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CATALYSIS BY SALTS OF METALS OF VARIABLE OXIDATION STATE IN LIQUID-PHASE OXIDATION REACTIONS

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INTRODUCTION

The catalysis of the oxidation of organic substances by the addition of compounds of variable-valency metals is an important section of chemical kinetics. The mechanism of this catalysis includes elementary stages which are typical of ionic and radical reactions. We are therefore dealing with the border-land between the two most important types of chemical reactions: those in which ions take part, and free-radical processes. This type of catalysis has particular theoretical interest and practical significance for the stimulation of slow branched-chain reactions (processes with degenerate branching).

The catalysts normally used in the oxidation of hydrocarbons are the salts of organic acids with such metals as cobalt, manganese, iron, copper, chromium, lead, and nickel. The salt catalysts are widely used in laboratory practice and in various industrial processes. Potassium permanganate, for instance, is used as catalyst for the oxidation of paraffins by atmospheric oxygen in the production of fatty acids; cobalt and manganese acetates are used as catalysts for the oxidation of acetaldehyde to acetic acic and anhydride. The catalysts permit oxidation at a lower temperature, i.e., under milder conditions, and so decrease the development of more extensive oxidation processes. The study of the mechanism of such processes is also of undoubted interest in biochemistry, since such metals are components of many enzymes. For instance, the cytochromes (enzymes which take part in tissue respiration) contain iron.

A large number of investigations on the catalysis of liquid-phase oxidation reactions by metals of variable oxidation state have been reported in the last ten years. These experimental data provide the general outlines of the mechanism of the action of salt catalysts in the oxidation of aldehydes and hydrocarbons.

The acceleration of certain oxidation-reduction reactions by salts of iron and copper has long been known[1]. In 1931 Haber and Willstätter[2] based the mechanism of the action of ions of variable oxidation state on chain oxidation and decomposition reactions. They introduced the concept of the elementary reaction between the ion and the reacting compound, in which the oxidation state of the ion changes and a free radical is formed. This radical then commences the chain reaction. This mechanism was proved 20 years later by Bawn and coworkers[3-6] in the oxidation of aldehydes, which is catalysed by cobalt salts. The mechanism of salt catalysis proved much more complex in the oxidation reactions of hydrocarbons: after taking part in the oxidation reaction, the catalyst reacts with the oxidised products, causing the process to take place in several successive stages. Tsyskovskii and Kiseleva[7] showed that in the oxidation of kerosene, the catalyst accelerates the reaction only at its outset, and is then precipitated and does not

further affect the course of the oxidation. The present authors have studied the mechanism of the catalysis of the oxidation of n-decane and cyclohexane by cobalt and manganese salts[8-12].

In the absence of a catalyst, the autooxidation of hydrocarbons takes place by means of degenerate-branching chain reactions[13]. In the pure hydrocarbon free radicals may be formed by reaction with oxygen:

$$RH + O_2 \rightarrow R\cdot + HO_2^{\cdot},$$

$$2RH + O_2 \rightarrow 2R\cdot + H_2O_2.$$

Each radical causes a chain in which hydrocarbon and oxygen molecules form the hydroperoxide[14]:

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

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

With a dissolved-oxygen concentration greater than 10^{-3} M (when the partial pressure of oxygen is above 100 mm Hg) the radicals R· are very rapidly converted into peroxide radicals, so that $[R\cdot] \ll [RO_2^{\cdot}]$. The breaking of the chain therefore takes place as a result of collision and reaction between two peroxide radicals, e.g., by the reaction[15]

$$2R_1R_2CHOO\cdot \rightarrow R_1COR_2 + R_1R_2CHOH + O_2.$$

From time to time the hydroperoxide formed decomposes into free radicals by the reactions

$$ROOH \rightarrow RO\cdot + \dot{O}H,$$

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

At a sufficiently high temperature this method of formation of free radicals (degenerate branching of chains) becomes predominant in the reaction. When considering the action of catalysts on the oxidation of hydrocarbons, it is therefore necessary to bear in mind the possible occurrence of the above elementary reactions. The action of catalysts has a number of special features. The main property of a catalyst is its ability to initiate chains, i.e. to create free radicals in the reaction zone. It is also necessary to take into account the ability of the catalysts to break chains. There are cases where the action of catalysts may be likened to an initial "push" of the branched-chain process, after which the further presence of the catalyst in the reaction zone becomes unnecessary. There are also many cases where a change in the properties of the catalyst and the loss of its activity leads to a decrease in the rate of reaction. Sometimes the catalyst influences the composition of the oxidation products. The mechanisms of these phenomena will be reviewed here.

INITIATION OF CHAINS BY CATALYSTS

The uncatalysed oxidation of hydrocarbons usually proceeds with a self-accelerating effect and with a typical period of induction. Catalysts of variable oxidation state as a rule accelerate the oxidation and reduce the induction period, for instance cobalt, chromium, and manganese naphthenates in the oxidation of cyclohexane[16] and cobalt acetate in the oxidation of tetralin[17]. In the oxidation of cyclohexane in the presence of cobalt stearate at 130°, the more catalyst is introduced, the shorter the induction period[10]. Salt catalysts sometimes slow down the oxidation; these cases will be considered later.

The accelerating action of catalysts of variable oxidation state is due to their ability to generate free radicals. The

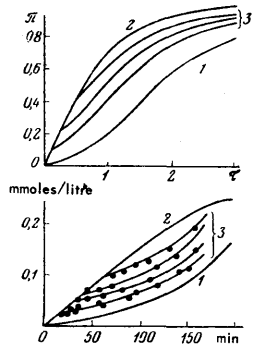


Fig. 1. Kinetic curves for the accumulation of the intermediate in oxidation: 1) without a catalyst; 2) with a catalyst; 3) with removal of the catalyst from the reaction zone. Upper figure — theoretical curves constructed from formulae (I) – (II) with $\omega_0 = 1$. Lower figure — kinetics of the accumulation of cyclohexanone at 130°, using 0.06 mole% of St_2Co.

direct participation of the catalyst in chain initiation is demonstrated by experiments in which the catalyst dissolved in the hydrocarbon is removed from the reaction zone[10] (the cobalt catalyst precipitates on cooling partially oxidised cyclohexane, and the oxidation continues after filtration).

Fig.1 shows kinetic curves for the accumulation of cyclohexanone (an intermediate in the oxidation of cyclohexane) in experiments in which the cobalt catalyst was removed from the reaction zone; after such removal, the rate of accumulation of cyclohexanone immediately falls. These results support the view that the catalyst is an agent which ensures a high rate of formation of free radicals. To demonstrate this, consider a simple mechanism for the oxidation as a degenerate-chain reaction with a single intermediate. Let the initial reactant RH be converted by a chain mechanism into the intermediate product P at a rate $k_2[RH]n$, where n is the concentration of free radicals. The product P decomposes by the chain mechanism at a rate $k_3[P]n$ and produces degenerate branching of the chains at a rate $k_4[P]$. The catalyst sets up a constant high rate of chain-initiation W_0. With quadratic termination of the chains, the stationary concentration of free radicals is

$$n = \left(\frac{W_0 + k_4[P]}{2k_6}\right)^{1/2},$$

where k_6 is the rate of quadratic termination of chains. The rate of accumulation of P in the presence of the catalyst is described by the differential equation

$$\frac{d[P]}{dt} = (k_2[RH] - k_3[P])\left(\frac{W_0 + k_4[P]}{2k_6}\right)^{1/2}.$$

Converting to dimensionless parameters, we obtain

$$\pi = \frac{k_3[P]}{k_2[RH]}, \qquad \tau = k_3\left(\frac{k_2k_4}{2k_3k_6}[RH]\right)^{1/2} t, \qquad \omega_0 = \frac{k_3W_0}{k_2k_4[RH]},$$

$$\frac{d\pi}{d\tau} = (1 - \pi)\sqrt{\omega_0 + \pi}.$$

Integrating this equation with the initial conditions $\pi = 0$ and $\tau = 0$, we obtain for the accumulation of P with time:

$$\pi = \left(\frac{Ae^{a\tau} - 1}{Ae^{a\tau} + 1}\right)^2 a^2 - \omega_0, \qquad A = \frac{a + \sqrt{\omega_0}}{a - \sqrt{\omega_0}}, \qquad a = \sqrt{1 + \omega_0}. \quad \text{(I)}$$

In the absence of the catalyst, when $\omega_0 \cong 0$,

$$\frac{d\pi}{d\tau} = (1-\pi)\sqrt{\pi}, \qquad \pi = \left(\frac{e^{\tau}-1}{e^{\tau}+1}\right)^2. \qquad \text{(II)}$$

The removal of catalyst from the reaction zone at a time t is equivalent to saying that at the corresponding moment of dimensionless time τ, ω_0 becomes zero (more exactly, becomes very small). Up to time τ_1 the accumulation of P is described kinetically by formula (I), and from time τ_1, by the formula

$$\pi = \left(\frac{Be^{\tau}-1}{Be^{\tau}+1}\right)^2, \qquad B = \frac{\sqrt{1+\pi_1}+\sqrt{\pi_1}}{\sqrt{1-\pi_1}-\sqrt{\pi_1}}, \qquad \text{(III)}$$

which is obtained by integration of the equation

$$\frac{d\pi}{d\tau} = (1-\pi)\sqrt{\pi},$$

with the initial conditions $\tau = \tau_1$, $\pi = \pi_1$.

Fig.1 shows the kinetic curves for the accumulation of P constructed from formulae (I)–(III). The calculated results are in good agreement with experiment.

The rate of chain initiation can be measured by making use of strong liquid-phase oxidation inhibitors[18,19]. The inhibitor is added to the hydrocarbon, and the rate of formation of free radicals determined from the rate of disappearance of the inhibitor (which usually decomposes only by reaction with free radicals). In the oxidation of lubricating oil in the presence of iron and copper stearates, the use of inhibitors has shown[20] that the rate of chain initiation at the commencement of the reaction is directly proportional to the concentration of catalyst (at sufficiently low concentrations). At the start of the oxidation of cyclohexane, with a cobalt stearate concentration of 0.06 mole%, the rate of chain initiation is 4.7×10^{-7} mole litre^{-1} sec^{-1}.[21] In the absence of catalyst, and at a higher temperature, the initial rate of formation of chains in the oxidation of cyclohexane is much lower — 0.46×10^{-7} mole litre^{-1} sec^{-1}.[19] These results show that the catalysts accelerate the reaction by providing a high rate of formation of chains.

