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1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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CRITICAL PHENOMENA IN THE OXIDATION OF HYDROCARBONS IN THE PRESENCE OF INHIBITORS IN OPEN SYSTEMS

According to modern views, the processes of oxidation of hydrocarbons in the liquid phase are chain, markedly branched reactions. The chemical mechanism of such reactions may be represented by the following sequence of elementary stages:

$$\begin{array}{rll}
0) & \mathrm{RH} + \mathrm{O_2} \xrightarrow{\omega} \mathrm{R}^\bullet & \text{chain initiation;} \\
1) & \mathrm{R}^\bullet + \mathrm{O_2} \xrightarrow{k_1} \mathrm{RO}_2^\bullet & \\
2) & \mathrm{RO}_2^\bullet + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \mathrm{R}^\bullet & \} \text{ chain propagation;} \\
3) & \mathrm{ROOH} \xrightarrow{k_3} \mathrm{RO}^\bullet + \mathrm{OH}^\bullet & \text{marked branching;} \\
4) & \mathrm{RO}_2^\bullet + \mathrm{RO}_2^\bullet \xrightarrow{k_4} & \\
i) & \mathrm{RO}_2^\bullet + \mathrm{InH} \xrightarrow{k_i} \mathrm{ROOH} + \mathrm{In}^\bullet & \} \text{ chain termination.}
\end{array}$$

N. N. Semenov (^1) showed that, when the oxidation process is carried out in the presence of inhibitors, there must exist a certain critical concentration of the inhibitor, below which an autocatalytic reaction will be observed, and above which there will be a very slow stationary process.

Experimental proof of the existence of a critical inhibitor concentration was obtained in work (^2). Studying the kinetics of the accumulation of hydroperoxides in the oxidation reaction of n-decane in the presence of the inhibitor α-naphthol, we showed that at an α-naphthol concentration above the critical one, decane is practically not oxidized, and only the decomposition of hydroperoxides accumulated in the system by the time the inhibitor was introduced is observed. With an insignificant decrease in the concentration of α-naphthol, the character of the process changes sharply—the reaction develops autocatalytically, similarly to the process proceeding in the absence of inhibitor.

Figure 1

Figure 1: Figure 1

Recently, works have been published in which the critical character of the dependence of the induction period of polypropylene oxidation on the concentration of inhibitors—phenol derivatives and amines—was established ($^{3,}4$).

The phenomenon of a critical inhibitor concentration in the oxidation of *n*-decane has thus far been studied by us in a closed system. However, these phenomena must also be observed when the process is carried out in open systems, i.e., systems exchanging with the external medium not only energy but also matter. The rate of exchange is characterized by the parameter $v = W/V$, where W is the volume of substance entering the vessel per unit time, and V is the volume of the reacting mixture.

The change in the concentration of the reaction components in an open system is the result not only of chemical transformations but also of material exchange. A characteristic feature of an open system is the esta-

appearance after some time (depending on the rates of chemical transformations and the rate of exchange) of a steady state.

A mathematical analysis of the kinetic scheme describing the oxidation of hydrocarbons in the presence of an inhibitor in an open system was carried out by V. M. Andreev. It was shown that, with continuous feeding of the inhibitor into the reaction vessel together with the initial hydrocarbon and continuous removal of the reaction products at the same rate, two types of kinetic curves for the accumulation of the primary reaction product (peroxides) may occur, corresponding either to a stationary or to an autocatalytically accelerated development of the process. At a certain critical concentration of the inhibitor, a sharp change in the value of the stationary peroxide concentration should be observed, corresponding to a transition from one mode of the process to another.

Fig. 1. Kinetic curves for the accumulation of hydroperoxides in the oxidation reaction of *n*-decane in an open system at 135° and at the following concentrations of α-naphthol (in mole/ml). 1 —pure decane without inhibitor; 2 —$3.0 \cdot 10^{-9}$; 3 —$7.50 \cdot 10^{-9}$; 4 —$9.0 \cdot 10^{-9}$; 5 —$9.05 \cdot 10^{-9}$; 6 —$9.2 \cdot 10^{-9}$; 7 —$1 \cdot 10^{-8}$.

