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Articles

Kinetic Model of Ethyl Benzene Oxidation Catalysed by Manganese Salts

Tatiana V. Bukharkina,* Olga S. Grechishkina, Nikolai G. Digurov, and Nadezhda V. Krukovskaya

Department of Carbon Materials Technology, Faculty of Organic Compounds, D.I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Square, Moscow 125047, Russia

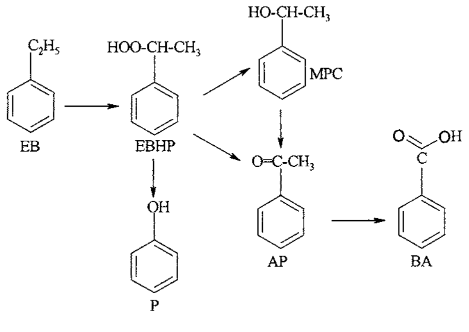
Abstract:
A practical model was developed for liquid-phase Mn^{3+}-catalysed oxidation of ethyl benzene by O_2. The model describes time profiles of concentrations of ethyl benzene and two intermediate oxidation products (methyl phenyl carbinol and acetophenone). The kinetic model of acetophenone oxidation to benzoic acid was also obtained. The influence of the main products of the ethyl benzene oxidation on the reaction kinetics is discussed. It was established that the addition of ethyl benzene hydroperoxide does not affect the reaction rate; the addition of methyl phenyl carbinol inhibits the reaction. The addition of acetophenone promotes the reaction and neutralises the inhibiting effect of methyl phenyl carbinol. The proposed reaction mechanism includes free-radical ethyl benzene oxidation. The process is initiated by the acetophenone interaction with Mn^{3+} ion, and the chain is propagated due to the hydroperoxide interaction with ethyl benzene. The chain termination is quadratic. The length of the oxidation chain was calculated. The inhibition is caused by the manganese bonding to form an inactive complex. The obtained system of differential rate equations adequately describes the process.

Introduction

The kinetic model of ethyl benzene (EB) oxidation is relevant for many commercial processes. This model would become eventually more valuable if it were to include the reactions of the intermediates. In some cases these intermediates can become desired products themselves. Also, they can participate in the oxidation of the starting EB and change the rate of its consumption. This work is devoted to EB oxidation in the presence of the main reaction products and aimed at the building of a mathematical model of the process that can be used for equipment design. The information on the reactions occurring in the system is vital for the construction of the model. Thus, EB can interact either with Mn(III) or with free radicals. The latter can be formed both in the decomposition of the first intermediate, that is, ethyl benzene hydroperoxide (EBHP), and in the oxidation of other intermediates: methyl phenyl carbinol (MPC) or acetophenone (AP) to benzoic acid (BA). It is evident that all these compounds can influence the rate of ethyl benzene (EB) consumption and the type of the kinetic equations in the model. Preliminary experiments[1] showed that the initial rate of EB oxidation is described by the following equation:

$$r_0 = k[\mathrm{EB}]_0\sqrt{[\mathrm{Mn}^{3+}]}$$

The following reactions occur in the system:



It is evident that these data are not sufficient for the construction of the kinetic model. Therefore, we had to

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* Author for correspondence. Fax: +7 (095) 978 9569. E-mail: htum@muctr.edu.ru.

(1) Bukharkina, T. V.; Grechishkina, O. S.; Digurov, N. G.; Krukovskaya, N. V. *Org. Process Res. Dev.* **1999**, *3*, 400−403.

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investigate the reactions of the intermediate products leading to the final product of EB oxidation, that is, benzoic acid. We also investigated the influence of the intermediates on the ratio of catalyst species in different oxidation states. As a result, we obtained the system of differential equations that correctly describes the process.

Experimental Section

Kinetic Procedure. All the runs were carried out under intensive mixing at standard pressure and 120 °C. In the preliminary experiments it was established that the initial reaction rate became independent of the stirrer speed at 2000 rpm and of oxygen flow above 0.5 L/min. All the kinetic experiments were run under these conditions, thus ensuring the absence of mass-transfer effects. The solvent was pure ethyl benzene or its mixture with chlorobenzene. To remove all traces of EBHP, EB prior to the reaction was passed through the column packed with alumina and distilled. After the purification, no traces of EBHP were found. The reactor was a glass cylinder vessel of 80−120 mL volume, equipped with turbine mixer, gas inlet pipe, sampler, contact thermometer, and Dean−Stark head for the isolation of water from the gaseous reaction products, which were condensed in the reflux cooler. The reaction temperature was kept constant within ±0.5 °C due to the system control thermometer-relay.

After assembling the setup the Dean−Stark head was filled with ethyl benzene. The reactor was loaded with reaction components. Then the mixer and heating were turned on. After the reaction temperature was reached, oxidant gas was fed into the reactor. This moment was assumed as the beginning of the reaction. The gas flow was controlled with the flow meter.

The reaction was monitored by taking samples of the reaction mixture with time.

