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Kinetics of the Oxidation of Mixtures of Organic Substances in the Liquid Phase

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The available literature data on the kinetics of the co-oxidation of organic substances by oxygen in the liquid phase are surveyed. The methods for the determination of the rate constants for reactions involving chain propagation by peroxy-radicals in the oxidation of mixtures are analysed and the experimental kinetic parameters of the co-oxidation of binary mixtures of organic compounds of different classes are presented. The general rules governing the kinetics of oxidation reactions in mixtures are considered and the methods whereby the rates and selectivities of the oxidation reactions of individual mixture components can be regulated are demonstrated.
The bibliography includes 111 references.

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I. INTRODUCTION

One of the most highly developed fields in the study of oxidation reactions of organic substances is that of the theory of the homolytic oxidation of organic substances in the liquid phase. Detailed studies have now been made of the kinetics and mechanism of the oxidation of representatives of many classes of organic compounds,[1-5] but it should be noted that, because these processes yield reactive oxygen-containing products, which subsequently react, the oxidation of the individual substances takes place only in the very initial stage of the reaction. In subsequent stages the process proceeds as the coupled oxidation of the starting material and its primary oxidation products, which is normally the main cause of the low selectivity with respect to the required product at advanced stages of the reaction.

In order to regulate the oxidation process and to increase its rate and selectivity, it is necessary to known the fundamental features of the joint oxidation of various substances and in particular the parameters of the so-called "cross" reactions needed to establish the relations between the structures and the reactivities of molecules and radicals in elementary oxidation reactions.

Investigations of the oxidation of mixtures has now yielded many results important for the theory and practice of liquid-phase oxidation. These include primarily the discovery of systems where the intermediate radicals derived from one substance function as the reactants in the reaction with another substance in the course of the oxidation process, which leads to the formation of the desired product. An example of such a reaction is the joint oxidation of aldehydes and unsaturated hydrocarbons which has been studied in detail by Emanuel' and co-workers.[6-9] This reaction has been proposed[6] as an effective method for the preparation of olefin oxides.

Numerous studies have been devoted to the coupled oxidation of olefins and aldehydes (see Filippova and Blyumberg's review[10]). It has been shown that[11-13] critical phenomena are observed in the oxidation of mixtures of decane with ethylbenzene, which is due to the reactions of alkyl radicals with the hydrocarbons; the contribution of these reactions to the overall process kinetics is very considerable and controls the characteristic features of the process under the given conditions. The coupled oxidation of benzene and alcohols by molecular oxygen in aqueous solutions at 430–470 K has been investigated.[14,15] Benzene is resistant to oxidation under these conditions, while under co-oxidation conditions phenol is formed and the hydroxylating reagent is in this instance the peroxy-radical $HOO^{\cdot}$. Coupled reactions leading to the decarboxylation of organic acids both in their individual oxidation and in mixtures with other substances have been studied in detail;[4,16] the kinetic features of the process have been established. The influence of various factors on the kinetics of the coupled oxidation of benzene and cyclohexane at 460–520 K has been studied.[17,18]

The kinetics of the joint oxidation in systems containing aromatic alkyl-substituted hydrocarbons and benzaldehyde have been investigated.[19,20] Studies have been made[21-24] of the kinetics of the joint oxidation of lower olefins and the considerable influence of the mixture composition and reaction conditions on the yield of the olefin oxide and the oxidation products has been demonstrated. Aspects of the practical applications of the oxidation reactions of mixtures of hydrocarbon have been examined.[25,26]

The studies on the joint oxidation of organic substances in the liquid phase can be divided by convention into two groups. The first includes studies of the reactions occurring under the conditions of a branched chain process, which continues until advanced stages, and the process kinetics are described in this instance by a cumbersome system of non-linear differential equations whose solution is possible only by numerical methods with a computer. Theoretical analysis of the kinetics of such processes involves many difficulties and can be achieved only in isolated simplified cases. The other group of studies has been devoted to the co-oxidation processes occurring under the conditions of an unbranched chain

reaction to low degrees of conversion of the starting materials. Here the reaction scheme is much simpler and there is a possibility of determining the kinetic parameters of all the elementary steps. The results of studies of the second group are mainly discussed in the present review.

II. KINETICS OF UNBRANCHED RADICAL-CHAIN OXIDATION REACTIONS OF MIXTURES

Rigorous analysis of the kinetics of the oxidation reactions of mixtures is greatly facilitated when the reaction is carried out under conditions such that there is no chain branching. The kinetics of the oxidation of binary mixtures under the conditions of an unbranched chain reaction were investigated and analysed for the first time by Walling and McElhill,[27] who used the familiar Mayo-Walling copolymerisation equation[28] to describe the dependence of the rate of oxidation on composition. Subsequently this equation in one or other modification was used in the study of many binary mixtures of organic substances.

The general approach to the solution of the kinetic problems arising in the description of unbranched chain processes in multicomponent systems involving free radicals of different structure has been developed by Tsepalov.[29] Using this approach, it is possible to describe the kinetics of the co-oxidation reactions occurring with quadratic, linear, or mixed chain termination and also under the conditions of low oxygen pressures where one cannot neglect the reactions of alkyl radicals. The only limitation to its application is the need for fairly long chains.

In relation to the simplest case, namely the oxidation reaction of a multicomponent mixture occurring with long chains and initiated at a rate W_i at an oxygen pressure ensuring the complete conversion of alkyl radicals into peroxyradicals and with quadratic chain termination, the reaction mechanism can be formulated as follows:

$$\begin{aligned} R_iH &\rightarrow R_i^{\cdot}, \\ R_i^{\cdot} + O_2 &\rightarrow R_iO_2^{\cdot}, \\ R_iO_2^{\cdot} + R_jH &\rightarrow R_iOOH + R_j^{\cdot}, \\ R_iO_2^{\cdot} + R_jO_2^{\cdot} &\rightarrow \text{inactive products.} \end{aligned} \qquad (1)$$

The subscripts i and j vary from 1 to n, where n is the number of components. Under stationary conditions and for long reaction chains, the following equations are valid:

$$W_i = \sum_{ij} k_{tij} [R_iO_2^{\cdot}] [R_jO_2^{\cdot}], \qquad (2)$$

$$\sum_j k_{pij} [R_iO_2^{\cdot}] [R_jH] = \sum_j k_{pij} [R_jO_2^{\cdot}] [R_iH]. \qquad (3)$$

The system of equations can be formulated thus:

$$\sum_j (k_{pij} [R_jH] - b_i\delta_{ij}) [R_jO_2^{\cdot}] = 0, \qquad (4)$$

where

$$b_i = \sum_j k_{pij} [R_jH],$$

and δ_{ij} is the Kronecker delta. Solutions of this system have the following form:

$$[R_jO_2^{\cdot}] = CA_{kj}, \qquad (5)$$

where A_{kj} is the algebraic supplement to the element a_{kj} in the determinant of Eqns.(4). The constant C is determined from Eqns.(2) and (5):

$$C = \left[W_i \Big/ \left(\sum_{ij} k_{tij} A_{ki} A_{kj} \right) \right]^{1/2}. \qquad (6)$$

It can be determined analogously also for processes with linear and mixed chain termination.

The rate of consumption of each component is described by the expression[29]

$$\frac{d[R_iH]}{dt} = C \sum_j k_{pji} A_{kj} [R_iH]$$

and the overall rate of reaction is determined as the sum of the rates of consumption of all the components:

$$W = C \sum_{ij} k_{pij} A_{ki} [R_jH].$$

An important special case of a multicomponent system is a two-component system, which has been investigated in very many theoretical as well as experimental studies. The complete scheme for the initiated oxidation of the binary mixture at oxygen pressure sufficiently high to be able to neglect all the reactions of alkyl radicals apart from their interaction with oxygen can be formulated as follows:[27,28]

$$\begin{aligned} R_1H,\ R_2H &\xrightarrow{W_i} R_1^{\cdot},\ R_2^{\cdot}, \\ R_1^{\cdot} + O_2 &\rightarrow R_1OO^{\cdot}, \\ R_2^{\cdot} + O_2 &\rightarrow R_2OO^{\cdot}, \\ R_1OO^{\cdot} + R_1H &\xrightarrow{k_{p11}} R_1OOH + R_1^{\cdot}, \\ R_1OO^{\cdot} + R_2H &\xrightarrow{k_{p12}} R_1OOH + R_2^{\cdot}, \\ R_2OO^{\cdot} + R_1H &\xrightarrow{k_{p21}} R_2OOH + R_1^{\cdot}, \\ R_2OO^{\cdot} + R_2H &\xrightarrow{k_{p22}} R_2OOH + R_2^{\cdot}, \\ \left.\begin{aligned} R_1OO^{\cdot} + R_1OO^{\cdot} &\xrightarrow{k_{t11}} \\ R_1OO^{\cdot} + R_2OO^{\cdot} &\xrightarrow{k_{t12}} \\ R_2OO^{\cdot} + R_2OO^{\cdot} &\xrightarrow{k_{t22}} \end{aligned}\right\} & \text{ inactive products.} \end{aligned} \qquad (7)$$

