U. D. C. 541.124.7

CRITICAL PHENOMENA IN CHAIN REACTIONS WITH DEGENERATE BRANCHING

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I. INTRODUCTION

Limiting (critical) phenomena constitute the clearest and most characteristic feature of branched chain reactions. These phenomena are shown quantitatively in a sharp change in reaction velocity at certain (limiting or critical) values of the external parameters (pressure, temperature, diameter of vessel, etc.). The essential nature of critical phenomena was explained by Semenov's theory of branched chains, supported by a large amount of experimental work by Soviet and foreign scientists. The limits of an autocatalytic chain reaction are certain boundary conditions under which an increase in the concentration of active centres carrying reaction chains becomes possible or impossible. In chain ignitions these conditions are represented by equality of the rates at which the elementary processes of chain branching and termination are occurring. Study of the chain ignition of hydrogen, phosphorus, etc. revealed numerous limiting phenomena (critical pressure, temperature, vessel diameter), and the effect on them of various factors, such as treatment of the walls of the vessel, the action of inert gases and active additions, was investigated.

Besides branched chain reactions, whose development at pressures exceeding the critical value involves ignition of the reactant mixture, slow autocatalytic reactions are known, among them the oxidation of hydrocarbons and other organic substances in both gas and liquid phases. These slow autocatalytic processes were termed by Semenov chain reactions with degenerate branching (or reactions of degenerate chain explosion) [1,2].

According to the theory of degenerate branching, the explanation of the peculiarities of slow oxidation is that, in the course of such reactions, radicals are involved only in the elementary processes of chain propagation and termination, i.e. that the main chain "develops at the normal rate (very rapidly) and is not accompanied by branching in the usually accepted sense" [2]. However, a relatively stable intermediate product is formed in the unbranched primary chain, which, on undergoing some independent reaction (decomposition, oxidation), is responsible for the formation of radicals, i.e. the appearance of secondary chains. "We can regard these secondary chains formally as branches of the primary chain, although a chain of 'degenerate branching' may appear a very considerable time after destruction of the primary chain".

If the number of chains increases by such a mechanism, development of the process is non-stationary:

$$w = \frac{\nu n_0 (k_1 + k_2)}{\varphi} (e^{\varphi t} - 1),$$

where w is the reaction velocity, ν the length of the unbranched chain, n_0 the rate of generation of chains, $\varphi = k_2(\nu - 1) - k_1 = (\nu\delta - 1)/\theta$ is the autocatalytic factor of the reaction, and k_2 and k_1 are the rate constants for decomposition of the intermediate product into radicals and into stable compounds respectively. The parameter $\delta = k_2/(k_2 + k_1)$ is the probability of chain formation involving the stable intermediate, and $\theta = 1/(k_2 + k_1)$ is the mean life of this compound in the reaction. The magnitude of the autocatalytic factor is determined by the low rate of breakdown of the intermediate product into radicals, so that conversion of the starting materials slowly accelerates with time.

The decisive part played by stable intermediate products in the occurrence of slow autocatalytic chain reactions is now supported by a large mass of experimental results. Analysis of kinetic equations [3-6] and also experimental data show that the peculiarities of reactions of this class are determined both by the mechanism of conversion of the intermediate product (radical, molecular, chain) and by the type of chain termination (linear or quadratic).

With variation in the external conditions (diameter of vessel, pressure of mixture, concentration of inhibitor) the autocatalytic factor $\varphi = (\nu\delta - 1)/\theta$ of the degenerate branched chain reaction may be either positive (when $\nu\delta > 1$) or negative (when $\nu\delta < 1$). Hence limiting phenomena should be observed in slow, non-stationary chain reactions, as in chain ignition, if the condition $\nu\delta = 1$ is satisfied [1,2,7-9].

In gas-phase reactions, destruction of chains occurs by the collision of active centres with the surface of the reaction vessel, and the rate of chain termination is proportional to the concentration of radicals (linear termination). In this case the length of the chain ν depends on the diameter and surface state of the reaction vessel and on the pressure of the reactant mixture. The existence of a critical vessel diameter and a critical pressure in the gas-phase oxidation of hydrocarbons has been shown experimentally [10-13].

In the liquid phase the high density of the substance makes the diffusion of active centres to the walls of the reaction vessel difficult, and chain termination occurs by the recombination of radicals (quadratic chain termination). In the quadratic recombination of radicals the length of the chain is independent of any external parameter. Linear chain termination occurs in the liquid phase in the presence of compounds such as phenols, naphthols, amines, etc., which contain a weakly bound hydrogen atom in the hydroxyl or amino-group. The active radicals which effect the chain conversion of the starting materials react with these compounds and are replaced by the corresponding phenoxyl or imino-radicals, which are incapable of chain propagation, so that the chain terminates.

If the rate of chain termination on an inhibitor exceeds the rate of quadratic recombination of radicals, the length of the chain decreases, and induction periods appear in the oxidation. With different inhibitor concentrations, the process of oxidation during the induction period may be stationary ($\varphi < 0$) or may develop autocatalytically ($\varphi > 0$) depending on the length of the chain. The existence of critical inhibitor concentrations, at which a sharp change occurs in the induction period in the liquid-phase oxidation of hydrocarbons, has now been shown experimentally [14,15].

The present Review examines the problem of limiting (critical) phenomena occurring in reactions with degenerate branching of the chains, non-chain consumption of an intermediate product, and linear chain termination.

II. KINETIC EQUATIONS OF A CHAIN REACTION WITH DEGENERATE BRANCHING, LINEAR CHAIN TERMINATION, AND NON-CHAIN CONSUMPTION OF AN INTERMEDIATE PRODUCT

The fundamental mechanism of a chain reaction with degenerate branching comprises the following elementary reactions of radicals r and stable intermediate products x

0) $A+B \xrightarrow{k_0} r$ — chain initiation,

1) $r' + B \xrightarrow{k_1} r + C$
2) $r + A \xrightarrow{k_2} r' + x$ — chain propagation,

3) $x \xrightarrow{k_3} r$ — degenerate branching,
$x \xrightarrow{k_3', k_3''[M]}$ — stable products,

4) r + (wall, inhibitor) $\xrightarrow{g}$ chain termination.

On the basis of this scheme, the variation in concentration of radicals r and the intermediate product x during the reaction is represented by the equations

$$\frac{dr}{dt} = w_0 + k_3 x - gr, \tag{1}$$

$$\frac{dx}{dt} = ar - kx. \tag{2}$$

Chain initiation occurs very slowly in reactions of saturated molecules of the starting materials, its rate being $w_0 = k_0[A][B]$.

The radicals r and r', which are formed in the system, carry reaction chains in which the intermediate product x is formed. The length of the chain is $\nu = a/g$, where $a = k_2[A]$ and g are respectively the kinetic coefficients of chain propagation and termination. The intermediate product x may undergo various reactions during the process. Breakdown of x into radicals (or other reaction) results in an increase in the rate of formation of active centres, i.e. in autocatalysis of the process; the parameter k_3 is the effective rate constant of decomposition of the intermediate product in this way.

The intermediate product can decompose or react with some other molecule M to form stable, valency-saturated compounds, k_3' and $k_3''[M]$ being the effective rate constants of these processes. The parameter $k = k_3 + k_3' + k_3''[M]$ is the overall rate constant for consumption of the intermediate product in the various ways.

In oxidation reactions the intermediate product can be consumed also by a chain mechanism

$$x + r \xrightarrow{k_4} r' + \text{products}.$$

The rate of this process will depend on the concentration of intermediate product and radicals. In the initial stages of conversion, when the concentrations x and r are small, the rate of the chain consumption of the intermediate product $w_{ch} = k_5 xr$ is small, and is ignored in the above scheme.

Eqns. (1) and (2) have the solutions

$$r = \frac{w_0}{(ak_3 - gk)}\left[\frac{(k\lambda_2 + gk - ak_3)}{(\lambda_2 - \lambda_1)}e^{\lambda_1 t} - \frac{(k\lambda_1 + gk - ak_3)}{(\lambda_2 - \lambda_1)}e^{\lambda_2 t} - k\right], \tag{3}$$

$$x = \frac{aw_0}{(ak_3 - gk)}\left[\frac{\lambda_2}{(\lambda_2 - \lambda_1)}e^{\lambda_1 t} - \frac{\lambda_1}{(\lambda_2 - \lambda_1)}e^{\lambda_2 t} - 1\right], \tag{4}$$

where λ_1 and λ_2 are the roots of the characteristic equation $\lambda^2 + (g + k)\lambda - (ak_3 - gk) = 0$ of this system:

$$\lambda_{1,2} = \frac{(g+k)}{2}\left(\pm\sqrt{1 + \frac{4(k_3\nu - k)}{(g+k)(1 + k/g)}} - 1\right).$$

If the inequality

$$(k_3\nu - k) \ll (g + k)(1 + k/g), \tag{5}$$

is satisfied, the exponents are

$$\lambda_1 = \frac{(k_3\nu - k)}{(1 + k/g)}, \quad \lambda_2 = -(g + k).$$

The inequality (5) is satisfied if $g \gg k$ or $g \ll k$.

The parameter $1/g = \tau_r$ represents the average life of the radical r, while $1/k = \theta$ is the average life of the intermediate product x. With degenerate branching of the chains, the life of the stable intermediate product should obviously be far longer than that of the radical: $\theta \gg \tau_r$, so that $g \gg k$. If we write $\varphi = k_3\nu - k$, we find that, when $g \gg k$, the exponents are $\lambda_1 = \varphi$ and $\lambda_2 = -g$, and the solutions of Eqns. (1) and (2) become

$$r = \frac{w_0 k_3 \nu}{g\varphi}\left(e^{\varphi t} - \frac{k}{k_3\nu}\right) - \frac{w_0}{g}e^{-gt} = \frac{w_0 k_3 \nu}{g\varphi}\left(e^{\varphi t} - \frac{k}{k_3\nu}\right)_{t \approx 1/g}, \tag{6}$$

$$x = \frac{\nu w_0}{\varphi}(e^{\varphi t} - 1) + \frac{\nu w_0}{g}e^{-gt} = \frac{\nu w_0}{\varphi}(e^{\varphi t} - 1)_{t \approx 1/g}. \tag{7}$$

The solutions (6) and (7) are evidently valid when $dr/dt = 0$, i.e. if the concentration of radicals can be regarded as quasistationary.

Inequality (5) is a condition of quasistationary character either in relation to the concentration of radicals ($dr/dt = 0$), when $g \gg k$, or for the concentration of the intermediate product, when its life θ in the reaction is far shorter than the life of the radicals τ_r, i.e. when $g \ll k$.

The latter case can obviously occur in branched chain reactions†. The inequality (5) can be satisfied whatever

† Fresh results have recently been obtained on the mechanism of branching in chain ignitions [16]. These indicate that the increase in the number of active centres in branched chain reactions is a consequence of the transformation of excited saturated molecules x^*, which are formed in the strongly exothermic stage of chain propagation, and concentrate the heat of reaction in the excitation of vibrational and rotational degrees of freedom.

In the oxidation of hydrogen, for example, chain branching occurs in the reactions

$$H + O_2 \rightarrow HO_2^*,$$
$$HO_2^* \rightarrow HO + O.$$

When $k \gg g$ and condition (5) applies, the concentration of x^* can be regarded as quasistationary, and Eqns. (1) and (2) as equivalent to the equation

$$\frac{dr}{dt} = w_0 + (a\delta^* - g)r = w_0 + (f - g)r,$$

where δ^* is the probability of radical formation from an excited molecule x^*, and $f = a\delta^*$ is the kinetic coefficient of chain branching.

the relationship among the kinetic constants a, k_3, g, and k, if the system is close to a limit, when $k_3\nu \to k$, i.e. $\lambda_1 \to 0$. However, it can be satisfied also if the system is remote from a limit, when $k_3\nu > k$. This case has already been discussed[3] for the degenerate branching of chains.

In degenerate chain branching ($g \gg k$) the condition of quasistationarity with respect to the concentration of radiclas is given by the inequality

$$k_3\nu - k \ll g \quad \text{or} \quad k_3\nu \ll g,$$

if the reaction system is remote from the limit, when $k_3\nu > k$. This inequality can be written[3]

$$\nu \ll \frac{\theta}{\tau_r} \quad \text{or} \quad \nu \ll \sqrt{\frac{\theta}{\tau_m}}, \qquad (5')$$

where $\tau_m = 1/a$ is the life of a radical in the reaction of chain propagation. If $\tau_r \leq 1$ s, while $\theta \simeq 10^3$–10^6 s, which corresponds to the average life of stable intermediate products — aldehydes, hydroperoxides — in the autoxidation of hydrocarbons, condition (5′) is valid with a chain length of $\nu = 10^3$–10^6 steps. In the autoxidation of hydrocarbons the chain length ν is far smaller than this value.

In the analysis of the kinetic equations of chain reactions with degenerate branching it will henceforward be assumed that the condition of quasistationarity is satisfied for the concentration of radicals.