The setup for the EB oxidation under anaerobic conditions was eventually the same as described above only it lacked the Dean−Stark head. To maintain an inert atmosphere argon or nitrogen were fed into reactor instead of air.

Analysis Procedure. The concentrations of MPC, AP, BA, and phenol were determined by GLC. The EBHP concentration was determined by iodometric titration, and concentration of Mn(III) by UV-spectroscopy. The EB concentration was determined as the difference between its initial concentration and the sum of organic reaction product concentrations.

1. Iodometric Titration. The 1-mL sample of the reaction mixture was put into a stoppered flask. To the flask was added 10 mL of AcOH and 5 mL of 10% KI solution. The flask was kept in the dark for 25 min. The evolved I_2 was titrated with 0.05 N $Na_2S_2O_3$ solution. The EBHP concentration was calculated according to the equation:

$$c = \frac{V_{Na_2S_2O_3} - V_0}{2V} N_{Na_2S_2O_3}$$

where c is EBHP concentration, $V_{Na_2S_2O_3}$ is the volume of titrant used, mL, V_0 is the volume of titrant is for the titration of the “blank” sample, mL; V is the sample volume, mL; $N_{Na_2S_2O_3}$ is the normality of the titrant in mol/L.

The mean relative error of the analysis is ±5%.

2. GLC Analysis. Analysis of the reaction mixture was performed on the gas chromatograph “Tsvet” model 500 with FID and glass 1 m × 3 mm i.d. column packed with INERTON super AW-DMCS ($d = 0.16-0.2$ mm) with 5% FFAP. Injector temperature 220 °C, column temperature 100−160 °C (3 min isotherm at 100 °C, temperature programming 10 °C/min up to 160 °C, 15 min isotherm at 160 °C).

The concentrations were determined with the help of the internal standard (*n*-octanol for AP and MPC and *p*-nitroacetophenone for BA and phenol). Triphenylphosphin was added to all samples of reaction mixture. It selectively converted HPEB to MPC, then internal standards were added.

The mean relative error of the analysis is ±5%.

3. UV Spectroscopy. To 1 mL of the sample was added 3 mL of freshly distilled acetic acid. The optical density of the obtained solution was measured on “Specord-M40” UV−vis spectrophotometer at 460 nm. The concentration of Mn^{3+} was determined by the calibration curve linking [Mn^{3+}] with the solution optical density.

The mean relative error of the analysis is ±5%.

Results and Discussion

The Effect of the Hydroperoxide Addition. In the noncatalysed oxidation free radicals are produced by the thermal destruction of hydroperoxides.[2,3] This destruction which can proceed both by radical and molecular pathways is also catalysed by metal ions.[4,5] If the molecular mechanism is prevailing, then the hydrocarbon oxidation rate would not be increased by the addition of hydroperoxide despite the increase in its decomposition rate as compared with noncatalysed process. Air oxidation of EB in the presence of Mn(II) salts in the absence of organic additives at 140 °C begins after fairly long induction time. During that time reaction mixture is only slightly coloured, and no reaction products are accumulated. The oxidation begins after rapid and complete transfer $Mn^{2+} \rightarrow Mn^{3+}$. Oxidation proceeds rapidly at first, later slows, and eventually stops. Transformation of EB to MPC and AP via EBHP starts after induction time. In all possibilities, inhibition is the result of some kind of catalyst deactivation. However, when the oxidation is carried out in the absence of inhibiting products of EBHP decomposition (i.e., phenol and MPC), the reaction gives benzoic acid in nearly quantitative yield.

On addition of EBHP to the starting reaction mixture, all manganese ions were immediately oxidised to Mn^{3+}. The consumption of EB occurred without an induction time. All kinetic curves were congruent with those observed in the runs without added EBHP after the induction time. The same results were obtained with addition of cumene hydroperoxide

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(2) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Tsepnye Reakcii Okisleniya Uglevodorodov v Zhidkoi Phaze* [*Liquid-Phase Chain Hydrocarbon Oxidation*]; Nauka: Moscow, 1965.

(3) Emanuel, N. M.; Gal, D. *Okislenie Etilbenzola* [*Ethyl Benzene Oxidation*]; Nauka: Moscow, 1984.

(4) Bal’kov, B. G.; Skibida, I. P.; Maizus, Z. K. *Izv. AN SSSR, Ser. Khim.* **1970**, 1780−1785.

(5) Skibida, I. P.; Brodskii, M. S.; Gervits, M. Ya.; Goldina. L. A.; Maizus, Z. K. *Kinet. Katal.* **1973**, *14*, 885−890.