The equation for the overall rate of oxidation assumes the following form in this instance:

$$W = W_i^{1/2} \frac{r_1 [R_1H]^2 + 2 [R_1H] [R_2H] + r_2 [R_2H]^2}{\left(\frac{r_1^2}{a_1^2} [R_1H]^2 + 2\Phi \frac{r_1 r_2}{a_1 a_2} [R_1H] [R_2H] + \frac{r_2^2}{a_2^2} [R_2H]^2 \right)^{1/2}}, \qquad (8)$$

where $r_i = k_{pii}/k_{pij}$, $a_i = k_{pii}/k_{tii}^{1/2}$, and $\Phi = k_{t12}/(k_{t11}k_{t22})^{1/}$ Analysis of this equation[30] made it possible to obtain an expression for the estimation of the effect of adding one of the components on the overall rate of oxidation and also on the rate of oxidation of each component. The form of the curve describing the dependence of the overall rate of reaction on the ratio of the concentrations of the mxiture components for variable kinetic parameters[30] and also on the absolute rate constants for chain termination in the oxidation of each component[31] has been analysed. The form of the curves describing the dependence of the overall rate of oxidation of a binary mixture and its individual components on composition has been investigated.[32-34]

The expression for the dependence of the rate of co-oxidation on composition can be simplified as follows.[34] The concentrations of the components will be expressed in terms of the volume fractions, i.e. $[R_1H] = [R_1H]_0(1 - x)$ and $[R_2H] = [R_2H]_0$, where x is the volume fraction of the second component and $[R_1H]_0$ and $[R_2H]_0$ are the molar concentrations of the components.

The boundary values of the derivatives of W with respect to x constitute a criterion which is a comparatively simple fucntion of the co-oxidation parameters and makes it possible to differentiate quantitatively various types of co-oxidation curves. Thus, for $x \rightarrow 0$, the expression for such a derivative is

$$\left(\frac{dW}{dx}\right)_{x\to 0} = W_i^{1/2} (2a_1 [R_2H]_0/r_1 - a_1 [R_1H]_0 - \Phi r_2 a_1^2 [R_2H]_0/r_1 a_2).$$

We shall consider three special cases which are possible for each of the boundary values of the derivatives, i.e. for derivatives corresponding to $x = 1$ and $x = 0$.

1. The slope of the tangent of the boundary point is zero, so that we have the straight lines AA_1 and BB_1 in Fig.1, i.e. the derivative is zero.

2. The direction of the tangent coincides with the line connecting the rates of oxidation of the individual components—a linear relation obtains.

3. The direction of the tangent coincides with the line describing the variation of the rate of oxidation of an individual component in an inert solvent and we have the lines AA_3 and BB_3 in Fig.1.

Having formulated and simplified the equations corresponding to each case, we obtain a set of expressions describing the relation between the co-oxidation parameters for the given boundary value of the derivative; they are written against the corresponding lines in Fig.1. Having denoted by the numerals 1–8 the sectors separated by these lines, we can divide all the co-oxidation curves into 16 types depending on the sector in which the parts of the curve corresponding to depleted mixtures are located.

Fig.2 presents certain types of such curves. A system of inequalities limiting the possible values of the co-oxidation parameters can be associated with each type of curve. The "greater than" and "less than" symbols defining the inequalities in a given sector are shown in Fig.1. For example, the following inequalities correspond to curves *1–5*:

$$r_2 < 2a_2/\Phi a_1;\ r_1 > 2a_1/a_2\Phi$$

and the inequalities

$$r_2 < 2a_2/\Phi a_1;\quad r_2 < 2a_2/\Phi a_1 - a_2^2 r_1/\Phi a_1^2;$$
$$r_2 < 2[R_1H]_0/[R_2H]_0 - \Phi a_2 r_1 [R_1H]_0/a_1 [R_2H]_0;$$
$$r_2 > 2a_2/a_1 - \Phi a_2^2 r_1/a_1^2$$

correspond to curves *2–7*.

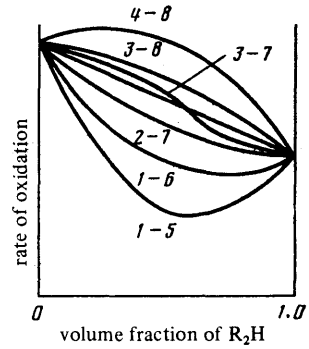


Figure 2. Types of co-oxidation curves.[34]

Using the given systems of inequalities and bearing in mind that only positive values of the parameters have a physical significance, it is possible to define rigorously the region in

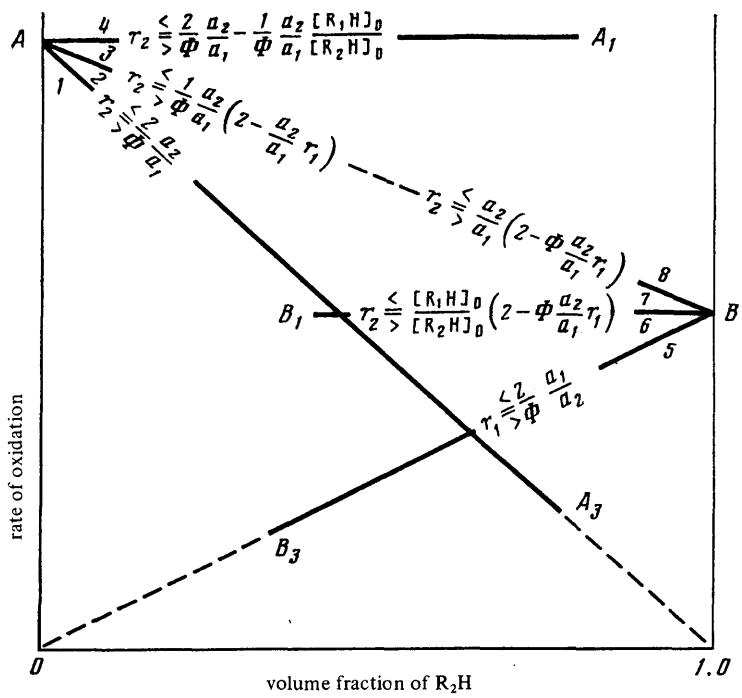


Figure 1. Equations relating the co-oxidation parameters for different boundary values of the derivative of the overall rate with respect to composition.[34]

which the co-oxidation parameters vary for each type of curve (Fig.3). As an example of the employment of the data in Fig.3, we shall analyse the problem of the type of co-oxidation parameters we should have for a system the dependence of the rate of oxidation of which on composition is described by a curve with a maximum, i.e. a curve of type 4–8. The range of parameters 4–8 corresponds to this curve (Fig.3). Bearing in mind that all the relations presented in Fig.1 have been obtained for $a_1 > a_2$, one may conclude that an essential condition for a curve with a maximum is as follows: r_1 and r_2 should be small, not greater than 2. In practice this implies that the rate constants for the "cross" reactions k_{pij} should be comparable in magnitude or greater than the constants k_{pii}, i.e. the contribution of "cross" chain propagation reactions should predominate.

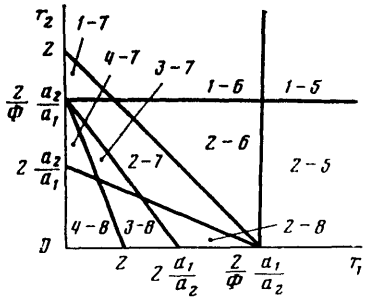


Figure 3. The ranges of the co-oxidation parameter for different types of curves.[34]

The inequalities obtained can be used also to solve the converse problem, which is of practical importance, namely the specification of the limits of the region in which the co-oxidation parameters are sought for a given type of co-oxidation curve by statistical analysis.

