{-3}$  and  $w_8 = 3.6 \times 10^{-3}$  mol l<sup>-1</sup>s<sup>-1</sup> at  $[O_3] = 4.5 \times 10^{-4}$ ,  $[ArCH_3] = 0.5$ , and  $[Cat] = 1.9 \times 10^{-2}$  mol/l;  $t = 100^\circ\text{C}$ ;  $k_3 = 1.85$  l mol<sup>-1</sup> s<sup>-1</sup>; and  $k_8 = 0.83$  l mol<sup>-1</sup>s<sup>-1</sup>). Hence, it follows that reaction (VIII) is the main channel involving the substrate into the process of oxidation.

Thus, we experimentally found that the catalytic oxidation of 4-nitrotoluene with an ozone–air mixture is a nonchain ion–radical process, which includes reactions (V), (VI), (VIII), (IX), (XI), and (XVII).

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