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The Problems of the Selectivity of Chemical Reactions

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The review discusses the problem of the selectivity of chemical processes of different classes. Mathematical expressions are given for the selectivity of reactions of simple types and for radical-chain processes and a relation is demonstrated between the selectivity and the kinetic parameters of the reaction. Factors controlling the selectivity by influencing the mechanism of the process and its kinetics are considered—chemical and physical factors (catalysing, inhibiting, and complex-forming additives, factors associated with control of the reaction by carrying it out at low temperatures, by employing laser radiation and magnetic and electric fields, etc.).
Data on reaction selectivity and ways of improving it are considered in relation to specific examples of oxidation, polymerisation, cracking, and halogenation reactions involving organic substances.
The bibliography includes 102 references.

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I. INTRODUCTION

The problem of the effective utilisation of natural raw materials is of fundamental importance in modern chemistry. The high selectivity and rate of a chemical reaction involving a low expenditure of energy and apparatus of minimum size have become the main criteria of the practical usefulness of a chemical process. The solution of the problem of the optimisation of a process presupposes the knowledge of the kinetic parameters and mechanism of the given chemical reaction, i.e. the chemical kinetics. Thus chemical kinetics have become the scientific basis of chemical engineering.

This review is devoted to the problem of the selectivity of simple and complex (including a large number of elementary stages) chemical reactions and the physicochemical and kinetic factors which determine the selectivity.

II. SELECTIVITY, CONVERSION, AND REACTION YIELD

The concept of the "quantitative yield" of the reaction product, which is frequently employed, corresponds to the idea of a high process selectivity. However, the quantitative definition of the term "selectivity" must be more rigorous, particularly in view of the fact that different definitions are stated in the literature.

The integral selectivity S_P (with respect to the product P) of the reaction

$$\underset{\text{initial compounds}}{\text{A, B, ...}} \longrightarrow \underset{\text{intermediates}}{\pi_1, \pi_2 \ldots\ldots} \quad \underset{\text{final products}}{\text{P, P}_1 \ldots}$$

is defined by the relation

$$S_P(t) = \frac{f\Delta P}{\Delta A} = \varphi_P / C_A = \frac{f\int_0^t w_P \, dt}{\int_0^t |w_A| \, dt}, \qquad (1)$$

where ΔP is the amount (or concentration when the volume is constant) of the product P formed, w_P the rate of its accumulation, ΔA the amount of unreacted initial substance A in relation to which the selectivity is determined, $|w_A|$ the absolute rate of consumption of A, f a normalising factor related to the stoichiometric coefficients of the chemical equation, $\varphi_P = f\Delta P/A_0 = \int_0^{f\Delta P} dP/A_0$ the yield of the product P (A_0 is the initial amount of substance A), and $C_A = \Delta A/A_0$ the degree of conversion of substance A; the form of the function $w(t)$ is determined by the specific reaction mechanism.

Thus the selectivity characterises the fraction of the initial substance converted into the product P. It is a function of time and hence also of the degree of reaction, the rate constants for the elementary processes, and the concentrations of the substances involved in the reaction.

The relation between S and C, i.e. between the selectivity and the degree of conversion, can be formulated thus:

$$S(C) = \frac{f}{C_A}\int_0^{\Delta P} \frac{dP}{A_0} = -\frac{1}{C_A}\int_0^{C_A} \frac{f\,dP}{dA} dC_A = \frac{1}{C_A}\int_0^{C_A} \sigma \, dC_A, \qquad (2)$$

since $dC_A = -dA/A_0$, $C_A = 0$ when $A = A_0$, and the degree of conversion is equal to C_A when $A = A_0 - \Delta A$.

The quantity

$$\sigma = -\frac{f\,dP}{dA} = -\frac{f\,dP/dt}{dA/dt} = -\frac{fw_P}{w_A} \qquad (2a)$$

is called the differential selectivity. In relation to reactions in flow systems, σ may be used as an independent selectivity criterion. For an ideal mixing reactor, Eqn. (2a) reduces to a formula analogous to Eqn. (1). In a flow system under steady-state conditions at constant volume of the reaction mixture, the following relations hold:

$$w_P = v_P [P]_{st},$$
$$w_A = v_0 [A]_0 - v_A [A]_{st},$$

where v_0, v_A, and v_P are the specific rates of supply and removal of A and of removal of the product P respectively. We then have

$$\sigma = \frac{fw_P}{|w_A|} = \frac{fv_P [P]_{st}}{|v_0 [A]_0 - v_A [A]_{st}|}; \qquad (3)$$

where $v_0 = v_A = v_P$, we find

$$\sigma = f [P]_{st}/([A]_0 - [A]_{st}) = f [P]_{st}/(\Delta [A])_{st},$$

i.e. in the steady state the differential selectivity is identical with the integral selectivity.

In closed systems σ does not characterise the selectivity adequately and may actually become negative. In certain cases (heterogeneous catalytic processes) an integral selectivity criterion is used in the form

$$S' = \Delta P_i \Big/ \sum_{j \neq i} \Delta P_j = \int_0^t w_{P_i} dt \Big/ \int_0^t \sum_{j \neq i} w_{P_j} dt, \qquad (1a)$$

where ΔP_i is the amount (concentration) of the product P_i and $\sum_{j \neq i} = \Delta P_j$ is the total amount of all the reaction products with the exception of P_i.

III. SELECTIVITY OF REACTIONS OF SIMPLE TYPES

In chemical kinetics the entire wide variety of chemical reactions reduce to a limited number of kinetic types: reactions of simple orders and simple consecutive, parallel, reversible, autocatalytic, and chain processes. Complex chain reactions are frequently described by simple kinetic laws, so that the problem of selectivity is considered primarily in relation to a set of first-order reactions occurring simultaneously.

1. Reaction of the type

$$A \xrightarrow{k} mP .$$

In this case

$$-d[A]/dt = f\,d[P]/dt,$$

i.e. $|w_A| = fw_P$, where $f = 1/m$, and, according to Eqns. (1) and (2), we have $S(t) = 1$ and $S(C) = 1$.

Thus the selectivity of simple chemical reactions taking place in one stage and leading to the formation of a single desired product only is always equal to unity throughout the chemical reaction (Fig. 1).

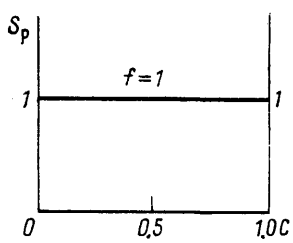


Figure 1. The selectivity in a simple irreversible reaction.

2. The parallel reactions

$$A \begin{cases} \xrightarrow{k_1} m_1 P_1 \\ \xrightarrow{k_2} m_2 P_2 \\ \dashrightarrow \ldots . \\ \xrightarrow{k_k} m_k P_k \end{cases}$$

The rate of consumption of the initial substance A is given by

$$-d[A]/dt = \sum_i k_i [A],$$

and the formula

$$d[P_j]/dt = m_j k_j [A].$$

expresses the rate of accumulation of P_j. Consequently

$$S_{P_j}(t) = S_{P_j}(C) = f_j k_j / \sum_i k_i = \text{const},$$

where $f_j = 1/m_j$. Evidently, the selectivities $S(C)$ and $S(t)$ of parallel first-order reactions are also independent of both the time and the degree of reaction (they remain constant throughout the reaction) and are determined by the stoichiometry of the reaction and the rate constants for the individual stages.

When the order n of even one of the parallel stages (l) is other than unity ($n \neq 1$), we have

$$-d[A]/dt = \sum_{i \neq l} k_i [A] + n k_l [A]^n,$$

$$d[P_j]/dt = m_j k_j [A],\ d[P_l]/dt = m_l k_l [A]^n;$$

$$S_j(t) = \frac{f_j \int_0^t k_j [A]\, dt}{\int_0^t \left(\sum_{i \neq l} k_i [A] + n k_l [A]^n \right) dt} \quad (\text{for } j \neq l),$$

$$S_l(t) = \frac{f_l \int_0^t k_l [A]^n\, dt}{\int_0^t \left(\sum_{i \neq l} k_i [A] + n k_l [A]^n \right) dt},$$

where $f_j = 1/m_j$ and $f_l = n/m_l$.

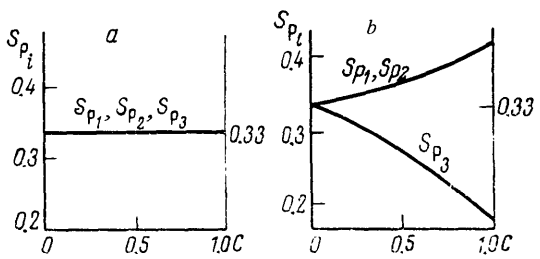


Figure 2. The selectivity in parallel reactions: *a*) three first-order reactions ($k_1 = k_2 = k_3$); *b*) two parallel first-order reactions and one second-order reaction $\{k_1 = k_2 = k_3[A]_0\}$.

Although these equations can in fact be integrated, they lead to complex formulae, so that it is much more convenient to calculate the function $f_j(C)$. The expressions for differential selectivity required in these calculations are formulated as follows:

$$\sigma_{j(j \neq l)} = \frac{f_j k_j}{\sum_{i \neq l} k_i + n k_l [A]^{n-1}} = \frac{f_j k_j}{\sum_{i \neq l} k_i + n k_l [A]_0^{n-1} (1-C)^{n-1}} \quad (4)$$

for all the products formed in first-order reactions and

$$\sigma_l = \frac{f_l k_l}{\sum_{i \neq l} k_i [A]^{1-n} + n k_l} = \frac{f_l k_l}{\sum_{i \neq l} k_i [A]_0^{1-n} (1-C)^{1-n} + n k_l} \quad (5)$$

for the product formed in the nth order reaction.

It is seen from Figs. 4 and 5 that, as the initial substance A is consumed, the differential process selectivity with respect to any product changes monotonically. When $n > 1$, the quantity σ_j ($j \neq 1$) increases monotonically with the degree of reaction and σ_l diminishes monotonically; on the other hand, when $n < 1$, σ_j diminishes and σ_l increases. It follows from Eqn. (2) that, for the monotonic variation of the differential selectivity σ, the integral selectivity S varies in parallel with the latter. Accordingly, when $n > 1$, an increase in the degree of conversion entails an increase of S_j and a decrease of S_l, while under conditions where $n < 1$, the opposite situation obtains, i.e. S_j decreases and S_l increases (Fig. 2). For integral values of n, the expressions for the integral selectivities may also be obtained in terms of quadratures, for example, for $n = 2$ and $m_j = 1$, we have

$$S_j = \frac{k_j}{2k_l [A]_0 C} \ln\left(1 - \frac{k_l [A]_0 C}{\sum_{i \neq l} k_i + 2k_l [A]_0}\right);$$

$$S_l = 2\left\{1 + \frac{\sum_{i \neq l} k_i}{2k_l [A]_0 C} \ln\left(1 - \frac{2k_l [A]_0 C}{\sum_{i \neq l} k_i + 2k_l [A]_0}\right)\right\}.$$

3. A sequence of first-order reactions:

$$A \xrightarrow{k_1} m_1 \pi_1 \xrightarrow{k_2} m_2 \pi_2 \longrightarrow \cdots \longrightarrow \pi_{k-1} \xrightarrow{k_k} m_k P.$$

The system of differential equations for this process is of the form

$$\left.\begin{aligned} &-d[A]/dt = k_1 [A], \\ &d[\pi_1]/dt = m_1 k_1 [A] - k_2 [\pi_1], \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ &d[\pi_{k-1}]/dt = m_{k-1} k_{k-1} [\pi_{k-2}] - k_k [\pi_{k-1}], \\ &d[P]/dt = m_k k_k [\pi_{k-1}]. \end{aligned}\right\} \quad (6a)$$

Accordingly the differential selectivities are given by

$$\left.\begin{aligned} &-\sigma_{P_1} = \frac{f_1 d[\pi_1]}{d[A]} = -1 + \frac{k_2}{m_1 k_1} \cdot \frac{[\pi_1]}{[A]}, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &-\sigma_{P_{k-1}} = \frac{f_k d[\pi_{k-1}]}{d[A]} = \frac{f_{k-1} m_{k-1} (k_{k-1} [\pi_{k-2}] - k_k [\pi_{k-1}])}{k_1 [A]}, \\ &-\sigma_{P_k} = \frac{f_k d[P]}{d[A]} = \frac{f_k m_k k_k [\pi_{k-1}]}{k_1 [A]}, \end{aligned}\right\} \quad (6)$$

where $f_k = 1/\prod_{i=1}^{k} m_i$.

By integrating Eqns. (6), it is possible to obtain an expression for the integral selectivity $S(C)$ corresponding to any product. The selectivity with respect to π_1

$$S_{\pi_1}(C) = m_1 \frac{(1-C)^{k_2/k_1} - (1-C)}{(1 - k_2/k_1) C} \quad (7)$$

decreases from 1 to 0 with increase of the degree of conversion (Fig. 3). For $k_2/k_1 < 2$, $S_{\pi_1}(C)$ changes relatively little up to high degrees of conversion [the plot of the function $S_{\pi_1}(C)$ has a convex region]. For $k_2/k_1 > 2$, $S_{\pi_1}(C)$ varies sharply under the conditions of low values of C [the function $S_{\pi_1}(C)$ is concave].

For selectivity with respect to π_2, we have

$$S_{\pi_2}(C) = \frac{m_1 m_2 k_1 k_2}{(k_2 - k_3)} \cdot \frac{1}{C}\left\{\frac{(1-C)^{k_2/k_1}}{k_2 - k_1} - \frac{(1-C)^{k_3/k_1}}{k_3 - k_1} + \frac{(1-C)(k_2 - k_3)}{(k_3 - k_1)(k_3 - k_2)}\right\}.$$

When $t \to 0$ and $t \to \infty$, the function $S_{\pi_2}(C) \to 0$, so that the maximum selectivity with respect to π_2 is attained for an optimum degree of conversion of the initial substance (Fig. 3).

For all subsequent intermediates, S also passes through a maximum, but the formulae for selectivity become more cumbersome. Naturally the process selectivity with respect to any product is higher the lower the rate of its consumption. This is clearly seen from Eqns. (6): the lower the constant k_K the higher the value of $\sigma_{\pi_{k-1}}$ and hence also of $S_{\pi_{k-1}}(C)$.

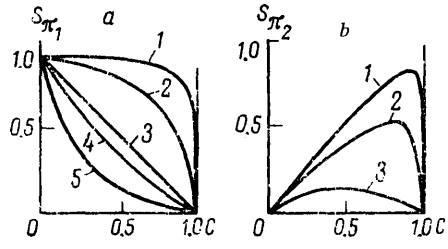


Figure 3. The selectivity in the formation of products in a first-order consecutive reaction A → π_1 → π_2 → P: *a*) for the first intermediate and different rate constant ratios k_2/k_1 [1) 0.1; 2) 0.5; 3) 2; 4) 3; 5) 10]; *b*) for the second intermediate, $k_2/k_1 = 2$ and different k_3/k_1 ratios [1) 0.1; 2) 0.5; 3) 10].

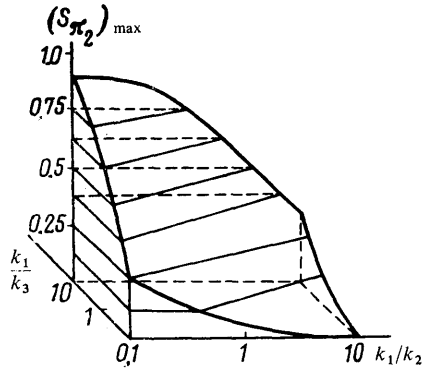


Figure 4. Selectivity with respect to the second intermediate in consecutive first-order reactions as a function of the ratio of the rate constants for individual stages.

A high selectivity with respect to an intermediate may be obtained if the rate constant for its consumption is significantly lower than the rate constant for its formation. Fig. 4 shows how the maximum process selectivity with respect to the second intermediate $(S_{\pi_2})_{max}$ varies for different ratios of the rate constants k_1, k_2, and k_3. Evidently, the highest selectivities are attained when $k_1 \gg k_3 \ll k_2$. The selectivity with respect to the final product

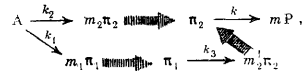
$$S_P(C) = 1 - \sum_{i=1}^{k-1} S_{\pi_i}$$

decreases monotonically with increase of C.

In order to achieve the transformation into the function $S(t)$, it is sufficient to use the time variation of the degree of conversion, i.e. the equation of the kinetic curve. In the case where the consumption of the initial substance follows first-order kinetics, the relation between C and t is

$$C = (1 - e^{-k_1 t}).$$

4. Consecutive-parallel reactions. The selectivity in the formation of any products of a complex consecutive-parallel reaction is determined by the stability of the reaction products and the probability that the reaction proceeds via different parallel pathways. For example, in the complex consecutive-parallel reaction



the differential process selectivity σ_1 with respect to the first product π_1 is determined by the factor associated with the parallel mechanism of the conversion of A into this product, namely $\alpha_{(A \to \pi_1)} = k_1/(k_1 + k_2)$, and the factor associated with the instability of the product π_1, namely $\beta_1 = k_3[\pi_1]/k_1[A]$, and can be formulated as follows:

$$\sigma_1 = \alpha(1 - \beta_1) = \alpha\gamma_1. \qquad (8a)$$

The quantity $\gamma_1 = 1 - \beta_1$ characterises the accumulation of π_1 and may be called the accumulation factor.

The second product is formed via two pathways: directly from A and from the first intermediate π_1. The selectivity in the formation of π_2 is therefore determined by the sum of the selectivities in its formation via the two pathways. The selectivity in the formation of π_2 directly from A is determined from a formula analogous to Eqn.(8a):

$$\sigma_2(A \to \pi_2) = (1 - \alpha)\gamma_2 = (1 - \alpha)(1 - \beta_2),$$

where

$$\beta_2 = k[\pi_2]/(k_2[A] + k_3[\pi_1]),$$

The selectivity in the formation of π_2 via the second pathway, i.e. from π_1, is determined by the product of the factor associated with the parallel mechanism of the formation of π_1 from A (α), the π_1 instability factor (β_1), and the π_2 accumulation factor (γ_2):

$$\sigma_2(\pi_1 \to \pi_2) = \alpha\beta_1(1 - \beta_2) = \alpha\beta_1\gamma_2;$$

i.e.

$$\sigma_2 = \gamma_2(1 - \alpha + \alpha\beta_1). \qquad (8b)$$

If the selectivity with respect to π_2 is proportional to the π_2 accumulation factor, then the selectivity with respect to the product P is proportional to the π_2 instability factor and is given by

$$\sigma = \beta_2(1 - \alpha + \alpha\beta_1). \qquad (8c)$$

Eqns.(8a), (8b), and (8c) form a system of differential equations, the substitution of the solution of which in Eqn. (2) yields expressions for the integral selectivities with respect to all products.

The integral selectivity with respect to π_1 is described by a formula analogous to Eqn.(7):

$$S_{\pi_1}(C) = \alpha \frac{(1 - C)^{k_3/(k_1 - k_2)} - (1 - C)}{(1 - k_3/(k_1 + k_2))C} \qquad (9)$$

and decreases from 1 to 0 with decrease in the degree of conversion, as for the product π_1 of the consecutive reaction (Fig. 5). The selectivity with respect to the product π_2 varies in accordance with the equation

$$S_{\pi_2}(C) = m_2 \frac{k_1}{C}\left\{\frac{[k_2/k_1 + k_3/(k_3-k_2-k_1)](1-C)}{k_1+k_2-k} + \right.$$
$$\left. + \frac{k_3}{(k_3-k_2-k_1)(k_3-k)}(1-C)^{k_3/(k_1+k_3)} + \frac{[k_2/k_1 + k_3/(k_3-k)]}{k-k_2-k_1}(1-C)^{k/(k_1+k_3)}\right\}.$$

$S_{\pi_2}(C)$ may pass through a maximum for $k_2/k_1 < k_3/k$ (Fig. 5). Under these conditions, the product π_2 is formed predominantly owing to the conversion of π_1, i.e. is in essence the second intermediate in the sequence of transformations.

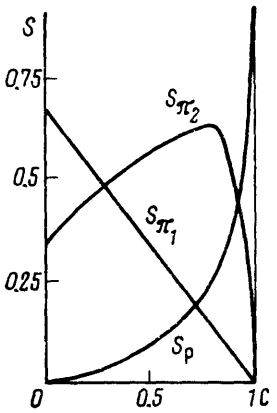


Figure 5. Selectivity in consecutive-parallel reactions. Calculation carried out for $k_1 = 2k_2$, $k = 1.5k_2$, and $k_3 = 6k_2$.

The selectivity with respect to the final product P_1 in this mechanism, as in any other sequence of reactions, increases with increased degree of conversion. Here the time variation of the degree of conversion

$$C = (1 - e^{-(k_1+k_3)t})$$

makes it possible to transform the $S(C)$ relation into the expression for the time dependence of the selectivity in the formation of the products $S(t)$.

Expressions for the selectivities in the formation of products in a chemical process of any complexity may be obtained similarly.

IV. KINETIC ANALYSIS OF THE GENERAL SCHEME FOR A RADICAL-CHAIN REACTION AND SELECTIVITY

The kinetic mechanism of a chain process includes elementary steps of three types: (1) the formation of active centres propagating the chain; (2) chain propagation (steps involving the chain transformation of the substance, chain interconversion of the active chain-propagating centes), and (3) chain termination (destruction of active centres) [1-3]. If the chains are fairly long, then chain termination has almost no influence on the composition of the reaction products. The products formed during the process may interact with any active centres in the system, giving rise to secondary active species, whose reactivity as a rule differs from that of the primary species. Thus chain interaction assumes a significant importance.

The general mechanism of the radical-chain process can be represented in the following form when account is taken of the chain interaction mechanism (A) (see also Fig. 6).

Sources of free radicals:

$$\underset{\text{initial substances (initiation)}}{A, B, \ldots} ; \quad \underset{\text{intermediates (degenerate branching)}}{\pi_j} \rightsquigarrow \underset{\text{primary radicals}}{r_0^{\cdot}, r_j^{\cdot}} \rightsquigarrow \underset{\text{radical chain carriers}}{R_k^{\cdot}},$$

Chain formation:

$$A(B) \xrightarrow{k_0} r_i^{\cdot} \quad \text{(chain initiation)},$$
$$\pi_k \xrightarrow{k_{3k}} f r_k^{\cdot} \quad \text{(chain branching by the product } \pi_k),$$
$$A(B) + r_l^{\cdot} \xrightarrow{k_1} R_0^{\cdot} + P \quad \text{(formation of chain-propagating radical } R_0^{\cdot}).$$

Chain propagation

$$\left.\begin{aligned} A + R_0^{\cdot} &\xrightarrow{k_{2.1}} \pi_1 + R_0^{\cdot\prime} \\ B + R_0^{\cdot} &\xrightarrow{k_{2.2}} R_0^{\cdot} \end{aligned}\right\} \quad \text{(main chain in the conversion of the initial substance)}$$

$$\pi_i + R_i^{\cdot} \xrightarrow{k_2^{ii}} \pi_l + R_i^{\cdot} \quad \text{(secondary chain in the conversion of intermediates)}$$

$$\left.\begin{aligned} A + R_k^{\cdot} &\xrightarrow{k_{2.k}} \pi_s + R_0^{\cdot\prime} \\ \pi_j + R_0^{\cdot} &\xrightarrow{k_2^{0j}} \pi_1 + R_j^{\cdot} \\ \pi_i + R_k^{\cdot} &\xrightarrow{k_2^{ki}} \pi_s + R_i^{\cdot} \end{aligned}\right\} \quad \text{(chain interaction)},$$

Chain termination

$$R_i^{\cdot} + R_j^{\cdot} \xrightarrow{k_{4.1}} P_{\text{term}} \quad \text{(quadratic chain termination in the interaction of active centres)}$$
$$R_i^{\cdot} \xrightarrow{k_{4.2}} P'_{\text{term}} \quad \text{(linear chain termination, for example in the interaction between a radical and the inhibitor)}.$$

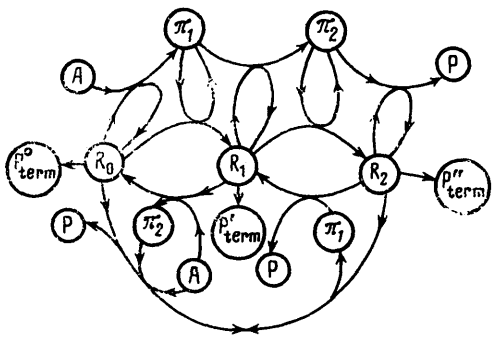


Figure 6. The pathways in a consecutive radical-chain reaction.