III. METHODS FOR THE DETERMINATION OF THE RATE CONSTANTS FOR ELEMENTARY REACTIONS IN CO-OXIDATION PROCESSES

The rate constants for the reactions of the radicals derived from one mixture component with the molecules of other components determine the specific features of the kinetics of the oxidation of the components of the mixture. In addition, they make it possible to compare the reactivities of many different molecules in reactions with the same radical and of a series of different radicals in reactions with the same molecule. At the present time there exist two methods for the determination of such constants. These are the Howard–Ingold method, based on the measurement of the rate of oxidation of one substance in the presence of the hydroperoxide of the other, and the joint oxidation method; we shall consider each of them.

1. The Howard–Ingold Method

A method has been proposed[35] for the determination of the rate constants for "cross" reactions based on the study of the kinetics of the oxidation of the hydrocarbon R_1H in the presence of the hydroperoxide R_2OOH. At high hdyroperoxide concentrations, the peroxy-radicals $R_1OO^\bullet$ and $R_2OO^\bullet$ are fully "exchanged" and the mechanism assumes the following form:

$$R_1H \rightarrow R_1^\bullet,$$
$$R_1^\bullet + O_2 \rightarrow R_1O_2^\bullet,$$
$$R_2OO^\bullet + R_1H \rightarrow R_2OOH + R_1^\bullet,$$
$$R_1OO^\bullet + R_2OOH \rightarrow R_1OOH + R_2OO^\bullet,$$
$$2R_2OO^\bullet \rightarrow \text{inactive products.}$$

The rate of reaction in this instance, subject to the condition that long chains obtain, is given by

$$W = \frac{k_{p21}}{k_{t22}^{1/2}} [R_1H] W_i^{1/2},$$

where k_{p21} and k_{t22} are the rate constants for the reactions of the peroxy-radicals formed from the hydroperoxide with the moelcules of R_1H and for quadratic chain termination respectively.

The applicability of this method has been demonstrated in relation to the oxidation of many organic substances—both hydrocarbons and their various derivatives substituted by functional groups.[36–42] However, on the basis of the results of their own study of the oxidation of tetralin in the presence of t-butyl hydroperoxide, Niki and Kamiya[43] cast doubt on the accuracy of the Howard–Ingold method. In reply to this criticism, Howard and Chenier[44] reinvestigated the same system and showed the need to ensure the complete "exchange" of the peroxy-radicals of the substance oxidised for the peroxy-radicals derived from the hydroperoxide and to make corrections for the evolution and absorption of gases in chain initiation and termination reactions.

However, the above factors are not the only ones which can significantly influence the validity of the values of the constants determined. When an attempt was made to apply this method to the determination of the rate constants for the reactions of cumenyl- and t-butyl-peroxy-radicals with polystyrene and adamantane at 348 K in solutions in chlorobenzene, results were obtained indicating a significant contribution of the chain decomposition reactions of the hydroperoxide to the given process.[45] Such decomposition, accompanied by the evolution of oxygen, leads to an unduly low measured rate of oxidation and hence introduces an error into the measured rate constant.

Thus, together with the undoubted advantages of the Howard–Ingold method, such as simplicity of the experiment and of the interpretation of the results, reliability of the results, particularly at low temperatures, and also the possibility of using it for substances with molecules having several reaction centres (the measured rate constant is then equal to the sum of the partial rate constants for the reactions of the hydroperoxy-radical with each of its centres), this method suffers from many disadvantages. The most significant of these are the rigorous requirements for the purification of the hydroperoxide and the difficulties arising from this in the determination of reproducible data, the possible complication of the process by the chain decomposition of hydroperoxides even at comparatively low temperatures (350 K), and the lack of availability of many hydroperoxides as a result of their lability.

2. The Co-oxidation Method

The method involving the joint oxidation of two substances for the determination of the co-oxidation parameters from which the rate constants for the "cross" reactions can be determined was developed much sooner than the Howard–Ingold method but the number of rate constants determined

with its aid is smaller because in many instances the accuracy of the value thus obtained is low. There exist several ways of determining the co-oxidation parameters from the results of the study of the kinetics of the co-oxidation of mixtures of two substances: (a) those based on the measurement of the consumption of the starting materials or the accumulation of each hydroperoxide; (b) those based on the measurement of the dependence of the overall rate of oxidation on the mixture composition.

The first group includes methods in which equations relating the ratio of the consumptions of the reactants (or the accumulations of the hydroperoxides) to the ratio of their concentrations in the mixture are employed:[46,47]

$$\frac{-\Delta[R_1H]}{-\Delta[R_2H]} = \frac{\Delta[R_1OOH]}{\Delta[R_2OOH]} = \frac{r_1[R_1H]/[R_2H]+1}{r_2[R_2H]/[R_1H]+1}, \qquad (9)$$

These methods have been used in a number of studies.[27,48-50] Their analysis, carried out by Niki et al.,[49] shows that small errors in the determination of concentrations lead to large errors in the determination of r_1 and r_2. Thus a 5% error in the measurement of [RH] leads to 10–30% errors in the calculated co-oxidation parameters.

The methods based on the use of Eqn.(9) are widely used for the determination of copolymerisation parameters. After the publication of the studies of Mayo and Lewis[46] and Fineman and Ross,[47] these methods were frequently modified in order to avoid their principal disadvantage, which is a marked dependence of the constants obtained on random experimental errors and also on the choice of coordinates in the linearisation of the plot of the dependence of the composition of the copolymer on the composition of the initial mixture.[51]

A significant fundamental limitation, which precludes in some cases the application of this group of methods to the determination of the co-oxidation parameters, should be noted: in order to measure the rate of consumption of a component or the rate of accumulation of the hydroperoxide with the required accuracy, one must carry out the reaction up to a significant degree of conversion: this leads to the accumulation of hydroperoxides in the system in amounts such that the contribution of their reactions

$$R_1OO^{\cdot} + R_2OOH \rightarrow R_1OOH + R_2OO^{\cdot},$$
$$R_2OO^{\cdot} + R_1OOH \rightarrow R_2OOH + R_1OO^{\cdot}$$

to the process becomes considerable. Analysis of the influence of the concentrations of the hydroperoxides formed on the accuracy of the parameters determined shows that even at concentrations of approximately 10^{-3} M the deviations can be significant.[34]

In the determination of the co-oxidation parameters from the dependence of the overall rate of oxidation on mixture composition, Eqn.(8) is employed. In the first study of this type[49,52-54] the following procedure was used: the system of non-linear equations containing three unknowns (r_1, r_2, Φ) is reduced to a system with two unknowns by eliminating one parameter on the basis of one of the equations; the resulting equations are solved in pairs by numerical or graphical methods. A disadvantage of this method is an unduly high statistical weight of one of the experiments and the consequent difficulty of a rigorous estimation of the accuracy of the parameters obtained.

Following the development of computers, it became possible to employ the methods of statistical analysis for the solution of this problem.[55,56] The accuracy of the estimates of the parameters is determined in this instance by the accuracy of the measurement of the rate of oxidation (it is usually fairly high) and also by the form of the co-oxidation curve. In particular, it has been shown[34] that, for a linear dependence of the rate of oxidation on mixture composition (and the volume fraction of the component), such a relation cannot be used to calculate the co-oxidation parameters. The latter are in this case related by equations of the type

$$r_2a_1/a_2 + \Phi r_1a_2/a_1 = 2,$$
$$r_1a_2/a_1 + \Phi r_2a_1/a_2 = 2,$$

which precludes the calculation of the unknowns r_1, r_2, and Φ, because there are only two equations. A partial solution is provided by the equation

$$\Phi = 1;\ 1/r_2 = r_1 = a_1/a_2.$$

A significant increase in the accuracy of the determination of the co-oxidation parameters can be achieved by a specific experimental design[56,57] which consists in the evaluation from preliminary estimates of the co-oxidation parameters of the ratio of the component concentrations for which the determinant of the information matrix has the maximum value; using the calculated ratio of the component concentrations, the next experiment is then performed and its results are employed in the recalculation of the co-oxidation parameters.

Table 1. Estimates of r_1, r_2, and Φ for the cumene–*o*-xylene system.[57]

No. of points	r_1	r_2	Φ
Uniform distribution of co-ordinates with respect to the composition axis			
6	1.76±0.52	0.638±0.030	1.34±0.48
12	1.27±0.22	0.658±0.017	0.99±0.26
Experimental design			
12	1.12±0.13	0.648±0.013	0.75±0.11

As an example, we present data obtained in the study of the co-oxidation of cumene and *o*-xylene[57] (Table 1). The data presented in Table 1 show that experimental design results in a considerable increase in the accuracy of the determination of all the co-oxidation parameters, particularly r_1 and Φ. The quantity r_2 for the given system (and for other systems of this type) is already determined with a satisfactory accuracy as a result of the first (non-optimal) measurements at six points distributed uniformly along the composition axis.

