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Liquid-phase Oxidation of Aldehydes

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Published information on the kinetics and the mechanism of the low-temperature liquid-phase oxidation of various classes of aldehydes-aliphatic, aromatic, unsaturated—is surveyed, and the mechanism of the elementary stages under various conditions —with thermal and photochemical initiation, in the presence of catalysts, in various solvents—is discussed. The mechanism of the concerted oxidation of aldehydes with other organic compounds is also reviewed. Numerical data on these reactions are given in tables. Applications of the oxidation of aldehydes in chemical technology are described. A list of 134 references is included.

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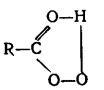
I. INTRODUCTION

The liquid-phase oxidation of organic compounds, the scientific principles of which were developed by Emanuel[1], is used in many processes of modern chemical technology, in particular in the manufacture of acetic acid and acetic anhydride from acetaldehyde. The oxidation of aldehydes to peroxy-acids, as well as the concerted oxidation of aldehydes and alkenes, shows great practical promise[2]. The oxidation of aldehydes is also of considerable theoretical interest, since they serve as convenient model subjects for study of the kinetics and the mechanism of slow chain reactions with degenerate branching.

The first kinetic studies of the gas-phase oxidation of aldehydes[3,4] belong to the early period when Semenov was establishing the theory of chain reactions[5]. The first and later publications[6,7] give data on the rate of change of pressure and the accumulation of oxidation products of acetaldehyde in the region of slow oxidation and under conditions of cold and hot ignition; the reaction mechanism is also discussed.

Systematic investigations of the kinetics and the mechanism of the gas-phase oxidation of acetaldehyde made by Emanuel' and his coworkers[8-13] were summarised in a review[14]. Oxidation at 125-185°C was found to involve two consecutive chain reactions—(i) oxidation of acetaldehyde with its quantitative conversion into an intermediate hydroperoxide and (ii) interaction of acetyl hydroperoxide with acetaldehyde to form the final products—acetic acid, carbon dioxide and monoxide, ethylene, and water. The surface state of the reaction vessel had a considerable influence on both stages of the process. A discovery of great interest for the modern theory of chain reactions was the existence[9-15] of acyl hydroperoxides (peroxy-acids) in two states with a reversible transition between them as the temperature was varied; the heat of transition was 8 kcal mole^{-1}. On rapid cooling ("quenching") of the reacting gaseous mixture of aldehyde and oxygen, the peroxy-acid present passes into a state of enhanced reactivity, apparent in a fall in the ignition temperature when the mixture is reheated after quenching.

The change in the reactivity of peroxy-acids is due to the formation of an intramolecular hydrogen bond with transfer of the acidic proton from one oxygen atom to another.



followed by rearrangement of the valency bonds in the molecule[14,15].

The direct recording of acylperoxy-radicals AlkCOOO· by electron spin resonance has yielded fresh information on the kinetics and the mechanism of the gas-phase oxidation of acetaldehyde at 230-350°C. Peracetic acid is formed by the interaction of acetylperoxy-radicals at $CH_3COOO\cdot$ with acetaldehyde, is the chief intermediate responsible for degenerate chain branching in the oxidation of acetaldehyde, and decomposes mainly heterogeneously on the surface of the reaction vessel.

The oxidation by molecular oxygen of aldehydes in the liquid phase takes place under far milder conditions than in the gas phase. An increasingly large number of papers have appeared on the kinetics of these reactions. There are a few reviews[17-19], but they were published about twenty years ago, and furthermore pay insufficient attention to the elementary mechanism of the process. The present Review covers work on the kinetics and the mechanism of the liquid-phase oxidation of aldehydes by molecular oxygen† completed mainly during recent years. The numerical data obtained in these investigations—bond lengths, equilibrium constants, rate constants and activation energies of individual stages—are given in Tables 1 and 2.

The first experimental confirmation of the radical-chain mechanism of the oxidation of aldehydes was the abnormally high quantum yield (up to 15 000) obtained in the photochemical oxidation of heptanal and benzaldehyde[20].

† Henceforward the term "oxidation" will be used to imply liquid-phase oxidation by molecular oxygen.

Chain oxidation of aldehydes is effected both thermally and in the presence of various initiators and catalysts. The bonding energy $E_{C(O)-H}$ is relatively small (77–79 kcal mole^{-1}) in aldehydes[21], so that thermal initiation of oxidation is always very significant. In view of the ready oxidisability of aldehydes the value ~80 kcal mole^{-1} seems more justified than 87 kcal mole^{-1} [22,23] (furthermore, it should be the same for different types of aldehydes—acetaldehyde, benzaldehyde, and acrylaldehyde). Values of 74 and 88 kcal mole^{-1} have been published[24] for benzaldehyde and acetaldehyde respectively. It is beyond the scope of the present Review to discuss the accuracy of the values obtained for $E_{C(O)-H}$. If the chain-propagation rate constant k_2 is taken to be a measure of this bonding energy, however, such a large difference between the values for benzaldehyde and acetaldehyde is unjustified. Furthermore, this bonding energy should be smaller in acrylaldehyde than in acetaldehyde[25], which is also inconsistent with the above results[22,23].

Table 1. Length of chain in the oxidation of aldehydes.

Aldehyde	Initiation	Chain length	Temp., °C	Ref.
Benzaldehyde	$h\nu$	15 000	5	20
Heptanal	$h\nu$	4 000	5	17
Acetaldehyde	$h\nu$	10 000	5	1
Benzaldehyde	O_3	50 000	5	1
Butyraldehyde	O_3	200 000	5	1
Decanal	azoisobutyronitrile	8 450	25	1
Benzaldehyde	azoisobutyronitrile	1 050	25	1
Methacrylaldehyde	thermal oxidation	590	26	76
Benzaldehyde	»	450	45	76
Heptanal	»	500	25	38
Heptanal	»	198	43	30
Isobutyraldehyde	$h\nu$	150	10	35
Isobutyraldehyde	$h\nu$	1 200*	10	35
	thermal oxidation	250	20	29

* At low partial pressures of oxygen.