The mechanism of chain initiation by cobalt ions has been studied in detail in the oxidation of benzaldehyde in glacial acetic acid solution at room temperature with cobalt acetate as catalyst[5,6]. The rate of oxidation $V \propto [RCHO]^{3/2}[\text{catalyst}]^{1/2}$. The strong decelerating influence of added β-naphthol shows that the reaction is a chain process. With quadratic chain termination the velocity of the chain reaction must be $v = \text{const.}[RCHO]\sqrt{w_i}$, where w_i is the rate of formation of free radicals. Consequently, in the presence of the catalyst the rate of chain initiation must be proportional to $w_i \propto [RCHO][\text{catalyst}]$. Experiments with added inhibitor enabled the rate of chain initiation to be determined. It was found that $w_i = k_4[RCHO][\text{catalyst}]$ and $k_4 = 3 \times 10^9 \exp(-14{,}800/RT)$ litre mole^{-1} sec^{-1}. The kinetics of the reaction of Co^{3+} with benzaldehyde in acetic acid solution were studied in independent experiments in the absence of oxygen; the velocity constant found for the reaction of Co^{3+} with RCHO was practically identical with the velocity constant for chain initiation in the experiments with the inhibitor. This agreement proves conclusively that the chains are initiated by reaction of cobalt(III) with benzaldehyde. The mechanism of the catalysed oxidation of benzaldehyde is in entirely consistent with the scheme

$$RCO\cdot + O_2 \rightarrow RCOOO\cdot, \qquad (1)$$

$$RCOOO\cdot + RCHO \rightarrow RCOOOH + RC\dot{O}, \qquad (2)$$

$$Co^{2+} + RCOOOH \rightarrow Co^{3+} + OH^- + RCOO\cdot, \qquad (3)$$

$$Co^{3+} + RCHO \rightarrow Co^{2+} + RCO\cdot + H^+, \qquad (4)$$

$$Co^{3+} + RCOOOH \rightarrow Co^{2+} + RCOOO\cdot + H^+, \qquad (5)$$

$$2RCOOO\cdot \rightarrow \text{mol. products}. \qquad (6)$$

The perbenzoic acid formed by the oxidation oxidises the cobalt(II) to cobalt(III) in a fast step. The reaction between cobalt(III) and perbenzoic acid does not play any substantial part, since it takes place very slowly. The limiting stage in the cycle of cobalt oxidation–state changes is the reaction of cobalt(III) with the benzaldehyde. Each reaction involving a change in the oxidation state of the catalyst is accompanied by the formation of a free radical; the rate of chain initiation is, naturally, determined by the limiting stage, the reaction of cobalt(III) with the aldehyde. Under stationary conditions of initiation and termination of chains,

$$2k_4[Co^{+3}][RCHO] = 2k_6[RCO_3\cdot]^2,$$

$$[RCO_3\cdot] = \left(\frac{k_4[Co^{+3}][RCHO]}{k_6}\right)^{1/2},$$

$$v = k_2[RCHO][RCO_3\cdot] = \frac{k_2 k_4^{1/2}}{k_6^{1/2}}[RCHO]^{3/2}[Co^{3+}]^{1/2},$$

which is found experimentally.

The oxidation of acetaldehyde[4] differs from the oxidation of benzaldehyde in the formation of a peroxide X by the reaction

$$CH_3CHO + CH_3\overset{\overset{O}{\|}}{C}-OOH \rightleftarrows X$$

The peroxide X has been assigned the structure

$$CH_3-\underset{\displaystyle OOH}{\underset{|}{CH}}-O-\overset{\overset{O}{\|}}{C}-CH_3.$$

The equilibrium constant $K = \dfrac{[X]}{[CH_3CHO][CH_3COOOH]} = 0.3$ at 25°.

In the presence of catalysts (cobalt, manganese, and copper acetates) the peroxide X is rapidly decomposed, oxidising Co^{2+} and Mn^{2+} to Co^{3+} and Mn^{3+}. The rate of oxidation of acetaldehyde in acetic acid solution is $-\dfrac{d[O_2]}{dt} = k[CH_3CHO]^{3/2}[\text{catalyst}]^{1/2}[O_2]^0$, $k = 67$ litres mole^{-1} min^{-1} at 25°. As in the oxidation of benzaldehyde, the rate of chain initiation by the catalyst is limited by the reaction

$$Co^{3+} + CH_3CHO \rightarrow Co^{2+} + CH_3\dot{C}O + H^+.$$

Therefore

$$w_i = k_4[RCHO][Co^{3+}], \quad n = (k_4[RCHO][Co^{3+}]/k_6)^{1/2},$$

$$\frac{d[O_2]}{dt} = k_2[RCHO]\,n = k_2\sqrt{\frac{k_4}{k_6}}[RCHO]^{3/2}[Co^{3+}]^{1/2}.$$

The peroxide X reacts with the catalyst more rapidly than peracetic acid. The velocity constant for the reaction of Mn^{2+} with X at 25° is 10^3 litres mole^{-1} sec^{-1}, while for the reaction of Mn^{2+} with CH_3COOOH it is 61 litres mole^{-1} sec^{-1}.[4]

Woodward and Mesrobian[17] studied the oxidation of tetralin in acetic acid solution in the presence of cobalt acetate, and showed that the maximum concentration of hydroperoxide in this reaction is

$$[ROOH]_{max} \propto \left(\frac{[RH]}{[(CH_3COO)_2\cdot Co]}\right)^2,$$

and the maximum rate of absorption of oxygen,

$$-\frac{d[O_2]}{dt} \propto [RH]^2,$$

is independent of the concentration of catalyst. Experiments on the decomposition of the hydroperoxide in a nitrogen atmosphere showed that

$$-\frac{d\,[\mathrm{ROOH}]}{dt} = k_3\,[\mathrm{ROOH}]\,[(\mathrm{CH_3COO})_2\mathrm{Co}]^2,$$

k_3 = 40 litre^2 mole^{-2} sec^{-1} at 81°. These facts agree well with the reaction mechanism proposed by the authors:

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

$$\mathrm{RO_2^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot, \qquad (2)$$

$$\mathrm{ROOH} + 2(\mathrm{CH_3COO})_2\mathrm{Co} \rightarrow \text{free radical}, \qquad (3)$$

$$2\mathrm{RO_2^{\cdot}} \rightarrow \text{mol. products}. \qquad (6)$$

According to this mechanism,

$$\frac{d\,[\mathrm{ROOH}]}{dt} = k_2\,[\mathrm{RH}]\,[\mathrm{RO_2}\cdot] - k_3\,[\mathrm{ROOH}]\,[\mathrm{Ac_2Co}]^2,$$

$$[\mathrm{RO_2}\cdot] = \left(\frac{k_3\,[\mathrm{ROOH}]\,[\mathrm{Ac_2Co}]^2}{2k_6}\right)^{1/2}, \quad [\mathrm{ROOH}]_{max} = \frac{k_2^2\,[\mathrm{RH}]^2}{2k_3k_6\,[\mathrm{Ac_2Co}]^2},$$

$$-\left(\frac{d\,[\mathrm{O_2}]}{dt}\right)_{max} = k_2\,[\mathrm{RH}]\,[\mathrm{RO_2}\cdot] = \frac{k_2^2\,[\mathrm{RH}]^2}{2k_6}.$$

The relationships obtained from this mechanism agree with the experimental data. The energies of activation were obtained from the temperature variation of k_3 and $-(d[\mathrm{O_2}]/dt)_{max}$: E_2 = 8.2 kcal mole^{-1} and E_3 = 23 kcal mole^{-1}.

The oxidation of aldehydes shows convincingly that the initiation of chains by salts of such metals is closely bound up with the change in their oxidation state. A change in oxidation state of cations such as those of cobalt and manganese has been observed in many studies of catalysed oxidation. Oxidation of cobalt(II) and manganese(II) is easily observed from the change of colour of their solutions. A solution of cobaltous stearate or naphthenate in a hydrocarbon is pale violet if the salt contains water of crystallisation, or pink if it is anhydrous. In a hydrocarbon which is being oxidised, the cobalt is converted to the +3-state, and the solution takes on an intense green colour[8,10,21-25]. The spectrum of cobalt(III) from an oxidised hydrocarbon is the same as the spectrum of a solution of pure cobaltic acetylacetonate[21,24]. The spectrum of cobalt (III) in solution in a hydrocarbon has an absorption maximum at 600 mμ, a minimum at 520 mμ, and strong absorption in the ultra-violet. Study of the kinetics of the accumulation of cobalt(III) in cyclohexane which is being oxidised has shown that not all of the cobalt is converted to the +3-state during the course of the reaction; the concentration of Co^{3+} reaches a maximum and then decreases (Fig. 2).

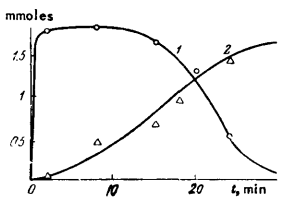


Fig. 2. Kinetic curves for the accumulation of 1) Co^{3+} and 2) hydroperoxide in the catalysed oxidation of cyclohexane (124°, 3 mmoles of cobalt stearate per litre).

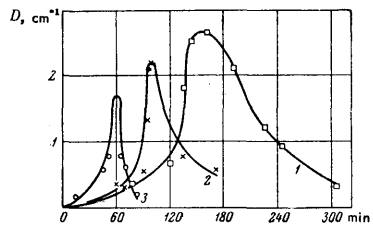


Fig. 3. Kinetics of accumulation of Mn^{3+} during the oxidation of n-decane with a catalyst concentration 0.012 M at: 1) 120°; 2) 130°; 3) 140°.

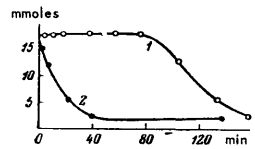


Fig. 4. Change of oxidation state of iron in the oxidation of cyclohexane: 1) at 110° with 0.018 mole% of St_3Fe; 2) at 130° with 0.017 mole% of St_2Fe.

A solution of a manganous salt in a hydrocarbon is colourless. During the oxidation a brown colour appears, typical of manganese in a higher oxidation state[7,8,21,24,26]. The spectrum of an oxidised manganese catalyst coincides with that of manganese(III) benzoate[24], and consequently manganese, like cobalt, is converted to the +3-state during the oxidation. The concentration of manganese(III) in the course of the oxidation of n-decane[26] passes through a maximum (Fig.3); the maximum concentration of Mn^{3+} is 20-30% of its total concentration of 0.012 moles per litre. Manganese is completely converted to the +3-state in the oxidation of cumene and tetralin[26]. This difference is due to the different composition of the oxidation products in these reactions and to their differing reducing action on Mn^{3+}.

A change in the oxidation state of iron in an oxidised hydrocarbon has been demonstrated[12] (Fig.4). The more rapid the oxidation (the higher the reaction temperature), the more rapid is the onset of the reduction of iron(III) to iron(II). This shows the close link between the formation of the oxidation products and the reduction of the catalyst. The reduction of copper(II) to copper(I) has been observed in the oxidation of decane[27].

The oxidation of aldehydes and observations on the catalysed oxidation of hydrocarbons and the reaction between salts of such metals and hydroperoxides indicate the close connection between oxidation–state changes of the catalysts and their part in chain initiation. It is often found that the start of a catalysed oxidation coincides with a change in the oxidation state of the catalyst, which is easily seen from

the change of colour of the solution. In the oxidation of acetaldehyde with manganese acetate[28], of branched-chain paraffins with cobalt stearate[22], and in the oxidation of decane[8], α-pinene[29], and cyclohexane[10] with cobalt stearate, it has been observed that the oxidation commences after an induction period, and coincides with a change in the oxidation state of the catalyst (with a rapid oxidation of Co^{2+} to Co^{3+} and of Mn^{2+} to Mn^{3+}).

