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The Coupled Reactions of Oxidation by Hydrogen Peroxide

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The results of basic studies of chemical coupling in the gas-phase oxidation of various substrates by hydrogen peroxide have been analysed. The general characteristics of the mechanism of chemical coupling in gas-phase and liquid-phase oxidation by hydrogen peroxide have been examined.
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I. INTRODUCTION

Many reactions of practical importance involving the direct oxidation of various substrates by molecular oxygen do not correspond to present-day requirements, since practically all existing technical processes take place with a low selectivity.

In the development of present-day oxidation processes in chemical technology, the use of chemically combined forms of oxygen (O_3, H_2O_2, ROOH, etc.) and the principles of coupled processes are acquiring increasing importance.

Interest in the study of oxidation in coupled chain reactions has increased considerably as a result of the work of Academician N.M.Emanuel' and his school,[1,2] who were the first to formulate the concept of radical forms of coupled chemical reactions: "...the radicals generated by one of the reactions taking place in the system act as active reagents for another reaction which does not occur to a significant extent by itself under these conditions".

This statement forms the basis of the mechanism of the coupled oxidation of various substrates by hydrogen peroxide.

The present review examines reactions involving coupled oxidation by hydrogen peroxide, in which it has been shown that H_2O_2 can be used effectively both to discover new chemical reactions and to intensify and simplify the technology of oxidation processes of practical importance.

Hydrogen peroxide has various applications, and its world production has been estimated as several hundred thousand tons.

The use of H_2O_2 in industry in most cases has led to an improvement in the quality of production, a decrease in its cost, a decrease in environmental pollution, and increase in productivity, simplification of the technology, etc.

Because of its intermediate position in the redox triad

$$O_2 \underset{-2H}{\overset{2H}{\rightleftarrows}} H_2O_2 \underset{-2H}{\overset{2H}{\rightleftarrows}} H_2O$$

H_2O_2 shows a dual reactivity, and can act as an electron donor or as an electron acceptor, depending on the nature of the substrate.

Studies of reactions involving H_2O_2 have dealt chiefly with methods of preparation, the mechanism of the homogeneous and heterogeneous decomposition of H_2O_2, and the use of H_2O_2 as polymerisation initiator and as oxidising agent for the liquid-phase oxidation of organic substrates using transition metal compounds or enzymes as catalysts. Until recently there were practically no published data on the use of H_2O_2 as an oxidising agent in the gas phase.

II. CHEMICAL COUPLING IN GAS-PHASE OXIDATION BY HYDROGEN PEROXIDE

The use of hydrogen peroxide as an oxidising agent in the gas phase (as shown below) makes it possible to oxidise effectively aromatic compounds, alcohols, halogen-containing compounds,[3] and even nitrogen.[4] It is assumed that the oxidation is due to the existence of chemical coupling.[5,6] The primary reaction in this case is

$$H_2O_2 + H_2O_2 \rightarrow \underset{\text{intermediates}}{[\dot{O}H,\ H\dot{O}_2]} \rightarrow 2H_2O + O_2 \quad \Delta G^{\circ}_{298} = -58.8 \text{ kcal mole}^{-1} \qquad (1)$$

The $HO_2^{\bullet}$ free radicals formed in this reaction bring about the oxidation of the substrate according to the overall equation

$$H_2O_2 + \text{acceptor} \rightarrow \text{reaction products} . \qquad (2)$$

In the H_2O_2–acceptor–H_2O system, hydrogen peroxide is converted into the active form as the radical $HO_2^{\bullet}$ (in which the acceptor–donor properties of H_2O_2 are preserved), which transfers the inductive action of the primary reaction to the secondary reaction. The $HO_2^{\bullet}$ radical acts as it were as the intermediary agent between the coupled reactions, and the "active oxygen" in it is responsible for the selective oxidation.[6]

1. The Coupled Dehydrogenation of Various Substrates by Hydrogen Peroxide

Experimental studies to detect chemical coupling in gas-phase oxidation by hydrogen peroxide[6,7] were carried out in a flow system using an integral reaction vessel (ideal displacement conditions), whose design made it possible to introduce H_2O_2 into the reaction zone.

To determine which species is responsible for oxidation in the RH–H_2O_2–H_2O system, the model system chosen was the coupled dehydrogenation of ethylbenzene by a 15% aqueous solution of hydrogen peroxide and by molecular oxygen. For comparison of the results, the O_2 was supplied in quantities equivalent to its concentration in 15% aqueous H_2O_2 solution.[7,8]

Experiments on the coupled dehydrogenation of ethylbenzene (ETB) in the range 580–620 °C showed that the use of hydrogen peroxide gives high yields of styrene, equal to 39.3 mass % and 90 mass %, calculated respectively for the initial ETB and the ETB reacted, at 620 °C. At the end of the reaction, no condensation products (CP) were detected, and the volatile products consisted chiefly of CO_2, in quantities not exceeding 1% by weight.

In the dehydrogenation of ethylbenzene by molecular oxygen, the yields of styrene are much lower (8–10 mass %) than in the first case, and condensation products are formed in quantities of up to 1.7% by wt. on the walls of the quartz reaction vessel. In addition, the quantity of O_2 in the gaseous products reaches 80 % by volume, whereas the gaseous products of the conjugated dehydrogenation by hydrogen peroxide do not contain molecular oxygen. Thus the dehydrogenating agent in the system is hydrogen peroxide, that is the coupled dehydrogenation by hydrogen peroxide takes place by a mechanism which differs fundamentally from that of high-temperature oxidation by molecular oxygen. Although by itself the formation of an oxygen atom by the decomposition of H_2O_2 in a hydrocarbon medium by a heterogeneous process is unlikely, nevertheless to eliminate the possibility of the participation of the atoms of O_2 in the dehydrogenation, the decomposition of nitrous oxide was used as a source of oxygen atoms: [9]

$$N_2O \rightarrow N_2 + O^{\cdot}$$

The degree of decomposition of N_2O in the presence of butane and cyclohexane at 500–600 °C is 25 mole % and 30 mole % respectively, [10,11] indicating that the decomposition of N_2O is independent of the presence of hydrocarbons in the medium.

In addition to unsaturated compounds, a large number of side products (H_2, CH_4, C_2H_6, C_2H_4) were found in the products of the transformation of C_4H_{10}. The dehydrogenation of C_6H_{12} in the presence of H_2O_2 is also characterised by a much higher selectivity at higher degrees of conversion, compared with the reaction in the presence of N_2O, where the only active intermediate species is atomic oxygen (see Table 1). [11,23]

Table 1. The coupled dehydrogenation of cyclohexane with the participation of hydrogen peroxide and nitrous oxide. [11,23]

System	C_6H_{10}, mass %	C_6H_8, mass %	C_6H_6, mass %	Selectivity, %
$C_6H_{12}+H_2O_2$	20	4	3	98
$C_6H_{12}+N_2O$	9	2	7	80

Thus the mechanism of dehydrogenation by hydrogen peroxide differs from that of oxidative dehydrogenation by molecule oxygen and nitrous oxide. The participation of an oxygen atom as an active reaction centre in the conjugated oxidation of the substrate by hydrogen peroxide is therefore unlikely, and elementary reactions involving it need not be considered in the reaction mechanism. This conclusion is confirmed by a study of the dehydrogenation of butane both by hydrogen peroxide and by nitrous oxide. [10]

To establish the possibility that surfaces influence the nature of the reaction of H_2O_2 with hydrocarbons, the conjugated dehydrogenation of various alkylbenzenes was studied in reaction vessels treated with inorganic salts. [12] The results of these experiments indicate that in all cases the reaction shows an appreciable sensitivity to the nature of the surface of the reaction vessel. The yields of the desired products decrease in the order:

$$B_2O_3 > \text{untreated reaction vessel} > K_2B_4O_7 > KBr > KCl > BaBr_2$$

The results correlate with data from Ref. 13, where it was shown that a quartz surface treated with metal salts influences the rate of the destruction of $HO_2^{\cdot}$ radicals, which decreases in the same salt sequence. This indicates that the surfaces which are most active in chain termination as a result of the destruction of $HO_2^{\cdot}$ are least favourable for the conjugated dehydrogenation of hydrocarbons.

