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Kinetics of the Liquid-Phase Oxidation of Cyclooctene in the Presence of MnO_2

B. I. Chernyak, M. V. Nikipanchuk, G. M. Mishchenko, Yu. B. Trach, and I. Yu. Pyrig
Lvovskaya Politekhnika State University, Lviv, Ukraine

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Abstract—The kinetics of the liquid-phase oxidation of cyclooctene by molecular oxygen in the presence of a MnO_2 catalyst is studied. It is found that MnO_2 is an initiator of this reaction and has no effect on the steps of chain propagation and termination. The oxidation occurs by a radical chain mechanism with the escape of radicals to the bulk of the reaction mixture. Radicals are formed by the interaction of the olefin with the solid catalyst surface. The kinetic parameters of the reaction are calculated.

INTRODUCTION

The oxidation of olefins by molecular oxygen provides an opportunity to manufacture a number of valuable oxygen-containing products. The use of catalysts makes it possible, in a number of cases, to conduct a reaction in the desired direction and to improve the selectivity to one of the components. In this respect, heterogeneous catalytic systems are considered to be more promising. These systems offer a number of advantages over homogeneous systems, among which are the ease of separating the catalyst from the reaction mixture, the possibility of reusing the catalyst, etc.

In this work, we studied the initial steps of the liquid-phase oxidation of cyclooctene by molecular oxygen in the presence of the solid catalyst MnO_2 and azodiisobutironitrile (AIBN), which is a homogeneous initiator.

EXPERIMENTAL

Chemically pure cyclooctene was additionally distilled on a glass-packed distillation column with an efficiency of 30 theoretical plates. The degree of purification was monitored using a chromatographic technique and by comparing the reproducibility of results obtained by the oxidation of different portions of the hydrocarbon.

Gaseous oxygen was used as an oxidant; prior to entering the reaction system, it was passed through a bed of soda lime and calcium chloride to remove moisture.

Commercial MnO_2 (chemically pure) with a specific surface area of 7 m^2/g as measured by nitrogen desorption served as a catalyst. The catalyst had the structure of β-MnO_2 rutile-type crystals of the tetragonal system (lattice parameters: $a = 4.398$ Å and $c = 2.867$ Å). It was found in special experiments that MnO_2 is insoluble in the reaction system.

Reagent grade chlorobenzene was used as a solvent, which was additionally purified according to a standard procedure.

Cyclooctene oxidation was carried out in a glass reactor equipped with a magnetic stirrer and constant-temperature jacket to keep the temperature constant to within ± 0.1°C. At a stirring intensity of >600 rpm, a kinetic regime was maintained; that is the rate of oxygen consumption was independent of the stirring intensity, reactor volume, and O_2 partial pressure. The rate of oxidation was determined by oxygen consumption, measured with a gas-metric setup described in [1].