II. UNCATALYSED OXIDATION

The general scheme of the liquid-phase oxidation of organic compounds consists[1] of consecutive and parallel elementary stages of chain initiation, propagation, branching, and termination. We shall examine data on each of these stages for the liquid-phase oxidation of aldehydes.

Initiation of Chains

Chains may be initiated in liquid-phase oxidations by the reactions

$$\mathrm{RCHO} + \mathrm{O_2} \xrightarrow{k_0} \mathrm{HO_2^{\cdot}} + \mathrm{RCO^{\cdot}}; \quad (1)$$

$$\mathrm{RCHO} + \mathrm{RCHO} + \mathrm{O_2} \xrightarrow{k_{0'}} \mathrm{H_2O_2} + \mathrm{RCO^{\cdot}}; \quad (2)$$

$$\mathrm{RCHO} + \mathrm{RCHO} \xrightarrow{k_{0''}} 2\,\mathrm{RCO^{\cdot}} + \mathrm{H_2} \quad (3)$$

Table 2. Kinetic parameters of elementary stages in the oxidation of aldehydes (subscripts as in text).

Parameter	Aldehyde	Numerical value	Temp., °C	Solvent	Ref.
$k_{0''}$, M^{-2} s^{-1}	decanal	$1.6\cdot10^{8}\exp(-11\,600/RT)$	5—20	n-decane	28
	»	$2.5\cdot10^{-6}$ *	20	»	
	acetaldehyde	$2.7\cdot10^{8}\exp(-17\,200/RT)$	60—100	benzene	26
	»	$5.3\cdot10^{-8}$ *	20	»	
	benzaldehyde	$6.3\cdot10^{7}\exp(-16\,400/RT)$	30—50	acetic acid	32
	»	$4\cdot10^{-5}$ *	20	»	
	decanal	$8\cdot10^{4}\exp(-15\,600/RT)$	5—20	none	27
	»	$2\cdot10^{-7}$ *	20	»	
	isobutyraldehyde	$8.7\cdot10^{-8}$	20	chlorobenzene	29
$k_{0''}$, M s^{-1}	benzaldehyde	$2.1\cdot10^{-5}$	43	o-dichlorobenzene	30
	isobutyraldehyde	$6.3\cdot10^{8}\exp(-19\,500/RT)$	10—30	chlorobenzene	29
	»	10^{-7} *	43	»	
	methylacrylaldehyde	$2.9\cdot10^{4}\exp(-17\,300/RT)$	−17÷+30	none	41
	»	$2.9\cdot10^{-8}$ *	43	»	
	»	$3.8\cdot10^{2}\exp(-13\,600/RT)$	26—45	»	76
	»	$1.5\cdot10^{-7}$ *	43	»	
	ethylacrylaldehyde	$10^{4}\exp(-15\,700/RT)$	−17÷+30	»	41
	propylacrylaldehyde	$6.3\cdot10^{4}\exp(-17\,500/RT)$	−17÷+30	»	41
	isopropylacrylaldehyde	$2.7\cdot10^{3}\exp(-14\,600/RT)$	−17÷+30	»	
	crotonaldehyde	$1.75\cdot10^{4}\exp(-14\,900/RT)$	−14÷+20	»	31
	»	$7\cdot10^{-7}$ *	43	»	
	acrylaldehyde	$6.3\cdot10^{-2}$***	40	benzene	89
k_2, M^{-1} s^{-1}	benzaldehyde	$5\cdot10^{4}\exp(-1\,800/RT)$	5—20	n-decane	28
	»	$1.9\cdot10^{3}$ *	0	»	
	»	$1.2\cdot10^{4}$	0	chlorobenzene	39
	acetaldehyde	$1.6\cdot10^{3}$	0	»	
	heptanal	$3.9\cdot10^{3}$	0	»	
	octanal	$3.3\cdot10^{3}$	0	»	
	cyclohexanal	$1.4\cdot10^{3}$	0	»	
	trimethylacetaldehyde	$3.4\cdot10^{3}$	0	»	
	decanal	$1.4\cdot10^{6}\exp(-4\,200/RT)$	5—20	none	27
	»	$6.3\cdot10^{2}$ *	0	»	
	isobutyraldehyde	$3.5\cdot10^{5}\exp(-6\,000/RT)$	10—30	chlorobenzene	29
	»	5.5 *	0	»	
	methylacrylaldehyde	$9.3\cdot10^{3}\exp(-4\,300/RT)$	−17÷+30	none	41
	»	3.5 *	0	»	
	ethylacrylaldehyde	$4.6\cdot10^{4}\exp(-5\,000/RT)$	−17÷+30	»	
	propylacrylaldehyde	$2.7\cdot10^{3}\exp(-3\,500/RT)$	−17÷+30	»	
	isopropylacrylaldehyde	$7.3\cdot10^{3}\exp(-9\,300/RT)$	−17÷+30	»	
	methylacrylaldehyde	$4.1\cdot10^{3}\exp(-4\,600/RT)$	26—45	»	76