The kinetic estimation of the decomposition of H_2O_2 to $HO_2^{\cdot}$ and $^{\cdot}OH$ free radicals is of interest in this connection. The decomposition of H_2O_2 in the gas phase has been fairly well studied, and takes place by the following mechanism: [14–16]

	$\lg A$, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
$H_2O_2 + M \xrightarrow{k_1} 2\dot{O}H + M$	17.08	45
$H_2O_2 + \dot{O}H \xrightarrow[k_2]{} HO_2^{\cdot} + H_2O$	13.0	1.8
$HO_2^{\cdot} + \text{wall} \xrightarrow{k_3} HO_{2\,ads}$	1.0	8.2
$^{\cdot}OH + \text{wall} \rightarrow OH_{ads}$	0.3	7.0

where M is the total number of molecules in the reaction volume, and A the pre-exponential factor.

According to this scheme

$$\frac{[HO_2^{\cdot}]}{[\dot{O}H]} = \frac{k_1}{k_2}[H_2O_2] \qquad (3)$$

which makes it possible to estimate the ratio of the concentrations of the active centres in the system.

Under the conditions of the experiment, [4] the ratio (3) usually lies in the range 10^3–10^7, that is the concentration of the radical $HO_2^{\cdot}$ in the gas phase is many powers of ten greater than that of $^{\cdot}OH$.

Thus dehydrogenation in the presence of H_2O_2 evidently takes place by a free-radical mechanism, and the rate of the process is determined mainly by the concentration of $HO_2^{\cdot}$ in the system.

The mechanism of dehydrogenation by hydrogen peroxide can be illustrated by several examples.

The kinetics and yield of the products of the dehydrogenation of ETB by hydrogen peroxide [7,17] in the temperature range 500–600 °C at volume rates of supply of ethylbenzene of 0.2–0.8 h^{-1} and ratios $C_6H_5C_2H_5 : H_2O_2$ in the range from 1:1 to 1:4 depend on the ratio of the surface area (S) to the volume (V). Under optimum conditions the yield of styrene reaches 40% by weight with a selectivity of 90% by weight.

The mechanism of the process involves the following elementary stages: [17]

$$H_2O_2 \rightarrow 2\dot{O}H - 52.0 \text{ kcal mole}^{-1} \qquad (4)$$

$$H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O + 26.7 \text{ kcal mole}^{-1} \qquad (5)$$

$$C_6H_5C_2H_5 + \dot{O}H \rightarrow C_6H_5\dot{C}_2H_4 + H_2O + 42.9 \text{ kcal mole}^{-1} \qquad (6)$$

$$C_6H_5\dot{C}_2H_4 \rightarrow C_6H_5C_2H_3 + H - 52.7 \text{ kcal mole}^{-1} \qquad (7)$$

$$C_6H_5C_2H_5 + H\dot{O}_2 \rightarrow C_6H_5\dot{C}_2H_3 + H_2O + \dot{O}H + 26.7 \text{ kcal mole}^{-1} \qquad (8)$$

$$H_2O_2 + H \rightarrow H_2O + \dot{O}H + 68.4 \text{ kcal mole}^{-1} \qquad (9)$$

$$C_6H_5C_2H_5 + HO_2^{\cdot} \rightarrow C_6H_5\dot{C}_2H_4 + H_2O_2 + 14.7 \text{ kcal mole}^{-1} \qquad (10)$$

$$HO_2^{\cdot} + \text{wall} \rightarrow HO_{2\,ads} \qquad (11)$$

$$^{\cdot}OH + \text{wall} \rightarrow OH_{ads} \qquad (12)$$

This scheme includes three paths for the chain formation of styrene in the $C_6H_5C_2H_5$–H_2O_2–H_2O system.

The hydroxyl radical formed in elementary stage (4) is consumed in the bulk phase by two possible reactions, (5) and (6). Comparison of the kinetic parameters of the elementary stages (5) and (6), whose activation energies are 1–2 kcal $mole^{-1}$ [14] and 5–8 kcal $mole^{-1}$ [18] respectively, shows that the rate of reaction (5) is much greater than that of reaction (6). Thus in the $C_6H_5C_2H_5$–H_2O_2–H_2O system, of

the two paths by which $^{\cdot}OH$ are consumed, stage (5) is more probable. A noteworthy feature is that the formation of hydrocarbon radicals by the reaction $RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O$ would have led, in subsequent stages of development of the process, to the formation of new free radicals $RO^{\cdot}$ and $RO_2^{\cdot}$. Their transformations should lead to the appearance of oxygen-containing substances and products of oxidative cracking in the reaction products, in addition to unsaturated compounds.[19] The products of the dehydrogenation of ethylbenzene do not include organic oxygen-containing compounds, however; at relatively low yields of styrene (about 20 mass %), products of oxidative cracking are not detected either.[7]

Thus the elementary reaction (8) is apparently the most probable.[17] Usually, the activation energy of stage (10) $E_{10} > 12.5$ kcal mole^{-1} ($\lg A_{10} = 9.4$ cm^3 mole^{-1} s^{-1}),[20] and for stage (8), E_8 does not exceed 11.0 kcal mole^{-1} ($\lg A_8 = 9.6$ cm^3 mole^{-1} s^{-1}).[17,21] For chain termination reactions by the destruction of the free radicals $^{\cdot}OH$ and $HO_2^{\cdot}$ on the walls of the quartz reaction vessel, their accommodation coefficients were determined:[13,17] $\varepsilon_{OH} = 0.5 \times 10^{-6}$ and $\varepsilon_{HO_2} = 0.2 \times 10^{-5}$.

Thus estimation of the rates of the elementary stages (4) to (12) indicates that coupled dehydrogenation is an unbranched chain reaction, in which chain propagation involves two stages:

$$H_2O_2 + \dot{O}H \xrightarrow{k_5} H\dot{O}_2 + H_2O \qquad (5)$$

$$C_6H_5C_2H_5 + H\dot{O}_2 \xrightarrow{k_8} C_6H_5\dot{C}_2H_3 + H_2O + \dot{O}H \qquad (8)$$

overall reaction

$$C_6H_5C_2H_5 + H_2O_2 = C_6H_5C_2H_3 + 2H_2O \qquad (13)$$

The proposed mechanism and the method of stationary states gave a kinetic equation[21] for the reaction rate which adequately describes the experimental data in the temperature range 500–620 °C:

$$-d[\mathrm{ETB}]/dt = k_{\mathrm{eff}}[\mathrm{ETB}][H_2O_2]$$

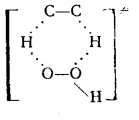
$$k_{\mathrm{eff}} = \frac{k_1 k_8}{k_{11}} = 0.35 \cdot 10^{16} \exp(-55300/RT) \text{ litre mole}^{-1}\text{s}^{-1}$$

The expression for k_{eff} does not contain the rate constant of reaction (5), so that the limiting step in chain propagation is reaction (8), which involves $HO_2^{\cdot}$.

The dehydrogenation of ethylbenzene by hydrogen peroxide (13) is a coupled reaction, since it is induced by the decomposition of H_2O_2 (the primary reaction). Both processes in the system are complex, and take place via a common intermediate active species, the $HO_2^{\cdot}$ radical,[7,22] and in the mechanism of the conjugated dehydrogenation a central position is occupied by the new elementary stage

$$\text{>CH–CH<} + HO_2^{\cdot} \rightarrow \text{>C=C<} + H_2O + \dot{O}H \qquad (5)$$

This reaction involves the formation of the six-membered transition state



which subsequently decomposes to give H_2O, alkene, and the free radical $^{\cdot}OH$, which is more active than the original $HO_2^{\cdot}$.