In general, the one-electron transfer reaction between a molecule (a species of saturated valency) and a metal of variable oxidation state, must invariably lead to the formation of a free radical or atom. For example, in the reaction between cobalt(II) and a molecule A:B, cobalt(III) and a free radical or atom is formed:

$$Co^{2+} + A{:}B \rightarrow Co^{3+} + A\cdot + B^{-} \text{ (or } A^{-} + B\cdot).$$

An analogous effect is observed in the reverse transition of cobalt from the +3-state to the +2-state:

$$Co^{3+} + A{:}B \rightarrow Co^{2+} + A^{+} + B\cdot \text{ (or } A\cdot + B^{+}).$$

The classical example of oxidation-reduction reactions in which such cations participate are the reactions of peroxides with the ions of iron, copper, and cobalt. Since these reactions are closely related to the catalysed oxidation of hydrocarbons, they will be considered in more detail. Hydroperoxides are the primary molecular products of the oxidation of hydrocarbons, and play an important role in uncatalysed oxidation, since they ensure degenerate chain branching.

Of great significance also is the participation of hydroperoxides in catalysed oxidation reactions, in which reaction between a hydroperoxide and the catalyst is a powerful source of free radicals. A mechanism for the decomposition of peroxides by cations of variable oxidation state was first proposed by Haber and Weiss[30], with the decomposition of hydrogen peroxide in the presence of ferrous ions as an example. The primary elementary reaction between hydrogen peroxide and Fe^{2+} is

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + \cdot OH.$$

The resulting hydroxyl radical causes chain decomposition of the hydrogen peroxide; in the presence of a monomer (e.g. methyl methacrylate) the hydroxyl radicals cause radical polymerisation[31]. The velocity constant of the reaction between Fe^{2+} and H_2O_2 is $k = 1.8 \times 10^9 \exp(-10\,000/RT)$ litres mole^{-1} sec^{-1}.[31]

Hydroperoxides also decompose very rapidly in aqueous solution in the presence of iron ions, with the formation of alkoxy radicals:

$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + OH^{-} + RO\cdot,$$

as was shown by Kharasch[32], who decomposed cumene, tetralin and t-butyl hydroperoxides with iron ions in the presence of butadiene; the reaction products included the compounds (A) and (B), formed by the addition of the alkoxy radical to a butadiene molecule, with subsequent recombination of the radicals:

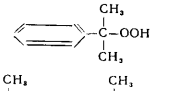
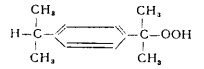
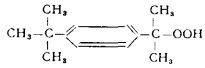
$$ROCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OR, \quad (A)$$

$$ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR. \quad (B)$$

Table 1 gives the velocity constants for reactions of Fe^{2+} with ROOH[33,34].

The thermal decomposition of the hydroperoxides to form free radicals takes place with an energy of activation ~30 kcal/mole. The iron ions react with the hydroperoxides with much lower energies of activation of 10-12 kcal/mole. The rate of reaction of cumene hydroperoxide with Fe^{2+} relative to its rate of thermal decomposition at 100° is $4.1 \times 10^8[Fe^{2+}]$, i.e. with $[Fe^{2+}] = 10^{-5}$ M, the reaction between ROOH and Fe^{2+} is 4000 times as rapid as the thermal decomposition.

TABLE 1. Velocity constants for the reaction of Fe^{2+} with ROOH for some hydroperoxides.

Hydroperoxide	Velocity constant, litres mole^{-1} sec^{-1}
	1.07×10^{10} exp (−12 000/RT)
	4.0×10^{9} exp (−10 800/RT)
	1.8×10^{9} exp (−9900/RT)

In the oxidation of hydrocarbons the catalysis is not by ions, but by the molecules of salts of metals of variable oxidation state; therefore the reaction between the hydroperoxide and the catalyst takes place with the formation of a free radical and a new polar bond (and not an ion, as in aqueous solution), for example:

$$St_2Co + ROOH \rightarrow RO\cdot + St_2CoOH,$$

where St = n-$C_{17}H_{35}COO$.

This reaction apparently takes place more slowly than the analogous one in aqueous solution, but much faster than the thermal decomposition of the hydroperoxide. The rapid decomposition of hydroperoxides in solution in hydrocarbons in the presence of small amounts of the stearates or naphthenates of cobalt, manganese, and iron is well known, and the strong catalytic action of these salts on the decomposition of hydroperoxides is not open to doubt. However, the kinetics and mechanism of the catalysed decomposition of hydroperoxides in solution in hydrocarbons have been little studied. The kinetics of the reaction between manganese stearate and n-decyl hydroperoxide have been studied[35]; this reaction takes place very rapidly, with decomposition of the hydroperoxide and oxidation of part of the manganese(II) to manganese(III). The kinetic curves depicting the change of optical density of the reactants, indicating the formation of manganese(III) are shown in Fig.5. The amount of manganese oxidised to the +3-state is less than the quantity of hydroperoxide decomposed, but with increase of the ratio $a = \frac{[St_2Mn]_0}{[ROOH]_0}$, the ratio $b = \frac{[Mn^{3+}]}{[ROOH]_{decomp}}$ also increases: when $a = 3.23$, $b = 48\%$, and when $a = 9.7$, $b = 80\%$. In addition to the reaction between St_2Mn and ROOH, there is apparently an induced decomposition of the hydroperoxide also. The initial rate of oxidation of manganese(II) is $k\,[St_2Mn]\,[ROOH]$, where $k \cong 2.8 \times 10^{11} \exp(-18{,}000/RT)$ litres mole^{-1} sec^{-1}. At 90° $k = 4.1$ litres mole^{-1} sec^{-1}, while for the reaction between Fe^{2+} and ROOH in aqueous solution, $k = 910$ litres × × moles^{-1} sec^{-1}. Since manganese is a more active cata-

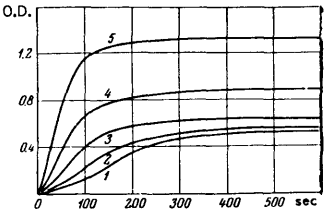


Fig. 5. Kinetic curves for the change of optical density of a solution of St_2Mn and n-decyl hydroperoxide in decane, showing the oxidation of the catalyst by the hydroperoxide at: 1) 80°; 2) 85°; 3) 90°; 4) 95°; 5) 104°. $[St_2Mn] = 4.86 \times 10^{-3}$ M, $[ROOH] = 1.56 \times 10^{-3}$ M.

lyst than iron, this difference must be due to the much greater reactivity of ions than of molecules of the organic-acid salts. However, the reactivity of such catalysts in the decomposition of hydroperoxides must still be considered as very high even in hydrocarbon solutions. For example, the rate of reaction of manganese stearate (0.01 M) with n-decyl hydroperoxide at 140° is 3.7×10^4 times the rate of decomposition of this hydroperoxide into free radicals in the decane being oxidised, where the velocity constant for the decomposition is $k = 6 \times 10^8 \exp(-24{,}000/RT)$ sec^{-1} [36]. In catalysis with ferric salts the catalyst first forms a complex with the hydroperoxide, which then decomposes to form free radicals[37,38]:

$$FeSt_3 + ROOH \rightleftarrows [FeSt_3 \ldots ROOH],$$

$$[FeSt_3 \ldots ROOH] \rightarrow FeSt_3 + RO\cdot + \cdot OH.$$

The formation of an analogous complex has been observed in the decomposition of ethylbenzene hydroperoxide in the presence of copper stearate[39].

This account has shown convincingly that the reaction between catalysts of variable oxidation state and hydroperoxides plays an important part in the mechanism of the catalysed oxidation of hydrocarbons.

Figs.3 and 4 show that in the hydrocarbon being oxidised, reduction of the oxidised form of the catalyst also occurs. It has been suggested that this takes place only as a result of reaction with the hydroperoxide;

$$St_2CoOH + ROOH \rightarrow St_2Co + RO_2\cdot + H_2O.$$

This reaction takes place in aqueous solutions[40], but it is much slower than the reaction between Co^{2+} and ROOH, and in fact takes place between the cobalt and hydroperoxide ions:

$$Co^{3+} + ROO^- \rightarrow Co^{2+} + RO_2\cdot.$$

In a hydrocarbon, where the hydroperoxide is known not to dissociate, this reaction takes place extremely slowly, if at all. Moreover, it does not explain the reduction of the catalyst to the lower oxidation state during the reaction, as the following kinetic calculation shows. Let us denote the reduced form of the catalyst by M^{2+} and the oxidised form by M^{3+}, and let us examine the kinetics of the accumulation of M^{3+} during the oxidation, assuming that both forms of the catalyst react only with the hydroperoxide. Let the catalyst be introduced at the commencement of the reaction in the lower oxidation state, M^{3+} being formed by reaction between M^{2+} and ROOH with a velocity constant k_3, and disappearing by reaction with ROOH with a velocity constant k_5. The rate of accumulation of M^{3+} is

$$\frac{d[M^{3+}]}{dt} = (k_3[M^{2+}] - k_5[M^{3+}])[ROOH].$$

$$\frac{dx}{dt} = (x_p - x)(k_3 + k_5)[ROOH], \text{ where } x = \frac{[M^{3+}]}{[M^{2+}]_0} \text{ and } x_p = \frac{k_3}{k_3 + k_5},$$

hence,

$$x = x_p\left(1 - e^{-\int_0^t (k_3+k_5)[ROOH]\,dt}\right).$$

Irrespective of the actual form of the kinetic curve for the accumulation of the hydroperoxide, $\int_0^t [ROOH]dt > 0$ and increases with t. Consequently, in the course of this reaction, $x \rightarrow x_p$, and having reached this kinetic equilibrium value, remains constant, i.e. the concentration of M^{3+} in the course of the reaction cannot decrease. To obtain a concrete form of $x = x(t)$, let us assume that chain initiation during the oxidation occurs by reactions (3) and (5), for simplicity of calculation assuming that $k_3[M^{2+}] + k_5[M^{3+}] \cong k_3[M^{2+}]_0$, that chain termination is quadratic (velocity constant k_6), and that the loss of peroxide at the commencement of the reaction can be ignored. Then the rate of formation of hydroperoxide in this reaction will be

$$\frac{d[ROOH]}{dt} = k_2[RH]\left(\frac{k_3[M^{2+}]_0[ROOH]^{1/2}}{k_6}\right)$$

(k_2 relates to the reaction between RO_2 and RH),

$$[ROOH] = A\,t^2, \quad A = \frac{k_2^2 k_3[RH]^2[M^{2+}]_0}{k_6},$$

and for the accumulation of the oxidised form of the catalyst we have the formula

$$x = x_p(1 - e^{-\tau^3}), \quad \tau = \left[\frac{(k_3 + k_5)A}{3}\right]^{1/3} t. \qquad \text{(IV)}$$

Fig.6 shows that in such a reaction the oxidised form of the catalyst accumulates at an increasing rate (auto-acceleration) until its concentration reaches a constant value and then remains unchanged.