1. Limiting Condition of a Chain Reaction with Degenerate Branching

It is evident from Eqns. (3) and (4) and Eqns. (6) and (7) that the concentrations of radicals r and of the reaction product x will increase with time, i.e. that the process will be autocatalytic, provided that $k_3\nu > k$ ($\lambda_1 > 0$, $\varphi > 0$).

When $k_3\nu < k$ ($\varphi < 0$, $\lambda_1 < 0$) the concentrations of x and r, and hence the reaction velocity $-dA/dt = ar$, will, after a certain time $t \simeq 1/|\varphi|$, become constant:

$$r \to \frac{w_0 k}{g|\varphi|}, \qquad (8)$$

$$x \to \frac{\nu w_0}{|\varphi|}. \qquad (9)$$

The possibility of a chain reaction with degenerate branching passing into a "degenerate unbranched stage" when limiting conditions are reached has been demonstrated previously[3].

The equality $k_3\nu = k$ is the condition for a process to pass from autocatalysis to a steady state. The parameter $\delta = k_3/k$ is none other than the "probability of formation... of a chain when one molecule of intermediate product is involved, i.e. a parameter (formally identical with the previous δ) defining the probability that a chain will branch at a given step" [2].

Thus if a stable intermediate product leads to the formation of active centres in a chain reaction, the limiting condition at which this reaction will be autocatalytic is $\nu\delta = 1$, when ν intermediate product molecules formed in the primary chain yield one secondary chain on further reaction.

Since $\nu = 1/\beta$, the limiting condition is that the probabilities of termination β and of degenerate branching of the chain should be equal: $\beta = \delta$.

2. Autocatalytic Factor in a Chain Reaction with Degenerate Branching and Transition through Limiting Values of the Parameters

The autocatalytic factor in a chain reaction with degenerate branching is the difference between the kinetic coefficients $k_3\nu$ and k, which represent respectively the rate of formation of intermediate product in those chains which have arisen from its breakdown into radicals $k_3 x\nu$ and the total rate of consumption of the intermediate product in the reaction kx:

$$\varphi = k_3\nu - k = k_3\nu(1 - 1/\nu\delta).$$

The expression for φ can be written

$$\varphi = k_3\nu(1 - \nu_{cr}/\nu) = k_3\nu\psi, \qquad (10)$$

where $\psi = 1 - \nu_{cr}/\nu$ and $\nu_{cr} = 1/\delta$ is the chain length at which the autocatalytic factor is zero.

In the liquid-phase oxidation of hydrocarbons the chain length can be varied by additions of inhibitors InH:

$$\nu = k_2[RH]/k_i[InH],$$

where k_2 and k_i are the rate constants for reaction of $RO_2^{\cdot}$ radicals with the hydrocarbon RH and with the inhibitor respectively. We then have $\psi = 1 - [InH]_{cr}/[InH]$.

In the gas-phase oxidation of hydrocarbons, chain termination takes place on the wall of the reaction vessel. The termination rate constant g depends on the diameter of the vessel (kinetic region) and on the pressure of the mixture and the diameter (diffusion region of chain termination).

In gas-phase reactions the rate of chain propagation will depend on the pressure of the mixture, since $a = k_2[RH] = k_2 N\gamma p$, where N is the number of molecules at pressure $p = 1$ mmHg and the temperature of the reaction vessel, γ is the mole fraction of the reactant in the gaseous mixture, and p is the total pressure of the reaction mixture.

If chain termination is determined by the probability of the capture of radicals by the surface of the reaction vessel ($\epsilon_r < 1$, kinetic region of chain termination), we have $g = \epsilon_r u_r/d$, where u_r is the mean thermal velocity of a molecule and d the diameter of the vessel. The chain length in gas-phase oxidation will depend on the pressure of the mixture and the diameter of the vessel:

$$\nu = a/g = \frac{k_2 N\gamma}{u_r \epsilon_r} pd.$$

In this case $\psi = 1 - p_{cr}/p$ for variation of the pressure of the mixture in a vessel of given diameter, and $\psi = 1 - d_{cr}/d$ for variation of the diameter of the vessel at constant pressure.

It follows from Eqn. (10) that, with degenerate chain branching, the autocatalytic factor is determined by the rate constant for decomposition of the intermediate product into radicals k_3 and by the length of the chain ν, and depends on ψ, which measures how far the reaction system is from the limit under given experimental conditions (e.g. how much less is the inhibitor concentration [InH], or how much higher, when $\psi > 0$, is the pressure of the mixture p, than the corresponding limiting values).

In a branched chain reaction the autocatalytic factor is given by the difference between the kinetic coefficents of chain branching f and chain termination g:

$$\varphi_{br} = f - g = f(1 - f/g) = f\psi.$$

In the oxidation of hydrogen above the lower limit in the kinetic region of chain termination ($\epsilon < 1$), the autocatalytic factor is

$$\varphi_{br} = 2a_2(1 - p_{cr}/p) = 2a_2\psi, \qquad (11)$$

where $\psi = 1 - p_{cr}/p$, $f = 2k_2[O_2] = 2a_2$, and k_2 is the rate constant of the chain-branching reaction $H + O_2 \xrightarrow{k_2} HO^{\cdot} + {}^{\cdot}O^{\cdot}$. It is seen from Eqns. (10) and (11) that the autocatalytic factors of a branched reaction and of a reaction with degenerate branching are proportional to the rate constant (a_2, k_3) of the process in which the number of active centres increases.

In branched chain reactions the increase in the number of active centres is determined by rapid reactions of radicals with saturated molecules. In such processes the transition from a slow steady-state reaction, involving a negligible rate of initiation of chains (when $\varphi < 0$), to a rapid autocatalytic process (when $\varphi > 0$) is very sharp, with little departure of the external parameters from the critical values, i.e. with a very low value of ψ.

The consumption of the starting materials in the chain ignition of hydrogen is described by the formulae

$$\Delta[O_2] = \frac{n_0}{4a_2\psi} e^{\varphi t} \text{ when } \varphi > 0 \text{ and } t > \frac{1}{\varphi},$$

$$\Delta[O_2] = n_0 t\left(1 + \frac{1}{2|\psi|}\right) \text{ when } \varphi < 0,$$

where $\Delta[O_2] = [O_2]_0 - [O_2]_t$. When $\varphi > 0$, the time t_1 during which the amount $\Delta[O_2]$ of oxygen is used up is

$$t_1 = \frac{2.3 \log A}{\varphi} = \frac{2.3 \log A}{f\psi}, \qquad (12)$$

where

$$\varphi = 2a_2\psi = f\psi, \; A = \frac{4a_2\psi^2\Delta[O_2]}{n_0}.$$

When $\varphi < 0$, the time t_2 during which the oxygen concentration falls by $\Delta[O_2]$ is

$$t_2 = \frac{\Delta[O_2] \cdot 2|\psi|}{n_0 \cdot (1 + 2|\psi|)} \qquad (13)$$

The ratio t_2/t_1 gives the factor by which the time for a definite consumption of the starting materials $\Delta[O_2]$ increases on passing from $\varphi > 0$ to $\varphi < 0$:

$$t_2/t_1 = C\frac{f}{n_0}, \qquad (14)$$

in which

$$C = \frac{\Delta[O_2]\psi^2}{1.15(1 + 2|\psi|)\log A}.$$

In a stoichiometric mixture of hydrogen and oxygen[9] at 800°K and p_{cr} = 7.6 mmHg, we have $a_2 = 310\ s^{-1}$. At the pressure $p_1 = 1.1p_{cr}$, i.e. with $\psi = 0.1$, the autocatalytic factor is $\varphi_{br} = 62\ s^{-1}$, and the time required for 10% of the oxygen to be consumed is $t_1 = 0.2$ s from Eqn. (12). At the pressure $p_1 = 0.9p_{cr}$ ($\psi = -0.1$) the time $t_2 = 3000$ s‡. Thus for a change in pressure of 20%, from $1.1p_{cr}$ to $0.9p_{cr}$, the reaction time increases by a factor of $t_2/t_1 = 1.5 \times 10^4$.

‡ The rate constant of chain initiation in the oxidation of hydrogen[9] is $k_0 \simeq 10^{-22}$ at 800°K. For a stoichiometric mixture of oxygen and hydrogen at 7.6 mmHg the rate of initiation is $n_0 = 10^{-22}[H_2][O_2] = 3.0 \times 10^{-10}$ M s^{-1}.

With degenerate branching of the chains, autocatalysis of a reaction is determined by the rate of formation of primary radicals from molecular intermediate products.

In the oxidation of hydrocarbons the rate constant for decomposition of the hydroperoxide into radicals is $k_3 = 10^{-3}$–$10^{-6}\ s^{-1}$; the autocatalytic factor in these reactions, many orders of magnitude smaller than φ_{br}, is therefore quite remote from the limit ($\psi \to 1$) and thus close to the limit ($\psi \to 0$). This is the reason for the slow increase in rate of a chain reaction with degenerate branching and the less sharp transition through the limiting values of the external parameters.

"Long before critical conditions are approached, the increase in rate is so slow that we find it difficult to fix the sharpness of the transition from complete absence of reaction when $\delta - \beta < 0$ to autocatalysis when $\delta - \beta > 0$". [1]

The variation in reaction time on passing through limiting values of the parameters in the case of degenerate chain branching can be analysed in a similar manner to that used for the branched chain oxidation of hydrogen. The starting materials are consumed in the chain process at the rate $-d[RH]/dt = ar$, where $a = k_2[RH]$, in which k_2 is the rate constant of chain propagation. If the reaction is autocatalytic ($\varphi > 0$), it follows from Eqn. (6) that, after a certain time $t \simeq 1/\varphi$, the variation in radical concentration is described by the equation

$$r = \frac{w_0}{g\psi} e^{\varphi t}.$$

In this case, integration of the equation for the consumption of hydrocarbon with the initial conditions [RH] = $= [RH]_0$ at $t = 0$ leads to the expression

$$\Delta[RH] = \frac{w_0}{k_3\psi^2}(e^{\varphi t} - 1),$$

which is valid when the extent of conversion of the starting materials is small.

Hence the time required for an amount $\Delta[RH]$ of the starting materials to be consumed in an autocatalytic process is

$$t_1 = \frac{2.3 \log A}{\varphi} = \frac{2.3\,\delta(1 - \psi)\log A}{k_3\psi}, \qquad (12')$$

where

$$A = \frac{\Delta[RH] \cdot k_3\psi^2}{w_0} + 1$$

and from Eqn. (10)

$$v_{\varphi > 0} = \frac{1}{\delta(1 - \psi)}.$$

The variation in radical concentration during the steady state of the process ($\varphi < 0$) is described by Eqn. (8). In this case $\Delta[RH]$ increases with time according to the equation

$$\Delta[RH] = \frac{w_0(1 + |\psi|)v_{\varphi<0}}{|\psi|} t_2$$

and the time t_2 for consumption of an amount $\Delta[RH]$ of the starting materials under steady-state conditions of the process is

$$t_2 = \frac{\Delta[RH] \cdot \delta|\psi|}{w_0}, \qquad (13')$$

where $v_{\varphi<0} = 1/\delta(1 + |\psi|)$ from Eqn. (10).

The change in reaction time on passing through $\varphi = 0$ is given by the ratio

$$t_2/t_1 = C\frac{k_3}{w_0}, \qquad (14')$$

where

$$C = \frac{\psi^3\Delta\,[RH]}{(1-|\psi|)\,2.3\log A}.$$

Eqns. (12) and (12'), (13) and (13'), and (14) and (14') for the dependence of reaction time on kinetic constants with branching and with degenerate chain branching are analogous to one another.

It follows from Eqns. (14) and (14') that the abruptness of the change in reaction time on passing from autocatalytic to steady-state conditions depends on the relationship between the rate constant for chain branching f (or degenerate branching k_3) and the rate of initiation of chains n_0 (w_0).

Table 1 gives for comparison values of t_1, t_2, and t_2/t_1 found for the oxidation of hydrogen and calculated from Eqns. (12')–(14') for a reaction with degenerate chain branching and different values of the rate constant for dissociation of the intermediate product into radicals. In Table 1 the times t_1 and t_2 relate to the consumption of 10 mole % of the starting materials respectively at $\psi = 0.1$ and $\psi = -0.1$, the rate of initiation of chains is $w_0 = 3\times10^{-10}$ M s^{-1}, $\delta = 1$, and the concentration of the starting materials is $[RH]_0 = 0.002$ M (in the gas phase this concentration corresponds to 100 mmHg at 423°C).

The calculations show that, in slow non-stationary reactions, a quite abrupt transition through $\varphi = 0$ will be observed provided that the ratio $k_3/w_0 \geq 10^7$ litres mole^{-1}. With $k_3/w_0 \leq 10^6$ no significant change should occur in the reaction time on passing through $\varphi = 0$, and limiting phenomena are not observed. It is obvious that critical phenomena in periodic processes can be observed in sufficently rapid reactions, when $k_3 \simeq 10^{-2} - 10^{-3}$ s^{-1}.