Thus the available theoretical and experimental data lead to a new and chemically specific mechanism of conjugated dehydrogenation, involving the primary (inducing) reaction of H_2O_2 decomposition and the secondary (induced) reaction of conjugated dehydrogenation.[6]

The use of H_2O_2 makes it possible to carry out effectively the incomplete dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene; under other conditions this reaction is thermodynamically difficult.[23]

The conjugated dehydrogenation of cyclohexane by hydrogen peroxide can take place over a wide temperature range (450–630 °C) at different volume rates of supply of cyclohexane (0.1–1.0 h^{-1}) and H_2O_2 concentrations of 5–30% by weight. Under the optimum conditions at 580 °C, a conditional contact time $\tau = 4.2$ s, and a volume ratio of cyclohexane to aqueous H_2O_2 solution (20% by weight) of 1:3, the yields of cyclohexene and cyclohexadiene are 20% by weight and 4% by weight respectively, with a selectivity with respect to double bonds of 97% by weight.

Fig. 1 gives typical kinetic curves showing the consumption of cyclohexane and the accumulation of reaction products at 580 °C; the kinetic curves for the accumulation of cyclohexadiene and benzene are *S*-shaped.[23] These kinetic data indicate that the reaction products (cyclohexadiene and benzene) are formed by the successive dehydrogenation of the more saturated analogues. Thus the reaction products are formed in the successive stages:

		$\lg A_{\mathrm{eff}}$, cm^{3}mole^{-1}s^{-1}	E_{eff}, kcal mole^{-1}
$H_2O_2 +$	$C_6H_{12} \xrightarrow{k_{\mathrm{eff}\,1}} C_6H_{10} + H_2O$	24.95	63.0
	$C_6H_{10} \xrightarrow{k_{\mathrm{eff}\,2}} C_6H_8 + H_2O$	23.95	53.0
	$C_6H_8 \xrightarrow{k_{\mathrm{eff}\,3}} C_6H_6 + H_2O$	22.86	49.0

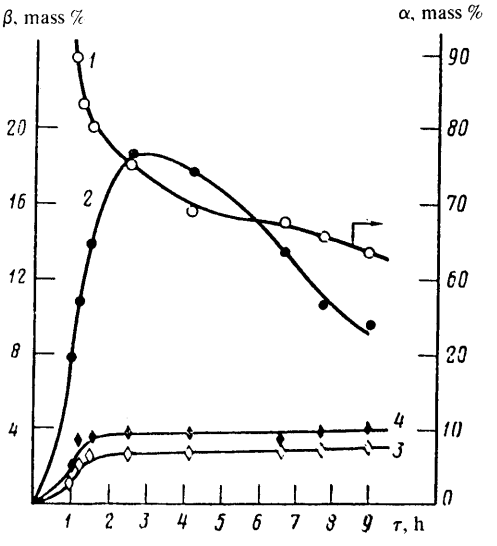


Figure 1. Kinetic curves giving the consumption (α) of cyclohexane (*1*) and the accumulation (β) of cyclohexene (*2*), cyclohexadiene (*3*), and benzene (*4*) in the coupled dehydrogenation of cyclohexane; $V_0 = 0.237$ h^{-1}, ratio C_6H_{12} : 20% aqueous H_2O_2 solution = 1:3 (by volume), 580 °C, τ is the conditional contact time.[23]

Each of the successive reactions described by the chain unbranched scheme (4), (8), and (11) represents a combination of the stages of chain initiation, propagation, and termination.

A system of kinetic equations providing an adequate description of the experimental data has the form:[24,25]

$$-\frac{d[C_6H_{12}]}{dt} = k_{eff\,1}[C_6H_{12}][H_2O_2]$$

$$-\frac{d[C_6H_{10}]}{dt} = k_{eff\,1}[C_6H_{12}][H_2O_2] - k_{eff\,2}[H_2O_2][C_6H_{10}]$$

$$\frac{d[C_6H_8]}{dt} = k_{eff\,2}[H_2O_2][C_6H_{10}] - k_{eff\,3}[H_2O_2][C_6H_8]$$

The overall dehydrogenation process is effectively described by a chain radical scheme with the following rate constants for the reaction of $HO_2^{\cdot}$ with cyclohexane and alkenes:

			lg A, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
$HO_2^{\cdot}$ +	C_6H_{12}	C_6H_{10}	11.65	15.2
	$C_6H_{10} \rightarrow \dot{O}H + H_2O +$	C_6H_8	10.65	13.2
	C_6H_8	C_6H_6	9.86	9.2

The high selectivity of the process (95–99% by weight) and the absence of oxygen-containing reaction products makes it possible to eliminate a number of technological operations involving the separation of an appreciable quantity of components difficult to separate. Moreover, the high selectivity makes possible more complete utilisation of the raw materials.

An important task is the synthesis of pyridine bases and their derivatives, and the preparation of the corresponding N-oxides.[26] The realisation of the mechanism of chemical coupling in the oxidation of 4-ethylpyridine (4-ETP) by hydrogen peroxide[27] led to the development of a new method for obtained 4-vinylpyridine (4-VNP) and 4-vinylpyridine N-oxide. In a reaction vessel made entirely of quartz, in the range of volume rates of supply of 4-ETP 0.065–0.783 h^{-1} at a ratio of 4-ETP and 20% aqueous H_2O_2 solution of 1:3, the reaction takes place with a high selectivity up to 640 °C. Under the optimum conditions (620 °C), the yield of 4-VNP is 20.9% by weight with a selectivity of 92% by weight. Under the same conditions in a reaction vessel filled with quartz granules, the yield of 4-VNP increases considerably and amounts to 44.3% by weight with a selectivity of 96% by weight (Table 2).[28]

Table 2. Influence of the S/V ratio on the yield of 4-VNP.[28]

S/V ratio, cm^{-1}	Yield of 4-VNP (mass %) in relation to temperature, °C		
	600	620	640
Empty reactor, $S/V = 0.8$	15.2	20.9	21.8
With quartz packing, $S/V = 8.2$	39.1	44.3	46.7

The increase in the yield of 4-VNP when the reaction zone is filled with quartz granules is probably related to the fact that under the conditions studied, in a reaction vessel with quartz packing, the homogeneous decomposition of H_2O_2 is accompanied by the heterogeneous decomposition

$$H_2O_2 + \text{wall} \longrightarrow \dot{O}H + \text{wall–OH} \qquad (14)$$

With chain initiation by reaction (14) there is a gain of energy relative to the homogeneous reaction, equal to the heat of formation of the M–OH bond. Other conditions being equal, increase in the value of the factor S/V apparently leads to an increase in the concentration of active centres and hence in the yield of desired product.

The kinetic parameters of the overall reaction and the stage involving the reaction of 4-ETP with $HO_2^{\cdot}$ are given below:[29]

	lg A, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
4-ETP + H_2O_2 = 4-VNP + $2H_2O$	23.8	51.0
4-ETP + $HO_2^{\cdot}$ → 4-VNP + H_2O + $^{\cdot}OH$	10.8	10.2

In the liquid phase and at low temperatures, H_2O_2 can be used for the N-oxidation of pyridine bases, using organic acids and their anhydrides as catalysts. The synthesis of N-oxides without the use of a catalyst is of interest, since components giving decomposition products difficult to remove from the system are introduced.