Parameter	Aldehyde	Numerical value	Temp., °C	Solvent	Ref.
E_2, kcal mole^{-1}	benzaldehyde	2.3	25—50	benzene	36
	»	1.0	42—85	*o*-dichlorobenzene	30
	»	6.8 **	20—35	acetic acid	38
	»	7.8 **	20—45	»	37
	heptanal	4.0	10—30	none	35
k_3, , s^{-1}	benzaldehyde	$6.3\cdot10^{12}\exp(-30\,000/RT)$	60—70	benzene	47
	acetaldehyde	$10^{14}\exp(-32\,000/RT)$	75—95	toluene	46
k_6, M^{-1} s^{-1}	benzaldehyde	$2.1\cdot10^6$	5	n-decane	28
	»	$7.5\cdot10^8$	0	chlorobenzene	39
	acetaldehyde	$2.6\cdot10^7$	0	»	
	heptanal	$2.65\cdot10^7$	0	»	
	octanal	$2.6\cdot10^7$	0	»	
	cyclohexanal	$4.8\cdot10^6$	0	»	
	trimethylacetaldehyde	$4.0\cdot10^6$	0	»	
	decanal	$7.5\cdot10^6$	5	n-decane	27
	»	$3.4\cdot10^6$	5	»	28
	methylacrylaldehyde	$2.4\cdot10^4\exp(-1\,900/RT)$	−17÷+30	none	41
	»	$7.5\cdot10^2$ *	0	»	
	»	$1.3\cdot10^5\exp(-900/RT)$	26—45	»	76
	»	$1.5\cdot10^4$ *	0	»	
	ethylacrylaldehyde	$8.8\cdot10^4\exp(-1\,000/RT)$	−17÷+30	»	41
	propylacrylaldehyde	$5.4\cdot10^5\exp(-1\,200/RT)$	−17÷+30	»	
	isopropylacrylaldehyde	$2.5\cdot10^6\exp(-2\,800/RT)$	−17÷+30	»	
	crotonaldehyde	$1.7\cdot10^5\exp(-1\,600/RT)$	−14÷+20	»	31
	»	10^4 *	0	»	
	isobutyraldehyde	$9.5\cdot10^7\exp(-4\,100/RT)$	10—30	chlorobenzene	29
	»	$5.5\cdot10^4$ *	0	»	
k_7, s^{-1}	acetaldehyde	$10^{10}\exp(-5\,000/RT)$	40—70	benzene	42
K_9, M	acetaldehyde	$3.4\cdot10^{-1}$ **	25	acetic acid	60
	»	$2.7\cdot10^{-1}$	25	»	58
	»	$2.6\cdot10^{-1}$ **	25	»	
	»	$1.6\cdot10^8\exp(-5\,500/RT)$	0—25	toluene	59
	»	$1.6\cdot10^{-1}$ *	25	»	59
	acrylaldehyde	1.3 **	30	none	55
k_{-9}, s^{-1}	acetaldehyde	$5\cdot10^5\exp(-12\,000/RT)$ **	5—25	acetic acid	94
$k_{9'}$, s^{-1}	acetaldehyde	$1.25\cdot10^{10}\exp(-19\,000/RT)$	−20÷0	ethyl acetate	61
	»	$1.6\cdot10^{-4}$ *	25	»	
	»	$6.7\cdot10^{-5}$	20	toluene	62
	»	$1.1\cdot10^{-4}$	25	acetaldehyde	49
$k_{9''}$, M^{-1} s^{-1}	benzaldehyde	$2.1\cdot10^3\exp(-10\,000/RT)$	42—85	*o*-dichlorobenzene	30
	»	$1.3\cdot10^{-4}$ *	30	»	
	»	$2.8\cdot10^{-4}$	29	acetic anhydride	66
	»	$10^5\exp(-11\,900/RT)$	30—45	acetic acid	37
	»	$2.5\cdot10^{-4}$ *	30	»	37
E_{-9}, kcal mole^{-1}	acetaldehyde	13.0	25	toluene	59
$E_{9'}$, kcal mole^{-1}	acetaldehyde	15.0			17
K_{15}, M^{-2}	benzaldehyde	$6.8\cdot10^{12}\exp(-13\,300/RT)$	20—45	acetic acid	37
k_{15}, s^{-1}	benzaldehyde	$2.3\cdot10^4\exp(-7\,500/RT)$	20—45	acetic acid	37

* Calculated from authors' data.
** Cobalt acetate as catalyst.
*** Copper and iron phthalocyanines as catalyst.

From published bonding energies in reactant and product molecules the negative heats of reactions (1)–(3) for aldehydes having $E_{C(O)-H} \simeq 80$ kcal mole^{-1} can be estimated as 35, 20, and 55 kcal mole^{-1} respectively. Thus the termolecular reaction (2) is energetically the most favourable. In experimental kinetic investigations, however, various workers have observed both bimolecular and termolecular initiation. Reaction (2) has been established in the oxidation of acetaldehyde[26], decanal[27,28], and benzaldehyde[34]; initiation by reaction (3) occurs in the oxidation of isobutyraldehyde[29], benzaldehyde[30], α-alkylacrylaldehydes, and crotonaldehyde[31]. The pre-exponential factor of reaction (2) for saturated aldehydes is 10^3–10^5 M^{-2} s^{-1}; that of reaction (3) for unsaturated aldehydes is 10^3–10^4 M^{-1} s^{-1}, with E = 15–17 kcal mole^{-1}. In the oxidation of isobutyraldehyde initiation occurs mainly by reaction (3), the pre-exponential factor is 6×10^8 M^{-1} s^{-1}, and E = 19.5 kcal mole^{-1} (calculated from the Reviewers' experimental results).

The rate constant of initiation in the oxidation of benzaldehyde exceeds those for aldehydes of other types by factors of 10^2.[30] Available experimental results do not enable any unambiguous relation to be established between the structure of an aldehyde and the mechanism of the initiation of oxidation chains.

Initiation of the oxidation of aldehydes may occur also by the reaction[33]

$$RCH_2CHO + O_2 \rightarrow R\dot{C}HCHO + HO_2^{\cdot} \qquad (4)$$

whose negative heat of reaction should be 25–30 kcal mole^{-1}. The radical $\cdot$CHR.CHO may give rise to formic acid, small quantities of which are present among the products of the oxidation of aldehydes containing two or more carbon atoms. It is formed as a result of decomposition of the hydroperoxide:

$$RCH(OOH)-CHO \rightarrow OH^{\cdot} + RCH(\dot{O})-CHO \rightarrow RCHO + HCO^{\cdot};$$
$$HCO^{\cdot} + OH^{\cdot} \rightarrow HCOOH.$$

Abstraction of hydrogen from a methylene or a methyl group in an aldehyde is promoted by the presence of a catalyst [34].

