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# Study of Reaction of Isomeric Acetoxytoluenes with Ozone in Liquid Phase in the Presence of Manganese Bromide Catalyst

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**Abstract**—The kinetics of the ozone reaction with isomeric acetoxytoluenes in acetic anhydride in the presence of sulfuric acid and mixed manganese bromide catalyst was studied. Under these conditions it is possible to stop the oxidation process at the stage of formation of hydroxybenzaldehydes in the form of the respective acetoxybenzylidendiacetates (63–70%). The reaction products contain also acetoxybenzyl acetate (16–18%) and a small amount of acetoxybenzyl bromide (2%). The mechanism of oxidation–reduction catalysis with manganese bromide complex explaining the experimental data was considered.

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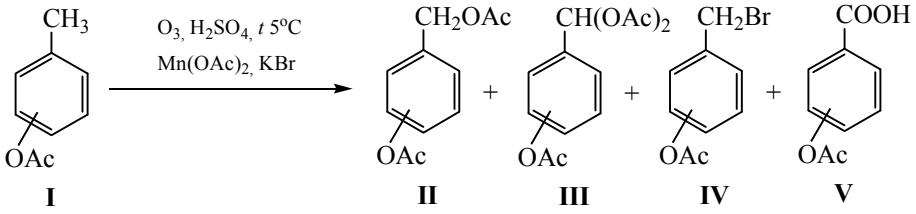
It was shown earlier [1, 2] that the selective oxidation of hydroxytoluenes with ozone proceeding without destroying the aromatic ring could be carried out in acetic anhydride solution, in the presence of manganese acetate and sulfuric acid, the catalyst of acylation. The main reaction products in the conditions of catalysis are hydroxybenzyl alcohols in the form of the acetoxybenzylacetates (**II**), formed in a yield reaching 59–63%. Attempts to obtain in these conditions hydroxybenzaldehyde in the form of acetoxybenzylidendiacetate (**III**) as the main product failed, the yield was less than 17–19%.

To solve this problem, in the present study we investigated the effect of potassium bromide additives on the kinetics of the process and the product composition of catalytic oxidation of acetoxytoluenes (**I**) with ozone, since the alkali metal bromides were known to enhance the depth, selectivity, and the reaction rate in the catalytic oxidation of alkylaromatic hydrocarbons with ozone [3]. The experimental procedure and analysis technique were described in [2].

At atmospheric pressure and 5ºC (Fig. 1) the ozonization of 4-acetoxytoluene **Ic** in acetic anhydride in the presence of a catalytic additive of sulfuric acid, manganese acetate, and potassium bromide proceeds with the formation of 4-acetoxybenzylidenediacetate **IIIc** mainly (70%). In the reaction mixture there are also present 4-acetoxybenzyl acetate **IIc** (18%) and 4-acetoxybenzyl bromide (2%). At the exhaustive oxidation of **Ic,** 4-acetoxybenzoic acid accumulates in the system. Similar results were obtained at the oxidation of 3-acetoxytoluene **Ib.** In the case of ozonization of 2-isomer **Ia** the selectivity of oxidation of methyl group is somewhat lower (see data in the end of the article), which is probably due to the steric effects of substituents.




**I** **II** **III** **IV** **V**

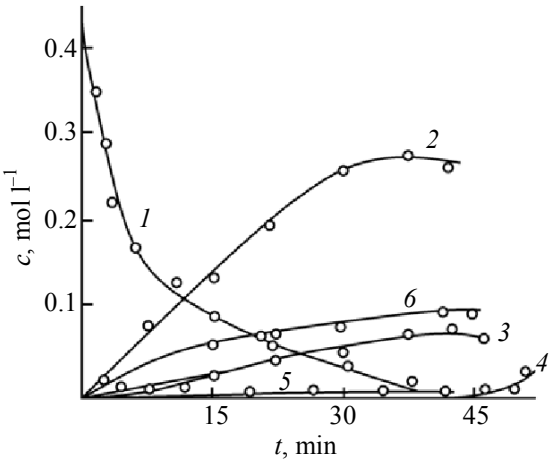



**Fig. 1.** Kinetics of oxidation of **Ic** with ozone in acetic anhydride in the presence of manganese bromide catalyst at 5ºC. $[I]_0 = 0.4$; $[Mn(OAc)_2]_0 = 0.1$; $[KBr]_0 = 0.1$; $[H_2SO_4]_0 = 1.2$; $[O_3]_0 = 4{,}2 \cdot 10^{-4}$ mol $l^{-1}$. Compounds: (*1*) **I,** (*2*) **III**, (*3*) **II**, (*4*) **V**, (*5*) **IV**, and (*6*) $[Mn^{2+}Br^{\bullet}]$; *c* is concentration, mol $l^{-1}$; *t* is reaction time, min.