The oxidation of 4-ETP by hydrogen peroxide showed that the maximum yield of 4-VNP N-oxide (Fig. 2)[30] is achieved at 300 °C. Under the optimum conditions at this temperature, the chief reaction product is 4-VNP N-oxide, the yield of which is 33% by weight with a selectivity of 98%. Increase in temperature from 200 °C to 300 °C increases the yield of N-oxide, probably because of an increase in the rate of the production of active centres in the decomposition of H_2O_2. Further increase in temperature from 300 °C to 400 °C leads to a decrease in the yield and the selectivity of formation of 4-VNP N-oxide. At a temperature of 400 °C, 19.8% 4-VNP, 91% pyridine, and only about 7% by weight of the N-oxide are formed.

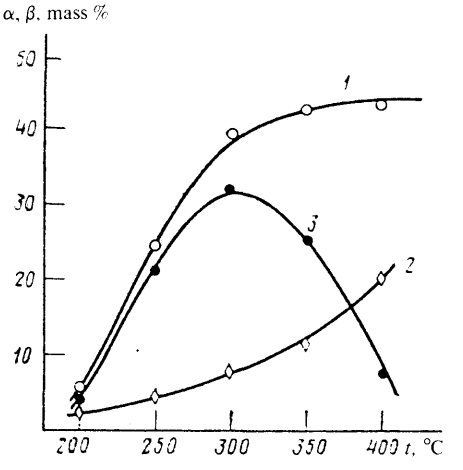


Figure 2. Influence of temperature on the degree of conversion (α) of 4-ETP (*1*) and the yields (β) of 4-VNP (*2*) and 4-VNP N-oxide (*3*) in the coupled oxidation of 4-ETP; $V_0 = 0.045\ h^{-1}$, [4-ETP]:[H_2O_2] = 1:3, H_2O_2 concentration 30% by weight.[30]

Thus depending on the oxidation conditions, the coupled oxidation of 4-ETP by hydrogen peroxide can be directed towards the formation of 4-VNP or its N-oxide.

The possible coupled dehydrogenation of alkenes by hydrogen peroxide was confirmed by the dehydrogenation of propene to allene and of isopentenes to isoprene.[31,32]

The familiar oxidative dehydrogenation of propene to allene in the presence of iodine[33] at a temperature of 625–700 °C is characterised by low yields of allene, 3.6% by weight, and a

low selectivity of its formation (6% by weight). In the case of the coupled dehydrogenation of propene under the optimum conditions (at 700 °C), the yields of allene and methylacetylene are ~20% by weight and 10% by weight respectively[34] (Fig.3). With increase in temperature above 700 °C, the yield of methylacetylene continues to increase, whereas that of allene decreases.

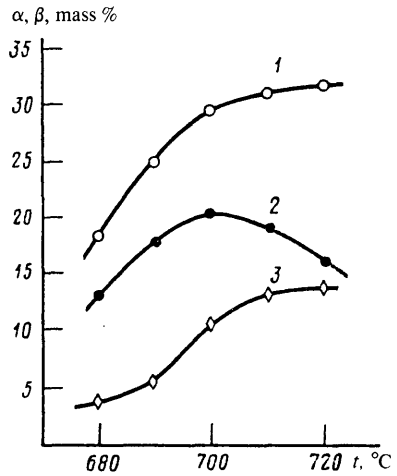


Figure 3. Influence of temperature on the degree of conversion (α) of propene (*1*) and the yields of allene (*2*) and methylacetylene (*3*) in the coupled dehydrogenation of propene; contact time 0.045 s.[34]

Fig.4 indicates that the coupled dehydrogenation of isopentenes with isomer compositions close to that of industrial fractions gives a fairly high yield of isoprene (25% by weight, with a selectivity of 75% by weight).[32] An advantage of this reaction over the oxidative catalytic dehydrogenation of isopentenes,[35] in spite of the relatively low selectivity, is the absence of the effect of retardation of the process by reaction products.

Of practical interest is the coupled dehydrogenation of industrial fractions of di-isopropylbenzene containing 57% *m*-di-isopropylbenzene and 34% *p*-di-isopropylbenzene by weight;[36] the yield of *p*-di-isopropenylbenzene in the dehydrogenation product reaches 30% by weight. The authors cited[36] compared the results with data on the catalytic dehydrogenation of di-isopropylbenzene on Shell-105 catalyst, and concluded that the yield and selectivity of the process are much higher in the coupled dehydrogenation of *p*-di-isopropylbenzene.

There are other examples of the preparation of alkenes of practical importance by coupled dehydrogenation, and these are considered below.

To some extent, the increase in the production of chloroalkenes[37] by existing technology is restricted by the loss of chlorine in byproducts, so that the development of methods for the dehydrogenation of chloroalkanes free from this disadvantage appears promising.

The oxidative dehydrogenation of ethyl chloride by air over a catalyst consisting of chromium oxide deposited on Al_2O_3 [38] is of interest in this connection. This process has a low yield and selectivity, however, since at the optimum temperature of 367 °C the yield of vinyl chloride is 17% by weight for a degree of conversion of 21% by weight. Some of these unsatisfactory features can be eliminated by the development of a new method for obtaining vinyl chloride, namely the coupled dehydrogenation of ethyl chloride by hydrogen peroxide.[39] Under the optimum conditions at a temperature of 450 °C, the yield of vinyl chloride is 37.8% by weight for a degree of conversion of 52% by weight, which is more than double the values for the process in Ref.38. It should be borne in mind the halogenoalkenes with more complex structures can also be synthesised in this way.

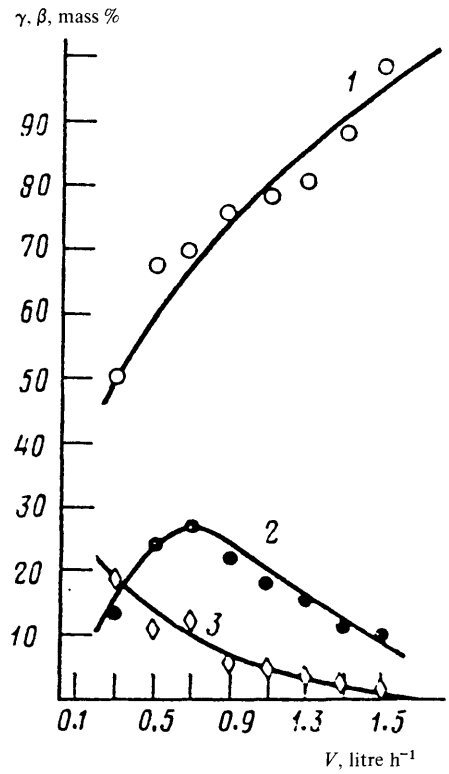


Figure 4. Influence of the rate of supply of the mixture of isopentenes and nitrogen ($V_{iso\text{-}C_5H_{10}} : V_{N_2} = 1:10$) on the selectivity of the coupled dehydrogenation (γ) (*1*), the yield of isoprene (*2*), and the total yield of side products (*3*); rate of supply of 20% aqueous H_2O_2 solution 0.185 ml h^{-1}, temperature 553 °C.[32]

The oxidative dehydrogenation of organic alcohols provides a relatively new approach to the development of industrial processes for obtaining aldehydes and ketones.[40–42] In this respect, the most successful from the technological viewpoint is the method for obtaining acetaldehyde by oxidising ethanol (at 350–490 °C) in an alcohol–air mixture in the presence of fused vanadium oxide or alkali metal vanadates catalysts with alkali metal sulphates or chlorides as promoters.[42] The yield of the desired product is 65.9% by weight, calculated on the alcohol passed, for a degree of conversion of 69.2% by weight. An unsatisfactory feature of the method[42] is the relatively low yield of the desired product and the increase in the complexity of the process with the use of an expensive catalyst.

To simplify the process and increase the yield of product, the oxidative dehydrogenation of C_2H_5OH has been carried out[43] by means of hydrogen peroxide by a conjugated mechanism. By varying different parameters of the reaction in the range 450–550 °C, it is possible, without using catalysts, to achieve fairly high yields of acetaldehyde (up to 87% by weight with a selectivity of not less than 97% by weight).