Chain Propagation

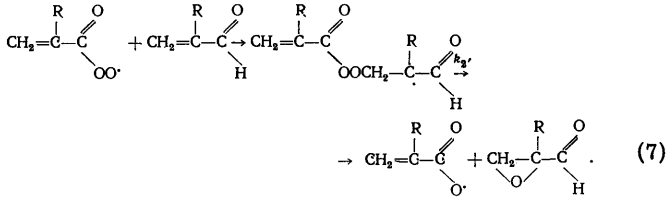
A chain is propagated by addition of an oxygen molecule to an acyl radical and abstraction of hydrogen from an aldehyde molecule by the acylperoxy-radical formed:

$$RCO^{\cdot} + O_2 \xrightarrow{k_1} RCOOO^{\cdot}; \quad (5)$$
$$RCOOO^{\cdot} + RCHO \xrightarrow{k_2} RCOOOH + RCO^{\cdot}. \quad (6)$$

Reaction (5) is exothermic ($\sim$ 20 kcal mole^{-1}) and is very rapid, with rates of 10^7–10^8 M^{-1} s^{-1} and almost zero activation energy ($E_1 = 2.0 \pm 1.5$ kcal mole^{-1} was given [35] for the oxidation of heptanal). Reaction (6), leading to the formation of peroxy-acids, is also exothermic, but less strongly so than reaction (5). The activation energy E_2 = 4–6 and 3–5 kcal mole^{-1} respectively for saturated aliphatic [27,29,35] and unsaturated [31] aldehydes, the corresponding pre-exponential factors being 10^5–10^6 and 10^3–10^4 M^{-1} s^{-1}, so that rates of chain propagation are higher in the oxidation of saturated aldehydes (by factors of 10–10^2). In the oxidation of benzaldehyde E_2 has the values 1–2 and 6–8 kcal mole^{-1} in the absence of a catalyst [28,30,36] and in the presence of cobalt acetate respectively [37,38]; the pre-exponential factor is 50 000 M^{-1} s^{-1}. [28] Values differing almost tenfold have been given [28,39] for the rate constant k_2 for benzaldehyde, the lower of which is fivefold the rate constant k_2 for decanal [27] and coincides with those obtained [39] for saturated aliphatic aldehydes. According to these measurements [39] k_2 for benzaldehyde is almost tenfold those for aliphatic aldehydes, e.g. acetaldehyde. Thus values of k_2 determined by different workers vary by almost a whole order of magnitude. The lower rate of chain propagation (and hence of the overall oxidation) with unsaturated aldehydes can be explained [25] by features of the intermediate complex formed in reaction (6) with compounds having conjugated double bonds. The hypothesis that reaction (6) involves the intermediate complex [$RO_2^- : \overset{+}{H}\,\overset{+}{R}'$] was put forward [40] for the oxidation of substituted aromatic ethers.

It can now be accepted that the rates of oxidation of unsaturated aldehydes are substantially lower than those of the corresponding saturated aldehydes [31]. This is probably due not only to different rates of chain propagation but also to the rate of initiation.

The mechanism of the oxidation of unsaturated aldehydes (α-alkylacrylaldehydes) involves not only reaction (6) but also another chain-propagating reaction, between an acylperoxy-radical and the double bond of the aldehyde [41]:



(7)

Occurrence of this reaction is supported by the presence of α-alkylepoxypropionaldehydes among the oxidation products from α-alkylacrylaldehydes.

Chain propagation in the oxidation of aldehydes may involve not only RCOOO$\cdot$ radicals but also acyloxy-radicals RCOO$\cdot$ formed by cleavage of peroxy-acids at the RCOO–OH bond:

$$RCOO^{\cdot} + RCHO \xrightarrow{k_2''} RCOOH + RCO^{\cdot}. \quad (8)$$

This reaction, leading to the formation of acids, competes with decomposition of the acyloxy-radicals [42,43], which occurs at 20–70°C with considerable rapidity. At sufficient aldehyde concentrations reaction (8) predominates. This is confirmed by experiments on the decomposition of acetyl peroxide in the presence of 3 M acetaldehyde in benzene solution at 70°C, in which the yield of acetic acid per mole of peroxide decomposed exceeded fourfold the yield of carbon dioxide [44]. The rate constant k_2'' was not estimated.

Branching of Chains

Degenerate branching of chains probably plays a less significant role in the liquid-phase oxidation of aldehydes than in the oxidation of hydrocarbons. This may be deduced from a comparison of the rate of thermal initiation by reaction (2) with the rate of radical decomposition of peroxy-acids

$$RCOOOH \xrightarrow{k_3} RCOO^{\cdot} + OH^{\cdot}. \quad (9)$$

The activation energy of reaction (9) for peracetic and perbenzoic acids is [45–47] 30–33 kcal mole^{-1} (which corresponds to the energy of the oxygen–oxygen bond in a peroxy-acid). The pre-exponental factor is 10^{13}–10^{14} s^{-1}, which is fully consistent with the unimolecular reaction (9): the factor would have been considerably smaller for induced decomposition of the peroxy-acids. The rate constant of reaction (9) at 70°C is $k_3 = 10^{13} = \exp(-30\,000/RT) = 10^{-6}$ s^{-1}. When the concentration of the peroxy-acid is 0.2 M, the rate of degenerate chain branching by reaction (9) is 2×10^{-7} M s^{-1}. Yet the rate of chain initiation by reaction (2) in the oxidation of acetaldehyde under these conditions is 1.05×10^{-6} M s^{-1} [48] (or 3.6×10^{-7} M s^{-1} [44]). Thus the rate of degenerate branching (9) is even somewhat smaller than the rate of initiation (2). A similar conclusion was reached [30] from a comparison of the rates of decomposition of perbenzoic acid and of thermal initiation of chains in the oxidation of benzaldehyde. Peroxy-acids can evidently decompose also by a bimolecular reaction

$$2RCOOOH \rightarrow RCOOO^{\cdot} + RCO^{\cdot} + H_2O$$

analogous to the reaction for hydroperoxides. The rate constant of this reaction for peroxy-acids has not been measured. In the oxidation of hydrocarbons $k_3 = 10^6$ M^{-1} s^{-1} at 40–60°C. [1]

A possibility in the low-temperature oxidation of aldehydes is that chain branching may occur by breakdown of an addition product of peroxy-acid and aldehyde (henceforward termed for brevity an "adduct") [49]. Addition of a small quantity of the adduct (1-hydroxyethyl peracetate) to a solution of acetaldehyde in acetic acid eliminated the induction period and accelerated considerably oxidation of the aldehyde at 18°C. Under the experimental conditions this peroxy-compound broke down mainly by a molecular mechanism, but a small fraction ($\sim$0.1%) of the peroxide decomposed into radicals. Unfortunately, the paper did not contain sufficient data for the rate of initiation to be

estimated, and only the actual fact of the initiating action of the adduct at low temperatures can be established. With rise in temperature the importance of this mode of degenerate chain branching will probably diminish because of a shift in the adduct equilibrium towards formation of the corresponding peroxy-acid and the aldehyde.

