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Abstract

Full Text

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ON THE ROLE OF STABLE INTERMEDIATE PRODUCTS IN COMPLEX CHAIN REACTIONS

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The kinetics of complex chain reactions that proceed with the formation of a series of stable intermediate products (SIP) (for example, peroxides, aldehydes, alcohols, etc., in the oxidation of hydrocarbons) differs from the kinetics of simple chain reactions (the reaction of hydrogen with chlorine, the oxidation of hydrogen and of carbon monoxide at low pressures, etc.) in that, in complex chain reactions, as the SIP accumulate, the mechanism of the process changes. At the beginning of the reaction, when the concentration of SIP is small, the active particles (atoms and radicals) react mainly with the initial substances. As the SIP accumulate, the active particles react simultaneously both with the initial substances and with the SIP, which leads to a change in the mechanism in the course of the process.

The rate of an unbranched chain process is described by the equation

$$w = a_0\nu = a_0\frac{a}{g}, \tag{1}$$

where a_0 is the rate of initiation of active centers; ν is the chain length; a is the rate constant of chain propagation; g is the rate constant of termination.

In the case of quadratic termination of active centers, a_0 and g will enter equation (1) to the power 1/2. This will not introduce any substantial changes into our reasoning; therefore, the ideas developed below concerning the role of SIP are fully applicable also to quadratic termination.

In complex chain reactions, cases are possible in which SIP initiate active centers at a higher rate than do the initial substances. This phenomenon formed the basis of N. N. Semenov' s theory of degenerate branching (1) and was considered by us (2). In this case the reaction rate is described by the equation

$$w = (a_0 + hx)\nu = (a_0 + hx)\frac{a}{g}, \tag{2}$$

where hx is the rate of degenerate branching; x is the concentration of SIP capable of initiating active centers at a higher rate than the initial substances; h is the constant of the elementary process of degenerate branching.

The theory of degenerate branching is at present generally accepted; however, in complex chain reactions, degenerate branching is not the only process by which SIP affect the course of the reaction. In complex chain reactions, a case is possible in which SIP affect not the initiation process a_0, but the chain length ν. Here it is necessary to distinguish two fundamentally different cases: I —an increase and II —a decrease of the chain length ν as SIP accumulate.

I. **Increase in chain length as stable intermediate products accumulate.** Consider the scheme

0. $\mathrm{RH} + \mathrm{O_2} = \dot{\mathrm{R}} + \dot{\mathrm{H}}\mathrm{O_2}$.
1. $\dot{\mathrm{R}} + \mathrm{O_2} = \mathrm{RO\dot{O}}$.
2. $\mathrm{RO\dot{O}} + \mathrm{RH} = \mathrm{ROOH} + \dot{\mathrm{R}}$.
3. $\mathrm{RO\dot{O}} + \mathrm{ROOH} = \mathrm{ROOH} + \dot{\mathrm{R}}'\mathrm{OOH}$.
4. $\dot{\mathrm{R}}'\mathrm{OOH} = \mathrm{A} + \dot{\mathrm{O}}\mathrm{H}$.
5. $\dot{\mathrm{O}}\mathrm{H} + \mathrm{RH} = \mathrm{H_2O} + \dot{\mathrm{R}}$.
6. $\dot{\mathrm{O}}\mathrm{H} + \mathrm{ROOH} = \mathrm{H_2O} + \dot{\mathrm{R}}'\mathrm{OOH}$.
7. $\mathrm{RO\dot{O}} \rightarrow$ termination.

This scheme should not be regarded as chemically proven and verified experimentally. We present it only as an illustration.

As is seen from the scheme, the rate of the hydrocarbon-consumption reaction will be

$$w = a_2[\mathrm{RO\dot{O}}] + a_5[\dot{\mathrm{O}}\mathrm{H}]. \tag{3}$$

Applying the steady-state condition and expressing the concentrations of the radicals $[\mathrm{RO\dot{O}}]$ and $[\dot{\mathrm{O}}\mathrm{H}]$ in terms of the concentrations of the initial substances, for the reaction rate we obtain

$$w = a_0 \frac{a_2 + k_3[\mathrm{X}]}{a_7}, \tag{4}$$

where [X] is the concentration of the stable intermediate products (in the present case, hydroperoxide) reacting with the low-activity radical $\mathrm{RO\dot{O}}$. a_2 and a_7 are, respectively, the constants of chain propagation and termination.

As is seen from equation (4), the chain length increases by the amount $\frac{k_3[\mathrm{X}]}{a_7}$. If process 3 were absent, the chain length would be a_2/a_7.

