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Kinetics of the Early Stages of Oct-1-ene and Cyclooctene Oxidation with Molecular Oxygen in the Presence of MoS_2

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Abstract—The kinetics of the early stages of the liquid-phase oxidation of oct-1-ene and cyclooctene with molecular oxygen in the presence of MoS_2 and *tert*-butyl hydroperoxide is reported. MoS_2 initiates oct-1-ene oxidation and inhibits cyclooctene oxidation. This is explained by the different reactivities of the hydroperoxide-containing complexes in the radical generation reaction. A kinetic scheme is suggested, and kinetic parameters of the process are calculated.

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INTRODUCTION

Hydrocarbon oxidation with molecular oxygen is used in various processes in the chemical and petrochemical industries. Large amounts of oxygen-containing products result from these processes, and these products are widely employed in many industries, so the investigation of hydrocarbon oxidation is very important. One way of intensifying oxidation processes and enhancing their selectivity is by using catalysts. The changes in the rate and selectivity of an oxidation process in the presence of a catalyst is due to the effect of the catalyst on particular steps of this process, such as chain initiation, propagation, and termination.

Transition metal compounds are efficient catalysts for the oxidation of hydrocarbons, particularly, olefins. A number of metal compounds obtained by self-propagating synthesis were studied in the oxidation of non-1-ene and benzaldehyde with molecular oxygen, and MoS_2 was shown to inhibit this process [1]. At the same time, molybdenum disulfide catalyzes the oxidation of *n*-decane [2].

Furthermore, it was found in our laboratory that MoS_2 exerts different effects on the liquid-phase oxidations of the linear olefin oct-1-ene and its cyclic analogue cyclooctene with molecular oxygen. In order to reveal the possible causes of the different effects of MoS_2, we studied the oxidation of these olefins in greater detail.

EXPERIMENTAL

Oct-1-ene (high-purity grade) and cyclooctene (Acros Organics) were distilled. Chlorobenzene (high-purity grade) to be used as the solvent was dried and distilled. Azodiisobutyronitrile (AIBN) was purified by recrystallization from ethanol. *tert*-Butyl hydroperoxide (TBHP) was synthesized using a standard procedure [3]. Molybdenum disulfide MoS_2 (high-purity grade) had a particle size of 3–10 μm and a specific surface area of 5.5 m^2/g, as determined by the nitrogen desorption method.

Oxidation was carried out in a glass reactor with a temperature-controlled jacket and a magnetic stirrer using a gasometric setup [4] at a pressure of 1×10^5 Pa and T = 353 K. The stirring velocity was 1000 rpm, which ensured the kinetically controlled regime of the process. The volume of the reaction mixture was 2 ml. Changes in the reaction mixture volume within 1–4 ml were found to exert no effect on the oxidation rate. To rule out the influence of the oxidation products on the kinetics of the process, the initial oxidation rates were determined by the extrapolation of the oxygen consumption curves (Fig. 1) to the initial point in time.

The hydroperoxide content was determined by iodometric titration. The other components of the reaction mixture were identified on a Hewlett Packard HP 6890 N chromatograph (DB-1 capillary column packed with dimethylsiloxane) and on a Hewlett Packard HP 5890 II chromatograph with a Hewlett Packard HP 5971 mass spectrometric detector (DB-5 ms capillary column packed with 5% diphenylpolysiloxane and 95% dimethylpolysiloxane). The oven temperature was varied in a temperature-programmed mode within the range of 323–523 K at a rate of 10 K/min. The carrier gas was helium.

