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Liquid-Phase Ethyl Benzene Oxidation Catalysed by Manganese Salts

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Abstract:

The liquid-phase oxidation of ethyl benzene by O_2 catalysed by manganese stearate ($MnSt_2$) in a stirred batch reactor has been studied. The main reaction products are ethyl benzene hydroperoxide, methyl phenyl carbinole, and acetophenone. It was established that the reaction includes four basic macro-stages: an induction period, a period of accelerated ethyl benzene consumption, a period of slowing-down, and an inhibition step. It was shown that the initial rate of the second step is described by the equation $r_0 = k[EB]_0\sqrt{[Mn^{3+}]}$. The observed experimental data allowed the supposition that the reaction proceeds by the radical-chain mechanism with participation of hydroperoxide radicals. The overall process is possibly initiated by Mn^{3+} ions.

Introduction

The number of studies devoted to the liquid-phase oxidation of ethyl benzene (EB) is enormous.[1−7] In general, these studies follow two trends: those devoted to the industrial process improvement and those aimed at the reaction mechanism. There are a lot of experimental data in the both fields, and some of the facts were explained. Nevertheless, there is no general conception which would combine both of these trends.

The approach based on the determination of the most essential reagent interactions and their further isolation from the multitude of all the possible reactions proved to be the most fruitful in our previous studies of oxidation of aromatic hydrocarbons in acetic acid. It allowed us to obtain the adequate description of the kinetics of the main product formation and to choose the suitable catalytic system and reaction conditions. On the other hand, the obtained description is, strictly speaking, not complete from the theory viewpoint, but quite feasible practically. However, it is based on the chemistry of the process, and the proposed mechanism includes experimentally verified steps. The same approach was applied in the present work devoted to study of the ethyl benzene oxidation in the apolar media catalysed by the salts of manganese (II) and (III), i.e., $MnSt_2$ (St = stearate) and $Mn(OAc)_3$. The aim of the study was: (a) to establish the pathway of the main product formation and (b) to determine the influence of the reaction products on the activity of the catalyst.

Results and Discussion

The preliminary experiments showed that the basic reaction products are ethyl benzene hydroperoxide (EBHP), methyl phenyl carbinole (MPC), acetophenone (AP), benzoic acid (BA), and phenol (P). We also determined the main oxidation dependencies. In particular, the induction time was observed after the oxidant gas was fed. During this time there was no product formation, and the oxidation state of the catalytic metal ions did not change. The duration of this time depended on reaction conditions. The increase in EB and Mn(II) concentrations resulted in the prolongation of the induction time. Then the solution quickly acquired the dark brown colour typical for Mn(III) salts, and the evolution of water and accumulation of the reaction products (EBHP, MPC, and AP) began. The oxidation process itself can be provisionally divided into two steps. During the first step the EBHP concentration was low (at least 10-fold lower than those of the other reaction products) and virtually constant. During the second step the reaction mixture slowly lost its colour, the EBHP concentration increased quickly, and the rate of EB consumption decreased compared with that in the first step. Also there were observed small amounts of BA and P. After some time, the oxidation stopped completely, reagent concentrations did not change, and the solution acquired pale yellow colour. During the experiment the EB concentration dropped, and that of MPC passed through the maximum and other components accumulated. The rates of EB consumption and products accumulation were the largest during the first step at the low EBHP concentration.

Thus, in all of the oxidation experiments the process included four steps: (I) induction period, (II) period of “stationary” EBHP concentration and maximum reaction rate, (III) period of EBHP accumulation, and (IV) retardation. The typical kinetic curves are shown in Figures 1 and 2.

Table 1 lists the mass balance of EB oxidation by oxygen.

According to the kinetic curves and data in Table 1 the general oxidation scheme can be presented as shown in Scheme 1). It is known that P is formed by its acid-catalysed decomposition. The indirect evidence of this pathway is seen in Table 1. The accumulation of phenol begins simultaneously with the appearance of BA in the reaction mixture.

