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Advances in the Study of the Mechanism of the Gas-phase Oxidation of Aldehydes

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The results of studies of the kinetics and mechanism of the gas-phase oxidation of aliphatic aldehydes are examined in relation to CH_2O, CH_3CHO, and C_2H_5CHO, which are intermediates in the oxidation of hydrocarbons and the general rules governing the course of these degenerate-branched chain processes are established. Attention has been concentrated on the role of heterogeneous factors. It is shown that heterogeneous chain branching as a consequence of the radical decomposition of CH_3CO_3H or $C_2H_5CO_3H$ takes place in the low-temperature oxidation of acetaldehyde and propionaldehyde; the experimental data on the heterogeneous radical decomposition of organic peroxy-compounds are considered.
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I. INTRODUCTION

Aldehydes are the main intermediates in the oxidation of hydrocarbons and the study of the mechanisms of their oxidation can help in determining such mechanisms. The characteristic features of the oxidation of aldehydes are described satisfactorily from the standpoint of the concept of degenerate branched chain reactions.[1-9] The determination of the true mechanism of these processes constitutes an important stage in the further development of the theory of chain reactions and also in the development of the scientific principles of the direct preparation of the compounds involved such as peroxyacids, acids, hydrogen peroxide, etc. which are widely used in various branches of the national economy.

Recent studies of the dependence of the kinetics of the oxidation of CH_3CHO and C_2H_5CHO on the nature of the surface of the reaction vessel over a wide temperature range revealed a number of unusual features.[10-14] This led to the revision of the ideas concerning the character of certain elementary stages, in particular the chain branching stage.

One of the important problems in the kinetics of the gas-phase oxidation reactions involves the elucidation of the causes of the appreciable rate of oxidation of acetaldehyde and propionaldehyde at temperatures below 473 K down to room temperature and the inertness of formaldehyde at these temperatures,[13,14] although the C–H bond energies in the CHO groups of the above compounds are identical.

The negative temperature coefficient (NTC) of the maximum rate of oxidation of aldehydes (CH_3CHO and C_2H_5CHO) observed comparatively recently,[15,16] stimulated studies whose aim was to elucidate the causes of the appearance of this coefficient both in the case of aldehydes and hydrocarbons.

The present state of the experimental and theoretical investigations is analysed in the present review in relation to the oxidation reactions of CH_2O, CH_3CHO, and C_2H_5CHO and the development of ideas concerning the mechanism of these reactions, particularly from the standpoint of allowance for the role of heterogeneous factors, is traced. The characteristic features and the general rules governing these processes have been elucidated and an approach to the development of a method for the selective gas-phase oxidation of aldehydes to acids and peroxyacids by appropriate treatment of the surface of the reaction vessel (treatment with a particular substance) or by altering the surface to volume (S/V) ratio has been formulated on their basis.

II. CHARACTERISTIC FEATURES OF THE KINETICS OF THE OXIDATION OF ALDEHYDES

The oxidation reactions of formaldehyde and acetaldehyde have now been investigated in detail. The conclusions reached have been extended to propionaldehyde, which is legitimate in view of the experimental demonstration of common features[5] of the oxidation of CH_3CHO and C_2H_5CHO. The principal results of the kinetic studies for formaldehyde have been discussed in review articles[6-9] and in a communication.[17] Studies devoted to acetaldehyde and propionaldehyde have been described in Refs.5–9 and 18–25 and Refs.5–9, 12, 14, 26, and 27 respectively.

The principal result of these investigations, common to all the aldehydes, is that the reactions proceed via a degenerate branched chain mechanism with autoacceleration. It has been shown for the photochemical oxidation of acetaldehyde and propionaldehyde that the chains in these reactions are long (~1000 units).[28-31] The chain character of the process is indicated also by the inhibition of the reaction by the addition of small amounts of a number of compounds.[32-35] The chain mechanism of the reaction involving formaldehyde has been demonstrated by the decreased rate of the process with increase of the S/V ratio.[36]

The product responsible for chain branching is a peroxy-compound—hydrogen peroxide in the high-temperature oxidation of formaldehyde and a peroxyacid in the oxidation of acetaldehyde and propionaldehyde. This conclusion is based on the acceleration of the reaction following the addition of RCO_3H [37-40] and also by the results of experiments[5] using the "quenching" method. After rapid cooling to 298 K, the acetaldehyde–oxygen mixture which has partly reacted at 488 K ignites spontaneously at a lower temperature on reheating. A similar phenomenon has been observed also for synthetic $CH_3CHO + O_2$ mixtures with added peroxyacetic acid. The degenerate chain branching has been attributed[5] to peroxyacetic acid and its existence in two forms has been

suggested—more and less stable forms, the former being partly converted into the latter during quenching.

The chain branching stage was initially attributed to the reactions of the peroxyacid, namely the decomposition of the peroxy-complex [$RCO_3H.RCHO$][8,27,39,41,42] or the homogeneous decomposition of RCO_3H.[32,33,43,44] The formation of a peroxy-complex was claimed on the basis of the inconsistency observed in a number of instances between the decrease of pressure in the system and the pressure of the RCO_3H formed, which was particularly clearly manifested at $T <$ 353 K.[39] The only criterion of the occurrence of the branching stage with participation of the peroxy-complex below 423 K is believed to be[39] the dependence of the maximum rate of the oxidation reaction on the square of the aldehyde concentration, which follows from the mechanism adopted (on the assumption of long chains and the neglect of the rate of initiation in mixtures with a high aldehyde content):

$$RCHO + O_2 \rightarrow R\dot{C}O + H\dot{O}_2,$$
$$R\dot{C}O + O_2 \rightarrow RC\dot{O}_3,$$
$$RC\dot{O}_3 + RCHO \rightarrow RCO_3H + R\dot{C}O$$
$$\left.\begin{array}{l} 2R\dot{C}O \rightarrow \\ R\dot{C}O + RC\dot{O}_3 \rightarrow \\ 2RC\dot{O}_3 \rightarrow \end{array}\right\} \text{chain termination},$$
$$RCO_3H \rightarrow RC\dot{O}_2 + \dot{O}H$$
$$RCO_3H + RCHO \rightarrow \text{radicals},$$
$$R = CH_3,\ C_2H_5.$$

It has been stated[45] that the maximum rate calculated from the $p-t$ curves (p is the pressure and t the time) cannot serve as criterion of the correctness of the choice of a particular branching reaction in view of the low accuracy of its determination.

The hypothesis that a peroxy-complex is formed in a gas phase with subsequent decomposition into radicals in space or on the reactor surface is relatively unjustified and has been put forward mainly by analogy with the situation observed in the liquid-phase oxidation.[46] A number of studies have been devoted to the question of the existence of the peroxy-complex in the gas phase.[47-50] Solely on the basis of the iodometric analysis of the reaction products, the formation of the aldehydomonoperacetate (AMP) via the following pathway has been claimed:

$$CH_3CHO + CH_3CO_3H \rightarrow CH_3{-}\underset{\displaystyle OO}{\overset{\displaystyle OH}{C}}{-}H \quad \overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3.$$

AMP then decomposes:

$$AMP \left\langle \begin{array}{l} \longrightarrow CH_3CHO + CH_3CO_3H; \\ \longrightarrow 2CH_3CO_2H. \end{array} \right.$$

In contrast to the liquid-phase acetaldehyde oxidation reaction, in which the presence of an adduct has been confirmed by NMR,[51,52] no such convincing evidence is available for the gas-phase process.

As regards the homogeneous decomposition of RCO_3H its contribution to the branching process at temperatures up to 473 K is low owing to the high activation energy[53-55] and it is difficult to account for the higher rates of oxidation of CH_3CHO at low temperatures by its formation.