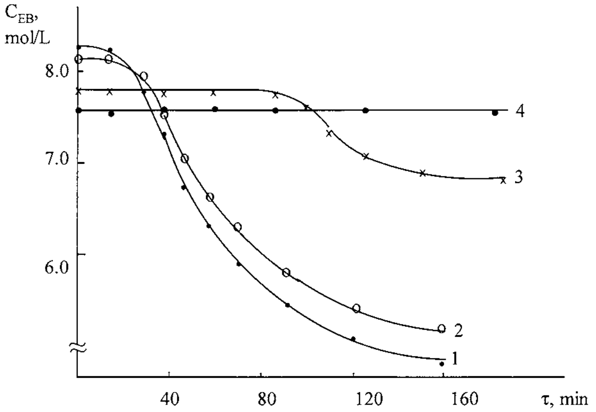

Figure 1. **Influence of added MPC on the ethyl benzene oxidation. Initial concentrations (in mol/L): [EB] = 8.17. [$MnSt_2$] = 0.0075. (Curve 1) [MPC] = 0. (Curve 2) [MPC] = 0.10. (Curve 3) [MPC] = 0.33. (Curve 4) [MPC] = 0.44.**

to the reaction mixture. The continuous feed of hydroperoxides after induction time also did not change the rate of EB consumption.

The decomposition of EBHP under Ar catalysed by manganese(II) stearate ($MnSt_2$) is extremely fast, and at 120 °C it yields MPC, AP, and all manganese(II) is oxidised to Mn^{3+}. Thus, it can be supposed that main role of EBHP during the oxidation is the generation of Mn^{3+} rather than abstracting hydrogen atoms from EB. This hypothesis also corresponds with the published[4] data that EBHP decomposition catalysed by Mn proceeds mainly by the molecular pathway. The low steady-state concentration of EBHP during the reaction is explained by its high decomposition rate. This concentration stays low until the moment of the catalyst poisoning when the rate of the process significantly drops.

The Influence of Added Methyl Phenyl Carbinol, Acetophenone, Benzoic Acid, and Phenol. The kinetic curves obtained in the presence of MPC added at the start of the oxidation are shown in Figure 1. It is seen that the increase in MPC concentration results in the elongation of the induction time, and the reaction rate drops. The oxidation is halted completely at the MPC concentration of 0.44 mol/L. Moreover, the maximum obtained Mn^{3+} concentration is lower than the initial concentration of manganese stearate. This was observed only in the presence of added MPC. The samples of the reaction mixture contained the brown MnO_2 precipitate. The oxidation of MPC did not proceed in the absence of EB, and begins only after the addition of AP. In the presence of AP no inhibition was observed. It may be supposed that the catalyst poisoning is due to the MPC oxidation and competes with manganese−AP interaction. This interaction prevents the irreversible inactivation of the catalyst.

The addition of AP at the beginning of the reaction resulted both in the reduction of the induction time and in the increase in the initial rate of ethyl benzene oxidation (see Figure 2). It should be noted that the rate of EB consumption grows with the increase in the initial AP concentration. This implies that the kinetic equation for the EB oxidation should include the AP concentration. It is reasonable to suppose that AP participates in the initiation step. The rate of this step can be estimated by studying AP oxidation under the conditions of ethyl benzene reaction.

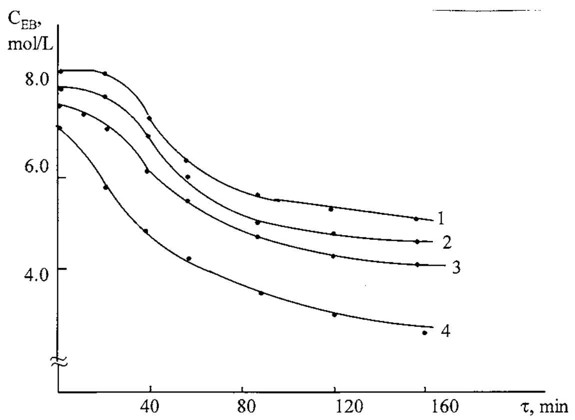

Figure 2. **Influence of added AP on the ethyl benzene oxidation. Initial concentrations (in mol/L): [EB] = 8.17. [$MnSt_2$] = 0.0075. (Curve 1) [AP] = 0. (Curve 2) [AP] = 0.14. (Curve 3) [AP] = 0.32. (Curve 4) [AP] = 1.06.**

The addition of benzoic acid eliminated the induction time. A bell-like dependence of the initial rate on benzoic acid concentration was obtained.

The addition of phenol inhibited EB oxidation. Its addition at the beginning resulted in virtually infinite induction time. When it was added after the induction, the reaction was drastically slowed.

The results show that AP and Mn^{3+} participate in the initiation step. The acting concentration of Mn^{3+} is the result of its reactions with oxygen-containing reaction products. These may be both red−ox processes and simple binding of manganese into a complex. The experimental data show that the accumulation of Mn(III) in high concentration is the result of reactions with participation of acetophenone and benzoic acid. Thus, the next step was the study of their possible transformations.