Termination of Chains

In the liquid-phase oxidation of aldehydes termination is effected by the recombination of radicals:

$$RCO\cdot + RCO\cdot \xrightarrow{k_4} \text{Molecular products} \quad (10)$$

$$RCO\cdot + RCOOO\cdot \xrightarrow{k_5} \text{Molecular products} \quad (11)$$

$$RCOOO\cdot + RCOOO\cdot \xrightarrow{k_6} \text{Molecular products} \quad (12)$$

The relative rates of these reactions are directly dependent on the concentration of dissolved oxygen: at low concentrations termination occurs predominantly by reaction (10); with excess of oxygen, because of the higher rate of reaction (5) than of (6), the system contains almost solely RCOOO· radicals, the only termination reaction is (12), and the rate of oxidation becomes independent of the oxygen concentration. The dependence of the rate of oxidation on the concentrations of the starting materials is given by the formula

$$W = W_\infty \left[1 + \frac{k_5}{k_6}\frac{k_2[RH]}{k_1[O_2]} + \frac{k_4}{k_6}\left(\frac{k_2[RH]}{k_1[O_2]}\right)^2\right]^{-1/2},$$

where

$$W_\infty = \frac{k_2}{k_6^{1/2}}[RH]W_i^{1/2},$$

in which W_i is the rate of initiation.

Experimental results for the dependence of the rate of oxidation of acetaldehyde in benzene solution on the concentration of dissolved oxygen[50] are well reproduced by this formula. The rate becomes independent of the oxygen concentration when the latter reaches 0.2 M.[50]

A similar dependence of reaction velocity on partial oxygen pressure was obtained[35] for the oxidation of benzaldehyde. At low oxygen concentrations, when $[C_6H_5CHO]/p_{O_2} \geq 0.01$ M mm^{-1}, the rate of reaction is linearly dependent on the partial pressure, but with ratios ≤ 0.002 M mm^{-1} (which corresponds to 0.1 M oxygen) it is independent of the oxygen pressure. The intermediate range of $[C_6H_5CHO]/p_{O_2}$ ratios is characterised by a fractional kinetic order with respect to molecular oxygen. It is interesting that the limiting oxygen concentration (0.1–0.2 M) at which the rate of oxidation of the aldehyde ceases to depend on the oxygen pressure far exceeds the values usual for the oxidation of hydrocarbons (e.g. $\sim 10^{-5}$ M for ethyl linoleate[51] and tetrahydronaphthalene[1]). An explanation offered[50] for this was that the rate constant of reaction (10), in competition with reaction (5), is greater for acyl radicals RCO· than for alkyl radicals R·.

In practice the oxidation of aldehydes is almost always conducted under conditions such that chain termination occurs solely by reaction (12). It was usually considered that no activation energy was involved, but values $E_6 =$ 1–3 and 4 kcal mole^{-1} were obtained in the oxidation of unsaturated aldehydes[31] and of isobutyraldehyde[29] respectively. The pre-exponential factors of reaction (12) are 10^4–10^5, 10^6–10^7, and 10^8 M^{-1} s^{-1} for unsaturated aldehydes, saturated aliphatic aldehydes, and benzaldehyde. The difference in these factors for different groups of aldehydes remains difficult to understand (especially the low values for unsaturated aldehydes[31]). The activation energy of chain termination also requires further experimental study. In the oxidation of unsaturated aliphatic aldehydes[41] termination may occur also by means of the radical $CH_2:C\dot{R}.CO.O.O.CH_2.CR(CHO)\cdot$, whose transformation leads to formation of the polyperoxide

$$CH_2{=}C(R){-}C(O){-}OO{-}CH_2{-}\overset{R}{\overset{|}{C}}(CHO){-}OO{-}CH_2{-}\overset{R}{\overset{|}{C}}(CHO){-}OO{-}\cdots$$

Only fragmentary data are available on the nature of the molecular products of chain termination in the oxidation of aldehydes. For example, butane-2,3-dione, formed by the recombination of acyl radicals, has been identified[52] among the oxidation products from acetaldehyde in benzene solution with low concentrations of oxygen at 70°C. The oxidation of benzaldehyde in acetic acid[53] yields benzoyl peroxide, perhaps because of chain termination by reaction (12). Acetic anhydride among the oxidation products of acetaldehyde was attributed[54] to chain termination by the reaction RCO· + RCOO·, but no experimental results were given in support.

Because of the great length of the chain, products of termination are formed in very small quantities, and cannot always be identified. Table 1 gives data on the length of the chain in the oxidation of aldehydes.

Mechanism of Formation of Molecular Products

Molecular products may be formed both from the radicals responsible for the chain process and from valency-saturated molecules. The RCOO· radicals formed at the stage of degenerate branching by decomposition of peroxy-acids readily undergo decarboxylation:

$$RCOO\cdot \xrightarrow{k_7} R\cdot + CO_2. \quad (13)$$

However, if an aldehyde is present in the system, competition by reaction (8) noted above results in formation of a far smaller quantity of carbon dioxide than from decomposition of the peroxy-acid in an inert solvent. Thus addition of acetaldehyde in the decomposition of acetyl peroxide in benzene solution at 70°C lowered the yield of carbon dioxide from 80 to only 25 mole % of the peroxide decomposed[44].

Carbon dioxide may be formed also from acylperoxy-radicals:

$$RCOOO\cdot \rightarrow RO\cdot + CO_2. \quad (14)$$

However, no experimental results have been published on this reaction. It has merely been postulated[55] among other hypothetical reactions possible in the oxidation of acrylaldehyde.