In this formulation the general mechanism for a chain reaction has a distinct structure, which emphasises the presence in the system of many sources of free radicals, distinguishes the units of the main and secondary chains

and the interaction steps between the chains, and contains traditional types of elementary stages such as chain branching and termination†.

In examining the characteristics of a chain process use was made of fundamental concepts such as chain length ν and the rate of formation of radicals w_i in the chain initiation and branching stages. The length of the chain in the consumption of the initial substance A $[\nu_-^{(A)}]$ or in the consumption of any intermediate π_j $[\nu_-^{(\pi_j)}]$ is equal to the ratio of the rate of interaction of A or π_j with the free radicals to the rate of destruction of the latter, w_{term}. Since w_{term} in chain processes is usually equal to w_i, we have the following expressions for the chain lengths in the consumption process:

$$\nu_-^{(A)} = \left(\sum_i k_{2,i} [\dot{R}_i]\right)[A]/w_i,$$
$$\nu_-^{(\pi_j)} = \left(\sum_i k_2^{ij} [\dot{R}_i]\right)[\pi_j]/w_i, \qquad (10)$$

where $k_{2,i}$ and k_2^{ij} are the rate constants for the interaction of the radicals with A and π_j. If the intermediate π_k is formed as a result of the interaction of an active centre $\dot{R}_i$ with any substance involved in the process, the chain length in the formation of π_k is proportional to the concentration of $\dot{R}_i$ and is determined by the relation

$$\nu_+^{(\pi_k)} = \left(\sum_i k_2^{ki} [\pi_i]\right)[\dot{R}_i]/w_i, \qquad (11)$$

where $\pi_0 = A$.

The chain lengths in the formation (ν_+) and consumption (ν_-) of the same substance are not identical and the difference between them characterises the change in the concentration of the substance during the process (the concentration of the latter increases and falls respectively when $\nu_+ > \nu_-$ and $\nu_+ < \nu_-$). The ratio of the rates of formation and consumption of the substances involved in the process is determined by the relative concentrations of the active centres in the system. For fairly long chains, the steady-state concentration of radicals is established as a result of their interconversion during the interaction between the chains. The rate of formation of the given radical in the chain is equal to the rate of its chain transformation:

$$\left(\sum_i k_2^{ij} [\dot{R}_i]\right)[\pi_j] = \left(\sum_i k_2^{ki} [\pi_i] + k_{2,k} [A]\right)[\dot{R}_k] \qquad (12)$$

where π_j is the substance from which the active centre $\dot{R}_k$ is formed as a result of the interaction with the active centre $\dot{R}_i$.

Eqns.(12) constitute a system of algebraic linear homogeneous equations, whose number is equal to the number of types of radicals involved in the process. The rank of the coefficients matrix for this system of equations is smaller by unity than the number of equations. The relative concentration of any active centre can therefore be determined from Eqns.(12):

$$[\dot{R}_j] = \frac{D_{ij}}{D_i} [\dot{R}_i], \qquad (13)$$

where D_i is the determinant corresponding to the coefficients matrix of Eqns.(13), from which the ith row and the ith column have been eliminated and D_{ij} is the determinant, analogous to D_i, obtained from the initial matrix by the transposition of the ith and jth columns.

On substituting Eqn.(13) into Eqns.(10) and (11) and then into Eqn.(2), we find an expression for the dependence of the process selectivity on the degree of conversion of the initial substance for a purely chain process when the contribution of molecular processes is insignificant:

$$S_{\pi_j} = \frac{1}{C} \int_0^C \frac{\sum_i (k_2^{ki} [\pi_i] D_{0k} - k_2^{kj} D_{0i} [\pi_j])\, dC}{D_0 \sum_i k_2^{0i} [\pi_i]}. \qquad (14)$$

Eqn.(14) for the selectivity in the formation of any substance in an arbitrary chain process permits the following conclusions.

1. The selectivity is independent of the absolute concentration of the active centres in the system, i.e. of the rate of their formation (the integrand does not contain the absolute concentration of active centres).

2. Since the selectivity is independent of the absolute concentration of active centres, the factors which alter the rates of a chain process by altering the absolute concentration of active species (the effects of initiators and weak inhibitors) do not affect the process selectivity.

3. In the common instance where the reactivity of a radical in its reaction with molecules is independent of the nature of the radical and the rate constant for this reaction is determined solely by the properties of the molecules, the ratio

$$k_2^{ij}/k_2^{ik} = \varphi_{jk} = \text{const}$$

for the given j and k. The selectivity of a chain process of this kind is determined in the same way as the selectivity in a non-chain process proceeding via the same pathway without the participation of active centres. For a non-chain process, the ratios of the rate constants for the interconversion of the substance φ_{jk} are equal to the ratios of the rate constants for the interaction of the substances with the active centres in the chain process.

The selectivity of the chain process $S_{P_{term}}$ with respect to the product P_{term} formed in the chain initiation or termination step is a function of the chain length in the consumption of the initial substance:

$$S_{P_{term}} = \frac{n}{C} \int_0^C \frac{dC}{\nu_-^{(A)} + m}, \qquad (15)$$

where n is the number of molecules of P_{term} formed in a single chain termination step and m the number of molecules of the initial substance consumed during the initiation and termination of a single chain. The maximum selectivity with respect to termination products is attained for the minimum chain lengths $[\nu_-^{(A)} = 1]$. For non-linear chain termination, the quantity $\nu^{(A)}$ is a function of the rate of initiation and the process selectivity depends in this instance on the rate of initiation.

† In the text below the following numbering of the rate constants for individual elementary steps has been adopted: k_0 is the chain initiation rate constant, $k_{2,i}$ the rate constant for the ith reaction propagating the chain in the consumption of the initial substance, $k_{3,i}$ the rate constant for the ith chain branching reaction, and $k_{4,i}$ the rate constant for the ith chain termination reaction. The constants k_2^{ij} refer to secondary reaction chains; the first superscript refers to the reacting radical and the second to the given substance.

The absolute selectivity in the formation of P_{term} in a process with long chains is low, since the differential selectivity in the integrand of Eqns.(15) is inversely proportional to the chain length. At advanced stages of the reaction the chain length in the consumption of the initial substance diminishes owing to the decrease of the concentration of the latter. The integrand of Eqn.(15) then increases and there is a corresponding increase of the process selectivity with respect to the product P_{term}. For short chain lengths, the rate of initiation begins to influence also the process selectivity with respect to the products formed in the chain propagation reaction.

The case discussed above refers to processes where the formation and consumption of all the initial substances and reaction products take place only with participation of free radicals, (i.e. via a chain mechanism). When molecular reaction pathways or short chains occur, the characteristics of the variation of $S(C)$ and $S(t)$ change somewhat, in particular the process selectivity begins to depend on ν and w_i. A quantitative calculation of the selectivity of a chain process during which the chain length becomes small involves the solution of non-linear integrodifferential equations even in the simplest cases.

As an example of such a process, we shall consider a degenerate branched chain oxidation reaction where the hydrocarbon is consumed via a single pathway:

$$\begin{aligned}
&\mathrm{ROOH} \xrightarrow{k_1} (\mathrm{RO}^{\cdot} + \mathrm{OH}^{\cdot}),\\
&\mathrm{RO}^{\cdot} + \mathrm{RH} \xrightarrow{+O_2} \mathrm{ROH} + \mathrm{RO}_2^{\cdot},\\
&\mathrm{OH}^{\cdot} + \mathrm{RH} \xrightarrow{+O_2} \mathrm{H_2O} + \mathrm{RO}_2^{\cdot},\\
&\mathrm{RO}_2^{\cdot} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \mathrm{RO}_2^{\cdot},\\
&\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_4} \mathrm{R'{=}O} + \mathrm{ROH} + \mathrm{O_2}.
\end{aligned} \qquad (B)$$

Application of the principle of the quasi-steady-state nature of the process with respect to the concentrations of the radicals $RO_2^{\cdot}$, $OH^{\cdot}$, and $RO^{\cdot}$, yields a system of differential equations describing the process kinetics:

$$\begin{aligned}
&d[\mathrm{ROOH}]/dt = k_2[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] - k_3[\mathrm{ROOH}],\\
&d[\mathrm{RH}]/dt = k_2[\mathrm{RO}_2^{\cdot}][\mathrm{RH}] - fk_3[\mathrm{ROOH}],\\
&[\mathrm{RO}_2^{\cdot}] = (fk_3[\mathrm{ROOH}]/k_4)^{1/2},
\end{aligned}$$

(f is the probability of the release of radicals into space during the hydroperoxide decomposition step) and hence the equation relating the concentration of the hydroperoxide and the hydrocarbon:

$$\frac{d[\mathrm{ROOH}]}{d[\mathrm{RH}]} = \frac{\nu - 1/f}{\nu + 1}, \qquad (16)$$

where

$$\nu = \frac{k_2[\mathrm{RH}]}{(fk_3k_4[\mathrm{ROOH}])^{1/2}}.$$

The concentration of the hydroperoxide at any concentration of RH may be calculated by Eqn.(16) and the process selectivity may be determined for different degrees of conversion. The highest selectivity in a process of this kind is attained when $1 \ll \nu \gg 1/f$. Fig. 7 presents the results of a numerical calculation of S_{ROOH} for different values of the parameter $k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}$ ($f = 1$).

In this process the hydroperoxide is the first intermediate and, as in a usual consecutive reaction, the selectivity in its formation decreases monotonically with increased degree of conversion of the initial substance. However, in contrast to a non-chain process, the decrease of selectivity is not associated with the consumption of the hydroperoxide but with the decrease of the chain length in its formation caused by the increase of its concentration and by the corresponding increase of the rate of initiation. The form of the function $S_{\mathrm{ROOH}}(C)$ is therefore independent of the rate constant for the decomposition of the hydroperoxide, but depends on the parameter determining the oxidation chain length $\{k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}\}$ and on the probability of the release of radicals into space during the hydroperoxide decomposition step (f). For this reason, the greatest change in selectivity for any values of the parameters occurs at the beginning of the process, for low degrees of conversion of RH, where the concentration of the hydroperoxide and the rate of initiation vary to the maximum extent.

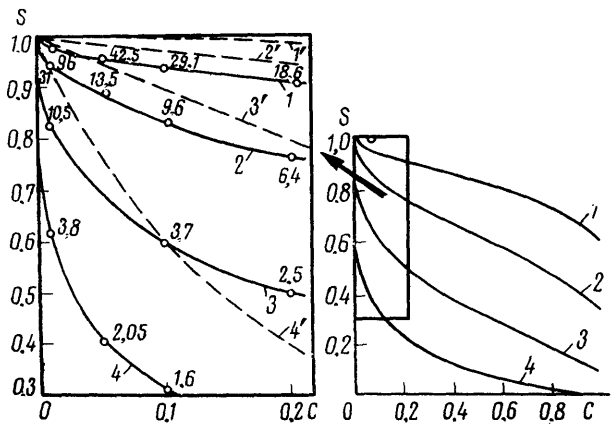


Figure 7. The selectivity in the formation of the hydroperoxide in a degenerate branched chain process as a function of the degree of conversion of the hydrocarbon oxidised for $f = 1$ and different values of the parameter $k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}$: 1) 10; 2) 3.16; 3) 1; 4) 0.316. The numerals opposite the calculated points denote the chain lengths under these conditions: 1′)–4′) the selectivities in the formation of the first intermediate in a simple consecutive reaction for the rate constant ratios k_2/k_1 = 0.1, 0.5, 2, and 10 respectively.

Fig. 7 presents the variation of the selectivity of the chain process discussed above and in a non-chain consecutive reaction (with the same sequence in the formation of products) for low degrees of conversion. In a consecutive reaction with low rate constants for the consumption of the first intermediate ($k_2/k_1 < 2$) the process selectivity corresponding to low degrees of conversion varies little and the function $S_{\pi_1}(C)$ is convex (Fig. 3). In a chain process the function $S_{\mathrm{ROOH}}(C)$ is always concave for low degrees of conversion, i.e. $S_{\mathrm{ROOH}}(C)$ changes sharply for low values of C. This form of the relation is due to the decrease of the chain length in the formation of the hydroperoxide owing to the increase of the rate of formation of active centres.

Thus kinetic analysis of the mechanism of a radical-chain process shows that the selectivity for the formation of chain propagation products in a reaction with long chains is independent of the rate of chain initiation and the absolute concentration of radicals. The characteristics

of the variation of $S(C)$ are then largely analogous to those observed for the selectivity in a non-chain process proceeding via the same pathway. For short chains, S begins to depend on w_i and hence on ν. The selectivity in the formation of chain termination products P_{term} always depends on the rate of initiation (chain length) and assumes significant values only for fairly short chains.

V. FACTORS CONTROLLING SELECTIVITY

The best indication of the importance of chemical kinetics in experimental and practical research is the effective employment of kinetic parameters for controlling the rates and selectivities of chemical reactions.

For a long time the set of available factors capable of influencing a chemical reaction remained almost unchanged—the action of heat (heating, temperature rise), the influence of sunlight and chemical additives, and catalysis. Towards the end of the XXth century progress in science and engineering introduced into chemistry the action of ionising radiation, laser radiation, shock waves, the use of low temperatures (in contrast to the usual endeavour to increase the reaction temperatures), continuous processes, and modification and immobilisation of enzymes and cells as factors influencing the reaction. The principles of chemistry were given a profound and rigorous theoretical basis. This led to considerable possibilities in controlling chemical reactions, provided that their kinetics and mechanisms have been established, and to the possibility of altering the mechanism and kinetics when it is necessary and desirable from the scientific or technical point of view.

According to the formulae for selectivity, temperature as a rule influences the factors associated with a parallel-reaction mechanism (α) and the instability of the intermediate (β). Selective inhibition of undesirable and coupled processes leads to a change of α. In coupled processes these quantities depend on the relative activities of the radicals propagating the oxidation chain.

The introduction of complex forming agents (including solvents) also alters α and β owing to the decrease of the reactivity of the active centres. In certain cases (for short chains) the selectivity in a radical-chain processes depends on the chain length ν, which may be varied by the introduction of initiating additives or inhibitors which increase the rate of chain termination. The latter procedure is used in polymerisation, where a change in the viscosity and structural properties of the medium makes it possible to increase the molecular weight of the polymer and to alter the nature of the molecular weight distribution. The procedure involving the increased lifetime of the radical in the solid polymer led to the discovery of a new type of polymerisation—the radiation-induced graft polymerisation.

A new factor which increases selectivity is associated with the technique in which the reaction is carried out at low and ultralow temperatures (down to ~100 K) where many processes show high rates and high selectivities in the region corresponding to the transition of the system from the vitreous to the supercooled liquid state.

In the region of heterogeneous catalysis new possibilities arose in connection with the use of modified catalysts which propagate the process via a purely heterogeneous mechanism. A characteristic feature of such modified catalysts is the possibility of activating only one of the species involved in the chemical reaction (for example, O_2 in an oxidation process) and, conversely, a decrease of the ability of the catalyst to form complexes with other species (for example, the decreased rate of decomposition of the hydroperoxide in the autoxidation of hydrocarbons). In the presence of such catalysts the process selectivity is as a rule very high.

Homogeneous catalysis has become a fairly effective factor for influencing the selectivity in many chemical processes. The increase of the selectivity of radical-chain processes in the presence of homogeneous catalysts is associated with the selective acceleration of individual elementary stages.

Fundamentally new possibilities for increasing selectivity have arisen from the employment of catalysts which make it possible to propagate the process with participation of radicals bound in a complex with the catalyst (Lewis acids in polymerisation, dinuclear iron complexes in chlorination, etc.). In the presence of such catalysts reactions as a rule take place in the coordination sphere of the metal with a high selectivity.

Research based on the principles of the simulation of enzymatic systems has developed. The application of multicomponent homogeneous catalytic systems has led to many reactions which proceed with a selectivity which is actually higher than that in enzymatic processes.

The application of infrared laser chemistry has already given rise to instances where the reactivities and rates of conversion of individual substances were increased. These effects are used, in particular, for isotope enrichment. Thus under the influence of a HF laser, which emits coherent radiation in the region of 2.7 μm, CH_3OH molecules undergo selective excitation in a CH_3OH-CD_3OH mixture, and then become capable of reacting with Br_2 at high rates[4]:

$$CH_3OH + nh\nu \rightarrow CH_3OH^*,$$
$$CH_3OH^* + Br_2 \rightarrow \text{bromination products.}$$

By employing a 90 W HF laser, it is possible to enrich an equimolar CD_3OH-CH_3OH mixture to a 95% deuteromethanol content over a period of 1 min. Unfortunately laser chemistry has not as yet found applications in the solution of problems of increasing the selectivity in radical-chain processes to an extent which it merits.

Reactions in strong magnetic and electromagnetic fields will probably become common. The first examples of the use of magnetic and electric fields showed that the method is likely to be useful for increasing the selectivity in many chain processes.

The possibility of increasing the selectivity in chemical processes arising in connection with the employment of reactors where the reaction takes place under continuous conditions (ideal mixing and plug flow vessels) is beginning to attract much attention. Many reviews and monographs have been devoted to the simulation and optimisation of chemical reactors[5-7]. However, a fundamental deficiency of these studies is the employment of overall reaction mechanisms in the calculations, whereas knowledge and use in the calculations of specific chemical schemes for the elementary reaction rate constants might be very important. The importance of this approach becomes evident when account is taken of the fact that the method used to carry out the process may have a significant influence on the characteristics of the individual stages and hence the entire process. For example, a significant factor is that, by carrying out the reaction in an open system, one may promote the attainment of steady-state concentrations differing from those corresponding to thermodynamic equilibrium. Thus, for a simple reversible first-order reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$ in an open system, the

ratio of the steady-state concentrations of P and A is

$$\frac{[P]_{st}}{[A]_{st}} = \frac{k_1([A]_0 + [P]_0) + v[P]_0}{k_{-1}([A]_0 + [P]_0) + v[A]_0} \neq \frac{k_1}{k_{-1}},$$

where $[A]_0$ and $[P]_0$ are the concentrations of A and P in the solutions supplied to the vessel and v is the flow rate.

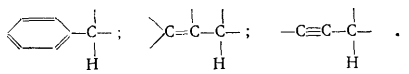
Thus analysis of specific chemical mechanisms plays in all cases an important role in the solution of problems associated with the optimisation of chemical processes. Certain specific examples of selective reactions and methods of increasing selectivity are considered below in relation to oxidation, polymerisation, cracking, and halogenation of organic substances.

VI. LIQUID-PHASE OXIDATION REACTIONS

Liquid-phase reactions involving the oxidation of organic substances are exceptionally widely used as objects of theoretical and experimental studies in the field of radical chain reactions and they are therefore important for chemical practice.

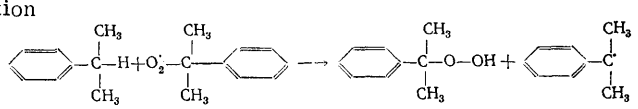
1. Dependence of Reaction Selectivity on Chain Length

A high selectivity in the formation of hydroperoxides at low temperatures is characteristic of the chain oxidation of aromatic alkyl derivatives, α-olefins, and other hydrocarbons with reactive C–H bonds activated by conjugation with an aromatic ring or with unsaturated carbon–carbon bonds:



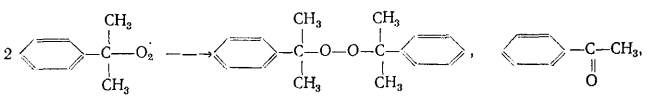
In this case the process is a degenerate branched chain reaction proceeding via mechanism (B) (see Section IV).

In the oxidation of cumene the chain propagation reaction



leads to the formation of a single primary product—isopropylphenyl hydroperoxide.

The recombination of radicals results in the formation of other oxygen-containing products (dicumenyl peroxide, acetophenone, methylphenylmethanol, etc.):



O_2 etc.

In the low-temperature initiated oxidation of hydrocarbons the initiator serves as the source of free radicals in the system and the hydroperoxide does not undergo further transformations. For low degrees of conversion of the hydrocarbon and the initiator, the chain length is almost constant and can be altered by varying the rate of initiation. Under the conditions considered, Eqns. (14) and (15) are transformed as follows:

$$\left.\begin{aligned} S_{ROOH} &= \frac{\nu}{\nu + m} = \frac{\nu_-^{(O_2)}}{\nu_-^{(O_2)} + 1.5} \to 1 \\ S_{P_{term}} &= \frac{1}{\nu + m} = \frac{1}{\nu_-^{(O_2)} + 1.5} \to 0 \end{aligned}\right\} \text{(when } \nu_-^{(O_2)} \gg 1.5\text{)}.$$

If the rate of reaction is followed from the absorption of oxygen $[\nu = \nu_-^{(O_2)}]$, the coefficient m proves to be 1.5, since two O_2 molecules are absorbed in the chain initiation stage for each free radical formed and evolution of one half of an O_2 molecule corresponds to each $RO_2^{\cdot}$ recombination step.

Fig. 8 presents the dependence of the selectivity in the low-temperature sensitised oxidation of isopropylbenzene on chain length. Evidently, in conformity with the above analysis, for long chains $[\nu_-^{(O_2)} > 10]$, the selectivity in the formation of the hydroperoxide is almost independent of ν. For short chains $[\nu_-^{(O_2)} < 10]$, a dependence of this kind does appear. The reaction selectivity with respect to chain termination products changes much more, whatever the chain length ν, than the selectivity with respect to the hydroperoxide.

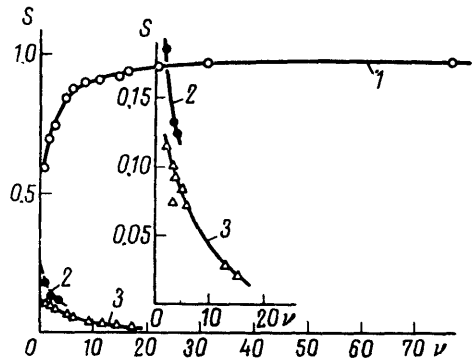
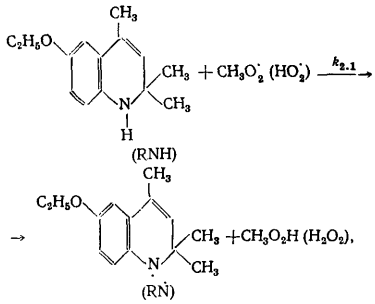
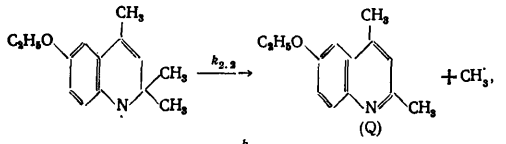


Figure 8. The yields of hydroperoxide (curve *1*), dicumenyl peroxide (curve *2*), and acetophenone (curve *3*) in relation to the amount of absorbed oxygen (in mole %) for different chain lengths in the initiated oxidation of isopropylbenzene. Initiator—azobisisobutyronitrile; solvent—chlorobenzene; temperature 60°C.

The chain oxidation of 6-ethoxy-2,2,4-trimethylethyl-1,2-dihydroquinoline (ethoxyquin, RNH) in chlorobenzene at a temperature >100°C is distinguished by a high selectivity in the formation of 6-ethoxy-2,4-dimethylquinoline (Q).[8] The chain propagation and termination can be represented by the following reactions:

(2.1)



(2.2) 

(2.3) $CH_3^{\cdot} + O_2 \xrightarrow{k_{2.3}} CH_3O_2^{\cdot}$,

(4) $RN^{\cdot} + RN^{\cdot} \xrightarrow{k_4}$ products.

The unit of the ethoxyquin oxidation chain consists of a sequence of reactions (2.1), (2.2), and (2.3).

The high selectivity in the oxidation of ethoxyquin to the quinoline at high temperatures is due to the fact that in this process ethoxyquin reacts solely via the reactive N–H bond and the free radical RN˙ decomposes via only one pathway ($\alpha = 1$). Quinoline does not undergo further transformations and is the final reaction product: $\beta = w_{-}^{(Q)}/w_{+}^{(Q)} = 0$. The reaction chain length is high ($\nu \geq 50$ units) and the selectivity in the oxidation of ethoxyquin to quinoline is more than 95–97 mole % (Fig. 9). The radical RN˙ decomposes [reaction (2.2)] with a high activation energy (~20 000 cal mole^{-1}), so that at low temperatures (<50°C) there is virtually no chain oxidation of ethoxyquin. At low temperatures ethoxyquin is used as an effective antioxidant. The high inhibiting activity of ethoxyquin is due to the high rate of reaction (2.1), which takes place with participation of peroxy-radicals ($RO_2^{\cdot}$ + RNH → RO_2H + RN˙) and with virtual absence of the decomposition of the RN˙ radical.