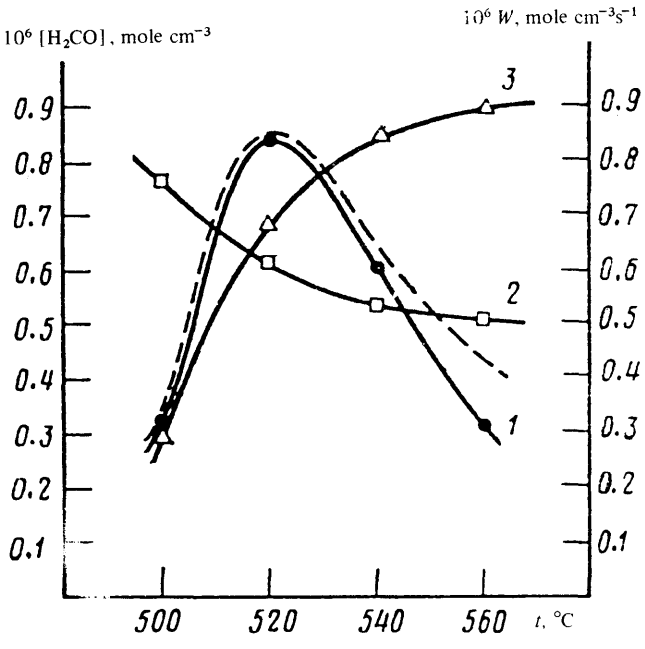


Figure 5. Temperature dependence of the H_2CO concentration (*1*) and the rates of accumultation (*W*) of $HO_2^{\cdot}$ (*2*) and $^{\cdot}CH_3$ (*3*) in the oxidation of methane by hydrogen peroxide; [CH_4] : [25% aqueous H_2O_2 solution] = 1 : 1, contact time τ = 1.2 *s*; the broken line gives the calculated curve for the accumulation of H_2CO.[50]

The high efficiency of the use of H_2O_2 in the oxidation of alcohols can also be illustrated by the dehydrogenation of s-butyl alcohol (2-BA) to methyl ethyl ketone (MEK). The oxidative dehydrogenation of 2-BA to MEK is now carried out using as catalysts metals such as gold and silver;[44,45] in the temperature range 520–600 °C, the yield of MEK is 70–85% by weight with a selectivity of 93–96% by weight. In spite of the high selectivity and degree of conversion to MEK, the presence of various side products such as acetaldehyde, acetone, diacetyl, CO, and CO_2 creates additional technological difficulties in the separation of MEK from the reaction medium.

In the liquid-phase oxidation of 2-BA,[46] although it is possible to avoid the use of precious metal catalysts, the characteristics of the process (the yield of MEK is 23.5% by weight with a selectivity of 79.4% by weight) are much inferior to those of the catalytic processes. Moreover, at 115–135 °C, it is necessary to use a pressure of 9–20 atm, to carry out the process and also to use initiating additives to decrease the induction period. The coupled dehydrogenation of 2-BA by hydrogen peroxide is free from most of these disadvantages, and makes it possible to increase the selectivity to 99% by weight, and to simplify the technology of the process, since it can be carried out at atmospheric pressure without using catalysts or special additives. The process is carried out in the gas phase at 460–560 °C with a yield of MEK of 26–44% by weight.

The possibility of obtaining unsaturated hydrocarbons and their derivatives by the conjugated decomposition of H_2O_2 and dehydrogenation of organic compounds indicates that this method is to some extent general.

2. The Coupled Oxidation of Methane to Formaldehyde by Hydrogen Peroxide

A large number of studies in the last ten years have been devoted to the incomplete oxidation of methane. The increased interest in the development of this method is due to the fact that methane is a practically inexhaustible natural raw material, whose possible utilisation will make it possible to satisfy completely the requirements of the national economy for methanol and formaldehyde.

The study of the mechanism of the oxidation of methane by oxygen in the presence of small quantities of H_2O_2 [47,48] has shown that H_2O_2 has a promoting action in the formation of formaldehyde. The intermediate species formed in the reaction are the free radicals $HO_2^{\cdot}$ and $CH_3O_2^{\cdot}$, whose transformations give the final reaction product H_2CO. In this reaction, H_2O_2 remains an intermediate product and accumulates in extremely small quantities.[47] The main oxidising agent is molecular oxygen, and the mechanism of the oxidation with added H_2O_2 does not differ significantly from the mechanism of the oxidation by O_2 in the absence of H_2O_2.

At the same time, the oxidation of various substrates by hydrogen peroxide in the gas phase takes place by a mechanism which is different from that involving molecular oxygen.[48]

The oxidation of methane to formaldehyde can be carried out with a high efficiency by the coupled oxidation of CH_4 in the presence of H_2O_2.[49,50]

The yield of H_2CO in the oxidation of CH_4 by hydrogen peroxide passes through a maximum with increase in the reaction temperature (Fig.5).[50] This form of the dependence is clearly related to the fact that H_2CO undergoes secondary reactions at temperatures above 520 °C. The maximum yield of H_2CO (39% by weight) calculated on the methane passed is reached at 520 °C, and at higher temperatures H_2CO is oxidised to CO. The concentration of CO in the reaction products increases with increase in temperature.

In the oxidation of methane by hydrogen peroxide, the following reaction becomes important:

$$CH_4 + OH^{\cdot} \rightarrow CH_3^{\cdot} + H_2O \quad \lg A = 12.5\ cm^3 mole^{-1} s^{-1}\ E = 2.0\ kcal\ mole^{-1} \qquad (15)$$

The concentration of $HO_2^{\cdot}$ in the H_2O_2–H_2O–CH_4 system will be determined by the ratio of the rates of reactions (5) and (15). At a molar ratio $CH_4 : H_2O_2$ = 1 : 1, corresponding to the optimum condition for obtaining formaldehyde, the ratio $[HO_2^{\cdot}]/[^{\cdot}OH] = 0.22 \times 10^4$, and the rates of the elementary reactions (5) and (15) with allowance for the reaction

$$CH_3^{\cdot} + HO_2^{\cdot} \rightarrow H_2CO + H_2O \qquad (16)$$

are practically equal and lie in the range $(0.46–0.60) \times 10^{-6}$ mole cm^{-3} s^{-1}.

Thus the radical $^{\cdot}OH$ formed in reaction (4) reacts with H_2O_2 and CH_4 at practically identical rates.

In this respect, the oxidation of CH_4 by hydrogen peroxide occupies a unique position, since in the presence of other compounds, for example ethylbenzene, cyclohexane, etc., the concentration ratio $[HO_2^{\cdot}]/[^{\cdot}OH] \gg 10^4$,[17] that is the main active centre is $HO_2^{\cdot}$. Under the optimum conditions for the

oxidation of methane, the concentrations of $^{\cdot}CH_3$ and $HO_2^{\cdot}$ are related by the inequality $[HO_2^{\cdot}]/[^{\cdot}CH_3] < 10^2$. This indicates that the cross recombination by reaction (16) is the main route to the formation of H_2CO. Other alternative routes to the formation of formaldehyde have been examined,[15] such as:

	$\lg A$, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$	
$\dot{C}H_3 + H\dot{O}_2 \rightarrow CH_3\dot{O} + \dot{O}H$	13.51	≈ 0	(17)
$CH_3\dot{O} + \dot{C}H_3 \rightarrow H_2CO + CH_4$	13.4	≈ 0	(18)

The elementary stages (17) and (18) apparently do not play a signficant role, since the formation of the methoxy radical by reaction (17) should have led to the accumulation of methanol in the system by reaction (19), and this is not observed:[50]

$$CH_3\dot{O} + CH_4 \rightarrow CH_3OH + \dot{C}H_3 \qquad (19)$$

The addition of CH_3OH to the CH_4–H_2O_2–H_2O system leads to the unambiguous conclusion that CH_3OH is not an intermediate product of the selective oxidation of CH_4 by hydrogen peroxide.[50,51]

Under the conditions of the selective oxidation of CH_4 by hydrogen peroxide, the formation of CO and CO_2 is not observed, so that at relatively low temperatures and short contact times, the elementary stages involving their formation were not included in the proposed mechanism for the oxidation of CH_4.

