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Catalysis of Reaction between Ozone and 4-Hydroxytoluene in Acetic Anhydride

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Abstract—Kinetics and products of 4-hydroxytoluene oxidation with ozone–air mixture in the presence of transition metal acetates as catalysts have been studied. Main steps of the catalytic series have been considered, and a mechanism of redox catalysis has been proposed which conforms to the experimental data and enables control over the direction, depth, and selectivity of the oxidation. Only manganese(II) acetate has been found to exhibit high catalytic activity in the presence of catalytic amounts of mineral acids. Manganese(II) acetate largely suppresses electrophilic reaction of ozone with the aromatic ring, so that the main reaction direction is oxidation of the methyl group with formation of 4-acetoxybenzyl acetate as the major product (62.6%) and 4-acetoxybenzylidene diacetate as a minor one (10.2%).

Keywords: 4-hydroxytoluene, 4-acetoxytoluene, ozone, acetic anhydride, catalyst, oxidation
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We previously showed that 4-hydroxytoluene reacted with ozone in the form of acetoxytoluene in the sulfuric acid–acetic anhydride medium, and that the process involved competing reactions of ozone with the methyl group and aromatic ring (ozonolysis) [1] (Scheme 1).

In all the cases, oxidation of methyl group stopped at the stage of formation of acetylated benzyl alcohol and benzaldehyde, the final product being 4-acetoxybenzoic acid. The selectivity with respect to the methyl group oxidation did not exceed 20.5%. In the present work we examined the reaction of 4-hydroxytoluene with ozone in the presence of transition metal salts in order to enhance the selectivity of the methyl group oxidation [2].

The ozonation of 4-acetoxytoluene in acetic anhydride at 278 K in the presence of transition metal salts revealed improved selectivity for the methyl group oxidation, and the major products were 4-acetoxybenzyl acetate and 4-acetoxybenzylidene diacetate. The transition metal salts acted as oxidation catalysts, and ozone reacted preferentially with metal cation M^{n+}

Scheme 1.

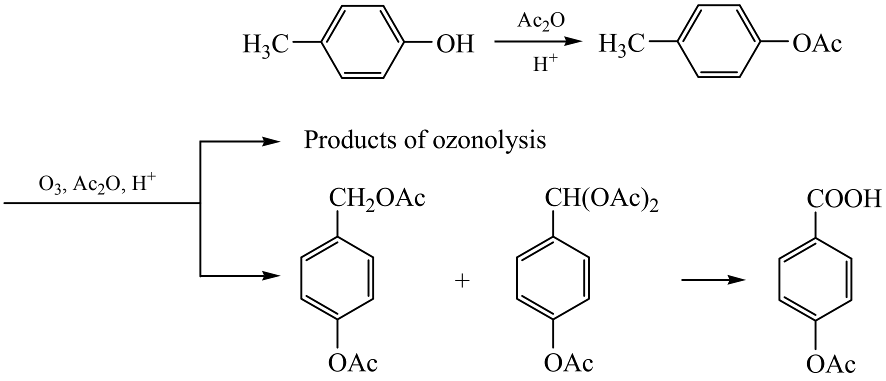

Table 1. Selectivity of oxidation of 4-acetoxytoluene with ozone in acetic anhydride in the presence of sulfuric acid and transition metal salts; 278 K; $[\text{4-AT}]_0 = 0.4$, $[\mathrm{M(OAc)_2}]_0 = 0.1$, $[\mathrm{H_2SO_4}]_0 = 1.2$, $[\mathrm{O_3}]_0 = 4.0 \times 10^{-4}$ mol/L

Metal salt	E_r^{298} M/M$^+$	Yield of oxidation products, %	
		4-acetoxybenzyl acetate	4-acetoxybenzylidene diacetate
$\mathrm{Co(OAc)_2}$	1.810	13.7	7.3
$\mathrm{Mn(OAc)_2}$	1.510	63.3	14.0
$\mathrm{Cr(OAc)_2}$	0.740	36.1	6.3
$\mathrm{Ni(OAc)_2}$	0.407	30.2	3.1

to give its oxidized form $\mathrm{M}^{(n+1)+}$ (1) which was in turn reduced according to reaction (2) with formation of benzyl radicals, and the latter were oxidized into final products [3].

$$\mathrm{M}^{n+} + \mathrm{O_3} + \mathrm{H}^+ \rightarrow \mathrm{M}^{(n+1)+} + \mathrm{O_2} + \mathrm{HO}^{\cdot}, \tag{1}$$

$$\mathrm{AcOC_6H_4CH_3} + \mathrm{M}^{n+1} \rightarrow \mathrm{AcArCH_2^{\cdot}} + \mathrm{Me}^{n+} + \mathrm{H}^+. \tag{2}$$

The selectivity of the oxidation of 4-acetoxytoluene depended on the redox potential of the $\mathrm{M}^{n+}/\mathrm{M}^{(n+1)+}$ couple and was found to increase in the Ni(II) < Cr(II) < Mn(II) series, being the highest in the presence of manganese(II) acetate (Table 1).

