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## Abstract

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## PHYSICAL CHEMISTRY

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# CRITICAL PHENOMENA UNDER THE ACTION OF INHIBITORS ON CHAIN DEGENERATE-BRANCHED REACTIONS

The essence of the critical phenomena discovered in the study of chain-branched reactions is that, at certain values of the parameters (vessel size, temperature, pressure), an insignificant change in them sharply changes the character of the course of the process. The theory of critical phenomena for rapid chain-branched reactions associated with ignition of the reacting mixture was developed by N. N. Semenov (^1).

It follows from N. N. Semenov' s theory of slow chain reactions with degenerate chain branching that critical phenomena should also occur in these cases. For gaseous reactions the conclusions of the theory were confirmed by the example of the oxidation of arsine (^2), ethane (^3), acetylene (^4), and certain other hydrocarbons ($CH_4$, $C_3H_8$, $C_2H_4$, $C_3H_6$) (^5), for which the existence of critical phenomena upon changing the vessel size was discovered.

Recently, in studying the oxidation reaction of *n*-decane in the presence of copper stearate, it was shown that critical phenomena are also inherent in oxidation processes in the liquid phase (^6). In this work a dual function of copper stearate was found: small amounts accelerate the reaction, while with increasing $CuSt_2$ concentration a distinct inhibiting action is observed. The existence of a critical concentration of copper stearate was established; below it an autocatalytic process develops with measurable induction periods (2–4 hours), while above it the induction period sharply increases and an almost complete cessation of the reaction occurs.

The authors explained the existence of a critical concentration of copper stearate within the framework of the generally accepted oxidation scheme, assuming branching and termination of chains on $CuSt_2$ molecules. Considering the mechanism of chain degenerate-branched reactions, N. N. Semenov proposed that in liquid-phase oxidation reactions there should exist a critical inhibitor concentration above which the process proves to be stationary, and below which it is self-accelerating ($\frown$7).

The scheme of the oxidation process in the presence of an inhibitor may be written in the following form:

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R} \cdot + \mathrm{HO_2} \cdot \quad \text{chain initiation}$$

$$\left.\begin{aligned} \mathrm{R} \cdot + \mathrm{O_2} &\xrightarrow{k_1} \mathrm{RO_2} \cdot \\ \mathrm{RO_2} \cdot + \mathrm{RH} &\xrightarrow{k_2} \mathrm{ROOH} + \mathrm{R} \cdot \end{aligned}\right\} \quad \text{propagation}$$

$$\mathrm{ROOH} \xrightarrow{k_3} \mathrm{RO} \cdot + \mathrm{OH} \cdot \quad \text{branching}$$

$$\mathrm{RO_2} + \mathrm{InH} \xrightarrow{k_i} \quad \text{chain termination}$$

At present it may be considered established that the death of radicals on inhibitor molecules is practically the only path of chain termination up to complete consumption of the inhibitor. The system of differen-

differential equations describing the kinetics of the process has the form:

$$\frac{d[\mathrm{RO_2}^{\cdot}]}{dt} = w_0 + k_3[\mathrm{ROOH}] - k_i[\mathrm{InH}][\mathrm{RO_2}^{\cdot}];$$

$$\frac{d[\mathrm{ROOH}]}{dt} = k_2[\mathrm{RO_2}][\mathrm{RH}] - k_3[\mathrm{ROOH}].$$

At a constant inhibitor concentration, the solution of this system of differential equations is represented by the following functions:

$$[\mathrm{RO_2}] = A_0 + A_1 e^{\lambda_1 t} + A_2 e^{\lambda_2 t} = f_1(t);$$

$$[\mathrm{ROOH}] = B_0 + B_1 e^{\lambda_1 t} + B_2 e^{\lambda_2 t} = f_2(t),$$

where $A_0, A_1, A_2, B_0, B_1, B_2$ are parameters that depend on the initial conditions and do not depend on $t$; and $\lambda_1, \lambda_2$ are the roots of the characteristic equation

$$\lambda^2 + [k_i[\mathrm{InH}] + k_3]\lambda + k_3[k_i[\mathrm{InH}] - k_2[\mathrm{RH}],$$