The rate of accumulation of the stable intermediate product X:

$$\frac{d[\mathrm{X}]}{dt} = a_2[\mathrm{ROO\dot{}}] - k_6[\mathrm{X}][\dot{\mathrm{O}}\mathrm{H}]. \tag{5}$$

Substituting the values of [ROȮ] and [ȮH], expressed through the concentrations of the initial substances, into equation (5) and solving it under the assumption that at the beginning of the process the concentration [X] is equal to zero, we obtain:

$$\xi = \frac{e^{2\varepsilon\tau} - 1}{e^{2\varepsilon\tau} + 1}, \tag{6}$$

where

$$\xi = \frac{[\mathrm{ROOH}]}{\left[\frac{a_2 a_5}{k_3 k_6}\right]^{1/2}} \quad \text{—dimensionless concentration;}$$

$$\varepsilon = \left[\frac{a_5 k_3}{k_6 a_2}\right]^{1/2} \quad \text{—dimensionless parameter;}$$

$$\tau = \frac{a_0 k_3}{a_7} t \quad \text{—dimensionless time.}$$

Substituting the values of [ROȮ], [ȮH], and [X] into equation (3), for the dimensionless reaction rate we obtain:

$$\theta = 1 + \varepsilon \frac{e^{2\varepsilon\tau} - 1}{e^{2\varepsilon\tau} + 1}, \tag{7}$$

where

$$\theta = \frac{w a_7}{a_0 a_2}.$$

As is evident from equation (7), the reaction rate increases with time, tending toward the maximum value

$$\theta = 1 + \varepsilon.$$

The dimensionless parameter ε shows the effectiveness of the increase in the reaction rate (chain length) as a result of the propagation process involving SPI.

Figure 1 shows the dependence of the reaction rate on time for various values of ε. The calculation was made according to equation (7), without taking into account consumption of the initial substance.

As was to be expected, at the initial moment of time the reaction rate is equal to unity, since we began counting time from the moment when stationarity was established, and defined the dimensionless rate as the ratio of the current reaction rate to the stationary one. If $\varepsilon = 0$, then there is no acceleration, and the reaction proceeds at a constant rate equal to unity.

Fig. 1

II. Decrease of the chain length as SPI accumulates. Let us consider the scheme

0. $\mathrm{RH} + \mathrm{O_2} = \dot{\mathrm{R}} + \mathrm{HO_2}$.
1. $\dot{\mathrm{R}} + \mathrm{O_2} = \mathrm{RO\dot{O}}$.
2. $\mathrm{RO\dot{O}} = \mathrm{A} + \mathrm{R'\dot{O}}$.
3. $\mathrm{R'\dot{O}} + \mathrm{RH} = \mathrm{B} + \dot{\mathrm{R}}$.
4. $\mathrm{R'\dot{O}} + \mathrm{A} \to \mathrm{B} + \dot{\mathrm{R}}''$.
5. $\dot{\mathrm{R}}'' + \mathrm{B} \to \mathrm{RO\dot{O}}$.
6. $\mathrm{RO\dot{O}} \to$ death.

This scheme should also be regarded as illustrative.

According to this scheme, as a result of reactions of the stable intermediate products A and B, the active radical $[\mathrm{R'\dot{O}}]$ is converted into the weakly active $\mathrm{RO\dot{O}}$, which leads to a decrease in the chain length.

Applying the steady-state method for active centers to the rate of consumption of hydrocarbons, we obtain:

$$w = a_0 \frac{a_2}{a_6} \frac{a_3}{a_3 + k_4[\mathrm{X}]} \tag{8}$$

[X] is the concentration of intermediate product A.

In the absence of process 4, the chain length would be equal to a_2/a_6. Process 4 decreases the chain length by a factor of

$$\frac{a_3}{a_3 + k_4[\mathrm{X}]}.$$

As is evident, the more SPI A accumulates in the system, the smaller the chain length and, consequently, the lower the reaction rate. The rate of accumulation of A is

$$\frac{d[\mathrm{A}]}{dt} = a_2[\mathrm{ROO\dot{}}] - k_4[\mathrm{A}][\mathrm{R'O\dot{}}]. \tag{9}$$

Expressing the concentrations $[\mathrm{ROO\dot{}}]$ and $[\mathrm{R'O\dot{}}]$ in terms of the concentrations of the initial substances and solving equations (8) and (9) under the assumption that at the beginning of the reac-

···the concentration of the SIP A is equal to zero, we obtain the dependence of the reaction rate on time:

$$\theta = \frac{2}{1 + \sqrt{1 + 4\varepsilon\tau}}, \tag{10}$$

where

$$\theta = \frac{wa_b}{a_0 a_2},$$

θ, ε, and τ have the same meaning as in equation (7).

Figure 2 shows the dependence of the reaction rate on time, calculated from equation (10) for various values of ε. The calculation was carried out without taking burnout into account.

Fig. 2

Thus, as is evident from the schemes I and II considered, in complex chain reactions proceeding with the formation of a number of stable intermediate products, the chain length may change in the course of the reaction, which in turn will lead to a change in the reaction rate. If, as a result of the reaction of an SIP with a radical, a radical is formed that is more active than the initial one, chain lengthening takes place. In the opposite case, as the SIP accumulates, the chain length decreases. It should be noted that the laws of acceleration and retardation may differ depending on the specific mechanism of the complex process.

The twofold action of stable intermediate products on the course of complex chain reactions considered above makes it possible to approach the explanation of certain kinetic features of processes of this kind.

The cessation of hydrocarbon oxidation long before complete consumption of the initial substances, the constant rate of reaction up to very large degrees of conversion (observed for methane, benzene, and others), the discrepancy between the reaction order determined from the course of the process and that

determined from the initial concentration of the starting hydrocarbon, autocatalysis by intermediate and final products, and the catalytic and inhibiting action of the same substances in different reactions may receive a satisfactory explanation within the framework of the ideas set forth.

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