It was found by special-purpose experiments that MoS_2 has no effect on the decomposition rate of the homogeneous initiator AIBN. Purified and freshly distilled oct-1-ene and cyclooctene without TBHP and AIBN in the presence or absence of MoS_2 underwent no oxidation for 2 h. Under oxygen partial pressures

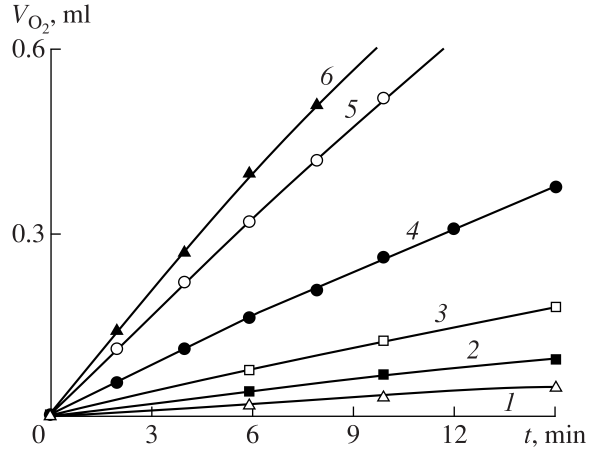

Fig. 1. Oxygen consumption kinetics in the oxidation of (*1*–*3*) cyclooctene ($[TBHP]_0$ = 0.2 mol/l, $[cyclooctene]_0$ = 1.3 mol/l) and (*4*–*6*) oct-1-ene ($[TBHP]_0$ = 0.2 mol/l, $[octene]_0$ = 5.1 mol/l) at a MoS_2 content of (*1*) 1.25, (*2*) 0.4, (*3, 4*) 0, (*5*) 0.45, and (*6*) 1.25 g/l. $T = 353$ K, $P_{O_2} = 9 \times 10$ Pa.

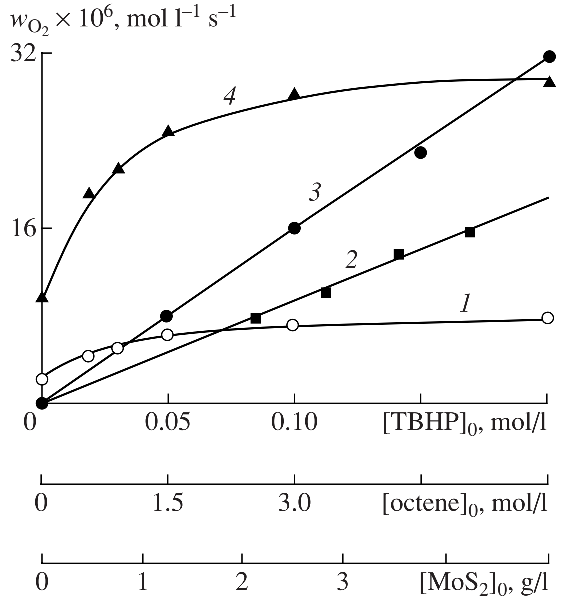

Fig. 2. Experimental data points and calculated dependences of the initial rate of oct-1-ene oxidation in the presence of MoS_2 on the catalyst content ($[octene]_0$ = 5.1 mol/l) at $[TBHP]_0$ = (*1*) 0.05 and (*4*) 0.2 mol/l and on the concentrations of (*2*) oct-1-ene ($[TBHP]_0$ = 0.1 mol/l, $[MoS_2]_0$ = 5 g/l) and (*3*) TBHP ($[octene]_0$ = 5.1 mol/l, $[MoS_2]_0$ = 5 g/l) at $T = 353$ K, $P_{O_2} = 9 \times 10^4$ Pa.

(P_{O_2}) higher than 5×10^4 Pa, the oxidation rate both in the absence and in the presence of MoS_2 was independent of the oxygen pressure. The major oxidation products of the olefins both in the presence and in the absence of MoS_2 were the corresponding hydroperoxide, alcohol, ketone, epoxide, and acids.

