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Abstract

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ON THE ROLE OF THE NONSTATIONARITY OF THE PROCESS IN THE STIMULATION OF DEGENERATELY BRANCHED CHAIN REACTIONS IN THE LIQUID PHASE

(Presented by Academician V. N. Kondrat' ev, 25 XII 1957)

Recently, in a number of works, one of us has shown that the oxidation processes of liquid hydrocarbons ([1–5]) and liquefied hydrocarbon gases ([6]) can be substantially accelerated if the process is acted upon by one or another oxidation initiator—gaseous catalysts HBr ([1]), NO_2 ([2,3]), penetrating radiation, inert radioactive gases ([5])—only for a comparatively short interval of time, while the reaction is still in the induction period. Further action of the initiator proves unnecessary or even harmful for the development of the process, because of the undesirable secondary processes it causes. In these works an explanation was also given of the observed phenomena from the standpoint of the theory of chain reactions with degenerate branching advanced by N. N. Semenov ([7]).

In the oxidation of hydrocarbons proceeding by a chain mechanism with degenerate branching, the formation of active centers takes place in two ways:

1) from the initial substances—the hydrocarbon RH and oxygen O_2—by the reaction

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot} \qquad (1)$$

which proceeds with a small rate constant w_0 (chain initiation);

2) as a result of the decomposition or some other transformation of an intermediate product P (in liquid-phase oxidation this is usually the decomposition of the hydroperoxide ROOH), proceeding with the rate $k_p[P]$ (degenerate branching).

As long as $w_0 + k_p[P]$ is small, the rate of oxidation is low and the reaction is in the induction period. If, by the use of some initiator, a higher rate of initiation

w_i is ensured, the reaction is accelerated and the induction period decreases. However, the initiator accelerates the reaction only so long as $w_i > w_0 + k_p[\mathrm{P}]$. When the concentration of hydroperoxide reaches such values that $k_p[\mathrm{P}] \gg w_i$, the initiator ceases to affect the rate of the oxidation process, i.e., its action on the system ceases to give any positive effect.

A mathematical consideration of the kinetics of a chain degenerately branched reaction as a function of the intensity and duration of initiation shows that, in the case of linear chain termination, an increase in w_0 leads to a considerable shortening of the induction period ([3,4,6]). However, in liquid-phase oxidation the predominant chain-termination process is quadratic termination. The corresponding kinetic consideration was carried out in the work of E. T. Denisov and one of us ([8]). In that work, in calculating the concentration of active centers, it was assumed to be quasistationary. Such an approximation, however, is not correct when the rates of initiation are not sufficiently high. Indeed, the equation for the accumulation of active centers in the case of quadratic destruction has the form $dn/dt = w_i -$

$-k_r n^2$, which, for a given w_i, leads to the relation $n = \sqrt{w_i/k_r}\ \mathrm{th}\ \sqrt{k_r w_i}\, t$. Thus, the time required to establish the stationary concentration is a quantity of the order of $1/\sqrt{k_r w_i}$. At small w_i this time may prove to be large. Therefore, in the initial stages of the process the stationarity condition will not be fulfilled. Application of the stationarity condition leads, in particular, to the conclusion that the reaction proceeds without a noticeable induction period, which in many cases is in contradiction with experimental data.

In the present work a calculation has been carried out of the kinetics of a chain reaction with pronounced branching and quadratic chain termination, taking into account the nonstationarity of the process in the initial period of its development. The main question here is the influence of the rate and duration of initiation on the initial stage of the reaction, chiefly on the magnitude of the induction period. Therefore the calculation has been performed without taking into account the consumption of the intermediate product, which begins to have a significant effect on the kinetics of the process only at deeper stages of conversion. Further, it is assumed that termination occurs by recombination of the radicals $\mathrm{RO_2}^{\cdot}$, which, as a rule, takes place at oxygen pressures close to atmospheric. Under these assumptions, the system of equations describing the kinetics of accumulation of the intermediate product has the form

$$\frac{d[\mathrm{RO_2}]}{dt} = w_0 + k_p[\mathrm{ROOH}] - k_r[\mathrm{RO_2}^{\cdot}]^2,$$

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{RO_2}][\mathrm{RH}]. \qquad (2)$$

Here k_r and k are, respectively, the rate constants of the recombination reaction of the radicals $\mathrm{RO_2}^{\cdot}$ and of the chain-propagation reaction

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}.$$

We introduce the dimensionless variables ξ, η, and τ, and the dimensionless parameter ω_0

$$[RO_2] = \frac{\sqrt{kk_p[RH]}}{k_3}\,\xi; \qquad [ROOH] = \frac{k[RH]}{k_r}\,\eta;$$

$$t = \frac{\tau}{\sqrt{kk_p[RH]}}; \qquad \omega_0 = \frac{k_r w_0}{kk_p[RH]}.$$

In dimensionless variables the differential equations (2) take the form

$$\frac{d\xi}{d\tau} = \omega_0 + \eta - \xi^2,$$

$$\frac{d\eta}{d\tau} = \xi. \tag{3}$$

Integration of the system (3), with the initial conditions $\eta = 0$, $\xi = 0$ at $\tau = 0$, leads to the integral

$$\tau = \int_0^{\eta} \frac{dx}{\sqrt{x - \left(\frac{1}{2} - \omega_0\right)\left(1 - e^{-2x}\right)}}.$$

Since we have neglected the consumption of hydroperoxide, this relation may be considered applicable only at small depths of conversion, of the order of 1%.