With small values of $k_3 \simeq 10^{-5} - 10^{-6}$ s^{-1} for the rate constant of breakdown of the intermediate product into radicals, even if the rate of initiation is very small (e.g. $w_0 = 10^{-12}$–10^{-13} M s^{-1}) and the ratio t_2/t_1 is large, the absolute values of t_2 and t_1 are so large that it is not possible to study such a process in the vicinity of the limit.

III. CRITICAL PHENOMENA IN THE GAS-PHASE OXIDATION OF HYDROCARBONS

Autoxidation of hydrocarbons in the gas phase occurs at temperatures above 200°C and pressures from a few millimetres of mercury to atmospheric. At such high temperatures and low densities of the hydrocarbon, the main reaction of the peroxy-radical is isomerisation and decomposition with formation of a molecule of a valency-saturated compound and another radical:

$$RO_2^{\cdot} \rightarrow R'CHO + R''O^{\cdot},$$
$$R''O^{\cdot} + RH \rightarrow R''OH + R^{\cdot},$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}.$$

Chain propagation with formation of a hydroperoxide is characteristic of liquid-phase oxidation, whereas in the gas phase it occurs at low temperatures (below 300°C).

Only traces of peroxy-compounds (mainly in the form of hydrogen peroxide, a secondary product) are detected in the products of the autoxidation of hydrocarbons in the gas phase above 300°C, and the only intermediate products are aldehydes [17-24]. The concentration of aldehydes reaches a high value during the reaction. In the oxidation of methane (p_{CH_4} = 110 mmHg at 491.5°C), for example, the maximum concentration of formaldehyde reaches 0.45 mole % of the initial hydrocarbon [21] ($[CH_2O] = 6\times10^{15}$ cm^{-3}). In the oxidation of propane ($p_{C_3H_8}$ = 116 mmHg at 350°C) the formaldehyde concentration is p_{CH_2O} = 11.5 mmHg ($[CH_2O] = 1.5\times10^{17}$ cm^{-3}) and that of acetaldehyde p_{CH_3CHO} = = 4.5 mmHg ($[CH_3CHO] = 5.8\times10^{16}$ cm^{-3}). [19] The concentration of radicals in the gas-phase oxidation of hydrocarbons is lower than the limit of sensitivity of modern methods of measurement: $r < 10^{13}$ cm^{-3}. Thus in slow, non-stationary oxidations of hydrocarbons, the concentration of stable intermediate products x is many orders of magnitude greater than the concentration of radicals r:

$$\frac{[RCHO]}{[RO_2]} = \frac{x}{r} > 10^3.$$

It follows from Eqns. (6) and (7) that the concentration ratio of radicals to intermediate product x, with quasi-stationary conditions for the concentration of radicals (when $t > 1/\varphi$), is

$$\frac{x}{r} = \frac{g}{k_3} \gg 1.$$

This is the relationship between the concentrations of stable intermediate products and radicals which is observed in actual processes.

It has now been shown by various methods [22-25] that, in the gas-phase oxidation of hydrocarbons, aldehydes are the only intermediate products involved in the degenerate branching of chains.

The most probable mechanism of degenerate branching is oxidation of the aldehydes according to the equation

$$(3)\ R'CHO + O_2 \rightarrow R'CO^{\cdot} + HO_2^{\cdot} - Q.$$

In a stoichiometric mixture of methane and oxygen at a total pressure of 235 mmHg and at 423°C, the rate of formation of radicals due to oxidation of the intermediate product (formaldehyde) is [22]

$$w_{deg\ br} \simeq f\times10^{-10}\exp(-32\,000/RT)[O_2][CH_2O] \simeq 2\times10^{-4}[CH_2O],$$

where $f = 10^{-2}$ is the steric factor.

Under these experimental conditions the rate of chain initiation is

$$w_0 \simeq 10^{-10}\exp(-55\,000/RT)[O_2][CH_4] \simeq 10^{-11}\ \text{M s}^{-1}.$$

Consequently the reaction is characterised by the ratio $k_3/w_0 \simeq 10^7$ litres mole^{-1}, where $k_3 = 2\times10^{-4}$ s^{-1} is the effective rate constant of radical formation by oxidation of

TABLE 1. Abruptness of transition through limiting values of parameters in branched chain and degenerate branched reactions.

	Rate constant f or k_3, s^{-1}	f/n_0 and k_3/w_0	t_1	t_2	t_2/t_1
Oxidation of hydrogen	6.2×10^2	2×10^{12}	0.2 s	3×10^3 s	1.5×10^4
Degenerate branched reaction	$3\cdot10^{-2}$	10^8	1.32 h	55 h	40
	$3\cdot10^{-3}$	10^7	7.5 »	55 »	7
	$3\cdot10^{-4}$	10^6	26 »	55 »	2
	$3\cdot10^{-5}$	10^5	46 »	55 »	1.2
	$3\cdot10^{-6}$	10^4	50 »	55 »	1.1

the intermediate product. According to the above calculations, with this ratio the transition through the limiting conditions should be far less abrupt than in the oxidation of hydrogen, as is confirmed by experimental results [13]. In the oxidation of methane at 423°C with p_{O_2} = 157 mmHg and p_{CH_4} = 78 mmHg, the life of the radicals $CH_3^{\cdot}$ and $^{\cdot}OH$ in the reactions of chain propagation is [9] $\tau_m = 5 \times 10^{-6}$ s. If the length of the chain is $\nu \simeq 100$ steps [26], the life of the chain is $\tau_\gamma = \tau_m \nu \simeq 5 \times 10^{-4}$ s. However, the average appearance time of a radical (i.e. of a secondary chain) by the breakdown of ν = 100 aldehyde molecules formed in the primary chain is $1/k_3\nu \simeq 50$ s. Hence it follows that, in processes of slow oxidation, propagation of chain — from the moment it is formed until it is destroyed — occupies a far shorter time than does formation of a fresh chain by breakdown of the intermediate product into radicals [2].

Apart from being used up in degenerate chain branching, the aldehydes are involved in several other reactions, which do not result in the formation of radicals. In the oxidation of methane, for example, it is supposed that formaldehyde may decompose on the walls of the reaction vessel [21]:

$$CH_2O \xrightarrow{\text{wall}} \text{products}.$$

Thus the probability of degenerate branching of the chains is less than unity ($\delta < 1$). In later stages of the reaction the aldehydes are consumed by a chain mechanism, e.g.

$$CH_2O + {}^{\cdot}OH \rightarrow H_2O + HCO^{\cdot}.$$

It has been shown [3] that, with consumption of the intermediate product by a chain mechanism and linear termination of chains, a steady-state concentration of the intermediate product is established, and the rate of oxidation becomes constant. After the induction period is over, however, the chain consumption of aldehydes in the gas-phase oxidation of hydrocarbons, and of hydroperoxides in the liquid-phase process, proceeds at an appreciable rate with a high radical concentration. In the early stages of conversion, therefore, the chain consumption of intermediate products can be disregarded. In the oxidation of methane it has been shown [25] that $\varphi\tau$ is approximately constant during the initial stages of the reaction (up to 10% conversion), which is consistent with a mechanism of the process which ignores the chain consumption of formaldehyde.

The gas-phase oxidation of hydrocarbons is greatly dependent on the state and treatment of the walls of the reaction vessel. The reaction velocity increases with increase in the diameter of the vessel and in the pressure of an inert gas [5,10,13]. This indicates that the destruction of active centres occurs on the surface of the reaction vessel. It has been established [5] that, in the oxidation of methane, chain termination takes place in the region of diffusion-controlled kinetics.

With chain termination on the surface of the vessel, a critical diameter d_{cr} and a critical pressure p_{cr} should be observed, their values being determined from the condition $\varphi = 0$. The existence of these critical parameters has been found in the gas-phase oxidation of various compounds. A study [10] of the oxidation of acetylene under flow conditions at 320°C and 400 mmHg in tubes of different diameters showed that the reaction occurred slowly at 2 and 4 mm, and quite rapidly at 6, 10, and 20 mm diameter. A change in diameter of the vessel from 4 to 6 mm produced a thirtyfold increase in reaction velocity. Thus the experimental results indicate the presence of a critical diameter $d_{cr} \simeq 4$ mm.

The existence of critical conditions d_{cr}, p_{cr}, and t_{cr} was found in the oxidation of ethane [11]. The increase in pressure during the process (Fig. 1), in a vessel of diameter 5 mm at 708°C and pressures of 134, 98, and 94.5 mmHg, was represented by the exponential law

$$\Delta p = N(e^{\varphi t} - 1).$$

The kinetic curves changed from concave to convex at pressures of 92–60 mmHg, and the variation in pressure was described by the equation to a steady-state process $\Delta p = A(1 - e^{-kt})$. A change in shape of the kinetic curves representing the autocatalytic and the steady-state process was observed with change in the experimental temperature and in the diameter of the vessel. In all cases the $\Delta p_{max} - p_0$ relationship changed abruptly at the critical values of the diameter, the pressure, and the temperature (Fig. 2). It was assumed [11] that, in the oxidation of ethane, the homogeneous reaction was accompanied by oxidation on the walls of the vessel, which prevented a sharper development of critical reaction conditions.

Critical phenomena are clearly evident in the oxidation of arsine [12]. A stoichiometric mixture of arsine and oxygen could remain in a spherical vessel of diameter d = = 10 cm at 50°C without change for an indefinite time if the pressure was lower than p_{cr} = 143 mmHg. At higher pressures the mixture slowly reacted, the pressure falling and As_2O_3 being deposited on the walls of the vessel. Reaction ceased when the pressure had fallen to a certain value p_{cr}. At constant temperature and pressure a critical diameter d_{cr} was shown to exist, which was linked with p_{cr} by the constancy of their product $p_{cr}d_{cr}$, a relationship known from the kinetics of chain ignitions. At a pressure of 94 mmHg, for example, the critical diameter is d_{cr} = = 15 cm, and at 143 mmHg it is 10 cm. The temperature dependence of the critical diameter is given by the relation $\log d_{cr} = A/T + B$. Thus the temperature dependence of d_{cr} exhibits the same regularities as does that of branched chain reactions.

An investigation has been made [13] of the effect of the diameter of the vessel on the rate of oxidation of a number of saturated and unsaturated hydrocarbons (methane, ethane, propane, ethylene, propene, and acetylene). Fig. 3 shown the dependence on vessel diameter of the time

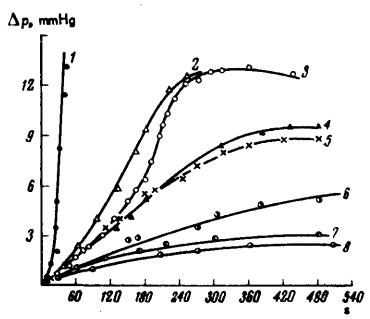


Fig. 1. Kinetic curves of increase in pressure in the oxidation of ethane (in a $C_2H_6 + 3.5O_2$ mixture at 708°C in a quartz vessel with d = 5 mm) at various initial pressures (mmHg) of the reactant mixture:
1) 134; 2) 98; 3) 94.5; 4) 91.5; 5) 92; 6) 90.5; 7) 80; 8) 60.

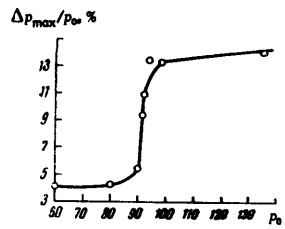


Fig. 2. Dependence of maximum increase in pressure in the oxidation of ethane on the initial pressure of the reactant mixture ($C_2H_6 + 3.5O_2$) at 700°C with d = 5 mm.

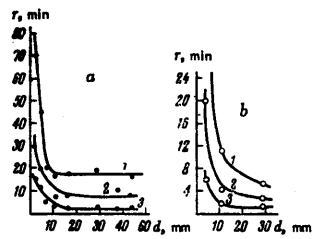


Fig. 3. Dependence of induction period on diameter of vessel in oxidation of: *a*) propene in $C_3H_6 + 3O_2$ mixture at 360°C; *b*) methane in equimolecular mixture with oxygen at 530°C; at various initial pressures (mmHg): 1) 150; 2) 200; 3) 300.

required for the reaction velocity to reach its maximum value (the induction period) in the oxidation of methane and propene. It is seen that a more or less sharp break occurs at a certain diameter, below which the reaction velocity falls sharply.

IV. PHENOMENON OF A CRITICAL INHIBITOR CONCENTRATION IN THE LIQUID-PHASE OXIDATION OF HYDROCARBONS IN BATCHES

1. Kinetics of the Inhibited Oxidation of Hydrocarbons from the Viewpoint of Limiting Phenomena

From a consideration of the fundamental mechanism of the oxidation of hydrocarbons with chain termination on an inhibitor, Semenov showed that a critical inhibitor concentration $[InH]_{cr}$ should exist, above which the process will be stationary, i.e. very slow, and below which it should be autocatalytic [9].