In addition, the following stage was not taken into account in the oxidation scheme[15]

$$CH_4 + H\dot{O}_2 \rightarrow \dot{C}H_3 + H_2O_2 \quad \lg A = 13.3\ cm^3 mole^{-1} s^{-1}\ E = 18\ kcal\ mole^{-1}$$

since it has a low probability, because of its high activation energy. Chain termination as a result of the destruction of $^{\cdot}CH_3$:[51]

$$^{\cdot}CH_3 + wall \rightarrow CH_{3\,ads}\ \lg A = 0.68\ s^{-1}\ E = 13.3\ kcal\ mole^{-1} \qquad (20)$$

was added to the elementary reactions (4), (5), (11), (12), (15), and (16).

The overall equation for the coupled oxidation of methane by hydrogen peroxide taking account of these stages has the following form:

$$CH_4 + 2H_2O_2 = H_2CO + 3H_2O \qquad (21)$$

These studies indicated that the most probable mechanism is one in which the chemical coupling between the decomposition of H_2O_2 and the oxidation of methane takes place through common intermediates, namely the free radicals $^{\cdot}OH$ and $HO_2^{\cdot}$.[50]

The proposed mechanism of formation of H_2CO was used to compile the following system of kinetic equations, which provide an adequate description of the experimental data (see Fig.5):[50]

$$-\frac{d[CH_4]}{dt} = k_{15}[CH_4][\dot{O}H]$$

$$\frac{d[\dot{O}H]}{dt} = 2k_4[H_2O_2][M] - k_5[H_2O_2][\dot{O}H] - k_{15}[CH_4][\dot{O}H] - k_{12}[\dot{O}H]$$

$$\frac{d[H\dot{O}_2]}{dt} = k_5[H_2O_2][\dot{O}H] - k_{16}[\dot{C}H_3][H\dot{O}_2] - k_{11}[H\dot{O}]_2$$

$$\frac{d[\dot{C}H_3]}{dt} = k_{15}[CH_4][\dot{O}H] - k_{16}[\dot{C}H_3][H\dot{O}_2] - k_{20}[\dot{C}H_3]$$

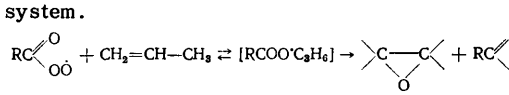
In the calculation, on the basis of Ref.52, it was assumed that the pre-exponential factor for the elementary stage (16) $\lg A_{16} = \lg A_{17}$. It was assumed that the activation energy of the recombination of the free radicals is close to zero.

Thus these studies gave the conditions for the selective coupled oxidation of methane by hydrogen peroxide to give formaldehyde, and a mechanism was proposed for the process.

3. The Coupled Oxidation of Propene by Hydrogen Peroxide

The catalytic epoxidation of alkenes by combined oxygen (ROOH, H_2O_2, peroxyacids) in the liquid phase has been discussed in a detailed review,[53] where it is possible to find detailed information on the kinetics and mechanism of the homogeneous catalysis of these processes in the presence of compounds of group V and VI elements.

Of particular interest is a single-stage method for obtaining alkene oxides by the conjugated oxidation of the alkenes with other organic compounds which are more easily oxidised, namely aldehydes, ketones, etc.[2,24] The active oxygen of peroxide radicals is used for the epoxidation of the alkene in this system.



These studies showed that it is possible in principle to carry out the epoxidation of alkenes by peroxide radicals, the simplest representative of which is the $HO_2^{\cdot}$ radical.

In recent years, from considerations of cost and availability, increasing use is being made of H_2O_2 as an oxidising agent for the selective oxidation of propene.[55] In the direct epoxidation in the liquid phase, however, hydrogen peroxide has a low reactivity, and it is therefore necessary to use various means of activating it, such as the reaction with carboxylic acids or with various inorganic anhydrides, which is accompanied by the formation of active compounds. In some studies,[56,57] the epoxidising agents used were peroxyacids formed by the reaction of H_2O_2 with formic and acetic acids. Of particular interest in this connection are the reactions involving the epoxidation of alkenes by peroxyacids at the moment of their formation from the acid anhydrides and H_2O_2. In the formation of alkene oxides by the reaction of the alkenes on the series of oxides of Ti, W, V, Ge, Mo, U, and Ru as catalysts, the most effective catalysts are tungsten oxides or tungstic acid, formed by the reaction of the oxides with H_2O_2.[58]

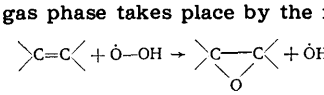
A non-trivial route to the synthesis of the important products propylene oxide, acrolein, and allene is provided by the gas-phase oxidation of propene by hydrogen peroxide by a coupled mechanism.[31,59]

Studies of the mechanism of the gas-phase and liquid-phase oxidation of hydrocarbons are giving a clear indication of the range in which a particular reaction path takes place, in relation to the specific conditions under which it is carried out.[60]

Thus depending on the conditions of the process (temperature, contact time, component ratio, H_2O_2 concentration, S/V ratio), the reaction of propene with hydrogen peroxide may lead to the epoxidation of propene, or to its oxidation to acrolein, or to coupled dehydrogenation.

In the range 500–580 °C, the main reaction is the coupled epoxidation of propene by hydrogen peroxide (Fig.6), and under the optimum conditions the average yield of propene oxide is 50 mass %.[59]

As already noted, in the gas-phase coupled oxidation by hydrogen peroxide in a flow system under stationary conditions, the $HO_2^{\cdot}$ concentration is greater than the $^{\cdot}OH$ concentration by several powers of ten. This fact, and also published data[53] on the epoxidation of alkenes by alkyl peroxide radicals, indicate that the epoxidation of alkenes by $HO_2^{\cdot}$ radicals in the gas phase takes place by the reaction:



The rate of epoxidation by alkyl peroxide radicals is determined by their structure. In the epoxidation of propene by hydrogen peroxide in the gas phase at 500–580 °C and a

contact time $\tau = 4.4$ s, the activity of $HO_2^{\cdot}$ as epoxidising species is greater than that of $RO_2^{\cdot}$.

The range 580–600 °C is an intermediate range in which the epoxidation of propene is accompanied by the simultaneous oxidation of propene to acrolein at a comparable rate. At 600–640 °C and $\tau = 1.2$ s, the main reaction product is acrolein, and its yield may reach 80 mass %.