Experimentally, quite a different picture is found (Figs.2 and 3). The rapid reduction of the oxidised form of the catalyst in the course of the oxidation may be due to accumulation of easily oxidised oxidation products which are produced after the hydroperoxide. Let us make one change

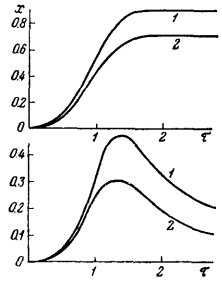


Fig. 6. Theoretical kinetic curves for the accumulation of the oxidised form of the catalyst in an oxidation reaction. Upper figure - M^{2+} and M^{3+} react only with the hydroperoxide [formula (IV): 1) $b = 0.9$; 2) $b = 0.7$]. Lower figure - M^{3+} is reduced by products formed from the hydroperoxide [formula (V): 1) $a = 0.5$; 2) $a = 1$].

in the above scheme, replacing the reaction M^{3+} with ROOH by the reaction

$$(M^{3+} + K \rightarrow M^{2+} + \text{radical } [3^1]),$$

where K is a product of the chain conversion of the hydroperoxide, formed at a rate $k[ROOH]n$:

$$\frac{d[K]}{dt} = k[ROOH]\sqrt{k_3[M^{2+}]_0[ROOH]/k^6};$$
$$[K] = B\,t^4; \quad B = {}^1/_3 A^{3/2} k \sqrt{k_3[M^{2+}]_0/k_6}.$$

The oxidised form of the catalyst will then accumulate at the rate:

$$\frac{d[M^{3+}]}{dt} = k_3[M^{2+}][ROOH] - k_4[M^{3+}][K]$$

or in dimensionless variables

$$\frac{dx}{d\tau} = (1-x)\tau^2 - ax\tau^4, \qquad (V)$$

where

$$x = \frac{[M^{3+}]}{[M^{2+}]_0}, \quad \tau = (k_3A)^{1/3}t, \quad a = k_4B(k_3A)^{-5/3}.$$

Fig.6 (lower curve) shows the change of x during the reaction, calculated with this formula; it is seen that this mechanism gives a good explanation of the experimentally observed kinetic curves for the accumulation of the oxidised form of the catalyst. Oxidation-reduction reactions between the catalyst and hydrocarbon oxidation products, such as alcohols, ketones, and aldehydes, are quite probable. It is known, for instance, that in aqueous acid solutions Co^{3+} rapidly oxidises formaldehyde and methyl and ethyl alcohols[41,42]. Analogous reactions apparently take place in solution in a hydrocarbon much more slowly, but at 100°–150° they may proceed fairly rapidly. These facts show convincingly that the reaction of cobalt(III) with aldehydes and other easily oxidised products of the incomplete oxidation has undoubted advantages over the reaction between Co^{3+} and ROOH→. It is appropriate here to recall that in the oxidation of aldehydes in acetic acid solutions the reaction of Co^{3+} with RCHO→ is much more rapid than the reaction between Co^{3+} and RCOOOH→.

In studying the catalysed oxidation of cyclohexane[21], it was noted that the rapid reduction of cobalt(III) coincides with the appearance of aldehydes in the cyclohexane. It is apparently these aldehydes which reduce the cobalt(III) during the oxidation reaction. Since the hydrocarbon undergoing oxidation contains hydroperoxides and aldehydes, the catalyst is continually being converted from one oxidation state to the other and back. Each transition is accompanied by the formation of a free radical, which starts a chain of conversions:

$$ROOH + St_2Co \rightarrow RO\cdot + St_2CoOH,$$
$$St_2CoOH + R_1CHO \rightarrow St_2Co + H_2O + R_1\dot{C}O.$$

Alcohols and ketones may react with the oxidised form of the catalyst similarly to aldehydes. Since the composition of the oxidation products changes continuously during the oxidation reaction, there is a continuous change in the relative amounts of oxidised and reduced forms of the catalyst. At the start of the reaction, only a hydroperoxide is formed, so that the concentration of the oxidised form increases. With the appearance of products possessing reducing properties (aldehydes, alcohols, etc.), the oxidised form of the catalyst is rapidly reduced, and its concentration diminishes.

The reaction of the catalyst with the oxidation products, with the formation of free radicals, may be considered as a degenerate branching of the chains which is accelerated by the catalyst. Of great interest, therefore, is the possibility of the initiation of chains by the catalyst in the initial system, containing only the hydrocarbon, dissolved oxygen, and the catalyst. If the catalyst is added to the hydrocarbon in a higher oxidation state, it can apparently form free radicals by the reaction

$$St_3Co + RH \rightarrow St_2Co + StH + R\cdot.$$

Free radicals are in fact formed by this type of reaction in the oxidation of trimethylethylene in acetic acid solution[43]. The study of the reactions of cobalt(III) with olefines has shown that the reaction of Co^{3+} with RH is rapid in aqueous acid solutions at room temperature[44]. The energy of activation of such a reaction is 27–29 kcal/mole, with a pre-exponential factor of 10^{20} litres $mole^{-1}$ sec^{-1}. At room temperature, k (Co^{3+}, olefine) varies from 0.3 to 6 litres $mole^{-1}$ sec^{-1}, depending on the hydrocarbon. Such reactions must proceed more slowly in solution in a hydrocarbon, where the catalyst is undissociated, but possibly occur at a rate sufficient to provide a reliable source of free radicals. In later stages of the oxidation such reactions do not apparently play a decisive part, reactions of the catalyst with the oxidation products predominating.

Catalysts such as cobalt and manganese salts are usually added to the hydrocarbon in the oxidation state(II). The question arises: do they participate in chain initiation at the start of the reaction, or does their initiating activity appear only with the appearance of a hydroperoxide? The possibility has been suggested[11,45] of chain initiation by reaction between cobalt(II) and oxygen under certain conditions:

$$St_2Co + O_2 \rightleftarrows St_2Co \ldots O_2,$$
$$St_2Co \ldots O_2 + RH \rightarrow St_2CoOOH + R\cdot$$
$$\text{or } St_2Co \ldots O_2 + RH \rightarrow St_2CoOH + RO\cdot.$$

Results supporting this mechanism were obtained in the oxidation of linoleic acid in benzene in the presence of cobalt stearate[45]. The rate of this reaction is independent of the concentration of hydroperoxide and is given by $\frac{d[ROOH]}{dt} = k[RH][St_2Co]$. Changing the polarity of the medium by adding nitrobenzene strongly affects the rate of the reaction (Table 2). Uri suggested that the catalyst forms a complex with oxygen which then reacts with another molecule of catalyst to form free radicals. A polar solvent (nitrobenzene) solvates the cobalt cations and hinders the formation of the complex with oxygen, and consequently, the formation of free radicals:

$$St_2Co + O_2 \rightleftarrows St_2Co \ldots O_2,$$
$$St_2Co \ldots O_2 + St_2Co(HX) \rightarrow St_2Co + St_2CoX + HO_2$$

The activity of a catalyst of variable oxidation state depends primarily upon the cation. To a first approximation, the higher the redox potential of its cation, the more active is the catalyst (Table 3)[46]. Table 3 shows that there is only a qualitative relationship between the maximum rate of oxidation and the redox potential. The relative activities of the catalysts change on passing from one oxidation process to another. This is quite understandable, since the ability of a catalyst to initiate a chain depends not only on its cation, but also on the composition of the reaction products, their activity in reactions with the catalyst, and the state of the catalyst in the reaction. In most cases the most active

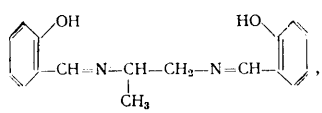
TABLE 2. Effect of the polarity of the solvent on the rate of oxidation of methyl linoleate (0.2 M) with 1.87×10^{-4} mole of St_2Co per litre.

Nitrobenzene, vol.%	Molar ratio of benzene to nitrobenzene	Rate of oxidation, mmoles $\times l^{-1} \times mole^{-1} h^{-1}$
0	—	14.4
25	3.74	13.4
30	2.70	12.3
35	2.14	7.6
40	1.74	3.88
45	1.42	1.86
50	1.16	0.68
75	0.385	0.0
100	—	0.0

catalysts are the salts of cobalt and manganese.

The lower the temperature, the more pronounced is the effect of the catalyst on the oxidation. At a low temperature the catalysed oxidation is much more rapid than the uncatalysed; as the temperature is raised, the difference in these rates decreases, because at a sufficiently high temperature the chain oxidation process can develop rapidly independently: the salt catalyst rapidly precipitates because of the accumulation of acids, and almost ceases to participate in the reaction.

The addition to the hydrocarbon of compounds which form complexes with metals of variable oxidation state affects their activity[47] because of the blocking action of the complex-forming agent, and possibly, because of a change in its redox potential. These complexing agents are used in practice; for example, very slight traces of copper in petrol (0.01 p.p.m.) decrease its stability. Disalicylidene-1,2-diaminopropane,



which forms chelate complexes with copper and deactivates it, is added to the petrol as a stabiliser[48,49].

The data on the catalysed oxidation of organic compounds leads to the following conclusion. In oxidation reactions catalysts of variable oxidation state play an active part in the initiation of chains. They react with the oxidation products (hydroperoxides, aldehydes, etc.), and in so doing change their oxidation state and produce free radicals. Each catalyst molecule can participate many times in the initiation of chains, converting the molecular oxidation products into free radicals. In this respect such catalysts differ substantially from initiators of the peroxide and azo-compound types. It must be emphasised that the detailed mechanism of the initiation of chains by catalysts has been insufficiently studied. Wide, strictly quantitative investigations of the individual elementary reactions in which various catalysts take part, are required.

TABLE 3. Effect of the redox potential of the catalyst on the maximum rate of oxidation of 2.5-dimethylhexane (61.4 mmoles) with 0.11 mmole of the stearates of various metals.

Catalyst cation	Max. rate of oxidation, mmoles of O_2 per hour per 61.4 mmoles of RH	Redox potential of cation (eV)
Co^{2+}	35	1.82
Mn^{2+}	32	1.51
Ce^{4+}	20	1.55
Fe^{3+}	13	0.77
Cd^{2+}	4	—

BREAKING OF CHAINS BY CATALYSTS OF VARIABLE OXIDATION STATE

The initiation of chains with participation of a catalyst takes place as a result of reactions of one or more "saturated-valency" molecules with a cation of variable oxidation state, in which the oxidation state of the catalyst changes and free radicals are formed. In principle the reverse reactions are also possible, reactions of free radicals with cations of variable oxidation state, leading to loss of the free valency. Since peroxide radicals are strong oxidising agents, they would be expected to react with the reduced form of the catalyst, e.g. by the reaction

$$RO_2\cdot + St_2Co \rightarrow ROO{-}CoSt_2 \text{ (or } St_2CoOH + \text{ketone)}.$$

In such a reaction, the peroxide radical forms a coordinate link, $RO_2{-}CoSt_2$, with the cation of variable oxidation state, using an unpaired electron of the cobalt(II). Reversible reactions of such ions are well known in aqueous solution, for example[50,51],

$$Fe^{3+} + OH^- \rightleftarrows Fe^{2+} + \cdot OH \text{ and } Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + HO_2\cdot + H^+$$

Thus, the ability of such cations to donate or accept an electron in reactions with molecules leads to the formation of free radicals, and in their reactions with free radicals, to the loss of these, with the formation of molecular products. In oxidation reactions such a catalyst initiates chains by reacting with molecular products, and breaks them by reacting with free radicals. The initiating action of the catalyst is usually much the stronger, and masks its inhibitory effect. The breaking of chains on variable-oxidation-state catalysts has been detected where the initiating action of the catalyst ceased to be effective after a time, and the catalyst (cobaltous or manganous stearate) showed only its inhibiting action[11,21]. The experiments were carried out as follows. The catalyst was added to cyclohexane, heated to 100°–110°, and the concentration of oxidation products and cobalt(III) was determined by sensitive analytical methods in samples of the oxidised cyclohexane taken during the course of the oxidation. When the catalyst had a high cobalt(III) content, the oxidation began immediately, at a constant and fairly high rate (Fig.7).