The literature data for the determination of the co-oxidation parameters from the dependence of the overall rate on composition show that this method, particularly when combined with statistical analysis and experimental design, ensures a satisfactory accuracy of the determination of the co-oxidation parameters. The existing experimental methods are fairly simple and permit the measurement of the quantities required for the calculation with a high accuracy. Another advantage of this method is that it makes it possible to obtain the parameters of the reactions also in cases where oxidation results in hydroperoxides which are unstable or difficult to isolate in a pure form.

Among the disadvantages of this method, one should include in the first place the dependence of the accuracy of the determination of the parameters on the form of the co-oxidation curve, which is why it cannot be applied to a whole series of systems. A significant limitation of the method can be in

many instances also the following factor. Studies of the oxidation of mixtures of substances whose molecules contain several C–H bonds with different energies have shown that the reaction kinetics are described satisfactorily by Eqn.(8). However, the kinetic parameters determined in this case are effective quantities and the expression for these include many constants for elementary reactions.[57–59]

We may also note that the effective rate constants for the chain termination reaction can be determined by the methods of non-stationary kinetics (the chemiluminescence[60] and interrupted illumination[61] methods) and in the case of a binary mixture they are described by the expression[62]

$$k_{t,\,\mathrm{eff}} = \frac{k_{t11}k_{p21}[\mathrm{R_1H}]^2 + 2k_{t12}k_{p21}k_{p12}[\mathrm{R_1H}][\mathrm{R_2H}] + k_{t22}k_{p12}^2[\mathrm{R_2H}]^2}{(k_{p21}[\mathrm{R_1H}] + k_{p12}[\mathrm{R_2H}])^2}.$$

For a multicomponent mixture, we have[63]

$$k_{t,\,\mathrm{eff}} = \frac{\sum_{ij} k_{tij}A_{ki}A_{kj}}{\left(\sum_i A_{ki}\right)^2}.$$

Table 2. The co-oxidation parameters of the cumene–R_2H systems.

No.	R_2H	T, K	r_1	r_2	Φ	Refs.
1	Ethylbenzene	333	0.5	0.8	1.3	[53]
	"	333	0.44	0.97	0.73	[64]
	"	333	1.3	1.0	1.2	[54]
	"	340.6	0.55	1.0	1.3	[65]
	"	348.5	0.59	1.0	1.2	[65]
	"	353	0.49	0.98	0.79	[64]
2	Tetralin	353	0.13	4.6	—	[48]
	"	353	0.21	5.0	4.3	[49]
	"	363	0.04	16	6	[66]
3	Toluene	333	3.0	0.2	0.8	[54]
	"	348	2.6	0.21	1.0	[57]
4	*p*-Xylene	333	2.1	1.0	2.1	[54]
	"	348	1.24	0.72	1.0	[57]
5	Mesitylene	333	2.2	0.8	1.1	[54]
	"	348	0.94	0.77	0.9	[57]
6	n-Propylbenzene	333	2.8	0.4	1.2	[54]
	"	348	1.4	0.72	1.0	[68]
7	n-Butylbenzene	333	1.9	0.9	1.2	[54]
8	Isobutylbenzene	348	3.5	0.10	1.0	[68]
9	s-Butylbenzene	348	2.0	0.30	0.8	[68]
10	Isopentylbenzene	348	2.3	0.50	4.6	[68]
11	Cyclopentylbenzene	333	0.1	4.0	—	[53]
12	Cyclohexylbenzene	333	0.55	0.75	0.75	[52]
	"	348	1.4	0.55	2.6	[68]
13	Neopentylbenzene	348	6.8	0.12	2.1	[68]
14	4-Methylpyridine	348	4.0	0.09	1.3	[70]
15	2-Methylpyridine	348	3.2	0.053	1.6	[70]
16	3-Methylpyridine	348	3.0	0.17	1.6	[70]
17	2-Isopropylpyridine	348	1.7	0.55	1.6	[70]
18	β-Bromoethylbenzene	348	1.6	1.4	1.0	[68]
19	*m*-Xylene	348	1.5	0.52	0.93	[57]
20	*o*-Xylene	348	1.12	0.65	0.8	[57]
21	Pseudocumene	348	0.63	1.24	0.9	[57]
22	2-Ethylpyridine	348	0.63	0.46	1.2	[70]
23	Diphenylmethane	348	0.42	2.2	1.4	[65]
24	Durene	348	0.32	2.12	0.9	[57]
25	4-Ethylpyridine	348	0.30	0.45	0.8	[70]
26	1,1-Diphenylethane	348	0.18	2.8	8.3	[69]
27	3-Ethylpyridine	348	0.17	0.69	0.64	[70]
28	Pentamethylbenzene	348	0.112	3.42	0.8	[57]
29	Hexamethylbenzene	348	0.087	8.83	1.0	[57]

by the simplest kinetic scheme corresponding to the mechanism with quadratic chain termination by peroxy-radicals and the oxidation takes place with fairly long chains.[1] The mechanism of the low-temperature oxidation reaction of mixtures of aromatic alkyl-substituted hydrocarbons is described by a simple kinetic scheme and it is therefore possible to calculate the kinetic co-oxidation parameters. At a quantitative level, i.e. with determination of the co-oxidation parameters, studies have now been made on more than 60 systems (Tables 2 and 3).

Table 3. The co-oxidation parameters for binary systems of aromatic alkyl-substituted hydrocarbons.

No.	R_1H	R_2H	T, K	r_1	r_2	Φ	Refs.
1	Tetralin	Mesitylene	333	6.5	0.15	1	[54]
2	Tetralin	n-Propylbenzene	333	6.7	0.1	1	[54]
3	Tetralin	*p*-Xylene	333	4.6	0.15	0.6	[54]
4	Tetralin	Pseudocumene	333	4.3	0.15	1.4	[54]
5	Tetralin	s-Butylbenzene	333	4.0	0.25	0.9	[54]
6	Tetralin	n-Butylbenzene	333	3.5	0.15	1.4	[54]
7	Tetralin	*o*-Xylene	333	3.1	0.15	0.6	[54]
8	Tetralin	Ethylbenzene	333	3.0	0.2	0.8	[54]
9	Tetralin	*m*-Xylene	333	2.6	0.1	0.6	[54]
10	Tetralin	Cymene	333	1.8	0.4	1.1	[54]
11	Ethylbenzene	Mesitylene	333	0.5	1.2	1.0	[54]
12	Ethylbenzene	*p*-Cymene	333	0.8	1.25	0.9	[54]
13	Ethylbenzene	n-Propylbenzene	333	1.0	0.8	1.0	[54]
14	Ethylbenzene	s-Butylbenzene	377	1.6	0.6	1.0	[54]
15	Ethylbenzene	n-Butylbenzene	377	0.8	1.2	1.2	[54]
16	Ethylbenzene	Neopentylbenzene	348	4.9	0.54	1.8	[71]
17	Ethylbenzene	Isobutylbenzene	348	2.5	0.35	1.0	[71]
18	Ethylbenzene	Toluene	348	2.2	0.2	3.0	[67]
19	Ethylbenzene	β-Bromoethylbenzene	348	1.8	0.25	0.9	[71]
20	Ethylbenzene	n-Hexylbenzene	348	1.8	0.62	1.4	[71]
21	Ethylbenzene	Diphenylmethane	348	0.31	1.2	2.5	[67]
22	Ethylbenzene	s-Butylbenzene	348	0.53	1.14	1.0	[71]
23	Ethylbenzene	Isopentylbenzene	348	0.7	0.7	2.0	[71]
24	Ethylbenzene	Cyclohexylbenzene	348	0.33	0.9	1.8	[71]
25	*o*-Xylene	*m*-Xylene	377	3.0	0.1	0.9	[54]
26	*o*-Xylene	*p*-Xylene	377	1.6	1.0	0.6	[54]
27	*m*-Xylene	*p*-Xylene	377	1.0	1.6	0.6	[54]
28	*o*-Xylene	n-Butylbenzene	377	0.5	1.8	1.1	[54]
29	Diphenylmethane	Toluene	348	6.3	0.10	3.0	[69]
30	1,1-Diphenylethane	Toluene	348	5.2	0.07	3.6	[69]
31	3-Isopropylpyridine	3-Methylpyridine	348	3.7	0.28	1.2	[72]
32	2-Isopropylpyridine	3-Methylpyridine	348	2.2	0.30	1.1	[72]
33	4-Isopropylpyridine	3-Methylpyridine	348	1.8	0.36	0.8	[72]
34	1,1-Diphenylethane	Diphenylmethane	348	1.3	0.51	3.2	[67]
35	s-Butylbenzene	n-Butylbenzene	377	0.3	2.0	1.1	[54]
36	*p*-Cymene	Toluene	333	2.2	0.4	1.0	[54]

Table 4. The parameters of the co-oxidation of aromatic alkyl-substituted hydrocarbons with alkanes.