If the percentage conversion is denoted by p, then for η we obtain

$$\eta = \frac{p}{100} \cdot \frac{k_r}{k}.$$

Since all experiments on the initiating effect on the initial stage of the process were carried out on paraffin hydrocarbons, the present···

the calculation was carried out for the case of a model branched paraffin—isodecane. In the absence of quantitative data on the energy of the tertiary C—H bond in isodecane and on the rate of decomposition of isodecyl hydroperoxide, we shall use the corresponding data for isobutane and tert-butyl hydroperoxide (9):

$$k_p = 10^{15} e^{-39000/RT}.$$

Fig. 1

Figure 1: Fig. 1

The heat effect of reaction (1) is −42 kcal (taking the energy of the breaking C–H bond as 89 kcal (10), and the energy of the H–O_2 bond as 47 kcal (11)); and since such a process can scarcely have a noticeable activation barrier (a strongly endothermic reaction with a linear activated complex), then

$$w_0 = f \cdot 10^{-10} e^{-42000/RT} [\mathrm{RH}][\mathrm{O_2}].$$

At 127° C, i.e., 400° K, this gives, taking $[\mathrm{RH}] = 10^{21}$, $[\mathrm{O_2}] = 10^{18}$,

$$\omega_0 \approx \frac{k_\Gamma}{k} f \cdot 10^{-9}.$$

In Fig. 1 the solid lines show the kinetic curves of hydroperoxide accumulation calculated for the cases $k_\Gamma/k = 10^3$ (a) and 10^5 (b). The dotted lines in the same figures show the curves calculated using the quasi-steady-state condition. It is seen that in both cases this condition leads to sharply overestimated values of η, and the induction period disappears.

In Fig. 2, for the same values of the parameter k_Γ/k, kinetic curves of hydroperoxide accumulation are given for different values of w_0. For a noninitiated reaction, in calculating w_0 it was assumed that $f = 10^{-4}$, since it is known that the steric factor in reactions of hydrocarbons in the liquid phase is much less than unity. The values of w_0 for the initiated process were taken equal to 10^{10} and 10^{12} mole/cm$^3 \cdot$ sec, which approximately corresponds to the conditions of the experiments carried out on the oxidation of paraffin initiated by γ-radiation from a cobalt source (4), and on the oxidation of isodecane (5), initiated by radon. It is seen that an increase in w_0 (ω_0) leads to a shortening of the induction period, up to its complete disappearance at a sufficiently large value of ω_0.

Fig. 1. Calculated kinetic curves of hydroperoxide accumulation, obtained by a rigorous solution of system (3) (solid curves) and using the quasi-steady-state condition (dotted curves). *a*–$k_\Gamma/k = 10^3$, $\omega_0 = 10^{-10}$; *b*–$k_\Gamma/k = 10^5$, $\omega_0 = 10^{-8}$

From Fig. 3 it is seen that the calculation carried out under the assumption of quasi-steadiness of the process gives a completely incorrect idea of the scale of the effect of the initiator on the oxidation kinetics.

The curves for initiated oxidation shown in Fig. 2 were calculated under the assumption of direct initiation throughout the entire process. For the values of the parameters $k_\Gamma/k = 10^3$, $\omega_0 = 10^{-2}$, the calculation was also carried out for the case of initiation during $\tau = 1.2$. The kinetic curve practically does not differ from the curve obtained with continuous initiation of the same intensity. The

Fig. 2 and Fig. 3: calculated kinetic curves for hydroperoxide accumulation

Figure 2: Fig. 2 and Fig. 3: calculated kinetic curves for hydroperoxide accumulation

kinetic curves obtained by calculation are similar in character to those observed in

experiment. Thus, the curves in Fig. 2a are similar to the kinetic curves obtained when the oxidation of paraffin was initiated in the initial period by nitrogen dioxide or by γ-radiation from Co^{60} ([4]). The curves in Fig. 2b are, in their type, close to the kinetic curves obtained in the oxidation of isodecane initiated by radon ([5]). It is significant that these curves were obtained for reasonable values of the parameters ω_0 and ω_i. The absence of information on the mechanism of the initiating action of NO_2 does not make it possible to estimate ω_0 in this case, and for gaseous initiation one can speak only of qualitative agreement between the calculated and experimental curves.

Fig. 2. Calculated kinetic curves for hydroperoxide accumulation.
a $-k_r/k = 10^3$, $\omega_0 = 10^{-10}$ (1) (uninitiated oxidation), $\omega_i = 10^{-2}$ (2) and $\omega_i = 1$ (3);
b $-k_r/k = 10^5$, $\omega_0 = 10^{-8}$ (1), $\omega_i = 1$ (2) and $\omega_i = 100$ (3).
The dotted line shows the curve with initiation during the interval $\tau = 1.2$. The arrow marks the time at which initiation is stopped.

Fig. 3. Calculated kinetic curves for hydroperoxide accumulation for the case $k_r/k = 10^3$, without initiation (curves 1, 1′) and with initiation $\omega_i = 1$ (curves 2, 2′), obtained by the exact solution of system (3) (solid curves) and with use of the quasi-stationarity condition (dotted curves).

Thus, the exact solution of the system of differential equations describing the kinetics of accumulation of the intermediate product in oxidation reactions with quadratic chain termination makes it possible to explain the induction periods observed experimentally and to understand the effects of initial stimulation of these processes.

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