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# Oxidation of 2,4-Dinitrotoluene with Ozone in the Presence of a Stop Reagent

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**Abstract**—Liquid-phase oxidation of 2,4-dinitrotoluene with ozone in the presence of acetic anhydride as stop reagent and manganese(II) acetate as catalyst was studied. The major products of oxidation with ozone in acetic anhydride are 2,4-dinitrobenzyl alcohol (65.8%) and 2,4-dinitrobenzaldehyde (18.8%) in the form of the corresponding acetates. A reaction scheme accounting for the results obtained is considered.

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2,4-Dinitrobenzyl alcohol (2,4-DNBAl) and 2,4-dinitrobenzaldehyde (2,4-DNB) are widely used as intermediates in fine organic synthesis [1, 2]. 2,4-DNBAl is mainly prepared by hydrolysis of 2,4-dinitrobenzyl chloride [3]. The drawbacks of this method are low product yield and formation of large amounts of toxic chlorine-containing wastewaters.

This study deals with oxidation of 2,4-dinitrotoluene (2,4-DNT) with an ozone–air mixture and is aimed to develop a low-waste procedure for preparing 2,4-DNBAl in a high yield.

We showed previously [4] that 2,4-DNT is oxidized with ozone in an acetic acid solution in the presence of cobalt(II) acetate to 2,4-dinitrobenzoic acid (2,4-DNBAc) in 87.6% yield. The process cannot be stopped at the steps of formation of 2,4-DNBAl or 2,4-DNB because of their high reactivity in reactions with ozone.

As a continuation of these studies, we examined the possibility of stopping the oxidation at the step of 2,4-DNBAl formation by performing the reaction in the presence of a stop reagent, acetic anhydride, which can convert labile intermediates into acetates, more resistant to ozone [5].

Our studies showed that the major products of 2,4-DNT ozonation at 20°C and atmospheric pressure

in acetic anhydride in the presence of sulfuric acid and catalytic amounts of manganese(II) acetate are 2,4-dinitrobenzyl acetate (2,4-DNBAt) (65.8%) and 2,4-dinitrobenzylidene diacetate (2,4-DNBDA) (18.8%) (see figure). 2,4-DNBAc was detected in the solution



Oxidation of 2,4-DNT with ozone in acetic anhydride in the presence of manganese(II) acetate at 20°C. Reaction conditions:  $[ArCH_3]_0 = 0.40$ ,  $[H_2SO_4]_0 = 1.20$ ,  $[O_3] = 4 \times 10^{-4}$ ,  $[Mn(OAc)_2]_0 = 0.06$  M; space velocity of the ozone–air mixture 0.83 s<sup>-1</sup>. (c) Concentration of oxidation products and ( $\tau$ ) time. (1) 2,4-DNT, (2) 2,4-DNBAt, (3) 2,4-DNBDA, (4) 2,4-DNBAc, and (5) manganese(III) acetate.

Reaction	<i>k</i> , L mol <sup>-2</sup> s <sup>-1</sup>		Activation energy,
	5°C	20°C	kJ mol <sup>-1</sup>
2,4-DNT + O <sub>3</sub>	0.010	0.080	$29.0 \pm 3.0$
2,4-DNBA1 + O <sub>3</sub>	0.540	1.660	$23.5 \pm 2.0$
2,4-DNB + O <sub>3</sub>	0.420	1.340	$25.1 \pm 2.0$
2,4-DNBAt + $O_3$	0.004	0.023	$32.5 \pm 3.0$
2,4-DNBDA + $O_3$	0.002	0.015	$35.8 \pm 3.0$
$Mn(II) + O_3$	10.200	47.600	$22.8 \pm 2.0$
2,4-DNT + Mn(III)	0.010	0.020	$37.0 \pm 4.0$

**Table 1.** Rate constants of the catalytic cycle of 2,4-DNT oxidation with ozone in the presence of manganese(II) acetate in acetic anhydride. Initial concentrations:  $[ArH]_0 = 0.10-0.40$ ,  $[H_2SO_4]_0 = 1.20$ ,  $[Mn(OAc)_2]_0 = 0.06$ ,  $[O_3] = 4 \times 10^{-5}$  M

after exhaustive oxidation of 2,4-DNT. It should be noted that cobalt(II) acetate exhibits no catalytic properties in the presence of sulfuric acid.

the formation of 2,4-DNT oxidation products is shown in the scheme. Under the conditions of catalysis with manganese(II)

The oxidation inhibition at the step of formation of the alcohol and, to a lesser extent, aldehyde is due to the conversion of nascent hydroxy and carbonyl groups into acetate and acylal groups, which are Under the conditions of catalysis with manganese(II) acetate in acetic anhydride and in the presence of sulfuric acid, 7 min after starting the ozone feeding, the Mn(III) concentration in the system reached 0.06 M and then did

more resistant to ozone (Table 1). The sequence of



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#### Scheme.

not further change up to the end of the oxidation (see figure). In the initial period of the reaction, 2,4-DNBAt and 2,4-DNBDA are accumulated at a rate lower than the maximal rate (see figure, curves 2, 3). The attainment of the maximal rate of their formation coincides in time with the conversion of Mn(II) to Mn(III). Ozone should be fed continuously. If ozone feeding is stopped, the 2,4-DNT oxidation and accumulation of the final products first decelerate and then cease at all, and Mn(III) transforms into Mn(II).