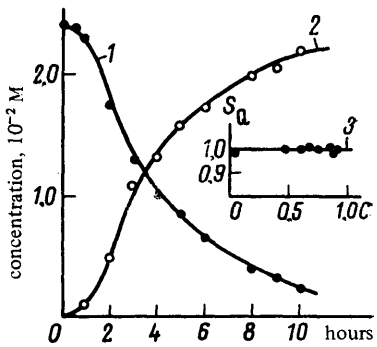


Figure 9. Kinetic curves for the consumption of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline in the oxidation process (curve *1*) and for the accumulation of 6-ethoxy-2,4-dimethylquinoline (curve *2*); curve *3* represents the selectivity in the formation of quinoline for different degrees of conversion of ethoxyquin. Solvent—chlorobenzene; temperature—120°C.

2. The Influence of Thermal Molecular Decomposition and Chain Consumption of Hydroperoxides on the Selectivity of the Hydroperoxide Oxidation of Hydrocarbons

A high selectivity in the formation of hydroperoxides from aromatic alkyl-substituted hydrocarbons (ethylbenzene, isopropylbenzene, etc.) may obtain at elevated temperatures under conditions where the process occurs in the absence of initiating additives. Active centres are formed in this case when the hydrocarbon reacts with oxygen (chain initiation) and in the decomposition of intermediates (degenerate branching).

Fig. 10 presents kinetic curves for the accumulation of α-phenylethyl hydroperoxides and the consumption of ethylbenzene $\{\Delta[RH]\}$ during its autoxidation [9]. The selectivity in the oxidation of ethylbenzene to the hydroperoxide and its variation with the degree of conversion of the hydrocarbon were calculated from these data (Fig. 10, curve *3*). When the degree of conversion reaches 0.2, the selectivity in the formation of the hydroperoxide falls to 0.82. This decrease cannot be explained solely by the increased rate of initiation in the system, as in the example discussed above [see Fig. 7, Eqn. (16)], since the parameter $k_2[RH]_0/(k_0k_4)^{1/2} = 36M^{1/2}$ in ethylbenzene under the given conditions. According to the calculated data presented in Fig. 7, the process selectivity should greatly exceed 0.9 when $C = 0.2$.

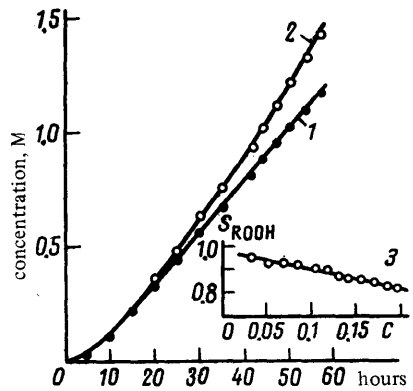


Figure 10. Kinetics of the autoxidation of ethylbenzene at 120°C: 1) the consumption of ethylbenzene $\Delta[RH]$; 2) the accumulation of hydroperoxides; 3) dependence of reaction selectivity with respect to the hydroperoxide $S = [ROOH]/\Delta[RH]$ on the degree of conversion of the hydrocarbon $\Delta[RH]/[RH]_0$. The amount of unconsumed hydrocarbon was calculated from the total amount of products.

The decrease of selectivity during the reaction is caused by the increase of the rates of secondary transformations of the hydroperoxide, which as a rule involves thermal and chain decompositions:

$$RO_2^{\cdot} + ROOH \xrightarrow{k_2^{01}} R'' + \text{alcohol, ketone (chain decomposition)},$$

$$R'' + RH \xrightarrow[(+O_2)]{} R'H + RO_2^{\cdot}.$$

Taking this reaction into account and also the thermal decomposition of the hydroperoxide, the oxidation of ethylbenzene may be represented as a consecutive chain reaction:

$$RH \xrightarrow{+RO_2^{\cdot}} ROOH \left\{ \begin{array}{l} \xrightarrow{+RO_2^{\cdot}} \text{chain decomposition} \\ \xrightarrow{\quad} \text{molecular decomposition} \end{array} \right\} \text{products.}$$

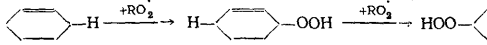
Eqn. (2) for the dependence of process selectivity on the degree of conversion of the initial substance with allowance for chain interaction may be put in the following form:

$$S = \frac{1}{C}\int \frac{\nu(1-\beta)}{(\nu+1+\nu')}\,dC,$$

where $\nu + \nu'$ is the chain length in the consumption of the hydrocarbon and ν is the chain length in the formation of the hydroperoxide. The selectivity with respect to the hydroperoxide must be to a large extent determined by its instability factor:

$$\beta_{ROOH} = \frac{w_-^{(ROOH)}}{w_+^{(ROOH)}} = \frac{k_2^{01}[RO_2^{\cdot}][ROOH] + k_3[ROOH]}{k_2[RO_2^{\cdot}][RH]} = \frac{\nu' + 1/f}{\nu},$$

where $w_-^{(ROOH)}$ is the overall rate of consumption of the hydroperoxide and $w_+^{(ROOH)}$ is the rate of its formation. The quantity β changes during the process (Fig. 10) from 0.06 to 0.4 (for C = 3–20%), which reduces the reaction selectivity with respect to the given product. Paraffins and naphthenes are oxidised at measurable rates at higher temperatures than aromatic alkyl-substituted hydrocarbons. The rate constants for the thermal and chain decomposition of the hydroperoxide are also higher. Under these conditions, β_{ROOH} may be large for lower degrees of conversion of the hydrocarbon, so that the selectivity in the oxidation of paraffins to hydroperoxides is lower than for aromatic alkyl-substituted derivatives. The main cause of the decrease of selectivity in the oxidation of cyclohexene to the monohydroperoxide is its subsequent chain oxidation to the dihydroperoxide, which occurs, like the oxidation of the initial cyclohexene, with participation of the reactive α-C–H bond [10]:



In contrast to the chain consumption of the hydroperoxides of aromatic alkyl-substituted hydrocarbons discussed above, in this elementary stage the OOH functional group of the monohydroperoxide is preserved. Together with the unimolecular decomposition of the hydroperoxide into free radicals and the chain consumption of the hydroperoxide in a secondary chain (with the rate constant k_2^{01}), the oxidation of cyclohexene involves the thermal decomposition of cyclohexenyl hydroperoxide via the reaction

$$RO_2H + HO_2R \overset{K}{\rightleftharpoons} [ROOH \ldots HOOR] \xrightarrow{k_{3.1}} RO^{\cdot} + H_2O + RO_2^{\cdot}.$$

However, the rate of the chain consumption of the hydroperoxide is significantly higher than the rate of its thermal molecular decomposition, so that the cyclohexenyl hydroperoxide "instability factor" may be formulated thus:

$$\beta_{ROOH} = (k_{eff} + k_2^{01}[RO_2^{\cdot}])[ROOH]/\alpha_{(RH\to ROOH)}\,k_2[RO_2^{\cdot}]\cdot[RH] \simeq \simeq k_2^{01}[ROOH]/\alpha_{(RH\to ROOH)}\,k_2[RH],$$

where $k_{eff} = k_{3.1}K$ is the effective rate constant for the decomposition of ROOH and $\alpha(RH \to ROOH) = k_{2.1}/(k_{2.1} + k_{2.2})$ is the factor associated with the parallel-reaction echanism of the main chain in the oxidation of cyclohexene i the monohydroperoxide [$\alpha(RH \to ROOH)$ at 0.7 at 70°C].

Fig. 11*a* presents kinetic curves for the consumption of cyclohexene and the accumulation of cyclohexenyl monohydroperoxide and dihydroperoxide. It is seen from the nature of the kinetic curves that the monohydroperoxide is an intermediate and the dihydroperoxide is a product of the subsequent transformation of the monohydroperoxide. The selectivity in the oxidation of cyclohexene to the monohydroperoxide diminishes from 70 to 20 mole % as the reaction proceeds owing to the increase of the parameter βROOH as C increases from 0 to 60% (Fig. 11*b*).

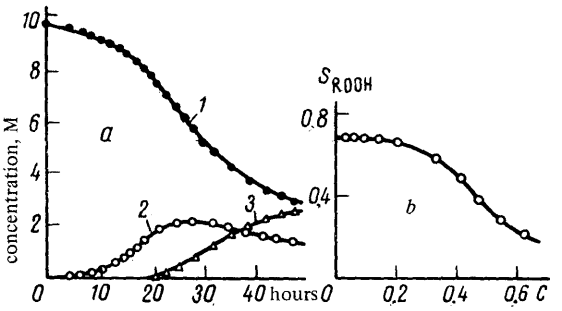


Figure 11. *a*) Kinetic curves for the consumption of cyclohexene (curve *1*) and the accumulation of cyclohexenyl monohydroperoxide (curve *2*) and dihydroperoxide (curve *3*) in the autoxidation of cyclohexene at 70°C; *b*) variation of the selectivity with respect to the monohydroperoxide with increase in the degree of conversion of the hydrocarbon.

3. The Selectivity in a Chain Reaction for the Parallel Consumption of the Hydrocarbon Via Different Pathways

In the general case the hydrocarbon molecule may contain several reaction centres (C–H, C=C, and other bonds), which have different reactivities or their reactivities in relation to reactions with free radicals are similar. The selectivity in the conversion of hydrocarbons into a particular product depends on the ratio of the rate constants for the parallel pathways in the consumption of the hydrocarbon (the quantity α_j). As an example, we may consider the autoxidation of cyclohexene for low degrees of conversion [10]. Cyclohexene is consumed via two parallel pathways with participation of the C–H and C=C bonds and different active centres ($RO_2^{\cdot}$ and $PO_2^{\cdot}$, $RO^{\cdot}$):

(2.1) $$\begin{cases} RO_2^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.1}} ROOH + RO_2^{\cdot}, \\ PO_2^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.1}} POOH + RO_2^{\cdot}, \end{cases}$$

(2.2) $$\begin{cases} RO_2^{\cdot} + RH \xrightarrow{k_{2.2}} P^{\cdot}, \\ PO_2^{\cdot} + RH \xrightarrow{k_{2.2}} P^{\cdot}, \end{cases}$$

(2.3) $$P^{\cdot} \begin{cases} \xrightarrow{k_{2.3}} RO^{\cdot} + \text{epoxycyclohexane}, \\ \xrightarrow[(+O_2)]{k'_{2.3}} PO_2^{\cdot}, \end{cases}$$

(2.4) $$RO^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.4}} ROH + RO_2^{\cdot},$$

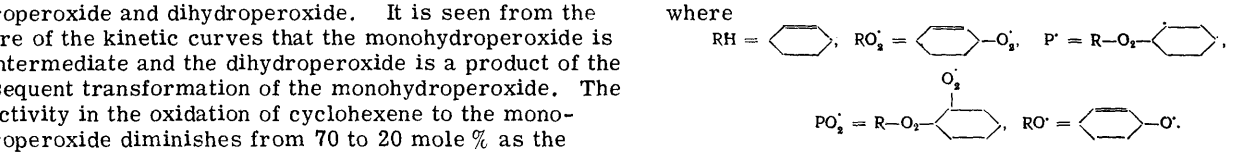
(2.5) $$RO^{\cdot} + RH \xrightarrow{k_{2.5}} P^{\cdot},$$

(4.1) $$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_{4.1}}$$

(4.2) $$PO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_{4.2}} \text{products;}$$

(4.3) $$RO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_{4.3}}$$

where



Analysis of this scheme on the assumption that $k_{2.1}/(k_{2.1} + k_{2.2}) = k_{2.4}/(k_{2.4} + k_{2.5})$ and $k_{4.1} = k_{4.2} = k_{4.3} = k_4$ leads to the following expressions for the concentration of free radicals

$$[RO_3^{\cdot}] = \frac{\alpha}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

$$[PO_3^{\cdot}] = \frac{(1-\alpha)\alpha'}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

$$[RO^{\cdot}] = \frac{k_p}{k_a}\frac{(1-\alpha')(1-\alpha)}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

where $k_p = k_{2.1} + k_{2.2}$ and $k_a = k_{2.4} + k_{2.5}$ are the overall rate constants for the consumption of cyclohexene in the interaction with peroxy- and alkoxy-radicals respectively, $\alpha = k_{2.1}/k_p$ and $1 - \alpha = k_{2.2}/k_p$ are the factors associated with the parallel-reaction mechanism of the consumption of cyclohexene involving the participation of the C–H and C=C bonds respectively and $\alpha' = k'_{2.3}[O_2]/\{k_{2.3} + k'_{2.3}[O_2]\}$ is the factor associated with the parallel-reaction mechanism of the consumption of the radical P′ via the pathway leading to the formation of PO_2. As in the case considered above, one of the pathways [reaction (2.1)] involves the formation of cyclohexenyl hydroperoxide and products containing a terminal hydroperoxy-group (ROOH), while the other leads to the formation of products resulting from the "saturation" of the carbon–carbon double bond (polymeric peroxide products, epoxycyclohexane, etc.).

The rates of formation of the sum of products [ROOH] + [POOH] + [ROH]‡ = Δ[C–H] and the sum of products which do not contain double bonds {Δ[C=C]} are given by the expressions

$$d\Delta[C-H]/dt = \alpha\nu w_i,$$
$$d(\Delta[C=C])/dt = (1-\alpha)\nu w_i,$$

where

$$\nu = \{k_p([RO_3^{\cdot}] + [PO_3^{\cdot}]) + k_a[RO^{\cdot}]\}[RH]/w_i = k_p[RH]/(w_i k_4)^{1/2}[\alpha + \alpha'(1-\alpha)]$$

is the chain length in the consumption of cyclohexene. For a low degree of conversion, where the degrees of the secondary reactions of the products ROOH and POOH are negligibly small, and subject to the condition that the chain is long ($\nu + 1 \simeq \nu$), we have the following relations according to Eqn. (2):

$$S_{[ROOH]+[POOH]+[ROH]} = S_{\Delta[C-H]} = \frac{1}{C}\int_0^C \frac{d([ROOH]+[POOH]+[ROH])}{d[RH]}dC = \alpha,$$

$$S_{\Delta[C=C]} = \frac{1}{C}\int_0^C \frac{d(\Delta[C=C])}{d[RH]}dC = (1-\alpha).$$

If the rate constants for the parallel reactions involving the consumption of the hydrocarbon are associated with different activation energies, the selectivities vary with temperature. Indeed, when

$$k_{2.1} = k^0_{2.1}\exp(-E_1/RT),\quad k_{2.2} = k^0_{2.2}\exp(-E_2/RT) \text{ and } E_1 \neq E_2$$

the selectivities are given by the following relations:

$$S_{\Delta[C-H]} = 1\Big/\left[1 + \frac{k^0_{2.2}}{k^0_{2.1}}\exp(-\Delta E/RT)\right],$$

$$S_{\Delta[C=C]} = 1\Big/\left[1 + \frac{k^0_{2.1}}{k^0_{2.2}}\exp(\Delta E/RT)\right],$$

‡ Account is taken of the alcohol formed solely as a result of reactions (2.3) and (2.4).

where $k^0_{2.1}$ and $k^0_{2.2}$ are pre-exponential factors and $\Delta E = E_2 - E_1$ is the difference between the activation energies. According to these formulae, when $\Delta E > 0$, the selectivity of the reaction via pathway (2.1) decrease with increase of temperature and the selectivity of that via pathway (2.2) increases. This case obtains in the oxidation of cyclohexene. The rate constants for the elementary chain propagation reactions are

$$k_{2.1} = 2.7 \cdot 10^8 \exp(-7000/RT) \text{ litre mole}^{-1}\,s^{-1},$$
$$k_{2.2} = 1.44 \cdot 10^9 \exp(-14\,000/RT) \text{ litre mole}^{-1}\,s^{-1}.$$

Fig. 12*a* presents data for the selectivity in the oxidation of cyclohexene corresponding to degrees of conversion not exceeding 20 mole %, where the rates of the molecular and chain consumption of hydroperoxides are low, i.e. $\beta ROOH \simeq 0$.[10] It is seen that $S_{ROOH} = 0.7$ (70%) and $S_{\Delta[C=C]} = 0.3$ (30%) at 70°C and $S_{ROOH} = S_{\Delta[C=C]} = 0.5$ (50%) at 100°C. Fig. 12*b* presents the variation of the selectivity over a wide temperature range. In conformity with the formulae quoted above, the selectivity in the oxidation of cyclohexene to hydroperoxides diminishes and that for the oxidation to products formed as a result of the addition of peroxy-radicals to the C=C bond increases.

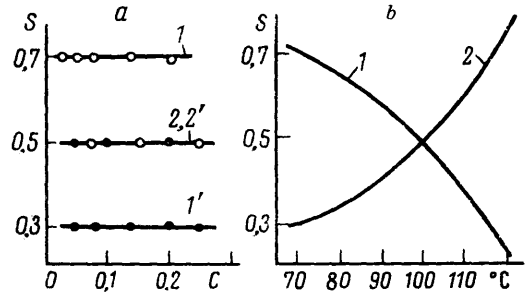


Figure 12. *a*) Dependence of the selectivity in the autoxidation of cyclohexene to the hydroperoxide (S_{ROOH}) (lines *1* and *2*) and to products formed as a result of the oxidation of the C=C bond ($S_{\Delta[C=C]}$) (lines *1′* and *2′*) on the degree of conversion of the hydrocarbon $C = \Delta[RH]/[RH]_0$ at 70°C (lines *1* and *1′*) and 100°C (lines *2* and *2′*); *b*) temperature variation of the selectivities S_{ROOH} (curve *1*) and $S_{\Delta[C=C]}$ (curve *2*) (calculated data).

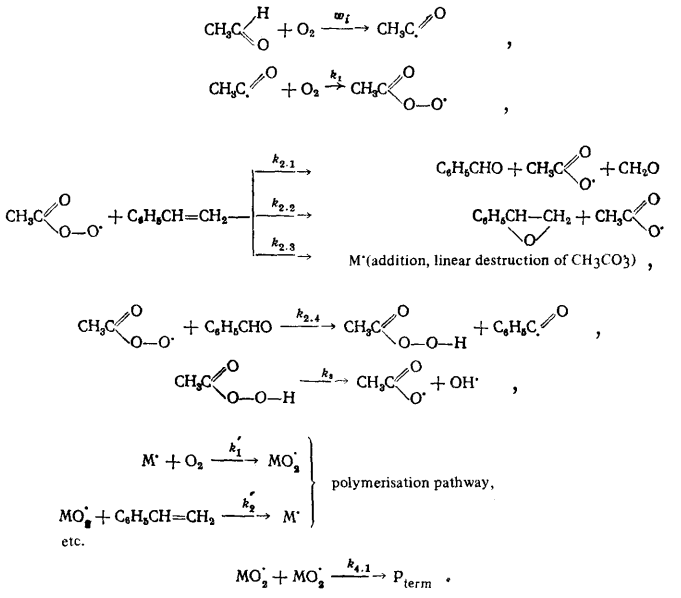
4. Selective Inhibition of Undesirable Chain Pathways

In chain reactions proceeding via several active centres with different activities and reactivities, there is a possibility of several parallel pathways some of which lead to the desired product:

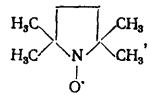
$$r^{\cdot} + A \begin{cases} \xrightarrow{} \pi \xrightarrow{r^{\cdot}} P \text{ (desired product)}, \\ \xrightarrow{} M^{\cdot} \xrightarrow{A} P_1 \text{ (side product)}. \end{cases}$$

This also happens when the reactant exhibits a dual reactivity and can be consumed via several pathways under the reaction conditions.

The conditions governing the possibility of the selective inhibition of the undesirable chain pathway are a difference between the activities of the radicals r˙ and M˙ and the absence of their interconversion (the radicals belong to different chains which do not interact). This case obtains in the joint oxidation of styrene and acetaldehyde [11]:



Stable iminoxy-radicals Im˙, in particular tanol



which react with alkyl radicals (M˙ and $CH_3\dot{C}=O$) at much higher rates than with peroxy-radical ($MO_2^{\cdot}$ and $RC(=O)-O^{\cdot}$) may be used as the inhibitors of the undesirable polymerisation pathway in this process. Additional chain termination reactions then occur in the system:

$$RC^{\cdot}=O + Im^{\cdot} \xrightarrow{k_{4.2}} P'_{term} ,$$

$$M^{\cdot} + Im^{\cdot} \xrightarrow{k_{4.3}} P''_{term} .$$

Selective inhibition of the polymerisation pathway is possible when the following condition is fulfilled:

$$w_1 > w_{4.2} \text{ and } w'_1 < w_{4.3} . \quad (17)$$

Ultimately this implies that the rate of linear termination by the $RO_2^{\cdot}$ radicals must exceed the rate of the interaction of $R\dot{C}=O$ with Im˙, while the rate of recombination of $MO_2^{\cdot}$ must be much lower than the rate of destruction of M˙ radicals by the inhibitor:

$$w_{2.3} > w_{4.2} \text{ and } w_{4.1} < w_{4.3} . \quad (18)$$

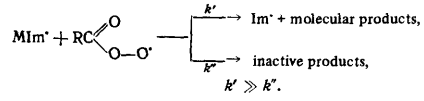
Conditions (17) and (18) hold at an inhibitor concentration

$$\frac{(k_{2.1}+k_{2.2})[C_6H_5C_2H_3]}{k_{4.2}} > [Im^{\cdot}] > \frac{(w_0 k_{4.1})^{1/2}}{k_{4.3}} . \quad (19)$$

As a rule, condition (19) is fulfilled at very low concentrations [Im˙] and requires the artificial maintenance of a steady-state inhibitor concentration in the system during the process.

The inhibition of the polymerisation pathway by the addition of tanol may be achieved by maintaining a steady-state concentration [Im˙] as a result of the regeneration of the inhibitor via the mechanism

$$M + Im^{\cdot} \rightarrow MIm^{\cdot},$$



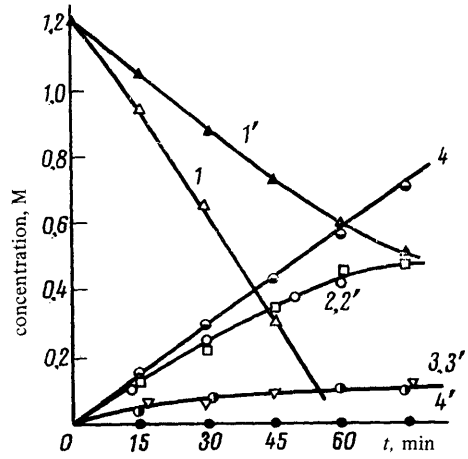


Figure 13. Kinetic curves for the consumption of styrene (curve *1*) and the accumulation of benzaldehyde (curve *2*), 1-phenyloxiran (styrene oxide) (curve *3*), and the polymer (curve *4*) in the joint oxidation of styrene and acetaldehyde in benzene at 70°C; the primed numerals have the same significance but in the presence of 0.002 M of tanol. The instant when the induction period ends was adopted as the time $t = 0$.

Table 1.

Reaction	Required product	Degree of conversion, mole %	Selectivity w.r.t. unsaturated compound which has reacted, mole %	
			without inhibitor	in the presence of Im
Coupled oxidation of styrene and acetaldehyde	1-Phenyloxiran	80.0	40.0	80.0
Coupled oxidation of aryl chloride and acetaldehyde	Chloromethyloxiran	6.0	7.0	65.0
Liquid-phase oxidation of methylacroleine	Methacrylic acid	50.0	30.0	80.0

Fig. 13 presents kinetic curves for the consumption of styrene and the accumulation of its conversion products in the joint oxidation of styrene and acetaldehyde without an inhibitor and in the absence of the iminoxy-radical. Evidently the inhibition of the consumption of styrene is associated with the suppression of its polymerisation (curves *1* and *1'*). To facilitate the comparison, the instant when the consumption of the initial substances begins is adopted as the time $t = t_0$ in both cases. Selective inhibition makes it possible to increase greatly the selectivities of many oxidation processes (Table 1).