The formation of carbon dioxide in the oxidation of acetaldehyde by air was studied[56] in benzene solution under 50 atm at 60°C. Hardly any carbon dioxide was formed in a glass reaction vessel, which indicated that reaction (14) occurs predominantly by a heterogeneous mechanism. This is confirmed by the increased yield of carbon dioxide produced by increasing the ratio of surface to volume of the reaction vessel.

Carbon monoxide is probably formed by the decomposition of acyl radicals[57]:

$$RCO\cdot \xrightarrow{k_{8'}} CO + R\cdot \quad (15)$$

Acids are formed in the oxidation of aldehydes as a result of reaction between the aldehyde and the peroxy-acid:

$$RCOOOH + RCHO \overset{K_9}{\rightleftarrows} X, \quad (16)$$

$$X \xrightarrow{k_9'} 2\,RCOOH. \quad (17)$$

It was suggested[58] that this reaction involves the intermediate formation of a compound X (an "adduct") having the structure R.CH(OOH)–O.CO.R. A detailed study was made of the kinetics of the formation of acetic acid in the oxidation of acetaldehyde[28]. The experimental results were fully described by the kinetic scheme involving intermediate formation of the adduct. The equilibrium constant K_9 for acetaldehyde is 0.1–0.3 M at 25°C [55,58-60], and E_9 = 5.5 kcal mole^{-1}. [59] Values of the rate constant k_9' obtained by several workers [49,61,62] for decomposition of the adduct showed satisfactory agreement. Activation energies E_9' = 19 and 15 kcal mole^{-1} were obtained[61,17]. The many independent determinations and the good agreement among the results indicate that K_9 and k_9' may well be among the most reliably determined elementary constants in the oxidation of aldehydes.

There is considerable disagreement as to which classes of aldehydes form an adduct. This was regarded[55,58,63,64] as occurring only in the oxidation of aliphatic aldehydes, whereas aromatic aldehydes underwent direct oxidation

$$RCOOOH + RCHO \xrightarrow{k_9''} 2RCOOH. \quad (18)$$

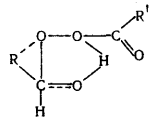
Infrared spectroscopy did not reveal formation of an adduct in the oxidation of benzaldehyde[65], but the opposite conclusion was reached from kinetic[66,67] and spectroscopic[68] data. Formation of an adduct was stated[25,69] to occur in the oxidation of acrylaldehyde, but the same authors gave a scheme[57] from which the adduct was absent. The present Reviewers consider that unambiguous evidence of the existence of an adduct would be its isolation in pure form from the reaction mixture at low temperatures. This method was adopted[70] in studying the oxidation of acetaldehyde and butyraldehyde. Isolation of an adduct had been achieved earlier[71] in the oxidation of another saturated aliphatic aldehyde, undecanal. The question of the formation of an adduct in the oxidation of aromatic and unsaturated aliphatic hydrocarbons cannot be regarded as settled.

In the early investigations by infrared spectroscopy[72] a hydroperoxide form of adduct was assumed to be present. Examination of the nuclear magnetic resonance spectra of products of the low-temperature oxidation of acetaldehyde led to the conclusion[70] that the adduct could have two possible structures

$$CH_3C(O)—OO—CH(OH)—CH_3;\quad CH_3—\underset{\diagdown\,O\,\diagup}{C}—O—CH(OH)—CH_3,$$

(*a*) (*b*)

of which (*a*) was the more probable. Almost all authors who postulated formation of an adduct during oxidation assumed a similar structure. Kinetic study of the decomposition of adducts from acetaldehyde and butyraldehyde established[70] that decomposition occurred mainly by a molecular mechanism via a cyclic intermediate complex of type



The presence of adducts is characteristic of the low-temperature of oxidation of acetaldehydes. The quantity of adduct in the mixture is considerably diminished by raising the temperature merely to 10–20°C, and the main oxidation product becomes acetic acid[73].

Carboxylic acids may be formed in the oxidation of aldehydes not only by breakdown of an adduct but also directly from peroxy-acids as a result of their molecular decomposition:

$$RCOOOH \rightarrow RCOOH + \tfrac{1}{2}O_2 \quad . \quad (19)$$

This reaction was postulated on the basis of results obtained by several workers [26,30,74,75] in kinetic studies of the decomposition of peroxy-acids. An almost 100% yield of carboxylic acid was obtained based on the peroxy-acid decomposed, and evolution of molecular oxygen was observed. The fact that inhibitors and initiators of radical reactions had no effect on the decomposition of peroxy-acids was further evidence of molecular decomposition. The activation energy of reaction (19), 16–24 kcal mole^{-1}, is less than for the radical decomposition of peroxy-acids. Decomposition of peracetic acid is a first-order reaction with respect both to this acid and to acetic acid[76].

III. PHOTOCHEMICAL OXIDATION—INITIATION OF CHAINS

In the photochemical oxidation of aldehydes the reaction mixture is usually exposed to ultraviolet radiation of wavelength 2500–4000 Å. On absorbing a quantum the aldehyde molecule passes into an excited singlet state S_1, from which a radiationless transition can occur to a metastable triplet state T_1.

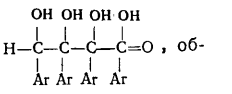
At sufficient aldehyde concentrations the excited molecules are deactivated by interaction with aldehyde molecules in the ground state, while free radicals are produced, and initiate the chain process. Since the lifetime of the T_1 state greatly exceeds that of S_1, radicals are most probably formed by autodeactivation of the T_1 state. In the gas phase, e.g. with benzaldehyde, the lifetimes of S_1 and T_1 states are 1.6 μs and 2 ms respectively[77]. In the photochemical oxidation of benzaldehyde the initiation of chains was regarded[78] as resulting mainly from reaction between an aldehyde molecule in the triplet state and an unexcited molecule:

$$C_6H_5CHO + h\nu \rightarrow C_6H_5\dot{C}H—\dot{O};$$
$$C_6H_5\dot{C}H—\dot{O} + C_6H_5CHO \rightarrow C_6H_5\dot{C}O + C_6H_5\dot{C}HOH.$$

This quite widely held view on the mechanism of chain initiation in the photochemical oxidation of aldehydes [79,80] is contradicted by results obtained at low partial pressures of oxygen (54–450 mm) in an investigation[81] of the oxidation of decanal in decane solution with λ = 3130 Å at 10°C. It was concluded[81] that at low oxygen pressures radicals are initiated mainly by reaction between an oxygen molecule in an S_1 state and an unexcited aldehyde molecule. At higher pressures both S_1 and T_1 are involved in radical formation.