Oxidation of Acetophenone in the Presence of the Manganese Catalyst. It is known[6] that AP oxidation in an acetic acid solution is a nonchain process rate-limited by the Mn^{3+}−AP interaction. The same reaction can proceed when ethyl benzene, chloro-, or dichlorobenzene is used as the solvent. Thus, it was necessary to study both the anaerobic oxidation of AP by Mn^{3+} ions using $Mn(OAc)_3{\cdot}2H_2O$ under Ar atmosphere and its oxidation to benzoic acid by oxygen in the presence of $Mn(OAc)_2{\cdot}4H_2O$ catalyst. The formation of complexes in the system Mn^{3+}−Mn^{2+}−AP−BA has been studied earlier,[7] and the results obtained were used in the construction of the kinetic model. The results of UV spectroscopy showed that in the chloro- and dichlorobenzene solutions exist free ions Mn^{3+}, Mn^{2+} together with associates $Mn^{2+}\cdots Mn^{2+}$, $Mn^{3+}\cdots Mn^{3+}$, and $Mn^{3+}\cdots Mn^{2+}$. All these catalytic species can interact with AP and BA, thus influencing the reaction kinetics.

Anaerobic Oxidation of Acetophenone by Manganese (III) Acetate. The reaction kinetics was studied in the presence of benzoic acid that was necessary to ensure a

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(6) Mil'ko, S. B.; Rzhevskaya, N. N. Digurov, N. G. *Izv. VUZOV, Ser. Khim.* **1990**, *33*,

(7) Bukharkina, T. V; Digurov, N. G.; Mil'ko, S. B.; Shelud'ko, A. B. *Org. Process Res. Dev.* **2000**, *4*, 404−408

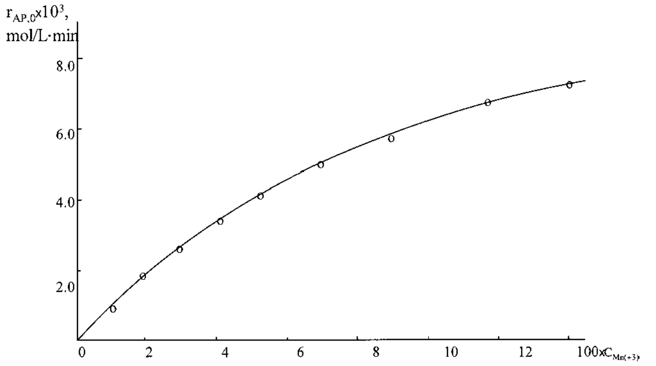


Figure 3. **Dependence of the initial rate of the anaerobic AP oxidation by Mn(III) (r_0) on its initial concentration $C_{Mn(3+)}$ at 110 °C.**

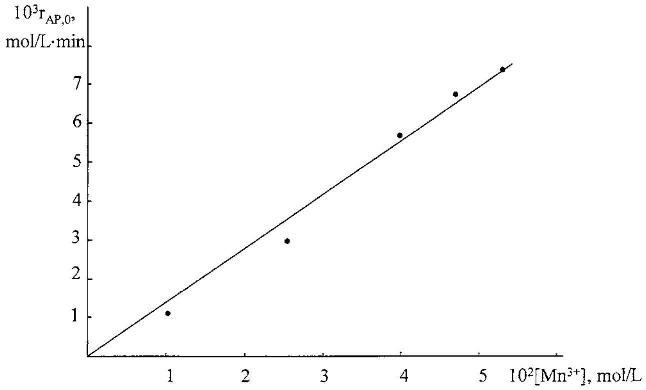
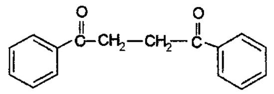


Figure 4. **Dependence of the initial rate of the anaerobic AP oxidation by Mn(III) (r_0) on the concentration of monomeric [Mn^{3+}].**

homogeneous reaction mixture. The only oxidation product was 1,4-diphenylbutane-1,4-dione:



The mass balance experiments showed that one mole of $Mn(OAc)_3$ is consumed per one mole of acetophenone, thus making it possible to monitor the reaction by Mn^{3+} consumption. It was established that the reaction does not proceed to completion and is inhibited by Mn^{2+} ions. That was confirmed by experiments with the addition of $Mn(OAc)_2$ to the reaction mixture. The dependence of the initial rate of Mn^{3+} consumption on the initial overall analytical Mn^{3+} concentration is nonlinear, as shown in Figure 3. This allowed us to suppose that only free manganese(III) ion is the oxidant. Its concentration can be calculated according to the mass balance equation:

$$C_{Mn(3+)} = [Mn^{3+}] + 2K_1[Mn^{3+}]^2$$

where $C_{Mn(3+)}$ is the overall (analytical) manganese(III) concentration, mol/L; [Mn^{3+}] is the concentration of the monomer Mn(III), mol/L; $K_1 = 16$ L/mol is the equilibrium constant of the following reaction:[7]

$$2Mn^{3+} \rightleftarrows Mn^{3+}\cdots Mn^{3+}$$

These relationships are valid only for the beginning of the reaction when no Mn^{2+} species are present.