5. Homogeneous Catalysis in Oxidation Reactions

Activation of oxygen. One of the possible ways of increasing the rates and selectivities of chemical processes involves the use of homogeneous catalysts—variable-valence metal compounds. This has been established by the activation of O_2, $RO_2^{\cdot}$, or ROOH when they are incorporated in the coordination sphere of the metal. The formation of complexes with all these species has been recorded by various physical procedures. The formation of a complex of O_2 with vitamin B_{12} [a cobalt(II) complex], which involves the generation of the Co(III).O_2^- species, has been established by ultraviolet spectroscopy (Fig. 14*a*),[12] the formation of complexes of Co(II)L_2 with ROOH has been demonstrated by NMR (Fig. 14*b*),[13,14] and the formation of complexes of Ni^+ with $RO_2^{\cdot}$ has been demonstrated by ESR (Fig. 14*c*).[15]

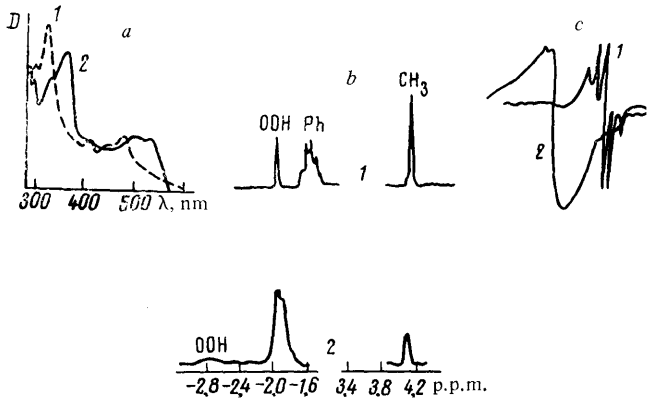


Figure 14. *a*) The spectra of vitamin B_{12} [Co(II)] in methanol at −80°C in an anaerobic medium (curve *1*) and of the B_{12}–oxygen complex formed at $p_{O_2} \simeq 1$ atm (curve *2*); *b*) the NMR spectra of cumenyl hydroperoxide (c = 0.45 M) in the 1 : 1 CCl_4–CH_2Cl_2 mixed solvent in the absence of a catalyst (curve *1*) and after the addition of 0.0245 M bis-(*o*-vanillideneanisidine)cobalt(II) (curve *2*) at −20°C; *c*) EPR signals due to the nickel(I) species formed in the Ni(acac)$_2$ + $Al(C_2H_5)_3$ system (curve *1*) and the complex $(CH_3)_3$–C–OC.Ni(I) (curve *2*). Solvent—benzene; temperature—23°C.

The use of metal salts rarely leads to an appreciable increase of process selectivity when catalysts of this kind form complexes with virtually all active species and oxygen-containing reaction products (particularly with hydroperoxides and alcohols), since under these conditions the reactions of all the intermediates are accelerated non-selectively. For this reason, the use of metal-complex catalysis is most promising for increasing the selectivity. In this case the use of appropriate ligands or electron-donating additives makes it possible to alter the structure and properties of the catalyst in such a way that the incorporation of one of the reacting species in the coordination sphere becomes unfavourable, and, conversely, the degree of coordination of other substances to the catalyst is enhanced.

Electron-donating ligands greatly increase the ability of cobalt compounds to form adducts with oxygen. The formation of such adducts may be observed by EPR (Fig. 15).[16] The equilibrium constant K_{O_2} for the formation of the complex $Co^{\delta+}L_2(B).O_2^{\delta-}$ via the reaction

$$CoL_2(B) + O_2 \overset{K_{O_2}}{\rightleftharpoons} Co^{\delta+}L_2(B).O_2^{\delta-}$$

increases with increase of the basicity constant of the base B. Fig. 1 illustrates the dependence of K_{O_2} on the basicity constant of B (pK_B) for the *NN'*-ethylenebis-(benzoylacetoneiminato)cobalt(II) complexes with various electron-donating additives. The inclusion of electron-donating molecules of B in the coordination sphere of cobalt simultaneously lowers the oxidation potential of the complex. There is a correlation between K_{O_2} and the polarographic half-wave potential of the complex. The greater the basicity of B, the lower the value of $E_{1/2}$, i.e. the higher the capacity of the complex $CoL_2(B)$ for being oxidised and hence the higher the degree of electron transfer in $Co^{\delta+}L_2(B).O_2^{\delta-}$, which must increase the activity of the oxygen complex in the formation of free radicals:

$$Co^{\delta+}L_2(B)\,O_2^{\delta-} + RH \rightarrow CoL_2(B) + HO_2^{\cdot} + R^{\cdot}$$

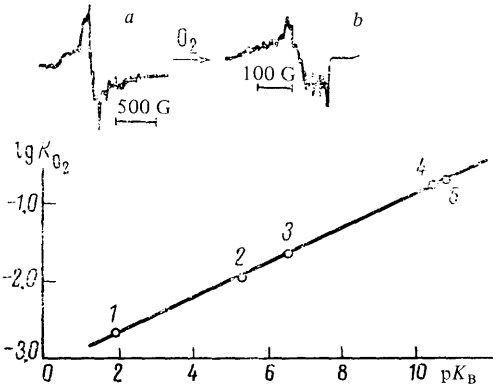


Figure 15. Dependence of the equilibrium constant K_{O_2} for the formation of the O_2 complexes of the adducts of *NN'*-ethylenebis(benzoylacetoneiminato)cobalt(II) with different bases B [1) cyanopyridine; 2) pyridine; 3) 3,4-lutidine; 4) isobutylamine; 5) n-butylamine] on the basicity constants of the latter. The EPR spectra of the adducts *NN'*-ethylenebis(benzoylacetoneiminato)cobalt(II) with pyridine Co(II)L_2Py (*a*) and the complex Co(II)L_2Py.O_2 (*b*).

The decomposition of hydroperoxides by complexes incorporating electron-donating molecules may be retarded owing to steric hindrance to the formation of complexes with the hydroperoxide. There is accordingly an increase of selectivity in the oxidation of hydrocarbons to hydroperoxides. Thus ethylbenzene is oxidised to the hydroperoxide in the presence of cobalt naphthenate with a selectivity $S \simeq 5$ mole % for a degree of conversion $C \simeq 6$ mole %.[17] The introduction of a chelating ligand with pronounced electron-donating properties (quinoline-carboxylic acid) into the solution increase S to 18.9 mole % for C = 8.2 mole % (Table 2).[17]

Nickel compounds, which exhibit a low activity in the decomposition of hydroperoxides but are capable of greatly activating oxygen, make it possible to carry out the oxidation of ethylbenzene with an appreciable selectivity for comparatively high degrees of conversion (Table 2). The selectivity in the oxidation of cyclododecane to ROOH in the presence of bis(acetylacetonato)nickel reaches 46.8 mole % for a degree of conversion of 26.1 mole %.[18] When ethylbenzene is oxidised in the presence of the same catalyst, the selectivity S_{ROOH} = 70 mole % for C_{RH} = 10 mole %. The introduction into the system of small amounts of electron-donating ligands (such as dimethylformamide and NaSt) retards the decomposition of the hydroperoxide and leads to a corresponding appreciable increase of process selectivity (Fig. 16).[19]

Table 2. Selectivity in the oxidation of hydrocarbons to hydroperoxides.

Catalyst	Hydrocarbon	C, mole %	S_{ROOH}, mole %
Cobalt naphthenate	Ethylbenzene	5.9	5.0
Chelate complex of cobalt naphthenate and quinolinecarboxylic acid (B)	Ethylbenzene	8.2	18.9
Bis(acetylacetonato)nickel	Ethylbenzene	10.0	70.0
Bis(acetylacetonato)nickel	Cyclododecane	26.1	46.8

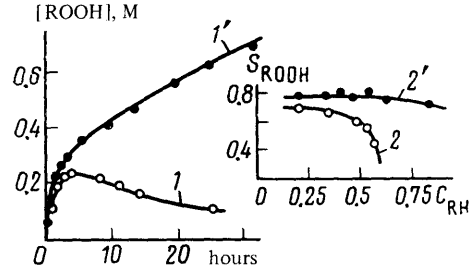


Figure 16. Kinetic curves for the accumulation of hydroperoxides (curves *1* and *1'*) and the dependence of the selectivity in the formation of the hydroperoxide S_{ROOH} on the degree of conversion of the hydrocarbon (curves *2* and *2'*) in the oxidation of ethylbenzene in the presence of 0.003 M Ni(acac)$_2$ (curves *1* and *2*) and a mixture of 0.003 M Ni(acac)$_2$ and 0.003 M dimethylformamide (curves *1'* and *2'*) at 120°C.

The selectivity in the formation of hydroperoxide decomposition products. The composition of the products formed in the decomposition of hydroperoxides in the presence of a catalyst depends on the nature of the solvent[20,21]. The decomposition in the ROOH–catalyst system proceeds via two pathways: with formation of free radicals and molecular products. Both pathways proceed via the formation of a single intermediate complex in accordance with the mechanism[22]

$$\mathrm{Co(acac)_2 + ROOH \rightarrow Co(acac)_2ROOH \rightarrow}$$
$$\rightarrow [\underbrace{\mathrm{Co(acac)_2^+,\ OH^-,\ RO^\cdot}}_{\text{(cage)}}] \begin{cases} \xrightarrow{k'} \mathrm{Co(acac)_2OH + RO^\cdot} \\ \xrightarrow{k''} \mathrm{Co(acac)_2 + R'COR'' + H_2O} \end{cases},$$

The rate constant ratio k''/k' which determines the fraction of molecular decomposition, depends on the rate of diffusion of RO$^\cdot$ from the solvent cage, and increases with increase of the viscosity of the medium (Fig. 17). The ratio of the rate constants for the molecular and radical decompositions of hydroperoxides, which lead in many instances to the formation of different products, depends on the nature of the catalyst, the hydroperoxide, and the solvent[22] (Table 3).

Table 3.

Catalyst	Hydroperoxide	Solvent	$\frac{W_p}{W_\Sigma}\times 100\%$	Catalyst	Hydroperoxide	Solvent	$\frac{W_p}{W_\Sigma}\times 100\%$
$CoSt_2$	Tetralinyl	Chlorobenzene	1.2	$Ni(acac)_2$	Tetralinyl	Chlorobenzene	2.0
$CoSt_2$	Cumenyl	Chlorobenzene	36.4	$Ni(acac)_2$	α-phenylethyl	Benzene	4.1
$CoSt_2$	t-Butyl	Benzene	100.0	$NiSt_2$	α-phenylethyl	Ethylbenzene	1.2
$Co(acac)_2$	Cumenyl	Benzene	96.0				

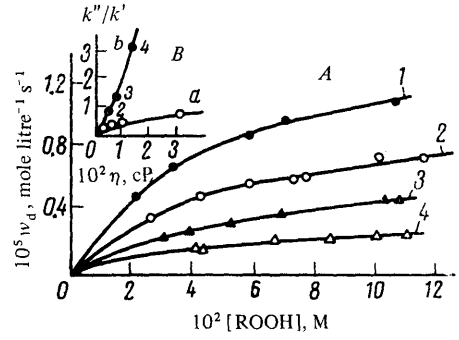


Figure 17. *A*) Dependence of the rate of decomposition of cumenyl hydroperoxide in the presence of 5×10^{-4} M Co(acac)$_2$ on [ROOH] in benzene (curve 1) and in solvents with mobile C–H bonds [2) ethylbenzene; 3) a mixture of 60 vol.% of tetralin and benzene; 4) tetralin]; *B*) dependence of k''/k' on η for the decomposition of cumenyl hydroperoxide in inert solvents (*a*) and in solvents with mobile C–H bonds (*b*). Points *2*, *3*, and *4* were obtained from the data represented by curves 2, 3, and 4 in Fig. *A*.

Cumenyl hydroperoxide decomposes in the presence of $CoSt_2$ via a chain mechanism with formation of dimethylphenylmethanol and acetophenone:

$$\mathrm{C_6H_5C(CH_3)_2OOH + CoSt_2 \rightarrow C_6H_5C(CH_3)_2CO^\cdot + Co(OH)St_2},$$
$$\mathrm{C_6H_5C(CH_3)_2OOH + Co(OH)St_2 \rightarrow C_6H_5C(CH_3)_2OO^\cdot + CoSt_2 + H_2O},$$
$$\mathrm{C_6H_5C(CH_3)_2OOH + C_6H_5C(CH_3)_2O^\cdot \rightarrow C_6H_5C(CH_3)_2OH + C_6H_5C(CH_3)_2OO^\cdot},$$
$$\mathrm{2\,C_6H_5C(CH_3)_2OO^\cdot \rightarrow C_6H_5C(CH_3)_2OH + C_6H_5C(=O)CH_3}.$$

The stoichiometric equation for the process is

$$3\,C_6H_5C(CH_3)_2OOH \rightarrow 2\,C_6H_5C(CH_3)_2OH + C_6H_5C(=O)CH_3 .$$

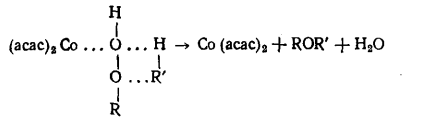
As expected on the basis of the mechanism, the process selectivity with respect to dimethylphenylmethanol $S_{C_6H_5C(CH_3)_2OH} \simeq 70$ mole %.

The selectivity in the chain decomposition of the hydroperoxide may be increased by adding hydrogen donors which react readily with peroxy-radicals and lead to a change in the chain termination mechanism. For example, the introduction of an inhibitor leads to the replacement of the $RO_2^{\cdot}$ (the source of the ketone) recombination reaction by the reaction

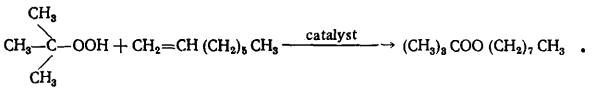
$$C_6H_5C(CH_3)_2OO^{\cdot} + InH \rightarrow C_6H_5C(CH_3)_2OOH + In^{\cdot}.$$

The experimental process selectivity then increases to 95 mole %.[4]

The activation of the hydroperoxide in the catalyst sphere makes it possible to achieve many bimolecular reactions of ROOH with hydrocarbons. In the decomposition of cumenyl hydroperoxide in the presence of hydrocarbons with a mobile C–H bond, there is an appreciable increase in the contribution of molecular decomposition of the hydroperoxide, although the overall rate of decomposition remains constant. The ether ROR′ is then formed in the system as a result of the reaction between the hydrocarbon and the activated hydroperoxide via the mechanism[23]

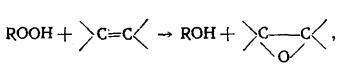


where ROOH = $C_6H_5C(CH_3)_2OOH$ and R′H = . When ROOH interacts with the hydrocarbon R′H, there is a possibility of the formation of the asymmetric peroxides ROOR′:



In the decomposition of t-butyl hydroperoxide in cyclohexene, oct-1-ene, or cumene in the presence of copper, manganese or cobalt salts the selectivity in the formation of asymmetric peroxides reached 90 mole %.[25]

Molybdenum, vanadium, and tungsten compounds are known to catalyse the bimolecular reaction[26,27]



which constitutes the basis of the highly selective synthesis of olefin oxides (the "chalcone process"). It has been shown recently that this reaction proceeds via the intermediate formation of a complex of ROOH with the catalyst. The formation of such complexes is indicated by the broadening of the absorption band of the hydroperoxide protons in the NMR spectrum of t-butyl hydroperoxide under the influence of dioxobis(cyclohexanediolato)molybdenum[28,29] and bis(acetylacetonato)molybdenyl[30].

The change in the hydroperoxide decomposition pathway and the increased selectivity of this process are the most important factors, which make it possible to increase the selectivity in oxidation reactions.

The change in the chain reaction pathway. The high selectivities (above 95 mole %) in the oxidation of aromatic alkyl-substituted hydrocarbons to organic acids may be achieved by employing cobalt bromide in acetic acid as the catalyst. Manganese(II) compounds are used as promoting additives, which lead to an additional increase of reaction selectivity. The mechanism of catalysis by cobalt compounds in the presence of bromide ions still remains controversial.

Although the specific mechanism of the formation of acids is not clear, it may be that the oxidation proceeds via a radical-chain mechanism where the catalyst is involved in the chain propagation reaction according to the following mechanism:

Formation of cobalt bromide:

$$CoAc_2 + NaBr \rightleftharpoons CoAcBr\,(Co\,(II)\,Br^-) + NaAc.$$

Chain initiation:

$$ROOH + Co\,(II) \rightarrow RO^{\cdot} + Co\,(III) \xrightarrow{RH} ROH + R^{\cdot} + Co\,(III),$$

$$ROOH + Co\,(III) \rightarrow RO_2^{\cdot} + Co\,(II).$$

Chain propagation:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$

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

$$RO_2^{\cdot} + Co\,(II) \xrightarrow{HAc} ROOH + Co\,(III),$$

$$RO_2^{\cdot} + Co\,(II)\,BrH^+ \rightarrow ROOH + Co\,(III)\,Br^- \rightarrow ROOH + Co\,(II)\,Br^{\cdot}.$$

Bromide chain propagation:

$$Co\,(III)\,Ac_3 + Co\,(II)\,Br^- \rightarrow Co\,(II)\,Ac_2 + Co\,(III)\,Br^{\cdot}Ac \rightarrow Co\,(II)\,Br^{\cdot}Ac$$

$$Co\,(II)\,Br^{\cdot}Ac + RH \rightarrow Co\,(II)\,Ac_2 + HBr + R^{\cdot} \rightarrow Co\,(II)\,Br^{-}\overset{\cdot}{A}c + HAc + R^{\cdot}.$$

Overall reaction:

$$Co\,(III)\,Ac_3 + RH \rightarrow Co\,(II)\,Ac_2 + HAc + R^{\cdot}.$$

Chain termination:

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow R'\text{—}\underset{R''}{\overset{|}{C}}O + ROH + O_2 .$$

In the presence of the cobalt bromide catalyst, the chain oxidation pathway, consisting in alternate reactions of the $R^{\cdot}$ radicals with O_2 and of $RO_2^{\cdot}$ radicals with the hydrocarbon, is replaced by a new more complex chain pathway which leads to a higher process selectivity.

This apparently occurs as a result of the suppression of the undesirable pathways involving the formation of peroxy-radicals and the hydroperoxide.

6. Simulation of Enzymatic Processes

In the development of selective oxidation processes it is frequently proposed to use the principles of the simulation of enzymatic oxidation which in many cases involve a high selectivity with respect to the substrate oxidised. A characteristic feature of the mechanism of an enzymatic process is activation of the reactants, coupling of the reactions, and a highly organised matrix [templet] nature of the process.

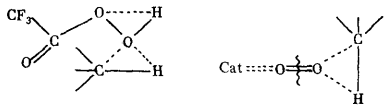
Hydroxylation. In biological systems this process takes place under the influence of mono-oxygenases as a coupled reaction involving the oxidation of the substrate and on organic reductant AH_2 present in the system[31]:

$$AH_2 + RH + O_2 \rightarrow A + ROH + H_2O .$$

The ratios of the amounts of the alcohol formed, the unconsumed organic reductant, and the oxygen absorbed are 1 : 1 : 1. The selectivity in the oxidation reaction with

respect to the substrate reaches 100 mole % for low degrees of conversion.

It is suggested that the enzymatic oxidation of hydrocarbons proceeds via the oxenoid mechanism [32] in a concerted process in which an oxygen atom of the O_2 molecule, activated by the enzyme, is inserted in a C–H bond of the substrate without the formation of free radicals. In chemical systems the oxenoid mechanism can occur when acyl hydroperoxides react with RH and in the catalytic epoxidation of olefins by hydroperoxides:



Depending on the nature of the enzyme and the substrate, the oxidation proceeds via different mechanisms. In the hydroxylation of 2,6-di-t-butyl-4-methylphenol, catalysed by an enzymatic system containing cytochrome P-450, the accumulation of the hydroperoxide was observed at early stages of the oxidation process. It appears that in this instance oxygen is inserted, without the association of the O–O bond, via the mechanism [33]

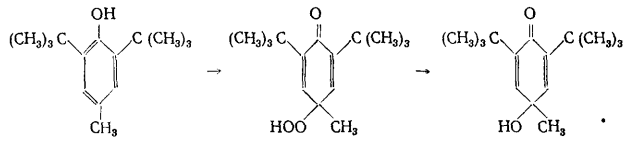
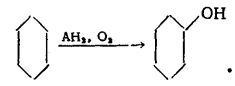


Table 4. Coupled oxidation of cyclohexane (S_1 and S_2 are respectively the selectivities in the formation of the alcohol and the ketone in terms of consumed cyclohexane and S_3 is the selectivity in the formation of the alcohol in terms of the consumed reductant).

System	S_1, mole%	S_2, mole %	S_3, mole %	System	S_1, mole %	S_2, mole %	S_3, mole %
Mono-oxidase	100	—	100	$SnCl_2$	100	—	5
Fe^{2+} + ascorbic acid	75	25	4	$TiCl_2$	95	5	8
Haemin + thio-salicylic acid	60	40	8	$FeCl_2$	80	20	9

In recent years numerous attempts were made to simulate enzymatic oxidation processes. The condition which must be met by such simulation is believed to be the simultaneous transfer of two electrons to the O_2 molecule [34]. Such electron transfer is possible in the oxidation of a metal capable of transferring two or more electrons [for example, $SnHPO_4$, $SnCl_2$, $MoCl_3$, and $Mo(CO)_6$ in Table 4] or of a ligand in a system of the Fe^{2+}–ascorbic acid type. However, in the known model systems there is at present no direct evidence for the occurrence of the oxenoid hydroxylation mechanism, characteristic of enzymatic systems, i.e. O is inserted in a C–H bond in a single step. On the other hand, model systems make it possible to hydroxylate alkanes with a high selectivity (Table 4) under mild conditions. In such systems the process apparently proceeds via a coupled radical chain mechanism.

The principle of the coupled oxidation of hydrocarbons and tin compounds has been used for the selective oxidation of hydrocarbons to alcohols (hydroxylation):



The selectivity in the formation of alcohols with respect to the hydrocarbon is close to 100 mole %. [34,35] This result has been obtained in the coupled oxidation of cyclohexane and $SnCl_2$ in acetonitrile at 20°C with formation of cyclohexanol as the only cyclohexane conversion product. The kinetic mechanisms for the oxidation of cyclohexane in the absence of $SnCl_2$ and after the introduction of bivalent tin into the reaction are compared below:

"Classical" oxidation mechanism	Coupled oxidation of RH and tin
(0) $RH \rightarrow R^{\cdot}$	(0) $\begin{cases} Sn(II) + O_2 \rightarrow Sn(III) + HO_2^{\cdot} \\ HO_2^{\cdot} + RH \rightarrow H_2O_2 + R^{\cdot} \end{cases}$
(1) $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$	(1′) $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$
(2) $RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$	(2′) $RO_2^{\cdot} + Sn(III) + H_2O \rightarrow ROH + Sn(IV)OH^-$
(3) $ROOH \rightarrow RO^{\cdot}$	(3′) $ROOH + Sn(II) \rightarrow RO^{\cdot} + Sn(III)OH^-$
(4) $RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$	(4′) $RO^{\cdot} + Sn(III) + H_2O \rightarrow ROH + Sn(IV)OH^-$
(5) $ROOH \rightarrow$ ketone	(5′) $ROOH + Sn(II) + H_2O \rightarrow Sn(IV)(HO^-)_2 + ROH$
(6) $RO_2^{\cdot} + RO_2^{\cdot} \rightarrow$ molecular products	(6′) $Sn(III) + Sn(III) \rightarrow Sn(II) + Sn(IV)$

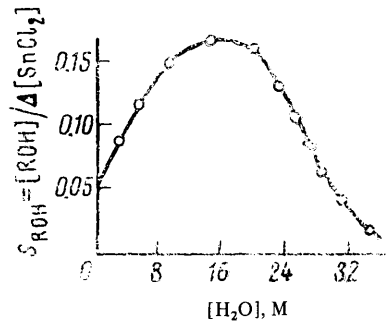


Figure 18. Dependence of the selectivity in the formation of cyclohexanol with respect to unconsumed $SnCl_2$ on the concentration of water in the coupled oxidation of cyclohexane and $SnCl_2$ at 20°C.

The high process selectivity is due to the replacement of the chain propagation reaction (2) involving the hydrocarbon by reaction (2′) involving Sn(III) in the reaction chain and is also due to a change in the hydroperoxide decomposition pathway. In the presence of tin(II) the hydroperoxide decomposes via a molecular pathway with formation of an alcohol [reaction (5)]. The selectivity of this process with respect to the reductant ($SnCl_2$) is low (up to 5 mole %), which may imply a considerable consumption of the reductant in processes which are useless from the standpoint of the formation of the desired product (the alcohol). The selectivity in the utilisation of the reductant may be somewhat increased by altering the composition of the medium. Thus, when the reaction is carried out in a mixed solvent (acetonitrile–water), the reaction selectivity with respect to the reductant increases to 20 mole % (Fig. 18).

Epoxidation of olefins. The coupled oxidation reactions may become a promising method for increasing the selectivity of processes of this type. In order to obtain the required product, active centres propagating a parallel chain process involving the conversion of the second component of the coupled pair are employed.

Catalytic systems for the direct oxidation of propene to epoxypropane are being actively sought at the present time. A yield of epoxypropane not less than 75 mole % relative to the unconsumed propene is believed to be economically useful. In the absence of a catalyst in glass, Teflon, or titanium reactors the selectivity in the direct oxidation of propene to epoxypropane does not exceed 50 mole % relative to the unconsumed propene (even for a low degree of conversion—up to 10–20 mole %).[36]

Fig. 19 presents kinetic curves for the oxidation of propene in chlorobenzene at 150°C and 50 atm. When propene is oxidised under these conditions, more than 20 products are formed, 14 of which are listed in Fig. 19; others are formed as impurities. In view of such complex mixture compositions, the isolation of the individual products presents significant technical difficulties.