According to present-day ideas, the oxidation of a hydrocarbon in the presence of an inhibitor comprises the following set of elementary stages

$$\left.\begin{array}{l}(0.1)\ RH + O_2 \xrightarrow{w_0} R^{\cdot} \\ (0.2)\ 2RH + O_2 \xrightarrow{w_0} R^{\cdot}\end{array}\right\}\ \text{— initiation of chains,}$$

$$\left.\begin{array}{l}(1)\ R + O_2 \xrightarrow{k_1} RO_2 \\ (2)\ RO_2 + RH \xrightarrow{k_2} ROOH + R^{\cdot} \\ (2')\ R' + RH \xrightarrow{k_2'} R'H + R^{\cdot}\end{array}\right\}\ \text{— chain propagation,}$$

$$(3)\ ROOH \xrightarrow{k_3} nR'\ (= RO, OH)\quad \text{— degenerate chain branching with autoxidation,}$$

$$\left.\begin{array}{l}(3')\ ROOH \xrightarrow{k_3'} \\ (3'')\ ROOH + M' \xrightarrow{k_3''[M']}\end{array}\right\}\ \text{— stable products,}$$

$$(4)\ ROOH + M^{n+} \longrightarrow R'\ \text{— degenerate chain branching in presence of a catalyst,}$$

$$(5)\ RO_2 + RO_2 \xrightarrow{k_5} \text{products,}$$

$$(6)\ RO_2 + InH \xrightarrow{k_6} ROOH + In^{\cdot},$$

$$(7)\ RO_2 + In \xrightarrow{k_7} \text{products,}$$

$$(8)\ In^{\cdot} + In \xrightarrow{k_8} \text{products.}$$

In this scheme R′ denotes a primary radical RO or OH, formed by the breakdown of a hydroperoxide, and M′ is a sulphide, phosphite, etc., which decomposes hydroperoxides with the formation of valency-saturated compounds. Many quantitative data are now available on the rates of the elementary reactions in liquid-phase oxidation. The most probable mechanism of chain initiation is the bimolecular reaction (0.1) for a hydrocarbon of bond energy $Q_{RH} > > 90$ kcal mole^{-1} and the termolecular reaction (0.2) for a hydrocarbon of bond energy $Q_{R-H} < 90$ kcal mole^{-1}. [27] The value of w_0 is 10^{-11}–10^{-8} M s^{-1} depending on the temperature and the nature of the hydrocarbon [27,28].

The autocatalytic character of the liquid-phase oxidation of hydrocarbons is associated with the formation of radicals by the breakdown of hydroperoxides, the stable intermediate products formed in the reaction of chain propagation. Comparison, by a kinetic tracer method, of the rates of consumption of hydroperoxides and of accumulation of the final products (ketones, alcohols, acids) in the oxidation of n-decane [29] (at 140°C), and also in the oxidation of cyclohexane [30] (155°C) has demonstrated rigorously that hydroperoxides are the primary and practically the only intermediate products in the liquid-phase autoxidation of hydrocarbons.

A great amount of work has been done on the mechanism of the dissociation of hydroperoxides into radicals and the part played by this process in accelerating oxidation processes (degenerate chain branching). Radicals are formed by the unimolecular breakdown of hydroperoxides at the weak O–O bond and as a result of a bimolecular reaction with the hydrocarbon [31–33]:

$$ROOH \left\langle \begin{array}{l} \longrightarrow RO^{\cdot} + {}^{\cdot}OH \\ \xrightarrow{+RH} R^{\cdot} + RO^{\cdot} + H_2O \end{array} \right\}\ \text{reaction mechanism (3).}$$

The experimental data in Table 2 show that at 100–140°C, when the liquid-phase autoxidation of hydrocarbons takes place at a measurable rate, the radical decomposition constant of the hydroperoxides is $k_3 \simeq 10^{-6}$–10^{-4} s^{-1}.

TABLE 2. Rate constants for the dissociation of hydroperoxides into radicals.

Hydroperoxide	k_3, s^{-1}	k_3, s^{-1}, at 100–140°C	Ref.
n-Decyl	$6\cdot10^{8}\exp(-24\,800/RT)$	$1.5\cdot10^{-6}$—$5.0\cdot10^{-5}$	34
Cyclohexyl	$1.2\cdot10^{13}\exp(-34\,000/RT)$	$1.2\cdot10^{-7}$—$4\cdot10^{-6}$	35
Decahydronaphthyl	$8.5\cdot10^{13}\exp(-32\,100/RT)$	$1.2\cdot10^{-5}$—$7.9\cdot10^{-5}$	36

The dissociation of a hydroperoxide into radicals can be initiated by a metal of variable valency (by a cobalt, copper, manganese, nickel, or iron salt). Radical formation in the presence of such a metal in glacial acetic acid[37] results from the reactions

$$ROOH + M^{n+} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [ROOH \cdot M^{n+}],$$

$$[ROOH \cdot M^{n+}] + M^{n+} \xrightarrow{k_c} RO^{\cdot} + M^{n+}_{f} + M^{3+}(OH),$$

$$[ROOH \cdot M^{n+}] + M^{3+}(OH) \xrightarrow{k_d} RO_2 + 2M^{n+} + H_2O.$$

It follows from the stoichiometric equation for this process

$$2ROOH \rightarrow RO^{\cdot} + RO_2^{\cdot} + H_2O,$$

that one radical is formed per hydroperoxide molecule decomposed. The rate of breakdown of the hydroperoxide in the presence of a metal of variable valency is proportional to the hydroperoxide concentration:

$$-d[ROOH]/dt = k_4[ROOH],$$

where $k_4 = 2k_ck_a[M^{n+}]^2/k_b$ at low catalyst concentrations $[M^{n+}]$, and $k_4 = k_a[M^{n+}]$ at high concentrations thereof. Under the actual conditions of the catalysed oxidation of hydrocarbons (tetrahydronaphthalene[38], ethylbenzene[39], n-decane[40], cyclohexane[41]) in the presence of salts of metals of variable valency, $k_4 = 0.001$–$0.1\ s^{-1}$.

In the mechanism of the breakdown of hydroperoxides, reactions in which stable molecules are formed directly — reactions (3′) and (3″) — must be taken into account as well as those leading to the production of radicals. The formation of valency-saturated compounds by the unimolecular decomposition of substances in the liquid phase is associated with a "cage effect", consisting in recombination of a proportion of the radicals without their escaping from the "cage" of the solvent[42]. For example, the hydroperoxide of n-decane in this hydrocarbon as medium at 130°C breaks down into radicals at a rate, measured from the consumption of inhibitor, which is 0.6 of the total rate of decomposition: i.e. 1.2 radicals are formed per hydroperoxide molecule decomposed. The remaining 0.4 of the total rate of decomposition represents reactions in which molecular products are formed[43].

A hydroperoxide breaks down without radical formation on reaction with alkyl and aryl sulphides[44,45], selenium compounds[46], and phosphoric esters[47–49]:

$$(3'')\ ROOH + R'SR \longrightarrow ROH + R'S(O)R.$$

The role of a hydroperoxide in the autocatalysis of oxidation is governed by competition between reactions (3) or (4) and reactions (3′) and (3″), i.e. by the value of $\delta = k_3/k$.

In the liquid phase the diffusion of radicals to the walls of the vessel is made very difficult by the high density of the substance, and liquid-phase oxidation in the absence of inhibitors is characterised by quadratic chain termination with recombination of the radicals. At oxygen pressures of $p_{O_2} \simeq 200$–300 mmHg the concentration of alkyl radicals R$^{\cdot}$ is far lower than that of $RO_2^{\cdot}$ radicals, and therefore chain termination occurs by reaction (5).

The rate constant for the recombination of $RO_2^{\cdot}$ radicals has been measured for various hydrocarbons[50–56], and its value of $k_5 = 10^5$–10^7 litres mole^{-1} s^{-1} is almost independent of temperature ($E_5 \leq 2$ kcal mole^{-1}). In the absence of inhibitor, the variation in radical concentration is given by the equation

$$d[RO_2]/dt = w_0 + nk_3[ROOH] - k_5[RO_2]^2 = 0,$$

from which it follows that the radical concentration is $[RO_2^{\cdot}] = \sqrt{w_i/k_5}$, where $w_i = w_0 + nk_3[ROOH]$ is the rate of initiation of radicals. The length of the chain ν and the rate of oxidation of the hydrocarbon w are

$$\nu = a/g = k_2[RH]/\sqrt{w_ik_5},$$

$$w = k_2[RH]\sqrt{w_i/k_5}.$$

The parameter $g_{qu} = \sqrt{w_ik_5}$ is the effective rate constant for the destruction of $RO_2^{\cdot}$ radicals by quadratic chain termination.

The rate of oxidation of a hydrocarbon is diminished by the presence of an amine, a phenol, or a naphthol, containing an OH, NH_2, or > NH group. Much work has been done on the mechanism of the action of inhibitors and on the kinetics of inhibited oxidation in connection with the practical problems of the stabilisation of various substances (fats, oils, petroleum products, and polymeric materials) against oxidative degradation. Progress in the practical application of antioxidants and in studying the mechanism of their action has been summarised in several reviews and monographs[57–59].

The retardation of oxidation processes in the presence of compounds containing the above groups results from the abstraction of the weakly bound hydrogen by $RO_2^{\cdot}$ radicals with the formation of relatively inactive In$^{\cdot}$ radicals, reaction (i). The parameter $g_{in} = k_i[InH]$ is the kinetic coefficient of the loss of $RO_2^{\cdot}$ radicals in reactions with the inhibitor. The mechanism of the action of inhibitors represented by reaction (i) is supported by kinetic data on the rates of oxidation of hydrocarbons in the presence of inhibitors[61–65], by isotopic[63], spectroscopic[66], and chemiluminescent methods[67], and by several other data[68].

Various methods have been proposed[64,69,70] for measuring the rate constant k_i, which depends on the nature of the inhibitor, the medium (hydrocarbon), and the temperature. Values of $k_i \simeq 10^3$–10^5 litres mole^{-1} s^{-1} have been obtained for inhibitors of varying efficiency. The activation energy for abstraction of a hydrogen atom from an inhibitor molecule by $RO_2^{\cdot}$ radicals is $E_i \simeq 3$–8 kcal mole^{-1}.

The structure and the reactivity of In$^{\cdot}$ radicals have been studied by chemical[71] and physical methods. Most of the recent information on their structure and reactions has been obtained by the electron spin resonance method[72], by means of which In$^{\cdot}$ radicals have been detected in the oxidation of polypropylene in the presence of 1- and 2-naphthols, 4-methyl-2,6-di-t-butylphenol, diphenylamine, and other inhibitors[72,73]. The reaction products from inhibitors under oxidising conditions have been found to include compounds In–RO_2 and In–In, in which the In$^{\cdot}$ radical has either a phenoxy or a quinonoid structure. These compounds could be formed in reactions (7) and (8).[57] If the In$^{\cdot}$ radical is involved in chain termination by reaction (7),

the number of chains m destroyed on one inhibitor molecule exceeds unity ($m \geq 1$).

It has been found that many inhibitors containing one OH or NH_2 group terminate two oxidation chains ($m = 2$), and that bifunctional compounds terminate four oxidation chains ($m = 4$):[67,74,75] i.e. under these conditions the In$^\cdot$ radicals disappear only in reaction (7). The rate constant of this reaction has been determined[76] as $k_7 \simeq 10^9$ litres mole^{-1} s^{-1} for the tetrahydronaphthylperoxy-radical and the phenoxy--radical. Thus this constant is larger than k_i by factors of 10^2–10^4.

The stability of the In$^\cdot$ radical and its ability to react with saturated hydrocarbon molecules

$$(9)\ \mathrm{In}^\cdot + \mathrm{RH} \rightarrow \mathrm{R}^\cdot + \mathrm{InH},$$

vary according to the nature, positions, and number of substituents in the molecule of the initial inhibitor. The rate constant for the abstraction of a hydrogen atom by 2,4,6-tri-t-butylphenoxy-radicals from various hydrocarbons (n-decane, 2,4,6-trimethylheptane, ethylbenzene, cumene) is small ($E_9 \simeq 20$–27 kcal mole^{-1}).[77] In the case of other In$^\cdot$ radicals (in particular from phenol), however, it is supposed that both reaction (9) and

$$(10)\ \mathrm{In}^\cdot + \mathrm{ROOH} \rightarrow \mathrm{InH} + \mathrm{RO}_2^\cdot,$$

are very rapid[63,78,79]. In reactions (9) and (10) the In$^\cdot$ radicals are involved in chain transfer, which substantially lowers the efficiency of the inhibitors. Phenols whose radicals are involved in the chain-transfer processes (9) and (10) are relatively ineffective. The peculiarities of the retardation of oxidation processes by inefficient inhibitors have been analysed[57,63,78,79]. The possibility of various reactions of phenols and amines and their radicals, and hence the overall efficiency of the retardation of an oxidation process by inhibitors, depend on the conditions of oxidation, in particular on the temperature. Above 150°C phenols and amines are consumed mainly by direct oxidation. It is assumed that this process can result in the initiation of chains[45,80]. Little work has been done on the products of the direct oxidation of inhibitors or on their effect on the oxidation of a hydrocarbon.