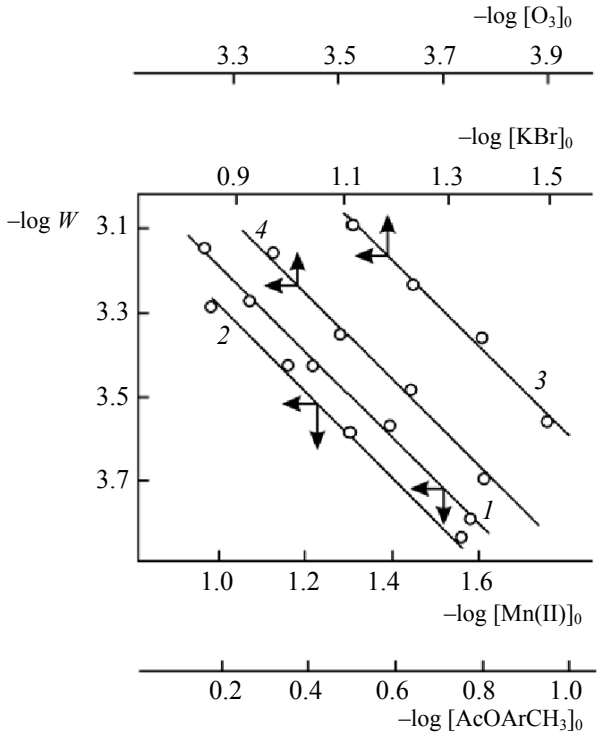



**Fig. 2.** Dependence of the rate of oxidation of **Ib** on the concentration of: (*1*) manganese acetate, (*2*) substrate, (*3*) potassium bromide, and (*4*) ozone, at 5ºC; *W* is the reaction rate, mol $l^{-1}$ $s^{-1}$.

Quantitative composition of manganese bromide catalyst affects significantly the selectivity and the ratio of oxidation products (Table 1). Maximum yield of **III** and higher selectivity of oxidation of compounds **I** is reached at the molar ratio $[Mn(OAc)_2]_0$:$[KBr]_0$ = 1:1 (initial concentrations of manganese acetate and potassium bromide is 0.1 mol $l^{-1}$), further increase in the KBr concentration does not lead to significant changes (Table 2). The linear relationship of log *W*–log $[Mn^{2+}]$ vs. log $[Br^{-}]$ is found, the reaction order with respect to the catalyst is close to 1 (Fig. 2). The higher rate and selectivity of oxidation of the methyl group in the presence of potassium bromide is due to the fact that the rate of initiation of selective oxidation of **I** in reactions with $Mn^{2+}Br^{\bullet}$ [Eq. (5)] is almost three times higher than the rate of initiation of the oxidation with manganese acetate [Eq. (4)] (Table 2). High selectivity of the oxidation occurs therewith at a decrease in the manganese concentration in the manganese bromide catalyst by 40% (Table 2).

The rate and selectivity of oxidation **I** → **III** depend on temperature: At the increased temperature the overall rate of oxidation and selectivity of methyl group oxidation grow with formation of **III**, and the fraction of **II** is reduced (Table 3). At a first glance, this dependence contradicts the experimental data: according to the experiment, at the overall trend to increase in the rate, the rate of selective oxidation [Eq. (5)] grows faster than the rate of ozonolysis [Eq. (19)] ($E_5$ = 34.4, $E_{19}$ = 20.3 kJ $mol^{-1}$, Table 2). However, kinetic studies of the ozone reaction with the reaction products showed that the patterns obtained can actually occur, since the dependence of oxidation rate on temperature increases in the sequence: $W_{17} > W_{16} > W_5$ ($E_{17}$ = 47.5, $E_{16}$ = 40.5, $E_5$ = 34.4 kJ $mol^{-1}$, Table 2).