Despite the highest redox potential and high catalytic activity in the oxidation of arenes [3, 4], cobalt(II) acetate showed no catalytic activity in the presence of $\mathrm{H_2SO_4}$.

In order to get a deeper insight into the mechanism of redox catalysis in reactions of arenes with ozone, we examined the reaction of ozone with manganese(II) and cobalt(II) acetates and the reactions of Mn(III) and Co(III) acetates with 4-acetoxytoluene in acetic anhydride in the presence of sulfuric acid. The reaction of $\mathrm{O_3}$ with $\mathrm{Mn(OAc)_2}$ at 278–303 K was of the first order with respect to the both reactants (Fig. 1). The kinetic parameters of that reaction at different temperatures are given in Table 2. In the absence of sulfuric acid, the electronic absorption spectra of ozonized solutions of manganese acetate were similar to those of Mn(IV) solutions (Fig. 2) [5, 6]. The solution was brown, also typical of Mn(IV) ions. In the presence of sulfuric acid exhaustive oxidation of Mn(II) yielded Mn(III), as confirmed by the absorption spectrum of the resulting solution (Fig. 2).

In agreement with the published data [7–9], ozonation of transition metal complexes with organic ligands followed mainly a two-electron intramolecular mechanism. According to our data, in the absence of sulfuric acid the oxidation was described by Eq. (3), and in the presence of sulfuric acid Eq. (4) was held.

$$\mathrm{Mn^{2+} + O_3 + 2H^+ \rightarrow Mn^{4+} + O_2 + H_2O}, \tag{3}$$

$$\mathrm{Mn^{2+} + O_3 + H^+ \rightarrow Mn^{3+} + O_2 + HO}. \tag{4}$$

In the absence of sulfuric acid, manganese(II) rapidly reacted with ozone, and the k_2 value attained 4.45×10^3 L mol^{-1} s^{-1} at 303 K. Sulfuric acid slowed down the oxidation of Mn(II): the rate constant k_2 at 303 K was lowered by two orders of magnitude in the presence of 1.2 mol/L of sulfuric acid (Table 2). Likewise, the reaction of cobalt(II) acetate with ozone was of the first order with respect to the both reactants, and Co(II) was oxidized to Co(III).

$$\mathrm{Co^{2+} + O_3 + H^+ \rightarrow Co^{3+} + O_2 + HO^{\cdot}}. \tag{5}$$

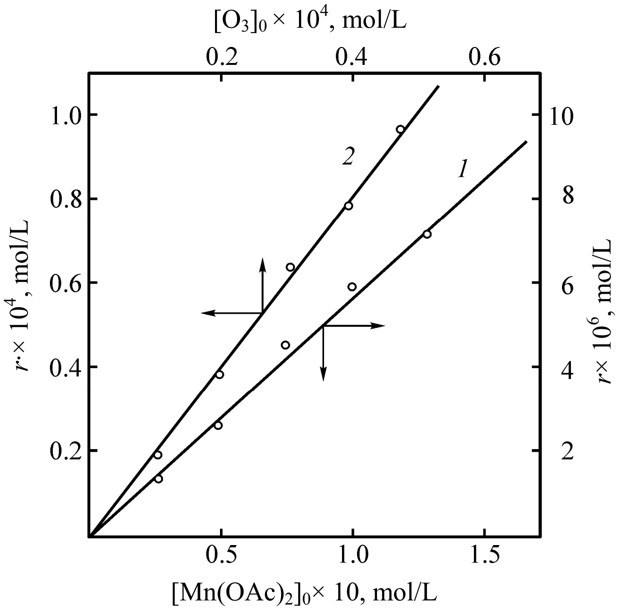

Fig. 1. Plots of the rate of oxidation of 4-acetoxytoluene at 278 K versus concentrations of (*1*) manganese(II) acetate at $[\mathrm{O_3}]_0 = 4.0 \times 10^{-4}$ mol/L and (*2*) ozone at $[\mathrm{Mn(OAc)_2}]_0 = 0.1$ mol/L.