R_1H	R_2H	T, K	r_1	r_2	Φ	Refs.
Tetralin	*cis*-Decalin	333	12	0.42	—	[48]
Pinane	Cyclohexylbenzene	333	2	0.4	0.4	[53]
Ethylbenzene	n-Decane	350	2.0	0.17	4.5	[55]
Ethylbenzene	2,7-Dimethyloctane	350	1.5	0.37	2.6	[55]
Pinane	Cyclopentylbenzene	333	0.9	1.7	4.0	[53]
Cumene	*cis*-Hexalin	333	0.58	1.56	—	[48]
Cumene	Decalin	333	0.5	0.27	1	[52]
Cumene	Pinane	333	0.4	0.7	4.0	[73]

IV. OXIDATION OF BINARY MIXTURES OF ORGANIC SUBSTANCES

The liquid-phase oxidation of aromatic alkyl-substituted hydrocarbons has been studied in greatest detail, which can be explained primarily by the fact that the kinetics of the oxidation reactions of such individual compounds are described

One of the most thoroughly investigated systems is the cumene–ethylbenzene system. The co-oxidation parameters for this system, measured in various investigations, agree well with one another (Table 2). The quantity Φ for the vast majority of systems is close to unity and its derivations from unity for some systems (see, for example, systems 10 and 12 in Table 2 and system 23 in Table 3) are probably

associated with the fact that in such cases Φ is an effective quantity, because the molecules of the substance undergoing co-oxidation in the presence of cumene always have several reaction centres. For systems 13 and 26 (Table 2) and 16, 18, 23, 24, 29, 30, and 34 (Table 3), the deviation of Φ from umity can be associated with the low accuracy of the determination of the co-oxidation parameters from the dependence of the overall rate of oxidation on composition, which is close to linearity for such systems.

The results of the study of the oxidation reactions of binary mixtures of aromatic alkyl-substituted hydrocarbons together with alkanes are presented in Table 4. Considerable deviations of Φ from unity are oosrved in these systems.

Table 5. The co-oxidation parameters for binary mixtures with oxygen-containing derivatives of hycrocarbons.

System	r_1	r_2	Φ	Refs.
Cumene-n-butyl ether	0.17	2.3	0.21	[74]
Cumene-isopropyl ether	0.11	2.2	0.55	[74]
Cumene-tetrahydrofuran	0.11	5.8	0.07	[74]
Cumene-2-methyltetrahydrofuran	0.11	17.5	0.5	[74]
Cumene-$(C_6H_5)(CH_3)(CH)_2O$	0.5	9.5	0.87	[74]
Tetralin-isopropyl ether	2.2	0.67	0.4	[74]
Tetralin-tetrahydrofuran	5.8	1.2	0.5	[74]
Tetralin-dibenzyl ether	0.7	2.4	2.6	[74]
Tetralin-benzyl ether	0.88	0.48	—	[48]
n-Butyl ether-isopropyl ether	0.65	1.6	1.7	[74]
Dibenzyl ether-$(C_6H_5)(CH_3)(CH)_2O$	4.3	0.45	0.3	[74]
Dibenzyl ether-2-methyltetrahydrofuran	2.5	0.48	1.2	[74]
Isopropyl ether-$(C_6H_5)(CH_3)(CH)_2O$	0.84	0.61	2.1	[74]
Tetrahydrofuran-methyltetrahydrofuran	0.56	1.6	0.8	[74]
1-Phenyl-1-propanol-cyclohexanol	1.8	0.43	0.7	[73]
1-Phenyl-1-propanol-2-butanol	1.1	0.34	1.44	[73]
1-Phenyl-1-propanol-tetralin	0.52	0.25	2.45	[73]
Cumene-cyclohexanone	0.2	0.4	—	[73]
Cumene-o-chlorobenzyl alcohol	0.97	2.2	6.5	[34]
Ethylbenzene-benzyl alcohol	0.80	2.3	0.7	[34]
Diphenylmethane-benzyl alcohol	0.26	8.0	0.7	[34]
Bibenzyl-benzyl alcohol	0.27	5.7	1.6	[34]
Cumene-n-butyl benzoate	2.6	0.08	1.1	[75]
Cumene-benzyl acetate	3.9	0.55	4.8	[75]
Cumene-benzyl butyrate	7.1	0.9	2.6	[75]
Cumene-2-heptylcyclohexanone	0.7	2.1	0.5	[76]

Studies have been made of systems comprising oxygen-containing derivatives of hydrocarbons (Table 5). One should note that, in the oxidation of ethers, the intraradical isomerisation reactions of the peroxy-radicals are significant.[4] Allowance for these reactions in the kinetics co-oxidation scheme leads to a relation between the rate of oxidation and mixture composition more complex than Eqn.(8). The co-oxidation parameters obtained using Eqn.(8) for systems containing ethers should therefore be regarded as effective quantities, i.e. as quantities incorporating the rate constants for both the intramolecular transport reaction and other elementary stages.

Eqn.(8) describes satisfactorily the dependence of the rate of oxidation of mixtures on composition for systems incorporating an aromatic alkyl-substituted hydrocarbon and an alcohol, ether, or ketone (systems 1–9 and 17–26 in Table 5), but the problem of whether or not the co-oxidation parameters are also effective quantities in this instance remains open. The point is that the determination of these parameters requires the alteration of the ratio of the hydrocarbon and the oxygen-containing derivative within very wide limits, which leads to considerable changes in the properties of the medium. The change in the properties of the medium can influence significantly the rate constants for the individual elementary stages[2] and the rate constants entering into Eqn.(8) may therefore prove not to be invariant over the entire range of concentrations of the components.

Apart from the systems presented in Table 5, studies have also been made of the kinetics of the co-oxidation of more than 50 binary mixtures of oxygen-containing compounds with polyhydric alcohols or esters in the range of compositions where the concentration of one component (R_1H) is much higher than that of the other (R_2H).[79] In this case the kinetic reaction scheme is simplified as a consequence of the low contribution of the $R_2OO^{\bullet} + R_2H$ and $R_2OO^{\bullet} + R_2OO^{\bullet}$ reactions, which makes it possible to determine experimentally the quantity α defined by the formula[79]

$$\alpha = 2\frac{k_{p12}}{k_{p11}} - \frac{1}{2}\frac{k_{t12}}{k_{t11}} \cdot \frac{k_{p12}}{k_{p21}}.$$

In many systems the second term is much smaller than the first, which enabled Degtyareva et al.[79] to estimate the quantities k_{p12}/k_{p11}, i.e. $1/r_1$. Thus $1/r_1$ for various alcohols in the n-hexadecane (R_1H)–alcohol (R_2H) systems has the following values respectively at 403 K: 2.8 for 1-decanol; 4.5 for 2-octanol; 2.2 for butane-1,3-diol; 12 for 1,1,1-tri-(hydroxymethyl)propane.

In the joint oxidation of aromatic alkyl-substituted hydrocarbons in alcohols, a sharp decrease of the rate of oxidation is observed following the addition of small amounts of an alcohol to the hdyrocarbon.[73,80] In relation to the cumene–benzyl alcohol system, it has been shown[81,82] that in this case the contribution of the reactions involving chain propagation by peroxy-radicals derived from the alcohol is negligible, which makes it possible to describe the dependence of the overall rate of oxidation W on the alcohol concentration $[R_2H]$ by the familiar[4] equation for inhibited oxidation:

$$\frac{W_0}{W} - \frac{W}{W_0} = 2\frac{k_{p12}}{(k_{t11}W_i)^{1/2}}[R_2H], \qquad (10)$$

where W_0 is the rate of oxidation of the hdyrocarbon without added alcohol. The same equation describes the kinetics of the co-oxidation of mixtures of hydrocarbons with amines.[83]

Binary systems containing aldehydes were the first systems in which co-oxidation has been investigated.[27] The parameters r_1 and r_2 for a number of systems have been determined from the kinetics of the accumulation of acids in the first hours of the co-oxidation reactions of substituted benzaldehydes (Table 6). Binary mixtures containing aldehydes and cyclohexadiene,[76] whose co-oxidation parameters have been determined using Eqn.(9), have also been investigated in detail.