Here we shall consider the kinetic laws of inhibited oxidation and experimental results on critical concentrations of efficient inhibitors, not involved in any reaction other than those of chain termination. The features of this phenomenon with amines and phenols as inhibitors at high temperatures of 180–220°C, when these compounds undergo reactions other than chain termination, have been discussed in other papers[60,80–84].

According to the above mechanism, the variation in radical concentration is governed by the equations

$$\frac{d[\mathrm{R}]}{dt} = w_0 + k_2[\mathrm{RO}_2][\mathrm{RH}] + k_2'[\mathrm{R}'][\mathrm{RH}] - k_1[\mathrm{R}][\mathrm{O}_2] = 0,$$

$$\frac{d[\mathrm{R}']}{dt} = nk_3[\mathrm{ROOH}] - k_2'[\mathrm{R}'][\mathrm{RH}] = 0,$$

$$\frac{d[\mathrm{RO}_2]}{dt} = k_1[\mathrm{R}][\mathrm{O}_2] - k_2[\mathrm{RO}_2][\mathrm{RH}] - k_i[\mathrm{RO}_2][\mathrm{InH}] - k_7[\mathrm{RO}_2][\mathrm{In}] - k_5[\mathrm{RO}_2]^2 = 0,$$

$$\frac{d[\mathrm{In}^\cdot]}{dt} = k_i[\mathrm{RO}_2][\mathrm{InH}] - k_7[\mathrm{RO}_2][\mathrm{In}] - k_8[\mathrm{In}]^2 = 0.$$

From the last equation it follows that the concentration of In$^\cdot$ radicals can be written

$$[\mathrm{In}] = \frac{k_i[\mathrm{RO}_2][\mathrm{InH}]}{k_7[\mathrm{RO}_2] + k_8[\mathrm{In}]} = \frac{\alpha k_i[\mathrm{InH}]}{k_7},$$

where $\alpha = k_7[\mathrm{RO}_2]/(k_7[\mathrm{RO}_2] + k_8[\mathrm{In}])$ is the probability of chain termination by In$^\cdot$ radicals. Adding up the first three equations, we obtain for the variation in concentration of $RO_2^\cdot$ radicals the equation

$$w_0 + nk_3[\mathrm{ROOH}] = k_i[\mathrm{RO}_2][\mathrm{InH}] + k_7[\mathrm{RO}_2][\mathrm{In}] + k_5[\mathrm{RO}_2]^2 = mk_i[\mathrm{RO}_2][\mathrm{InH}] + k_5[\mathrm{RO}_2]^2, \quad (15)$$

where $m = 1 + \alpha$ is the number of chains destroyed on one inhibitor molecule. With $\alpha = 0$, when the constant k_7 is zero, we have $m = 1$; and with $\alpha = 1$ and $k_8 = 0$, we find that $m = 2$. Thus the parameter m can have values of $2 \geq m \geq 1$.

From Eqn. (15) the concentration of $RO_2^\cdot$ radicals can be expressed

$$[\mathrm{RO}_2^\cdot] = \frac{mk_i[\mathrm{InH}]}{2k_5}\left(\sqrt{1 + \frac{4k_5w_i}{m^2k_i^2[\mathrm{InH}]^2}} - 1\right).$$

When $mk_i[\mathrm{InH}] \ll \sqrt{w_i k_5}$, i.e. when $g_{\mathrm{lin}} \ll g_{\mathrm{qu}}$, the quadratic termination of chains predominates over linear termination, and the inhibitor does not retard the reaction.

If

$$mk_i[\mathrm{InH}] \gg \sqrt{w_i k_5}, \text{ i.e. } g_{\mathrm{lin}} \gg g_{\mathrm{qu}}, \quad (16)$$

the radical concentration is

$$[\mathrm{RO}_2] = \frac{w_i}{mk_i[\mathrm{InH}]} = \frac{w_0 + nk_3[\mathrm{ROOH}]}{mk_i[\mathrm{InH}]}. \quad (17)$$

In this case the chain length $\nu_{\mathrm{inh}} = k_2[\mathrm{RH}]/mk_i[\mathrm{InH}]$ becomes less than the length ν_{qu} in the absence of inhibitor:

$$\frac{k_2[\mathrm{RH}]}{mk_i[\mathrm{InH}]} < \frac{k_2[\mathrm{RH}]}{\sqrt{w_i k_5}}.$$

In the presence of efficient inhibitors, therefore, induction periods appear in the oxidation process right up until the inhibitor is practically completely exhausted, when the relationship (16) ceases to be satisfied. The inequality (16) determines the inhibitor concentration [InH] at which linear termination predominates over quadratic termination[85,86].

This inequality is responsible for the fact that an inhibitor may retard oxidation when introduced at the start of the reaction ($w_i \simeq w_0$), but prove ineffective when introduced at later stages, when the rate of initiation w_i far exceeds the rate of generation of chains w_0. With linear termination of chains on the inhibitor, the variation in hydroperoxide concentration during the reaction is given by the equation

$$\frac{d[\mathrm{ROOH}]}{dt} = (k_2[\mathrm{RH}] + k_i[\mathrm{InH}])\frac{(w_0 + nk_3[\mathrm{ROOH}])}{mk_i[\mathrm{InH}]} - k[\mathrm{ROOH}],$$

which can be written

$$\frac{d[\mathrm{ROOH}]}{dt} = \nu' w_0 + \varphi[\mathrm{ROOH}], \quad (18)$$

where

$$\nu' = \frac{k_2[\mathrm{RH}]}{mk_i[\mathrm{InH}]} + \frac{1}{m} = \nu + \frac{1}{m},$$

is the chain length taking into account the hydroperoxide formed in the chain-termination reaction (i), and $\varphi = k_3 n\nu' - k$ is the autocatalytic factor of the process. If ν and φ do not vary with time, integration of Eqn. (18) with the initial conditions $[\mathrm{ROOH}]_0 = 0$ at $t = 0$ leads to the equations

$$[\mathrm{ROOH}] = \frac{\nu' w_0}{\varphi}(e^{\varphi t} - 1) \quad (19)$$

and

$$[RO_2^{\cdot}] = \frac{w_0 k_3 \nu'}{m k_i [InH]\varphi}\left(e^{\varphi t} - \frac{k}{n k_3 \nu'}\right). \quad (20)$$

These equations are identical with Eqns. (6) and (7) for the variation in concentration of radicals and of intermediate product obtained on analysing the general scheme of a chain reaction with degenerate branching when $n = 1$ and $g = mk_i[InH]$. Therefore the consumption of hydrocarbon

$$-d[RH]/dt = k_2[RO_2^{\cdot}][RH]. \quad (21)$$

during the induction period of inhibited oxidation should be governed by the relations (12′) and (13′), as well as by Eqn. (14′), which defines the abruptness of the change in induction period on passing through the critical inhibitor concentration.

Fig. 4 (curves *1–3*) illustrates the dependence, calculated from Eqns. (12′) and (13′) of induction period on inhibitor concentration. The time required for 0.01 mole% of the hydrocarbon to be consumed was taken as the end of the induction period; formation of hydroperoxide in the termination reaction was ignored. Calculations were made with experimental values of the elementary rate constants obtained in a study of the liquid-phase oxidation of hydrocarbons: $k_2 = 2.0$ litres mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres × × mole^{-1} s^{-1}, $k_3 = 10^{-2}$ (1), 10^{-3} (2), and 10^{-5} (3) s^{-1}, $w_0 = 10^{-10}$ M s^{-1}, [RH] = 5.0 M, $k = k_3$, $m = 1$, and $n = 1$.

Fig. 4 shows that, with the ratio $k_3/w_0 = 10^8$ and 10^7 litres mole^{-1} (curves *1* and *2*), the induction period

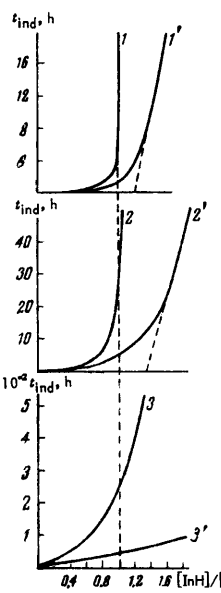


Fig. 4. Dependence of induction period (time required for 0.01% conversion of the hydrocarbon) on inhibitor concentration for different values of the rate constant k_3 (s^{-1}) for dissociation of the hydroperoxide into radicals: 1) and 1′) 10^{-2}; 2) and 2′) 10^{-3}; 3) and 3′) 10^{-5}; 1)–3) inhibitor concentration maintained constant; 1′)–3′) inhibitor used up (calculated values).

increases quite sharply at the critical inhibitor concentration. When the ratio is $k_3/w_0 = 10^5$ litres mole^{-1} (curve *3*), the induction period varies smoothly throughout the concentration range of the inhibitor; limiting phenomena are not found with such ratios of k_3 to w_0.

2. Value of Critical Inhibitor Concentration

The critical concentration of the inhibitor is evaluated from the condition that the autocatalytic factor of the process φ should vanish, i.e. that

$$\nu_{cr} + 1/m = 1/n\delta \quad (22)$$

and is given by

$$[InH]_{cr} = \frac{k_2[RH]n\delta}{k_i(m - n\delta)}. \quad (23)$$

According to Eqns. (22) and (23), at values of $n\delta \geqslant m$, oxidation should develop with autocatalysis at any inhibitor concentration — even with very short chains — owing to the hydroperoxide formed in the chain-terminating reaction (*i*). When, however, $\nu \leqslant 1$, reaction of $RO_2^{\cdot}$ radicals with the inhibitor should be accompanied by that of the primary radicals RO and OH (= R′) formed by dissociation of the hydroperoxide. In this case the mechanism of the process should be supplemented by the reactions

$$(i')\ R' + InH \xrightarrow{k_i'} R'H + In^{\cdot},$$

$$(7')\ R' + In \xrightarrow{k_7'} \text{products}.$$

These reactions should yield an alcohol or water, products which do not result in autocatalysis of the process. The occurrence of reactions between the R′ radicals and the inhibitor under oxidation conditions has been demonstrated experimentally [28].

If these reactions take place, and provided that $k_i/k_i' = k_2/k_2' = k_7/k_7'$, the concentrations of the radicals can be written

$$[R'] = \frac{nk_3[ROOH]}{k_2'[RH] + mk_i'[InH]}, \quad [RO_2^{\cdot}] = \frac{w_0 + \gamma n k_3[ROOH]}{mk_i[InH]},$$

where

$$\gamma = \frac{k_2'[RH]}{k_2'[RH] + mk_i'[InH]} = \frac{\nu}{\nu + 1},$$

is the probability of the formation of peroxy-radicals $RO_2^{\cdot}$ from the primary radicals R′, i.e. the probability of propagation of the chain by R′ radicals. In this case we have for m

$$m = 1 + \frac{\alpha(1+a)}{1+a\alpha}, \text{ where } a = \frac{k_i'[R']}{k_i[RO_2^{\cdot}]}.$$

Just as in the preceding case $m = 1$ when $\alpha = 0$, and $m = 2$ when $\alpha = 1$.

The autocatalytic factor of the process in Eqns. (19) and (20) becomes $\varphi = k_3 n\gamma(\nu + 1/m) - k$, while the limiting condition is given by

$$(\nu_{cr} + 1/m)\gamma_{cr} = \frac{(\nu_{cr} + 1/m)\nu_{cr}}{(\nu_{cr} + 1)} = \frac{1}{n\delta}, \quad (22')$$

from which it follows that in general, with various chain lengths taken into account, the critical inhibitor concentration is given by the formula

$$[InH]_{cr} = \frac{k_2[RH]n\delta\gamma_{cr}}{k_i(m - \gamma_{cr}n\delta)}. \quad (23')$$

It is seen from Eqn. (22′) that the critical concentration should be finite for any relationship between the parameters $2 \geqslant m \geqslant 1$ and $n\delta \leqslant 2$. We have

$$\nu_{cr} = \frac{1}{2}\left(\frac{1}{n\delta} - \frac{1}{m}\right) + \sqrt{\frac{1}{4}\left(\frac{1}{n\delta} - \frac{1}{m}\right)^2 + \frac{1}{n\delta}},$$

when $n\delta \ll m$, the chain length $\nu_{cr} \gg 1$, $\gamma_{cr} \simeq 1$, and the critical inhibitor concentration is

$$[InH]_{cr} = \frac{k_2[RH]n\delta}{k_i m}.$$

When $n\delta = m$ the critical inhibitor concentration is

$$[InH]_{cr} = \frac{k_2[RH]}{k_i\sqrt{m}}.$$

3. Effect of Inhibitor Consumption on Abruptness of Change in Induction Period on Passing through the Critical Inhibitor Concentration

Eqns. (19) and (20) for the variation in concentration of radicals and hydroperoxide have been obtained on the assumption that the chain length ν and the autocatalytic factor φ remain unchanged during the reaction. This might have been the case if the inhibitor concentration had been maintained constant. However, the chief feature of inhibited oxidation is the consumption of inhibitor, which occurs at the rate

$$-d[InH]/dt = k_i[RO_2][InH] = \frac{w_0 + nk_3[ROOH]}{m}. \qquad (24)$$

If inhibitor is consumed, the effective rate constant of chain termination $g_{1in} = mk_i[InH]$ continuously diminishes, while the chain length and the autocatalytic factor increase, during the reaction.