The involvement of hydrogen peroxide in chain branching in the high-temperature oxidation of formaldehyde has been demonstrated[56] by the disappearance of the induction period following the addition of the maximum amount of H_2O_2 observed in the course of the reaction.

There has been no unanimous view concerning the mechanism of the low-temperature oxidation. The nature of the peroxy-compounds, i.e. H_2O_2[7,57,58] or HCOOOH,[4,8,59,60] has been the subject of controversy for a long time. This uncertainty was caused, on the one hand, by the deficiencies of the method of iodometric analysis used by the authors, which failed to yield an unambiguous answer and has been criticised at one time,[3] and, on the other hand, by the possibility of the formation of an organic peroxide, in particular dioxymethyl peroxide, on interaction of CH_2O with H_2O_2 outside the reaction zone.[61]

The formation of HCO_3H has been postulated[60] solely on the basis of the presence of peaks corresponding to masses of 60, 61, and 62 in the mass spectrum of the CH_2O oxidation products, which is unjustified without a comparison with the mass spectrum of the authentic compound. A recent communication[62] quotes the mass spectrum of HCO_3H and presents a comparison with the results of the mass-spectrometric analysis of the products of the low-temperature oxidation of formaldehyde and a mixture containing CH_2O and H_2O_2. In the last two stages the spectra hardly differed. On this basis, it was concluded that the presence of peaks with m/e 60–62 in the analysis of the formaldehyde oxidation products is associated with the products of the interaction of CH_2O and H_2O_2 outside the reaction zone and not with the presence of HCO_3H.

The absence of HCO_3H from the low-temperature formaldehyde oxidation products in a reactor treated with boric acid has been established by analysing the organic peroxyacid in the presence of H_2O_2 using a photoelectric colorimeter (PEC) with the aid of benzidine[63] and *o*-toluidine[64] hydrochlorides. The kinetics of the consumption of CH_2O and the accumulation of H_2O_2 have shown that the chain branching in the low-temperature oxidation of CH_2O is caused by the bimolecular homogeneous decomposition of H_2O_2 into two $\dot{O}H$ radicals.[17]

An important factor in the determination of the mechanism of a chain reaction is the elucidation of the nature of the chain propagating active centre. Progress in this direction has been associated with the employment in the investigations of the kinetic method involving the freezing out of the radicals combined with EPR spectroscopy.[65]

According to published data, the chain propagating active centres in the oxidation of aldehydes are the peroxy-radicals $RC\dot{O}_3$ for acetaldehyde and propionaldehyde and $H\dot{O}_2$ for CH_2O. This conclusion has been based on the presence of acetyl peroxide in the products of the photochemical oxidation of acetaldehyde[66] and also the direct detection of peroxy-radicals by EPR in the thermal oxidation of CH_3CHO [18] and C_2H_5CHO.[12] The observation of the EPR signals due to the peroxy-radicals at low degrees of conversion of acetaldehyde and propionaldehyde (~10%) and the high selectivity of the reaction with respect to peroxyacids (~90%)[67] as well as the parallel course of the peroxy-radical and RCO_3H accumulation curves[18] served to identify the $RC\dot{O}_3$ radicals. An appreciable contribution to the EPR spectrum by radicals of the type $R\dot{O}_2$ was ruled out by the observation that the kinetics of the accumulation of their radicals were inconsistent with the kinetics of the accumulation of ethyl hydroperoxide.[26] Under the experimental conditions, the radicals accumulated in accordance with the rate law characteristic of an intermediate, while the yield of the hydroperoxide increased continuously.

The presence of $H\dot{O}_2$ radicals in the high-temperature oxidation of formaldehyde was indicated by the detection of hydrogen peroxide in the reaction products[57,61,68-71] and by the direct recording of the EPR spectra of the $H\dot{O}_2$ radical.[72]

The identification was based on a comparison of the spectra with the EPR spectra of the $HO_2^{\cdot}$ radicals quoted in the literature[73-76] and on the basis of the parallel behaviour of the radical and H_2O_2 accumulation curves.

The question of the nature of the chain propagating species under the conditions of the low-temperature oxidation of formaldehyde has been discussed[4] as a function of the actual pathway of the reaction of the HĊO radical with O_2 leading to the formation of HO_2 or $HCO_3^{\cdot}$ radicals.

$$\text{HĊO} + O_2 \begin{cases} \longrightarrow HO_2^{\cdot} + CO; & (1a) \\ \longrightarrow HCO_3^{\cdot}; & (1b) \\ \longrightarrow {\cdot}OH + CO_2. & (1c) \end{cases}$$

The results of studies in recent years of the reactions of the HĊO radicals with oxygen by infrared spectroscopy,[77] mass spectrometry,[78] and intracavity laser spectroscopy (ICLS) combined with flash photolysis,[79] as well as the direct detection of the $HO_2^{\cdot}$ radicals by EPR[80] indicate the preferential formation of $HO_2^{\cdot}$ radicals. The source of the HĊO radicals was either the reaction of formaldehyde with H atoms obtained by a high-frequency discharge in hydrogen or the photolysis of CH_2O.[81]

On the assumption that reaction (1a) takes place, its rate constant has been determined[78] by following directly the concentration of the HĊO radicals and on the basis of data concerning the competition of the reactions of the HĊO radicals with O_2 and O. In another study[77] a band corresponding solely to the $HO_2^{\cdot}$ radical was observed in the infrared spectrum of the products of the reaction of the HĊO radicals with oxygen at room temperature and no bands were found which could be attributed to the $HCO_3^{\cdot}$ radical. The study of the kinetics of the destruction of the HĊO radicals in the photolysis of CH_2O and CH_3CHO in the presence of O_2 by the ICLS method[79] made it possible to determine the rate constants for the overall reaction (1). On the basis of the lack of a dependence of k_1 on pressure in the range 0.2–76 kPa, it was concluded that either the $HO_2^{\cdot}$ radicals are formed preferentially or that the $HCO_3^{\cdot}$ radicals formed decompose rapidly into $CO(CO_2)$ and $HO_2^{\cdot}(\dot{O}H)$. Calculations by the LCAO method have shown[82] that an excited $HCO_3^{\cdot}$ radical is formed in reaction (1b) and can rapidly decompose into ȮH and CO_2. In view of the fact that the yield of CO_2 in the photolysis of CH_2O is low, it has been suggested that at room temperature reaction (1a) competes successfully with the stage (1b) indicated above.