It has been recommended that special additives which readily produce free radicals under the influence of light, e.g. butane-2,3-dione, be introduced in the oxidation of heptanal[35], in order to improve the efficiency of photochemical initiation. On absorption of a quantum (λ = 4358 Å) the dione passes into an excited singlet state, which is converted almost quantitatively into a triplet state. The latter is deactivated mainly by reaction with molecular oxygen, and free radicals are formed. With this method of initiation the rate of generation of chains is constant during oxidation.

Photochemical initiation is an efficient method of intensifying oxidation which finds practical application for obtaining oxidation products of aldehydes. In photochemical oxidation the above reactions of chain termination (10)–(12) are probably accompanied by destruction of radicals on the molecules of certain oxidation products. This may explain in particular why the oxidation of aldehydes gradually slows down with time. Thus it was suggested[82] that the compound



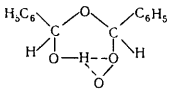
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formed in the liquid-phase photolysis of benzaldehyde, may act as an inhibitor. Preliminary photolysis of heptanal in an oxygen-free medium lowers the rate of a subsequent oxidation[17]. The oxidation of benzaldehyde slows down at a time when considerable quantities of aldehyde are still present in the mixture[30]. Some quantities (1–2%) of salicylaldehyde and phenol, which are inhibitors, have been shown to be present.

A study of the photochemical oxidation of benzaldehyde in the presence of quinol as inhibitor established that the absorption of one quantum by an aldehyde molecule initiates only one reaction chain[78]. Since the act of initiation produces two radicals, $C_6H_5CO\cdot$ and $C_6H_5CH(OH)\cdot$, this result was explained by the destruction of one of the radicals according to the scheme

$$C_6H_5\dot{C}HOH + C_6H_5CHO \rightarrow C_6H_5CH(OH)-O-\dot{C}H-C_6H_5 \xrightarrow{+O_2}$$
$$\rightarrow C_6H_5CH(OH)-O-CH(O\dot{O})-C_6H_5 .$$

It is assumed that the rate of this reaction in pure benzaldehyde will be comparable with the rate of the reaction between $C_6H_5CH(OH)\cdot$ and molecular oxygen. The resulting radical tends to form intramolecular hydrogen bonds



which is responsible for its characteristic reactivity.

The phenomenon of autoinhibition noted in papers on photochemical oxidation has been observed also in the thermal oxidation of benzaldehyde. This can be attributed both to the inhibiting effect of certain oxidation products and to possible deactivation of the catalyst in the later stages of catalytic oxidation[83]. Thus phenol has been detected in the thermal oxidation of benzaldehyde[66], and is formed as secondary product of the reaction between benzaldehyde and perbenzoic acid[63], its quantity being greater the more strongly electron-donating is the *para*-substituent in a substituted benzaldehyde.

IV. CATALYSED OXIDATION

Catalysts, mainly compounds of metals of variable valency, are widely employed to increase the rate and the selectivity of the oxidation of aldehydes. Published information relates mainly to homogeneous catalysts, but considerable interest has recently been taken in the use of heterogeneous catalysts. Introduction of a catalyst leads to a significant change in the mechanism of the process.

Initiation of Chains

Initiation may result from interaction of the catalyst with a molecule of a peroxy-acid or an aldehyde, which can be represented schematically

$$M^{n+} + RCOOOH \xrightarrow{k_3'} M^{(n+1)+} + OH^- + RCOO\cdot; \quad (20)$$

$$M^{(n+1)+} + RCHO \xrightarrow{k_3''} M^{n+} + H^+ + RCO\cdot; \quad (21)$$

$$M^{(n+1)+} + RCOOOH \xrightarrow{k_3'''} M^{n+} + H^+ + RCOOO\cdot. \quad (22)$$

Reaction (20), involving oxidation of the catalyst ion, is usually far more rapid than (21) and (22). Its rate depends on the nature of the metal ion[38,84], but for the most commonly used homogeneous catalysts—cobalt, copper, and manganese salts—its rapidity leads to the presence of the catalyst ions almost entirely in the state of higher valency during the reaction. The oxidised form of the ion may generate free radicals as a result of reaction with the initial aldehyde or with the peroxy-acid. The rates of these reactions were measured[38], and the rate of (21) for benzaldehyde was determined by independent measurements in a mixture of acetic and sulphuric acids. The rate constant obtained agreed satisfactorily with that of chain initiation determined from the consumption of inhibitor during the oxidation of benzaldehyde.

From this it was concluded that reaction (21) was responsible for chain initiation in the oxidation of benzaldehyde in the presence of a catalyst. This view was fairly widespread in the literature until quite recently, but it can hardly be accepted as soundly based. Firstly, the consumption of inhibitor can be related only to the total rate of interaction with radicals, whereas free radicals are formed primarily by the uncatalysed reaction (2) or (3). After a certain quantity of peroxy-acid has accumulated, radicals are formed by reactions (21) and (22). Considerable inaccuracy is due also to the fact that the measured[38] rate of reaction (21) is far too high, because the rate constant obtained in sulphuric-acid medium exceeds significantly its value in an inert solvent[37]. Moreover, the same work[38] gave $k_3'' = 0.05\ M\ s^{-1}$, and the rate constant of reaction (22) as $0.8\ M\ s^{-1}$, which contradicts the authors' statement that reaction (21) predominated in the initiation of chains. Measurements of the rates of reactions (21) and (22) in acetic-acid medium during the oxidation of benzaldehyde gave values of 8×10^{-11} and $7 \times 10^{-7}\ M\ s^{-1}$ at 30°C.[37] The rate of the uncatalysed initiation (2), determined under the same conditions for comparison, was $1.3 \times 10^{-8}\ M\ s^{-1}$. A similar ratio of rates of (21) and (22) has been observed[85] in the oxidation of *p*-tolualdehyde.