Table 2. Rate constants of the reaction of ozone with manganese(II) acetate in acetic anhydride

Temperature, K	Initial concentration, mol/L			k, L mol^{-1} s^{-1}	E, kJ mol^{-1}	A, L mol^{-1} s^{-1}
	$[Mn(OAc)_2]_0 \times 10^3$	$[O_3]_0 \times 10^5$	$[H_2SO_4]_0$			
278	2.3–18.1	1.6–4.5	1.0–1.2	19.2±2.0	26.6±3.0	(2.1±0.2)×10^6
283	2.3–18.1	1.6–4.5	1.0–1.2	24.5±2.4		
288	2.3–18.1	1.6–4.5	1.0–1.2	31.6±3.0		
303	2.3–18.3	1.6–4.5	1.0–1.2	59.4±6.0		
278	2.3–18.1	1.6–4.5	–	1000±100	48.3±4.0	(1.1±0.1)×10^{12}
283	2.3–18.1	1.6–4.5	–	1380±130		
288	2.3–18.1	1.6–4.5	–	1915±190		
303	2.3–18.3	1.6–4.5	–	4450±400		

The rate constant k_5 was of 9.1×10^2 L mol^{-1} s^{-1} at 303 K in the absence of sulfuric acid. Addition of the latter reduced k_5 to 1.0 L mol^{-1} s^{-1}. The findings may be rationalized taking into account the structure of the transition complex $[M^+ \cdots O_3]$ whose stability should be determined by the ligand environment. In the acetic anhydride medium, acetate anions and acetic anhydride molecules could act as ligands $[M(OAc)_x(Ac_2O)_y]$. Presumably, in the presence of sulfuric acid ligand exchange with participation of hydrogen sulfate anion led to the $[Me(OAc)_{x-a}(Ac_2O)_{y-b}(HSO_4^-)_{a+b}]$ complex, which hindered electron transfer from the metal to ozone in the intermediate complex $[M^{n+} \cdots O_3]$ [7].

It was surprising that cobalt(II) acetate showed no catalytic activity in the presence of sulfuric acid. Almost no oxidation of 4-acetoxytoluene was observed under those conditions (Fig. 3). Within the observation time the color of the solution remained pink which was typical of the reduced form of the catalyst. That is difficult to explain in terms of the existing views: cobalt generally exists mainly in the oxidized form under the conditions of methylbenzenes ozonation [2]. Cobalt should also be present in the oxidized form in the course of 4-acetoxytoluene oxidation, for the rate of accumulation of Co(III) ($r_5 = 7.2 \times 10^{-5}$ mol L^{-1} s^{-1}; k_5 = 1.0 L mol^{-1} s^{-1}, $[O_3]_0 = 4.0 \times 10^{-4}$ mol L^{-1}, $[Co(OAc)_2]_0$ = 0.18 mol L^{-1}) was an order of magnitude higher than the rate of consumption of 4-acetoxytoluene in the reaction with Co(III) in the presence of sulfuric acid, as calculated from the data in Fig. 3 (curve *1*). The pattern is very untypical of ozonolysis catalysis by cobalt acetate; we believe that it is possible only if there are other preferential paths of Co(III) consumption.

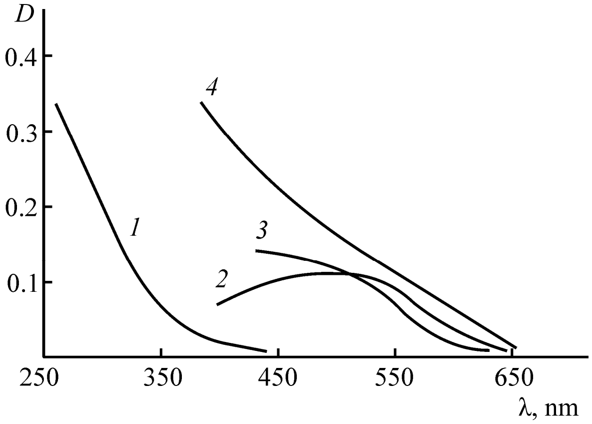

Fig. 2. Electronic absorption spectra of (*1*) Mn(OAc)$_2$, (*2*) Mn(OAc)$_3$, and ozonized Mn(OAc)$_2$ (*3*) in the presence and (*4*) in the absence of sulfuric acid.