The situation is different if cobaltous stearate is added to the cyclohexane in concentrations of 0.01–0.05 mole %; a small part of the cobalt is converted to the +3-state, but most remains in the +2-state; for a time the oxidation is inhibited. This inhibition ceases when the cobalt has been converted to the +3-state and a hydroperoxide appears (Fig.8). The more cobalt(II) is added, the longer is the period of inhibition. This indicates a deceleration of the reaction by cobalt(II). An even clearer inhibiting action of

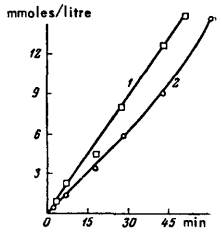


Fig. 7. Kinetic curves for the formation of 1) cyclohexanol and 2) cyclohexanone in the oxidation of cyclohexane in the presence of cobalt stearate containing 40% Co^{3+} (110°, $[Co^{3+}] + [Co^{2+}] = 0.07\%$).

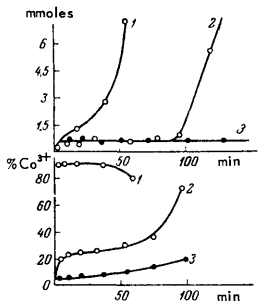


Fig. 8. Kinetics of the formation of cyclohexanone (upper figure) and of the change in the valency state of the catalyst (lower figure) in experiments on the oxidation of cyclohexane at 110° and 30 atm with various concentrations of St_2Co catalyst: 1) 0.003 mole%; 2) 0.02 mole%; 3) 0.07 mole%.

initiator of chains; it therefore behaves only as an inhibitor, reacting with free radicals and breaking the chains. An analogous effect is found in catalysis with manganese(II): at the start of low-temperature oxidation it functions as an oxidation inhibitor. From the very commencement of the reaction, cobalt(III) and manganese(III) act as chain initiators. The comparatively smooth converstion of cobalt(II) to cobalt(III) therefore causes a sudden change in the reaction, from inhibited to strongly catalysed.

Considering this in more detail, we shall attempt to construct the kinetic curves for the accumulation of the oxidised form of the catalyst and the oxidation products P, using a simple reaction scheme.

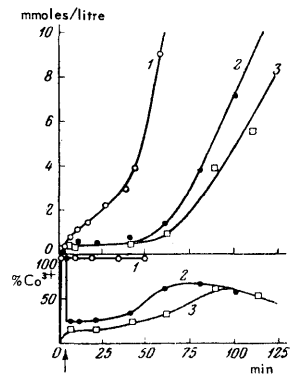


Fig. 9. Experiments on the oxidation of cyclohexane at 110° and 30 atm: 1) 0.003 mole% of St_2Co added initially; 2) 0.003 mole% of St_2Co added initially and a further 0.016 mole% in the fourth minute; 3) 0.018 mole% of St_2Co added initially. Upper figure - kinetics of the formation of the ketone; lower figure - kinetics of the formation of Co^{3+} in % of total Co concentration.

cobalt(II) on the oxidation of cyclohexane is observed when further catalyst is added to the reaction. A small quantity (0.003 mole %) of cobalt(II) added to the cyclohexane is completely converted to the +3-state, and the reaction starts immediately, without any inhibition (Fig.9, curve *1*). If to this reaction, once started, a further quantity of cobalt(II) is added, oxidation ceases for a time (Fig.9, curve *2*); the inhibition itself ceases with the conversion of a considerable part of the cobalt to the +3-state. An analogous effect is observed when a considerable quantity of cobalt(II) is needed in the reaction (Fig.9, curve *3*).

These facts are apparently contradictory — the more catalyst added to the hydrocarbon, the greater the inhibition of the oxidation — although it is known that cobalt(II) can initiate chains by reaction with a hydroperoxide. The behaviour of the catalyst in these experiments is explained in this way: at the start of the reaction, no hydroperoxide has yet been formed, and the cobalt(II) cannot act as an

Assume that in the chain-oxidation reaction, proceeding at a rate $k_2[RH]n$, the free radicals are formed mainly by the action of the oxidised form of the catalyst M^{3+} at a rate $k_4[RH][M^{3+}]$, and that the chains are broken with the participation of the reduced form of the catalyst at a rate $k_7[M^{2+}]n$, and without the participation of the catalyst at a rate $k_6'n$. Linear, and not quadratic, chain termination is assumed here for simplicity of calculation. At a stationary free radical concentration,

$$k_4[RH][M^{3+}] = (k_6' + k_7[M^{2+}])n\,,$$

$$\frac{d[P]}{dt} = k_2[RH]n = \frac{k_2 k_4 [RH]^2 [M^{3+}]}{k_6' + k_7[M^{2+}]}, \quad \text{or} \quad \frac{dy}{d\tau} = \frac{x}{a + 1 - x}, \qquad \text{(VI)}$$

$$y = y_0 + \int_{x_0}^{x} \frac{z\,d\tau}{a + 1 - z},$$

where x is the fraction of catalyst in the higher oxidation state:

$$x = \frac{[M^{3+}]}{[M^{2+}] + [M^{3+}]}, \quad a = \frac{k_6'}{k_7([M^{2+}] + [M^{3+}])}, \quad \tau = k_4[RH]\,t, \quad y = \frac{k_7[P]}{k_2[RH]}.$$

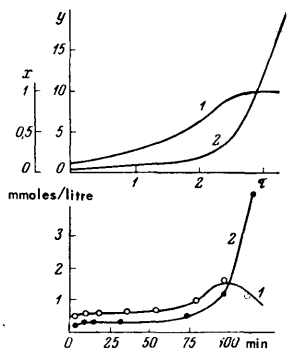


Fig. 10. Kinetic curves for the accumulation of 1) M^{3+} and 2) the oxidation product P in the initial period of the oxidation, with chain breaking by M^{2+} and chain initiation by M^{3+}. Upper figure - theoretical curves constructed from formulae (VI) and (VII) ($x_0 = 0.1$, $a = 0.05$, $y_0 = 0.05$). Lower figure - experimental data on the oxidation of cyclohexane at 110°, 30 atm, and St_2Co concentration 0.02 mole%: 1) Co^{3+}; 2) cyclohexanone.

Assuming that M^{3+} is formed only by reaction of M^{2+} with a free radical, we obtain

$$\frac{d[M^{3+}]}{dt} = \frac{k_4 k_7 [RH][M^{2+}][M^{3+}]}{k_6' + k_7[M^{2+}]} \quad \text{or} \quad \frac{dx}{d\tau} = \frac{x(1-x)}{a+1-x},$$
$$\ln \frac{x}{x_0} + a \ln \frac{1-x_0}{1-x} = \tau . \qquad \text{(VII)}$$

The change of x and y is shown in Fig.10, where they are compared with the kinetic curves for the accumulation of cobalt(III) and cyclohexanone in the oxidation of cyclohexane. The good agreement between calculation and experiment once more confirms the correctness of the suggested inhibitory action of cobalt(II) at the start of the reaction. The maximum in the experimental curve for the accumulation of cobalt(III) is associated with the appearance of aldehydes, which reduce the metal to the +2-state. The appearance in the reaction of a hydroperoxide converts even cobalt(II) from an inhibitor to a chain initiator.

The inhibiting action of cobalt(II) and manganese(II) is also shown by a number of other facts, which have not been correctly interpreted. Prolonged induction periods have been observed by Wibaut and Strong[22] in the oxidation of paraffinic hydrocarbons with cobaltous stearate; for example, in the oxidation of n-octane at 125°, in the presence of 1% cobalt stearate, the induction period is 10 h. The end of the induction period coincides with the rapid conversion of cobalt(II) to the +3-state. The addition of a hydroperoxide eliminates the induction period. In the oxidation of α-pinene[23] there is also a long induction period (8 h), but if cobaltic stearate is used instead of the cobaltous salt, the oxidation commences immediately, as is the case if cobalt(II) is added to α-pinene containing a hydroperoxide. The use of manganous stearate causes an induction period in the oxidation of Synthin[24]; the induction period is longer the more manganese stearate is used.

These facts are explained simply if breaking of the chains by the +2-state of the catalyst is taken into account. At the start of the reaction, the cobalt(II) [or manganese(II)] only breaks the chains, and so creates a long induction period. The addition of cobalt(III), which does not react with peroxide radicals but initiates chains, only accelerates the reaction, and there is no induction period. A hyderoperoxide added to the system, hydrocarbon — oxygen — catalyst reacts with cobalt(II) to form free radicals and thus eliminates the induction period.

In the later stages of the reaction the initiation of chains by the reaction of the reduced form of the catalyst with the hydroperoxide predominates over the breaking of chains by the catalyst molecules. Moreover, in the later stages of the oxidation the free radical concentration n is much greater than at the start of the process. Under these conditions the rate of quadratic chain termination, $k_6 n^2$, is much greater than the rate of linear chain termination by the catalyst, $k_7[M^{2+}]n$. Hence, in the later stages of the reaction the inhibitory action of the catalyst hardly appears. It can be detected by measuring the order of the reaction relative to the catalyst. With quadratic termination of chains and their initiation with the participation of one molecule of catalyst, $v \propto n \propto [\text{catalyst}]^{1/2}$. If the catalyst also participates in the breaking of chains, the order of the reaction relative to the catalyst concentration must be less than 0.5. In the oxidation of cyclohexene in the presence of the stearates of cobalt(II), copper(II), and manganese(II),[38] it was found that the order of the reaction relative to the manganese stearate concentration was 0.36, and relative to the copper stearate concentration, 0.40; with manganese stearate the induction periods are long. The inhibiting action of copper(II) on the oxidation of n-decane is significant[27]. In this reaction copper stearate produces an induction period which depends in a very singular fashion on the concentration of added catalyst. Up to a copper concentration of 0.6 mole % the induction period increases smoothly with concentration, but a further slight increase in its concentration causes a much increased induction period (Fig.11). The presence of a critical copper stearate concentration of 0.6 mole % in the oxidation of decane is connected with the double function of this catalyst and the

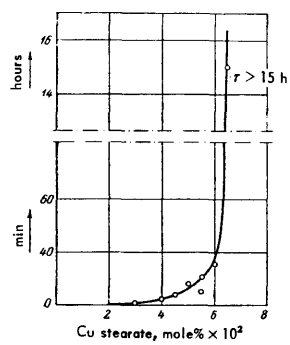


Fig. 11. Effect of the concentration of added copper stearate on the induction period in the oxidation of n-decane at 140°.

degenerate-branching chain mechanism of the reaction. The inhibiting action of copper stearate on oxidation reactions has been observed in the case of the oxidation of octenes[52] and paraffins[52]. On the other hand, the oxidation of ethylbenzene[52], cyclohexane[21], and lubricating oil[20] is accelerated by a copper catalyst. The inhibitory effect of copper(II) is usually found when it is present in fairly high concentration; traces of copper, as a rule, accelerate oxidation.

Catalysts of variable oxidation state (salts of cobalt, manganese, and copper) can thus not only initiate chains, but can break them also. Depending on the conditions, one of these functions predominates, so that the catalyst can act as an initiator or as an inhibitor. The detailed quantitative investigation of the inhibitory function of the catalyst merits very serious attention. It is important to compare the effectiveness of inhibition by different cations of variable oxidation state, to investigate how this effect varies with the medium (solvent), the nature of the anion of the catalyst, and the structure of the peroxide radicals, to determine the velocity constants of the elementary reactions of peroxide radicals with the catalyst, and so on. Investigations of this type are only just beginning, and data on all these questions are not available.