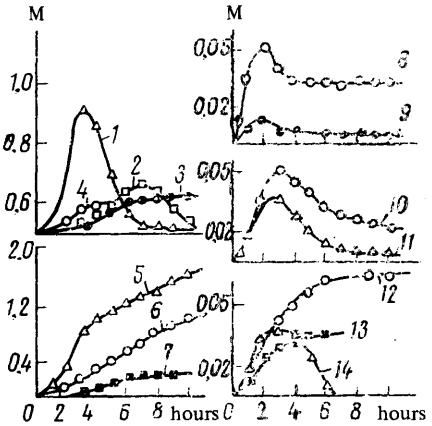
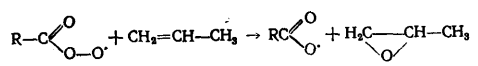


Figure 19. Kinetic curves for the accumulation of propene oxidation products: 1) epoxypropane; 2) propylene glycol; 3) propylene glycol formate; 4) CO_2; 5) formic acid; 6) acetic acid; 7) methyl formate; 8) acetaldehyde; 9) peroxide; 10) isopropyl alcohol; 11) allyl alcohol; 12) acetone; 13) methanol; 14) acrolein.

In the coupled oxidation of propene and acetaldehyde the epoxidation of the double bond proceeds with participation of acylperoxy-radicals formed as a result of the oxidation of the aldehyde[37]:



This reaction has a close analogy with enzymatic oxidation processes, since an oxygen atom is inserted (in a single elementary step) in the molecule of the substance undergoing oxidation with dissociation of the O–O bond. The coupled process proceeds at comparatively low temperatures (50–70°C) and is distinguished by high selectivities in the formation of acetic acid from acetaldehyde (~100%) and of epoxypropane from propene (~100%) (Fig. 20).

The main disadvantage of systems simulating enzymatic oxidation is the consumption of the reductant together with the main process. In many instances the selectivity relative to the unconsumed reductant proves to be very low. Consequently the main task involved in increasing the selectivity of the oxidation reaction is not so much the simulation of enzymatic processes as the creation of new effective catalytic systems which are in general highly effective and do not require the consumption of the second component (the reductant).

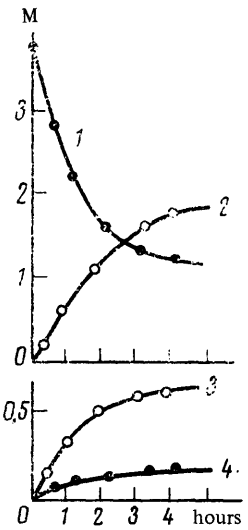


Figure 20. Kinetic curves for the consumption of acetaldehyde (curve *1*) and the accumulation of acetic acid (curve *2*) epoxypropane (curve *3*), and propylene (curve *4*) in the coupled oxidation of propene and acetaldehyde at 50 atm and 70°C.

All the enzymatic and model reactions discussed above involve the dissociation of the O–O bond. Catalytic processes in which oxygen adds via a hydrocarbon (olefin) activation stage are apparently more effective. Here oxygen is transferred to the substrate from water or adds on directly. The oxidation of olefins to carbonyl compounds catalysed by palladium(II) salts using $CuCl_2$ as a cocatalyst is an example of reactions of this type. The selectivity in the formation of low-molecular-weight aldehydes in such a process is >95 mole %.[38] The process develops via the mechanism

$$PdCl_4^{2-} + C_2H_4 + H_2O \rightarrow Pd^0 + CH_3CHO + 2H^+ + 4Cl^-,$$

$$Pd^0 + 2Cu^{2+} + 8Cl^- \rightarrow PdCl_4^{2-} + CuCl_3^-,$$

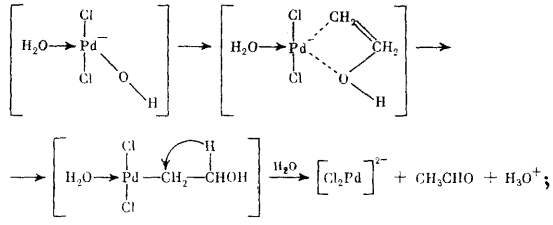
$$2\,CuCl_3^- + 1/2O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 4Cl^-.$$

The overall reaction is

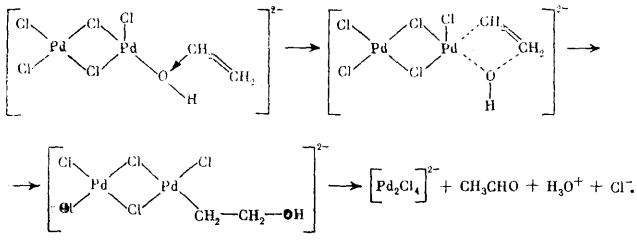
$$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO + 52.26 \text{ kcal mole}^{-1}.$$

A significant factor is the formation in the system of π-complexes $(C_2H_4)PdCl_2(OH^-)$, which undergo further transformations via two possible pathways:

pathway I:



pathway II:



Studies where heteropolyacids of complex composition and containing molybdenum and vanadium ions are used instead of $CuCl_2$ have developed[39]. This makes it possible to eliminate Cl^- ions from the process. The oxidation then proceeds with a high selectivity because of the absence of parallel chlorination reactions in which a considerable proportion of the unreacted hydrocarbon is consumed in the oxidation of higher olefins.

Alcohols and ketones are selectively oxidised to acids in alkaline media in the presence of copper complexes of *o*-phenanthroline (*o*-phen). The oxidation of methanol in the presence of $Cu(o\text{-phen})_2^{2+}$ in alkaline media leads to the formation of formaldehyde and acetic acid at very high rates even at 25–30°C.[40,41] Under the same conditions, certain aliphatic ketones (ethyl methyl ketone) are selectively oxidised to acids[42]. The process develops via the intermediate formation of a complex of the carbanion $CH_3C(O)\bar{C}HCH_3$ (A^-) with $Cu(o\text{-phen})_2^{2+}$:

$$[Cu(o\text{-phen})_2A^-]^+ \rightleftharpoons [Cu(o\text{-phen})_2A\cdot]^+,$$

$$[Cu(o\text{-phen})_2A\cdot]^+ + O_2 \rightarrow [Cu(o\text{-phen})AO_2^-]^+,$$

$$[Cu(o\text{-phen})_2AO_2^-]^+ + [Cu(o\text{-phen})_2]^{2+} + OH^- \rightarrow 2[Cu(o\text{-phen})_2]^+ + 2CH_3COOH.$$

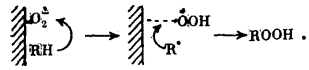
The last two cases may be regarded as examples of oxidation processes which are more favourable from the standpoint of their selectivity than even enzymatic processes.

7. Heterogeneous Catalysis in Oxidation Reactions

The liquid-phase oxidation of hydrocarbons in the presence of heterogeneous catalysts proceeds via two different mechanisms.

I. A heterogeneous-homogeneous process with formation of radicals on the surface of the catalyst and their subsequent transfer to the liquid phase[43–45]. The catalyst merely initiates the chain reaction, the process selectivity remaining the same as in the absence of the catalyst and only the rate of reaction being altered. The liquid-phase oxidation of ethylbenzene in the presence of Ag_2O may serve as an example[46]. The reaction proceeds via a chain mechanism with short chains and the formation of methylphenylmethanol and acetophenone in the chain termination steps. These catalysts are active in the decomposition of the hydroperoxide and the selectivity in the formation of ROOH is as a rule low.

II. A heterogeneous process without the liberation of radicals to the bulk phase[47] may proceed via the mechanism



The formation of the O_2^- species has been demonstrated in gas-phase oxidation in the presence of deposited catalysts and in the liquid-phase oxidation of cumene (Fig. 21).[48,49] The possibility, in principle, of obtaining high yields of peroxides then arises, since such catalysts do not as a rule decompose ROOH and free radicals are not formed in the bulk phase (the hydroperoxide does not decompose via a chain mechanism).

The conditions under which the $RO_2^{\cdot}$ radicals are not released into the bulk phase and hydrocarbons are oxidised on the catalyst surface as a result of the activation of oxygen are achieved by employing the method of the donor–acceptor modification of the catalyst[49]. The catalyst is modified by the introduction of additives to the gas, liquid, and solid phases. This entails a change in both the rate of the process and in its selectivity. When the Ag_2O catalyst is used, electron-accepting properties are shown by oxygen, the hydroperoxide, alcohol, 2,4,6-dicyanomethylenetrinitrofluorenone, etc. The activity of the modified catalysts in relation to the decomposition of the hydroperoxide is highly suppressed and the process selectivity with respect to the hydroperoxide is significantly increased.

Table 5. Selective catalytic systems for the oxidation of aromatic alkyl-substituted hydrocarbons to hydroperoxides.

Catalyst	Additive	S_{ROOH}, mole %	S_{ROH}, mole %	$S_{RC(O)R}$, mole %	*C*, mole %
	Oxidation of ethylbenzene				
Ag_2O	—	20.0	50.0	30.0	1.3
Ag_2O	Cumenyl hydroperoxide (Na salt)	81.0	11.0	8.0	0.5
Ag/Al_2O_3	—	20.0	50.0	30.0	2.5
Ag/Al_2O_3	Acetophenone + methylphenylmethanol	77.0	19.2	3.8	1.8
Ag/Al_2O_3	0.2 at.% Ca	54.5	19.5	26.0	0.6
Ag/Al_2O_3	0.2 at.% Ca + acetophenone + methylphenylmethanol	96.0	3.0	1.0	0.6
	Oxidation of tetralin				
Ag_2O	—	10.0	26.0	64.0	6.0
Ag/SiO_2	—	18.0	36.0	46.0	7.5
Ag/SiO_2	Tetralinol + tetralinone	93.0	2.2	1.8	6.3

Modification also occurs under the influence of the reaction products (Table 5). In this case the process selectivity increases with increased degree of conversion. Thus in the oxidation of tetralin the reaction is non-selective at early stages—the hydroperoxide, ketone, and alcohol accumulate in equal amounts[50]. With increase in the degree of conversion of tetralin, the decomposition of the hydroperoxide ceases and only oxygen is activated on the catalyst modified by the oxidation products, as a result of which tetralinyl hydroperoxide becomes the only reaction product (Table 5).

In order to increase the selectivity of the oxidation process, deposited catalysts are modified. The modification of the Ag/Al_2O_3 deposited catalyst by the addition of calcium makes it possible to increase the selectivity in the oxidation of ethylbenzene to the hydroperoxide from 20 to 54.5 mole %, while modification by the 0.2 at.% Ca–acetophenone–methylphenylmethanol system increases the selectivity S_{ROOH} to 96 mole %.[50]

Heterogeneous catalysis in coupled oxidation[51]. An important parameter of the synthesis of epoxypropane and acetic acid is the "coefficient of the utilisation of active oxygen", i.e. the selectivity in the formation of epoxypropane with respect to the aldehyde which has reacted (γ). In the absence of a catalyst (at 70°C in benzene under a pressure of 50 atm) $\gamma = 0.3$. The use of silver oxide as the heterogeneous catalyst makes it possible to increase γ considerably (Table 6). In this case the process proceeds with participation of complexes formed by peroxy-radicals with the catalyst:

$$CH_3COOO^{\cdot} + Ag_2O \rightleftarrows [CH_3COOO \ldots Ag_2O] \xrightarrow{+C_3H_6} \rightarrow CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_3 + Ag_2O + CH_3COO^{\cdot} \xrightarrow{CH_3CHO} CH_3COOH$$

Table 6. Coupled oxidation of propene and acetaldehyde at 70°C and 50 atm (solvent—benzene).

System	Selectivity, mole %		
	w.r.t. C_3H_6	w.r.t. CH_3CHO	w.r.t. CH_3CHO
	Epoxypropane		Acetic acid
Without catalyst	95.0	23.0	92.0
Ag_2O (1.0 g litre^{-1})	98.0	63.0	96.0

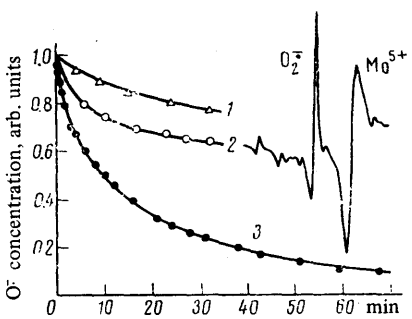
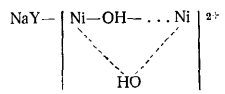


Figure 21. The EPR spectrum of the O_2^- radical-anion detected in the liquid phase on the surface of the Mo(V)/MgO heterogeneous catalyst and kinetic curves for its consumption in various hydrocarbons at 20°C: 1) ethylbenzene; 2) cumene; 3) cyclohexene.

Catalysis of oxidation on zeolites. Nickel-zeolite is a highly effective catalyst of the gas-phase oxidation of methanol by oxygen (350°C).[52] The process selectivity depends on the conditions in the preparation of the catalyst, particularly on the pH of the medium. In acid media the nickel on the zeolite exists in the form of isolated ions ($NaY \ldots Ni^{2+}$). The process on the catalyst then proceeds with formation of dimethyl ether as the main reaction product (acid–base mechanism).

When media close to neutrality (at pH from 7 to 7.6) are used, the nickel on the zeolite exists in the form of the complex



This complex exhibits a high magnetic susceptibility and an oxidation-reduction process proceeds on the catalyst. The presence of the OH group in the catalytic complex facilitates the electron transfer and the formation of formaldehyde and other oxidation products (Fig. 22). Thus, by altering the magnetic susceptibility of the catalyst, it is possible to influence the selectivity of oxidation processes.

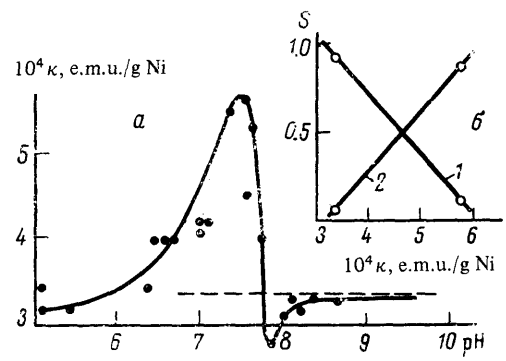


Figure 22. *a*) Dependence of the magnetic susceptibility of nickel (κ) in zeolites on the pH in the ion-exchange process; the dashed line represents the magnetic susceptibility of nickel ions; *b*) selectivity in the conversion of methanol: 1) into dimethyl ether CH_3OCH_3; 2) into oxidation products (CO_2, CO, and formaldehyde) as a function of the magnetic susceptibility of nickel-zeolite.

VII. RADICAL POLYMERISATION PROCESSES

The concept of selectivity applied to polymerisation processes may be considered in two ways: (1) the formation of a definite molecular structure for homopolymers or a definite tacticity, regularity, branching, and inhomogeneity of composition for copolymers; (2) the formation of a product with a specified molecular weight distribution (MWD) and specified average molecular weights (the distribution moments M_N).

The classical mechanism of radical polymerisation includes the following stages:

1. Initiation

$$R_0^{\cdot} + M \rightarrow M_1^{\cdot} .$$

2. Chain propagation:

$$M_n^{\cdot} + M \rightarrow M_{n+1}^{\cdot} ,$$
$$M_n^{\cdot} + X \rightarrow P_n + R_1^{\cdot} \text{ (chain transfer).}$$

3. Chain termination:

$$M_n^{\cdot} + M_m^{\cdot} \rightarrow P_{n+m} \quad \text{(recombination)},$$
$$M_n^{\cdot} + M_m^{\cdot} \rightarrow P_n + P_m \quad \text{(disproportionation)}.$$

The narrowest MWD for the polymer is obtained under isothermal conditions of synthesis and the width of the distribution is determined by the mechanism of the termination of the growing chains. Termination owing to the recombination of radicals leads to the so-called Schultz distribution ($\bar{M}_W/\bar{M}_N = 1.5$), while termination via the disproportionation of radicals leads to the normal distribution ($\bar{M}_W/\bar{M}_N = 2.0$). The reaction involving chain transfer to the monomer, solvent, initiator, etc. leads to an exponential distribution.

The width of MWD in radical polymerisation may be increased by various procedures which may be of practical importance in the industrial synthesis of products with the required physicochemical and rheological properties, provided that the "optimum" properties of the material occur in the region of broad MWD. It appears that this happens in the case of the main thermoplastics synthesised on a large scale: high- and low-density polyethylene, poly(vinyl chloride), and polystyrene. In order to improve the rheological properties of melts of these materials, the MWD must be fairly broad ($\bar{M}_W/\bar{M}_N \geq 2.0$).

1. Regulation of the Rates of Chain Termination in Radical Polymerisation

The classical concept of the mechanism of radical polymerisation as a typical chain reaction in which the chain length is regulated by the rate of chain termination makes it possible to control the polymerisation process by altering the rate of chain initiation[53]. It is also possible to control the elementary stages of the process by the interaction of the monomer and the chain propagation radical with the reaction medium.

The reactivities of monomers and radicals change as a result of their combination with the molecules of the medium. Certain modifying agents may alter the conjugation energy and the distribution of electron densities in the monomer and the radical. If the modifying agents participate in the formation of a transition complex, they naturally influence its energy, configuration, and chemical nature. This changes the free-radical chain propagation mechanism to a complex-radical mechanism. However, the influence of the medium cannot be reduced solely to chemical aspects of the interaction.

Regulation of the rates of chain termination. The use of the gel-effect. The influence of initiating additives. The elementary reaction involving the bimolecular destruction of macroradicals at early stages of homogeneous liquid-phase polymerisation is controlled by physical factors and depends on the physical characteristics of the reaction medium and the macromolecules formed.

The Norrish–Trommsdorff effect (gel-effect—acceleration of radical polymerisation after the accumulation in the system of a sufficient amount of the dissolved polymer) is an example of the dominant influence of physical factors on the kinetics of homogeneous polymerisation processes. The manifestation of the gel-effect is attributed to the aggregation of macromolecules and the formation in the polymerising system of a continuous three-dimensional fluctuation network, in which the macro-radicals are "stuck"[54,55]. This retards the destruction of the active centres via recombination or disproportionation. On the other hand, the active centres are accessible to the monomer molecules and the growth of the polymer chain continues for some time. For high degrees of conversion, the chain propagation reaction passes to the diffusion-dependent region.

The nature of the diffusion-dependent limitations imposed on the elementary reactions in radical polymerisation is determined by the physical characteristics of the macromolecules and the macroradicals and also by the intermolecular interactions in the system. Using the effects associated with the interaction of the monomers and radicals with the reaction medium, it is possible to control the elementary stages of radical polymerisation by means of both chemical and physical factors.

By creating a highly viscous system, by using low monomer concentrations, or by introducing additives which ensure high rates of chain initiation, it is possible to alter the rate of the biradical chain termination. An increase of the concentration of the initiator in the polymerising mixture makes it possible to maintain a specified MWD up to high degrees of conversion of the initial monomer. Such a system may approach "live" (without termination) polymerisation.

2. Polymerisation in the Devitrification of Reaction Mixtures (Supercooled Liquid)

Radical-chain polymerisation processes hardly occur when the system is in the vitreous state owing to the low mobility of the species and the low temperature despite the high concentration of active centres. However, these reactions proceed very effectively when the system passes from the vitreous to the supercooled liquid state. The fairly high viscosity of the supercooled liquid prevents the bimolecular destruction of the active centres and the reaction develops via a "live" chain mechanism (Table 7). The interaction of the reacting centre with the matrix of the monomer (for example, methyl acrylate) plays an important role in the selectivity of such reactions[56,57]. In the devitrification of the alcohol matrix the macroradical has a specific conformation which ensures its long life. As a result, intense polymerisation takes place in the system.

Table 7. Chain propagation rate constants ($cm^3\ s^{-1}$).

Polymerisation	$10^{12} \cdot k_p^0$	E, cal mole^{-1}	$10^9 \cdot k_p^0$	E, cal mole^{-1}	$10^{10} \cdot k_p^0$	E, cal mole^{-1}
	Crystal		Devitrification		Liquid	
Acrylic acid	6	11 000	5	10 700	20	3000
Methyl acrylate	—	—	1	10 000	2	4700
Methyl methacrylate	—	—	Does not polymerise		0.8	4700

Fig. 23 presents the EPR spectra of free polymer radicals obtained on γ-irradiation of frozen solutions of acrylic acid in ethanol (17%), recorded at different temperatures (with a gradual increase of the temperature of the solution). Spectrum I was obtained at 77 K and represents a superposition of the EPR spectra of the radicals $CH_3\dot{C}HOH$ and $CH_3\dot{C}HCOOH$. The stabilised electron also makes some contribution to the structure of the

spectrum. When the specimen is heated to 110 K (supercooled liquid), the radical concentration diminishes (the intensity of the spectrum falls). The EPR spectrum of the radical measured for the same system (spectrum II) consists of five well resolved components with the intensity ratios 1 : 2 : 2 : 2 : 1, which corresponds to the *B* conformation of the radical with the angle $\varphi = 75°$. In this system the interaction between the alkyl group and the COOH(*x*) group is weakened, which is the reason for the long life of the radicals (the formation of "live" radicals). With increase of temperature above 120 K, the polymer chain acquires the capacity for translational migrations. The macroradical coils up and has the usual conformation (*A* in Fig. 23) with the angle $\varphi = 15°$, which corresponds to a triplet EPR spectrum (spectrum III).

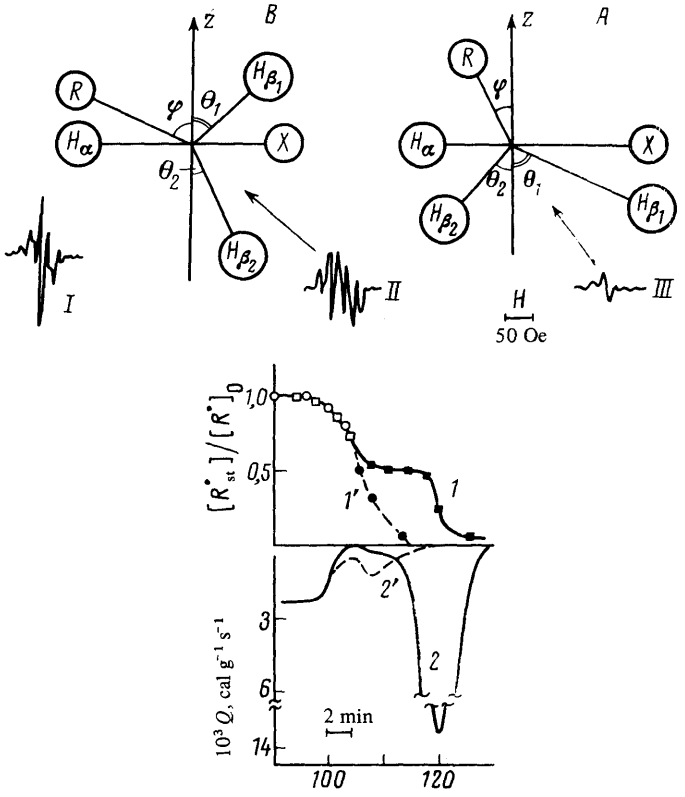


Figure 23. Temperature dependence of the steady-state concentration of radicals (curves *1* and *1'*) and of the rate of polymerisation (calorimetric curves *2* and *2'*) in γ-irradiated frozen solutions of acrylic (curves *1* and *2*) and methacrylic (curves *1'* and *2'*) acids in ethanol: I)–III) EPR spectra arising on heating the γ-irradiated acrylic acid solution in ethanol to 77, 110 (*B* conformation) and 125 K (*A* conformation) respectively.

The polymerisation of acrylic acid at 100–110 K with devitrification of the matrix (i.e. under conditions where "live" radicals are formed in the system) proceeds at very high rates. Curve *2* in Fig. 23 represents the change in the rate of polymerisation measured calorimetrically during the heating of the specimen. After a characteristic "step" associated with the transition to the supercooled liquid state, heat is evolved due to polymerisation. The radical concentration in this temperature range changes only slightly (Fig. 23, curve *1*). In the polymerisation of methacrylic acid the conformation corresponding to "live" radicals is not formed, since the presence of the methyl group prevents the interaction of the radical with the alcohol matrix. The lifetime of the radical is short, the radical concentration decreases monotonically with increase of temperature (Fig. 23, curve *1'*), and the post-polymerisation effect is not observed (Fig. 23, dashed curve *2'*).