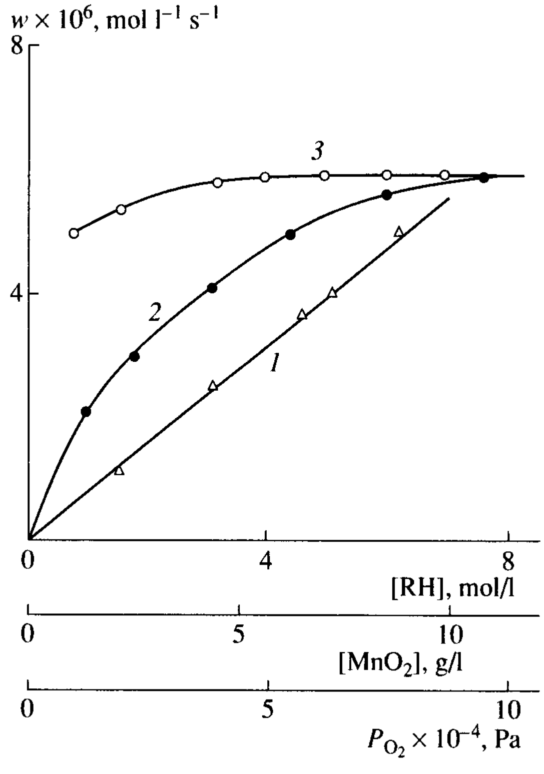

Fig. 1. Dependence of the initial rate of cyclooctene oxidation at 348 K on (*1*) the concentration of the olefin ($[MnO_2]$ = 10 g/l; $P_{O_2} = 1.1 \times 10^5$ Pa), (*2*) the amount of the catalyst ([RH] = 7.69 mol/l; $P_{O_2} = 1.1 \times 10^5$ Pa), and (*3*) the partial pressure of oxygen ([RH] = 7.69 mol/l; $[MnO_2]$ = 10 g/l).

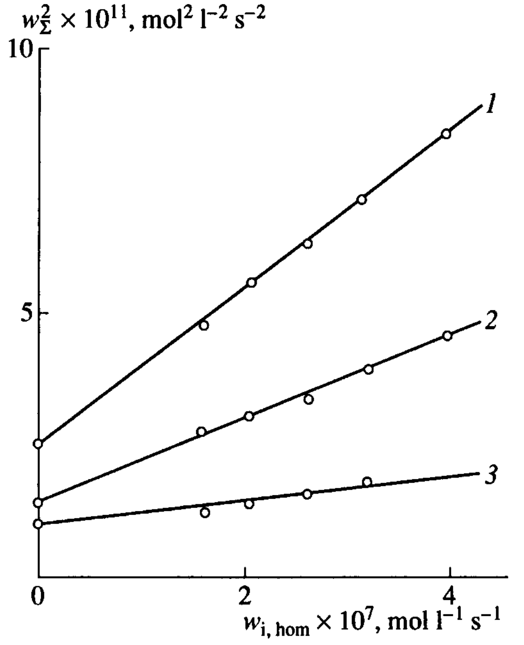

Fig. 2. Relationship between w_Σ^2 and $w_{i,\,hom}$ in the coordinates of equation (7) at the following olefin concentrations, mol/l: (*1*) 6.2, (*2*) 4.2, and (*3*) 3.5. $[MnO_2] = 10$ g/l; $P_{O_2} = 1.1 \times 10^5$ Pa; $T = 348$ K.

RESULTS AND DISCUSSION

Figure 1 shows the initial rates of cyclooctene oxidation as functions of the partial pressure of oxygen (P_{O_2}), the olefin concentration, and the catalyst concentration of the reaction system. It can be seen that the rate of cyclooctene oxidation in the presence of MnO_2 is almost independent of P_{O_2}; this fact is indicative of the zero order of the reaction with respect to oxygen. At the same time, the rate linearly depends on the olefin concentration; whence it follows that the reaction is of the first order with respect to the hydrocarbon. The reaction order with respect to the catalyst is 0.5.

Thus, in the initial period, the rate of cyclooctene oxidation in the presence of MnO_2 is described by the overall equation

$$w = k_{app}[RH][Cat]^{0.5}. \qquad (1)$$

The reaction orders with respect to the catalyst and oxygen can indicate that the radical chain propagation occurs in the bulk of the gas phase. This assumption was tested and supported by the kinetic method.

If a solid catalyst plays the role of an initiator of the radical chain oxidation reaction, the overall oxidation rate in the case of the simultaneous action of dissolved (AIBN) and solid (MnO_2) initiators is related to the rates of homogeneous and heterogeneous processes by the following equation [2]:

$$w_\Sigma = \sqrt{w_{hom}^2 + w_{het}^2}, \qquad (2)$$

where w_{hom} is the rate of oxidation with homogeneous initiation during AIBN decomposition and w_{het} is the rate of oxidation with heterogeneous initiation by MnO_2.

Comparing the experimental rates of oxidation in the presence of the dissolved initiator and the solid catalyst to the values calculated by equation (2), we can draw a conclusion on the role of the catalyst. Equation (2) is valid when the solid catalyst has no effect on the rate of decomposition of the dissolved initiator. Indeed, we found in special experiments that MnO_2 exerts no effect on the rate of AIBN decomposition.