In accordance with the obtained kinetic data, as well as with the general concepts of the mechanism of oxidation reactions catalyzed by metal-bromide catalysts [3, 8–10], we consider the results of kinetic

**Table 1.** Oxidation of **Ia** in the presence of manganese bromide catalyst of varied composition

| $[Mn(OAc)_2]_0$, mol $l^{-1}$ | $[KBr]_0$, mol $l^{-1}$ | Yield, % | |
|---|---|---|---|
| | | **IIIa** | **IIa** |
| 0.14 | – | 17.0 | 59.0 |
| 0.10 | 0.04 | 22.0 | 46.2 |
| 0.10 | 0.08 | 41.3 | 28.0 |
| 0.10 | 0.10 | 63.0 | 16.0 |
| 0.10 | 0.12 | 62.0 | 16.1 |
| 0.10 | 0.14 | 62.1 | 15.9 |

**Table 2.** Kinetic parameters of reactions of the catalytic cycle[a]

| Reaction no. | Reaction | $K$[b], l mol$^{-1}$ s$^{-1}$ | | $E$, kJ mol$^{-1}$ | $W^{5°C}$, mol l$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| | | 5°C | 30°C | | |
| 3 | $O_3 + Mn^{2+}Br^-$ | 20.30±2.00 | 55.00±5.50 | 22.1±2.2 | $8.1\times10^{-4}$ |
| 19 | **Ic** + $O_3$ | 0.59±0.05 | 0.82±0.05 | 20.3±2.0 | $0.9\times10^{-4}$ |
| 4 | **Ic** + $Mn^{3+}$ | $10.00\times10^{-3}$ | $19.52\times10^{-3}$ | 22.1±2.2 | $5.6\times10^{-4}$ |
| 5 | **Ic** + $Mn^{2+}Br^{\bullet}$ | $3.10\times10^{-2}$ | $12.10\times10^{-2}$ | 34.4±3.6 | $12.4\times10^{-4}$ |
| 6 | $AcOArCH_2^{\bullet} + O_2$ | $4.7\times10^{9}$ | | | $1.3\times10^{2}$ |
| 7 | $AcOArCH_2O_2^{\bullet} + AcOArCH_3$ | 2.3 | | | $3.2\times10^{-6}$ |
| 8 | $AcOArCH_2O_2^{\bullet} + Mn^{2+}Br^-$ | $10^2$ | | | $3.5\times10^{-5}$ |
| 9 | $AcOArCH_2O_2^{\bullet} + O_3$ | $10^2$ (20°C) | | | $1.4\times10^{-7}$ |
| 12 | $2AcOArCH_2O_2^{\bullet}$ | $10^8$ | | | $12.4\times10^{-4}$ |
| 13 | $AcOArCH_2O^{\bullet} + Mn^{2+}Br^-$ | $10^3$ | | | $3.5\times10^{-4}$ |
| 15 | $2AcOArCH_2O_2^{\bullet}$ | $10^8$ | | | $12.4\times10^{-4}$ |
| 16 | **IIc** + $Mn^{2+}Br^{\bullet}$ | $9.21\times10^{-3}$ | $31.34\times10^{-3}$ | 40.5±4.0 | $3.7\times10^{-4}$ |
| 17 | **IIIc** + $Mn^{2+}Br^{\bullet}$ | $4.92\times10^{-3}$ | $13.28\times10^{-3}$ | 47.5±5.0 | $2.0\times10^{-4}$ |

[a] The reaction rate determined from Fig. 1 is $9.5\times10^{-4}$ mol l$^{-1}$ s$^{-1}$. [b] $K_{19}$, $K_3$, $K_4$ and $K_5$, $K_{16}$, $K_{17}$ are calculated according to the data obtained in this study, the value of $K_6$ is that for the methyl radical [4], $K_9$ for the reaction $CH_3O_2^{\bullet}$ + $O_3$ [5], $K_7$, $K_8$, $K_{12}$ and $K_{15}$ were taken for the reaction of toluene with cobalt [6] corrected for the redox potential of $Mn^{2+}$ [7], $K_{13}$ = 10 $K_8$, taking into account the higher reactivity of alkoxy radical [7]. Acetoxyperoxyde radical concentration in the calculations was estimated based on the conditions of steady-state concentrations of reacting species: $K_5[AcOArCH_3][Mn^{2+}Br^{\bullet}] = K_{12}[AcOArCH_2O_2^{\bullet}]_2$, hence $[AcOArCH_2O_2^{\bullet}] = (K_5[AcOArCH_3][Mn^{2+}Br^{\bullet}])/K_{12}$.