An analysis has been made[87] of the effect of inhibitor consumption on the sharpness of the transition through $[InH]_{cr}$. The set of equations (15), (18), (21), and (24) for the concentration variation of radicals, intermediate product, inhibitor, and hydrocarbon was solved by numerical integration on an electronic computer. The values chosen for the elementary rate constants were $k_2 = 2.0$ litres × × mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres mole^{-1} s^{-1}, $k_5 = 2 \times$ $\times 10^7$ litres mole^{-1} s^{-1}, $w_0 = 10^{-10}$ M s^{-1}, $[RH] = 5.0$ M, $k_3 = 10^{-2}$–10^{-5} s^{-1}, $m = 1$, $n = 1$, and $k = k_3$. The formation of hydroperoxide by chain termination on the inhibitor was ignored in Eqn. (15).

The data given above showed that the values chosen for the rate constants simulate very closely actual processes of the autoxidation (with $k_3 = 10^{-4}$–10^{-5} s^{-1}) and the catalysed oxidation (with $k_3 = 10^{-2}$–10^{-3} s^{-1}) of hydrocarbons.

Figs. 5 and 6 illustrate kinetic curves for inhibitor consumption at k_3/w_0 ratios of 10^8 and 10^5 litres mole^{-1} (Figs. 5*a* and 6*a*) and the variation in the autocatalytic factor (Figs. 5*b* and 6*b*) during the process. Fig. 4 (curves *1′*–*3′*) gives the dependence of the induction period on the initial inhibitor concentration in this process. The end of the induction period is taken to be the time at which 0.01 mole % of the hydrocarbon has disappeared, when the inhibitor has already been completely exhausted. Figs. 5*b* and 6*b* show that the autocatalytic factor increases steadily during the process from negative values at $[InH] > [InH]_{cr}$ to positive values at $[InH] < [InH]_{cr}$.

At the ratio $k_3/w_0 = 10^8$ the inhibitor is consumed autocatalytically during the induction period (Fig. 5*a*) when

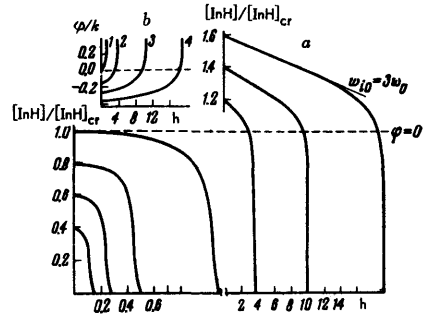


Fig. 5. *a*) Calculated kinetic curves for the consumption of inhibitor in the oxidation of a hydrocarbon with a ratio of the rate constant k_3 for dissociation of the hydroperoxide into radicals to the rate of generation of chains w_0 of $k_3/w_0 = 10^8$ litres mole^{-1}; *b*) variation in autocatalytic factor during reaction resulting from consumption of the inhibitor.

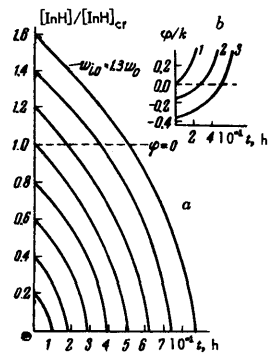


Fig. 6. *a*) Calculated kinetic curves for the consumption of inhibitor during the induction period in the oxidation of a hydrocarbon with a ratio of $k_3/w_0 = 10^5$ litres × × mole^{-1}; *b*) variation in autocatalytic factor during induction period resulting from consumption of inhibitor.

$[InH] < [InH]_{cr}$, but when $[InH] > [InH]_{cr}$ linear sections are present in which the inhibitor is consumed at a rate close to w_0. In this case the dependence of the induction period on the initial inhibitor concentration exhibits quite clear limiting phenomena (Fig. 4, curve *1′*). Autocatalytic consumption of the inhibitors 1- and 2-naphthols, 1- and 2-naphthylamines, and diphenylamine has been observed during the induction period in the oxidation of tetrahydronaphthalene (at 140°C),[27] cyclohexanone (at 120°C),[88] and hexadecane[89]. If the rate constant for dissociation of the intermediate product into radicals is small ($k_3 = 10^{-5}$ s^{-1}), the rate of initiation of chains due to degenerate branching may be close to the rate of generation of radicals. Fig. 6*a* shows that in this case the rate of consumption of inhibitor only slightly increases with time in comparison with the rate of generation of chains, and the induction period is proportional to the initial inhibitor concentration (Fig. 4, curve *3′*). A very frequent case is consumption of inhibitor at a constant rate, when the induction period is a

linear function of the inhibitor concentration. It follows from Figs. 6*a* and 4 that these regularities may be present at ratios of $k_3/w_0 \leq 10^5$ litres mole^{-1}. A constant rate of inhibitor consumption and a linear dependence of induction period on inhibitor concentration have been observed with the inhibitors *N*-phenyl-2-naphthylamine, 1-naphthol, and various alkylphenols in the oxidation of rubber[90], n-decane[87], ethyl methyl ketone, ethanol[91], and petrol[92].

Comparison of curves *1* and *1'*, *2* and *2'*, and *3* and *3'* in Fig. 4 shows that consumption of inhibitor diminishes the sharpness of the increase in induction period at the critical inhibitor concentration. It is seen from curves *1'* and *2'* that it is extremely difficult to determine $[InH]_{cr}$ when the transition through $\varphi = 0$ is unclear; extrapolation of the linear sections of the t_{ind}–$[InH]_0$ relationships yields values of $[InH]_{cr}$ which are too high.

However, the transition through $\varphi = 0$ should be sharp if $k_3/w_0 > 10^8$, and the experimental value of $[InH]_{cr}$ is close to the true value. The slope of the linear portions of curves *1'*–*3'* (Fig. 4) when $[InH] > [InH]_{cr}$ is close to the rate of generation of chains.

4. Results of Experimental Study of Critical Inhibitor Concentrations

Critical phenomena have been observed in the oxidation of n-decane in the presence of copper stearate as catalyst[93]. In this reaction the copper ions have a dual function, in that they catalyse the oxidation and act as inhibitor. The catalytic effect of copper stearate is already apparent at the very low concentrations of 10^{-5} mole % and right up to 0.060 mole %. At these concentrations the copper salt accelerates the formation of oxidation products — alcohols, ketones, and acids — in comparison with the uncatalysed reaction. At the same time the hydroperoxide concentration is diminished as compared with the uncatalysed reaction, more strongly the higher the copper stearate concentration. This fact indicates that the initiating effect of the copper salt is associated with an acceleration of the dissociation of hydroperoxide into radicals, as occurs with other metals of variable valency: $ROOH + Cu^{2+} \rightarrow RO_2$. Acceleration of the oxidation process, however, begins after a certain induction period has elapsed.

The plot of the variation in induction period with $CuSt_2$ concentration (Fig. 7) shows that the induction period gradually increases from 2 to 30 min up to $[CuSt_2] =$ = 0.06 mole %. Further slight increase in the copper stearate concentration by 0.005 mole % produces a sharp increase in the induction period of more than 15 h. Thus abrupt cessation of the reaction is observed at the critical copper stearate concentration of 0.065 mole %. This phenomenon may be associated with a transition at this concentration from autocatalytic ($\varphi > 0$) to steady-state ($\varphi < 0$) oxidation. The critical phenomenon in the presence of the copper salt is associated with the inhibiting action of copper ions.

The presence of a second, initiating action may explain the abrupt character of the transition to a steady state. The great rate of the catalysed dissociation of hydroperoxide into radicals ensures a rapid development of the reaction when $\varphi > 0$, and therefore the transition through the critical concentration $[CuSt_2]_{cr}$ occurs very sharply.

Critical phenomena are observed also in the oxidation of hydrocarbons in the presence of such typical inhibitors as phenols, naphthols, and amines. Figs. 8 and 9 show the dependence on inhibitor concentration of the induction period in the oxidation of ethylbenzene and n-decane in glacial acetic acid with cobalt acetate $CoAc_2$ as catalyst[40,87,94]. It is evident from these diagrams that a critical inhibitor concentration exists above which oxidation is sharply retarded, whereas induction periods are short at concentrations below $[InH]_{cr}$.

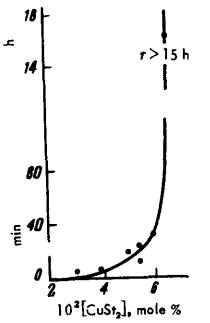


Fig. 7. Dependence of induction period in oxidation of n-decane on concentration of copper stearate at 140°C.

It has been shown[94] that the critical concentration of 1-naphthol varies little with temperature $E_{obs} = Ei - E_2 \simeq$ $\simeq$ 1 kcal mole^{-1}, is independent of the catalyst concentration (at $[CoAc_2] = 0.0056$–0.0565 M), and increases in proportion to the hydrocarbon concentration. These experimental results indicate that the effective activation energy and the dependence of the critical inhibitor concentration on the hydrocarbon concentration are consistent with Eqn. (23).

Table 3 lists experimental critical inhibitor concentrations together with values calculated from Eqn. (23) with

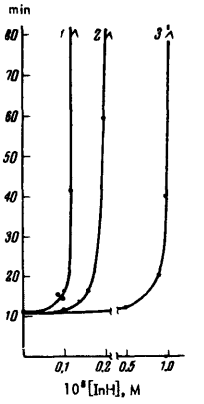


Fig. 8. Increase in induction period, in the oxidation of 2.6 M n-decane with 0.034 M cobalt acetate as catalyst in glacial acetic acid medium at 90°C, with increase in initial concentration of the inhibitors:
1) 1-naphthol; 2) tris-4-hydroxy-3,5--di-t-butylbenzylamine; 3) Ionol.

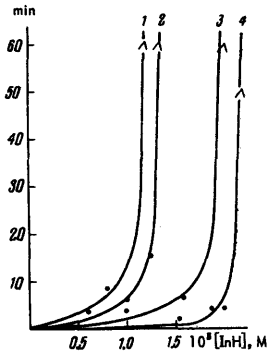


Fig. 9. Dependence of induction period, in the oxidation of ethylbenzene catalysed by 0.0113 M cobalt acetate at 60°C, on concentration of the inhibitors:
1) diphenylamine; 2) *N*-phenyl-2-naphthylamine; 3) 1-naphthol; 4) 2-naphthol.

TABLE 3. Comparison of experimental and calculated critical inhibitor concentrations in the catalysed oxidation of hydrocarbons.

Hydrocarbon	Inhibitor	$10^3[InH]_{cr}$, M		$\frac{[InH]_{calc}}{[InH]_{exp}}$
		expt.	calc.	
Ethylene-benzene*	Ionol	27.5	97	3.5
	1-naphthol	1.64	7.4	4.5
	N-phenyl-2-naphthylamine	1.3	10.5	8.1
	diphenylamine	1.0	8.9	8.9
	2-naphthol	1.8	34	19
n-Decane**	1-naphthol	0.2	0.56	3
	tris-4-hydroxy-3,5-di-t-butylbenzylamine	0.12	1.34	11
	Ionol	1.0	15	15

* From Ref. 94: [RH] = 3.24 M, $[CoAc_2]$ = 0.0113 M, [RH] : $[CH_3COOH]$ = 2 : 3, at 60°.

** From Ref. 40: [RH] = 2.6 M, $[CoAc_2]$ = 0.034 M, [RH] : $[CH_3COOH]$ = 1 : 1, at 90°C.

$n = 1$, $\delta = 1$, $m = 2$, and $\gamma = 1$. The ratio k_i/k_2 was determined by special methods in each case. The last column shows that the experimental values are lower than the calculated values. The discrepancy indicates that, at some stage in the oxidation or the breakdown of the hydroperoxide, new reactions, hitherto disregarded, appear in the system comprising the metal of variable valency and the inhibitor. Two hypotheses can be put forward to explain the increased effectiveness of antioxidants in the presence of cobalt ions.

In the calculation of the critical inhibitor concentration it was assumed that $\delta = 1$. However, the probability of degenerate branching may be less than unity, if the complex $[ROOH.CoAc_2]$ can react directly with the inhibitor to form valency-saturated compounds:

$$[ROOH \cdot Co(Ac)_2] + InH \rightarrow ROIn + Co(Ac)_2 + H_2O.$$

The second hypothesis is that the inhibitor may interact with the metal ion of higher valency to form an In radical:

$$(11)\ Co^{3+}(Ac)_2(OH) + InH \rightarrow Co^{2+}(Ac)_2 + H_2O + In^{\cdot}.$$

The occurrence of this reaction in the mechanism of inhibited oxidation in the presence of metals of variable valency is highly probable. Phenoxy, naphthyloxy, and other radicals are formed in the reactions of phenols and naphthols with hydroperoxides in the presence of cobalt salts and of such compounds as PbO_2, $(CH_3COO)_4Pb$, and $K_3[Fe(CN)_6]$, which contain the metal in the higher valency state [58,73,95-97]. If the In· radicals react with the $RO_2^{\cdot}$ radicals, the occurrence of reaction (11) will increase the rate of chain termination.