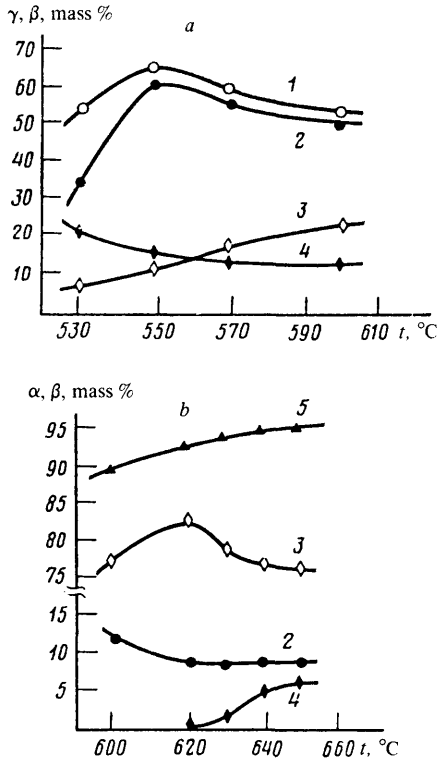


Figure 6. Temperature dependence of the selectivity (γ) (*1*), the yields (β) of propene oxide (*2*), acrolein (*3*), and side products (*4*), and the consumption of propene (α) (*5*) in its conjugated oxidation by hydrogen peroxide: *a*) 30 mass % H_2O_2, $V_{H_2O_2} = 1.3$ ml h^{-1}, $V_{C_3H_6} = 150$ cm^3 h^{-1}; *b*) 10 mass % H_2O_2, $V_{H_2O_2} = 3.78$ ml h^{-1}, $V_{C_3H_6} = 900$ cm^3 h^{-1}.[59]

Increase in temperature above 680 °C and $\tau = 0.045$ s leads to the formation of allene and methylacetylene as a result of the coupled dehydrogenation of propene (Fig. 3), and under the ultimate conditions the yields of these products are ~20% by weight and ~10% by weight respectively.[34]

Thus depending on the conditions, the coupled oxidation of propene may take place in three preferential directions:

$$CH_2{=}CH{-}CH_3 + H_2O_2 \rightarrow \left\{ \begin{array}{l} \rightarrow CH_2{-}\underset{\diagdown O \diagup}{CH}{-}CH_3 \\ \rightarrow CH_2{=}CH{-}CHO \\ \rightarrow CH_2{=}C{=}CH_2 \end{array} \right\} + \text{unwanted products}$$

In this system, as in the oxidations by hydrogen peroxide examined above, the coupling occurs according to schemes (1) and (2).[6]

It has thus been possible to determine the boundaries of the different mechanisms for the coupled oxidation of propene by hydrogen peroxide in relation to the conditions (temperature and contact time), and also to determine the intermediate ranges of the mechanisms of epoxidation and mild oxidation.

4. Coupled Oxidative Fixation by Hydrogen Peroxide

The problem of obtaining combined nitrogen from atmospheric nitrogen can now be solved by both reductive[61,62] and oxidative fixation. Several reactions for oxidising N_2 under severe conditions are known, for example the oxidation of N_2 by oxygen in an electric arc or plasma or under the influence of ionising radiation.[63] The direct oxidation of N_2 by oxygen is endothermic, and its realisation requires considerable expenditure of energy and gives low yields. It is therefore of considerable interest to develop nitrogen-fixation systems in which the principles of coupled reactions can be used.

The use of these principles in the oxidation of N_2 by hydrogen peroxide provides a new method for the fixation of nitrogen under conditions which are comparatively mild for reactions of this type.

The oxidation of nitrogen by hydrogen peroxide in a flow integral reaction vessel[64–66] makes it possible to obtain a yield of combined nitrogen of about 19% by weight.[68]

The mechanism of the oxidation of elementary nitrogen by hydrogen peroxide to N_2O includes a stage involving the reaction of N_2 with the $HO_2^{\cdot}$ radical, formed by the decomposition of H_2O_2:[69]

$$\begin{array}{l} H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O \\ N_2 + H\dot{O}_2 \rightarrow N_2O + \dot{O}H \\ \hline N_2 + H_2O_2 = N_2O + H_2O \quad \Delta G^{\circ}_{298} = -4.5 \text{ kcal mole}^{-1} \end{array} \qquad (22)$$

Nitrous oxide was identified by mass spectrometry and gas-adsorption chromatography. The aqueous fraction of the reaction products, assumed to contain nitrogen-containing acids, was analysed by mass spectrometry and by a qualitative test with $AgNO_3$,[67] although the latter does not exclude the possible formation of unknown forms of combined nitrogen which react with $AgNO_3$ to give a precipitate.

The effective rate constant of reaction (22), determined from the experimental data,[70] is:

$$k_{22} = 10^{14.46} \exp(-45\,700/RT) \text{ litre mole}^{-1}\text{s}^{-1}$$

The second-order rate constant for H_2O_2, calculated from the overall equation

$$H_2O_2 + M \rightarrow \text{products}$$

is

$$k_{\text{eff}} = 10^{14} \exp(-46300/\text{RT}) \text{ litre mole}^{-1}\text{s}^{-1}$$

The proposed mechanism makes it possible to obtain relationships which provide an adequate description of the experimental data in the temperature range 450–600 °C at an H_2O_2 concentration in the aqueous solution of 15–30% by weight at supply rates of 1–5 litre h^{-1} nitrogen and 8–24 ml h^{-1} H_2O_2.[71]

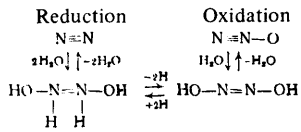
At 450 °C, the only product is nitrous oxide, the quantity of which amounts to 4% by weight, calculated on the original nitrogen. Beginning at 500 °C, the formation of combined nitrogen in the aqueous fraction of the reaction products is also observed, probably in the form of nitrogen-containing acids, the quantity of which increases to approximately 0.1% by weight with increase in the contact time.

Thus these studies have detected a new nitrogen-fixation system, which makes it possible to bind molecular nitrogen in an oxidative medium, as a result of chemical induction.

A distinguishing feature of the coupled oxidative fixation of N_2 by hydrogen peroxide is that the process takes place under relatively mild conditions compared with other similar reactions (at atmospheric pressure and at temperatures which are much lower than those usually required for the oxidation of nitrogen by oxygen).

In the biological fixation of molecular nitrogen, two different routes to its activation in the earliest stages of its fixation are possible: by reduction on the one hand and by oxidation on the other.[71] There is no proof, however, of oxidative fixation in the initial stages, although it is energetically more favourable.

According to Burris and Wilson, the following mechanism is involved in the initial stages of the biochemical fixation of N_2:[71]



In the oxidative part of this scheme, the question of the formation of nitrous oxide is not clear. Since hydrogen peroxide can induce chemical reactions, however, it has been possible to carry out the oxidative fixation of N_2 to N_2O by an energetically favourable path. All these studies make possible a new approach to the investigation of the mechanism of the biological fixation of N_2 and provide a new aspect to the nitrogen cycle.

III. CHEMICAL COUPLING IN LIQUID-PHASE OXIDATION BY HYDROGEN PEROXIDE

The catalytic decomposition of H_2O_2 in the liquid phase in the presence of iron(II) salts, discovered by Fenton,[72] is described by the following stepwise mechanism:[73]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \dot{O}H$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \dot{H}O_2 + H^+$$
$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^-$$
$$Fe^{3+} + \dot{H}O_2^- \rightarrow Fe^{2+} + H^+ + O_2^{\cdot-}$$
$$Fe^{2+} + \dot{H}O_2 \rightarrow Fe^{3+} + HO_2^-$$
$$H_2O_2 + \dot{O}H \rightarrow H_2O + \dot{H}O_2$$
$$H_2O_2 + O_2^{\cdot-} \rightarrow O_2 + OH^- + \dot{O}H$$

Salts of copper, chromium, vanadium, cobalt, and other transition metals can also be used to catlayse the decomposition of H_2O_2.

The catalytic generation of $^{\cdot}OH$ radicals, taking place as a result of the alternate oxidation and reduction of iron(II) and iron(III) ions, makes it possible to obtain free radicals at temperatures much lower than in thermal homolysis.