PHYSICOCHEMICAL PROPERTIES OF SOLUTIONS OF SALT CATALYSTS IN HYDROCARBONS

In addition to the chemical properties of catalysts, their physicochemical state in the hydrocarbon solution has a substantial influence. Knowledge of solutions of metal salts of organic acids in hydrocarbons provides a correct understanding of certain kinetic features of the catalysed oxidation of hydrocarbons and of the changes which the catalyst undergoes during the reaction as a result of the accumulation of various oxidation products. Catalysts of variable oxidation state are added to the hydrocarbon as salts of fatty or naphthenic acids; in a polar solvent the salts dissociate into ions, but in a hydrocarbon solvent dissociation does not occur. This is shown by conductivity measurements on hydrocarbon solutions of metal salts of fatty acids: the conductivity of benzene solutions of copper, nickel, and cobalt oleates is practically the same as that of pure benzene[53], and the conductivity of dilute toluene solutions of zinc, lead, copper, magnesium, and calcium oleates is little different from that of pure toluene[54]. As the salt concentration increases, the equivalent conductance also increases, because of the formation of micelles from the salt molecules, and their easier dissociation into ions[54].

Each molecule of carboxylic acid metal salt is a dipole, and the electrostatic attraction of these dipoles in the non-polar solvent causes the salt molecules to combine into micelles. The formation of micelles can be considered as a series of successive equilibria:

$$MA_2 + MA_2 \rightleftarrows (MA_2)_2,$$
$$MA_2 + (MA_2)_2 \rightleftarrows (MA_2)_3,$$
$$\cdots\cdots\cdots\cdots$$
$$MA_2 + (MA_2)_{n-1} \rightleftarrows (MA_2)_n.$$

Experimental proof of the association of salt molecules in the hydrocarbon solution is furnished by the higher molecular weight of the dissolved salt, determined ebullioscopically. For example, the molecular weight of copper stearate at a concentration of 0.02–0.08% in lubricating oil is 5000 instead of 347, and the molecular weight of iron stearate, at a concentration of 0.01–0.04%, is 1700 instead of 339.[20] The association of salts in toluene solutions has been studied in detail[55–57]. The degree of association increases with the salt concentration (Table 4), in good agreement with the existence of such equilibria.

TABLE 4. Micellar weights of various soaps in toluene*.

Zn laurate			Zn stearate			Cu stearate		
C	M	N	C	M	N	C	M	N
0.653	2310	4.98	0.938	3460	5.47	1.038	4040	6.43
1.335	2840	6.13	1.690	3400	5.38	1.647	4220	6.70
1.935	3040	6.56	2.650	3530	5.58	2.580	4470	7.10

* C = concn. of soap in g/100 g; M = micellar weight; N = number of slat molecules per micelle.

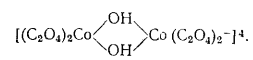
Since the combination of salt molecules into micelles occurs as a result of the electrostatic interaction between the dipoles of the molecules, the micellar weight must increase with the dipole moment, and this is found in practice (Table 5).

TABLE 5. Micellar weight of metal laurates as a function of dipole moment.

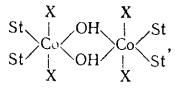
Metal	Micellar weight of laurate	Dipole moment of laurate
Zn	2600	0.29
Cu	3500	1.20
Mg	6000	1.66
Ni	20000	2.67

The degree of association depends on the length of the acid residue, and decreases as this length increases. The degree of association falls as the temperature is raised. To a first approximation, all these features of the behaviour of hydrocarbon solutions of salts of fatty acids can be explained by the electrostatic attraction of the polar molecules in the non-polar solvent. The mean interaction potential between two isolated dipoles $N = -2\mu_1^2\mu_2^2/3r^6kT$, where μ_1 and μ_2 are the dipole moments of the species, r is their radius, k the Boltzmann constant, and T the absolute temperature. It follows from this expression that the degree of association will be smaller the smaller the polarity of the cation of the salt, the larger the number of C atoms in the acid residue (the larger r), and the higher the temperature.

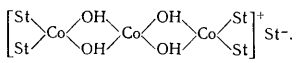
In some cases the association of catalyst molecules into larger particles takes place by the formation of polynuclear complexes, i.e. it is chemical in nature. For example, cobalt(III) tends to form polynuclear complexes of the type



The formation of the complex



where St is the stearic acid residue and X is water or alcohol, has been suggested in the catalysed oxidation of α-pinene[23]. Freidin[24] isolated the salt of cobalt(III) formed in the oxidation of Synthin and determined its empirical formula and molecular weight, concluding that the cobalt(III) is present in the hydrocarbon as the trinuclear complex:



The formation of salt molecules into micelles must be taken into account in considering the mechanism of the catalysed oxidation of hydrocarbons. The activity of the catalyst depends upon the degree of association of its molecules and the activity is proportional to a first approximation, to the number of catalyst particles in unit volume of the hydrocarbon being oxidised. The closer the approach of the catalyst solution to a true solution, the higher its activity, other conditions being equal. The influence of the acid residue on the catalyst activity is apparently due to this circumstance. The higher the molecular weight of the acid component of the salt, the more active is the catalyst[58,59]. Exceptions to this rule are apparently caused by the different methods of preparing the catalysts, which might contain water of crystallisation, might be partly present as a basic salt, and so on, which would affect the state of the catalyst in the hydrocarbon solution.

The combination of molecules of the salts into micelles is closely connected with the relation between the concentration of the catalyst and its effect on the reaction. If the catalyst forms a true solution in the hydrocarbon, the rate of initiation of chains by the catalyst should increase linearly with its concentration. The formation of micelles changes the picture: as the concentration of dissolved salt increases, the number of particles in unit volume first increases in proportion to the concentration, but then the increase slows down and practically levels off — further increase in the salt concentration causes an increase in the size of the micelles. Accordingly, the initiation of chains by the catalyst first increases as its concentration increases, and then this increase ceases. Fig.12 shows how the rate of chain initiation varies with the concentration of copper stearate in the oxidation of lubricating oil[20].

The rate of formation of free radicals determines the rate of oxidation, and so the same relation is observed between the maximum rate of the catalysed oxidation and the catalyst concentration[22,58,60-64]. Some workers consider this relation between the rate of oxidation and the catalyst concentration as proof that the catalyst takes part in the breaking of chains. Since the association of the catalyst molecules leads to an analogous picture and the effect of this association on the initiating capacity of the catalyst has been demonstrated experimentally[20], the above interpretation of the dependence of the rate of oxidation on the catalyst concentration is not necessarily valid. This is shown also by the fact that in acetic acid, where the catalyst forms a true solution, both the rate of chain initiation and the rate of oxidation increase linearly with the catalyst

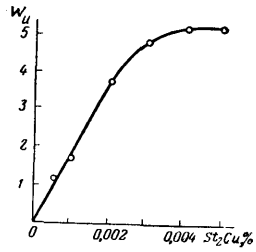


Fig. 12. Dependence of the rate of initiation w_u (in relative units) on the concentration of added copper stearate in the oxidation of liquid paraffin at 150°.

concentration[3,5,43]. It does not follow from this that variable-oxidation-state catalysts do not break chains in the advanced stages of the reaction; breaking of chains by the catalyst does apparently take place, but under these conditions the initiating function of the catalyst is much stronger than its inhibitory capacity. Moreover, with a high free-radical concentration in the later stages of the reaction, the rate of quadratic termination is high, and in comparison with this, the linear termination of chains by the catalyst molecules is insignificant. The inhibitory function of the catalyst is clearly shown, as we have seen, at the start of the reaction, when the catalyst does not initiate chains.

MACROSCOPIC STAGES IN THE CATALYTIC OXIDATION OF HYDROCARBONS

The vapour-phase oxidation of hydrocarbons in the presence of homogeneous catalysts takes place[65], as a succession of macroscopic stages separated in time[65]. The decisive part is played by the first macroscopic stage, the completion of which at the start of the process determines further development of the latter. Such separate stages were detected and studied in the oxidation of propane with hydrogen bromide as catalyst. It was shown that at the start, there is an initiating reaction which forms an intermediate product, and soon ceases. During the reaction this intermediate decomposes to form free radicals which initiate the second stage, the oxidation of propane to acetone. Later studies of the oxidation of propane, ethane, and methane in the presence of HBr, Cl_2, and NO_2, established that macroscopic stages in oxidation reactions with a homogeneous catalyst are widespread[65,66]. Macroscopic stages are also observed in the liquid-phase oxidation of hydrocarbons with catalysts of variable oxidation state. Tsyskovskii and Kiseleva[7,59] first drew attention to the fact that in the oxidation of kerosene with manganese naphthenate, the catalyst is in the dissolved state and initiates the reaction only at the start of the oxidation. The catalyst then precipitates completely and takes no further part in the oxidation. Knorre, et al.[8] studied the kinetics of the oxidation of n-decane in the presence of cobalt and manganese stearates, and showed that the catalyst first undergoes a change of oxidation state, and then precipitates and takes no noticeable part in the oxidation. Thus the catalysed oxi-

dation of hydrocarbons often takes place in two stages: in the first, the catalyst is in solution and accelerates the oxidation by initiating chains; in the second, it is in the precipitate, and takes no part in chain initiation. This sharp separation of the reaction into two stages is not always found: for instance, in the catalysed oxidation of cyclohexane the catalyst is not completely precipitated, so that its effect on the reaction decreases gradually during the course of the oxidation[10].

The presence of macroscopic stages in the catalysed oxidation of hydrocarbons is apparently caused by a change in the physicochemical stage of the catalyst in the hydrocarbon solution as the molecular oxidation products accumulate. In acetic acid, where the catalyst is always present as ions, macroscopic stages are not observed. In a hydrocarbon the catalyst is extremely sensitive to the presence of polar substances; its solubility depends greatly on the polarity of the medium and the anionic component of the salt. The formation of complexes with the oxidation products can affect its activity. Of the oxidation products which act upon the state of aggregation of the catalyst, the acids are important. It has often been found in experiments that the catalyst is precipitated in oxidation reactions as salts of acids formed by the oxidation. Thus in the oxidation of kerosene the catalyst precipitates as a salt of low-molecular weight acids formed in the reaction[59]; in the oxidation of cyclohexane, the cobalt, added as stearate, precipitates as the adipate[10]. However, the precipitation of the catalyst during the oxidation is not the result of a simple exchange reaction between the salt and the acid, but of a more complex physiocochemical process in which other reaction products, particularly water, take part as well as the acids.

Some workers have noted a decreased catalyst activity even when it is not precipitated. In the oxidation of cyclohexane in the presence of copper stearate the rate of oxidation falls rapidly in the course of the reaction; with the introduction of fresh catalyst, the reaction again proceeds rapidly, and then slows down[21] (Fig.13). Possibly, the catalyst loses its activity by undergoing a change in the chain initiation process itself, for example by reaction with a hydroperoxide. The activity of copper stearate also decreases rapidly in the catalysed decomposition of ethylbenzene hydroperoxide[39].

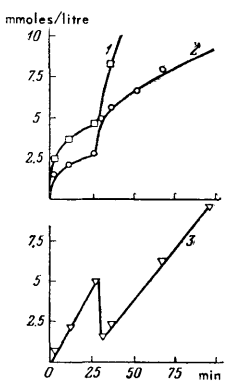


Fig. 13. Oxidation of cyclohexane at 110° with the introduction of St_2Cu (0.75 mmole/litre) initially, and 1.0 mmole/litre in the 60th minute: [30th minute? (Ed. of Translation)] 1) cyclohexanol; 2) cyclohexanone; 3) cyclohexyl hydroperoxide.