The overall rate of oxidation calculated by equation (2) at 348 K (10.26×10^{-6} mol l^{-1} s^{-1}) is close to the value 10.36×10^{-1} mol l^{-1} s^{-1} found in the experiment with the use of the initiator AIBN ([AIBN] = 5.02×10^{-3} mol/l) and the catalyst MnO_2 ($[MnO_2] = 10$ g/l). This fact can indicate that the chain is initiated at the surface of the solid catalyst MnO_2 and the propagates in the bulk.

Table 1. Rate of the catalytic initiation of cyclooctene oxidation at different concentrations of the olefin ($T = 348$ K; $[MnO_2] = 10$ g/l; $P_{O_2} = 1.1 \times 10^5$ Pa)

[RH], mol/l	$w_{i,\,het} \times 10^7$, mol l^{-1} s^{-1}	
	by equation (5)	by equation (6)
1.54	1.40	1.58
4.62	1.32	1.70
5.08	1.56	1.76
6.17	1.72	1.64
7.69	1.52	1.79

Table 2. Rate of initiation and the ratio between the rate constants of chain propagation and termination in the oxidation of cyclooctene in the presence of AIBN and MnO_2 ($[MnO_2] = 10$ g/l; [AIBN] = 5.02×10^{-3} mol/l; [RH] = 7.69 mol/l; $P_{O_2} = 1.1 \times 10^5$ Pa)

T, K	AIBN	MnO_2	
	$[(k_2+k_{2'})/\sqrt{k_6}]\times 10^3$, l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$[(k_2+k_{2'})/\sqrt{k_6} \times 10^3$, l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$w_{i,\,het} \times 10^7$, mol l^{-1} s^{-1}
338	1.25 ± 0.03	1.23 ± 0.02	1.02 ± 0.03
343	1.52 ± 0.02	1.46 ± 0.03	1.38 ± 0.02
348	1.68 ± 0.04	1.71 ± 0.06	1.81 ± 0.04
353	2.09 ± 0.02	1.95 ± 0.04	2.91 ± 0.02

Table 3. Effect of the exposure time of the reaction system with the inhibitor in an argon atmosphere on the duration of the induction period ($T = 348$ K; [RH] = 7.69 mol/l; $P_{O_2} = 1.1 \times 10^5$ Pa)

[AIBN] × 10^3, mol/l	[MnO$_2$], g/l	[β-Naphthol] × 10^3, mol/l	Exposure time in Ar, min	t_i, min	$w_{O_2} \times 10^6$, mol l^{-1} s^{-1}
5.02	0	0	0	–	8.35
5.02	0	1.8	0	7.3	8.19*
5.02	0	3.2	0	13.0	8.21*
5.02	0	1.8	7.3	0	8.20
5.02	0	3.2	13.0	1.0	8.25*
0	10	0	0	–	5.85
0	10	1.4	0	8.0	5.80*
0	10	2.3	0	13.3	5.75*
0	10	1.4	8.0	0	5.77
0	10	2.3	13.3	0.5	5.73*

* Rate of oxygen consumption after the induction period.

In this case, the rate of oxidation is described by the equation [3]

$$w = \frac{k_2 + k_{2'}}{\sqrt{k_6}}[\mathrm{RH}]\sqrt{w_i}, \qquad (3)$$

where k_2, $k_{2'}$, and k_6 are the rate constants of the corresponding steps, and w_i is the rate of initiation.

Experimental relation (1) agrees with rate equation (3) provided that the rate of initiation in the presence of the solid catalyst $w_{i,\mathrm{het}}$ is independent of the partial pressure of the oxygen and hydrocarbon concentration; i.e.,

$$w_{i,\mathrm{het}} = k_i[\mathrm{Cat}]. \qquad (4)$$

The values of $w_{i,\mathrm{het}}$ were determined using two independent methods: (1) by the inhibition method and (2) by the rate of oxygen consumption in the presence of the dissolved initiator AIBN and the solid catalyst MnO$_2$ in the system.