The study of Osif and Heicklen[83] showed that $k_{1b}/k_{1a} = 5 \pm 1$ in the determination of the rates of reactions (1a) and (1b) from the known concentrations of CO, CO_2 and HCO_2H. However, other pathways leading to the formation of HCO_2H,[84] which differ from the reaction sequence $HCO_3^{\cdot} \rightarrow HCO_3H \rightarrow HCO_2H$ and associated, in particular, with secondary processes occurring in the system owing to the presence of CH_2O and H_2O_2 were not ruled out.[61]

The kinetics of the photolysis of CH_2O in a mixture containing O_2 and in the presence of CO_2 have been investigated at 298 K.[84] The quantum yields of H_2, CO, and CO_2 and the consumption of O_2 were determined. Since $\Phi_{H_2} \gg 1$ and $\Phi_{CO} \gg 1$ (Φ is the quantum yield), the authors proposed a reaction mechanism on the basis of which the following expression was obtained for the ratio of the rate constants (M is any kind of species):

$$\frac{k_{1b}[M]}{k_{1b}[M] + k_{1a}} \geqslant 0.049 \pm 0.017.$$

The question of the nature of the chain propagating active centre in the low-temperature oxidation of CH_2O was finally resolved after the direct detection of the $HO_2^{\cdot}$ radicals.[17]

Convincing evidence that peroxy-radicals are the chain propagating active centres was obtained by analysing the kinetics of the thermal oxidation of aldehydes and the following of its features: (1) the attainment of the maximum concentration of the $RCO_3^{\cdot}$ or $HO_2^{\cdot}$ radicals (depending on the object of study) simultaneously with the attainment of the maximum rate of consumption of the aldehyde; (2) the quantitative correspondence between the change in the rates of consumption of the aldehyde and the concentrations of the corresponding peroxy-radicals as the experimental conditions are varies.[12,17,18,26,67,72]

Information concerning the elementary rate-limiting reaction

$$RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + R\dot{C}O$$

obtained indirectly by analysing the molecular products, has been published[31,85] and is presented in Table 1. The rate constants for this reaction have been determined[67] by measuring the concentration of the $RCO_3^{\cdot}$ radicals by EPR and the rate of accumulation of the peroxyacid in the gas-phase oxidation of CH_3CHO or C_2H_5CHO at low degrees of conversion. The rate constants are listed in Table 1.

Data concerning the elementary step

$$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + H\dot{C}O$$

have been obtained[86,87] and are also presented in Table 1.

Table 1. The rate constants for the reactions of peroxy-radicals with aldehydes.

Reaction	A, cm^3 molecule^{-1} s^{-1}	E_a, kJ mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	Remarks	Refs.
$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + H\dot{C}O$	$1.6 \cdot 10^{-12}$ $1.6 \cdot 10^{-11}$ $1.9 \cdot 10^{-11}$	44.7 59.3 43.5±12.5	$1.6 \cdot 10^{-15}$ —	773	Slow $H_2 + O_2 + N_2 + CH_2O$ oxidation reaction CH_2O oxidation reaction, EPR method	[86] [87]
$CH_3CO_3^{\cdot} + CH_3CHO \rightarrow$ $\rightarrow CH_3CO_3H + CH_3\dot{C}O$	— — $(5.7 \pm 2.2) \cdot 10^{-12}$	30±4 28.4±4.18 33.4±3.2	$(1.3 \pm 0.3) \cdot 10^{-17}$ — —	293 360—403 415—473	Photochemical CH_3CHO oxidation reaction, analysis of molecular products CH_3CHO oxidation reaction initiated by $(CH_3)_3COOH$ Thermal CH_3CHO oxidation reaction, EPR method	[31] [85] [67]
$C_2H_5CO_3^{\cdot} + C_2H_5CHO \rightarrow$ $\rightarrow C_2H_5CO_3H + C_2H_5\dot{C}O$	— $(7.0 \pm 1.3) \cdot 10^{-12}$	28±2 32.2±2.1	$(7.2 \pm 0.2) \cdot 10^{-17}$ —	295 438—488	Photochemical C_2H_5CHO oxidation reaction, analysis of molecular products Thermal C_2H_5CHO oxidation reaction, EPR method	[31] [67]

Notation: A is the pre-exponential factor, E_a the activation energy, k the rate constant, and T the temperature.

On the basis of data showing a decrease of the induction period and the slow hydrogen oxidation reaction in the presence of added formaldehyde, the reaction mechanism, involving the reactions of the active species with CH_2O has been analysed with the aid of a computer, which made it possible to estimate the rate constant at 773 K.[86] The rate constant for this reaction has been measured by EPR.[87] The approach was similar to that used by Paronikyan et al;[67] the source of the $HO_2^{\cdot}$ radicals was the CH_2O oxidation reaction.

III. THE ROLE OF HETEROGENEOUS FACTORS IN THE OXIDATION OF ALDEHYDES

In the early studies of the oxidation of formaldehyde, few data were published concerning the influence of heterogeneous factors.[36,88,89] A decrease of the reaction rate[36] or a change in the composition of the products with increase of the S/V ratio was noted. In particular, a sharp increase in the yield of CO_2 compared with CO has been observed.[88]

Experiments in a reactor which had been treated with boric acid, inert with respect to decomposition of peroxy-compounds, leads to an appreciable increase in their yield.[59,90]

The observed discrepancies between results obtained by different workers (for example, the presence of an induction period and peroxides[59,89-91] or their absence[92]) has been attributed[60] to differences between the rates of the heterogeneous decomposition of the peroxy-compound, namely HCO_3H, in different experiments. Despite the lack of clear-cut evidence for the formation of HCO_3H, the above study[60] is valuable because the influence of the nature of the surface on the character of the kinetics of the oxidation of formaldehyde was noted in it for the first time.

Studies[93,94] whose authors noted that the treatment of the reactor surface with KCl leads to the inhibition of the homogeneous reaction and did not assume that both the formation and destruction of the active species proceed heterogeneously merit attention.

The influence of the surface of the reaction vessel on the CH_2O oxidation reaction was studied in greater detail by Markevich and Filippova.[68] in clean reactors the reaction proceeds with formation of a considerable amount of hydrogen peroxide (~27% of the initial aldehyde), while in reactors treated with various substances (KCl, CsCl, and $K_2B_4O_7$) the peroxide is not observed and the reaction proceeds at an almost constant rate. A similar dependence of the yield of H_2O_2 on the nature of the surface has been observed in other investigations.[71,72,95,96] The different data obtained have been accounted for in terms of different rate constants for the heterogeneous destruction of hydrogen peroxide and $HO_2^{\cdot}$ radicals on different surfaces.

Thus the variable data definitely indicate the dependence of the yield of H_2O_2 on the nature of the surface. As regards radicals, the first experimental proof of their formation has been obtained by Vardanyan and co-workers.[72,87] In the high-temperature oxidation of CH_2O in an untreated reactor and a reactor treated with boric acid, the $HO_2^{\cdot}$ radicals,[72] whose concentration reached 0.1% of the initial aldehyde, were detected together with considerable amounts of hydrogen peroxide. In reactors treated with salts, hydrogen peroxide and the $HO_2^{\cdot}$ radicals were not detected. Direct experiments have shown[87] that the rate of the heterogeneous destruction of the $HO_2^{\cdot}$ radicals in an untreated reactor and in a reactor treated with boric acid is low but increases appreciably on passing to reactors treated with salts.

In terms of their influence on the rate of the formaldehyde oxidation reaction and the composition of its products, the surfaces investigated have been divided into two groups.[97] A similar subdivision has also been carried out in another study.[98] In the reactors of the first group (reactors pretreated by the reaction taking place or treated with boric acid) the rate of reaction is high and the oxidation proceeds via a degenerate branched chain mechanism and the agent responsible for the chain branching is hydrogen peroxide. The effective activation energies, determined from the maximum rate of consumption of formaldehyde, are 109–125 kJ mol^{-1}. In the reactors of the second group (reactors treated with a salt) the rate of reaction is almost constant and is appreciably lower; no hydrogen peroxide has been detected in the products. The influence of the surface is reflected in a sharp increase of the effective activation energies (209 kJ mol^{-1}) compared with the reactors of the first group. Similar characteristics of the dependence on the nature of the surface have been observed also in the low-temperature oxidation of formaldehyde in reactors treated with boric acid and CsCl.[17]