In the viscous supercooled liquid formed on devitrification, the duration of mutual contact between the reactants is much longer than in the gas and liquid phases. For this reason, the composition of the copolymer obtained in a viscous supercooled liquid is independent of the relative reactivities of the comonomers and is determined solely by their initial concentrations[58]. The composition of the acrylic acid–acrylamide copolymer does indeed fully correspond to the initial solution on devitrification of the alcohol matrix, while in solution the copolymerisation constants for these monomers are different and the composition of the copolymer differs from that of the initial solution. Thus the method makes it possible to synthesise polymers with a specified homogeneity of composition.

Structure formation by macromolecules. By controlling the macromolecular structure formation processes during the polymerisation, it is possible to exclude fully the reaction involving the destruction of macroradicals and thus pass to an outwardly homogeneous liquid system with radical polymerisation via the "live" chain mechanism[59–63].

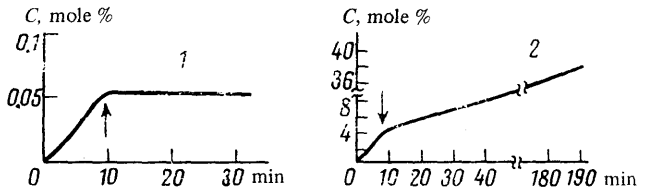


Figure 24. Kinetics of the polymerisation (*C* is the degree of conversion) of methyl methacrylate in bulk (curve *1*) and in a mixture with orthophosphoric acid (curve *2*). The arrow indicates the instant when light was switched off.

It has been shown that in the photoinitiated polymerisation of methyl methacrylate (MMA) in a mixture with orthophosphoric acid the reaction continues, after switch-off the initiation source, at a constant albeit somewhat lower rate up to high degrees of conversion (Fig. 24). The number of chains remains unaltered during post-polymerisation. The reaction proceeds as a result of the accumulation in the "light stage" of poly(methyl methacrylate) (PMMA) macroradicals, which are not involved in the bimolecular termination reaction[59,64,65]. The introduction of another monomer after the exhaustion of the

initial methyl methacrylate leads to the renewal of polymerisation and the formation of block-copolymers[66]. The cause of the preservation of the number of growing chains (macroradicals) in these outwardly homogeneous solutions is the formation of a stable fluctuation network with participation of PPMA macroradicals, strengthened by a network of hydrogen bonds between the $COOCH_3$ groups in the PMMA units and H_3PO_4.

Radical post-polymerisation without termination may be achieved also by the slow heating of vitreous monomers or their mixtures with complex-forming agents subjected to preliminary irradiation at $-196°C$ with γ-rays or ultraviolet light. The post-polymerisation of butyl methacrylate in the presence of $ZnCl_2$ may serve as an example of such a process. These processes may be followed by EPR and calorimetric methods[67]. In the transition through the devitrification regions some of the radicals accumulated as a result of irradiation are destroyed, while the remaining radicals continue to grow and further post-polymerisation proceeds virtually via a mechanism without chain termination.

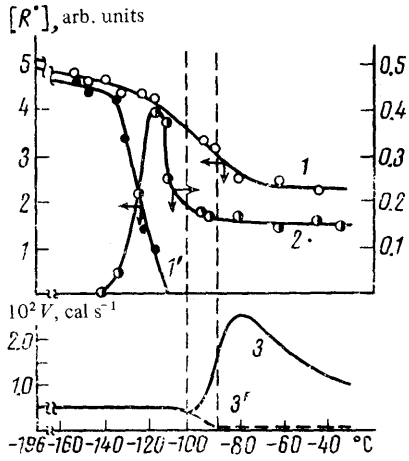


Figure 25. Post-polymerisations in the γ-irradiated butyl methacrylate (BMA)–$ZnCl_2$ system (1 : 0.45). Variation of the concentration of the sum of the radicals (curves *1* and *1′*) and oligomeric $(BMA)_n^{\cdot}$ radicals (curve *2*) and of heat evolution (curves *3* and *3′*) in the system on polymerisation in the presence of $ZnCl_2$ (curves *1–3*) and in the absence of a complex-forming agent (curves *1′–3′*). The dashed lines are the limits of the devitrification region.

The post-polymerisation proceeds with participation of oligomeric radicals. Irradiation of frozen solutions ($-196°C$) of butyl methacrylate (BMA) leads to the formation of monomeric radicals, the EPR spectrum of which consists of seven lines ($\Delta H = 22.5$ G). On raising the temperature to between $-150°$ and $-130°C$, a monomer molecule adds to the radical and oligomeric radicals are produced. The concentration of monomeric radicals falls and oligomeric radicals accumulate in the system. At temperatures between $-130°$ and $-110°C$ the system contains only oligomeric radicals (Fig. 25).

In the range between $-100°$ and $-80°C$ the main bulk of the radicals recombine, but, in contrast to the polymerisation of BMA in the absence of $ZnCl_2$, a steady-state concentration $[(BMA)_n^{\cdot}]$ is established in the system, which ensures rapid post-polymerisation at this temperature. This results in the formation of polymers with a fairly narrow MWD, whose molecular weights are specified by the irradiation dose and are defined by the formula

$$\overline{M}_n = \frac{q[BMA]}{[R^{\cdot}]},$$

where q is the degree of conversion, [BMA] the monomer concentration, and $[R^{\cdot}]$ the concentration of radicals.

Thus one of the problems involved in increasing the selectivity of polymerisation processes, namely the formation of a product with a specified molecular weight distribution, may be solved by influencing the rate of recombination of macroradicals by changing the reaction temperature, irradiation of the solution, or the introduction of complex-forming agents.

Radiation-induced graft polymerisation. Using the influence of the viscosity of the medium on the rate of bimolecular chain termination, it was possible to develop a new method of radiation-induced graft polymerisation[68]. The usual radiation-induced polymerisation of the monomer is comparatively slow or leads to the formation of a polymer with a low molecular weight. If a small polymer "seed" is subjected to preliminary irradiation and then introduced into the monomer, the degree of conversion increases by a factor of several hundred and a polymer with a high molecular weight is formed. The essential feature of the effect is that the radicals formed in the solid "seed" and propagating the polymerisation chain hardly recombine. As a result, the yield of the polymer and its molecular weight increase by several orders of magnitude.

The method has been applied to the synthesis of Teflon by the polymerisation of tetrafluoroethylene[68]. Irradiation of tetrafluoroethylene with a dose of 0.05 Mrad leads to the formation of Teflon with a low yield and a low molecular weight. The employment of a "seed" increases the yield of Teflon by a factor of 200 and its molecular weight by two orders of magnitude.

3. Polymerisation in Continuous Operation Reactors

An important factor influencing the MWD arises when the reactions are carried out in ideal mixing or plug flow reactors[69,70]. The broadening or narrowing of the MWD when the process passes from the periodic to the continuous-operation regime depends under these conditions on the lifetime of the active centre. A criterion of the broadening of the MWD on passing to the continuous-regime is the inequality $\tau_c \ll \tau$, where τ_c is the average lifetime of the active centres and τ the residence time of the species in the ideal mixing reactor. The method used to carry out the reaction also has a regulating effect on the composition of the polymer in copolymerisation.

Whereas the monomers reacting at different rates in a periodic-operation reactor give rise to a variable-composition copolymer, in an ideal mixing reactor the process proceeds at a constant rate, which results in the formation of a copolymer with a homogeneous composition[71]. In certain cases it is useful to carry out the polymerisation in a cascade of reactors with different process regimes.

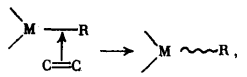
The optimum process conditions are determined in this instance by analysing the kinetic model of the process using mathematical simulation methods.

Such studies have been carried out for the radical polymerisation of styrene in bulk [72]. It was established that the optimum composition of the polymer may be achieved by carrying out the polymerisation in a cascade of reactors consisting of two series-connected ideal mixing reactors, in which the process is carried out in different temperature regimes, and an ideal plug flow reactor with an adiabatic regime.

The MWD of the final product is somewhat narrower compared with the calculated distribution owing to the mechanochemical effects in the extrusion of the melt. This procedure yields a product with $\bar{M}_W/\bar{M}_N = 2.7-3.0$, which is fairly close to the empirically observed "optimum" in the mechanical and rheological properties of a thermoplastic of this type.

4. Homogeneous Catalysis

The molecular weight distribution of the macromolecules may be narrowed by polymerising olefins in the presence of soluble catalysts. In such cases the polymer chain is grown in the coordination sphere of a transition metal:



i.e. the macroradical is linked to the metal throughout the entire polymerisation process. In contrast to purely radical processes, chain termination takes place mainly via unimolecular reactions. The chain-transfer reactions in these processes are inhibited and there is virtually no branching of the macromolecules.

The narrowest molecular weight distributions of polyethylene may be obtained by use of the soluble catalytic systems $(C_2H_5)_2TiCl_2 + AlR_2Cl$, in which the catalytic centres are homogeneous [73,74]. The general polymerisation mechanism can be represented as follows:

$$X^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot},$$
$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot},$$
$$M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot},$$
$$M_j^{\cdot} \xrightarrow{k_t} r_j + X^{\cdot},$$
$$M_j^{\cdot} \xrightarrow{k_d} r_j,$$

where X· and M are the active centre and the monomer and k_i, k_p, k_t, and k_d are the initiation, chain propagation, chain transfer, and chain termination constants. The theoretical form of the molecular weight distribution is defined by the expression

$$L_j = \{M_j + r_j\}_1^{\infty},$$

where M_j and r_j are the concentrations of "live", i.e. growing, and non-growing ("dead") chains. The theoretical MWD may be compared with experimental data using the integral expression [74]

$$\frac{jL_j}{\sum_{j=1}^{\infty} jL_j} \cdot 100 = W_j^{\cdot} = \frac{w_i}{2} + \sum_{\alpha=1}^{j-1} w_\alpha.$$

Calculations have shown that the ratio $\bar{M}_W/\bar{M}_N = 1.8-2.2$. The values obtained agree satisfactorily with the experimental ratios $\bar{M}_W/\bar{M}_N$.

Fig. 26 presents the MWD for polyethylene obtained by radical catalytic polymerisation. Evidently the use of a homogeneous catalyst leads to a sharp narrowing of the MWD, i.e. to an increase of the polymerisation selectivity.

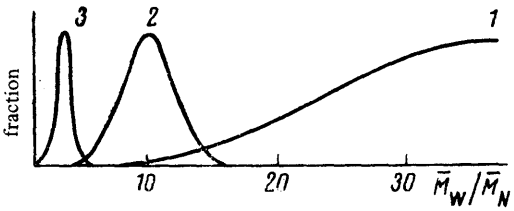


Figure 26. Molecular weight distributions for high-pressure (curve *1*) and medium-pressure (curve *2*) polyethylenes and in catalytic polymerisation in the presence of a homogeneous catalyst (curve *3*).

A narrow molecular weight distribution ($\bar{M}_W/\bar{M}_N \leq 2$) in polypropylene was obtained in a study [75] where propene was polymerised in heptane at low temperatures (between $-20°$ and $-60°C$) in the presence of the $VCl_4 + AlEt_2Cl$ catalytic system, which exists in a homogeneous state under these conditions. With increase of temperature (above $-10°C$), the solid catalyst appeared and the MWD was greatly broadened ($\bar{M}_W/\bar{M}_N$ increased to 30).

Catalysis of radical addition. Regulation of the composition of copolymers. Radical copolymerisation is usually regarded as a statistical process in which the probabilities of the addition of monomers to the growing chain are determined by their concentrations and the nature of the substituent at the double bond. In this case copolymerisation proceeds via the mechanism

$$(1.1)\ m_1^{\cdot} + M_1 \xrightarrow{k_{1.1}} \sim m_1 m_1^{\cdot} (\sim m_1^{\cdot}),$$
$$(1.2)\ m_1^{\cdot} + M_2 \xrightarrow{k_{1.2}} \sim m_1 m_2^{\cdot} (\sim m_2^{\cdot}),$$
$$(2.1)\ m_2^{\cdot} + M_1 \xrightarrow{k_{2.1}} \sim m_2 m_1^{\cdot} (\sim m_1^{\cdot}),$$
$$(2.2)\ m_2^{\cdot} + M_2 \xrightarrow{k_{2.2}} \sim m_2 m_2^{\cdot} (\sim m_2^{\cdot}),$$

where $m_1^{\cdot}$ and $m_2^{\cdot}$ are the terminal units of the growing polymer chain formed by the addition of the molecules M_1 and M_2 respectively; the first subscript in the constants refers to the terminal monomeric unit of the macroradical.

The composition of the copolymer depends on the rate constant ratios $k_{1.1}/k_{1.2} = r_1$ and $k_{2.2}/k_{2.1} = r_2$ and is defined by the formula

$$\frac{d[m_1^{\cdot}]}{d[m_2^{\cdot}]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad . \qquad (20)$$

There exist many binary systems where copolymerisation leads to the formation of copolymers with a rigorous alternation of monomeric units ($m_1m_2m_1m_2$), i.e. the limiting selectivity in the chain propagation reaction is reached. In certain cases this occurs also without the use of any special additives by virtue of the chemical nature of the specific monomer pairs. In particular, α-olefins, certain dienes, and vinyl ethers (M_1) form on radical initiation rigorously alternating copolymers with maleic anhydride, certain other maleic acid derivatives, and SO_2 (M_2).

However, combinations of this kind are more likely to be exceptional. In most instances the reactivities of the monomers do not promote a rigorous alternation of elementary steps of types (1.2) and (2.1) in the mechanism quoted above. In particular, α-olefins, vinyl ethers, and dienes are incapable of forming alternating copolymers with the majority of known monomers. Furthermore, the double bonds in olefins and vinyl ethers are relatively inactive and enter with difficulty into reactions of types (1.2) and (2.1). Their involvement in radical copolymerisation is therefore in general difficult. Finally, an additional obstacle arises in the case of α-olefins—degradative chain transfer to the monomer leading to the formation of relatively inactive radicals of the allyl type and the corresponding sharp decrease of the probabilities of all four chain propagation reactions.

The above complications can be overcome and rigorously alternating copolymers can be obtained from the above monomers of the M_1 group with vinyl monomers of the type CH_2=CHX, where X = COOR, CN, or C(O)R (acrylates, methacrylates, acrylonitrile, etc.) by carrying out the radical copolymerisation in the presence of complex-forming agents—Lewis acids ($AlRCl_2$, $SnCl_4$, $ZnCl_2$, etc.).

It has been shown by a number of methods, in particular by direct observations with the aid of EPR of the sequence of elementary steps (initiation and chain propagation) leading to the formation of the molecules of alternating copolymers, that the polymerisation is in all cases a radical-chain reaction initiated by monoradicals [64]. Depending on the nature of the monomers and the reaction conditions, chain propagation takes place via the consecutive addition of either individual monomers molecules or of donor–acceptor complexes ($M_1 \ldots M_2$) to the growing chain radical via the mechanism

$$(1.2)\quad \sim m_1^{\cdot} + M_2 \xrightarrow{k_{1,2}} \sim m_1 m_2^{\cdot},$$

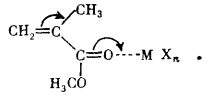
$$(2.1)\quad \sim m_2^{\cdot} + M_1 \xrightarrow{k_{2,1}} \sim m_2 m_1^{\cdot},$$

$$(1.2\ c)\quad \sim m_1^{\cdot} + (M_2 \ldots M_1) \xrightarrow{k^c_{1,2}} \sim m_1 m_2 m_1^{\cdot},$$

$$(2.1\ c)\quad \sim m_2^{\cdot} + (M_1 \ldots M_2) \xrightarrow{k^c_{2,1}} \sim m_2 m_1 m_2^{\cdot}.$$

The copolymerisation of maleic anhydride with 2,3-dimethylbutadiene [67,76] and phenyl vinyl ether [64], of methyl methacrylate with 2,3-dimethylbutadiene in the presence of $Al(C_2H_5)_2Cl$, [67,76,77] etc. are examples of systems where reactions (1.2) and (2.1) predominate. Chain propagation takes place via the addition of donor–acceptor complexes of the comonomers [reaction (1.2c) and 2.1c)] in the copolymerisation of SO_2 with 2,3-dimethylbutadiene or vinyl acetate [76] and of maleic anhydride with butyl vinyl ether [64]. All types of chain propagation reactions coexist simultaneously in many instances (copolymerisation of maleic anhydride with vinyl acetate [64,79]).

The mechanism of copolymerisation in the presence of Lewis acids includes the formation of a complex of the Lewis acid with free polymeric radicals ($\sim m_1^{\cdot}$ or $\sim m_2^{\cdot}$) or monomers [80–82]:



The formation of complexes of free radicals with $AlCl_3$, $AlBr_3$, etc. has been demonstrated by EPR on the basis of the systematic changes occurring in the EPR spectra of radicals in the presence of these compounds [80] (Figs. 27*A* and 27*B*).

Quantum-mechanical calculations have shown that donor–acceptor interactions between the radical and the species which adds to it lower the free energy of formation of the transition complex in the reactions

$$\sim m_1^{\cdot} + M_2 \rightarrow (\sim m_1 \ldots M_2) \rightleftarrows (\sim m_1^{-} \ldots M_2^{+}) \rightarrow \sim m_1 m_2^{\cdot}$$

or

$$\sim m_1 + (M_2 \ldots M_1) \rightarrow (\sim m_1 \ldots M_2^{\cdot} \ldots M_1) \rightleftarrows (\sim m_1^{-} \ldots M_2^{+} \ldots M_1) \rightarrow \rightarrow \sim m_1 m_2 m_1^{\cdot}.$$

Table 8. Copolymerisation of butyl methacrylate with 2,3-dimethylbutadiene in the presence of Lewis acids.

Initiator	Temp., °C	$\frac{[MX_n]}{[M_1]}$	r_1	r_2	$r_1 r_2$
		$MX_n = ZnCl_2$			
[ABIBN] = 0.005 M	50	0	0.45±0.01	0.47±0.03	0.212
		0.15	0.23±0.05	0.41±0.10	0.094
		0.25	0.10±0.01	0.40±0 03	0.040
		$MX_n = Al(C_2H_5)_2Cl$			
u.v. (λ > 313 nm)	15	0.10	0.11±0.042	0.048±0.036	0.0053
		0.25	0.058±0 018	0.013±0.015	0.0007
		0.15	0.044±0.027	0.010±0.024	0.004

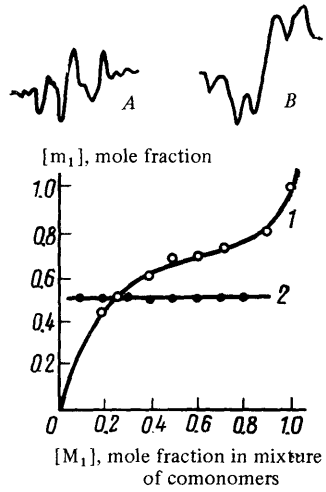


Figure 27. Copolymerisation of butyl methacrylate (M_1) with 2,3-dimethylbutadiene (M_2) at 23 °C in the presence of $Al(C_2H_5)_2Cl$ for different $[Al(C_2H_5)_2Cl]/[M_1]$ ratios: 1) 0.10; 2) 0.55; *A* and *B* are the EPR spectra of the polymeric radical $\sim m_1^{\cdot}$ and the complex $[\sim m_1^{\cdot} \ldots AlBr_3]$ for $[AlBr_3]/[M_1] = 1$.

As a result of the increase of the rate constants $k_{1,2}$ and $k_{2,1}$, the quantities r_2 and r_1 (see above) decrease with increased concentration of the complex-forming agent, which in this case actually behaves as the selective catalyst of radical addition (Table 8). For very low values of r_1 and r_2 ($r_1 \rightarrow 0$ and $r_2 \rightarrow 0$), the ratio of the monomeric units m_1 and m_2 in the copolymer is according to Eqn. (20)

$$d[m_1]/d[m_2] = 1 \quad \text{and} \quad [\overline{m_1}] = [\overline{m_2}],$$

and a fully alternating copolymer is formed regardless of the initial concentrations of the comonomers in solution. Fig. 27 illustrates the dependence of the copolymer composition (the fraction of m_1) on the composition of the mixture of comonomers in the copolymerisation of butyl methacrylate (M_1) with 2,3-dimethylbutadiene (M_2) in the presence of $Al(C_2H_5)_2Cl$.[80] With increase of catalyst concentration, there is an increase in the selectivity of the copolymerisation. For fairly high values of $[Al(C_2H_5)_2Cl]$, it is possible to attain conditions under which a fully alternating polymer is formed $\{[m_1] = [m_2] = 0.5\}$ over a wide range of monomer content M_1 in the mixture (from 5 to 95%). Alternating copolymerisation via reactions (1.2c) and (2.1c) is the limiting case of non-statistical radical processes.

It has been observed[64] in the copolymerisation of SO_2 with buta-2,3-diene that the nature of the terminal unit of the growing radical is specified by the nature (donor–acceptor properties) of the initiating radical and does not change in the course of chain propagation. Depending on the type of initiating radical, the radicals $\sim SO_2^{\cdot}$ and $\sim CH_2-\underset{CH_3}{\overset{\cdot}{C}}=\underset{CH_3}{\overset{\cdot}{C}}-CH_3$, which propagate two independent polymerisation chains, can therefore exist in different proportions. In the case under consideration, the introduction of the catalyst enhances the differences between the reactivities of the radicals in relation to the comonomers (r_1, $r_2 \to 0$ after the addition of the catalyst).

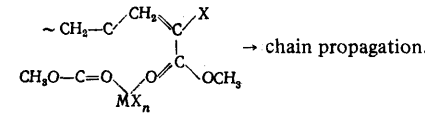
In the copolymerisation of monomers having functional groups of the same type (for example, COOR) in the presence of Lewis acids there is a possibility of another limiting case—the "disappearance" of the differences between the reactivities of the monomers in the chain propagation reaction ($r_1 \to 1$ and $r_2 \to 1$). This effect was observed in the copolymerisation of methyl methacrylate with methyl acrylate in the presence of $ZnCl_2$ and $AlBr_3$[83] and was subsequently confirmed in certain other systems[64].

Table 9. Copolymerisation of methyl methacrylate (M_1) with methyl acrylate (M_2) in the presence of complex-forming agents at 50°C.

Initiator	$\frac{[MX_n]}{[M_1]+[M_2]}$	r_1	r_2
	$MX_n = ZnCl_2$		
[ABIBN] = 0.005 M	0	2.23±0.13	0.36±0.1
	0.15	1.33±0.03	0.70±0.03
	0.45	0.90±0.03	0.90±0.09
	$MX_n = AlBr_3$		
u.v. (λ > 313 nm)	0.075	1.75±0.04	0.78±0.05
	0.15	1.11±0.04	0.91±0.1
	0.40	0.96±0.05	0.96±0.11

Table 9 lists the effective constants for the copolymerisation of methyl methacrylate (M_1) with methyl acrylate (M_2) in the presence of $ZnCl_2$ and $AlBr_3$.[83] When the catalyst MX_n is added, the composition of the copolymer, initially relatively enriched in M_1 units, approaches that of the mixtures of the monomers and becomes virtually identical with it when $[MX_n]/\{[M_1] + [M_2]\} = 0.2-0.5$; under these conditions, the effective copolymerisation constants are $r_1 = r_2 = 1$ (Fig. 28).

The equalisation of the relative activities of the comonomers following the introduction of complex-forming agents can be naturally accounted for within the framework of the hypothesis that chain propagation proceeds via a stage involving a cyclic transition complex with simultaneous coordination of the radical and the monomer to the MX_n molecule:



The mutual approach and appropriate orientation of the reaction centres of the monomer and the radical promote rapid addition. The probability of addition virtually ceases to depend on the true reactivities of the radical and the monomer. The mechanism of chain propagation in radical homo- and co-polymerisation in systems of this kind is in principle analogous to the typical mechanisms of coordination-ionic polymerisation. The stability of the complex of the modifying agent and the terminal unit of the growing radical increases owing to the delocalisation of the unpaired electron of the radical to the metal ion in MX_n.[80] The resulting possibility of the migration of MX_n with retention of the complex at the terminal unit of the growing chain increases the analogy with coordination-ionic polymerisation still further.

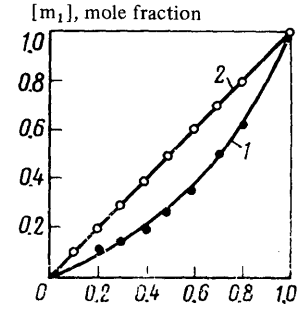


Figure 28. Copolymerisation of methyl methacrylate (M_1) with methyl methacrylate (M_2): 1) in the absence of complex-forming agent; 2) after the introduction of zinc chloride; $[ZnCl_2]/\{[M_1] + [M_2]\} = 0.25$; temperature 50°C.

5. The Influence of Magnetic and Electric Fields

An urgent problem in polymer chemistry is the synthesis of stereoregular and crystalline polymers. The selective formation of highly oriented polymers in radical polymerisation is promoted by the preliminary structural organisation of the medium in which the process is carried out, which may be achieved by applying a magnetic field or by the fixation of the monomeric liquid-crystal structure.