Catalyst Transformations in the Course of the Reaction. The change of reaction mixture colour during the

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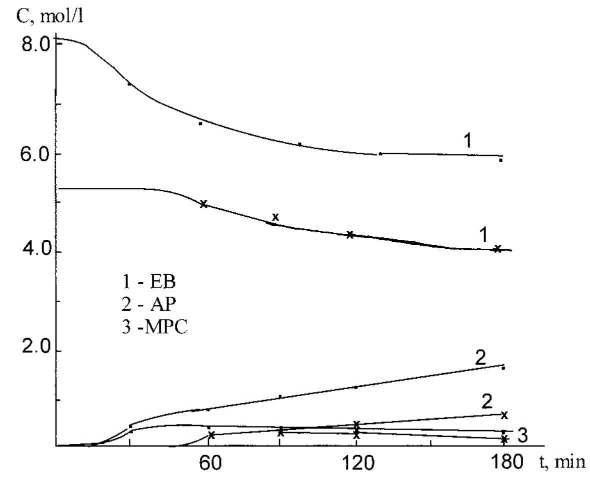


Figure 1. **EB oxidation at 120 °C. Initial concentrations (in mol/L): $[MnSt_2] = 0.0075$; [EB] = 5.25 (×), 8.17 (●). (1) EB, (2) AP, (3) MPC.**

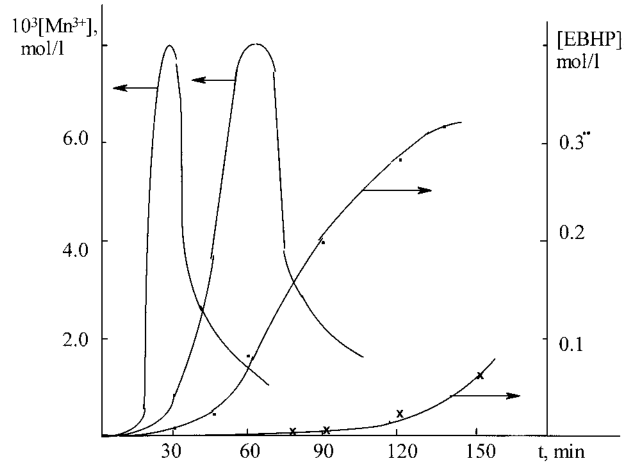
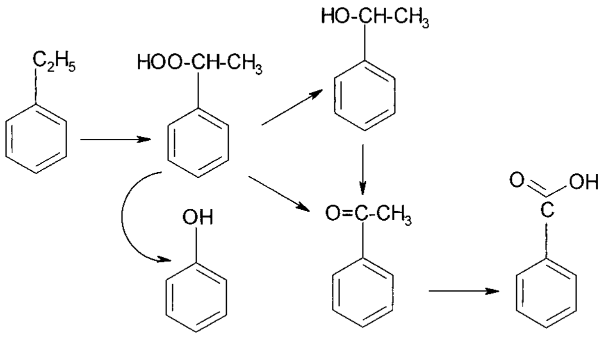


Figure 2. **Concentration profiles of Mn^{3+} and HPEB during EB oxidation. Initial EB concentrations (mol/L): 5.25 (×), 8.17 (●).**

Table 1. **The mass balance of EB oxidation $t = 120$ °C, $[MnSt_2]_0 = 0.0075$ mol/L**

	concentration, mol/L					
t, min	EB	AP	MPC	EBHP	BA	P
0	8.17	0	0	0	0	0
30	7.37	0.37	0.41	0.02	0	0
60	6.59	0.96	0.55	0.07	0	0
90	6.00	1.34	0.56	0.25	0.019	0.001
120	5.82	1.52	0.53	0.34	0.037	0.003
180	5.43	1.84	0.44	0.37	0.083	0.007

Scheme 1



reaction shows that the oxidation state of the catalytic species changes. Application of spectroscopy together with other methods allows us to monitor these changes and make justified assumptions concerning the concentrations of the different catalytic species. During the induction time the concentration of Mn^{3+} increases and then decreases steeply and disappears completely after the retardation. Introduction of the fresh portion of the catalyst eliminates the retardation. The catalyst can be introduced either as Mn(II) ($MnSt_2$) or Mn(III) [$Mn(OAc)_3$]. It means that there are no products that can bind Mn^{2+} or Mn^{3+} into inactive complex, thus the retardation of the reaction is caused by other factors. One may suppose that retardation is caused by binding of Mn^{2+} into some inactive form unable to transfer to Mn^{3+} or by its transfer to higher oxidation state. In all possibility it is caused by the formation of MnO_2 because in some runs, especially in the presence of large amounts of MPC, the sedimentation of the dark brown precipitate was observed.

Thus, comparison of the changes in the catalyst oxidation state with the reaction rate allows us to suppose that the active species is Mn^{3+}. Mn^{2+} inhibits the reaction but can be oxidised to Mn^{3+}. Manganese dioxide (MnO_2) formed in the end of the reaction is the irreversibly "poisoned" catalyst.