On the basis of experimental studies and the analysis of the available literature data, the following mechanism has been proposed[56,97] for the oxidation of CH_2O:

$$CH_2O + O_2 \rightarrow H\dot{C}O + HO_2^{\cdot},$$
$$H\dot{C}O + O_2 \rightarrow HO_2^{\cdot} + CO,$$
$$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + H\dot{C}O,$$
$$H_2O_2 + M \rightarrow 2OH + M,$$
$$\dot{O}H + CH_2O \rightarrow H_2O + H\dot{C}O,$$
$$\dot{O}H + H_2O_2 \rightarrow H_2O + HO_2^{\cdot},$$
$$H_2O_2 \xrightarrow{\text{wall}} \text{destruction},$$
$$HO_2^{\cdot} \xrightarrow{\text{wall}} \text{destruction},$$
$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2.$$

Extremely convincing evidence for the alteration of the rate of the heterogeneous destruction of peroxy-radicals on passing from reactors of the first group to those of the second has been obtained by EPR.[87,99-101] The heterogeneous decomposition of hydrogen peroxide follows from the comparative analysis of data obtained in a study of the gas-phase decomposition of hydrogen peroxide as a function of the nature of the surface in glass reactors, both thoroughly cleaned[102] and treated with boric,[103,104] phosphoric,[105] and hydrofluoric acids[106] in the temperature range 573–873 K. It has been noted that at approximately 693–698 K a transition from a heterogeneous to a homogeneous reaction is observed. The homogeneous reaction mechanism is indicated, in particular, by the sharp increase of the effective activation energy—from 42 to 230 kJ mol^{-1}.[105] An increase of the reactor diameter leads to a decrease in the rate of decomposition of radicals.[104] In a reactor treated with boric acid,[103,104] the decomposition of H_2O_2 is difficult, and, according to the authors of one of the investigations,[102] a thoroughly clean glass surface is more effective for the conservation of H_2O_2.

The need to include the homogeneous recombination of the $HO_2^{\cdot}$ radicals arises from the experimentally observed dependence of the maximum $HO_2^{\cdot}$ radical concentration on the concentration of the initial aldehyde; this dependence is described by a curve which tends to a limit.[72]

The validity of the proposed mechanism and the characteristic features of the dependence of the reaction kinetics on the nature of the surface which follow from it have been confirmed with the aid of a mathematical model.[107]

There is very little information about the influence of the nature and state of the surface of the reaction vessel on the kinetics of the oxidation of acetaldehyde and propionaldehyde

under static conditions. According to published data, the effective activation energies for the oxidation of CH_3CHO and C_2H_5CHO are much lower (37.6–83.6 kJ mol^{-1}) than for the oxidation of CH_2O, where the effective activation energy is 117–209 kJ mol^{-1}.[5,8]

Pease's study[108] merits special attention because of the novelty of the conclusions reached on the basis of extremely limited information concerning the influence of the nature of the surface on the composition of the products and the rate of the low-temperature oxidation of acetaldehyde. He showed that the rate of reaction is 4–5 times higher in a reactor treated with KCl than in one washed with nitric acid. The maximum yield of CH_3CO_3H was observed in a reactor washed with nitric acid, while the highest yield of CO_2 was noted in a reactor treated with KCl. The amount of CO_2 formed in packed reactors was appreciably higher. By analogy with formaldehyde[96] and H_2,[108] a sharp decrease in the rate of reaction was to be expected in the reactor treated with KCl, since it is known that in this case the rate of destruction of active centres is higher.[87,98]

On the basis of these experimental results, Pease[108] suggested that, in the gas-phase oxidation of CH_3CHO, the chains are initiated on the surface as a consequence of the decomposition of CH_3CO_3H or the $CH_3CO_3^{\cdot}$ radical. Later, the observed dependence of pressure pulsations on the nature of the surface of the reaction vessel in the oxidation of acetaldehyde was also attributed[41] to the heterogeneous decomposition of RCO_3H but this time via a molecular mechanism. According to the authors,[41] the heat evolved in this process initiates a cold flame. However, it has been shown recently that the initiation of the flame is more likely to be the cause rather than the consequence of thermal heating.[110]

Studies[111,112] of the influence of the nature of the surface of a reactor treated with metal halides on the oxidation of acetaldehyde have led to the conclusion that the surfaces catalysing the decomposition of RCO_2H also catalyse the oxidation of CH_3CHO.

A relation has been established in a number of studies[32,108,113] between S/V and the rate of oxidation of CH_3CHO. The proposed explanations are contradictory. Heterogeneous initiation and chain termination have been suggested by Pease,[108] while McDowell and Thomas[32] postulated only a homogeneous process as did their earlier investigation[114] and the study of Combe et al.[39]

Since the calculated activation energies proved to depend on S/V, it was suggested that the corresponding stage is heterogeneous. If the initiation had been homogeneous, one might expect an activation energy of 171.4 kJ mol^{-1},[115] while the value actually obtained[116] is 121.2 kJ mol^{-1}. The possibility of the heterogeneous chain initiation in the oxidation of acetaldehyde has been demonstrated by EPR.[117] The available data show that at low temperatures heterogeneous initiation can predominate over homogeneous initiation.

Data on the influence of the nature and cleanliness of the reactor surface on the rate of the process and its activation energy, obtained in two investigations,[24,44] also merit attention. A marked dependence of the rate of reaction and of the ratio of the yields of the products of the low-temperature oxidation of acetaldehyde (peroxyacetic and acetic acids) on the specific concentration of the substance deposited on the reactor surface has been established recently.[112] The maximum yield of CH_3CO_3H was observed in the reactor treated with a 0.1% KCl solution, while the yield of CH_3CO_2H changed only slightly.

Using the above set of reactions (see Section II) for the description of the acetaldehyde oxidation process, Dixon et al.[22] obtained activation energies ranging from 0 to 66.9 kJ mol^{-1} in the temperature range 318–393 K, on the basis of which they concluded that the branching process is heterogeneous. A similar hypothesis has been put forward by Hardacre et al.[44]

Inspection of the available experimental data obtained under static conditions establishes that a detailed analysis of the products has been carried out only for acetaldehyde. The complete absence of detailed kinetic results concerning the oxidation of propionaldehyde is noteworthy. The sensitivity of the reaction to the nature and state of the surface of the reaction vessel observed in a number of investigations has not been reflected in the proposed mechanisms, which in essence describe a homogeneous process. The conclusion concerning the proposed elementary stages has been reached only on the basis of the analysis of the molecular products. There are no clearly well-founded data concerning the nature of the chain branching stage. The mechanisms of the gas-phase oxidation of CH_3CHO and C_2H_5CHO have been constructed formally by analogy with the liquid-phase oxidation,[46,118,119] which has been studied in greater detail.

Table 2. Characteristics of the aldehyde oxidation reactions.