The dependence of the initial rate on [Mn^{3+}] is linear as shown in Figure 4. The addition of Mn^{2+} to the reaction mixture at the start resulted in reaction inhibition. It seems that mixed associates of Mn(III) and Mn(II) do not participate in the oxidation. Thus, the inhibiting effect of Mn^{2+} is caused by its binding with Mn^{3+} into an inactive complex. When the acetophenone is in a large excess ($[AP] \gg [Mn^{3+}]_0$), the reaction kinetics can be described by the following system:

$$-\frac{dC_{Mn(3+)}}{dt} = k_1[Mn^{3+}]$$

$$C_{Mn(2+)} = C_{Mn(3+)_0} - C_{Mn(3+)}$$

$$C_{Mn(2+)} = [Mn^{2+}] + 2K_2[Mn^{2+}]^2 + K_3[Mn^{2+}][Mn^{3+}]$$

$$C_{Mn(3+)} = [Mn^{3+}] + 2K_1[Mn^{3+}]^2 + K_3[Mn^{2+}][Mn^{3+}]$$

where $C_{Mn(2+)}$ is the overall (analytical) concentration of Mn(II), mol/L; $C_{Mn(3+)}$ is the overall (analytical) concentration of Mn(III), mol/L; [Mn^{2+}] is the concentration of the monomer Mn(II), mol/L; [Mn^{3+}] is the concentration of the monomer Mn(III), mol/L; $K_1 = 16$ L/mol is the equilibrium constant of the reaction:[7]

$$2Mn^{3+} \rightleftarrows Mn^{3+}\cdots Mn^{3+}$$

$K_2 = 70$ L/mol is the equilibrium constant of the reaction:[7]

$$2Mn^{2+} \rightleftarrows Mn^{2+}\cdots Mn^{2+}$$

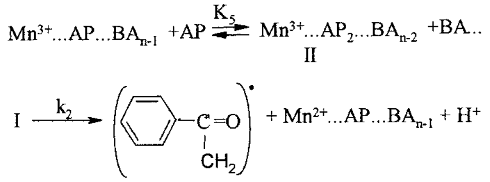
$K_3 = 370$ L/mol is the equilibrium constant of the reaction:[7]

$$Mn^{2+} + 2Mn^{3+} \rightleftarrows Mn^{3+}\cdots Mn^{3+}$$

The dependences of the rate constant k_1 on the initial acetophenone and benzoic acid concentrations are bell-like curves. The studies of the complex formation in the system containing Mn^{2+}, Mn^{3+}, BA, and AP showed that organic species compete for a position in the metal coordination sphere. Then k_1 can be expressed in terms of the ratio $[AP]_0/[BA]_0$ (both are in a large excess to the metal). This dependence is also bell-like.

$$k_1 = \frac{a[AP]_0/[BA]_0}{1 + b[AP]_0/[BA]_0 + c([AP]_0/[BA]_0)^2} \qquad (1)$$

The obtained equation allows us to propose the following scheme of transformations:



If the complex **II** is not able to transfer an electron from AP molecule to Mn^{3+} ion, then the rate constant is described by

Table 1. Constants of eq 2

run	t, °C	k_2, min^{-1}	K_4	$K_5 \times 10^3$
1	100	0.09	2.6	14
2	110	0.17	2.4	12
3	120	0.30	2.4	11
4	130	0.36	2.2	11

Table 2. Mass balance of the AP oxidation

time, min	0	30	60	120	180	240	300
[AP], mol/L	2.40	2.20	1.68	1.22	0.54	0.19	0.06
[BA], mol/L	0.50	0.70	1.20	1.65	2.32	2.64	2.76
[AP] + [BA], mol/L	2.90	2.90	2.88	2.88	2.87	2.83	2.82

eq 1 and the kinetic equation is as follows:

$$\frac{d[AP]}{d\tau} = \frac{dC_{Mn(3+)}}{d\tau} = \frac{-k_2k_3K_4C_{Mn(3+)}[AP]_0/[BA]_0}{1 + K_4[AP]_0/[BA]_0 + K_4K_5([AP]_0/[BA]_0)^2} \quad (2)$$

The constants of eq 2 are listed in Table 1. Strictly speaking, in eq 2 current concentrations of BA and AP should be used instead of the initial ones. Nevertheless, the use of the initial concentrations is justified as the concentration of benzoic acid during the reaction is constant and consumption of AP is negligible due to its large excess over Mn^{3+}.

Thus, we established that the rate of anaerobic AP oxidation by Mn^{3+} is determined by the concentration of the Mn^{3+} monomer species, and Mn(II) inhibits the reaction binding Mn(III) into an inactive complex. The complicated dependencies of the reaction rate upon BA and BA concentrations are the result of the complex formation.

Oxidation of Acetophenone by Oxygen in the Presence of the Manganese Catalyst. The reaction was run in the absence of mass-transfer effects. The main reaction product (97−99% yield) was benzoic acid.

The mass balance of the oxidation is listed in Table 2.