The kinetic features of 2,4-DNT oxidation in the presence of manganese(II) acetate and an increase in the selectivity of methyl group oxidation under these conditions suggest that ozone reacts primarily not with 2,4-DNT [reaction (1)], but with Mn(II) [reaction (2)] {at 20°C, [ArCH<sub>3</sub>]<sub>0</sub> = 0.4, [Mn(OAc)<sub>2</sub>]<sub>0</sub> = 0.06, [O<sub>3</sub>]<sub>0</sub> =  $4 \times 10^{-4}$  M;  $k_1 = 0.08$ ,  $k_2 = 47.6$  L mol<sup>-1</sup> s<sup>-1</sup>;  $r_2 : r_1 = 10$  (Table 1)}, generating active Mn(III) species that exhibit high substrate selectivity in oxidation of methylarenes at

the methyl group [6, 7] and are capable to react with 2,4-DNT with the formation of benzyl radicals [reaction (3)]:

$$ArCH_3 + O_3 \rightarrow ozonolysis products,$$
 (1)

$$Mn^{2+} + O_3 + H^+ \rightarrow Mn^{3+} + HO^{-} + O_2,$$
 (2)

$$ArCH_3 + Mn^{3+} \rightarrow ArCH_2 + Mn^{2+} + H^+.$$
(3)

High selectivity of 2,4-DNT oxidation to aromatic alcohol is possible only at sufficiently high concentration of the acylation catalyst, sulfuric acid (Table 2). With an increase in the acid concentration, the selectivity of the oxidation at the methyl group first increases, reaches a maximum at the acid concentration of 1.2 M, and does not increase further at higher acid concentrations. In the examined interval of sulfuric acid concentrations, the ratio of the products of the methyl group oxidation remains virtually constant (Table 2).

Our experimental data in combination with published data [8–11] allowed us to suggest the reaction scheme

**Table 2.** Influence of sulfuric acid concentration on the yield of products and selectivity of 2,4-dinitrotoluene oxidation at the methyl group. Reaction conditions:  $20^{\circ}$ C; initial concentrations:  $[ArCH_3]_0 = 0.10-0.40$ ,  $[Mn(OAc)_2]_0 = 0.06$ ,  $[O_3] = 4 \times 10^{-4}$  M; liquid phase volume 0.01 L; reaction time 2.5 h

[H <sub>2</sub> SO <sub>4</sub> ] <sub>0</sub> , M	C			
	2,4-DNBAt	2,4-DNBDA	DNBAc	Selectivity, %
0.6	37.1	12.5	22.0	71.6
0.8	48.2	16.3	30.8	95.3
1.0	55.3	19.1	22.3	96.7
1.2	65.8	18.8	12.5	97.1
1.4	59.2	20.0	18.0	97.2

**Table 3.** Influence of temperature on the selectivity of 2,4-DNT oxidation with ozone in an acetic anhydride solution. Reaction conditions: initial concentrations:  $[H_2SO_4] = 1.20$ ,  $[ArCH_3]_0 = 0.10-0.40$ ,  $[Mn(OAc)_2]_0 = 0.06$ ,  $[O_3] = 4 \times 10^{-4}$  M; 20°C; liquid phase volume 0.01 L; reaction time 2.5 h

<i>T</i> , °C	Co	Salactivity %		
	2,4-DNBAt	2,4-DNBDA	2,4-DNBAc	Selectivity, 70
10	62.5	17.5	10.9	90.9
20	65.8	18.8	12.5	97.1
30	53.0	13.4	31.1	97.5
40	45.2	10.5	42.5	98.2

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involving the radical ion nonchain mechanism of 2,4-DNT oxidation:

$$ArCH_2^{\cdot} + O_2 \rightarrow ArCH_2O_2^{\cdot}, \qquad (4)$$

$$ArCH_2^{\cdot} + O_3 \rightarrow ArCH_2O^{\cdot} + O_2, \tag{5}$$

$$ArCH_2O_2^{\cdot} + ArCH_3 \rightarrow ArCH_2O_2H + ArCH_2^{\cdot}, \qquad (6)$$

$$ArCH_2O_2^{\cdot} + Mn^{2+} + H^+ \rightarrow ArCH_2O_2H + Mn^{3+}, \quad (7)$$

$$ArCH_2O_2^{\cdot} + O_3 \rightarrow ArCH_2O^{\cdot} + 2O_2, \qquad (8)$$

$$ArCH_2O' + Mn^{2+} \rightarrow ArCH_2O^- + Mn^{3+}, \qquad (9)$$

$$ArCH_2O^- + CH_3 - \stackrel{+}{C} = O \rightarrow ArCH_2OCOCH_3.$$
(10)