Compound	c_0, %	T, K	10^{-16} w_{max}, cm^{-3} s^{-1}	Radical	10^{-13} c_r, cm^{-3}	Peroxide	10^{-16} c_p, cm^{-3}	Refs.
Reactors of first group								
CH_2O	1	850	42	$HO_2^{\cdot}$	12	H_2O_2	1	[71, 107]
CH_2O	5	718	1.8	$HO_2^{\cdot}$	2	H_2O_2	1	[17]
CH_3CHO	20	448	2	$CH_3CO_3^{\cdot}$	2.5	CH_3CO_3H	56	[11, 21]
CH_3CHO	2.5	498	0.3	$CH_3CO_3^{\cdot}$	5.6	CH_3CO_3H	6–6.2	[10, 19]
CH_3CHO	1.5	598	8	$CH_3CO_3^{\cdot}$	—	CH_3CO_3H	2	[19, 21]
CH_3CHO	1.5	623	10	$CH_3CO_3^{\cdot}$	10	CH_3CO_3H	0.72	[19, 21]
C_2H_5CHO	8	448	0.35	$C_2H_5CO_3^{\cdot}$	~1	$C_2H_5CO_3H$	8	[12]
C_2H_5CHO	2.1	564	0.3	$C_2H_5CO_3^{\cdot}$	1	$C_2H_5CO_3H$	1.3	[26]
Reactors of second group								
CH_2O	1	900	12	—	—	—	—	[71, 107
CH_2O	5	723	0.2–0.25	—	—	—	—	[17]
CH_3CHO	20	448	10	$CH_3CO_3^{\cdot}$	11	CH_3CO_3H	1.9	[11, 21]
CH_3CHO	2.5	498	0.28	$CH_3CO_3^{\cdot}$	3.6	CH_3CO_3H	0.3	[10, 19]
CH_3CHO	1.5	598	3.2	$CH_3CO_3^{\cdot}$	—	CH_3CO_3H	<0.1	[19, 21]
CH_3CHO	1.5	623	4	$CH_3CO_3^{\cdot}$	2.5	CH_3CO_3H	<0.1	[19, 21]
C_2H_5CHO	8	448	0.5	$C_2H_5CO_3^{\cdot}$	1.3	$C_2H_5CO_3H$	3.8	[12]
C_2H_5CHO	2.1	564	0.26	$C_2H_5CO_3^{\cdot}$	0.5	$C_2H_5CO_3H$	—	[26]

Notation: c_0 is the initial concentration of the aldehyde in air at atmospheric pressure, w_{max} the maximum reaction rate, c_r the maximum concentration of radicals, and c_p the maximum concentration of the peroxide.

The first detailed investigation of the kinetics of the oxidation of CH_3CHO and C_2H_5CHO as a function of the nature of the surface has been carried out by Oganesyan and coworkers[18–21] and by Oganesyan[26] respectively. At 448 K the rate of oxidation of CH_3CHO in a reactor of the second group is ~4–5 times higher than in a reactor of the first group; a 40% conversion of acetaldehyde in a reactor of the second group was observed for t = 25 s (t is the residence time of the reaction mixture in the reactor) and for t = 90 s in a

reactor of the first group. The maximum yields of the peroxyacids also differ. The yield in a reactor treated with a salt amounts to 5–7% relative to the initial aldehyde, while in a reactor conditioned by the reaction itself it is 18–20%. An increase of temperature to 499 K results in an interesting phenomenon: the rates of the process in reactors of both types are similar. Up to 25% conversion of acetaldehyde, its consumption in the two cases is described virtually by the same S-shaped curve. The yield of CH_3CO_3H is appreciable in reactors of the first group (17–18%) and low in those of the second group (a fraction of one per cent). Considerable amounts of CH_3CO_3H have been observed[19] in the temperature range 598–648 K in a reactor treated with boric acid, the amount diminishing with increase of temperature: the maximum yields of CH_3CO_3H are 10–11% at 598 K and only 2% of the initial aldehyde at 648 K. In a reactor treated with a salt the amount of CH_3CO_3H is apparently below the sensitivity of the analysis.

The fact that the reaction proceeds autocatalytically in reactors of both types merits attention. However, in contrast to the low-temperature range, the rate of consumption of the aldehyde in a reactor of the first group is ~3–4 times greater (at 623 K) than in a reactor of the second group. The concentrations of the peroxy-radicals are correspondingly greater in a reactor treated with boric acid; Table 2 presents certain characteristic data.

The decreased yield of the organic peroxide with increase of temperature is explained by the increased rate of decomposition of both RCO_3H and the CH_3CO and $CH_3CO_3^{\cdot}$ radicals. It has been established by EPR[10] that the rate of decomposition of the peroxide on a surface treated with a salt is much higher than on one treated with boric acid. In contrast to the low-temperature range, in a reactor treated with boric acid hydrogen peroxide is detected in the CH_3CHO oxidation products, the shape of its accumulation curve differing from that for RCO_3H. Measurable amounts of H_2O_2 are detected at a later stage in the reaction than is RCO_3H. For example, at 623 K and for $t = 0.3$ s the CH_3CO_3H concentration is 2%, while that of hydrogen peroxide is only 0.1%.

Studies of the kinetics of the low-temperature oxidation of propionaldehyde[12] showed that the kinetic behaviour of the system in reactors of both groups is similar to that observed for acetaldehyde. As before, the reaction takes place with autoacceleration, the rate of consumption of the aldehyde and the maximum concentration of the $RCO_3^{\cdot}$ radicals being higher in reactors of the second group. The yields of peroxypropionic acid also differ appreciably: at 423 K and for $t = 2$ min its yield is 1.7% in a reactor treated with KCl and 4.7% of the initial aldehyde in one treated with boric acid.

It has been established[12] that, although the yield of $C_2H_5.CO_3H$ in a reactor treated with KCl is lower, a new organic peroxide, namely ethyl hydroperoxide, as well as ethanol are detected in the reaction product; furthermore, ethylene, detected in a reactor treated with boric acid, is absent. It was concluded that, under conditions favourable for the decomposition of the peroxyacid, the $C_2H_5^{\cdot}$ radicals formed react with oxygen, giving rise to the $C_2H_5O_2^{\cdot}$ radicals, whose subsequent reaction with the aldehyde leads to the formation of ethyl hydroperoxide. The experimentally established influence of the nature of the surface on the yield of the products C_2H_4 and $C_2H_5O_2H$ led to the hypothesis that the reactions $C_2H_5^{\cdot} + O_2 \rightarrow C_2H_4 + HO_2^{\cdot}$ and $C_2H_5^{\cdot} + O_2 \rightarrow C_2H_5O_2^{\cdot}$ take place partly on the reactor surface under the experimental conditions.

With increase of the experimental temperature to 431–531 K, a change in the ratio of the rates of consumption of C_2H_5CHO and of the concentrations of the radicals is observed in reactors of both types, as in the case of acetaldehyde; the ratios are higher in a reactor of the first group (Table 2). It has been established that the yields of $C_2H_5CO_3H$ and $C_2H_5.O_2H$ depend on the nature of the surface of the reaction vessel. In the case of a surface which is effective for the decomposition of peroxides and radicals, the yield of the peroxyacid is lower and that of the hydroperoxide is higher. This has been explained by the fact that the formation of the hydroperoxide is due to the reactions of the $C_2H_5^{\cdot}$ radicals arising in the course of the decomposition of the C_2H_5CO radicals and the peroxyacid.

Analysis of experimental data (Table 2) has shown that, whereas from the standpoint of the involvement of the peroxy-compound in the chain-branching stage the oxidation reactions of formaldehyde, acetaldehyde, and propionaldehyde are similar, in terms of the influence of the nature of the reactor surface they are different. The oxidation of CH_3CHO and C_2H_5CHO proceeds with autoacceleration in reactors of all types. The main intermediate, responsible for the branching, is the corresponding peroxyacid RCO_3H, while the chain propagating active centres are the $RCO_3^{\cdot}$ radicals. The fact that in the low-temperature range the rate of reaction and the concentration of the chain propagating species are low in reactors treated with salts, which are effective inhibitors[3] of the epoxidation processes, despite the intense destruction of the radicals merits attention.

It has been shown for formaldehyde that the rate of reaction in reactors treated with salt is greatly reduced, while the concentration of the active centres becomes lower than the sensitivity of the analysis. The opposite behaviour has been observed for acetaldehyde and propionaldehyde. This is due to the fundamental difference between the natures of the chain branching stages in the oxidation of formaldehyde, on the one hand, and acetaldehyde and propionaldehyde, on the other. This is also indicated by the appreciable difference between the effective activation energies for the processes and the compositions of the reaction products as a function of the nature of the surface. Whereas in the case of CH_2O the activation energy varies from 108.7 kJ mol^{-1} for a surface treated with an acid to 209 kJ mol^{-1} for a surface treated with a salt, in the case of acetaldehyde and propionaldehyde, the activation energy is 37.6–83.6 kJ mol^{-1}, being smaller for a surface treated with a salt.

