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Abstract

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ON THE POSSIBILITY OF INCREASING THE YIELD OF HYDROPEROXIDE WHEN INITIATING THE OXIDATION OF CUMENE WITH HYDROGEN PEROXIDE

(Presented by Academician V. N. Kondrat' ev, 11 II 1960)

In connection with the radical nature of hydrocarbon oxidation reactions, the study of the initiation of this process is of interest. Short-term initiation of the chain process at the initial stage, proposed by N. M. Emanuel (1), leads to a shortening of the induction period and provides a reaction rate close to that of the process under continuous initiation, making it possible to avoid diverse secondary processes. The effectiveness of initiation is determined not only by the regime, but also by the activity of the radicals introduced into the system. As N. N. Semenov (2) points out, a measure of radical activity may be the so-called relative activity, characterizing the reactivity of a given radical with respect to some other one. Activity is mainly determined by the structure of the radical, which depends on the nature of the reacting substances. However, the effectiveness of initiation by some additive must change in the course of a complex process, during which various products are formed. In real systems, an initiator and an inhibitor are very often present simultaneously. In this case, the effectiveness of initiation must be determined not only by the rate of generation of new chains, but also by the rate of interaction of the initiator radicals with inhibitor molecules.

As an initiating additive in the oxidation of isopropylbenzene, we used hydrogen peroxide. The experimental procedure was described in previous communications (3, 4).

As it turned out, the action of hydrogen peroxide is highly specific and is determined to a great extent by the time at which it is introduced into the reaction system (Fig. 1). Initial short-term initiation does not lead either to acceleration of the reaction or to shortening of the induction period. Introduction of H_2O_2

into the reaction mass at later stages of the process, when the reaction has already slowed, leads to the opposite effect: the process is, as it were, disinhibited, and the rate of hydroperoxide formation increases sharply. Such an operation can be repeated upon renewed inhibition, with a similar effect up to practically complete burnout of the hydrocarbon. The yield of hydroperoxide thereby increases from 40 to 80%. Such a picture cannot be explained if the introduction of the initiator is regarded only as the creation of a high concentration of active particles in the system, as was done earlier. This phenomenon resembles rather the disinhibition of the reaction than its initiation.

In order to clarify the cause of this phenomenon, we carried out an experiment with initiation by hydrogen peroxide of the oxidation reaction of isopropylbenzene inhibited by an inhibitor (phenol). As is seen from Fig. 1 B, after the introduction of H_2O_2 the reaction resumes at its previous rate. Thus, the introduction of hydrogen peroxide into the system evidently causes selective destruction of the inhibitor, for example, by the reaction $C_6H_5OH +$

$+ \cdot OH \rightarrow C_6H_5O \cdot + H_2O$. The low-activity radicals $C_6H_5O\cdot$ then recombine.

All this suggests that the radicals formed during the decomposition of hydrogen peroxide are of low activity compared with the chain radicals and are practically incapable of reacting with the initial hydrocarbon, since in the opposite case a sharp increase in the rate would be observed when H_2O_2 is introduced into the initial system.

As the process develops, molecular intermediate products accumulate; as a rule, being compounds more reactive than the initial hydrocarbon, they become involved in the overall chain process, which cannot fail to affect the kinetic regularities of the reaction at its later stages. A consequence of such participation of intermediate products in the chain process—for example, according to the scheme $B + R\cdot \rightarrow B^* + RH$ (where B^* is a low-activity radical, and B is an intermediate product)—is the inhibition and cessation of the oxidation reaction, noted by many authors, long before the initial hydrocarbon has been consumed, i.e., at a time when the internal resources of the process are far from exhausted (6). Therefore, removal of the inhibiting products from the reaction zone, or their destruction, should lead to renewal of the process. This circumstance potentially contains the possibility of increasing the final yield of the target reaction products.

Fig. 1. Kinetic curves of hydroperoxide accumulation during the oxidation of cumene in an emulsion at a phase ratio of 1 : 4 at a temperature of 85°. The arrows indicate the moments at which H_2O_2 was introduced into the system in an amount of 0.015 g-mole/liter and phenol in an amount of 0.01 g-mole/liter.

Stopping a degenerate-branched reaction at the moment when the initiation rate is greatest requires the presence in the system of a highly effective inhibitor. Initiation of such a system by low-activity radicals, by increasing the overall concentration of active centers, should lead to a selective increase in the rate of consumption of the reactive product inhibiting the reaction; and the greater the

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Figure 1: Fig. 1. Kinetic curves of hydroperoxide accumulation during the oxidation of cumene in an emulsion at a phase ratio of 1 : 4 at a temperature of 85°. The arrows indicate the moments at which H_2O_2 was introduced into the system in an amount of 0.015 g-mole/liter and phenol in an amount of 0.01 g-mole/liter

initiation rate, the stronger this effect. Therefore, a brief but energetic action of hydrogen peroxide on such an inhibited reaction at a late stage should lead: 1) to the destruction of reactive intermediate products inhibiting the reaction; 2) to cessation of the chain process of hydroperoxide formation during the action; 3) to an increase in the rate of hydroperoxide formation to a value which, at the given hydroperoxide content, can provide the rate of degenerate branching after the action.

Let us note that the effect of disinhibition of the reaction will be observed only under the condition that the initiator radicals are less active than the chain radicals if the inhibitor is formed by a chain pathway, and always if it is molecular.