As follows from the data in Fig. 3, exhaustive ozonation of cobalt(II) acetate in acetic anhydride yielded Co(III) which fairly slowly reacted with acetic anhydride; according to our data, the effective rate constant of the reaction of Co(III) with acetic anhydride at 293 K was of 3.4×10^{-4} L mol^{-1} s^{-1}. As a result, the concentration of ozone in the reaction solution was almost constant after termination of its feeding to the system (Fig. 3, curve *3*). Addition of sulfuric acid promoted fast reduction of Co(III) to Co(II) (Fig. 3, curve *3*). Characteristically, 4-acetoxytoluene added to the system simultaneously with sulfuric acid almost was not oxidized within the observation period.

Our experimental data indicated fast reduction of Co(III) in the reaction with acetic anhydride in the presence of sulfuric acid. That fast reaction was likely allowed due to exchange of coordinated acetate ion and acetic anhydride molecule for hydrogen sulfate ion at the metal cation, which facilitated electron transfer from acetic anhydride molecule to Co(III). The kinetic data were consistent with the above conclusion: in the presence of sulfuric acid at 293 K the effective rate constant of the Co(III) reaction with acetic anhydride increased from 3.4×10^{-4} to 0.31 $L\,mol^{-1}\,s^{-1}$, i.e., by three orders of magnitude, so that the ratio r[Co(III) + Ac_2O]/r[Co(III) + 4-AT] attained $\sim 10^3$.

Similar studies carried out with manganese acetate showed that Mn(III) reacted with acetic anhydride in the presence of sulfuric acid at a considerably lower rate than did Co(III) ($k_{ef} = 1.7 \times 10^{-4}$ $L\,mol^{-1}\,s^{-1}$ at 293 K), which was responsible for the high catalytic activity in the ozonation of 4-acetoxytoluene (Table 3). At 293 K, [4-AT] = 0.4 $mol\,L^{-1}$, $[Ac_2O]_0 = 10$ $mol\,L^{-1}$, $[Mn(OAc)_3]_0 = 0.1$ $mol\,L^{-1}$, $[O_3] = 4 \times 10^{-4}$ $mol\,L^{-1}$, we found that k[Mn(III) + Ac_2O] = 1.7×10^{-4} $L\,mol^{-1}\,s^{-1}$, $k_1 = 31.6$ $L\,mol^{-1}\,s^{-1}$, and k[Mn(III) + 4-AT] = 2.1×10^{-2} $L\,mol^{-1}\,s^{-1}$; r[Mn(III) + 4-AT] = 0.8×10^{-3} $mol\,L^{-1}\,s^{-1}$ and r_3[Mn(III) + Ac_2O] = 1.7×10^{-4} $mol\,L^{-1}\,s^{-1}$.

To conclude, manganese(II) acetate is an efficient catalyst for the oxidation of 4-acetoxyoluene at the methyl group in acetic anhydride in the presence of sulfuric acid. At 273 K the oxidation results in formation of 4-acetoxybenzyl acetate (62.6%) and 4-acetoxybenzylidene diacetate (10.2%). Cobalt(II) acetate loses its catalytic activity in the presence of sulfuric acid.

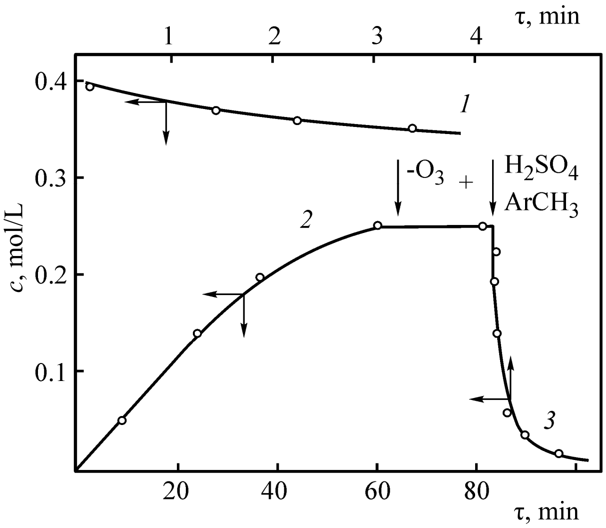

Fig. 3. Kinetics of (*1*) oxidation of 4-acetoxytoluene with Co(III) in the presence of sulfuric acid, (*2*) accumulation of Co(III) in the reaction of Co(II) with ozone in the absence of sulfuric acid, and (*3*) consumption of Co(III) in the presence of sulfuric acid and 4-acetoxytoluene; temperature 278 K; solvent acetic anhydride; $[H_2SO_4]_0 = 1.2$, $[4\text{-AT}]_0 = 0.4$ mol/L.