The kinetic manifestation of the influence of the nature of the surface on the formaldehyde oxidation reaction does not conflict with the idea that there is a stage involving the heterogeneous destruction of the $HO_2^{\cdot}$ radicals and H_2O_2—the product responsible for the branching. For two successive representatives of aliphatic aldehydes, this explanation is invalid. If the decomposition of the intermediate (the peroxyacid) were heterogeneous and involved the formation of molecular products only, the CH_3CHO and C_2H_5CHO oxidation reactions should have been retarded in reactors of the second group in the low-temperature range. Clearly, apart from the heterogeneous chain termination stage, a surface reaction which generates active centres in the gas phase must also occur. This reaction is the decomposition of the peroxyacid on the surface via a radical mechanism with liberation of some of the radicals into the gas phase.

The occurrence of the heterogeneous chain branching has been confirmed with adequate reliability by the autocatalytic character of the process observed regardless of the nature of the surface, the high rates of reaction, and the high concentrations of the active centres in a reactor whose surface (treated with a salt) is effective in the destruction of radicals.

The heterogeneous chain branching is also supported by the results of experiments involving adsorption on the cold surface of the reactor of small amounts of CH_3CO_3H, which leads to the auto-ignition of the acetaldehyde–oxygen mixture

on reheating as a consequence of the heterogeneous decomposition of CH_3CO_3H.[120,121] The temperature of the induced auto-ignition then depends both on the amount of the adsorbed CH_3CO_3H and on the S/V ratio; with increase of S/V, the auto-ignition temperature falls sharply.

According to the available data,[1-3] the increase of S/V leads as a rule to a decrease in the rate of the chain process, which indicates heterogeneous chain termination. However, the influence of the surface is not exhausted by this finding. In early investigations[122-131] the possibility of heterogeneous chain initiation and branching was assumed. The latter possibility was subjected to theoretical analysis in a number of investigations.[1,131-133] So far, there are few experimental data concerning heterogeneous branching. One may note studies[126-130] which dealt with the low-temperature oxidation of hydrocarbons: propane, ethane, and methane. The observed anomalous influence of the surface on the rate of the corresponding stage of the chain process, namely the increase of the rate with increase of S/V, was attributed to heterogeneous chain branching.

Yet another experimental piece of evidence for heterogeneous chain branching in the CH_3CHO and C_2H_5CHO oxidation reactions is provided by the discovery of the radical decomposition of the vapours of the organic peroxides CH_3CO_3H, HCO_3H, CH_3OOH, $C_2H_5CO_3H$, and $(CH_3)_3COOH$ on a solid surface with liberation of some of the radicals from the surface to the gas phase.[134-147] The experiments on the decomposition of the peroxy-compounds were performed mainly at atmospheric pressure in a stream of nitrogen containing small amounts of O_2 at temperatures from ambient up to 498 K. In a number of instances at low pressure the peroxyacid was supplied to the catalyst without dilution with an inert gas. The solid surfaces were those of the reactors of the first and second groups and also metallic platinum, gold, and silver. The residence time in the reactor was varied from several seconds to 10^{-3}–10^{-4} s. In the course of the experiments it was established that, in the absence of catalysts, the decomposition proceeds via a first-order reaction with respect to the peroxy-compound with formation of radicals, which are partly transferred to the gas phase. The detection of peroxy-radicals in the cold trap, placed in the EPR cavity, serves as experimental evidence for the radical decomposition. The heterogeneous character of the decomposition of the peroxy-compounds has also been confirmed by the low effective activation energies, not exceeding 54.3 kJ mol^{-1}.

The general character of the radical decomposition on many solid surfaces has been established in relation to peroxyacetic acid. The detection of the $CH_3CO_3^{\cdot}$ radicals[134] and analysis of the molecular products in the course of the decomposition on platinum[143] led to the conclusion that the peroxyacid dissociates with homolysis of the peroxide bond. This is supported by the finding that the amount of CO_2 formed reached 90% of the initial peroxide. The formation (in the course of the decomposition of organic peroxy-compounds) of OH_{ads} radicals adsorbed on the surface has been demonstrated as a result of the investigation of the methyl hydroperoxide decomposition reaction on a platinum wire in the presence of small amounts of added CO.[143] Under conditions ruling out homogeneous reactions, the formation of additional amounts of CO_2, attributed to the interaction of OH_{ads} with CO, has been observed.

It has been shown that, from the standpoint of the generation of radicals on the surface and their transfer into space, the activities of the catalysts decrease in the following sequence of metals:[141] Pt > Au > Ag, and in the following sequence of alkali metal chlorides:[144] LiCl > NaCl > KCl > RbCl > CsCl.

Comparison of the kinetics of the decomposition reactions of peroxyacetic acid on silver and potassium chloride led to the conclusion that the metallic catalyst is more effective, particularly as regards the generation of radicals and their transfer into the gas phase. Analysis[139] of the ratio of the concentrations of the molecular products of the decomposition of peroxypropionic acid (C_2H_4 and C_2H_4O) made it possible to exclude the transfer of the radicals R from the surface into space.

In a number of instances[134-139] the yield of radicals is appreciable, amounting to 10% of the amount of the decomposed peroxide. A recent study of the radical decomposition of t-butyl hydroperoxide showed that the yield of the $CH_3OO^{\cdot}$ radicals reaches 90% of the decomposed hydroperoxide.[147]

It has been suggested that the heterogeneous decomposition of organic peroxides be used as a source of peroxy-radicals and OH_{ads} radicals for the initiation of the low-temperature oxidation reactions of organic compounds in order to investigate radical reactions.[148]

On the basis of data for the decomposition of organic peroxides on a solid surface, the kinetic curves for the accumulation of the $RO_2^{\cdot}$ radicals, and the analysis of molecular products, the following fundamental elementary steps leading to the formation of radicals have been proposed:[14]

$$CH_3CO_3H_{ads} \rightarrow CH_3CO_{2\,ads}^{\cdot} + \dot{O}H_{ads},$$
$$CH_3CO_{2\,ads}^{\cdot} \rightarrow CH_{3\,ads}^{\cdot} + CO_2,$$
$$CH_{3\,ads}^{\cdot} + O_2 \rightarrow CH_3O_{2\,ads}^{\cdot}$$
$$CH_3O_{2\,ads}^{\cdot} \rightarrow \text{partial transfer of radicals into gas phase.}$$

An important result of the experimental study of the kinetics of the heterogeneous radical decomposition of a peroxy-compound (a peroxyacid) is that the rate of the decomposition reaction on the surface of glass treated with a salt (second group) exceeds that in a reactor treated with boric acid (first group). This result agrees with the observed higher rate of oxidation of acetaldehyde and propionaldehyde in reactors treated with a salt, supporting the view that the branching stage is heterogeneous.