Using the inhibition method, the rates of initiation were calculated by the equation

$$w_i = \frac{f[\mathrm{InH}]_0}{t_i}. \qquad (5)$$

β-Naphthol was used as an inhibitor.

The rate of the heterogeneous initiation of cyclooctene oxidation was determined from the overall rate of oxidation in the presence of AIBN and MnO$_2$ according to the equation

$$w_\Sigma = \frac{k_2 + k_{2'}}{\sqrt{k_6}}[\mathrm{RH}]\sqrt{w_{i,\mathrm{hom}} + w_{i,\mathrm{het}}}, \qquad (6)$$

which was linearized on the $w_\Sigma^2 - w_{i,\mathrm{hom}}$ coordinates as follows:

$$w_\Sigma^2 = \frac{(k_2 + k_{2'})^2}{k_6}[\mathrm{RH}]^2 w_{i,\mathrm{het}} + \frac{(k_2 + k_{2'})^2}{k_6}[\mathrm{RH}]^2 w_{i,\mathrm{hom}}. \qquad (7)$$

In this case, the slope of the straight line is

$$\tan\alpha = \frac{(k_2 + k_{2'})^2}{k_6}[\mathrm{RH}]^2,$$

and the intercept b on the axis of ordinates is equal to

$$b = \frac{(k_2 + k_{2'})^2}{k_6}[\mathrm{RH}]^2 w_{i,\mathrm{het}} = \tan\alpha w_{i,\mathrm{het}}.$$

On this basis, the rate of initiation by the solid catalyst and the value of $(k_2 + k_{2'})/\sqrt{k_6}$ were calculated by the following equations:

$$w_{i,\mathrm{het}} = \frac{b}{\tan\alpha},$$

$$\frac{k_2 + k_{2'}}{\sqrt{k_6}} = \frac{\tan\alpha}{[\mathrm{RH}]^2}.$$

Figure 2 shows the experimental w_Σ^2 $w_{i,\mathrm{hom}}$ plots obtained at different concentrations of the olefin. Table 1 summarizes the rates of heterogeneous initiation $w_{i,\mathrm{het}}$ in the presence of MnO$_2$ found by the two independent methods.

Table 1 indicates that the rate of radical formation due to the catalytic effect of MnO$_2$ is independent of the hydrocarbon concentration. It was also found that $w_{i,\mathrm{het}}$ remained constant; $w_{i,\mathrm{het}}$ was equal to 1.70×10^{-7} or 1.78×10^{-7} mol l^{-1} s^{-1} at different partial pressures of oxygen $P_{O_2} = 2 \times 10^5$ or 5×10^5 Pa, respectively.

Using the above values of $w_{i,\,het}$, we calculated the ratios between the rate constants of chain propagation and termination. Table 2 compares these ratios and the values obtained under analogous conditions using only the dissolved initiator.

As Table 2 indicates, the $k_2 + k_{2'}/\sqrt{k_6}$ ratios are almost the same in both homogeneous and heterogeneous initiation. It is likely that MnO_2 has no effect on the $(k_2 + k_{2'})/\sqrt{k_6}$ ratio between rate constants and on the $k_2 + k_{2'}$ and k_6 constants themselves, because it is highly improbable that this oxide affects the rates of chain propagation and chain termination to the same extent. Evidently, manganese dioxide participates only in the initiation step, whose rate is described by equation (4).

The temperature dependence of the $(k_2 + k_{2'})/\sqrt{k_6}$ ratio is linear in the Arrhenius coordinates, and the preexponential factor and the activation energy can be calculated. The general expression for $(k_2 + k_{2'})/\sqrt{k_6}$ as a measure of the oxidizability of cyclooctene in the presence of MnO_2 has the form

$$\frac{k_2 + k_{2'}}{\sqrt{k_6}} = (0.54 \pm 0.4) \times 10^2$$

$$\times \exp\left(-\frac{(30\,200 \pm 500)}{RT}\right) \mathrm{l}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1/2}.$$