RESULTS AND DISCUSSION

The plots of the initial oct-1-ene and cyclooctene oxidation rates versus the initial olefin and TBHP concentrations and the MoS_2 content ($[MoS_2]_0$) are presented in Figs. 2 and 3. It can be seen that the character of the effect of the olefin and TBHP concentrations on the oxidation rate is olefin-independent: for both olefins, as the concentrations of these substances are increased, the reaction rate increases linearly. At the same time, the MoS_2 effects differ substantially, depending on the olefin nature. Molybdenum disulfide increases the oct-1-ene oxidation rate to a certain value, whereas it inhibits the oxidation of cyclooctene. The dependence of the cyclooctene oxidation rate on the MoS_2 content is linear in the coordinates $1/w_{O_2}$ – $[MoS_2]_0$ (Fig. 4, line *1*).

This character of the influence of MoS_2 on the processes can be due to the effect of this compound on the chain propagation and termination processes. If this were the case, in the presence of AIBN, another initiator of radical processes, MoS_2 would also participate in these processes. However, as can be seen from the data in Fig. 4 (lines *2* and *4*), molybdenum disulfide exerts no effect on the oxidation of oct-1-ene and cyclooctene when the oxidation process is initiated by AIBN. This result indicates that MoS_2 exerts no effect on the chain propagation and termination steps and its influence on the oxidation reaction in the presence of TBHP arises from processes involving this hydroperoxide.

The results presented in Figs. 2 and 3 indicate that the plots of the oxidation rate versus the MoS_2 content do not come out of the point of origin: the process contains a noncatalytic component associated with radical generation by the noncatalytic TBHP decomposition during the oxidation of these olefins [5, 6].

The fact that the oxidation rate is independent of the MoS_2 content at large values of this parameter in the case of oct-1-ene and decreases in the case of cyclooctene is likely explained by complex formation processes in these systems. The reaction systems of oxidation with molecular oxygen have the same composition as the hydroperoxide epoxidation systems: they consist of an olefin, a hydroperoxide, and a catalyst. At the initial moment of the process, the hydroperoxide epoxidation system contains catalyst–olefin and catalyst–olefin–hydroperoxide complexes [3, 7–9]. The binding of the hydroperoxide into this complex is the likely cause of the inhibiting effect of MoS_2 on the oxidation with molecular oxygen. As a consequence, the concentration of free TBHP decreases and the radicals form in the system via the noncatalytic decomposition of TBHP.

The activating role of MoS_2 is likely related to the catalysis of radical formation by the interaction

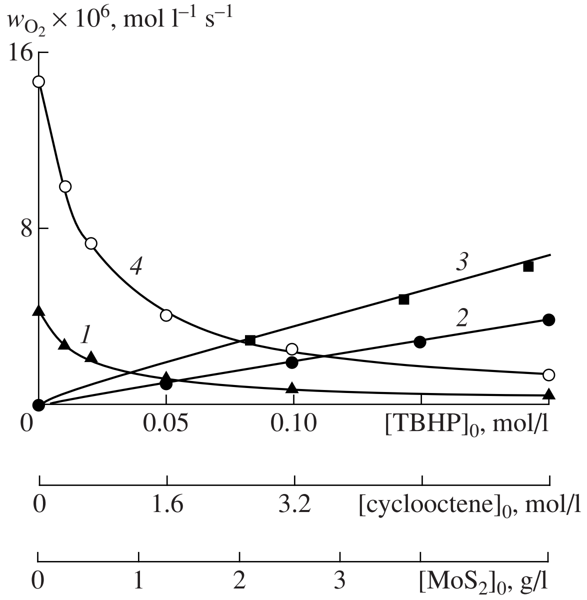

Fig. 3. Experimental data points and calculated dependences of the initial rate of cyclooctene oxidation in the presence of molybdenum disulfide on (*1*, *4*) the MoS_2 content at (*1*) [cyclooctene]$_0$ = 1.3 mol/l, [TBHP]$_0$ = 0.2 mol/l and (*4*) [cyclooctene]$_0$ = 6.1 mol/l, [TBHP]$_0$ = 0.15 mol/l and on the concentrations of (*2*) TBHP ([cyclooctene]$_0$ = 6.1 mol/l, [MoS$_2$]$_0$ = 2 g/l) and (*3*) cyclooctene ([TBHP]$_0$ = 0.15 mol/l, [MoS$_2$]$_0$ = 0.7 g/l) at T = 353 K, P_{O_2} = 9 × 10^4 Pa.

between the catalyst–olefin–hydroperoxide ternary complex and a TBHP molecule. In the case of cyclooctene oxidation, it is pertinent to assume that this complex is inactive in radical generation.