The free radicals formed in the reaction can react with practically any organic compound in acidic solutions.[74]

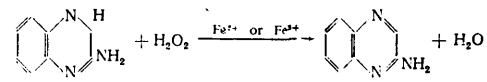
The oxidation of benzene in an aqueous solution of hydrogen peroxide in a Fenton system, which is taken as a classical example of a coupled process,[5] can be considered. The addition of an iron(II) salt to the C_6H_6–H_2O_2–H_2O system leads to the oxidation of benzene to phenol and biphenyl according to the following mechanism:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \dot{O}H$$
$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^-$$
$$C_6H_6 + \dot{O}H \rightarrow \dot{C}_6H_5 + H_2O$$
$$\dot{C}_6H_5 + \dot{O}H \rightarrow C_6H_5OH$$
$$\dot{C}_6H_5 + C_6H_5 \rightarrow C_6H_5 - C_6H_5$$

In this system, the phenomenon of induction is due to the fact that both reactions, that is the oxidation of C_6H_6 and Fe^{2+}, take place through common intermediate species, namely $^{\cdot}OH$ free radicals.[5]

As noted above, Fe^{2+} ions are effective catalysts for the decomposition of H_2O_2, so that the chemical conjugation in this system will not differ from that described in the previous section.[6]

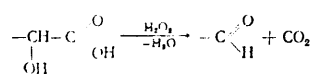
2-Amino-3,4-dihydroxyquinoxaline is comparatively readily dehydrogenated to give 2-aminoquinoxaline by H_2O_2 in the presence of traces of iron ions:[75]



The dehydrogenation takes place as a result of the reaction of the $^{\cdot}OH$ free radicals with the H(3) and H(4) hydrogen atoms of 2-amino-3,4-dihydroquinoxaline. The iron ions possibly bring about additional activation of the substrate molecule.

Free radicals also apparently play an important role in the degradation of carbohydrates by Ruff's method.[76]

The reaction of α-hydroxyacids with H_2O_2 in the presence of iron(III) salts takes place according to the overall equation:



In the successive transformation of D-glucose into D-arabinose



the stage involving the transformation of the aldonic acid into the 2-ketoaldonic acid is a dehydrogenation reaction. The role of H_2O_2 in this reaction is probably similar to that described above: the oxidising agents in this case are the highly active species formed by the decomposition of H_2O_2 in the presence of iron ions as catalyst.

The conjugated reactions of the decomposition of H_2O_2 and the oxidation of H_2CO and HCOOH in the presence of platinised graphites and Pt/(Pb with added Pb) was demonstrated in Ref.78. These studies showed that the ratio of the oxidation products is influenced significantly by the grade of graphite, the Pt deposition conditions, the reagent concentrations, and the percentage concentration of added Pb.

The detailed mechanism of the oxidation of dihydroxyfumaric and tartaric acids by hydrogen peroxide in the presence of iron and copper ions was studied in Ref.79.

In the gas phase under the conditions of conjugated oxidation by hydrogen peroxide, the $HO_2^{\cdot}$ concentration (2×10^{-9} mole cm^{-3}) is greater by many powers of ten than the $^{\cdot}OH$ concentration (7×10^{-13} mole cm^{-3}), and the ratio of the initial concentrations of $HO_2^{\cdot}$ and $^{\cdot}OH$ is about 10^4.[50]

In accordance with Eqn.(3), however, when the hydrogen peroxide is extensively diluted ($[H_2O_2] = 10^{-13}$ mole cm^{-3}), the system will contain chiefly $^{\cdot}OH$ radicals, and these will be responsible for the subsequent transformation of the substrate.

Since the reaction of the substrate with $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals leads to the formation of different products, the composition of the products should depend on the degree of dilution of H_2O_2. According to Ref.80, $^{\cdot}OH$ brings about nonselective oxidation, whereas $HO_2^{\cdot}$ brings about the selective gas-phase oxidation of substrates by hydrogen peroxide. Thus in an RH–H_2O_2–H_2O system, decrease in the concentration of the reagents leads to an increase in the degree of conversion and a decrease in the selectivity of the reaction, whereas a decrease in the concentration of the reagents

usually leads to an increase in the selectivity and a decrease in the yield of the reaction products. This situation is observed not only in the case of extremely low concentrations of H_2O_2 in the aqueous solution, but also in a liquid-phase (Fenton) system, in which the principal active centre is $^{\cdot}OH$.

Thus in a Fenton system it is impossible in principle to achieve highly selective oxidation of the substrate.

IV. THE ABILITY OF HYDROGEN PEROXIDE TO INDUCE OXIDATION, AND POSSIBLE NEW APPLICATIONS

The mechanism of chemical coupling in oxidation by hydrogen peroxide can be formulated as follows: the ability of hydrogen peroxide to induce chemical reactions is due to its decomposition to give active centres which take part in another reaction which does not take place spontaneously (for example nitrogen fixation, dehydrogenation, etc.).

An interesting question is whether more complex peroxy-compounds such as organic hydroperoxides and peroxides can induce chemical reactions.

The mechanism of the chain decomposition of the initiator most widely used in chemistry, namely di-t-butyl peroxide,[81] can be examined in this connection:

$$(CH_3)_3COH + \dot{C}H_2C(CH_3)_2\dot{O} \rightarrow CH_2\!\!<\!\!\begin{matrix}O\\ \\ \end{matrix}\!\!-C(CH_3)_2$$

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^{\cdot} \rightarrow 2(CH_3)_2CO + 2\dot{C}H_3 \rightarrow C_2H_6$$

$$\downarrow RH \qquad\qquad \downarrow RH$$

$$(CH_3)_3COH + \dot{R} \qquad CH_4 + R^{\cdot}$$

Di-t-butyl peroxide decomposes in the gas phase at 300 °C or in solution at pH ≥ 7 in different directions by a complex chain mechanism to give different reactions products: $(CH_3)_2COH$, $CH_2\!\!<\!\!\begin{matrix}O\\ \\ \end{matrix}\!\!-C(CH_3)_2$, CH_4, C_2H_6, and $(CH_3)_2CO$. The variety of chain decomposition paths is related to the formation of several active intermediate compounds, $(CH_3)_3CO^{\cdot}$, $^{\cdot}CH_2C(CH_3)_2O^{\cdot}$, $^{\cdot}CH_3$, and $R^{\cdot}$, whose transformation in the presence of the substrate (RH) gives a large number of side products.

Thus if attempts are made to use organic peroxides as components in conjugated reactions of mild oxidation, the above considerations related to the large number of active centres present a serious obstacle. In this system, the decomposition of the organic peroxide is accompanied by the chain oxidation of the substrate by different active centres to give the corresponding reaction products. Thus the absence of selectivity and the large number of chain reactions which can be initiated by organic peroxides create serious difficulties in the use of these hydroperoxides to induce reactions which do not take place spontaneously.

The ability of hydrogen peroxide to induce oxidative transformations of chemical substances as a result of chemical coupling not only extends the ways in which it can be used in new non-traditional directions but also leads to a deeper understanding of the mechanism of the action of H_2O_2 in many systems.

It can be confidently state that extension of the ranges of application of chemical coupling in general and in oxidation reactions in particular will stimulate progress in this field.

This will lead finally to the development of fundamentally new chemical-technological oxidation processes, corresponding to present-day requirements, that is the economic utilisation of energy resources and raw materials and an increase in the unit power of chemical reactors, without leading to environmental pollution. The low cost of H_2O_2 production by existing technology (chiefly by the anthraquinone method) provides a basis for increasing the use of H_2O_2 in modern industry. Thus the development of processes of oxidation by hydrogen peroxide corresponds to present-day requirements.

These studies raise another extremely important question for chemical technology, related to the unification of chemical production. It is surprising that unification, a powerful means of scientific and technical progress which has transformed many branches of industry, has hardly been introduced in chemical technology. This situation has probably arisen because almost every chemical reaction introduced has its own specific characteristics, which make it impossible to unify both chemical processes as a whole and individual technological units. To these characteristics can be added the use in industrial processes of specific catalysts with different compositions and structural properties, the formation of side products whose utilisation represents an independent problem, the purification of the desired product from side products, and the use of increased pressures and different phase states of the components of the reaction system.

The solution of the problem of the unification of chemical production will be found not in the development of separate chemical-technological processes differing considerably in their technological and chemical aspects, but in the development of chemical systems in which chemical reactions of the same type, having many common characteristics, can be realised.

Coupled reactions involving the oxidation of different substrates by hydrogen peroxide can justifiably be included among such chemical systems.

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