In the present work, an experimental study was made of the phenomenon of the critical concentration of inhibitor during the oxidation of *n*-decane in an open system.

The experiments were carried out according to the procedure described in work (^{5}). Five ml of decane containing inhibitor was poured into the vessel, and from the very beginning of oxidation the same solution of inhibitor in decane was continuously and automatically fed into the vessel at a rate of 2.6 ml/hr; in this case $v = 0.53$ hr^{-1}. Oxygen was bubbled through the reaction mixture at a rate of 1.6 l/hr, at the same time providing the necessary stirring of the mixture.

Figure 2

Figure 2: Figure 2

The course of the process was monitored from the accumulation of peroxides, which were analyzed iodometrically.

Figure 1 presents a series of kinetic curves for peroxide accumulation at a temperature of 135° and at different inhibitor concentrations. With an insignificant change in the inhibitor concentration from $9 \cdot 10^{-9}$ to $9.05 \cdot 10^{-9}$ mole/ml, the value of the stationary hydroperoxide concentration drops sharply (practically to zero).

The critical character of the dependence of the stationary peroxide concentration on the concentration of inhibitor in the decane fed into the reactor is also clearly seen in Fig. 2.

Fig. 2. Dependence of the stationary concentration of hydroperoxides on the concentration of inhibitor in the oxidation reaction of *n*-decane in an open system at 135°.

Thus, at α-naphthol concentrations below $9 \cdot 10^{-9}$ mole/ml, the oxidation process of *n*-decane develops as a degenerate-branched chain reaction, with the stationary peroxide concentration decreasing in proportion to the increase in the initial inhibitor concentration. When the inhibitor concentration is increased above the critical value, equal to $9 \cdot 10^{-9}$ mole/ml, the system passes into another stationary state, where the scale of chemical changes in the system is determined only by the initiation of primary active centers.

The kinetics of hydrocarbon oxidation in the presence of an inhibitor in an open system, in accordance with the mechanism given above, is described by the following–

by the following differential equations:

$$\frac{d[\mathrm{RO}_2^{\bullet}]}{dt} = \omega_0 + k_3[\mathrm{ROOH}] - k_4[\mathrm{RO}_2^{\bullet}]^2 - k_i[\mathrm{RO}_2^{\bullet}][\mathrm{InH}] - \nu[\mathrm{RO}_2^{\bullet}]; \tag{1}$$

$$\frac{d[\mathrm{ROOH}]}{dt} = k_2[\mathrm{RO}_2^{\bullet}][\mathrm{RH}] - k_3[\mathrm{ROOH}] - \nu[\mathrm{ROOH}]; \tag{2}$$

$$\frac{d[\mathrm{InH}]}{dt} = -k_i[\mathrm{RO}_2^{\bullet}][\mathrm{InH}] + \nu[\mathrm{InH}]_0 - \nu[\mathrm{InH}], \tag{3}$$

where $-\nu[\mathrm{RO}_2^{\bullet}]$, $-\nu[\mathrm{ROOH}]$, $-\nu[\mathrm{InH}]$, $\nu[\mathrm{InH}]_0$ are terms that take into account the change in the concentration of the corresponding components as a result of exchange and the continuous introduction of inhibitor into the reaction vessel.

The stationary state of the open system is described by the corresponding algebraic equations obtained from equations (1), (2), (3) by setting the derivatives equal to zero.