Based on the data obtained in this study, on the results of the investigation of olefin epoxidation with TBHP in the presence of molybdenum-containing compounds [3, 7–9], and on data obtained for noncatalytic olefin oxidation with molecular oxygen in the presence of TBHP [5, 6], we suggest the following scheme of radical formation during the oxidation of oct-1-ene and cyclooctene with molecular oxygen in the presence of MoS_2:

$$\text{olefin} + MoS_2 \xrightleftharpoons{K_1} X_1; \quad X_1 + \text{TBHP} \xrightleftharpoons{K_2} X_2,$$

$$2\text{TBHP} \xrightarrow{k_{\text{noncat}}} \text{radicals};$$

$$X_2 + \text{TBHP} \xrightarrow{k_{\text{cat}}} \text{radicals},$$

where k_{noncat} is the rate constant of the noncatalytic radical formation reaction, k_{cat} is the rate constant of radical formation involving the catalyst, and K_1 and K_2 are the equilibrium constants of the formation of the complexes X_1 and X_2.

According to this scheme, the chain initiation rate is

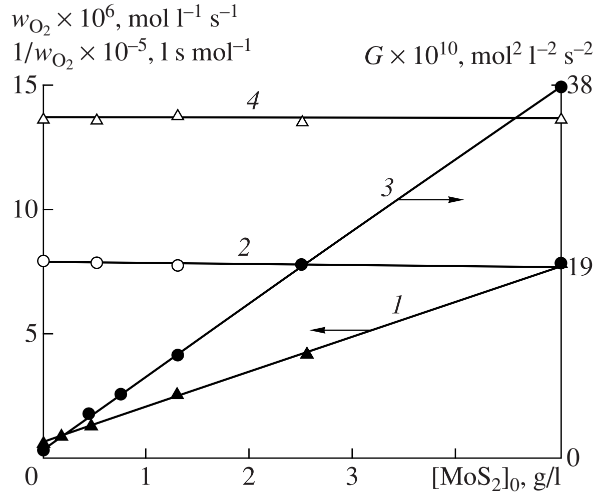

Fig. 4. Plots of (*1*) $1/w_{O_2}$, (*3*) G, and (*2*, *4*) w_{O_2} versus [MoS$_2$]$_0$ at T = 353 K, P_{O_2} = 9 × 10^4 Pa: (*1*) [cyclooctene]$_0$ = 6.1 mol/l, [TBHP]$_0$ = 0.2 mol/l; (*2*) [octene]$_0$ = 5.1 mol/l, [TBHP]$_0$ = 0, [AIBN]$_0$ = 1.0 × 10^{-2} mol/l; (*3*) [octene]$_0$ = 5.1 mol/l, [TBHP]$_0$ = 0.2 mol/l; (*4*) [cyclooctene]$_0$ = 5.1 mol/l, [TBHP]$_0$ = 0, [AIBN]$_0$ = 1.0 × 10^{-2} mol/l.

$$w_i = k_{\text{noncat}}[\text{TBHP}]^2 + k_{\text{cat}}[X_2][\text{TBHP}],$$

where $[X_2] = K_1K_2[\text{olefin}][\text{TBHP}][MoS_2]$.