A characteristic feature of the kinetics of the oxidation of mixtures incorporating aldehydes is a significant diminution of the rate of oxidation with time as a consequence of the formation in the course of the process of substances which probably possess inhibiting properties.[85,86] One of the general features of the kinetics of the oxidation of mixtures of aldehydes with organic substances of other classes is that the rate of reaction is strongly retarded not only by classical inhibitors but also virtually by all other substances with a mobile hydrogen atom or substances capable of undergoing addition reactions. Thus the oxidation of aldehydes is subjected to a powerful inhibiting effect by aromatic alkyl-substituted compounds,[76,84–86] olefins,[87–89] alcohols,[90,91] ketones,[92,93] and polycyclic hydrocarbons.[96] In some studies[86,95,96] it has been shown that the additive influences the rate of oxidation of the aldehyde via the usual mechanism of inhibited oxidation and canbe described by Eqn.(10). The kinetics of the oxidation of an aldehyde in the presence of a hydroperoxide can be described by the Howard–Ingold scheme

In the co-oxidation of two aldehydes one can observe an increase of the overall rate of oxidation of the mixture compared with the oxidation of the individual components,[77] which is associated with the increase of the rate of chain initiation in such mixtures. The maximum rate of chain initiation in the benzaldehyde–decanol mixture is attained for a 1 : 1 component ratio.

Table 6. The co-oxidation parameters for systems containing aldehydes.

System	T, K	r_1	r_2	Refs.
p-Chlorobenzaldehyde-*p*-methoxybenzaldehyde	303	0.15	2.36	[27]
p-Chlorobenzaldehyde-*p*-methylbenzaldehyde	303	0.24	2.15	[27]
p-Chlorobenzaldehyde-*m*-methylbenzaldehyde	303	0.33	2.20	[27]
p-Chlorobenzaldehyde-*p*-propylbenzaldehyde	303	0.28	1.87	[27]
p-Chlorobenzaldehyde-*p*-cyanobenzaldehyde	303	1.15	0.46	[27]
p-Chlorobenzaldehyde-benzaldehyde	303	0.54	1.62	[27]
m-Chlorobenzaldehyde-benzaldehyde	303	0.38	1.95	[27]
p-Methoxybenzaldehyde-benzaldehyde	303	2.22	1.0	[27]
p-Chlorobenzaldehyde-n-butyraldehyde	303	0.28	10.7	[27]
n-Heptanal-cyclohexadiene	273	0.64	1.65	[76]
n-Octanal-cyclohexadiene	273	0.64	1.65	[76]
n-Hexanal-cyclohexadiene	273	0.95	0.44	[76]
Pivaldehyde-cyclohexadiene	273	2.15	0.36	[76]
Benzaldehyde-cyclohexadiene	273	0.17	4.75	[76]
n-Heptanal-benzaldehyde	273	10	0.1	[76]
n-Decanal-benzaldehyde	273	8.6	0.2	[77]
Benzaldehyde-2-propanol	273	4	0.067	[78]
Benzaldehyde-benzyl alcohol	273	0.8	0.43	[78]

Table 7. The parameters of the co-oxidation of polystyrene with aromatic alkyl-substituted derivatives (348 K).[101]

System	r_1	r_2	Φ
PS-cumene	0.55	1.96	0.59
PS-diphenylmethane	0.62	1.25	1.21
PS-benzyl alcohol	0.72	20.3	2.64

Another important feature of the kinetics of the oxidation of binary mixtures containing an aldehyde is a considerable increase in the rate of oxidation of the second component, which is indicated by estimates of the rates from the co-oxidation parameters and by direct measurements.[76,79]

Data for the oxidation of mixtures of aldehydes with alkenes and also of alkenes with other substances have been examined in two studies[10,98] and are not presented in this review.

The joint oxidation of high-molecular-weight compounds in solutions and also their oxidation in mixtures with low-molecular-weight substances has so far been little studied. Only a few investigations[99,100] devoted to this problem are known. In the study of the co-oxidation reactions with participation of high-molecular-weight substances, difficulties due to the degradation of the polymers in the oxidation reaction and the influence of the co-oxidising component on the degradation arise compared with mixtures of low-molecular-weight substances (for which the principal object of study is the dependence of the rate of oxidation of the mixture and of the rates of oxidation of the individual components on composition).

It has been shown for the co-oxidation of cumene with polyethylene that the rate of degradation of the polymer diminishes linearly with increase of the concentration of cumene, although the rate of oxidation of the latter does not change in the presence of polyethylene.[99] The rate constant for the reaction of the cumenylperoxy-radical with polyethylene was determined in the same study. The rate of oxidation of cumene decreases appreciably with increase in the polystyrene content (PS) of the latter.[100] The dependence of the rate of oxidation of cumene on that of PS is described by a straight line in terms of the variables of the Eqn.(10), which enabled Guk et al.[100] to calculate the rate constant for the reaction of the cumenylperoxy-radical with PS.

For several systems, one of the components of which is polystyrene, the co-oxidation parameters have been determined (Table 7) from the overall dependence of the rate of oxidation on the composition of the binary mixture.[101] The calculation of the rate of oxidation of polystyrene in mixtures, carried out using the co-oxidation parameters obtained, showed that the addition of PS retards the oxidation of cumene and diphenylmethane but hardly influences the rate of oxidation of benzyl alcohol. Cumene and dimethylmethane in their turn accelerate the oxidation of PS, while benzyl alcohol inhibits this process. The addition of low-molecular-weight substances to a solution of polystyrene lowers the rate of its oxidative degradation.[102]

Different organic compounds have different effects on the degradation of PS in its oxidation in solution.[103] In terms of the magnitude of the inhibiting effect, they can be arranged in the sequence cumene < toluene < esters < cumenyl hydroperoxide < benzyl alcohol.

Shilov and Denisov[104] compared the relations between the rate of oxidation and composition in systems consisting of polyethylene, polypropylene, and their low-molecular-analogues—n-decane and 2,2,4-trimethylpentane respectively. In the co-oxidation of low-molecular-weight hydrocarbons a curve with a hump (of type 3–7 in Fig.2) is observed. For the polyethylene–polypropylene system, the rate of oxidation varies linearly with the composition of polymers, which has been explained[104,105] by the absence of cross-reactions in the given systems, i.e. the chain oxidation develops within each individual molecular coil.

Thus hitherto detailed studies have been made on the joint oxidation reactions of mixtures of aromatic alkyl-substituted compounds, alkanes, alkenes, alcohols, ketones, aldehydes, polyolefins, ethers, and esters. The reactions involving individual representatives of other classes have also been investigated. Thus, among chloro-derivatives, a study has been made of the joint oxidation reaction of benzyl chloride and cumene;[106] the overall rate of oxidation is found to decrease both after the addition of cumene to benzyl chloride and after the addition of benzyl chloride to cumene, i.e. the co-oxidation curve is of type *1–5*.

The kinetics of the co-oxidation of cumene in the presence of a series of amines have been investigated.[83,107] A characteristic feature of the kinetics of these processes is that small amounts of added amine diminish partly the overall rate of oxidation.

All the curves quoted in the literature for the dependence of the rate of reaction on the mixture composition are combined in Table 8 in six groups each of which includes several types (Fig.1).

The data in Table 8 show that, among the 164 systems investigated, only one is described by a curve with a maximum. Unfortunately the authors[74] do not quote the curve, stating only the co-oxidation parameters, the accuracy of the determination of which is insufficient to regard the conclusion concerning the shape of the curve as rigorously unambiguous.

Only approximately 7% of all the systems investigated exhibit small positive deviations from linearity, i.e. in these systems the rate of oxidation of the mixture is somewhat greater than the sum of the rates of oxidation of its components taken at the same concentrations in an inert solvent. Among the systems whose rate of oxidation varies with composition in accordance with a linear law, the majority are those in which the molecules of the components have similar chemical structures.

Table 8. The numbers of systems investigated described by different types of co-oxidation curves.

Composition-rate relation	Type of curve	Number of systems
Linear		35
With a maximum	*4—8*	1
With positive deviations	*3—8*	10
With negative deviations	*1—7, 2—7*	81
With a minimum	*2—6, 2—5*	35
With inflections	*1—8, 2—8, 3—5, 3—7*	2

Table 8 shows that the most characteristic feature established in the study of the kinetics of the co-oxidation of binary systems is a decrease of the overall rate of oxidation of the mixture compared with additivity, i.e. negative deviations from linearity.