Correlation of the Oxidation Rate with the Reactants Concentration. Preliminary experiments showed that EB autoxidation rate in the absence of hydroperoxides at 130 °C is negligible. This is confirmed by the published data.[2] First we correlated the initial rate of EB consumption with the composition of the reaction mixture at the second step of the process, i.e., at the "stationary" EBHP concentration. The initial rate was determined at the end of the induction time. In the majority of the runs (we will discuss the exceptions separately) the concentration of Mn^{3+} reaches at this moment its maximal value equal to initial $MnSt_2$ concentration.

The influence of the reactant concentrations was determined by varying them in the wide range using chlorobenzene as a solvent.

The obtained results showed that the EB oxidation rate increases with the growth of EB and $MnSt_2$ concentrations. To determine the type of the kinetic equation we plotted the initial rate of EB consumption (r_0) vs initial concentrations of the reactants (see Figure 3). Both plots are nonlinear. The EB concentration at the end of the induction time is virtually constant, and all the catalyst is in Mn(III) state. Due to this fact the initial rate r_0 was plotted vs Mn^{3+} concentration rather than vs that of $MnSt_2$. This dependence (Figure 3, curve 2) becomes linear in coordinates $r^0 - ([Mn^{3+}])^{1/2}$. At low EB concentrations $[Mn^{3+}]$ at the end of the induction period is lower than $[MnSt_2]_0$ and direct correlation of r_0 with [EB] is hardly possible. It is evident that the reaction mixture at this moment contains Mn^{3+}, Mn^{2+}, and EB. Thus, it is necessary to determine which catalytic species involves EB into the oxidation process and so determines the overall reaction rate. The comparison of the kinetic curves of EB

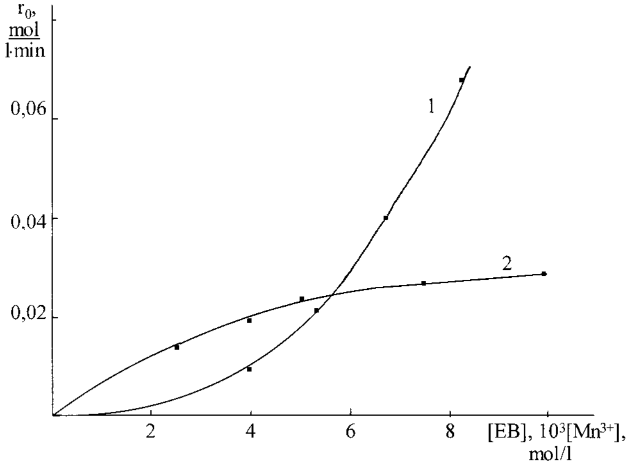


Figure 3. **Plot of the nitial rate of EB oxidation r_0 vs (EB) (1) and Mn^{3+} (2) concentrations at the end of the induction time.**

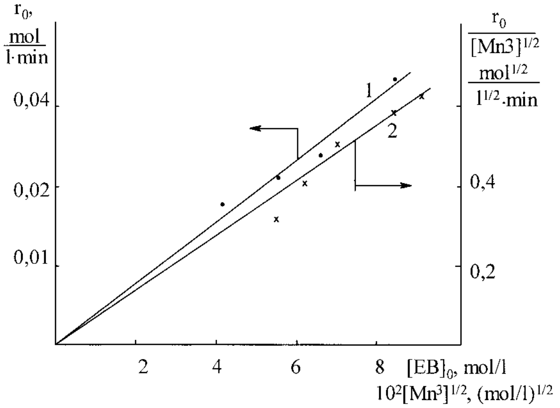


Figure 4. **Linearization of r_0 dependencies vs EB (1) and Mn^{3+} (2) concentrations.**

consumption with the plots of [Mn^{3+}] vs time shows that the oxidation does not start until a significant amount of [Mn^{3+}] is formed. It can mean that [Mn^{3+}] is the active catalytic species. To prove this hypothesis we ran the EB oxidation using $Mn(OAc)_3{\cdot}2H_2O$ as the catalyst. The induction period disappeared. All of the kinetic curves were congruent to those obtained at the same $MnSt_2$ concentration (0.0075 M) excluding induction time. It confirms our hypothesis that Mn^{3+} is the active catalytic species. Therefore, we plotted $r_0/([Mn^{3+}])^{1/2}$ vs $[EB]_0$, thus taking into account the change in the catalyst composition (Figure 4, curve 1). The obtained plot is virtually linear. Then the initial oxidation rate is described by the equation

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

where $[EB]_0$ is the initial EB concentration.