Fig. 29 presents the diffraction patterns for polymers obtained by the radical polymerisation of acryloyloxybenzoic acid in the liquid crystal phase (curve *1*) and in isotropic solution in heptyloxybenzoic acid (curve *2*).[84] Curve *1* is characterised by a series of sharp diffraction maxima. The degree of crystallinity of the polymer is 40% according to X-ray diffraction data, while polymerisation in solution leads to the formation of a polymer with an amorphous structure.

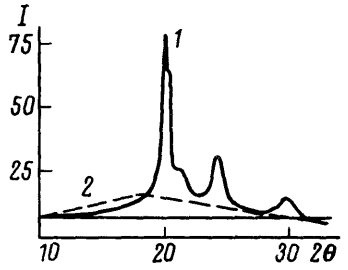


Figure 29. Diffractometer traces for polyacryloyloxybenzoic acid specimens obtained in the radical polymerisation of heptyloxybenzoic acid in bulk (curve *1*) and in solution in the monomer (curve *2*).

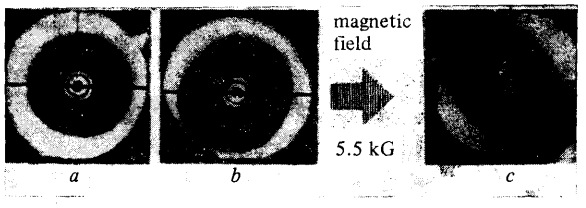


Figure 30. X-Ray diffraction patterns for the polymer of 4-n-hexyloxyphenyl 4'-acryloyloxybenzoate obtained by polymerisation from the isotropic phase (*a*), the liquid-crystal phase (*b*), and the liquid-crystal phase with application of a 5.5 G permanent field (*c*).

In the polymerisation of 4-n-hexyloxyphenyl 4'-acryloyloxybenzoate it was possible to obtain polymers with a high degree of orientation of the macromolecules by employing the intrinsic orientation order in the liquid crystal phase of the monomer as well as a magnetic field of 5.5 kG.[85] X-Ray diffraction patterns for the polymer obtained by radical polymerisation from the isotropic phase (*a*), the liquid-crystal phase (*b*), and the liquid-crystal phase with application of a steady magnetic field (*c*) are presented in Fig. 30.[85] The presence of denser regions on the diffraction rings indicates an increase in the anisotropy (degree of axial orientation of the macromolecules) of the specimens on passing from *a* to *c*. The polymer formed exhibits only axial orientation.

Magnetic and electric fields make it possible to influence the microstructures of polymeric specimens. Fig. 31 illustrates the changes in the isomeric composition of polybutadiene on polymerisation of butadiene under the influence of a magnetic field with the specimen (20% of butadiene in benzene) irradiated by ultraviolet light[86]. Dibenzothiazolyl sulphide was used as the sensitiser. Evidently, the polybutadiene obtained by polymerisation in the absence of a field contains ~30% of the *trans*-1,4-form. When a 5 kG magnetic field is applied, the content of *trans*-1,4-polybutadiene increases to 50%.

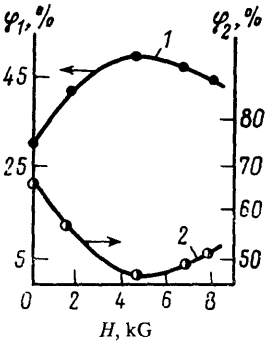


Figure 31. The influence of the magnetic field on the microstructure of polybutadiene formed on photochemical polymerisation at 25°C; sensitiser—dibenzothiazolyl sulphide (φ_1 and φ_2 are the yields of *cis*- and *trans*-polybuta-1,4-dienes).

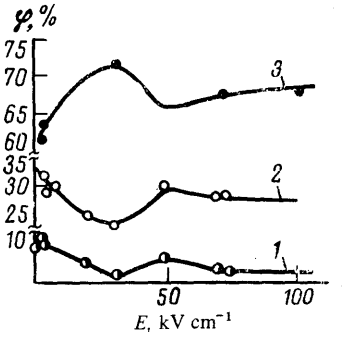


Figure 32. The contents of isotactic (curve *1*), heterotactic (curve *2*), and syndiotactic (curve *3*) triads in the polymerisation of methyl methacrylate in a permanent electric field at 60°C; initiator—azobisisobutyronitrile.

The mechanism of the phenomenon apparently includes the formation of an intermediate complex of the isomerising molecules with the free radical produced on photolysis of the sensitiser. The C=C bonds in the *trans*-position in the complex are ruptured and there are singlet–triplet transitions in the radical pairs. The role of the magnetic field is additional removal of the singlet–triplet degeneracy of the Zeeman interaction energy and an increase in

the probability of the *cis–trans* isomerisation through the triplet state via an adiabatic pathway.

The application of a permanent electric field, like that of a magnetic field, can influence strongly the tacticity of the poly(vinyl acetate) formed in the polymerisation reaction [87]. Fig. 32 illustrates the influence of the electric field on the stereoregularity of the poly(vinyl acetate) formed by radical polymerisation in the presence of azobisisobutyronitrile as the radical initiator at 60°C. A sharp increase of the tacticity of the polymer is seen at an electric field strength of ~30 kV cm^{-1}.

The above examples suggest that magnetic and electric fields are promising factors whereby the selectivity of polymerisation processes may be influenced.

6. Thermodynamic Properties of the Monomer and the Formation of the Crystal Structure of the Polymer

Changes in the thermodynamic properties of monomer solutions (concentration, solvent, and temperature) may alter the crystal structure of the resulting polymer. At high concentrations of the monomer (for example, trioxan) macromolecules with a high molecular weight are formed in solution.

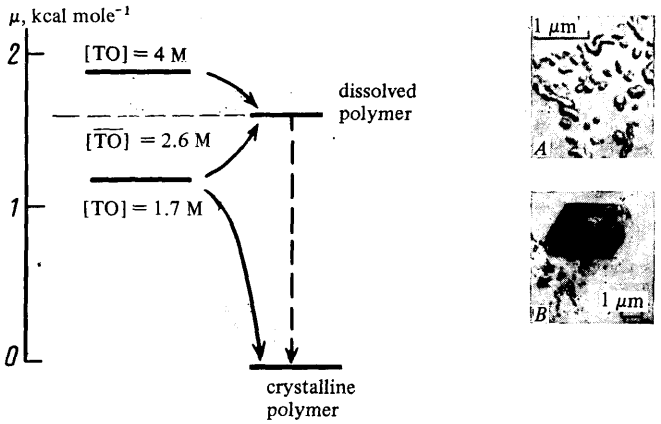


Figure 33. Thermodynamics of the polymerisation of trioxan; *A* and *B*—specimens of crystals formed on crystallisation of trioxan from solutions with [TO] > [$\overline{TO}$] and [TO] < [$\overline{TO}$]; {[$\overline{TO}$] = 2.6 M}.

Fig. 33 shows that the thermodynamic potential of trioxan (TO) in methylene chloride at a concentration of 4 M exceeds that of the polyformaldehyde macromolecule in this medium. The final product is formed in two stages—the macromolecule is formed initially and this is followed by its crystallisation from solution. At low concentrations of the monomer its thermodynamic potential is lower than that of the dissolved polymer molecule. The polymer molecules formed do not dissolve as the chain length increases and give rise to the solid crystalline phase almost immediately. Because of this, a crypto-crystalline polymer is formed in the former case, while in the latter case large crystals are produced (Fig. 33). [88,89]

The thermodynamic potentials of the polymer and the monomer also vary under the influence of temperature and the nature of the solvent.

Thus there are new possibilities for a thermodynamic approach to the regulation of the supermolecular structure of the polymer. The reaction is carried out under conditions close to the polymer ⇌ monomer equilibrium position. It is found that the formation of a polymer with an undesirable structure is thermodynamically impossible under these conditions.

7. Polymerisation Under the Influence of Shock Waves

The usefulness of shock waves in polymerisation reactions of many organic compounds has been demonstrated in recent years [90]. When a shock wave passes through solid organic monomers, even substances which do not undergo polymerisation under the usual conditions do polymerise (for example, benzene) [91]. The reaction is carried out in special "storage containers", the design of which makes it possible to protect substances subjected to compression by shock waves from decomposition (Fig. 34). Under these conditions, polymerisation is observed only at shock wave pressures exceeding a threshold value. The degree of reaction during the passage of the shock wave and the threshold polymerisation amplitude depend on the nature of the monomer.

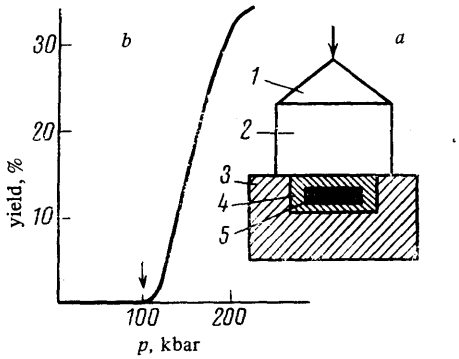


Figure 34. *a*) Schematic illustration of polymerisation under the influence of a shock wave: 1) generator of a planar detonation wave; 2) explosive; 3) housing; 4) container; 5) monomer; 6) dependence of the yield of polyacrylamide on the shock wave pressure. The arrow indicates the threshold pressure.

The use of shock waves makes it possible to obtain polymers with a much higher molecular weight than in the usual polymerisation. Thus, in the polymerisation of trioxan in a shock wave, the molecular weight of the polymer reaches 1.3×10^6, while in catalytic polymerisation it is 10^5. Depending on the conditions, polymerisation in a shock wave makes it possible to synthesise polymers with different structures.

The mechanisms of polymerisation in a shock wave cannot be reduced to a simple combination of compression and heating and apparently involves a new specific type of influence. The application of shock waves may be regarded as one of the possible factors for increasing process selectivity.

VIII. RADICAL PROCESSES IN THE CRACKING OF HYDROCARBONS

The selectivity in the formation of products in the cracking of hydrocarbons is determined by their structure. In paraffins and isoparaffins the difference between the energies of primary, secondary, and tertiary C–H bonds is as a rule small (390–410 kJ mole^{-1}). The energy of the C–C bond is virtually constant along the hydrocarbon skeleton (330–340 kJ mole^{-1}), its value being slightly higher only for the abstraction of terminal methyl groups (350–360 kJ mole^{-1}).[92] For this reason, the process at low temperatures (up to 500°C) is non-selective and leads to the formation of a wide range of products, for example[92a]:

(0) $CH_3-CH_2CH_2-CH_3 \rightarrow 2C_2H_5^{\cdot}$,

(0′) $CH_3-CH_2CH_2-CH_3 \rightarrow CH_3^{\cdot} + C_3H_7^{\cdot}$,

(2.1) $C_2H_5^{\cdot} + C_4H_{10} \rightarrow C_2H_6 + C_4H_9^{\cdot}$,

(2.2) $CH_3^{\cdot} + C_4H_{10} \rightarrow CH_4 + C_4H_9^{\cdot}$,

(2.3) $C_3H_7^{\cdot} + C_4H_{10} \rightarrow C_3H_8 + C_4H_9^{\cdot}$,

(2.4) $C_2H_5^{\cdot} \rightarrow H^{\cdot} + C_2H_4$,

(2.5) $C_3H_7^{\cdot} \rightarrow CH_3^{\cdot} + C_2H_4$,

(2.6) $H^{\cdot} + C_4H_{10} \rightarrow H_2 + C_4H_9^{\cdot}$,

(2.7) $CH_3-\dot{C}H-CH_2CH_3 \rightarrow C_3H_6 + CH_3^{\cdot}$,

(2.8) $\dot{C}H_2-CH_2-CH_2CH_3 \rightarrow C_2H_4 + C_2H_5^{\cdot}$,

$C_2H_5^{\cdot}, C_3H_7^{\cdot}, C_4H_9^{\cdot} \rightarrow$ chain termination.

1. The Influence of Temperature and Reactant Concentrations on Selectivity in Cracking

It is seen from the overall cracking mechanism that free radicals are transformed via several pathways in the chain propagation stages: unimolecular decomposition via reactions (2.4) and (2.5) and bimolecular interaction with the initial substance via reactions (2.1) and (2.3). Individual elementary stages are characterised by different activation energies, so there is the possibility, in principle, of altering the ratios of the rates of parallel elementary stages by changing the temperature (the selectivity is influenced via the value of α).

In the cracking of butane, the processs selectivity is determined by the competition between reactions (2.4) and (2.5), which lead to the formation of ethylene, and between reactions (2.1) and (2.3), which lead to the accumulation in the system of low-molecular-weight alkanes as side products. Table 10 presents the rate constants for these elementary stages[92].

The rate ratios $w_{2.4}/w_{2.1}$ and $w_{2.5}/w_{2.3}$, calculated using the above constants, increase with temperature and, when $t > 800$°C and the butane concentration in the gas phase $[C_4H_{10}] \simeq 10^{-3}$ mole cm^{-3}, the rate of the unimolecular decomposition of alkyl radicals is significantly greater than the rates $w_{2.1}$ and $w_{2.3}$ of the bimolecular conversion of $C_2H_5^{\cdot}$ and $C_3H_7^{\cdot}$ respectively. A decrease in the concentration of butane (for example, by diluting it with an inert gas) decreases the temperature at which the conditions $w_{2.4} > w_{2.1}$ and $w_{2.5} > w_{2.3}$ hold. Thus it is possible to increase the selectivity in the cracking of butane to ethylene by raising the temperature and by diluting butane with an inert gas. This procedure is used in industry, where pyrolytic processes, designed to obtain ethylene, are carried out at high temperatures and with dilution by steam.

Table 10. The rate constants for the chain propagation reactions in the cracking of butane.

Reaction	lg k_0 (cm^3 mole^{-1} s^{-1})	E, kJ, mole^{-1}	Reaction	lg k_0 (cm^3 mole^{-1} s^{-1})	E, kJ, mole^{-1}
(2.1)	2.0	42	(2.4)	14.2	126
(2.3)	9.8	40	(2.5)	15.4	142

2. Coupled Cracking. Transfer of the Reaction to a New Pathway

The transfer of the reaction to a new chain pathway by coupling processes makes it possible to alter the nature and activity of the radicals propagating the main chain and hence the selectivity in the cracking process. This principle has been used to increase the selectivity in the cracking of piperylene. At 650–700°C the cracking of piperylene proceeds with formation of cyclopentadiene (the selectivity $S_C \simeq 30$ mole % relative to the unconsumed piperylene) and butadiene ($S_b = 50$ mole %) (Table 11) and involves the mechanism[93]

$C_5H_8 \rightarrow C_5H_7^{\cdot} + H^{\cdot}$,

(1.1) $C_5H_7^{\cdot} + C_5H_8 \xrightarrow{k_{1.1}} C_5H_9^{\cdot} + C_5H_6$,

(2.1) $H^{\cdot} + C_5H_8 \xrightarrow{k_{2.1}} C_5H_9^{\cdot}$,

(0.1) $C_5H_9^{\cdot} \xrightarrow{k_{0.1}} CH_3^{\cdot} + C_4H_6$ (butadiene),

(3.1) $CH_3^{\cdot} + C_5H_8 \xrightarrow{k_{3.1}} C_5H_7^{\cdot} + CH_4$,

$(CH_3^{\cdot}, C_5H_9^{\cdot}, C_5H_7^{\cdot}) \rightarrow$ chain termination.

The introduction of hydrogen into the reaction causes the replacement by hydrogen atoms of the $CH_3^{\cdot}$ radicals whose subsequent transformation leads to the formation of cyclopentadiene. As a result, the unit of the cracking chain consisting of the sequence of reactions (1.1), (0.1), and (3.1) is replaced by the sequence of reactions (2.1), (0.1), and (3.2):

(3.2) $CH_3^{\cdot} + H_2 \xrightarrow{k_{3.2}} CH_4 + H^{\cdot}$.

Table 11. The selectivity in the cracking of piperylene.

System	S_C, mole %	S_b, mole %	System	S_C, mole %	S_b, mole %
In the absence of H_2	30	50	In the presence of added H_2	10	70

This change in the pathway increases the process selectivity with respect to butadiene (Table 11). When account is taken of the reaction involving chain transfer by $CH_3^{\cdot}$

radicals [reaction (3.2)], the above mechanism of the cracking of piperylene makes it possible to obtain expressions for the integral selectivity S_b in the formation of butadiene.

According to Eqn. (2a), the differential selectivity in the formation of butadiene is

$$\sigma_{C_4H_6} = \frac{k_{0.1}[C_5H_9^{\cdot}]}{k_{1.1}[C_5H_7^{\cdot}] + k_{2.1}[H] + k_{3.1}[CH_3^{\cdot}]} \quad . \qquad (21)$$

By expressing the concentrations of all the active centres in terms of the concentration of $CH_3^{\cdot}$ radicals and assuming that the chain is long, we find

$$[C_5H_7^{\cdot}] = k_{3.1}[CH_3^{\cdot}]/k_{1.1};\ [H^{\cdot}] = \frac{k_{3.2}[H_2]}{k_{2.1}[C_5H_8]}[CH_3^{\cdot}];$$

$$[C_5H_9^{\cdot}] = \frac{k_{3.1}[C_5H_8] + k_{3.2}[H_2]}{k_{0.1}}[CH_3^{\cdot}] \quad .$$

On substituting the values obtained in Eqn. (21), we obtain an expression relating the differential selectivity with respect to butadiene to the concentrations of the initial substances C_5H_8 and H_2:

$$\sigma_{C_4H_6} = (k_{3.1}[C_5H_8] + k_{3.2}[H_2])/(2k_{3.1}[C_5H_8] + k_{3.2}[H_2]) \quad .$$

In the absence of hydrogen S_b is independent of C and is equal to 0.5. As the hydrogen concentration increases, the differential process selectivity rises from 1/2 to 1. There is a corresponding change also in the integral selectivity. In the presence of hydrogen

$$S_b(C) = \frac{1}{2}\left[1 - \frac{k_{3.2}[H_2]_0}{2k_{3.1}[C_5H_8]_0 C}\ln\left(1 - \frac{2k_{3.1}[C_5H_8]_0 C}{k_{3.2}[H_2]_0 + 2k_{3.1}[C_5H_8]_0}\right)\right].$$

With increase of the degree of conversion, S_b changes from

$$S_b = \frac{1}{2}\left(1 - \frac{k_{3.2}[H_2]_0}{k_{3.2}[H_2]_0 + 2k_{3.1}[C_5H_8]_0}\right)$$

for very low degrees of cracking ($C \to 0$) to

$$S_b = \frac{1}{2}\left(1 - \frac{k_{3.2}[H_2]_0}{2k_{3.1}[C_5H_8]_0}\ln\left[1 - \frac{2k_{3.1}}{k_{3.2}}\left(\frac{[H_2]_0}{[C_5H_8]_0} + \frac{2k_{3.1}}{k_{3.2}}\right)^{-1}\right]\right)$$

for the degree of conversion $C = 1$. For example, calculation showed that, for the rate constant ratio $2k_{3.1}/k_{3.2} = 0.5$ and an equimolar mixture of piperylene and hydrogen $\{[H_2]_0/[C_5H_8]_0 = 1\}$, the process selectivity $S_b = 0.85$, while in the absence of hydrogen $S_b = 0.5$ regardless of the degree of conversion of the hydrocarbon, since both products—butadiene and cyclopentadiene—are formed simultaneously in the first stage of the chain unit [reaction (1)] when $[H_2O]_0 = 0$. Thus in the presence of added hydrogen there is an increase also of the integral process selectivity with respect to butadiene. This result is consistent with the data in Table 11. Consequently the procedure involving the introduction of hydrogen makes it possible to increase the process selectivity S_b with respect to butadiene and to decrease the selectivity S_c with respect to cyclobutadiene. The selectivity with respect to cyclobutadiene may be increased by introducing hydrogen atom acceptors (for example, HCl). In many instances the cracking of ethane coupled with the main process may be used as a source of hydrogen atoms.

The mechanism of the cracking of a toluene–ethane mixture [94] may be formulated in the following form:

$$H^{\cdot} + C_6H_5CH_3 \to CH_3^{\cdot} + C_6H_6,$$
$$CH_2^{\cdot} + C_6H_5CH_3 \to CH_4 + C_6H_5CH_2^{\cdot},$$
$$2C_6H_5CH_2^{\cdot} \to C_6H_5CH_2{-}CH_2C_6H_5,$$
$$C_2H_6 + C_6H_5CH_2^{\cdot} \to C_6H_5CH_3 + C_2H_5^{\cdot},$$
$$C_2H_5^{\cdot} \to C_2H_4 + H^{\cdot},$$
$$CH_3^{\cdot} + CH_3^{\cdot} \to C_2H_6.$$

The competitions between the fourth and fifth reactions determines the yield of biphenyl and that between the first two reactions determines the yield of benzene. Enrichment of the mixture in ethane leads to an increase in the concentration of hydrogen atoms and hence of the yield of benzene formed by the interaction of hydrogen atoms with toluene. The selectivity in the cracking of toluene to benzene increases (Table 12). The increase of the cracking selectivity with respect to styrene is association with the reactions

$$C_6H_5CH_2^{\cdot} + CH_3^{\cdot} \to C_6H_5C_2H_5 \to C_6H_5CH{=}CH_2 + H_2,$$
$$C_6H_5^{\cdot} + C_2H_4 \to C_6H_5C_2H_4^{\cdot} \to C_6H_5CH{=}CH_2 + H^{\cdot},$$
$$C_6H_5^{\cdot} + C_2H_3^{\cdot} \to C_6H_5CH{=}CH_2.$$

In the absence of ethane C_2H_4 and $C_2H_3^{\cdot}$ are not formed in appreciable amounts during the reaction.

Table 12. The selectivities in the formation of the main products of the coupled cracking of toluene (mole %; 840°C; contact time in flow system 0.1 s).

Cracking product	Toluene	43:57 toluene–ethane mixture (wt.%)	32:68 toluene–H_2 mixture (wt.%)
Benzene	45	70	98
Styrene and methylstyrene	13	20	1
Bibenzyl	20	2	—

IX. HALOGENATION OF HYDROCARBONS

The chlorination of hydrocarbons constitutes a sequence of chain reactions involving the chlorination of the initial hydrocarbon and its various chloro-derivatives formed during the process. The hydrocarbon chlorination processes have as a rule a low selectivity and proceed via the mechanism [95,96]

$$Cl_2 \to 2Cl^{\cdot},$$
$$RCH_3 + Cl^{\cdot} \to RCH_2^{\cdot} + HCl,$$
$$RCH_2^{\cdot} + Cl_2 \to RCH_2Cl + Cl^{\cdot},$$
$$RCH_2^{\cdot} + HCl \to RCH_3 + Cl^{\cdot},$$
$$RCH_2Cl + Cl^{\cdot} \to RCH_2^{\cdot} + Cl_2,$$
$$Cl^{\cdot} + Cl^{\cdot} + M \to Cl_2 + M,$$
$$Cl^{\cdot} + RCH_2^{\cdot} \to RCH_2Cl,$$
$$RCH_2^{\cdot} + RCH_2^{\cdot} \to \text{molecular products},$$
$$Cl^{\cdot} \to \text{destruction on the wall},$$
$$RCH_2Cl + Cl_2 \to RCHCl_2^{\cdot} + HCl.$$

When there is a possibility of the parallel formation of several positional isomers in the system owing to the similar reactivities of the primary, secondary, and tertiary C–H bonds (390–410 kJ mole^{-1}), it is extremely difficult to alter the ratio of the isomers (and hence to increase the process selectivity with respect to one of the isomers, i.e. to alter the quantity $\alpha = k_i/\Sigma k_j$). The ratio of positional isomers as a rule assumes the statistical value. The small differences between the strengths of the primary, secondary, and tertiary C–H bonds in the hydrocarbon chain have almost no influence on the isomer ratio owing to the high reactivity of Cl atoms. However, the selectivity of the chlorination reaction may be significantly

increased by carrying out the latter in solution and by reducing thereby the reactivity of chlorine atoms as a result of complex formation with the solvent. Chlorine atoms with a reduced reactivity are capable of "distinguishing" the C–H bonds in different positions, although the energies of the latter still do not differ greatly. The ratio of monochloro-derivatives (primary, secondary, and tertiary), formed at early stages in chain chlorination reactions, is determined by the rate constants for the reactions:

$$\mathrm{RCH(CH_3)CH_2CH_3} + \mathrm{Cl}\cdot \begin{cases} \xrightarrow{k_3} \mathrm{R\dot{C}(CH_3)CH_2CH_3} \\ \xrightarrow{k_2} \mathrm{RCH(CH_3)\dot{C}HCH_3} \\ \xrightarrow{k_1} \mathrm{RCH(CH_3)CH_2\dot{C}H_2} \end{cases}$$

$$S_{-CH_2Cl} = k_1/(k_1+k_2+k_3),$$
$$S_{>CHCl} = k_2/(k_1+k_2+k_3),$$
$$S_{>CCl} = k_3/(k_1+k_2+k_3),$$

i.e. $S_{-CH_2Cl} : S_{>CHCl} : S_{>CCl} = k_1 : k_2 : k_3$.