The benzyl radicals generated in reactions (2) and (3)under the conditions of our experiments ( $[O_2] >> [O_3]$ ), taking into account comparable rate constants of reactions of reactions (4) and (5)  $(10^7-10^8 \text{ L mol}^{-1} \text{ s}^{-1} [8, 9])$ , are presumably consumed in reaction (4) to form peroxy radicals, which then rapidly react with ozone (for cyclohexane,  $k_8 = 1.2 \times 10^4$  L mol<sup>-1</sup> s<sup>-1</sup> [9]) to form alkoxyl radical [reaction (8)]. Reactions (6) and (7) under the conditions of our experiments do not occur to noticeable extent; at  $[ArCH_2O_2] = 3 \times 10^{-6} \text{ M}$  (calculated using the Bodenstein–Semenov method),  $20^{\circ}$ C,  $[Mn^{2+}] =$  $6 \times 10^{-3}$ ,  $[O_3] = 4 \times 10^{-4}$ ,  $[ArCH_3]_0 = 0.4$  M,  $k_6 \approx 0.2$  [9],  $k_7 \approx 11.5$  [10], and  $k_8 \approx 1.2 \times 10^4$  L mol<sup>-1</sup> s<sup>-1</sup> [9],  $r_6 \approx 2.0 \times 10^{-1}$ 10<sup>-7</sup>,  $r_7 \approx 1.9 \times 10^{-7}$ , and  $r_8 \approx 1.3 \times 10^{-5}$  mol L<sup>-1</sup> s<sup>-1</sup>. Because alkoxyl radicals are strong oxidants [11], it was natural to expect, by analogy with peroxy radicals, their reaction in the bulk of the liquid phase with the reduced Mn(II) species to form the anion [reaction (9)], which subsequently reacts with acylium cation [reaction (10)] to form 2,4-DNBAt. Apparently, the formation of 2,4-DNBDA and 2,4-DNBAc in the steady-state mode follows the similar scheme.

The rate and selectivity of oxidation of 2,4-DNT to 2,4-DNBAt depend on the reaction temperature. The optimum reaction temperature is 20°C. At lower temperatures, the total selectivity somewhat decreases (Table 3), because an increase in temperature leads to an increase in the extent of oxidation: 2,4-DNBAt and 2,4-DNBDA become intermediates, and 2,4-DNBAc is formed (Table 3).

### EXPERIMENTAL

We used analytically pure grade acetic anhydride and chemically pure grade sulfuric acid. Crystalline 2,4-DNT was purified by repeated recrystallization from ethanol. Analytically pure grade manganese(II) acetate was used without additional purification.

The reactor (a glass column with a porous partition for dispersing the ozone-air mixture) was charged with 5 mL of acetic anhydride, 2,4-DNT to a concentration of 0.4 M, and calculated amounts of the catalyst and sulfuric acid. Then the setup was brought to the required temperature, and, after the steady-state mode of the ozonizer operation was reached, the ozone-air mixture containing  $4.0 \times 10^{-4}$  M ozone was passed at a rate of 30 L h<sup>-1</sup>. The ozone concentration in the gas phase was determined by spectrophotometry from the absorption in the range 254-290 nm. Identification of oxidation products and their quantitative determination in solution were performed by GLC on a chromatograph equipped with a flame ionization detector, using a column 3 m long and 4 mm in diameter, under the following conditions: stationary phase SE-30, 5 wt % on Inerton AW-DMCS; vaporizer temperature 250, thermostat temperature 90–225°C; carrier gas nitrogen; flow rates: nitrogen 1.8, hydrogen 1.8, and air 18 L h<sup>-1</sup>. 4-Nitrochlorobenzene was used as internal reference. The effective rate constants of the reactions of ozone with Mn<sup>2+</sup>, 2,4-DNT, and its oxidation products were determined by spectrophotometry using the procedure described in [12]; the rate constant of the reaction of 2.4-DNT with Mn<sup>3+</sup> was calculated for the case of irreversible second-order reactions [13].

#### CONCLUSIONS

The catalytic reaction of ozone with 2,4-dinitrotoluene in the presence of a stop reagent was studied. In an acetic anhydride solution in the presence of sulfuric acid and manganese(II) acetate, it is possible to prevent ozonolysis and direct the reaction of oxidation with ozone toward methyl group oxidation with the predominant formation of 2,4-dinitrobenzyl alcohol in the form of the corresponding benzyl acetate in 65.8% yield.

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