Figure 1

Figure 1: Figure 1

obtained by setting the determinant of the system equal to zero:

$$\begin{vmatrix} -k_i[\mathrm{InH}] - \lambda & k_3 \\ k_2[\mathrm{RH}] & -k_3 - \lambda \end{vmatrix} = 0.$$

The condition for the roots of the characteristic equation to pass through zero is equality to zero of the constant term

$$k_i[\mathrm{InH}] - k_2[\mathrm{RH}] = 0.$$

For negative values of $\lambda_1$ and $\lambda_2$, which occurs when $k_i[\mathrm{InH}] > k_2[\mathrm{RH}]$, a slow stationary development of the process should be observed. If, however, one of the values of $\lambda$ is positive, $k_i[\mathrm{InH}] < k_2[\mathrm{RH}]$, the process will develop autocatalytically.

In the present work we set ourselves the goal of obtaining experimental proof of the existence of the phenomenon of a critical inhibitor concentration in hydrocarbon oxidation reactions upon addition of typical inhibitors of radical-chain processes, and of measuring the magnitude of this concentration.

As the object of investigation, the oxidation reaction of *n*-decane was chosen in the presence of the inhibitor $\alpha$-naphthol, the concentration of which in the reacting mixture was kept constant during the experiment. The inhibitor was introduced into the already reacting mixture at a certain definite reaction time $t_1 = 2$ h, when the concentration of hydroperoxides in the reacting mixture had reached the value 0.17 mol.%.

**Fig. 1.** Kinetic curves of hydroperoxide accumulation in the oxidation reaction of *n*-decane at 130° at different concentrations of $\alpha$-naphthol (in mol/ml):
1—$8.2 \cdot 10^{-7}$,
2—$4.4 \cdot 10^{-7}$,
3—$3.3 \cdot 10^{-7}$,
4—$2.9 \cdot 10^{-7}$,
5—$3.1 \cdot 10^{-7}$,
6—$1 \cdot 10^{-7}$.

The course of the reaction was monitored from the kinetic curves of hydroperoxide accumulation. Constancy of the $\alpha$-naphthol concentration was achieved by continuous feeding of the inhibitor into the reaction vessel in amounts that compensated for the consumption of $\alpha$-naphthol in the course of the reaction. The inhibitor was fed in the form of a solution in decane (of the same degree of oxidation as the decane in the reaction vessel) at a rate of 1 ml/h. Fluctuations in the stationary inhibitor concentration during the period of dripping of the added solution did not exceed 0.5–1.5%. The liquid level in the reactor throughout the entire experiment

practically did not change, since the sampling for analysis corresponded to the volume of decane introduced with the inhibitor.

The concentration of $\alpha$-naphthol was determined spectrophotometrically at the absorption maximum of 583 m$\mu$, after its extraction from the sample with an alcoholic alkali solution and coupling with hydrochloric acid $p$-nitrophenyldiazonium ([8]). The rate of consumption of the inhibitor under the reaction conditions was determined by special experiments.

The kinetic curves for the accumulation of hydroperoxides at various concentrations of $\alpha$-naphthol are given in Fig. 1. The phenomenon of a critical inhibitor concentration is very clearly evident from these data. In the range of $\alpha$-naphthol concentrations from $8.2 \cdot 10^{-7}$ to $3.3 \cdot 10^{-7}$ M/ml, practically complete inhibition of the oxidation process of $n$-decane is observed. The kinetic curves for the change in the concentration of hydroperoxides in this region reflect only the process of decomposition of hydroperoxides.

When, however, the $\alpha$-naphthol concentration passes from $3.3 \cdot 10^{-7}$ to $3.1 \cdot 10^{-7}$ M/ml, i.e., with a very small decrease in inhibitor concentration, a sharp change in the character of the process occurs—the inhibited oxidation is replaced by a rapid reaction proceeding according to an autocatalytic law, analogous to the process in the absence of inhibitor.

The data obtained confirm the theoretical considerations set forth above concerning the existence of critical phenomena under the action of inhibitors on slow chain branched processes (reactions with degenerate branching).

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