It has been shown[40] that, when reaction (11) is taken into account, the critical inhibitor concentration is (with $\gamma = 1$)

$$[InH]_{cr} = \frac{k_2[RH]n\delta}{k_i}\sigma.$$

The parameter σ is defined by the formula

$$\frac{\sigma}{1-\sigma} = \frac{k_d[Co^{3+}][ROOH]}{k_{11}[Co^{3+}][InH]},$$

where k_d is the rate constant for the reaction of Co^{3+} with ROOH (see p. 267). If Co^{3+} reacts more rapidly with the hydroperoxide than with the inhibitor, $\sigma \rightarrow 1$. When $\sigma = 1$, the formula (23) is obtained for the critical inhibitor concentration. If, however, Co^{3+} reacts predominantly with the inhibitor, $\sigma < 1$, and the critical inhibitor concentration decreases.

Thus the formation of phenoxy-radicals in the reaction of Co^{3+} with an inhibitor should result in a lower critical inhibitor concentration, as is observed experimentally. The very abrupt cessation of oxidation at this critical concentration found in these experiments completely confirms the kinetic analysis of the transition through limiting conditions with degenerate chain branching. The rate constant for dissociation of the hydroperoxides of n-decane and ethylbenzene in the presence of cobalt acetate under these experimental conditions is of the order of $k_3 \simeq 10^{-2}\ s^{-1}$, while the rate of generation of chains is $w_0 \simeq 10^{-10}-10^{-11}\ M\,s^{-1}$. Thus the ratio $k_3/w_0 \geq 10^8-10^9$ litres $mole^{-1}$, which corresponds to the relationships *1* and *1'* in Fig. 4.

In all cases considered above, limiting phenomena were associated with change in the autocatalytic factor from positive to negative values in the initial stages of the reaction: i.e. the induction period depended on an external parameter, the inhibitor concentration. Cessation of an autocatalytic reaction which has already begun has been observed[98] when limiting conditions are reached during the process. The oxidation of n-decane was studied in the presence of potassium permanganate, which, just like copper stearate[93], has a dual role in the oxidation. Addition of 0.076–0.576 mole % of potassium permanganate halves the induction period in the oxidation of n-decane compared with autoxidation at the same temperature (140° C). The maximum concentration of peroxides in the presence of the permanganate is one-third of that in the uncatalysed reaction, owing to participation of the catalyst in its radical dissociation.

Potassium permanganate was found to have an inhibiting as well as an initiating and controlling function. Fig. 10 shows kinetic curves for the accumulation of acids at various permanganate concentrations. It is seen that a reaction which has developed is abruptly stopped at different degrees of conversion depending on the permanganate concentration. The limiting yield of acids decreases with increase in this concentration.

Separate experiments in which potassium permanganate was withdrawn showed that the cessation of the reaction is due to chain termination involving a manganese salt. It

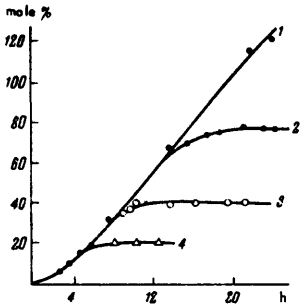


Fig. 10. Kinetic curves for the accumulation of acids in the presence of potassium permanganate (mole %):
1) 0.768; 2) 0.192; 3) 0.384; 4) 0.576.

follows from Eqn. (23) that the limiting condition can be reached if the hydrocarbon is exhausted to a definite concentration $[RH]_{cr}$. Fig. 11 shows that the hydrocarbon concentration at which reaction ceases is a linear function of the potassium permanganate concentration. This supports the conclusion that the cessation of oxidation in the presence of potassium permanganate is associated with the achievement of a limiting condition.

A critical solvent (benzene) concentration has been observed[99] in the oxidation of liquefied butane dissolved in it at temperatures and pressures close to the critical values (170°C and 50 atm). A certain relationship was observed to exist between the concentrations of butane and benzene

$$\gamma_{cr} = \frac{[RH]}{[C_6H_6] + [RH]},$$

below which butane is not oxidised at all, and above which the usual autocatalytic reaction develops.

Fig. 12*a* shows that the yield of acetic acid falls as the proportion of benzene in the initial mixture is increased, until a value corresponding to $\gamma = 0.28$ is reached, at which reaction ceases completely. This phenomenon can be seen in Fig. 12*b*, which illustrates the dependence on γ of the quantity of acetic acid formed during 2 h of the reaction. When mixtures having $\gamma > 0.28$ are taken for an experiment, reaction continues until the value $\gamma_{cr} = 0.28$ is reached (Fig. 12*c*).

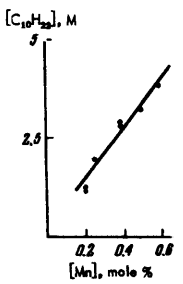


Fig. 11. Dependence of limiting hydrocarbon concentration on initial concentration of potassium permanganate.

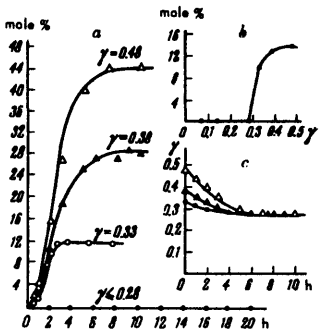


Fig. 12. *a*) Kinetic curves for the accumulation of acetic acid in the oxidation of liquefied butane in benzene at 170°C and 50 atm with various initial ratios γ of butane to benzene; *b*) dependence on γ of quantity of acetic acid formed in 2 h of reaction at 170°C and 50 atm; *c*) variation in γ during reaction.

It is assumed that in this reaction $RO_2^{\cdot}$ radicals add on to the benzene molecule, with the formation of relatively inactive radicals, which are incapable of chain propagation.

V. PHENOMENON OF A CRITICAL INHIBITOR CONCENTRATION IN THE CONTINUOUS OXIDATION OF HYDROCARBONS IN REACTION VESSELS WITH IDEAL MIXING (OPEN SYSTEMS)

All the experimental results discussed above on critical phenomena in the inhibited oxidation of hydrocarbons, and the kinetic analysis of this phenomenon, have related to batch processes occurring in a closed system. In such processes the starting materials are introduced into the reaction vessel in a single step at the start of the reaction, and remain together with the reaction products inside the reaction vessel until the end of the process. However, experimental results[14,100,101] show that the existence of limiting conditions in the inhibited oxidation of hydrocarbons is exhibited most clearly when the process is conducted continuously in reaction vessels with ideal mixing. In this method of conducting a process the starting materials enter continuously, at a rate u (in ml h^{-1}), a reaction vessel of volume V (ml), while a proportion of the reaction products are removed from the vessel at the same rate. Vigorous stirring should ensure a uniform concentration of the reaction components throughout the vessel. Such unclosed systems, which represent a flow system with perfect mixing, have been termed open systems, since every volume element is "open" for the entry of new substances[102].

The variation in concentration of the reactants in a continuous process can in general be represented by the equation

$$\frac{d[A_i]}{dt} = w_f - w_r + v[A_i]_0 - v[A_i].$$

where w_f and w_r are the rates of formation and removal of a component A_i by chemical reactions. The product $v[A_i]_0$ represents the rate of increase in concentration of this component resulting from its entry into the reaction vessel as a solution of concentration $[A_i]_0$; and the term

$-v[A_i]$ allows for the decrease in concentration of the component A_i due to the withdrawl of reaction products. The parameter v is the ratio $v = u/V$. When a process is conducted in this way, the concentration of each component A_i ceases to vary ($d[A_i]/dt = 0$) after a certain time, because the sum of the rates at which the concentration of the substance increases ($w_f + v[A_i]_0$) becomes equal to the sum of the rates at which the concentration decreases ($w_r + v[A_i]$).

In the steady state ($d[A_i]/dt = 0$) the rates w_f and w_r are constant, and the concentrations of the reactants remain unchanged indefinitely. The establishment of a steady-state chemical reaction in an open system is its most important feature [103-107].

In several cases of complex chemical reactions, the possibility has been shown both theoretically and experimentally of harmonic oscillations about the steady state [108-111].

In several cases the study of simple and complicated reactions under steady-state conditions, with the reaction conducted as a continuous process, permits the solution of many problems associated with the mechanism of the reaction. In particular, it is possible in open systems to study unstable intermediate products [103]. A new method has been proposed [112,113] for investigating, in complicated chain oxidations of hydrocarbons, the reactivities of various substances towards $RO_2^{\cdot}$ radicals, and for measuring the rates of formation and of consumption of the reaction products, etc.

The oxidation of a hydrocarbon has been studied [100,101] in the presence of an inhibitor in an open system. Fig. 13 illustrates the accumulation of hydroperoxide in the oxidation of n-decane in the presence of 1-naphthol as inhibitor. A reaction vessel of volume $V = 5$ ml was filled with n-decane containing 1-naphthol in concentrations which varied from experiment to experiment, and from the start of oxidation a similar solution was automatically and continuously fed into the vessel at a rate of $u = 2.6$ ml h^{-1}. Oxygen was bubbled through the oxidising hydrocarbon at 1.6 litres h^{-1}, and at the same time stirred the mixture. Fig. 13 shows that, with a continuous supply of pure n-decane in the absence of inhibitor (curve *1*) the concentration of the reaction product (hydroperoxide) increases to a certain value (0.8 mole %), after which the reaction proceeds at a constant rate.

If n-decane containing 1-naphthol enters the reaction vessel, increase in the inhibitor concentration over the range $(3-9) \times 10^{-6}$ M is accompanied by a lengthening of the induction period, but the previous steady state is established after the end of the induction period.

With further slight increase in the inhibitor concentration from 9×10^{-6} to 9.05×10^{-6} M a sudden change in the rate of the process occurs: the reaction does not emerge from the induction period, and oxidation does not take place. The critical character of the dependence of the induction period of the reaction and the hydroperoxide concentration in the steady state on the initial inhibitor concentration is evident from Fig. 13*b*.

Similar critical phenomena in the oxidation of n-decane in an open system have been observed with tris-4-hydroxy-3,5-di-t-butylbenzylamine as inhibitor (Fig. 14).

The relation between the phenomenon of a critical inhibitor concentration in a continuous process and the mechanism of oxidation has been analysed [94]. The variation in concentration of radicals r (= $RO_2^{\cdot}$), hydroperoxide x (ROOH), inhibitor i (InH), and hydrocarbon [RH] in an open system is described by the equations

$$dr/dt = w_0 + nk_3x - mk_ir - k_5r^2 = 0, \quad (25)$$

$$dx/dt = k_2[RH]r - (k_3 + k_3' + v)x, \quad (26)$$

$$di/dt = -k_ir - vi + vi_0, \quad (27)$$

$$d[RH]/dt = -k_2r[RH] - v[RH] + v[RH]_0. \quad (28)$$

In the experiments illustrated in Figs. 13 and 14, hydrocarbon and inhibitor enter the reaction vessel continuously at rates of $v[RH]_0$ and vi_0 respectively, and hydrocarbon, inhibitor, and hydroperoxide and other reaction products leave the reaction vessel continuously at rates of $-v[RH]$, $-vi$, and $-vx$ respectively, where [RH], i, and x are the concentrations of the corresponding substances in the reaction vessel. The change in concentration of radicals due to withdrawal of oxidation product ($-vr$) is insignificant, and can be neglected. In the equation for dx/dt the formation of hydroperoxide in chain termination on the inhibitor is disregarded, which is valid with sufficiently long chains ($\nu > 1$). With long chains the parameter γ, which determines the participation of RO and OH radicals in chain

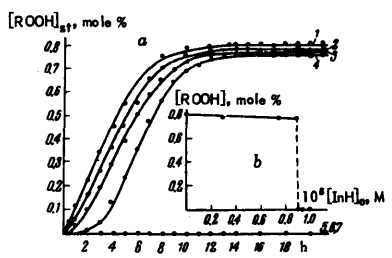


Fig. 13. *a*) Kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of n-decane in the presence of 1-naphthol (M): 1) 0; 2) 3×10^{-6}; 3) 7.5×10^{-6}; 4) 9.00×10^{-6}; 5) 9.05×10^{-6}; 6) 1.2×10^{-5}; 7) 1.4×10^{-5}. *b*) Dependence of steady-state concentration of hydroperoxide on initial concentration of 1-naphthol.