The typical profiles of AP consumption and BA and Mn(III) accumulation are shown in Figure 5. It is seen that after 20 min all manganese is present in the Mn(III) form, and its concentration does not change any more.

The primary treatment of the kinetic data was performed by the differential method. The concentration dependence of the AP consumption rate at the constant manganese concentration in coordinates $1/r$ − [AP]/[BA] is linear. Thus, the rate of the AP consumption can be expressed by the following equation:

$$\frac{d[AP]}{d\tau} = -\frac{k_3K_6[AP]/[BA]}{1 + K_6[AP]/[BA]}$$

The constants k_3 and K_6 were determined by the numerical integration of this equation. The fitting was performed using nonlinear least-squares regression minimising the sum of squares of residuals of measured and simulated data. The values at 110° C are $k_3 = 57 \times 10^4$ L/(mol•min), $K_6 = 3.2$. It is seen from Figure 5 that the deviation of experimental points from the theoretical curve falls within the limits of the experimental error.

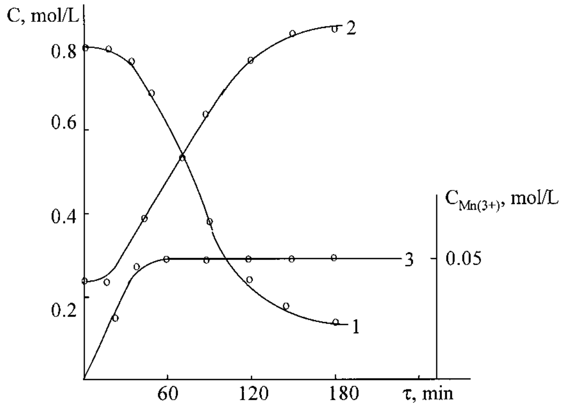


Figure 5. Oxidation of AP by oxygen in the presence of $Mn(OAc)_2$ at 110 °C. (Curve 1) AP. (Curve 2) BA. (Curve 3) Mn^{3+}. $[Mn(OAc)_2]_0 = 0.05$ mol/L.

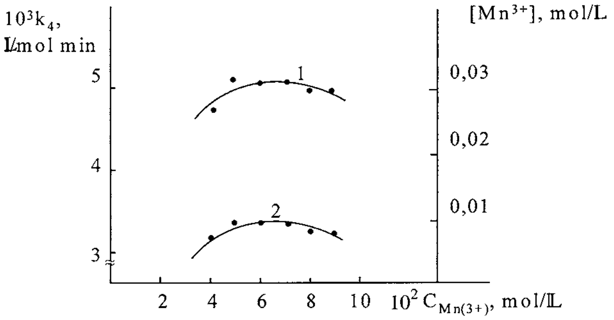


Figure 6. Dependence of monomeric $[Mn^{3+}]$ (curve 1) and k_4 rate constant (curve 2) on overall $C_{Mn(3+)}$

The dependence of the rate constant k_4 on the stationary analytical concentration Mn^{3+} is nonlinear as shown in Figure 6. This constant is linear-dependent on the calculated monomer species $[Mn^{3+}]$ concentration, that is, $k_3 = k_4[Mn^{3+}]$. At 110°C $k_4 = 0.21$ min^{-1}. Thus, the kinetics of the AP oxidation is described by the following equation:

$$\frac{d[AP]}{d\tau} = -k_4[Mn^{3+}]\frac{K_6[AP]/[BA]}{1 + K_6[AP]/[BA]}$$

The comparison of kinetics of AP oxygen and anaerobic oxidation (by $Mn(OAc)_3$ in Ar atmosphere) shows that they are described by the same equation with virtually identical numerical values of constants. Thus, at 110 °C $k_4 = 0.21 \pm 0.03$ min^{-1}, $k_2 = 0.17 \pm 0.02$ min^{-1}, $K_4 = 2.4 \pm 0.9$, $K_6 = 3.1 \pm 0.8$. Consequently, in our opinion, the oxidation of AP proceeds by the nonchain pathway. The rate-limiting step is the electron transfer from the AP molecule to Mn(III). Nevertheless, the produced radical intermediates also can participate in the EB oxidation. The feasibility of this pathway is confirmed by the promoting effect of AP addition in the EB oxidation.

Oxidation of Ethyl Benzene after Induction Time. The plausible scheme of the EB oxidation after induction time should explain the following phenomena:

1. The linear dependence of the oxidation initial rate on $[Mn^{3+}]^{1/2}$ together with the absence of EB interaction with $[Mn^{3+}]$ ions,