Thus, it appears possible to increase the yield of products in a chain degenerate-branched reaction if it is caused by inhibi-

by dilution of the main process with the reaction products. This method can be illustrated by a model scheme of a chain process.

$$A \to B \to C, \tag{1}$$

where the hydrocarbon A is converted by a chain route into product B, which gives pronounced branching, and then into product C, which terminates chains. Then the system of differential equations describing the kinetics of the process, under the assumption of quadratic chain termination, can be represented in the form

$$\begin{aligned} \frac{dn}{dt} &= w_0 + hB - k_3 nC - gn\sqrt{\frac{w_0 + hB}{g}}; \\ \frac{dB}{dt} &= (k_1 A - k_2 B)n; \\ \frac{dC}{dt} &= k_2 Bn, \end{aligned} \tag{2}$$

Fig. 2. Theoretical curve of accumulation of the intermediate product, which forms and is consumed by a chain route, calculated from equation (6) for $\beta = 0$ (1) and $\beta = 100$ (2). The arrow indicates the moment of destruction of product C.

Figure 2: Fig. 2. Theoretical curve of accumulation of the intermediate product, which forms and is consumed by a chain route, calculated from equation (6) for $\beta = 0$ (1) and $\beta = 100$ (2). The arrow indicates the moment of destruction of product C.

where w_0 is the rate of formation of active centers; k_1, k_2, k_3 are the rate constants of reaction of the active center carrying the chain with A, B, and C, respectively; h is the rate constant of the reaction of pronounced branching; g is the rate constant of chain-termination reaction; n is the concentration of active centers carrying the chain.

Fig. 2. Theoretical curve of accumulation of the intermediate product, which forms and is consumed by a chain route, calculated from equation (6) for values $\beta = 0$ (1) and $\beta = 100$ (2). The arrow indicates the moment of destruction of product C.

Introducing the dimensionless quantities

$$\frac{B}{A} = \eta; \quad \frac{C}{A} = \xi; \quad tk_1\sqrt{\frac{h}{g}}A = \tau; \quad \frac{k_2}{k_1} = \alpha; \quad k_3\sqrt{\frac{A}{hg}} = \beta; \quad \frac{w_0}{hA} = \omega_0,$$

we rewrite system (2) for the stationary course of the reaction in the form

$$\begin{aligned} \frac{d\eta}{d\tau} &= (1-\alpha\eta)\frac{\omega_0+\eta}{\beta\xi+\sqrt{\omega_0+\eta}}; \\ \frac{d\xi}{d\tau} &= \alpha\eta\frac{\omega_0+\eta}{\beta\xi+\sqrt{\omega_0+\eta}}. \end{aligned} \tag{3'}$$

Dividing ($3'$) by (3) and integrating the resulting expression under the condition $\xi = 0$ at $\eta = 0$, we obtain

$$\xi = -\eta - \frac{1}{\alpha}\ln(1-\alpha\eta). \tag{4}$$

If the logarithms are expanded in series and we confine ourselves to the first two terms, then equation (4) takes the form

$$\xi \simeq \frac{\alpha}{2}\eta^2. \tag{5}$$

After this, the integral of (3) is easily taken. Integrating equation (3) with allowance for equation (5), neglecting ω_0, under the condition $\eta = \eta_0$ at $\tau = \tau_0$, we obtain the expression

$$\frac{\beta}{2\sqrt{\alpha}}\left[\alpha(\eta_0 - \eta) + \ln\frac{1 - \alpha\eta_0}{1 - \alpha\eta}\right] + \ln\frac{1 + \sqrt{\alpha\eta_0}}{1 - \sqrt{\alpha\eta}}\,\frac{1 - \sqrt{\alpha\eta}}{1 + \sqrt{\alpha\eta_0}} = \sqrt{\alpha}(\tau - \tau_0). \qquad (6)$$

If, at the moment $\tau = \tau_1$, the substance C that inhibits the reaction is destroyed, then the course of the kinetic curve from this moment will be described by the equa-

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$$\frac{\beta}{2\sqrt{\alpha}}\left[\alpha(\eta_1 - \eta) + \ln\frac{1 - \alpha\eta_1}{1 - \alpha\eta}\right] + \ln\frac{1 + \sqrt{\alpha\eta}}{1 - \sqrt{\alpha\eta}}\,\frac{1 - \sqrt{\alpha\eta_1}}{1 + \sqrt{\alpha\eta_1}} + \frac{\alpha^{3/2}\beta}{2}\eta^2 \ln\frac{\eta_1}{1 - \alpha\eta_1}\,\frac{1 - \alpha\eta}{\eta} = \sqrt{\alpha}(\tau - \tau_1). \qquad (7)$$

The graph $\eta = f(\tau)$, calculated for various β, is shown in Fig. 2; the arrow indicates the moment of destruction of the inhibitor. A distinct increase in the reaction rate is clearly visible. It is evident that initiation of the system will be the more effective, the later the stage of the reaction that is subjected to the action. We note that in the patent literature there is an indication of increased yields of reaction products under short-term initiation during the course of the process (^{5}). It was found that, in the alkaline oxidation of alkylaromatic hydrocarbons, short-term ozonation with oxygen during the course of the reaction leads to an increase in the hydroperoxide yield at a high reaction rate. The amount of by-products of the reaction is thereby reduced. This method of initiating liquid-phase and emulsion oxidation of a hydrocarbon has prospects for practical application in order to increase hydroperoxide yields.

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CITED LITERATURE

1. N. M. Emanuel, DAN, 110, 245 (1956).
2. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1958.
3. R. V. Kucher, A. I. Yurzhenko, M. A. Kovbuz, DAN, 117, 638 (1957).

4. R. V. Kucher, M. A. Kovbuz, ZhFKh, 33, 429 (1959).
5. Swedish patents Nos. 140188, 145741.
6. N. M. Emanuel, *Scientific Notes of Moscow State University*, issue 174, 50 (1954).

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

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