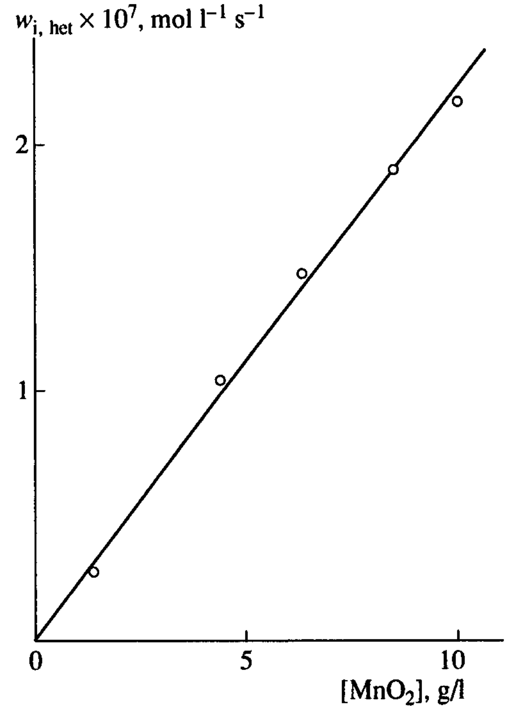

Fig. 3. Dependence of the rate of initiation on the amount of the catalyst ([RH] = 7.69 mol/l; $P_{O_2} = 1.1 \times 10^5$ Pa; T = 348 K).

We found no effect of the oxygen concentration on the rate of initiation in the kinetic experiments; however, it is possible that the formation of radicals proceeds with the participation of O_2. Thus, it was of importance to examine the participation of oxygen in the initiation step in the presence of MnO_2.

If oxygen takes part in the formation of radicals, the latter will not be produced in an inert atmosphere, and the inhibitor concentration will remain unchanged. By contrast, if the formation of radicals proceeds without oxygen participation, the consumption of the inhibitor will be independent of the presence or absence of oxygen in the system. To test this hypothesis, a catalyst treated in vacuum and then in an argon atmosphere was placed in a reactor with cyclooctene and β-naphthol. The mixture was also kept in argon at 348 K for a time equal to the induction period of the oxidation reaction at the corresponding inhibitor concentrations. Thereafter, the system was filled with oxygen, and cyclooctene was oxidized. The consumption of oxygen began almost immediately without an induction period. When the pretreatment with argon was not used, an induction period was observed, and the duration of this induction period (t_i) depended on the inhibitor concentration (Table 3). We conclude from these data that, during the exposure of the reaction mixture to an argon atmosphere in the absence of oxygen from the system, the inhibitor was consumed at almost the same rate as that in the process of oxidation. However, the same effect could also be observed when the inhibitor was completely adsorbed on the catalyst surface rather than consumed in reactions with free radicals.

To test this hypothesis, β-naphthol was added to the cyclooctene–MnO_2 system at room temperature, and the mixture was stirred for 30 min. Then, the catalyst was separated, and the filtrate was oxidized in the presence of AIBN. The relevant data are presented in Table 4, which indicates that the induction periods were practically equal in the oxidation of pure cyclooctene and the filtrate. Hence, it follows that the inhibitor was not adsorbed on the catalyst surface. The consumption of the inhibitor in an argon atmosphere was due to the reaction with free radicals in the bulk, and these radicals were formed in the RH–MnO_2 system without oxygen participation.

Taking into account the macrokinetic relations between the rate of cyclooctene oxidation and the olefin, catalyst, and oxygen concentrations and the linear dependence of the rate of initiation in the presence of MnO_2 on the amount of the catalyst (Fig. 3), we consider that, in the presence of MnO_2, radicals are generated at the catalyst surface according to the following scheme:

$$\mathrm{Cat} + \mathrm{RH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{RH}\cdots\mathrm{Cat}] \xrightarrow{k_i} \mathrm{R}^{\cdot}$$

Radicals formed at the surface pass into the bulk and propagate the oxidation chain.