2. The absence of reaction acceleration by hydroperoxide addition,

3. The acceleration of the process by AP addition and its inhibition by MPC addition.

Ethyl benzene hydroperoxide decomposes to MPC and AP with nearly 50% ratio. Assuming that the consumption of EB and MPC proceeds by the chain mechanism, the kinetics would be described by the following system of equations:

$$\begin{aligned} -\frac{\mathrm{d[EB]}}{\mathrm{d}\tau} &= k_5[\mathrm{ROO}^\bullet][\mathrm{EB}] \\ \frac{\mathrm{d[MPC]}}{\mathrm{d}\tau} &= \frac{k_5}{2}[\mathrm{ROO}^\bullet][\mathrm{EB}] - k_6[\mathrm{ROO}^\bullet][\mathrm{MPC}] \\ \frac{\mathrm{d[AP]}}{\mathrm{d}\tau} &= \frac{k_5}{2}[\mathrm{ROO}^\bullet][\mathrm{EB}] + k_6[\mathrm{ROO}^\bullet][\mathrm{MPC}] \end{aligned}$$

where k_5 is the rate constant of the reaction of the hydroperoxide radical with ethyl benzene, and k_6 is the rate constant of the reaction of the hydroperoxide radical with MPC.

If we assume that EBHP and $\mathrm{ROO}^\bullet$ concentrations are steady-state and the chain termination is a quadratic one, then we obtain:

$$\frac{\mathrm{d[EBHP]}}{\mathrm{d}\tau} = 0$$

$$\frac{\mathrm{d}[\mathrm{ROO}^\bullet]}{\mathrm{d}\tau} = k_4[\mathrm{AP}\cdots\mathrm{Mn}^{3+}] - k_7[\mathrm{ROO}^\bullet]^2 = 0$$

$$[\mathrm{ROO}^\bullet] = \sqrt{\frac{k_4[\mathrm{AP}\cdots\mathrm{Mn}^{3+}]}{k_7}}$$

where k_4 is the rate constant of the AP oxidation, and k_7 is the rate constant of the quadratic chain termination.

Spectroscopic investigation of the reaction mixture of EB oxidation revealed the presence of Mn(III) complexes with MPC ($\lambda = 402$ nm), and AP or benzoic acid ($\lambda = 490$ nm). The same complexes were observed in AP oxidation. In all possibility these complexes are in equilibria:

$$\mathrm{Mn}^{3+} + \mathrm{AP} \rightleftarrows \underset{\text{(III)}}{\mathrm{Mn}^{3+}\cdots\mathrm{AP}}$$

$$\mathrm{Mn}^{3+} + \mathrm{MPR} \rightleftarrows \underset{\text{(IV)}}{\mathrm{Mn}^{3+}\cdots\mathrm{MPC}}$$

$$\text{(III)} + \mathrm{MPC} \overset{\mathrm{K}_7}{\rightleftarrows} \text{(IV)} + \mathrm{AP}$$

To simplify the equations, molecules of benzoic acid incorporated into the coordination shell of Mn^{3+} are omitted.

If we assume that all Mn^{3+} is bound in the complexes (**IV**) and (**V**), then taking into account the equilibrium 3, the concentration of the active catalytic complex is:

$$[\mathrm{AP}\cdots\mathrm{Mn}^{3+}] = \frac{C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{[\mathrm{AP}] + K_7[\mathrm{MPC}]}$$

where K_7 is the equilibrium constant of the reaction 3, and $C_{\mathrm{Mn(3+)}}$ is the analytical Mn(III) concentration.

In this case, the steady-state concentration of peroxide radicals is equal to:

$$[\mathrm{ROO}^\bullet] = \sqrt{\frac{k_4 C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{k_7([\mathrm{AP}] + K_7[\mathrm{MPC}])}}$$

After that system 3 would became (not taking into account the rate of consumption of AP to benzoic acid)

$$\begin{aligned} -\frac{\mathrm{d[EB]}}{\mathrm{d}\tau} &= k_5[\mathrm{EB}]\sqrt{\frac{k_4 C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{k_7([\mathrm{AP}] + K_7[\mathrm{MPC}])}} \\ \frac{\mathrm{d[AP]}}{\mathrm{d}\tau} &= \left(\frac{k_5}{2}[\mathrm{EB}] + k_6[\mathrm{MPC}]\right)\sqrt{\frac{k_4 C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{k_7([\mathrm{AP}] + K_7[\mathrm{MPC}])}} \\ \frac{\mathrm{d[MPC]}}{\mathrm{d}\tau} &= \left(\frac{k_5}{2}[\mathrm{EB}] - k_6[\mathrm{MPC}]\right)\sqrt{\frac{k_4 C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{k_7([\mathrm{AP}] + K_7[\mathrm{MPC}])}} \end{aligned} \tag{4}$$

It should be noted that the rate of AP consumption (and BA accumulation) is the rate of initiation of chain EB oxidation. Let us compare these rates in the case of oxidation of pure EB at 30 min after the start of the reaction. At this moment reagent concentrations ($\mathrm{mol{\cdot}L^{-1}}$) are: $[\mathrm{EB}] = 6.80$, $[\mathrm{AP}] = 0.66$, $[\mathrm{MPC}] = 0.50$. Concentration of Mn^{3+} was 2×10^{-3} $\mathrm{mol{\cdot}L^{-1}}$. Then the rate of EB consumption $r_{\mathrm{EB}} = 0.018$ $\mathrm{L{\cdot}(mol{\cdot}min)^{-1}}$, the rate of benzoic acid accumulation $r_{\mathrm{BA}} = 0.57 \times 10^{-4}$ $\mathrm{L{\cdot}(mol{\cdot}min)^{-1}}$, and oxidation chain length is $0.018/(0.57 \times 10^{-4}) \approx 300$.