Substituting this quantity into the classical equation for the rate of hydrocarbon radical-chain oxidation with quadratic-law chain termination [10],

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{RH}]\sqrt{w_i},$$

where k_2 is the rate constant of chain propagation, k_6 is the rate constant of chain termination, and RH = hydrocarbon, we obtain the following equation for the oxidation rate of oct-1-ene and cyclooctene with molecular oxygen in the presence of MoS_2 and TBHP:

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{olefin}] \times \sqrt{k_{\text{noncat}}[\text{TBHP}]^2 + k_{\text{cat}}[X_2][\text{TBHP}]}. \tag{1}$$

According to the above kinetic scheme, the material balance with respect to molybdenum disulfide takes the form of

$$[MoS_2]_0 = [MoS_2] + [X_1] + [X_2]$$
$$= [MoS_2] + K_1[\text{olefin}][MoS_2]$$
$$+ K_1K_2[\text{olefin}][\text{TBHP}][MoS_2]$$

or

$$[MoS_2] = \frac{[MoS_2]_0}{1 + K_1[\text{olefin}] + K_1K_2[\text{olefin}][\text{TBHP}]},$$

where $[MoS_2]_0$ is the MoS_2 content of the reaction system.

Taking into account that [TBHP] is low, we can accept that

$$[MoS_2] = \frac{[MoS_2]_0}{1 + K_1[\text{olefin}]}.$$

The material balance with respect to the hydroperoxide is

$$[\text{TBHP}]_0 = [\text{TBHP}] + [X_2]$$

$$= [\text{TBHP}] + K_1K_2[\text{olefin}][\text{TBHP}][MoS_2],$$

and, accordingly, $[\text{TBHP}] = \dfrac{[\text{TBHP}]_0}{1 + K_1K_2[\text{olefin}][MoS_2]}$.

By substituting $[X_2]$, $[MoS_2]$, and [TBHP] into Eq. (1), we obtain the following equation for the initial oxidation rate:

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{olefin}]_0 \frac{[\text{TBHP}]_0}{1 + \dfrac{K_1K_2[\text{olefin}]_0[MoS_2]_0}{1 + K_1[\text{olefin}]_0}} \times \sqrt{k_{\text{noncat}} + \frac{k_{\text{cat}}K_1K_2[\text{olefin}]_0[MoS_2]_0}{1 + K_1[\text{olefin}]_0}}. \quad (2)$$

Our earlier data [3, 7, 9] indicate that $K_1[\text{olefin}]_0 \gg 1$ at high olefin concentrations in systems containing oct-1-ene, TBHP, and a molybdenum-containing catalyst. In the systems examined, this condition is fulfilled for the dependences of the oxidation rate on the catalyst content and hydroperoxide concentration. The oct-1-ene oxidation rate equation (2) will then take the form of

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{octene}]_0 \frac{[\text{TBHP}]_0}{1 + K_{2\text{oct}}[MoS_2]_0} \times \sqrt{k_{\text{noncat}} + k_{\text{cat}}K_{2\text{oct}}[MoS_2]_0}, \quad (3)$$

where $K_{2\text{oct}}$ is the equilibrium constant of the formation of the oct-1-ene-containing complex X_2.

For cyclooctene oxidation, as mentioned above, the ternary complex X_2 should be inactive in the radical formation reaction. The cyclooctene oxidation rate equation will then take the form of

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{cyclooctene}]_0 \frac{[\text{TBHP}]_0}{1 + K_{2\text{cycl}}[MoS_2]_0}\sqrt{k_{\text{noncat}}}, \quad (4)$$

where $K_{2\text{cycl}}$ is the equilibrium constant of the formation of the cyclooctene-containing complex X_2. According to this equation, the dependence of w_{O_2} on the MoS_2 content should be linear in the coordinates

$$\frac{1}{w_{O_2}} = \frac{1}{\dfrac{k_2}{\sqrt{k_6}}[\text{cyclooctene}]_0[\text{TBHP}]_0\sqrt{k_{\text{noncat}}}} + \frac{K_{2\text{cycl}}}{\dfrac{k_2}{\sqrt{k_6}}[\text{cyclooctene}]_0[\text{TBHP}]_0\sqrt{k_{\text{noncat}}}}[MoS_2]_0.$$

This was actually observed experimentally (Fig. 4, line *1*). The value of $K_{2\text{cycl}}$ was calculated as the ratio of the slope of the line to the ordinate intercept: it was found to be 2.1 l/g.