The establishment of the fact that the chain branching is heterogeneous has a number of consequences necessitating a detailed specification of the mechanism presented above by introducing certain possible surface processes involving the radicals formed. The following reactions may be included among them:

$$OH_{ads} + RCHO \rightarrow RCO_{ads} + H_2O, \quad (2)$$

$$RCO_{2\,ads} + RCHO \rightarrow RCO_2H + RCO_{ads}, \quad (3)$$

$$RCO_{ads} \rightarrow R_{ads} + CO, \quad (4)$$

$$RCO_{2\,ads} \rightarrow R_{ads} + CO_2. \quad (5)$$

Information concerning the possibility of the occurrence of reactions (4) and (5) has been published in a communication,[26] where it is shown that the yields of CO, CO_2, as well as C_2H_4 and $C_2H_5O_2H$ depend on the nature of the surface and increase with increase of S/V. The possibility of the occurrence of reaction (2) follows from the possibility of the reaction $OH_{ads} + CO \rightarrow CO_2 + H^{\cdot}$.[143] Depending on the experimental conditions (on the nature of the surface and the values of S/V), the ratio of the contributions of the heterogeneous and homogeneous stages can vary.

Modern ideas about the mechanism of the oxidation of acetaldehyde and propionaldehyde and, in particular, about the pathway leading to the formation of the products can be

formulated mainly in the form of the following sequence of elementary stages without claiming that it is complete:[21,26]

$$RCHO + O_2 \rightarrow R\dot{C}O + HO_2^{\cdot}, \quad (6)$$

$$R\dot{C}O + O_2 \rightarrow RCO_3^{\cdot}, \quad (7)$$

$$RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + R\dot{C}O, \quad (8)$$

$$RCO_3H \xrightarrow{\text{wall}} RCO_2^{\cdot} + \dot{O}H, \quad (9)$$

$$RCO_3H \rightarrow RCO_2^{\cdot} + OH, \quad (10)$$

$$RCO_2^{\cdot} + RCHO \rightarrow RCO_2H + R\dot{C}O, \quad (11)$$

$$\dot{O}H + RCHO \rightarrow H_2O + R\dot{C}O, \quad (12)$$

$$RCO_3^{\cdot} \xrightarrow{\text{wall}} \text{destruction}, \quad (13)$$

$$2RCO_2^{\cdot} \rightarrow \text{products}, \quad (14)$$

$$RCO_3^{\cdot} \rightarrow RO^{\cdot} + CO_2, \quad (15)$$

$$RO^{\cdot} + RCHO \rightarrow ROH + R\dot{C}O, \quad (16)$$

$$R\dot{C}O \rightarrow R^{\cdot} + CO, \quad (17)$$

$$RCO_2^{\cdot} \rightarrow R^{\cdot} + CO_2, \quad (18)$$

$$RO^{\cdot} + O_2 \leftrightarrow RCHO + HO_2^{\cdot}, \quad (19)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}, \quad (20)$$

$$RO_2^{\cdot} + RCHO \rightarrow RO_2H + R\dot{C}O, \quad (21)$$

$$R^{\cdot} + O_2 \rightarrow \text{olefin} + HO_2^{\cdot}, \quad (22)$$

$$RO_2^{\cdot} \rightarrow \text{olefin} + HO_2, \quad (23)$$

$$HO_2^{\cdot} + RCHO \rightarrow H_2O_2 + R\dot{C}O, \quad (24)$$

$$HO_2^{\cdot} + \dot{C}H_2O \rightarrow H_2O_2 + H\dot{C}O, \quad (25)$$

$$H_2O_2 + M \rightarrow 2\dot{O}H + M. \quad (26)$$

As already mentioned above, it is assumed that reactions (6), (9), (11), (12), (17), (18), (22), and (23) proceed both on the surface and in the gas phase.

The possibility of the homogeneous recombination of the $RCO_3^{\cdot}$ radicals is justified by experiments[66] in which acetyl peroxide was detected in the RCHO oxidation products and also by the tendency of the maximum concentration of the $RCO_3^{\cdot}$ radicals to reach a plateau with increase in the initial concentration of acetaldehyde.[18] The need to include reactions (24)–(26) arises from the direct detection of the $HO_2^{\cdot}$ radicals and hydrogen peroxide in the high-temperature oxidation of acetaldehyde and propionaldehyde.[26] Direct proof of the occurrence of the heterogeneous chain propagation stages can be provided by the study of the corresponding process at low pressures and temperatures under conditions ruling out homogeneous reactions.

Thus, whereas the mechanism of the oxidation of CH_2O can be regarded as in the main established, that of the oxidation of aliphatic aldehydes of the type RCHO requires further refinement in view of the observation that heterogeneous chain branching takes place.

IV. THE NEGATIVE TEMPERATURE COEFFICIENT OF THE MAXIMUM RATE OF REACTION

Studies devoted to the phenomenon of the negative temperature coefficient (NTC) of the maximum rate of reaction have been surveyed mainly in monographs.[2–4] The principal conclusion which follows from these investigations is that the phenomenon of the NTC is due to the thermal instability of a "critical" intermediate; however, the nature of this species is still controversial. The explanation proposed in a study,[149] where the competition of the reactions of radicals of the type $RO_2^{\cdot}$, $RO^{\cdot}$, $CH_3CO_3^{\cdot}$, and CH_3CO and of the interaction of the radicals $RO_2^{\cdot}$ and $CH_3CO_3^{\cdot}$ with acetaldehyde and the hydrocarbon respectively, leading to the formation of peroxy-compounds, in particular the peroxyacid responsible for the chain branching, merits special attention. With increase of temperature, the rate of formation of the peroxyacid diminishes, causing a fall in the overall rate of the reaction. Other workers adhere to a similar point of view.[150–151] The phenomenon of the NTC has been explained[152] by the competition between the chain propagation and isomerisation reactions of the radicals $RO_2^{\cdot}$ or $RCO_3^{\cdot}$.

The application of the EPR method to the study of the oxidation of propane made it possible to discover the chain propagating species for the reaction,[153,154] and to conclude that the phenomenon of the NTC is due to a change in the chain propagating species and the intermediates responsible for chain branching.[153] $RO_2^{\cdot}$ radicals and ROOH have been detected in the low-temperature range, while $HO_2^{\cdot}$ radicals and H_2O_2 have been found in the high-temperature range.

The phenomenon of the NTC in the aldehyde oxidation reactions has been investigated.[15,16] In the case of acetaldehyde the authors explained it by the contribution of the reverse reaction involving the decomposition of the $CH_3O_2^{\cdot}$ radicals; in the case of propionaldehyde the authors merely stated the fact of its existence. The kinetics of the oxidation of propionaldehyde at atmospheric pressure under flow conditions and at temperatures corresponding to the fall, the minimum, and the increase to a maximum reaction rate, namely 623, 683, and 803 K respectively, have been investigated comparatively recently by EPR.[155] In all cases the EPR spectra of peroxy-radicals were recorded. At 623 K considerable amounts of ethyl hydroperoxide and small amounts of peroxypropionic acid, formed from the peroxy-compounds, were found.

Analysis of the kinetics of the accumulation of C_2H_5OOH and peroxy-radicals enabled the authors[155] to conclude that the main contribution to the EPR spectrum comes from radicals of the type of $C_2H_5CO_3^{\cdot}$. The maximum concentration of the latter is attained (within the limits of experimental error) simultaneously with the attainment of the maximum rate of consumption of the aldehyde. This experimental finding served as proof that the chain propagating active centres in this temperature range are precisely the $RCO_3^{\cdot}$ radicals. The discovery of large amounts of CO and $C_2H_5.O_2H$ and the fact that the ratio $[CO]/[CO_2] > 1$ permitted the conclusion that the $R\dot{C}O$ decomposition stage makes a significant contribution. The decrease in the rate of consumption of the aldehyde at 683 K is accompanied by a decrease in the concentration of the peroxy-radicals and peroxy-compounds. A sharp increase of the concentration ratio $[CO]/[CO_2]$, which becomes ~10, is noteworthy. Such a sharp change in the ratio of the product concentrations has been explained[155] by the decrease of the rates of formation of the $C_2H_5CO_3^{\cdot}$ radical and organic peroxy-compounds as a consequence of the increase of the rate of decomposition of the $\dot{C}_2H_5CO$ radical, leading to a fall of the rate of the C_2H_5CHO oxidation reaction. At 803 K the $HO_2^{\cdot}$ radicals and

H_2O_2 were detected as intermediates, the maximum concentrations of the radicals and the rate of decomposition of propionaldehyde being attained almost simultaneously.

