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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Catalytic Oxidation of Toluene by Ozone in the Acetic Acid–Sulfuric Acid System

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Abstract—Oxidation of toluene by ozone was studied in the system constituted by acetic and sulfuric acids in the presence of manganese(II) acetate and sodium bromide. The effect of sulfuric acid and the catalyst on the yield of benzoic acid and on the oxidation rate was considered. The optimal ozonization conditions were determined. A scheme of redox catalysis that accounts for experimental data was suggested.

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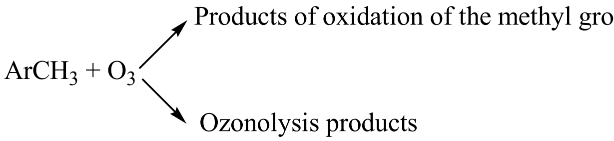
Toluene is oxidized by ozone in acetic acid predominantly with destruction of the aromatic ring [1]. The selectivity of oxidation at the methyl group can be raised by performing ozonization in the presence of variable-valence metals at 100°C [2]. The maximum yield of benzoic acid (71%) is achieved with Co(II) acetate. A less effective catalyst is Mn(II) acetate, in whose presence the yield of benzoic acid does not exceed 32%. The oxidation selectivity in the presence of Mn(II) acetate is low because the activity of Mn(IV) formed in the course of ozonization is low and it cannot compete under catalytic conditions with the reaction of disintegration of the aromatic system. At the same time, it is known that, in catalytic ozonization of nitrotoluenes in acetic anhydride in the presence of sulfuric acid additive, only Mn(III) is formed in the reaction mixture and oxidation occurs with high selectivity even at a temperature of 20°C [3, 4]. Of certain interest in this context is a study of the oxidation of toluene by ozone in acetic acid in the presence of Mn(II) acetate and sulfuric acid.

With sulfuric acid used in ozonization f toluene in acetic acid in the presence of Mn(II) acetate, benzoic acid could be obtained in 82.5% yield (Fig. 1). Benzyl alcohol and benzaldehyde are formed as intermediates in the reaction mass. As in the case of oxidation in acetic anhydride, 90% of manganese is in the trivalent state under the experimental conditions of the study (Fig. 1, curve *5*).

The amount of ozone consumed in catalytic oxidation conditions for formation of the carboxy group is 93% of that theoretically required. Cutting off the supply of ozone to the reaction mixture results in that Mn(III) is reduced to Mn(II) and the oxidation process is terminated. Thus, the role of ozone consists in permanent generation of the oxidized form of the metal that can selectively interact with the methyl group.

The experimental data obtained in the study and published evidence suggest the following scheme of toluene oxidation [2–4]:



$$\mathrm{ArCH_3 + O_3} \begin{cases} \nearrow \text{Products of oxidation of the methyl group} \\ \searrow \text{Ozonolysis products} \end{cases} \quad (1)$$

$$\mathrm{Mn^{2+} + O_3 \xrightarrow{H^+} Mn^{3+} + HO^{\cdot} + O_2}, \quad (2)$$

$$\mathrm{ArCH_3 + Mn^{3+} \longrightarrow Ar\dot{C}H_2 + Mn^{2+} + H^+}, \quad (3)$$

$$\mathrm{Ar\dot{C}H_2 + O_2 \longrightarrow ArCH_2OO^{\cdot}}, \quad (4)$$

$$\mathrm{ArCH_2OO^{\cdot} + O_3 \longrightarrow ArCH_2O^{\cdot} + 2O_2}, \quad (5)$$

$$\mathrm{ArCH_2O^{\cdot} + Mn^{2+} \xrightarrow{H^+} ArCH_2OH + Mn^{3+}}, \quad (6)$$

$$\mathrm{ArCH_2OO^{\cdot} \longrightarrow \text{Molecular products.}} \quad (7)$$

In the absence of a catalyst, the main reaction pathway is the destruction of the aromatic ring [reaction (1)] (Table 1, run no. 1). Introduction of Mn(II) acetate into the reaction zone makes it possible, owing to the faster reaction (2), to preclude direct interaction of ozone and toluene, with the methyl group oxidized by a reaction with Mn(III) (Table 2).