For the oxidation of oct-1-ene, Eq. (3) can be written as follows:

$$G = k_{\text{noncat}}\left(\frac{k_2}{\sqrt{k_6}}[\text{octene}]_0[\text{TBHP}]_0\right)^2 + k_{\text{cat}}\left(\frac{k_2}{\sqrt{k_6}}[\text{octene}]_0[\text{TBHP}]_0\right)^2 K_{2\text{oct}}[MoS_2]_0,$$

where $G = w_{O_2}^2(1 + K_{2\text{oct}}[MoS_2]_0)^2$.

Since G includes the unknown value of $K_{2\text{oct}}$, in order to plot the linear dependence of G on $[MoS_2]_0$, the optimized $K_{2\text{oct}}$ value maximizing the correlation coefficient calculated by least squares was inserted into G. The $K_{2\text{oct}}$ value thus determined was equal to 0.2 l/g at a correlation coefficient of 0.99 (Fig. 4, line *3*). The k_{cat} value equal to 2.3×10^{-3} l mol^{-1} s^{-1} was derived from the slope of this plot using the $k_2/\sqrt{k_6}$ value given in [11].

A comparison of the constants $K_{2\text{oct}}$ and $K_{2\text{cycl}}$ indicates a much higher stability of the complex containing cyclooctene, pointing out that the stability of a complex depends strongly on the structure of the molecules comprising the complex. On passing from the linear olefin oct-1-ene to the cyclic compound cyclooctene, the stability of the complex X_2 increases by one order of magnitude.

For the noncatalytic process, Eq. (2) is written in the following form:

$$w_{O_2} = \frac{k_2}{\sqrt{k_6}}[\text{olefin}]_0[\text{TBHP}]_0\sqrt{k_{\text{noncat}}}.$$

The k_{noncat} value was calculated from the plot of w_{O_2} versus the initial TBHP and olefin concentrations using the $k_2/\sqrt{k_6}$ values presented in [11] and [12] for oct-1-ene and cyclooctene, respectively. For both olefins, this constant at 353 K is equal to 6.0×10^{-5} l mol^{-1} s^{-1}.

In order to validate the assumptions made for the processes occurring in the reactions systems examined, we calculated the theoretical dependences of the initial oxidation rate on the catalyst content and TBHP concentration using Eqs. (3) and (4) and the rate constants obtained. These theoretical plots are shown in Figs. 2 and 3. The theoretical dependences on the olefin concentration were calculated by Eq. (2) using the $K_1 =$ 1.8 l/mol value [9] for oct-1-ene (for cyclooctene, we used the same value, although it should be larger).

It can be seen that the experimental data points virtually coincide with the calculated w_{O_2} values, possibly indicating that the assumptions made for the processes occurring in the systems examined are valid.

Thus, the data obtained for the early stages of the oxidation of oct-1-ene and cyclooctene with molecular oxygen in the presence of MoS_2 in the presence of TBHP indicate that the activating role of molybdenum disulfide is related to its participation in chain initiation, specifically, its catalytic effect on the radical formation reaction. The inhibiting effect of the disulfide is due to TBHP binding into an inactive MoS_2–olefin–hydroperoxide ternary complex. The formation of this complex reduces the concentration of free hydroperoxide capable of producing free radicals via noncatalytic decomposition. An increase in the stability of the ternary complex decreases its ability to participate in radical formation.

Our subsequent studies will be focused on the influence of molybdenum disilicide on the oxidation of other olefins.

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