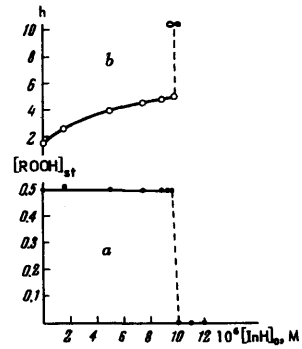


Fig. 14. Dependence, on concentration of tris-4-hydroxy-3,5-di-t-butylbenzylamine with inhibitor solution entering reaction vessel at a rate of $v = 1.83 \times 10^{-4}$ s^{-1} at 130°C, of: *a*) steady-state concentration of n-decane hydroperoxide; *b*) induction period.

propagation, is close to unity, and reactions of these radicals with the inhibitor can be disregarded. It is assumed that the In radicals are involved only in chain termination.

Provided that $k_5 r^2 \ll m k_i r i$, the equations for dr/dt and dx/dt can be combined to give

$$dx/dt = \nu w_0 + \varphi x,$$

where $\nu = k_2[RH]/mk_i i$ is the chain length, $\varphi = k_3(\nu - 1/\delta)$ the autocatalytic factor, and $\delta = k_3/(k_3 + k_3' + v)$ the probability of degenerate chain branching in the continuous process.

A feature of continuous reactions with perfect mixing of the components of the reaction mixture is the establishment of steady-state concentrations of the starting materials $[RH]_{st}$ and i_{st} and of the reaction products x_{st}, when the process occurs at a constant rate, so that $dx/dt = 0$, $di/dt = 0$, and $d[RH]/dt = 0$:

$$\nu w_0 + \varphi x_{st} = 0, \quad (26')$$

$$-k_i i_{st} r_{st} - v i_{st} + v i_0 = 0, \quad (27')$$

$$-k_2 r_{st}[RH]_{st} - v[RH]_{st} + v[RH]_0 = 0.$$

It follows from Eqn. (26′) that, under steady-state conditions of continuous oxidation with chain termination on an inhibitor, the autocatalytic factor should always be negative ($\varphi < 0$), since both νw_0 and x are positive. The inhibitor concentration in the steady-state i_{st} should therefore exceed the value $i_{\varphi=0}$ at which the autocatalytic factor is zero:

$$i_{st} > i_{\varphi=0} = \frac{k_2[RH]n\delta}{mk_i}. \quad (29)$$

Let us denote the steady state established during oxidation in the presence of an inhibitor as state (I). In this state the rate of reaction of the hydrocarbon is very small. It follows from Eqn. (26′) that the hydroperoxide concentration x_{st} at $\varphi < 0$ is given by

$$x_{st} = \frac{\nu w_0}{|\varphi|} = \frac{w_0}{nk_3(i_{st}/i_{\varphi=0} - 1)}.$$

When $i_{st}/i_{\varphi=0} = 1.4$, for example, the concentration of the intermediate product is $x_{st} = 1.1 w_0/k_3$ (with $n = 2$), and right up to the value $w_0/k_3 = 5 \times 10^{-4}$ M it is impossible to detect hydroperoxide in the steady state (I) by the usual iodometric method.

If the concentration of inhibitor falls to $i_{\varphi=0}$ during the oxidation, the autocatalytic factor of the process becomes zero.

Eqn. (26′) shows that, when $\varphi \geqslant 0$, the reaction cannot arrive at the steady state (I). When $\varphi > 0$, the reaction is autocatalytic, the concentration of radicals r increases, and inhibitor is consumed. A new steady state (II) is then established, associated with high rates of autocatalytic oxidation.

The oxidation of a hydrocarbon in the presence of an inhibitor in an open system has been simulated by the numerical integration of Eqns. (25)–(28) on an electronic computer. The parameters and elementary rate constants, obtained experimentally under conditions of the liquid-phase autoxidation of the hydrocarbons, chosen for the simulation were $w_0 = 10^{-10}$ M s^{-1}, [RH] = 5.0 M, $k_2 = 2.0$ litres mole^{-1} s^{-1}, $k_i = 2 \times 10^5$ litres mole^{-1} s^{-1}, $k_5 = 2 \times 10^7$ litres mole^{-1} s^{-1}, $k_3 = 10^{-4}$ s^{-1}, $k_3' = 0$, $v = 1.7 \times 10^4$ s^{-1}, $m = 1$, and $n = 1$.

Fig. 15 gives the calculated kinetic curves for the accumulation of intermediate product, and also the change in its concentration in the steady state and the induction period with different inhibitor concentrations. It is seen from Figs. 13–15 that the calculated relationships completely reproduce the rules observed experimentally.

Fig. 16 shows the variation in the autocatalytic factor of the process at inhibitor concentrations $[i_0]$ of $0.96[i_0]_{cr}$ (curve *2*) and $1.04[i_0]_{cr}$ (curve *1*). At an inhibitor concentration slightly exceeding the critical value, the autocatalytic factor remains negative until the steady state is established. At this innibitor concentration the rate of oxidation of the hydrocarbon is insignificant (Fig. 15*a*). At an inhibitor concentration below the critical value the autocatalytic factor is at first negative, passes through zero, and then assumes positive values. In this case the reaction is autocatalytic (Fig. 15, curve *3*).

Thus the critical phenomena in an open system represent a transition from a steady-state process ($\varphi < 0$) to an autocatalytic process ($\varphi > 0$), as occurs in a closed system.

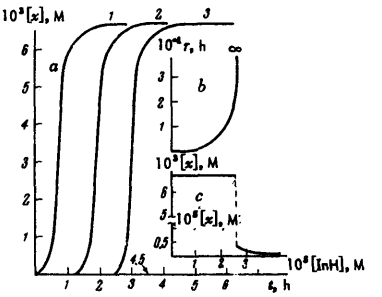


Fig. 15. *a*) Calculated kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of a hydrocarbon in the presence of an inhibitor at an initial concentration $[i_0]/[i_0]_{cr}$ of: 1) 0; 2) 0.8; 3) 0.96; 4) 1.04; 5) 1.2.
b) Variation in induction period in presence of inhibitor with continuous oxidation.
c) Dependence of steady-state concentration of hydroperoxide on concentration of inhibitor.

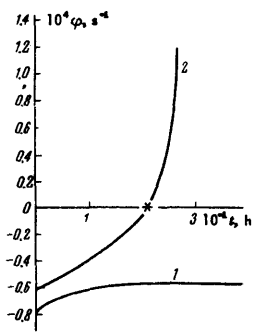


Fig. 16. Variation in autocatalytic factor during continuous oxidation of a hydrocarbon at inhibitor concentrations $[i_0]/[i_0]_{cr}$ of: 1) 1.04; 2) 0.96.

However, limiting conditions of oxidation are very sharply developed in an open system, and well-defined critical phenomena are observed even under conditions under which, in closed systems, the transition through $\varphi = 0$ is not accompanied by an abrupt change in the rate of the process (Fig. 4, curve *3*). The reason for this will become clear from a comparison of Fig. 16 with Figs. 5*b* and 6*b*, which illustrate the variation in the autocatalytic factor in continuous and batch processes.

In a batch process the inhibitor is introduced into the oxidising hydrocarbon in a single step, at the start of the reaction, and is continuously consumed during the reaction. The time of the steady-state development of the reaction (when $\varphi < 0$) in a closed system is limited by the time for the inhibitor to be exhausted to the critical concentration, and at any initial inhibitor concentration exceeding the critical value a transition will occur from the steady-state to the autocatalytic process ($\varphi > 0$) when the inhibitor has been consumed to the critical concentration.

In an open system the reaction cannot emerge from the steady state ($\varphi < 0$) for an infinite time. The advantage of an open system in revealing the limiting conditions of a process was emphasised[114] in connection with an analysis of the conditions of ignition in an exothermic reaction occurring in an adiabatic flow system with perfect mixing: "The boundary between spontaneous ignition and a steady state is absolutely sharp; physically this is connected with the fact that, in a flow system with a continuous supply of material, we can leave the system for an indefinite... time to reveal whether or not a steady state has been reached".

It has been shown theoretically[115] that several steady states may exist in an open system in which a composite process is occurring, consisting of a set of unimolecular and bimolecular reactions among N components. In particular, two stable steady states should occur in oxidation with a continuous supply of inhibitor together with the initial hydrocarbon to the reaction vessel.

The critical inhibitor concentration in an open system can be evaluated from Eqns. (26′) and (27′). These equations can be combined to give

$$x_{st}^2 - x_{st}\left[\frac{(mvi_0 - w_0)}{nk_3} - \frac{vk_2[RH]_{st}}{kk_i}\right] + \frac{vw_0k_2[RH]_{st}}{nk_3kk_i} = 0.$$

When $[i_0] > [i_0]_{cr}$, this equation has two positive roots, the smaller of which corresponds to the steady state (I), while the larger root defines an unstable state. When $[i_0] = [i_0]_{cr}$, the two roots are equal; and when $[i_0] < [i_0]_{cr}$, the equation has no positive root. Thus the value of $[i_0]_{cr}$ is determined from the condition that the above equation should have equal roots:

$$[i_0]_{cr} = (\sqrt{i_{\varphi=0}} + \sqrt{w_0/mv})^2. \qquad (30)$$

From the critical inhibitor concentration $[i_0]_{cr}$ we can determine by means of Eqns. (29) and (30) the relative activities k_i/k_2 of inhibitors towards chain radicals. For the inhibitors 1-naphthol and tris-4-hydroxy-3,5-di-t-butylbenzylamine the values of this ratio determined from experimental data (Figs. 13 and 14) were 3.8×10^5 and 6.5×10^4 respectively, which are very close to the values of 5.8×10^5 and 8.5×10^4 obtained by an independent method from experiments on the initiated oxidation of n-decane and by a chemiluminescent method[70].

Thus the striking property of branched chain processes — the existence of critical (limiting) phenomena — is clearly revealed in a variety of ways even with slow non-stationary processes with degenerate chain branching. Clear critical effects occur in the oxidation of organic compounds, especially in the condensed state (liquid phase). The presence of these effects, which confirms so vividly the branched chain character of the corresponding processes, should undoubtedly be taken into account in developing a general theory of the action of inhibitors (antioxidants), and will play its part in working out optimum conditions for the practical use of inhibitors, e.g. for the suppression of undesirable oxidative changes.

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PRESENT STATE OF THE THEORY OF THERMAL EXPLOSIONS

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I. INTRODUCTION

Studies of scientific and practical problems associated with thermal explosions have attracted considerable interest in recent years. These investigations are highly relevant not only to the development of the physics of combustion and of explosions, which includes the theory of thermal explosions as one of its subdivisions, but also to fundamental branches of knowledge such as chemical kinetics and the theory of heat transfer. The phenomenon of thermal explosion is used in the laboratory as a method of physicochemical research. Thermal explosion is the simplest among the forms of transformation of matter considered in the physics of combustion and of explosion. Therefore the formalism of the theory of thermal explosions finds application in the study of more complicated phenomena, such as the initiation of explosion by external (non-thermal) effects (impact, friction, etc.), multistage combustion, and detonation. The practical interest in thermal explosion processes arises mainly from problems of industrial safety in some types of operation with explosive systems (processing, manufacture of articles, explosive operations in high-temperature boreholes, etc.). In many cases, safe conditions excluding the possibility of spontaneous explosion can in principle be predicted, on the basis of the theory of thermal explosions.

The first quantitative formulation of the theory of thermal explosions was published in 1928 by Semenov [1], who used the simplest ideas on the evolution and extraction of heat to calculate critical conditions leading to thermal explosion, and the heating effect preceding explosion. This paper by Semenov laid the foundations for the development of the theory of thermal explosions, and stimulated numerous investigations in the 1930's, notably those of Todes, Ricę, Frank-Kamenetskii and others [2-10]. A generalised treatment of these researches, which we shall call the classical theory of thermal explosions, was given in a review by Semenov [11] and in monographs by Frank-Kamenetskii [12] and by Semenov [13].

Since gas-phase reactions were studied intensively in the investigation of chemical kinetics in the 1930's, the classical theory of thermal explosion deals mainly with gases. In later years, in connection with the great interest taken in condensed matter, systematic studies of thermal explosions in condensed media were begun. These studies contributed to the development of the general principles of the theory as well as to some specific aspects characteristic of condensed phases.

No reviews dealing with the work done since the formulation of the classical theory of thermal explosions have appeared in the literature. A few papers have been discussed [14] from the standpoint of the thermophysical aspects of the theory of thermal explosions. Thus the present review is of definite interest, since it gives an account of the present state of the theory of thermal explosions and suggests probable lines along which further development can be expected.

II. GENERALISATION AND DEVELOPMENT OF THE CLASSICAL THEORY OF THERMAL EXPLOSIONS

In the classical theory, the problem of thermal explosion is formulated as follows: given a region (or vessel) containing the reactant, knowing the kinetic laws of the evolution of heat and the mechanism of heat transfer within the region, and given the initial and boundary conditions, we are required to determine the basic parameters of the phenomenon (the critical conditions and the induction period). The actual expressions for the evolution and extraction of heat used in the classical theory are based on the simplest model of these phenomena, applicable to gaseous systems.

Generalising and making more concrete some initial premises adopted by Semenov, Frank-Kamenetskii, and