Because the rate constant of the interaction of ozone with toluene substantially exceeds that of its interaction with the oxidized form of the catalyst, the maximum yield of benzoic acid is possible at comparable concentrations of toluene and catalyst (Table 1, run no. 6).

The study demonstrated that sulfuric acid not only favors formation of Mn(III) in the system, but also affects the yield of the reaction product (Table 1, run nos. 6, 10–13). The yield of benzoic acid increases with the H_2SO_4 concentration primarily because the activity of the oxidized form of the metal in the reaction with toluene grows (Fig. 2) [the rates of interaction of ozone with Mn(II) acetate and ozone with toluene are independent of the sulfuric acid concentration in the range studied]. At sulfuric acid concentrations higher than 1.2 M, the consumption rate of toluene decreases (Fig. 3) and the yield of benzoic acid continues to grow (Table 1, run nos. 12 and 13). This occurs because the activity of Mn(III) increases at high concentrations of strong acids to such an extent that the reduction of trivalent manganese in the reaction with the solvent becomes noticeable (Fig. 2,

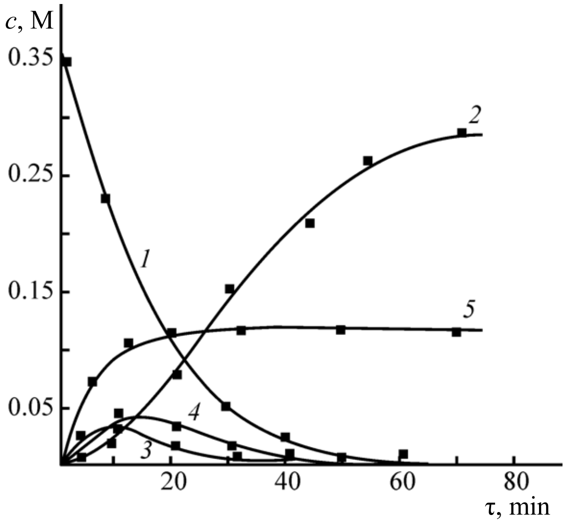


Fig. 1. Kinetics of (*1*) toluene consumption and (*2–5*) accumulation of (*2*) benzoic acid, (*3*) benzyl alcohol, (*4*) benzaldehyde, and (*5*) Mn(III) in ozonization in acetic acid in the presence of Mn(II) acetate and sulfuric acid at 60°C. $[ArCH_3] = 0.35$ M, $[O_3] = 4 \times 10^{-4}$ M, $[H_2SO_4] = 1.2$ M, $[Mn(OAc)_2] = 0.14$ M. (*c*) Concentration and (τ) reaction duration; the same for Figs. 2–4.

Table 1. Oxidation of toluene by ozone–air mixture. $[ArCH_3] = 0.35$ M, $[O_3] = 4 \times 10^{-4}$ M, gas flow rate 6.0×10^{-3} l s^{-1}

Run no.	[Mn(II)]	$[H_2SO_4]$	*T*, °C	τ, min	Yield of benzoic acid, %
	M				
1	–	1.2	60	140	11.2
2	0.02	1.2	60	120	41.8
3	0.05	1.2	60	110	64.2
4	0.08	1.2	60	100	74.1
5	0.1	1.2	60	90	78.2
6	0.14	1.2	60	75	82.5
7	0.14	1.2	20	90	70.6
8	0.14	1.2	40	80	75.4
9	0.14	–	60	130	24.6
10	0.14	0.4	60	100	68.3
11	0.14	0.8	60	85	76.1
12	0.14	1.6	60	95	84.7
13	0.14	2.0	60	125	86.8