The systems of inequalities which limit the values of the co-oxidation parameters are presented above in Table 1. However, they are too complex for practical analysis. In order to analyse the problem of what should be the relations between the parameters for a particular type of curve, the concept of reaction selectivity is employed.[108] We shall define the selectivities in the interaction of the reacting species in co-oxidation processes in the following manner.

1. The selectivity of the reactions of a molecule with two peroxy-radicals:

$$R_iOO^{\cdot} + R_nH \xrightarrow{k_{pin}} R_iOOH + R_n^{\cdot},$$
$$R_jOO^{\cdot} + R_nH \xrightarrow{k_{pjn}} R_jOOH + R_n^{\cdot},$$
$$S_{M_n/R_iR_j} = k_{pin}/k_{pjn};\ k_{pin} > k_{pjn}.$$

2. The selectivity of the reaction of a radical with molecules:

$$R_nO_2^{\cdot} + R_iH \xrightarrow{k_{pni}} R_nO_2H + R_i^{\cdot},$$
$$R_nO_2^{\cdot} + R_jH \xrightarrow{k_{pnj}} R_nO_2H + R_j^{\cdot},$$
$$S_{R_n/M_iM_j} = yk_{pni}/xk_{pnj};\ yk_{pni} > xk_{pnj},$$

where x and y are the numbers of equivalent atoms in the R_iH and R_jH molecules respectively.

3. The selectivity of the reaction with radicals:

$$\left.\begin{aligned} R_nO_2^{\cdot} + R_iO_2^{\cdot} &\xrightarrow{k_{tni}} \\ R_nO_2^{\cdot} + R_jO_2^{\cdot} &\xrightarrow{k_{tnj}} \end{aligned}\right\} \text{molecular products};$$
$$S_{R_n/R_iR_j} = k_{tni}/k_{tnj};\ k_{tni} > k_{tnj}.$$

For two-component mixtures, the quantities i, j, and n assume values of 1 and 2.

Using this notation, the condition for linearity can be formulated as the following equality:[34]

$$\frac{S_{R_1/R_1R_2}}{S_{M_1/R_1R_2}} + \frac{S_{M_2/R_1R_2}}{S_{R_2/R_1R_2}} = 2.$$

This equation holds in particular when the selectivities for all the species are equal, i.e. are independent of the reactivity.

The following inequality corresponds to the most general case, namely negative deviations from additivity:

$$\frac{S_{R_1/R_1R_2}}{S_{M_1/R_1R_2}} + \frac{S_{M_2/R_1R_2}}{S_{R_2/R_1R_2}} > 2. \qquad (11)$$

For many systems, the availability of experimental co-oxidation parameters and rate constants for the individual elementary reactions permits the calculation of the selectivities in formula (11). The results of such calculations make it possible to conclude that in systems containing hydrocarbons, alcohols, ethers, esters, and chloro-derivatives, the decrease of the rate of co-oxidation is caused by the higher selectivity of the reactions of peroxy-radicals compared with the reactions of molecules. In systems with aldehydes the decrease in the rate of oxidation is caused by the higher selectivity of the reactions of molecules. Analysis shows that, when the selectivity of the reactions of species depends appreciably on the reactivity (it is then unimportant whether the selectivity increases or diminishes with increasing reactivity), inequality (11) holds. The general relations governing the dependence of the selectivity on the reactivity of the reacting radicals and molecules under the conditions of a wide variation of their structures have not so far been established. It has been shown only for reactions of certain peroxy-radicals with the molecules of aromatic alkyl-substituted compounds that the selectivity of the radical changes in parallel with reactivity.[34] This is indicated by two facts.

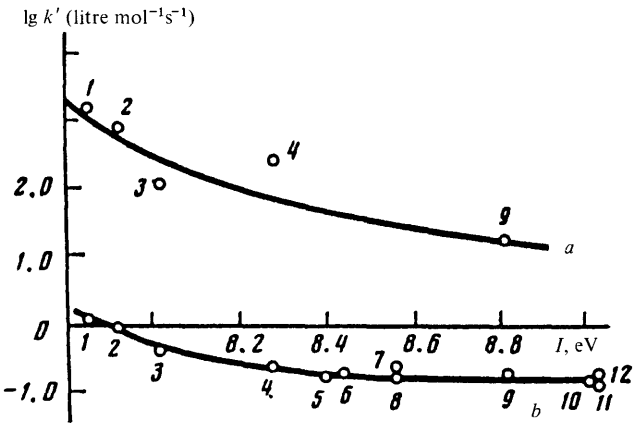


Figure 4. Dependence on the ionisation potentials of the molecules I of the partial rate constants k' for the reactions of the benzoylperoxy-radicals (a) and cumenylperoxy-radicals (b) with different substances: 1) hexamethylbenzene; 2) pentamethylbenzene; 3) durene; 4) pseudocumene; 5) mesitylene; 6) p-xylene; 7) o-xylene; 8) m-xylene; 9) toluene; 10)–12) picolines.[110]

Fig. 4 presents the variation of the partial (referred to a single reactive C–H bond) rate constants for the reactions of cumenyl peroxy- and benzoylperoxy-radicals with methyl-substituted benzene derivatives. It is seen that, with increased number of methyl groups in the ring, the partial rate constants also increase. The increase is more significant

for reactions of these molecules with the benzoylperoxy-radical, which is much more reactive than the cumenylperoxy-radical. This implies that the selectivity of the reaction of the more reactive radical, which is in this instance the benzoylperoxy-radical, is higher than the selectivity of the reaction involving the less reactive cumenylperoxy-radical.

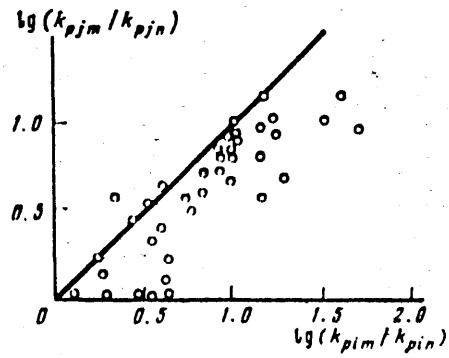


Figure 5. Relation between the selectivities of the reactions of peroxy-radicals; i is a more reactive radical than j; m is a more reactive molecule than n.[34]

The relation between the selectivities and reactivities of various peroxy-radicals can be traced also in terms of the co-oxidation parameters r_1 and r_2, which constitute the ratios of the rate constants for the reactions of two different peroxy-radicals for the same pair of molecules. We shall select from the binary systems investigated (Tables 2 and 3) those in which the oxidation of their components results in the formation of primary and tertiary, primary and secondary, or secondary and tertiary peroxy-radicals respectively. In order to determine which radical in the given pair is more reactive one can then employ the familiar reactivities in the series: primary > secondary > tertiary. The logarithm of the ratio of the rate constants for the reactions of the same pair of molecules with a less reactive radical is plotted in Fig. 5 against the logarithm of the ratio of the partial rate constants for the more reactive radical. Evidently most of the points lie below the line whose slope is unity, which demonstrates the greater selectivity of the reaction with the more reactive peroxy-radical.

V. THE SELECTIVITY OF THE REACTIONS OF THE COMPONENTS IN CO-OXIDATION

Using the approach developed by Emanuel'[109] for the estimation of the selectivities of liquid-oxidation reactions, we shall consider in greater detail the problem of the influence of the reactivity of the component on the rate and selectivity of the oxidation in mixtures.

In order to establish a relation between the co-oxidation parameters and the shape of the curve describing the dependence of the rate of oxidation of the individual components on the mixture composition, we shall make use of the limiting values of the derivative of the rate of oxidation of the component W with respect to its volume fraction in solution x for $x \to 0$ or $x \to 1$.

The systems of inequalities relating the kinetic co-oxidation parameters of various types of curves describing the rates of oxidation of the individual components are presented in Fig. 6. For example, the rate of oxidation of the second component in the region of mixtures enriched in the latter is higher than the rate of its oxidation in an inert solvent at the same concentration, provided that the following inequality holds: $r_1 < a_1/\Phi a_2$; in depleted mixtures the validity of the inequality $r_1 < a_1/a_2$ is sufficient for this purpose.