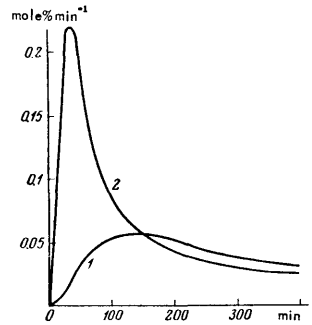


Fig. 14. Change of the rate of oxidation of n-decane at 140° in the course of the oxidation; 1) without catalyst; 2) with 0.3 mole% St_2Co.

The presence of an initial macroscopic stage is shown in the oxidation kinetics by the initial rapid increase in the rate of oxidation, which reaches a maximum and then rapidly falls (Fig.14). The decreased rate in later stages of the reaction is due to precipitation of the catalyst. At the commencement of the reaction the catalyst takes an active part in the initiation of chains, and, as hydroperoxides and other oxidation products accumulate, the rate of chain initiation by the catalyst grows. The appearance of products which cause precipitation of the catalyst or reduce its activity because of the formation of complexes, decreases the role of the catalyst in the initiation of chains. This naturally affects the rate of oxidation. The reason for the catalysed oxidation occurring in stages can be explained only in very general terms. Further and more detailed study of these phenomena is necessary, in particular, the development of methods for preventing the deactivation of the catalysts in the course of the oxidation.

CONTROLLING FUNCTION OF THE CATALYST IN OXIDATION REACTIONS

The role of the catalyst in an oxidation reaction is confined, in many cases, to its participation in the initiation and breaking of chains. Often, however, the catalysts affect not only the rate, but also the composition of the products of the oxidation, i.e. they have a controlling function. The direct influence of the catalyst on the composition of the oxidation products is seen in the catalysed oxidation of cyclohexane. The main intermediate oxidation products in the oxidation of cyclohexane are cyclohexanone and cyclohexanol. In the absence of catalyst the ketone forms in about twice the quantity of the alcohol; in the presence of cobalt stearate the amount of the alcohol is about 1.5 times that of the ketone[10,11].

The controlling action of the catalyst is not connected with its initiating capacity, as is shown by comparing the oxidation of cyclohexane in the presence of cobalt stearate and cobalt adipate (Fig.15). The latter is poorly soluble in cyclohexane and does not accelerate the oxidation, but both

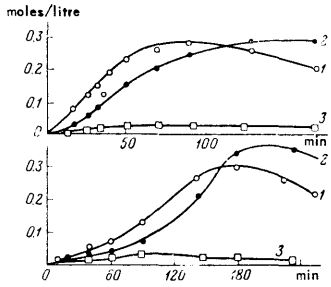


Fig. 15. Kinetic curves for the accumulation of 1) cyclohexanol, 2) cyclohexanone, and 3) cyclohexyl hydroperoxide in the oxidation of cyclohexane in the presence of 0.06 mole% St_2Co (upper figure) and 0.055 mole% of cobalt adipate (lower figure).

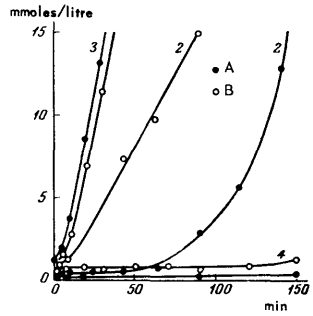


Fig. 16. Kinetic curves for the accumulation of cyclohexanone (A) and cyclohexanol (B) at the commencement of the oxidation of cyclohexane in the presence of 0.017 mole% St_2Co at: 1) 100°; 2) 110°; 3) 121°.

catalysts provide the alcohol : ketone ratio characteristic of the catalysed oxidation. If the catalyst is removed from the cyclohexane, this ratio rapidly changes and becomes that for the uncatalysed reaction.

The controlling action of the catalyst has been observed in the oxidation of paraffin with a manganese catalyst[67].

In the catalysed oxidation of cyclohexane the alcohol and ketone are formed and react by a chain mechanism[21]. The relative proportions of the products are completely determined by the chain-propagation reactions and are independent of the initiation and breaking of chains. This proportion can only be altered by acting upon the chain-propagation reactions; consequently, the influence of the catalyst on the composition of the products of the chain reaction must be the result of its participation in the chain-propagation reaction. In this connection, the following feature of the reaction is interesting. The addition of cobaltous stearate to cyclohexane at 100° slows down the formation of the ketone and the alcohol; at 120° the catalyst is immediately converted into the +3-state and both products simultaneously accumulate in the reaction. At 110° the catalyst is only partially converted into the +3-form, and the remaining cobalt(II) slows down the formation of the ketone, but not of the alcohol[11] (Fig.16). Analogous effects are found in the oxidation of cyclohexane with manganese stearate, where the alcohol begins to form much earlier than the ketone (Fig.17).[21] This indicates that in the presence of a catalyst, the alcohol and ketone are formed by two parallel independent routes. In the uncatalysed oxidation, they are formed according to the scheme[68,69]

$$\text{hydrocarbon} \rightarrow RO_2 \rightarrow \text{hydroperoxide} \begin{cases} \nearrow \text{alcohol} \\ \searrow \text{ketone} \end{cases} \rightarrow \text{acids}.$$

The catalyst apparently changes the routes of formation of these products, since this scheme cannot explain why the catalyst slows down the formation of the ketone, but not of the alcohol.

Experiments on the oxidation of cyclohexane with iron and nickel stearates have shown that at the start of the reaction there is parallel formation of the hydroperoxide, alcohol, and ketone[12] (Fig.18). This indicates the conversion of part of the peroxide radicals, in the presence of the catalyst, into the alcohol and ketone, without passing through

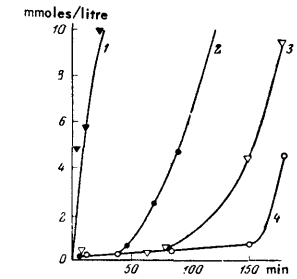


Fig. 17. Kinetic curves for the formation of 1) the alcohol and 2) the ketone in the oxidation of cyclohexane in the presence of 0.004 mole% St_2Mn, and similarly 3) and 4) in the presence of 0.017 mole% St_2Mn, at 110°.

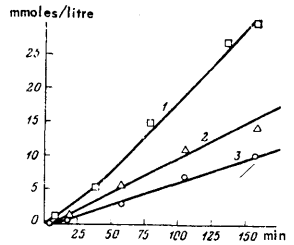


Fig. 18. Kinetic curves for the formation of 1) cyclohexanol, 2) cyclohexyl hydroperoxide, and 3) cyclohexanone at the commencement of oxidation of cyclohexane at 110° in the presence of 0.018 mole% St_3Fe.

the stage of hydroperoxide formation, i.e. it indicates that the catalyst participates in the chain-propagation reaction. To substantiate this conclusion, consider the two mechanisms for the chain oxidation of the hydrocarbon. Consider first the oxidation through hydroperoxide formation. Let the hydrocarbon be completely converted in the oxidation to hydroperoxide, at a rate $k_2[RH]^n$, and let the hydroperoxide

be converted by a chain mechanism to product P at a rate $k_4[\mathrm{ROOH}]n$. If the chains are initiated at a constant rate w_0, then with quadratic chain termination $n = \sqrt{w_0/2k_6}$, and the rates of accumulation of ROOH and P are

$$\frac{d[\mathrm{ROOH}]}{dt} = (k_2[\mathrm{RH}] - k_4[\mathrm{ROOH}])\sqrt{\frac{w_0}{2k_6}},$$

$$\frac{d[\mathrm{P}]}{dt} = k_4[\mathrm{ROOH}]\sqrt{\frac{w_0}{2k_6}}.$$

On introduction of the notation

$$\pi = \frac{[\mathrm{ROOH}]}{[\mathrm{ROOH}]_{max}}, \quad [\mathrm{ROOH}]_{max} = \frac{k_2[\mathrm{RH}]}{k_4},$$

$$\tau = k_4\sqrt{\frac{w_0}{2k_6}}[\mathrm{ROOH}]_{max}\, t, \quad \eta = \frac{[\mathrm{P}]}{[\mathrm{ROOH}]_{max}},$$

the equations take the form

$$\frac{d\pi}{d\tau} = 1 - \pi, \quad \frac{d\eta}{d\tau} = \pi.$$

hence $\pi = 1 - e^{-\tau}$, $\eta = \tau + e^{-\tau} - 1$.

At the start of the reaction $\frac{d\pi}{d\tau} = 1$ and $\frac{d\eta}{d\tau} = 0$.

The change of π and η with time is shown in Fig.19, where it is seen that at the start of the reaction π (curve *1*) increases linearly, and η autocatalytically (curve *2*).

Consider now the second mechanism, assuming part of the peroxide radicals to be converted by reaction with the catalyst M into product P and radical X, which can continue the chain. To a first approximation, it can be assumed, as before, that all the radicals combine quadratically at a rate $2k_6n^2$. Here the product P will form as a result of two reactions:

$$\mathrm{ROOH} + \mathrm{RO_2}\cdot\,(\text{or } \mathrm{X}\cdot), \text{ and } \mathrm{RO_2}\cdot + \mathrm{M} \qquad (7)$$

at a rate

$$\frac{d[\mathrm{P}]}{dt} = k_4[\mathrm{ROOH}]n + k_7[\mathrm{M}][\mathrm{RO_2}\cdot]$$

or in dimensionless variables

$$\frac{d\eta}{d\tau} = a + \pi,$$

where

$$a = \frac{k_2' k_7[\mathrm{M}][\mathrm{RH}]}{k_4[\mathrm{ROOH}]_{max}(k_7[\mathrm{M}] + k_2'[\mathrm{RH}])},$$

k_2' relates to the reaction X· + RH →

$$\eta = (a+1)\tau + e^{-\tau} - 1.$$

At sufficiently high values of a the kinetic curves for η are in this case similar to those of π (Fig.19). Comparison of Figs.18 and 19 shows the good agreement between the calculated and the experimental data. A similar situation is observed in experiments on the oxidation of cyclohexane in the presence of nickel and cadmium stearates (Table 6).

The participation of the catalyst in the chain-propagation reaction can be considered either as a reaction between a radical and the catalyst, forming a molecular product and a new radical, or as the formation of a complex between the catalyst and a free radical, the complex being active in the chain propagation reaction. Recent studies[70-72] indicate the formation of complexes between free radicals or atoms and molecules, for instance aromatic hydrocarbons. Similar

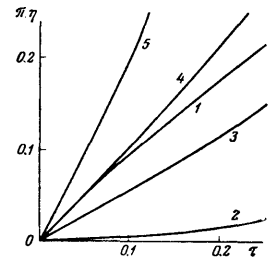


Fig. 19. Curves of π and η as functions of τ calculated from the formulae: 1) $\pi = 1 - e^{-\tau}$; 2) $\eta = \tau + e^{-\tau} - 1$; 3) $\eta = 3/2\,\tau + e^{-\tau} - 1$; 4) $\eta = 2\tau + e^{-\tau} - 1$; 5) $\eta = 3\tau + e^{-\tau} - 1$.