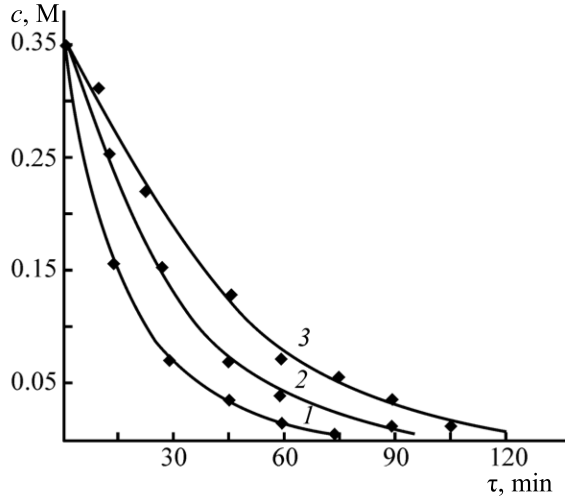


Fig. 2. Kinetics of toluene consumption at various sulfuric acid concentrations at 60°C. $[ArCH_3] = 0.35$ M, $[O_3] = 4 \times 10^{-4}$ M, $[Mn(OAc)_2] = 0.14$ M. $[H_2SO_4]$ (M): (*1*) 1.2, (*2*) 1.6, and (*3*) 2.0.

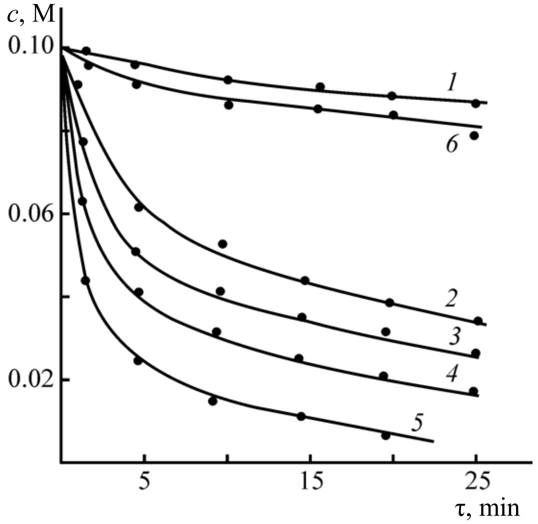


Fig. 3. Kinetics of Mn(III) consumption in acetic acid at various sulfuric acid concentrations. $[ArCH_3] = 0.35$ M, temperature 20°C. $[H_2SO_4]$ (M): (*1*) 0 (*2*) 0.4, (*3*) 0.8, (*4*) 1.2, (*5*) 2.0, and (*6*) 2.0 (in the absence of toluene).

curve *6*), together with the process of toluene oxidation.

It is known that the catalytic activity of variable-valence metal ions increases in the presence of alkali metal bromides [5]. As can be seen from the experimental data (Fig. 4), use of sodium bromide made it possible to accelerate the consumption of toluene and raise the yield of benzoic acid to 93.4%. Benzaldehyde and trace amounts of benzyl bromide were also found in the reaction mixture.

The increase in the catalytic activity of manganese acetate in the presence of NaBr is due to the formation of a manganese bromide complex $Mn^{2+}Br^-$ [5], which can involve a toluene molecule into oxidation at a higher rate, compared with Mn^{3+} (Table 2):

$$Mn^{2+} + Br^- \rightarrow Mn^{2+}Br^-, \qquad (8)$$

$$Mn^{2+}Br^- + O_3 \xrightarrow{H^+} Mn^{2+}Br^{\cdot} + HO^{\cdot} + O_2, \qquad (9)$$

$$Mn^{3+} + Br^- \rightarrow Mn^{2+}Br^{\cdot}, \qquad (10)$$

The yield of benzoic acid is the highest at $[Br^-]/[Mn^{2+}] = 1.1$ (Table 3). The observed decrease in the yield at higher contents of Br^- is in good agreement with the data of [6], according to which a number of complexes are formed, depending on the molar ratio between the metal and bromine, with the catalytic activity being the highest for metal monobromide. In the opinion of the authors of [6], this is due to the increased mobility of this complex, which facilitates substitution of AcO^- situated in the inner coordination sphere with a substrate molecule.

Consequently, with the ratio $[Br^-]/[Mn^{2+}]$ increaseing to above 1.1, manganese forms a complex with a higher content of bromine so that the rate at which toluene is involved in oxidation by reaction (11) decreases, and the fraction of methylbenzene undergoing destruction grows.