According to the above scheme, the rate of oxidation is described by the equation

$$w_{\mathrm{i,het}} = k_{\mathrm{i}}[\mathrm{RH}\cdots\mathrm{Cat}]. \quad (8)$$

Taking into account the steady-state condition and the material balance of the catalyst, the concentration of the surface complex can be found from the expression

$$[\mathrm{RH}\cdots\mathrm{Cat}] = \frac{k_1[\mathrm{Cat}]_0[\mathrm{RH}]}{k_1[\mathrm{RH}] + (k_{-1} + k_{\mathrm{i}})}. \quad (9)$$

The substitution of expression (9) into equation (8) gives

$$w_{\mathrm{i,het}} = \frac{k_{\mathrm{i}}k_1[\mathrm{Cat}]_0[\mathrm{RH}]}{k_1[\mathrm{RH}] + (k_{-1} + k_{\mathrm{i}})}. \quad (10)$$

If the catalyst affinity to the olefin is high, then $k_1[\mathrm{RH}] \gg k_{-1} + k_{\mathrm{i}}$, and equation (10) takes the form

$$w_{\mathrm{i,het}} = k_{\mathrm{i}}[\mathrm{Cat}]_0.$$

This equation is obeyed in actual practice (Fig. 3).

Because $w_{\mathrm{i,het}}$ is independent of both the olefin concentration and the partial pressure of oxygen, this value remains constant at a constant amount of the catalyst in the reaction mixture, and it can be considered as an apparent rate constant of initiation ($k_{\mathrm{i,app}}$). The temperature dependence of this constant in the presence of MnO_2 has the form

$$k_{\mathrm{i,app}} = (6.65 \pm 0.5) \times 10^2 \exp\left(-\frac{64\,400 \pm 800}{RT}\right) \mathrm{s}^{-1}.$$

Using the activation energy of initiation in the presence of MnO_2 equal to 64.4 ± 8 kJ/mol and the value $E_2 - 1/2E_6 = 33.1 \pm 3$ kJ/mol found from the temperature dependence of $(k_2 + k_{2'})/\sqrt{k_6}$ in the presence of the homogeneous initiator AIBN by the equation

$$E = E_2 - 1/2E_6 + 1/2E_{\mathrm{i}},$$

we can calculate the overall activation energy of cyclooctene oxidation in the presence of MnO_2. This value is 65.3 kJ/mol, which is consistent with the overall activation energy of cyclooctene oxidation in the presence of MnO_2 found from the temperature dependence of the rate of oxygen consumption (67.6 ± 3 kJ/mol).

Table 4. Effect of the adsorption of β-naphthol on the induction period of the inhibited oxidation of cyclooctene ($T = 348$ K; $[MnO_2] = 5.7$ g/l; $P_{O_2} = 1.1 \times 10^5$ Pa; [AIBN] = 5.05×10^{-3} mol/l)

[β-Naphthol] × 10^5, mol/l	Substrate	t_{i}, min
9.56	cyclooctene	16
9.56	filtrate	16
19.12	cyclooctene	32
19.12	filtrate	32

Thus, the experimental results provide support for the hypothesis that the oxidation of cyclooctene in the presence of MnO_2 proceeds by a radical chain mechanism. Manganese dioxide is a catalyst of the step of initiation because of the reaction with the cycloolefin, and it has no effect on the steps of chain propagation and termination.

REFERENCES

1. Tsepalov, V.F., *Zavod. Lab.*, 1964, no. 1, p. 111.
2. Gorokhovatskii, Ya.B., Kornienko, T.P., and Shalya, V.V., *Geterogenno-gomogennye reaktsii* (Heterogeneous–Homogeneous Reactions), Kiev: Tekhnika, 1972.
3. Emanuel', N.M., Zaikov, G.E., and Maizus, Z.K., *Rol' sredy v radikal'no-tsepnykh reaktsiyakh okisleniya organicheskikh soedinenii* (Role of a Medium in the Chain-Radical Oxidation Reactions of Organic Compounds), Moscow: Nauka, 1973.