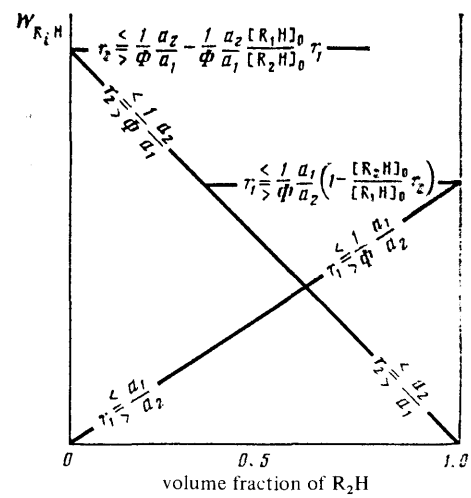


Figure 6. Equations relating the co-oxidation parameters for different derivatives of the rate of oxidation of the components with respect to composition.

The relations obtained[72] between the rate of oxidation of toluene and picoline (both these substances are relatively unreactive in liquid-phase oxidation reactions) and the composition of their mixture with cumene, whose reactivity is much higher, are presented in Fig. 7. These binary systems have been studied experimentally and their co-oxidation parameters have been obtained. Fig. 7 shows that a considerable increase of the rate of oxidation of the individual substances can be achieved in the co-oxidation reaction.

While the selectivity of the oxidation of an individual substance depends solely on the oxidation chain length and always diminishes when the substance is diluted by an inert solvent, the selectivity of the oxidation of the substance in the mixture is a complex function of the kinetic parameters and the concentrations of the components. In the simplest case of the oxidation of a mixture of two substances and subject to the condition $\Phi = 1$, the variation of the selectivity S_1 of the oxidation of the components R_1H and R_1OOH with composition is described by the expression[34]

$$\frac{1}{S_1} = 1 + \frac{(W_i k_{t11})^{1/2}}{k_{p11}[R_1H]_0 - (k_{p11}[R_1H]_0 - k_{p12}[R_2H]_0)\,x},$$

where $[R_1H]_0$ and $[R_2H]_0$ are the concentrations of the pure components and x is the volume fraction of the component R_2H. It follows from this equation that, in order to increase

the selectivity of the oxidation of a substance, it is necessary to add to it a second substance more reactive with respect to the peroxy-radicals $R_1OO^{\bullet}$.

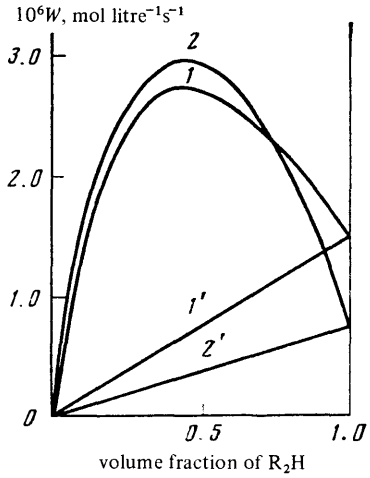


Figure 7. Dependence of the rates of oxidation of toluene (curves *1* and *1'*) and picoline (curves *2* and *2'*) on the composition of their mixtures with an inert solvent (curves *1* and *2*) and cumene (curves *1'* and *2'*) at 348 K.[72]

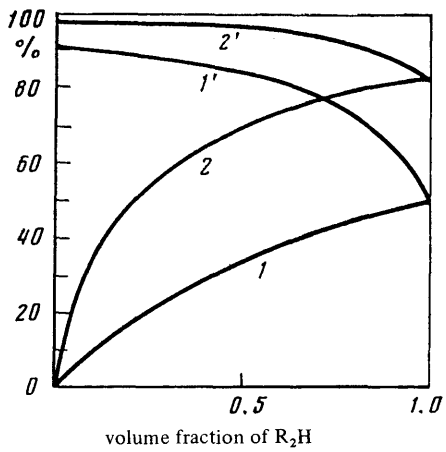


Figure 8. Dependence of the selectivity of the oxidation of the component R_2H on its content in a mixture with an inert solvent (curves *1* and *2*) and with the substance R_1H undergoing co-oxidation; $r_2 = 0.1$ (curves *1'* and *2'*) for different lengths ν of the oxidation chain: $\nu = 1$ (curves *1* and *1'*) and $\nu = 5$ (curves *2* and *2'*).

As an example, we calculated the dependence of the selectivity of the oxidation of the component R_2H in its mixture with a more reactive substance on the mixture composition for two oxidation chain lengths, namely 1 and 5; for clarity, short chains have been selected. The data presented in Fig. 8 show that, in contrast to the decrease of the selectivity on dilution of the substance R_2H by an inert solvent, the addition to R_2H of a more reactive substance entails an appreciable increase of the selectivity. For a chain length of unity, the selectivity of the oxidation of the pure substance is only 50%; on the other hand, in mixtures with a low content of this substance, the selectivity of its oxidation reaches as much as 90%. The selectivity of the oxidation of the second component also increases greatly for a chain length of 5 (from 83 to 98%).

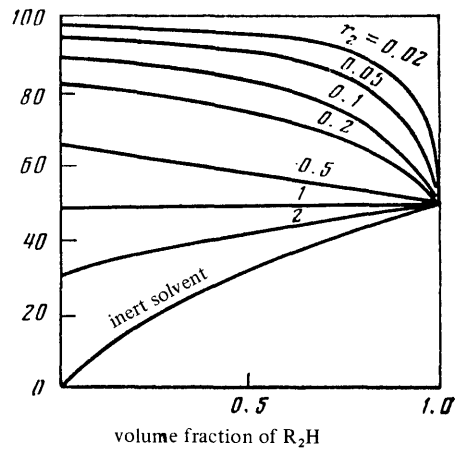


Figure 9. Dependence of the selectivity of the oxidation of the component R_2H on its content in a mixture with components R_1H having different reactivities.

In selecting the second mixture component, introduced in order to increase the selectivity of the oxidation of the required substance, its relative reactivity (relative to the given substance) is significant. The relations between the selectivity of the oxidation of the component R_1H and the mixture composition for different relative reactivities of the substance R_2H (this corresponds to different values of r_1) are presented in Fig. 9. Evidently, with increased reactivity of the second substance R_2H (a decrease of r_1 corresponds to this case), the selectivity of the oxidation of the first substance R_1H increases appreciably. Thus, in a mixture containing only 10 vol.% of a substance much more reactive than R_1H, the selectivity of the oxidation of the latter increases from 50 to 86%.[34]

The calculations and conclusions described above refer to reactions occurring under the conditions of initiated oxidation without degenerate chain branching. However, the results can be extended also to processes involving a mechanism with degenerate chain branching, provided that their main oxidation products are formed via the corresponding hydroperoxides.

Thus the oxidation of α-heptylcyclohexanone has been investigated[111] both separately and in mixtures with cumene. The results of kinetic studies showed that in co-oxidation the selectivity of the conversion of the ketone into an acid reaches 97%, while in the oxidation of the pure ketone it amounts to only 74% under the same conditions.

Thus in the oxidation of mixtures of substances with different reactivities a general feature is an increase of the selectivity of the conversion of the substance with the lowest

reactivity into hydroperoxides and products formed from the hydroperoxides in subsequent reactions.

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The data presented above permit the conclusion that the problems of describing the kinetics of unbranched chain oxidation reactions of organic substances under various conditions have been virtually solved. The examination and comparison of the available literature data for the kinetics of the co-oxidation of binary mixtures at low temperatures and high oxygen pressures showed that the principal feature of the dependence of the rate of oxidation of mixtures on composition is negative deviations of the rate of co-oxidation from additive values. The main cause of the appreciable negative deviations (observed in the oxidation of mixtures containing substances belonging to the classes investigated, with the exception of aldehydes) is a higher selectivity of the reactions of the peroxy-radical than that of the reactions of the initial molecule with peroxy-radicals formed in the given process. This can be used to select compositions which are difficult to oxidise.

Joint oxidation can serve as an effective means of regulating both the rate and selectivity of the oxidation of substances which are difficult to oxidise and can also be used to involve in the oxidation process substances which are hardly oxidised in a pure form under the given conditions.

In theoretical terms, the development of new experimental methods for the determination of the rate constants for various elementary liquid-phase oxidation cross-reactions is of interst. The co-oxidation method can be useful in the development of a procedure for the simultaneous synthesis of several chain products, which can be more economical than the synthesis of each of them separately. A more rigorous assessment of the likely usefulness of this method will become possible after the determination of the characteristic features of the kinetics of the joint oxidation at advanced stages of the process.

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