The fact that an excess amount of Br^- in the starting mixture is necessary is accounted for by the carryover

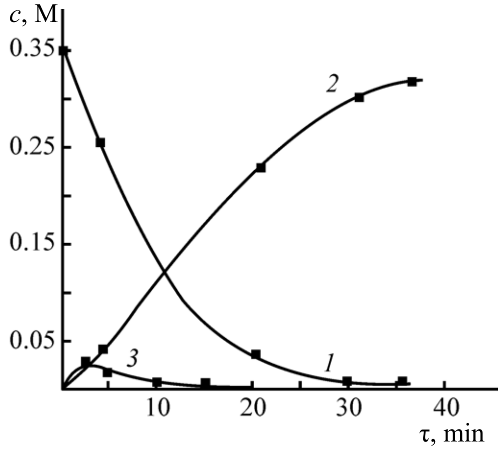


Fig. 4. Kinetics of (*1*) toluene consumption and (*2, 3*) accumulation of (*2*) benzoic acid and (*3*) benzaldehyde in ozonization in acetic acid in the presence of Mn(II) acetate, NaBr, and sulfuric acid at 60°C. $[ArCH_3] = 0.35$ M, $[O_3] = 4 \times 10^{-4}$ M, $[H_2SO_4] = 1.2$ M, $[Mn(OAc)_2] = 0.11$ M, $[NaBr] = 0.1$ M.

Table 2. Kinetic parameters of elementary reactions in catalytic oxidation of toluene by ozone in acetic acid in the presence of sulfuric acid. [H_2SO_4] = 1.2 M

Reaction	k, M^{-1}, at indicated T, °C		E, kJ mol^{-1}
	20	60	
1	0.78	5.2	38.5
2	1.3×10^{2}	4.3×10^{2}	24.2
3	7.2×10^{-3}	7.6×10^{-2}	47.8
10	1.9×10^{-2}	0.23	50.6

of molecular bromine formed in the course of oxidation and by the loss of bromine for formation of benzyl bromide.

EXPERIMENTAL

Toluene was oxidized in a hermetically sealed thermostated glass reactor equipped with a fast turbine stirrer and a bubbler 3 mm in diameter. With the stirrer working, the reactor was charged with 0.05 l of glacial acetic acid and calculated amounts of toluene, catalyst, and a strong acid, and an ozone–air mixture containing 4×10^{-4} M of ozone was delivered into the reactor. At a stirrer speed of 29.2 s^{-1} and the ozone–air mixture delivered at a rate of 6.0×10^{-3} l s^{-1}, the oxidation occurred under a kinetic control. The ozone concentration in the gas phase was determined spectrophotometrically from the absorption in the spectral range 254–259 nm, and the Mn(II) concentration in the reaction mixture, by the iodometric method. The variation of the concentrations of toluene and its oxidation products was monitored by gas-liquid chromatography with a flame-ionization detector on 3 m × 2 mm column packed with Inerton AW-DMCS support on which an SE-30 stationary phase is immobilized in an amount of 5% relative to the support mass under the following conditions: thermostat temperature increaseing by a program in the range 100–200°C in 10 min; flow rates of carrier gas (nitrogen), hydrogen, and air equal to 1.8, 1.8, and 18 l h^{-1}, respectively. As an internal standard served 4-nitrochlorobenzene.

Table 3. Oxidation of toluene by ozone–air mixture. [$ArCH_3$] = 0.35 M, [O_3] = 4×10^{-4} M, gas flow rate 6.0×10^{-3} l s^{-1}

[Mn(II)]	[NaBr]	Oxidation duration, min	Yield of benzoic acid, %
M			
0.1	0.03	60	75.4
0.1	0.07	50	86.1
0.1	0.11	40	94.3
0.1	0.15	55	85.6
0.14	0.11	55	87.5
0.7	0.11	65	73.2

CONCLUSIONS

(1) The main reaction pathway in oxidation of toluene in the system constituted by acetic and sulfuric acids is the destruction of the aromatic ring, with the yield of benzoic acid not exceeding 11.2%.

(2) Use of manganese(II) acetate as a catalyst makes it possible to raise the yield of the aromatic acid to 82.5%.

(3) Introduction of sodium bromide into the catalytic system raises both the oxidation rate of toluene and the yield of benzoic acid.

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