Analysis of the experimental data led the authors[155] to the conclusion that the chain propagating active centres in the region of the NTC consist predominantly of the $C_2H_5CO_3^{\cdot}$ radicals, whose concentration increases sharply with increase of temperature owing to their thermal instability and the thermal instability of the $C_2H_5\dot{C}O$ radicals. This causes an appreciable decrease of the concentration of the peroxy-compounds $C_2H_5CO_3H$ and C_2H_5OOH, which leads to a decrease in the rate of the process. On further increase of temperature, the rate of reaction again begins to rise, since the contribution by the degenerate chain branching process, responsible for the bimolecular decomposition reactions of hydrogen peroxide, begins to increase anew.

The results obtained permitted the conclusion that the phenomenon of the NTC in the oxidation of propionaldehyde is caused by the competition between the $C_2H_5\dot{C}O$ radical decomposition and oxidation reactions. As a consequence of this, the reaction mechanism changes, namely the nature of the chain propagating active centres and the peroxy-compounds responsible for the degenerate branching changes. In the region of the NTC these are the peroxy-radicals and organic peroxides, while at high temperatures the corresponding species are the $HO_2^{\cdot}$ radicals and hydrogen peroxide.

On the basis of the available information about the possibility of the heterogeneous decomposition of the $C_2H_5\dot{C}O$ radical,[26] one may expect an appreciable influence of the nature of the surface on the phenomenon of the NTC.[156] Depending on the change in the rate of decomposition of $C_2H_5\dot{C}O$, there is a possibility of narrowing or expanding the region of the negative temperature coefficient of the maximum rate of reaction.

In view of the fundamental similarity of the mechanisms of the oxidation of propionaldehyde and acetaldehyde, the above conclusions can be extended also to the oxidation of acetaldehyde in the region of the NTC of the maximum rate of reaction. The absence of the phenomenon of the NTC in the oxidation of CH_2O may be associated precisely with the fact that neither the $HCO_3^{\cdot}$ radicals nor HCO_3H are formed and the oxidation proceeds with formation of the $HO_2^{\cdot}$ radicals and hydrogen peroxide, albeit an appreciably lower rate, which however increases continuously with temperature, as a consequence of which the causes of the change in mechanism do not apply.

The ideas developed and the experimental data described above can help also in the understanding of the NTC phenomenon in the oxidation of hydrocarbons, in the course of which aldehydes and the corresponding peroxyacids are produced. The possibility of the formation of the latter at comparatively high temperatures (from 598 to 723 K) follows from experiments[19] carried out under flow conditions at atmospheric pressure and for short residence times of the reaction mixture in the reactor, i.e. under conditions which make it possible to remove relatively unstable products fairly rapidly from the reaction zone and to accumulate them until they attain concentrations susceptible to measurement.

V. CONCLUSION

Analysis of the experimental data on the oxidation of aldehydes makes it possible to explain the greater ease of the oxidation of CH_3CHO and C_2H_5CHO compared with CH_2O. This is associated in the first place with the fundamental difference in the character of the branching stage from the standpoint of both the nature of the products responsible for the branching and the site at which this reaction is localised (surface or space).

In the CH_3CHO and C_2H_5CHO oxidation reactions chain branching is caused by the heterogeneous radical decomposition of the corresponding peroxyacid, while in the CH_2O oxidation reaction it is due to the homogeneous bimolecular decomposition of hydrogen peroxide. As regards the behaviour of these two peroxy-compounds under corresponding conditions, it is known that peroxyacids decompose at a much higher rate and with a lower activation energy[134] than hydrogen peroxide.[157] The possibility of the heterogeneous radical decomposition of hydrogen peroxide has been demonstrated.[158-161] However, in the oxidation of formaldehyde at atmospheric pressure the rate of the heterogeneous radical decomposition of hydrogen peroxide is lower than the rate of its homogeneous bimolecular decomposition.

One cause of the low rates of oxidation of formaldehyde is the fact that the reaction chains are short,[2] in contrast to CH_3CHO and C_2H_5CHO, and that the chain propagating species in the reaction is the $HO_2^{\cdot}$ radical, whose interaction with the aldehyde proceeds with an activation energy of 46 kJ mol^{-1},[87] which is appreciably higher than the activation energies for the interaction of the $RCO_3^{\cdot}$ radicals with $CH_3.\dot{C}HO$ and C_2H_5CHO, amounting to 33.4 and 32.2 kJ mol^{-1} respectively.[67]

The formation of the peroxyacid in the oxidation of acetaldehyde and propionaldehyde and its absence in the oxidation of formaldehyde are caused by the different reactivities of the $H\dot{C}O$ and $R\dot{C}O$ radicals towards oxygen. The former reaction leads mainly to the formation of the $HO_2^{\cdot}$ radicals and the latter to the formation of the $RCO_3^{\cdot}$ radicals. Ultimately this is the reason why the formaldehyde oxidation reaction is somewhat isolated in the series of aliphatic aldehydes.

The experimental evidence for heterogeneous chain branching is important not only for the determination of the mechanism of the thermal oxidation of acetaldehyde and propionaldehyde but also for the further development of the theory of degenerate branched chain reactions, indicating the existence of a similar heterogeneous stage in many reactions exhibiting an "anomalous" sensitivity to the nature and state of the surface of the reaction vessel.

The survey of the experimental data permits the conclusion that the heterogeneous branching of homogeneous chains in the oxidation reactions of organic compounds proceeds more effectively at low temperatures and in the presence of long chains. From this standpoint, it is desirable to revise the existing schemes for the gas-phase oxidation of organic substances and to introduce, as far as possible, corrections to their mechanism, since in practice a corresponding reaction was not taken into account in constructing the mechanism, although the influence of the surface on these processes has not been denied in the literature.

The detection of peroxy-compounds in the high-temperature oxidation of aldehydes also indicates their involvement in chain branching in the oxidation reactions of hydrocarbons.

The results of studies[10,11,18-21,26] have led to a series of important practical conclusions, providing explanations of certain fundamental phenomena, which had been incomprehensible until recently. The observed[108] acceleration of the acetaldehyde oxidation reaction in reactors treated with KCl, as well as the influence of S/V and of the specific concentration of the KCl (deposited on the surface) on the rate and direction of the CH_3CHO oxidation reaction, the spontaneous inflammation of $CH_3CHO + O_2$ mixtures which have partly reacted at a lower temperature after their "quenching", and the spontaneous inflammation of artificial mixtures with added

peroxy-acetic acid[5] are explained by the degenerate chain branching. The observed pressure pulsations in the reactor treated with KCl at a lower temperature in the cold-flame oxidation of acetaldehyde are also caused by the radical decomposition of peroxyacetic acid, specifically by the increase of its rate on a given surface.

Thus the results of the study of the gas-phase oxidation of aldehydes obtained in recent years have significantly altered the existing ideas about the mechanisms of these processes. This has promoted the development of theoretical bases for technological processes for the preparation of valuable oxygen-containing compounds by treating the surface of the reactor or by altering the S/V ratio. In particular, ways have been found for increasing the selectivity in the oxidation of propionaldehyde to propionic[162] and peroxypropionic[12] acids and of acetaldehyde to peroxyacetic acid.[163]

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