studies in the framework of the classical scheme of unbranched chain reaction:

$$Mn^{2+} + Br^- \rightarrow Mn^{2+}Br^-, \quad (1)$$

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

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

$$AcOArCH_3 + Mn^{3+} \rightarrow AcOArCH_2^{\bullet} + Mn^{2+} + H^+, \quad (4)$$

$$AcOArCH_3 + Mn^{2+}Br^{\bullet} \rightarrow AcOArCH_2^{\bullet} + Mn^{2+}Br^- + H^+, \quad (5)$$

$$AcOArCH_2^{\bullet} + O_2 \rightarrow AcOArCH_2O_2^{\bullet}, \quad (6)$$

$$AcOArCH_2O_2^{\bullet} + AcOArCH_3 \rightarrow AcOArCH_2O_2H + AcOArCH_2^{\bullet}, \quad (7)$$

**Table 3.** Effect of temperature on the selectivity and rate of oxidation of **Ib**

| $T$, °C | $W\times10^4$, mol l$^{-1}$ s$^{-1}$ | Reaction products, mol l$^{-1}$ | | Total selectivity,% |
|---|---|---|---|---|
| | | **IIIb** | **IIb** | |
| 5 | 8.6 | 0.274 | 0.070 | 87.9 |
| 15 | 10.1 | 0.256 | 0.067 | 80.8 |
| 20 | 13.6 | 0.203 | 0.060 | 65.8 |
| 30 | 17.2 | 0.120 | 0.046 | 41.5 |

$$AcOArCH_2O_2^{\bullet} + Mn^{2+}Br^- + H^+ \rightarrow AcOArCH_2O_2H + Mn^{2+}Br^{\bullet}, \quad (8)$$

$$AcOArCH_2O_2^{\bullet} + O_3 \rightarrow AcOArCH_2O^{\bullet} + 2O_2, \quad (9)$$

$$AcOArCH_2O_2H \rightarrow AcOArCH_2O^{\bullet} + HO^{\bullet}, \quad (10)$$

$$AcOArCH_2O_2H + Mn^{2+}Br^- \rightarrow AcOArCH_2O^- + Mn^{2+}Br^{\bullet} + HO^{\bullet}, \quad (11)$$

$$AcOArCH_2O_2^{\bullet} \rightarrow 2\,AcOArCH_2O^{\bullet} + O_2, \quad (12)$$

$$AcOArCH_2O^{\bullet} + Mn^{2+}Br^- \rightarrow AcOArCH_2O^- + Mn^{2+}Br^{\bullet}, \quad (13)$$

$$AcOArCH_2O^- + CH_3{-}C{=}O \rightarrow AcOArCH_2OAc, \quad (14)$$

$$2\,AcOArCH_2O_2^{\bullet} \rightarrow AcOArCH_2OH + AcOArCHO + O_2, \quad (15)$$

$$AcOArCH_2OAc + Mn^{2+}Br^{\bullet} \rightarrow AcOArCH^{\bullet}OAc + Mn^2Br^- + H^+, \quad (16)$$

$$AcOArCH(OAc)_2 + Mn^{2+}Br^{\bullet} \rightarrow AcOArC^{\bullet}(OAc)_2 + Mn^{2+} + Br^- + H^+, \quad (17)$$

$$Ac_2O + H^+ \rightarrow CH_3{-}C{=}O + AcOH, \quad (18)$$

$$AcOArCH_3 + O_3 \rightarrow \text{ozonides}, \quad (19)$$

$$Br^- + O_3 + H^+ \rightarrow Br^{\bullet} + HO_3^{\bullet}, \quad (20)$$

$$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2, \quad (21)$$

$$AcOArCH_2^{\bullet} + Br_2 \rightarrow AcOArCH_2Br + Br^{\bullet} \quad (22)$$

In the absence of bromide ions the active form of the catalyst is the particle $Mn^{3+}$ [Eq. (2)], which

involves in the oxidation the methyl group of compound **I** with formation of acetoxybenzyl radical [Eq. (4)]. Introduction to the system of bromide ions leads to the formation of more active manganese bromide catalyst [Eqs. (1) and (3)]. At the ratio [Mn(II)]:[$Br^-$] = 1:1, compound **I** is involved in the oxidation reaction (5). When concentrations in the ozone–air mixture [$O_2$] >> [$O_3$] ≈ 22, the formed acetoxybenzyl radicals are transformed into acetoxyperoxyde radicals [Eq. (6)]. Further transformation of the latter in the framework of the considered scheme is possible when $W_i = W_t << W_r$, i.e. when the chain length $\nu = W_{exp}/W_i >> 1$. However, estimates show that in the experimental conditions this dependence is not observed: $W_i$ ($W_5$) = $W_t$ ($W_{12}$) >> $W_r$ ($W_7$, $W_8$, $W_9$), and the chain length $\nu = W_r/W_i = 3.5\times10^{-4}/12.4\times10^{-4} = 0.28$. Most likely, in the presence of manganese bromide catalyst, the oxidation of **I** develops by the ion-radical non-chain mechanism, whereby the oxidation products are mainly formed as a result of termination of acetoxyperoxy radicals.