TABLE 6. Initial rates of accumulation of peroxide, alcohol, and ketone in the oxidation of cyclohexane at 110° ($v = v_{\mathrm{ROOH}} + v_{\mathrm{alcohol}} + v_{\mathrm{ketone}}$)

Catalyst	Concn.	$\frac{v_{\mathrm{ROOH}}}{v}\times 100\%$	$\frac{v_{\mathrm{alcohol}}}{v}\times 100\%$	$\frac{v_{\mathrm{ketone}}}{v}\times 100\%$
St_3Fe	0.018	29	55	16
St_2Ni	0.024	32	34	34
St_2Cd	0.011	55	28	17

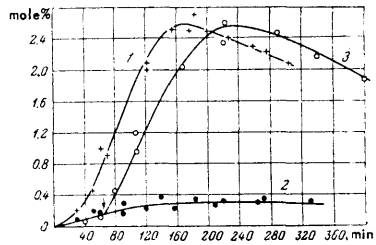


Fig. 20. Kinetics of the accumulation of hydroperoxide in the oxidation of n-decane at 140°: 1) without a catalyst; 2) with 0.3 mole% St_2Co; 3) with removal of the catalyst from the reaction zone (time of removal arrowed).

complexes may be formed between peroxide radicals and cations of metal salts; such complexes might gradually decompose or react with the hydrocarbon to form the alcohol or ketone. If the catalysts participate in the chain propagation reaction as suggested, the catalysts must influence the rate of chain propagation; in principle, this can be established by the intermittent-illumination method[73].

The suggested participation of the catalyst in chain propagation can explain the effect of the catalyst concentration on the maximum concentration of hydroperoxide and the maximum rate of reaction. It has frequently been observed that as the catalyst concentration is increased, the maximum concentration of hydroperoxide decreases, while the maximum reaction velocity increases. The catalyst causes the diminished hydroperoxide concentration, since its removal from the reaction zone produces a rapid increase in hydroperoxide concentration[69] (Fig.20).

These two simple facts are incorrectly explained in a number of proposed mechanisms. The following mechanism for the oxidation, for instance, is widely quoted:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot,\ RO_2 + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow M^+ + OH^- + RO\cdot, \quad (3)$$

$$2RO_2\cdot \rightarrow \text{mol. products}. \quad (6)$$

According to this mechanism, the maximum hydroperoxide concentration decreases with increased catalyst concentration:

$$\frac{d[ROOH]_{max}}{dt} = k_2[RH][RO_2\cdot] - (k_3[M]+k_1)[ROOH] = 0,$$

$$[RO_2\cdot] = \left[\frac{(k_1 + k_3[M])[ROOH]}{2k_6}\right]^{1/2},\ [ROOH]_{max} = \frac{k_2^2[RH]^2}{2k_6(k_3[M] + k_1)}.$$

However, the maximum rate of oxidation is independent of the catalyst concentration:

$$v_{max} = k_2[RH][RO_2\cdot] = \frac{k_2^2[RH]^2}{2k_6}.$$

When the maximum hydroperoxide concentration is reached, the process changes from a chain reaction to a radical reaction:

$$k_2[RH][RO_2\cdot] = (k_1 + k_3[M])[ROOH].$$

Such a mechanism is justified in some cases, e.g. in the oxidation of tetralin in acetic acid solution[17]. It does not, however, take into account the reaction between free radicals and the hydroperoxide, i.e. the chain decomposition of the hydroperoxide; let us consider therefore a mechanism which allows for this:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot,\ RO_2\cdot + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow M^+ + OH^- + RO\cdot, \quad (3)$$

$$ROOH + RO_2\cdot \rightarrow P + R'\cdot, \quad (4)$$

$$2RO_2\cdot \rightarrow \text{mol. products}. \quad (6)$$

If the chain decomposition of the hydroperoxide predominates, then

$$\frac{d[ROOH]_{max}}{dt} = (k_2[RH] - k_4[ROOH])n = 0,\ [ROOH]_{max} = \frac{k_2}{k_4}[RH],$$

$$v_{max} = k_2[RH]n = k_2[RH]\left[\frac{k_2[RH](k_1 + k_3[M])}{2k_4k_6}\right]^{1/2}.$$

This mechanism explains the growth of v_{max} with increase of [M], but is inconsistent with the dependence of $[ROOH]_{max}$ on [M].

Good agreement between experiment and calculation is obtained if the catalyst is assumed to take part in the chain propagation by the reaction given above with the additional step

$$RO_2\cdot + M \rightarrow X\cdot + P. \quad (7)$$

Let us denote the velocity constant of the reaction between RH and X· by k_2' and assume that the rate of second-order chain breaking is independent of the type of chain. The concentrations of $RO_2\cdot$ and X· in the reaction are in kinetic equilibrium:

$$k_2'[RH][X\cdot] = k_7[M][RO_2\cdot]$$

hence we find:

$$[RO_2\cdot] = \frac{k_2'[RH]n}{k_2'[RH] + k_7[M]},\ n = [RO_2\cdot] + [X\cdot].$$

The rate of accumulation of hydroperoxide in this reaction is

$$\frac{d[ROOH]}{dt} = k_2[RH][RO_2\cdot] - k_4[ROOH]n = \left(\frac{k_2k_2'[RH]^2}{k_2'[RH] + k_7[M]} - k_4[ROOH]\right)n,$$

hence

$$[ROOH]_{max} = \frac{k_2k_2'[RH]^2}{k_4(k_7[M] + k_2'[RH])}$$

and decreases with increase of [M].

The maximum rate of oxidation at small values of [M] increases with catalyst concentration, but the reaction remains a chain one all the time:

$$v_{max} = (k_2[RO_2\cdot] + k_2'[X\cdot])[RH] = k_2'[RH]^2\frac{k_2[RH] + k_7[M]}{k_2'[RH] + k_7[M]} \times$$

$$\times\sqrt{\frac{(k_1 + k_3[M])k_2k_2'}{2k_4k_6(k_2'[RH] + k_7[M])}} =$$

$$= k_2^2[RH]^2\sqrt{\frac{k_3[M]}{2k_4k_6(k_2[RH] + k_7[M])}}\ \text{(when } k_2 = k_2' \text{ and } k_3[M] \gg k_1).$$

Another reaction mechanism is also possible to explain the decrease in $[ROOH]_{max}$ and the increase in v_{max} as the catalyst concentration is increased. Assume that the hydroperoxide decomposes under the action of the catalyst by two routes: (*i*) without the formation of free radicals, and (*ii*) with the formation of free radicals, all the peroxide radicals being converted into hydroperoxide:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot\ RO_2 + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow PO\cdot + M + \cdot OH, \quad (3)$$

$$ROOH + M \rightarrow \text{mol. products}, \quad (5)$$

$$2RO_2 \rightarrow \text{mol. products}. \quad (6)$$

According to this mechanism,

$$[ROOH]_{max} = \frac{k_2^2[RH]^2(k_1 + k_3[M])}{2k_6[k_1 + (k_3 + k_5)[M]]^2} \simeq \frac{k_2^2k_3[RH]^2}{2k_6(k_3 + k_5)^2[M]},$$

$$v_{max} = \frac{k_2^2[RH]^2(k_1 + k_3[M])}{2k_6[k_1 + (k_3 + k_5)[M]]} \simeq \frac{k_2^2k_3[RH]^2}{2k_6(k_3 + k_5)}.$$

All the data obtained up to the present indicate a complex and multiple action of salt catalysts in an oxidation reaction. The catalysts react with oxidation products such as hydroperoxides and aldehydes to form free radicals. Moreover, some catalysts react with the free radicals and so break the chains; under certain conditions, such catalysts act as oxidation inhibitors. Furthermore, salt catalysts participate in chain-propagation reactions, and affect the composition of the resulting oxidation products. The catalysts undergo complex physicochemical modifications in the course of the oxidation. The final products of the reaction, particularly acids, precipitate the catalyst, and the reaction then proceeds with only very slight participation of the catalyst.

It is extremely important, however, that in spite of the great complexity of the catalysed oxidation of hydrocarbons, there is already sufficient understanding of a number of the phenomena involved to enable various problems in the control of the oxidation process to be recognised and solved.

Further study will undoubtedly lead to the establishment of a detailed mechanism, and to the explanation of the many singular features of catalysis by salts of metals of variable oxidation state. These studies will enable precise methods of controlled oxidation to be achieved in practice, based on the knowledge of the elementary processes involved in the catalysed oxidation of hydrocarbons and other organic substances.

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METHODS OF SYNTHESIS OF POLYPHENYL HYDROCARBONS

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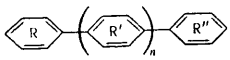
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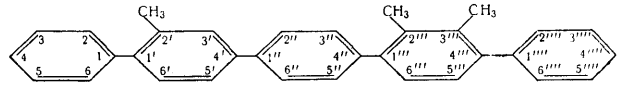
INTRODUCTION

The term polyphenyls is used for compounds whose molecules consist of a chain of substituted or unsubstituted phenyl and phenylene units.



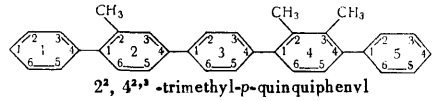
Each inner, phenylene, link of the molecule carries two aromatic residues in the *ortho*-, *meta*-, or *para*-position to one another; hence the existence of *ortho*-, *meta*-, and *para*-polyphenyls as well as mixed ones. The nomenclature is based on the use of latin numerical prefixes to give the number of aromatic nuclei in the molecule (e.g. terphenyl, quaterphenyl), the type of the polyphenyl also being indicated. The carbon atoms in each ring are numbered from the one linked to the preceding nucleus. In the "leading" phenyl radical the numbering starts either at the carbon linked to another nucleus or the one in the *para* -position to it. In the former case the rings are designated by primes, the position of the substituent being indicated by numerals. In the latter case the numeral denotes the ring containing the substituent and the numerical superscript the position of the substituent in the ring. Both methods are illustrated below:

1.



2′, 2″, 3‴-trimethyl-*p*-quinquiphenyl

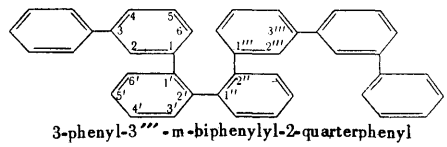
2.



$2^2, 4^{2,3}$-trimethyl-*p*-quinquiphenyl

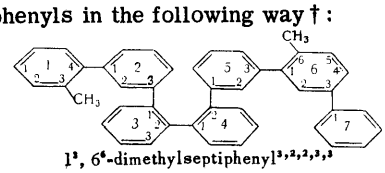
The second method is more convenient for compounds with a large number of rings[1].

Mixed polyphenyls are named by taking a part of the polycyclic chain with the same relative positions of the units and considering it as the main one, e.g.



3-phenyl-3‴-*m*-biphenylyl-2-quarterphenyl

We suggest an extension of the numeral method to mixed polyphenyls in the following way†:



$1^3, 6^6$-dimethylseptiphenyl$^{1^3,2^2,2^3,3^3}$,

the superscript numerals following the name indicating the points of attachment of subsequent rings, starting from the second one.

The interaction of non-condensed aromatic rings gives rise to a characteristic electronic structure of the polyphenyl chain and gives these compounds their specific properties which justify their classification as a separate group of compounds. Biphenyl is the first representative of the group of linear aromatic polycyclic hydrocarbons, just as the fused-ring analogue, naphthalene, is the first member of condensed aromatic hydrocarbons.

† The nomenclature based on the use of primes which has been more widely employed is adhered to in this review.