There are possible two pathways of EB involvement into oxidation: either

(1) by the reaction $Mn^{3+} + RH \rightarrow Mn^{2+} + R^{\bullet} + H^+$ or

(2) by the radical pathway $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
In the first case the reaction proceeds by the ion-radical mechanism and its rate is determined by the rate of one-electron transfer. The nonlinear rate dependence on Mn^{3+} concentration may be explained by its complexing with Mn^{2+}. The same mechanism of oxidation of alkylaromatics is described in ref 1. To test this hypothesis we oxidised EB by Mn(III) in Ar atmosphere. This reaction was run twice. In the first case the feed of O_2 was stopped when Mn^{3+} reached maximum and the reactor was flushed with Ar. In the second run EB was oxidised by $Mn(OAc)_3$ under Ar atmosphere. In both cases no products even in trace amounts were observed after 6 h at 120 °C. Thus, the first pathway is out of question. In all possibility the reaction proceeds by the radical chain pathway initiated with Mn^{3+} without EB participation and with the predominant square chain termination. In this case one can expect the linear dependence of reaction rate on [EB] and $[Mn^{3+}]^{1/2}$. The hydrocarbon is involved in the oxidation chain by the hydroperoxy radical, possibly by the EBHP radical.

Thus, it is evident that oxidation of EB proceeds by the radical chain mechanism and Mn^{3+} participates in the initiation step. The processes affecting the change of the catalyst composition in the course of the reaction still remain unclear. Also it is not known which factors cause catalyst activation and inactivation and whether these transformation are linked with the transformations of the oxidation products. These problems can be solved by studying the product influence on reaction kinetics and oxidation of the products themselves in the presence of the manganese catalyst.

Experimental Section

Kinetic Procedure. All of the runs were carried out under intensive mixing at the standard pressure and 120 °C. In the preliminary experiments it was established that the initial reaction rate became independent of the stirrer rate at 2000 rpm and of oxygen flow above 0.5 L/min. All of the kinetic experiments were run under these conditions, thus securing the kinetic region. The solvent was pure ethyl benzene or its mixture with chlorobenzene. To remove all traces of EBHP, prior to the reaction EB was passed through the column packed with alumina and distilled. After the purification no traces of EBHP were found. The experimental setup is shown in Figure 5.The reactor was a glass cylinder vessel (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.

Analysis Procedure

The concentrations of MPC, AP, BA, and phenol were determined by GLC. The EBHP concentration was deter-

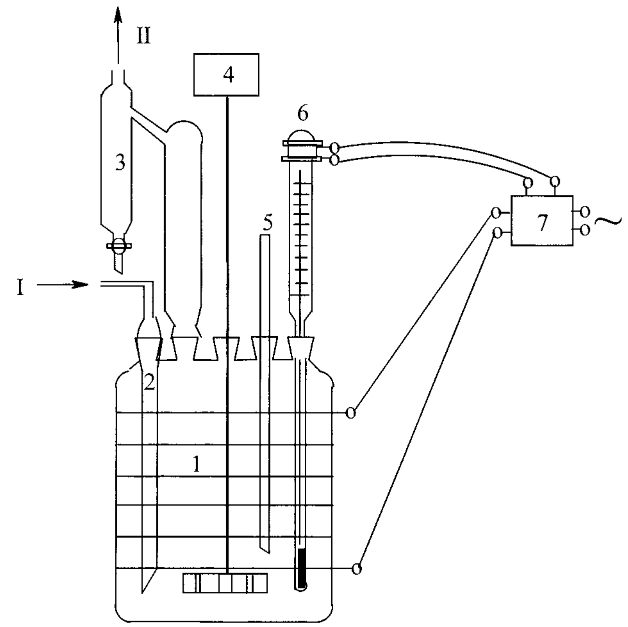


Figure 5. **Experimental setup: (1) reactor, (2) O_2 inlet, (3) Dean−Stark head, (4) −turbine mixer and drive, (5) sampler, (6) contact thermometer, (7) relay. (I) O_2 flow after flow meter, (II) flow of effluent gases and vapours to condenser.**

mined by iodometric titration, and concentration of Mn(III) by UV-spectrophotometry. The EB concentration was determined as the difference between its initial concetration and the sum of organic reaction product concentrations.

1. Iodometric titration. The 1 mL sample of the reaction mixture was put into 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 for the titration of the "blank" sample, V is the sample volume in 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-spectrophotometry. 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%.

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