It has been established experimentally that the use of different solvents, forming complexes with atomic chlorine and reducing its reactivity, leads to a greater process selectivity. Table 13 lists the rate constant ratios for the elementary steps in the interaction of chlorine atoms with C–H bonds in alkanes and aromatic alkyl-substituted hydrocarbons. Evidently, when the reaction is carried out in a solvent, the rate constant ratio increases sharply. The ratio k_3/k_1 for 2,3-dimethylbutane increases from 6 to 225 in CCl_4 (at 25 °C) and from 3.7 to 18.4 (at 55 °C) in anisole, i.e. when the reaction is carried out in a complex-forming solvent, the relative rate of the interaction of Cl with the t-C–H bond increases compared with the reaction involving the primary bond. There is a corresponding increase of the selectivity in the formation of 2-chloro-2,3-dimethylbutane. (In this calculation no account was taken of the possibility of further chlorination of the monochloro-derivatives.)

The regulating influence of the solvent increases with increase of its concentration owing to the shift of the equilibrium

$$\mathrm{Cl}\cdot + \mathrm{SH} \rightleftarrows \mathrm{Cl}\cdot\mathrm{SH}$$

towards the formation of the complex.

Table 13. The relative rate constants for the abstraction by a chlorine atom of tertiary and primary hydrogen atoms from 2,3-dimethylbutane (k_3/k_1) and α- and β-hydrogen atoms from aromatic hydrocarbons (k_α/k_β) in chlorination by molecular chlorine at 55 °C.[96]

Solvent	k_3/k_1	k_α/k_β		Solvent	k_3/k_1	k_α/k_β	
	2,3-dimethylbutane	ethylbenzene	cumene		2,3-dimethylbutane	ethylbenzene	cumene
Without solvent	3.7	14.5	42.2	Anisole	18.4	—	—
Without solvent	6.0*	—	—	Chlorobenzene	27.5*	—	—
t-Butyl alcohol	4.8	—	—	Benzene	49.0*	—	—
1,4-Dioxan	5.6	—	—	Carbon disulphide	225.0*	—	—
Nitrobenzene	4.9	2.7	5.2				

*Chlorination temperature 25 °C.

1. Selectivity of the Halogenation Reaction at Low Temperatures

By carrying out the reactions at low temperatures, it is possible to obtain high selectivities because of the possibility of increasing the sensitivity of the reaction to the energetic parameters of different stages[97]. It is possible to obtain the desired product in a high yield even for very low differences between the activation energies for the main and side reactions (ΔE). For example, in the parallel reactions

$$\mathrm{A} \begin{cases} \xrightarrow{k_1} \mathrm{P_1}\ (k_1 = k_{10}e^{-E_1/RT}), \\ \xrightarrow{k_2} \mathrm{P_2}\ (k_2 = k_{20}e^{-E_2/RT}) \end{cases}$$

with $E_1 - E_2 = \Delta E = 3$ kcal mole^{-1} (750 J mole^{-1}) and the pre-exponential factor ratio $k_{10}/k_{20} = 5$, the ratio of the selectivities in the formation of P_1 and P_2 is

$$\frac{S_{P_1}}{S_{P_2}} = \frac{k_1}{k_2} = \frac{k_{10}}{k_{20}}e^{-\Delta E/RT} = 5\cdot e^{-3000/RT}.$$

At 300 °C the ratio $S_{P_1}/S_{P_2} = 1.42$, so that $S_{P_1} = 0.59$ and $S_{P_2} = 0.41$ (the process is non-selective). In the same case at 100 K we have $S_{P_1}/S_{P_2} = 0.114$, $S_{P_1} = 0.10$, and $S_{P_2} = 0.90$, i.e. a high selectivity with respect to P_2 is achieved.

The wide-scale use of low temperatures has been retarded hitherto by the conviction that below 250 K the rates of chemical reactions are extremely low. However, studies in the last two decades have disproved this view. Many processes involving halogens occur at very high rates at 77–100 K, for example. Fig. 35 shows that the liquid-phase chlorination of olefins at low temperatures is faster than in the gas phase. Even in the solid phase at ~100 K, the reaction proceeds at appreciable rates. The selectivity data for the reaction between ethylene and Cl_2 illustrated in Fig. 35 show that substitution processes are completely suppressed at low temperatures, i.e. processes involving the dissociation of the C–H bond are altogether absent and high quantitative yields of 1,2-addition products are obtained.

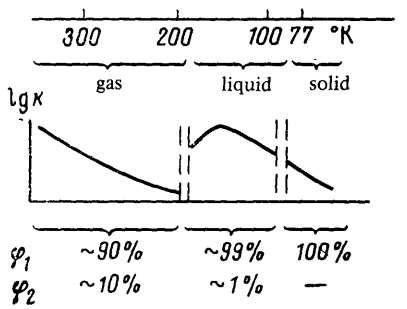


Figure 35. Chlorination of olefins in the gas phase, a supercooled liquid, and in the solid phase; k—rate constant for the dark reaction; φ_1 and φ_2—yields of addition and substitution products respectively.

The mechanism of the low-temperature reaction may be represented as follows:

$$\mathrm{C_2H_4} + \mathrm{Cl_2} \rightleftarrows \mathrm{C_2H_4\cdot Cl_2}\ (\Delta H \leqslant 10\ \mathrm{kJ\ mole^{-1}}),$$

this being followed by the molecular rearrangement

$$\mathrm{C_2H_4\cdot Cl_2} \rightarrow \text{cyclic transition state} \rightarrow \mathrm{C_2H_4Cl_2}$$

and the chain process

$$C_2H_4 \cdot Cl_2 \rightarrow C_2H_4Cl^{\cdot} + Cl^{\cdot} \rightarrow C_2H_3Cl + HCl.$$

The selective course of the process is associated with the involvement in the reactions of molecular complexes capable of a synchronous rearrangement under certain conditions to the reaction products or active radical species. The chain mechanism of the process at low temperatures is to a large extent suppressed owing to energy-dependent selectivity (based on the differences between the activation energies). When the low-temperature reaction is carried out in a solvent with pronounced complex-forming properties (HCl), the radical-chain component can be almost completely suppressed.

In liquid HCl, the process develops via the mechanism

$$Cl_2 + HCl \rightleftarrows Cl_2 \cdot HCl,$$
$$Cl_2 \cdot HCl + C_2H_4 \rightleftarrows (C_2H_4 \cdot Cl_2 \cdot HCl) \rightarrow C_2H_4Cl_2 + HCl.$$

Its activation energy is $E = 10-20$ kJ mole^{-1}.

The yield of the 1,2-dichloro-derivative is limited by the purity of the reactants and may be raised to 100%. In reactions with participation of halogens in non-polar media a negative temperature coefficient is frequently obtained. This effect can be accounted for by the occurrence of rapid reversible stages, in particular, complex formation stages. The activation energy for a consecutive reaction

$$A + B \overset{K}{\rightleftarrows} A \cdot B \overset{k}{\rightarrow} P,$$

where $K = K_0 e^{-\Delta H/RT}$ ($\Delta H < 0$) and $k_0 e^{-E/RT}$ ($E > 0$), is the sum of the positive activation energy E and the negative enthalpy of complex formation ΔH: $E_{obs} = E - |\Delta H|$. If $|\Delta H| > E$, a negative temperature coefficient is observed. The reaction proceeds with acceleration as the temperature is reduced to a value T_{max}, after which the rate begins to fall. The relation between T_{max} and E and ΔH is given by the equation

$$\frac{1}{T_{max}} = \frac{4.57}{|\Delta H|} \lg\left(\frac{|\Delta H| - E}{E}\right) + \frac{\Delta S}{|\Delta H|}.$$

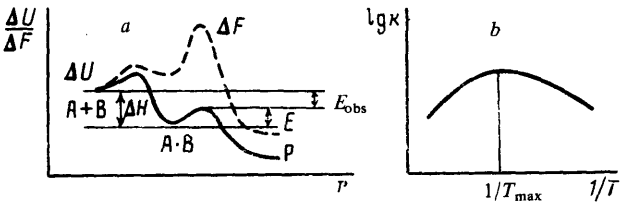
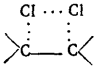


Figure 36. *a*) Reaction pathway characterised by a negative temperature coefficient (continuous line) and variation of ΔF in this process (dashed line); *b*) temperature variation of the rate constant for the reaction proceeding via the formation of a complex; T_{max} corresponds to complete binding of the components in the complex.

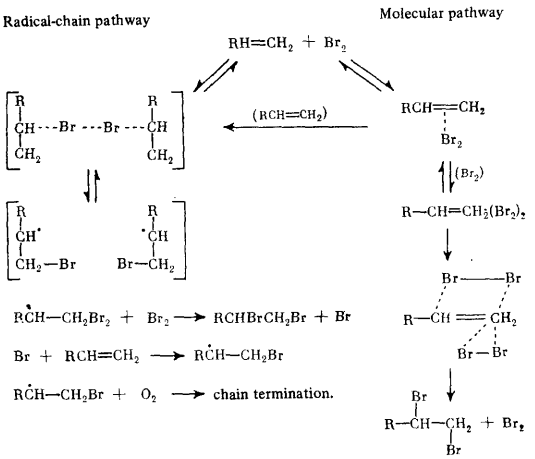
Fig. 36 illustrates the "energy–reaction pathway" scheme for a process with $E_{obs} < 0$ (the activation energy E_{obs} is an effective value). The reaction proceeds via this pathway when the complex AB (Fig. 36) is converted into the product via a cyclic transition state, for example



in the chlorination of olefins.

A high negative activation entropy is characteristic of processes of this kind, as a result of which the potential energy well for this type of transition state lies below the energy level of the initial molecules and $E_{obs} < 0$. When the temperature is reduced rapidly, the reactants are completely bound in an extremely stable complex AB. Many systems are known for which negative values of E_{obs} have been found: chlorine–olefin, bromine–olefin, iodine chloride and bromide–olefins, bromine–α-hydroxycyclopropanes, bromine–arylcyclopropanes, NOCl–epoxides, etc. The values of E_{obs} for the above processes are in the range between 0 and 60 kJ mole^{-1} and the maximum rate of the process is reached at 230–170 K. Thus there is a possibility of carrying out many reactions at high rates even at very low temperatures. Cryochemistry leads to new possibilities for selective reaction conditions.

In reality the interpretation of the nature of the negative temperature coefficient in halogenation is more complex[97]. At low temperatures energy-dependent selectivity is accompanied also by selectivity based on mechanisms in principle associated with the energetics of parallel reactions. The bromination of olefins at room temperature takes place simultaneously via two pathways:



The process may proceed via a synchronous rearrangement of the 2 : 1 bromine-olefin complex (molecular pathway). The existence of such complexes has been demonstrated experimentally and their structure has been confirmed by quantum-mechanical calculations. The rate in the molecular olefin transformation pathway is

$$w_m = k' [RCH=CH_2][Br_2]^2 \quad (E'_{obs} = -15 \div -30 \text{ kJ mole}^{-1}).$$

On the other hand, the synchronous process involving the dissociation and formation of bonds in the complex may lead to the formation of radicals (the radical-chain pathway). The rate in the radical-chain pathway is

$$w_c = k [RCH=CH_2]^2 [Br_2]^3.$$

The mechanism of the chain process involves reversible stages, for example, the reaction of bromine atoms with an olefin molecule:

$$Br + CH_2=CHR \rightleftarrows [Br \cdot CH_2=CHR].$$

For this reason, a negative temperature coefficient is also observed in the radical-chain reaction and is greater than in the molecular reaction. Depending on the nature of the group R, the activation energy E_{obs} varies from -20 to -60 kJ mole^{-1}. The ratio of the rates in the radical-chain and molecular pathways of the reaction with olefins is proportional to the olefin concentration:

$$w_c/w_m = (k/k') \cdot [RCH{=}CH_2].$$

The two processes give rise to different products (Table 14). By reducing the temperature and increasing the olefin concentration, it is possible to isolate the radical pathway, while the addition of inhibitors makes it possible to isolate the molecular pathway. Thus by altering the experimental conditions, one can isolate selectively the different pathways in the low-temperature halogenation reactions. Table 14 presents as an example data for the bromination of hex-1-ene. Analogous results were obtained in the chlorination of olefins and in reactions of halogens with epoxides and arylcyclopropanes.

Table 14. Hex-1-ene bromination products at 300 K (% of sum of products formed via a given pathway).

Product	Molecular pathway	Radical pathway
$CH_2BrCHBr(CH_2)_3CH_3$	97	50
$CH_2BrCH{=}CH(CH_2)_2CH_3$	3	34
$CH_2{=}CH{-}CH{-}Br(CH_2)_2CH_3$	—	12
$CHBr{=}CH(CH_2)_3CH_3$	—	4
$CH_2{=}CBr(CH_2)_3CH_3$		

The pathways in the low-temperature reactions can be additionally regulated by introducing complex-forming additives or solvents into the system. A high selectivity in additive chlorination has been noted when the reaction was carried out in liquid HCl. The role of the additive usually reduces to binding electron-accepting species (halogen atoms and molecules) in a complex, reducing their electrophilic properties, and increasing the process

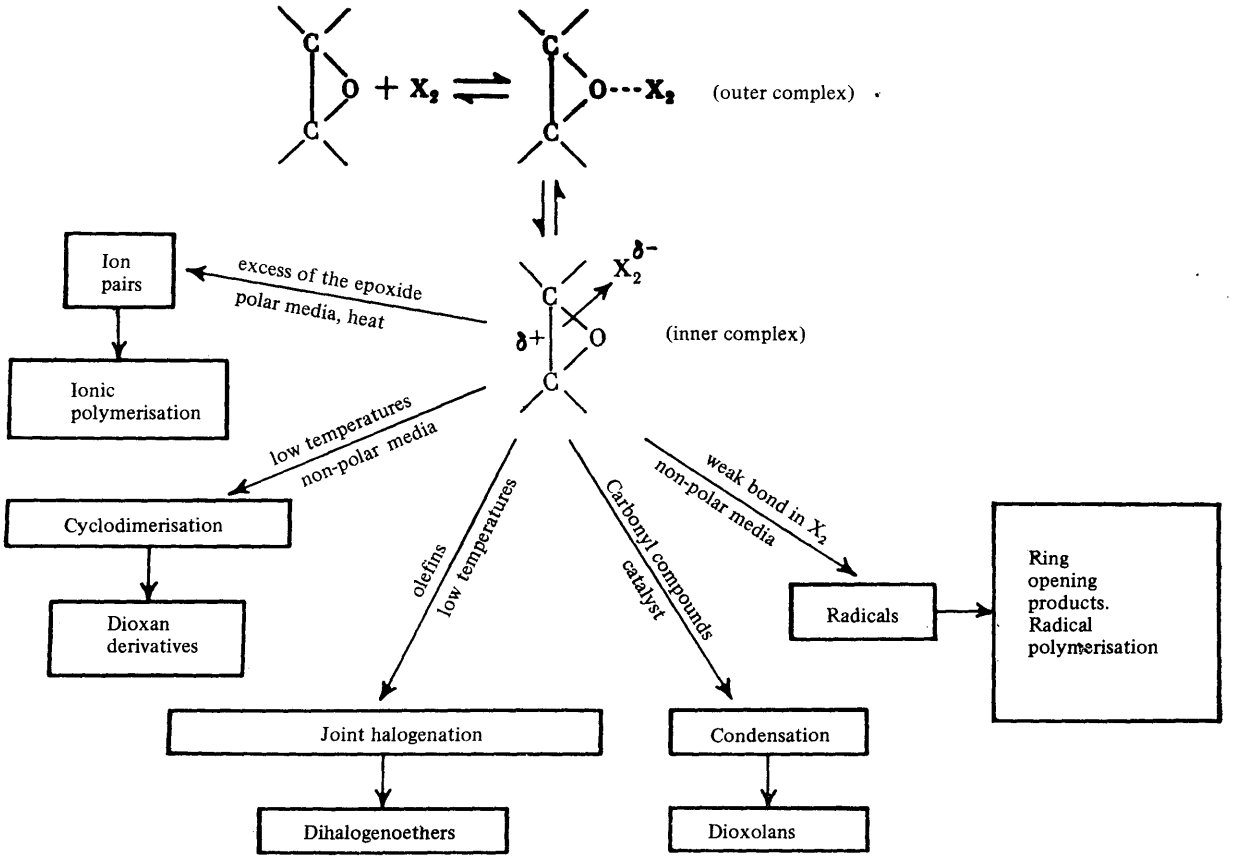


Figure 37. Reaction pathways in the halogen (X_2)–epoxide system.

selectivity. Selection based on different mechanisms can be achieved with the aid of complex-forming agents. Thus the addition of electron-donating compounds in the bromination of hex-1-ene suppresses the radical-chain pathway and makes it possible to obtain selectively the 1,2-addition product. The role of complex formation in energy-dependent selection was examined by Russell[98] as early as the 1960s. At low temperatures, where the energy-dependent selection is manifested most strikingly, these effects become particularly appreciable. When additive and substitutional chlorination of alkanes and chloroalkanes is carried out at 200–230 K in the presence of, for example, aromatic additives, 100% selectivity may be achieved.

The reactions of halogens with epoxides involve complex formation at the obligatory initial stage. Subsequent reaction of the complex proceeds via different pathways depending on the conditions: ionic polymerisation, molecular cyclodimerisation, and a radical-chain reaction involving the opening of the epoxide ring. In the presence of a third component (olefin, carbonyl compound, etc.) there is also a possibility of competition between the ionic, molecular, and radical mechanisms[99,100] (see the scheme in Fig. 37).

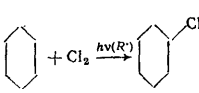
By varying the temperature and experimental conditions within wide limits, it is possible to isolate the molecular, radical, or ionic pathway in the halogenation reaction virtually in any system and hence one can obtain the product or the sum of products corresponding to only one of the possible pathways.

On transition of the system from the liquid to the frozen state, a new effective factor becomes available for controlling the rate and mechanism of the chemical reaction.

2. Catalytic Chlorination of Hydrocarbons

A common procedure for increasing the selectivity in radical reactions involves the introduction into the initiating systems of catalysts (organic or inorganic compounds), which behave as electron or ligand transferring agents. This approach does not always lead to the desired results, since the free radical in solution interacts not only with the catalytic transferring agent but also with other components of the medium.

A new approach to the solution of the problem of the selective synthesis of chloroalkanes involves carrying out the reactions under conditions where the reactants interact via the formation of radicals stabilised in the coordination sphere of a metal. It has been found that many halogen-containing iron compounds, where the metal ions exist in different oxidation states, for example hexakisacetonitrileiron(II) bis(tetrachloroferrate) $\{[Fe(II)\cdot(CH_3CN)_6][Fe(III)Cl_4]_2\}$, as well as other iron complexes, containing dimethylformamide or dimethyl sulphoxide as the neutral ligand, exhibit a high catalytic activity in the synthesis of chloroalkanes and make it possible to obtain different chloro-derivatives with a high selectivity[101]. The catalytic effect of dinuclear iron complexes has been demonstrated in chlorination by molecular chlorine, for example, in the reaction



and, when other chlorinating agents are used (for example, CCl_4):

$$CH_2{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2{-}CH_2)_nCl \text{ or}$$

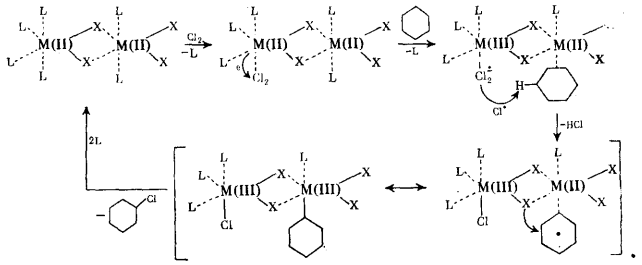
$$CH_2{=}CH{-}CH{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2{-}CH{=}CH{-}CH_2)_mCl\ .$$

Depending on the conditions under which it is synthesised and isolated and the conditions in the course of the catalytic reaction, the complex $[Fe(II)(CH_3Cl)_6][Fe(III)Cl_4]_2$ undergoes an intramolecular electronic transition, which leads to the formation of two different forms of Fe(II):

$$[Fe(II)L_6]\cdot[Fe(III)X_4]_2 \rightleftarrows [Fe(III)L_6]\cdot[Fe(II)X_4]\cdot[Fe(III)X_4] \rightleftarrows$$
$$\rightleftarrows [Fe(II)L_6] + [Fe(III)L_6] + [Fe(II)X_4] + [Fe(III)X_4]\ ,$$
$$[Fe(II)X_4] + [Fe(II)L_6] \rightleftarrows [Fe(II)L_6]\cdot[Fe(II)X_4]\ ,$$
$$[Fe(II)L_6][Fe(II)X_4] \rightleftarrows L_4Fe(II)X_2Fe(II)L_2X_2\ ,$$
$$(X{=}Cl;\ L = CH_3CN;\ (CH_3)_2NCHO;\ \text{or}\ (CH_3)_2SO)\ .$$

In the presence of catalysts containing at least two Fe(II) atoms the chlorination reactions proceed via the intermediate formation of the radical-anions Cl_2^- and CCl_4^- in the coordination sphere of the metal.

After the transfer of the ligand to the substrate (cyclohexane, ethylene, and butadiene) coordinated to a neighbouring metal atom or after the elimination of a hydrogen atom, the reactions proceed via the formation of a metal–carbon bond or a radical resonance-stabilised in the coordination sphere of the metal. The close proximity of the reacting species in the coordination sphere of a dinuclear bridge complex increases sharply the process selectivity or leads to the appearance of new chlorination pathways. Thus, in the chlorination of cyclohexane the selectivity in the formation of the monochloro-derivative via the radical-chain mechanism does not exceed 80 mole %. In the presence of catalysts of the above type the selectivity in the formation of cyclohexyl chloride reaches 98–99 mole %.[101] The process involves the formation of $C_6H_{11}^{\cdot}$ radicals, bound in a complex, via the mechanism

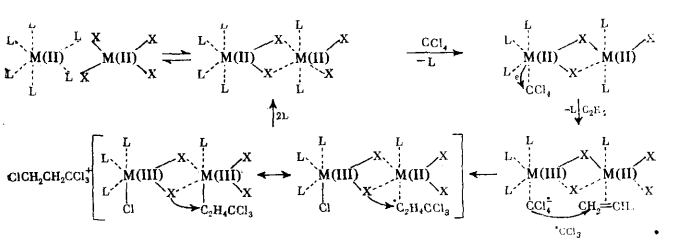


The chlorination of ethylene by carbon tetrachloride involves the reaction

$$CH_2{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2CH_2)_nCl$$

in which products with n = 1, 2, and 3 are formed.

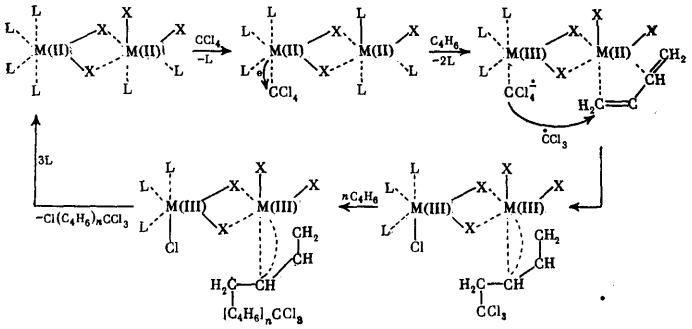
The use of a catalyst makes it possible to increase the selectivity in the formation of 1,1,1,3-tetrachloropropane (n = 1) from 30 to 95%. The catalytic process takes place in the coordination sphere of the metal, preventing the formation of isomers in which the number of carbon atoms is more than 3 ($n > 1$):



In the chlorination of butadiene[102] by CCl_4,

$$CH_2{=}CH{-}CH{=}CH_2 + CCl_4 \rightarrow Cl(CH_2CH{=}CHCH_2)_nCCl_3$$

the use of a catalyst leads to the formation of a chlorine-containing oligobutadiene—1,1,1,21-tetrachlorohene-icosane-3,7,11,15,19[$CCl_3(C_4H_6)_5Cl$, $n = 5$] with a selectivity of 95 mole %:



In the absence of the catalyst the above product is not formed at all.

It is seen from the examples quoted that the use of catalysts which propagate the process via an inner sphere mechanism in the coordination sphere of the metal constitutes an extremely effective procedure for altering the selectivity of chlorination reactions.

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