Terminating of acetoxyperoxy radicals can proceed predominantly by the reaction (12), since the reaction (15) suggests a parallel formation of **II** and **III**, which contradicts the experimental data. It seems that alkoxy radicals formed in the solvent cell in the experimental conditions go over into the bulk of solution (12) [7], where they react with a high rate with the reduced form of catalyst (13) forming the reaction products ($K_3/K_8 \approx 10.0$ [7]). The whole process development obviously corresponds to the sequence of reactions (6–12–13–14), but it does not stop at the stage of formation of compound **II** and continues until the formation of compounds **III** and **V** [Eqs. (16), (18) and then similarly to the reaction scheme (6)–(12)–(13)–(14)]. Formation of compound **IV** is probably a result of reactions (20)–(22).

It was noted (Fig. 1, curve *6*) that the concentration of active catalyst in solution at the initial time is close to zero, but it continuously increases with the decrease in the concentration of **I** and reaches maximum value (0.08 mol $l^{-1}$) during exhaustive oxidation of the substrate. The reason is that initially the reaction rate of oxidation of $Mn^{2+}$ $Br^-$with ozone ($W_3$) slightly exceeds the rate of its reduction in the reaction with the substrate ($W_5$) (at [$AcOArCH_3$]$_0$ = 0.4, [$O_3$]$_0$ =$4.0\times10^{-4}$; [$Mn^{2+}Br^-$]$_0$ = 0.07; [$Mn^{2+}$ $Br^{\bullet}$] = 0.03 mol $l^{-1}$; $K_3$ = 20.3, $K_5 = 3.1\times10^{-2}$ l $mol^{-1}$ $s^{-1}$, $W_3 = 5.7\times10^{-4}$, and $W_5 = 3.7\times10^{-4}$ mol $l^{-1}$ $s^{-1}$), so the concentration of $Mn^{2+}Br^{\bullet}$ in the system at the initial time is low (the color of the reaction mixture is light brown). Upon consumption of **I** and formation of less reactive **II** and **III** the rate of reduction of $Mn^{2+}Br^{\bullet}$ falls, resulting in an increase of its equilibrium concentration in the system (at the end of the oxidation the solution becomes of violet color). It is characteristic that at the initial time, when the concentration of $Mn^{2+}Br^{\bullet}$ in solution is low, the rate of oxidation of **I** is higher than the rate of formation of **III** (Fig. 1). In these conditions, **I** is oxidized by ozone mainly at the double bonds of the aromatic ring [Eq. (19)] with the formation of ozonides.

From the above follows that in the oxidation of **I** with ozone in the presence of manganese bromide catalyst the high selectivity of oxidation of the methyl group is achieved at comparable concentrations of catalyst and the substrate. Below are shown the data on the oxidation of **I** by ozone-air mixture in acetic anhydride in the presence of the manganese bromide catalyst at 5ºC: [$O_3$]$_0$ = $4.2\times10^{-4}$, [**I**]$_0$ = 0.4, [$Mn(OAc)_2$]$_0$ = 0.1, [KBr]$_0$ = 0.1, [$H_2SO_4$]$_0$ = 1.2 mol $l^{-1}$, $V_r$ =0.01 l.

| Comp. no. | Yield of the oxidation products, % | | |
|---|---|---|---|
| | **III** | **II** | **IV** |
| **Ia** | 63.0 | 16.0 | traces |
| **Ib** | 68.7 | 17.6 | 1.6 |
| **Ic** | 70.0 | 18.0 | 2.0 |

The oxidation proceeds by the ion-radical non-chain mechanism, comprising the following sequence of reactions: (5)–(6)–(12)–(13)–(14)–(17). Material balance of the process accounting for these reactions leads to the final Eq. (23), which corresponds to the experimentally observed first order with respect to the initial components (Fig. 2) [Eq. (24)]:

$$AcOArCH_3 + Mn^{2+}Br^- + O_3 \rightarrow AcOArCH_2O^- + Mn^{2+}Br^{\bullet} + HO^{\bullet} + 1/2O_2, \quad (23)$$

$$W = K_{eff}[AcOArCH_3]_0[Mn^{2+}Br^-]_0[O_3]_0. \quad (24)$$

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