EXPERIMENTAL

Experiments were carried out in a glass column equipped with a porous baffle to disperse the ozone–air mixture and maintained at a constant temperature in the range from 273–303 K; the reactions occurred in the kinetic mode. The column was charged with 10 mL of acetic anhydride, 0.4 $mol\,L^{-1}$ of 4-hydroxytoluene, 0.8 $mol\,L^{-1}$ of sulfuric acid, and the corresponding metal salt. 4-Hydroxytoluene underwent acylation during the reactants mixing; therefore, the oxidation of 4-acetoxytoluene was discussed above. Ozone–air mixture containing $(1.0–4.0) \times 10^{-4}$ $mol\,L^{-1}$ of ozone was then fed at a flow rate of 30 L/h. Ozone concentration in the gas phase was determined by spectrophotometry at λ 254–290 nm. Aromatic oxidation products were identified and quantified in solution with GLC using the LKhM-8MD chromatograph equipped with a flame-ionization detector and a 3 m × 4 mm column packed with 5 wt % of SE-30 on Inerton AW-DMCS; other conditions were as follows: injector temperature 523 K, oven temperature 463 K; carrier gas (nitrogen) and hydrogen flow rate 1.8 L/h; air flow rate 18 L/h.

The effective rate constants of ozone reactions with Mn(II) and 4-acetoxytoluene were determined by spectrophotometry as described in [10]. The rate constants of Mn(III) reaction with 4-acetoxytoluene

Table 3. Rate constants

Reaction	k, $L\,mol^{-1}\,s^{-1}$	r, $mol\,L^{-1}\,s^{-1}$
$Co(II) + O_3 + H^+ \rightarrow$	1.0	4.0×10^{-5}
$Co(III) + Ac_2O \rightarrow$	3.4×10^{-3}	3.4×10^{-3}
$Co(III) + Ac_2O + H^+ \rightarrow$	0.31	0.31
$Co(III) + ArCH_3 \rightarrow$	8.2×10^{-3}	3.3×10^{-4}
$Mn(II) + O_3 + H^+ \rightarrow$	31.6	1.3×10^{-3}
$Mn(III) + Ac_2O + H^+ \rightarrow$	1.7×10^{-4}	1.7×10^{-4}
$Mn(III) + ArCH_3 \rightarrow$	2.1×10^{-2}	8.4×10^{-4}

were determined graphically assuming irreversible second-order reaction [11].

REFERENCES

1. Galstyan, A.G., Sedikh, G.O., and Galstyan, G.A., *Ukr. Khim. Zh.*, 2007, vol. 73, no. 6, p. 104.
2. Galstyan, G.A., Tyupalo, N.F., and Galstyan, A.G., *Zhidkofaznoe kataliticheskoe okislenie aromaticheskikh soedinenii ozonom* (Liquid-Phase Oxidation of Aromatic Compounds with Ozone), Lugansk: Vostochnoukr. Nats. Univ. imeni V. Dalya, 2009.
3. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Liquid-Phase Chain Oxidation of Hydrocarbons), Moscow: Nauka, 1965.
4. Galstyan, G.A., Galstyan, T.M., and Mikulenko, L.I., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 255.
5. Davies, G., *Coord. Chem. Rev.*, 1969, vol. 4, no. 2, p. 199. DOI: 10.1021/ic50100a011
6. Hanotier, J., Hanotier-Bridoux, M., and de Radzitzky, P., *J. Chem. Soc., Perkin Trans. 2*, 1973, no. 4, p. 381. DOI: 10.1039/P29730000381
7. Grinberg, A.A., *Vvedenie v khimiyu kompleksnykh soedinenii* (Introduction to the Chemistry of Coordination Compounds), Leningrad: Khimiya, 1971.
8. Sapunov, V.N., *Kinet. Katal.*, 1974, vol. 15, no. 1, p. 30.
9. Uemura, S., Spencer, A., and Wilkinson, G., *J. Chem. Soc., Dalton Trans.*, 1973, no. 23, p. 2565. DOI: 10.1039/DT9730002565
10. Razumovskii, S.D. and Zaikov, G.E., *Ozon i ego reaktsii s organicheskimi soedineniyami* (Ozone and Its Reactions with Organic Compounds), Moscow: Nauka, 1974.
11. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Lectures on Chemical Kinetics), Moscow: Vysshaya Shkola, 1969.