Solving the system of algebraic equations leads to an expression for the dependence of the stationary concentration of radicals $[\overline{\mathrm{RO}_2^{\bullet}}]$ on the initial concentration of inhibitor $[\mathrm{InH}]_0$:

$$[\mathrm{InH}_0] = \left(\frac{[\overline{\mathrm{RO}_2^{\bullet}}]}{\nu} + \frac{1}{k_i}\right)\left(\frac{2a_2k_3}{k_3+\nu} - \nu + k_4[\overline{\mathrm{RO}_2^{\bullet}}]\right) + \frac{\omega_0}{[\overline{\mathrm{RO}_2^{\bullet}}]}, \tag{4}$$

where $[\overline{\mathrm{RO}_2^{\bullet}}]$ is the stationary concentration of radicals, and ω_0 is the rate of chain initiation.

Since from equation (2) there follows a linear relation between $[\overline{\mathrm{RO}_2^{\bullet}}]$ and $[\overline{\mathrm{ROOH}}]$,

$$[\overline{\mathrm{ROOH}}] = \frac{a_2}{k_3+\nu}[\overline{\mathrm{RO}_2}],$$

the form of the dependence of $[\overline{\mathrm{ROOH}}]$ on $[\mathrm{InH}]_0$ remains the same.

Graphically, this dependence is presented in Fig. 3. Mathematical analysis of equation (4) showed that, during the oxidation of hydrocarbons in the presence of an inhibitor, there exist two stable stationary states: ab and cd. The state bc is unstable and is not realized in practice. Thus, for example, if the inhibitor concentration is equal to [InH], and the initial concentration of peroxides at the moment when the reaction is brought to the continuous regime lies in the region l—m, then the open system will arrive at state m; but if the initial concentration of peroxides lies in the region l—n, then the open system will arrive at state n. It also follows from Fig. 3 that the critical concentration of inhibitor depends on the initial concentration of peroxides. In the oxidation of pure decane, the change in the open system as a function of the inhibitor concentration should proceed along the path $afcd$. It is precisely this segment that was obtained in our experiments (Fig. 2).

Fig. 3. Theoretical dependence of the stationary concentration of radicals on the inhibitor concentration during continuous oxidation of a hydrocarbon

For the critical concentration of inhibitor $[\mathrm{InH}]_{\mathrm{cr}}$ in the oxidation of pure decane, V. M. Andreev obtained the relation

$$[\mathrm{InH}]_{\mathrm{cr}} = 2\sqrt{\frac{2a_2k_3\omega_0}{k_i\nu(k_3+\nu)}} + \frac{2a_2k_3}{k_i(k_3+\nu)} + \frac{\omega_0}{\nu},$$

from which it follows that the ratio k_i/k_2 is equal to

$$\frac{k_i}{k_2} = \frac{2[\mathrm{RH}]k_3}{k_3 + \nu} \cdot \frac{1}{\left(\sqrt{[\mathrm{InH}]_{\mathrm{cr}}} - \sqrt{\omega_0/\nu}\right)^2}.$$

We determined the ratio k_i/k_2 for α-naphthol, using the value of $[\mathrm{InH}]_{\mathrm{cr}}$ determined by us, equal to $9 \cdot 10^{-9}$ mole/ml, and the following constants and

parameters: k_3—the rate constant of degenerate chain branching (^{6}); $v = 0.5\ \mathrm{h}^{-1}$; $[\mathrm{RH}] = 5.2 \cdot 10^{-3}$ mol/ml; $\omega_0 = 1.8 \cdot 10^{-9}$ mol/ml—the rate of chain initiation, determined from the rate of consumption of α-naphthol in the induction period in a closed system. With these parameters we obtain

$$k_i/k_2 = e^{(E_2 - E_i)/RT} = 1.33 \cdot 10^5.$$

The activation energy of the reaction of the radical $\mathrm{RO}_2^\bullet$ with an n-decane molecule is 15.1 kcal/mol (according to the data of (^{7})), taking into account the recently obtained value of the rate constant of chain branching (^{6}). Thus, the activation energy of the reaction of $\mathrm{RO}_2^\bullet$ with an α-naphthol molecule is 5.4 kcal/mol.

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Received
20 V 1961

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Note: Figure translations are in progress. See original paper for figures.