In principle, the rate of AP consumption to benzoic acid should be added to the rate of its accumulation. However, under the conditions of EB oxidation its contribution is negligibly small, as the oxidation of AP is the initiation of EB oxidation. When the chain length of EB oxidation is about 300, the rate of BA accumulation would be about 0.3% of the rate of EB consumption, that is, well within the limits of an experimental error. Nevertheless, when the concentrations of AP and EB are equal, this reaction should not be neglected.

For the rates of AP accumulation and consumption we obtain:

$$\frac{\mathrm{d[AP]}}{\mathrm{d}\tau} = -\frac{\mathrm{d[EB]}}{2\mathrm{d}\tau} + k_6\sqrt{\frac{k_4 C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{k_7([\mathrm{AP}] + K_7[\mathrm{MPC}])}}[\mathrm{MPC}] - k_4\frac{C_{\mathrm{Mn(3+)}}[\mathrm{AP}]}{[\mathrm{AP}] + K_7[\mathrm{MPC}]}$$

$$\frac{\mathrm{d[BA]}}{\mathrm{d}\tau} = -\frac{\mathrm{d[AP]}}{\mathrm{d}\tau}$$

The rate and equilibrium constants k_5 and K_7 were determined by the least-squares fit after numerical integration of the system of differential equations. The fitting was performed using nonlinear least-squares regression minimising the sum of squares of residuals of measured and simulated data. The concentration of Mn(III) in the each run was approximated by the polynomial function. The values of the constants are as follows:

$$k_5 = 12600 \pm 1000 \text{ L/(mol·min)}$$

$$k_6 = 4 \cdot k_6 \text{ L/(mol·min)}$$

$$k_7 = 1.2 \times 10^9 \text{ L/(mol·min)}$$

$$k_4 = 0.3 \text{ min}^{-1}$$

$$K_7 = 12.5 \pm 2.4$$

The rate constants k_6 and k_7 were found in the literature[3], k_4 is the rate constant of the AP oxidation.

The obtained system of differential rate eqs 4 adequately describes experimental dependencies of reaction rates on concentrations. It reflects all the effects that accompany the change in the composition of the reaction mixture during the second step of the EB oxidation in the presence of significant amounts of Mn^{3+}. The calculated and experimental values of current concentrations are listed in Table 3. It is seen that the discrepancies do not exceed the limits of the experimental error.

It is possible that accumulating phenol plays an important role in the process inhibition, but the present data do not allow us to make justified assumptions on the significant interactions during this stage of the process.

Conclusions

The results of the investigation of the EB oxidation in aprotic solvents (or without a solvent) allow us to conclude that this process is a radical-chain one. Ethyl benzene is included in the chain by interaction with $ROO^\bullet$ radicals. The radicals are not produced as the result of EBHP decomposition. The reaction is initiated by Mn^{3+} + AP interaction. Acetophenone itself is oxidised in the nonchain catalytic reaction in which the active catalytic species are regenerated. This process can be defined as the chain co-oxidation of ethyl benzene with the nonchain acetophenone oxidation.

***Table 3.* Experimental and calculated values of the reagent concentrations**[a]

	time, min	C_{EB}, mol/L		C_{MPC}, mol/L		C_{AP}, mol/L	
		exptl	calcd	exptl	calcd	exptl	calcd
$[EB]_0$ = 8.17 mol/L	0	7.96	7.96	0.13	0.13	0.08	0.08
	10	7.54	7.55	0.29	0.34	0.29	0.32
	20	7.15	7.10	0.41	0.50	0.48	0.52
	30	6.80	6.83	0.50	0.51	0.66	0.70
	40	6.50	6.64	0.55	0.52	0.81	0.83
$[EB]_0$ = 6.12 mol/L	0	6.00	6.00	0.07	0.07	0.05	0.05
	10	5.73	5.80	0.18	0.18	0.18	0.15
	20	5.48	5.45	0.27	0.29	0.31	0.32
	30	5.26	5.30	0.33	0.35	0.41	0.43
$[EB]_0$ = 5.25 mol/L	0	5.19	5.19	0.03	0.03	0.03	0.03
	10	5.00	5.01	0.12	0.13	0.13	0.10
	20	4.85	4.87	0.17	0.20	0.20	0.17
	30	4.69	4.71	0.23	0.27	0.28	0.26
	40	4.50	4.50	0.28	0.35	0.37	0.39
	50	4.38	4.40	0.31	0.36	0.43	0.47

[a] Temperature 120 °C, $[MnSt_2]_0$ = 0.0075 mol/L. The end of the induction time was taken as the start of the reaction.

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