Thus the main reaction responsible for the formation of free radicals in the catalytic oxidation of aldehydes is interaction of an oxidised form of a metal ion with a hydroperoxide. This reaction probably cannot be regarded as the elementary stage described by Eqn. (22). It must be remembered in particular that, in the presence of a catalyst, decomposition of the peroxy-acid induced by free radicals is possible. Such induced decomposition has been observed e.g. in the presence of cobalt and iron salts[86].

As shown for the oxidation of hydrocarbons[87], it is assumed that free radicals are generated in the oxidation of aldehydes through formation of an intermediate complex between the catalyst and an aldehyde or a peroxy-acid molecule. Kinetic evidence of the formation of complexes

with the catalyst has been obtained for perbenzoic acid[83], benzaldehyde[37], peroxypropionic acid[75], and peroxyacrylic acid[57]. It was shown[57] by spectroscopic methods that, when complex compounds are used to catalyse the oxidation of acrylaldehyde, an aldehyde molecule takes the place of one of the ligands, being coordinated through its carbonyl group with the central atom of the catalyst. The same views on the entry of an aldehyde molecule in hydrated form into the coordination sphere of the Co^{3+} ion have appeared[88] in a study of the oxidation of pyridinecarbaldehyde in aqueous medium. An oxygen molecule may enter the intermediate catalytic complex[89,90]. On the whole, however, the question of the existence and the role of catalytic complexes in chain initiation has been developed in considerably less detail than for the oxidation of hydrocarbons, where the decisive role of such complexes in the breakdown of hydroperoxides has been proved unambiguously by both kinetic and physical methods[91,92].

In the presence of a catalyst chains can be initiated not only by reactions (20)–(22) but also by detachment of hydrogen from the alkyl group[34,93]:

$$RCH_2CHO + Mn^{3+} \rightarrow R\dot{C}HCHO + Mn^{2+} + H^+. \quad (23)$$

Acyl radicals are then formed by a secondary reaction:

$$R\dot{C}HCHO + RCH_2CHO \rightarrow RCH_2CHO + RCH_2CO\cdot \quad (24)$$

This mechanism of initiation was supported by the isotope effect $k_H/k_D = 5.5–6.0$ obtained for α-deuterated acetaldehydes, whereas no isotope effect was present when the carbonyl hydrogen was replaced by deuterium. Additional evidence for reaction (23) is the detection in the mixture, on addition of an alkene, of products formed by addition of $\cdot CHR.CHO$ radicals to the double bond of the alkene[93].

In the homogeneous catalysis of the oxidation of aldehydes, as in the uncatalysed ocidation, chain-initiating reactions may involve either the free peroxy-acid or its addition product with the aldehyde (an "adduct"). The relative concentrations of adduct and free-peroxy acid, and hence their contributions to the generation of free radicals, depend mainly on the temperature and the aldehyde concentration. Cobalt salts accelerate decomposition of the adduct at temperatures above 10°C. A molecular reaction has been postulated[94] leading to oxidation of the cobalt by interaction between the catalyst and the adduct:

$$CH_3C(O)OOCH(OH)CH_3 + 2Co(OOCCH_3)_2 + CH_3COOH \rightarrow 2Co(OOCCH_3)_3 + CH_3CHO + H_2O.$$

Another postulate[95,96] is radical decomposition of the adduct:

$$Co^{2+} + CH_3CH(OH)—OO—C(O)CH_3 \rightarrow Co^{3+} + CH_3\dot{C}H(O)OH + CH_3COO^- .$$

These reactions become more important at high aldehyde concentrations, when the equilibrium between the peroxy-acid and the adduct is displaced towards formation of the latter. With decrease in the aldehyde concentration reaction (20) becomes the main process converting the metal ion to a higher valency state. The oxidised form of the metal is obviously able to interact not only with the peroxy-acid but also with the adduct to form free radicals.

Decomposition of Peroxy-acids

In the presence of a catalyst a peroxy-acid may undergo decomposition not only by reactions (20) and (22) but also by homolysis of the oxygen–oxygen bond, as has been proved[57,97,98] by the formation of carbon dioxide (resulting from decarboxylation of $RCOO\cdot$ radicals—products of the cleavage of peroxyacrylic and peroxytoluic acids at the peroxy-bond).

In the presence of catalysts peroxy-acids undergo not only radical but also molecular decomposition with formation of the corresponding carboxylic acids. Molecular breakdown has been established for peroxyacrylic[57], peroxypropionic[57], and peroxybutyric[90] acids. It is significant that this process is observed mainly when carboxylic acids are used as solvents. In the presence of a heterogeneous catalyst—silver oxide—decomposition of peracetic acid in the presence of acetic acid takes place by a molecular mechanism at temperatures of 20–40°C.[26] When the temperature is raised to 70°C, a small proportion of the peroxy-acid breaks down into radicals at the oxygen–oxygen bond. The rate of decomposition of the peroxy-acid diminishes with increase in the concentration of silver oxide.

Chain Propagation

In both catalysed and uncatalysed oxidation the chain-propagating reaction leads to formation of a peroxy-acid as primary molecular product. Involvement of the catalyst in propagation has been shown in the oxidation of hydrocarbons[99], but direct experimental evidence has not been obtained for aldehydes. However, the tenfold increase in the ratio $k_2/k_6^{\frac{1}{2}}$ obtained for the oxidation of benzaldehyde in the presence of a manganese salt relative to the uncatalysed process[100] suggests that the catalyst does affect the chain-propagating reaction. The heterogeneous catalyst Ag_2O may take part in propagation in the oxidation of aldehydes in the presence of unsaturated compounds[26].

Little information has been published on the effect of catalysts on the formation of molecular oxidation products. An acyl radical $RCO\cdot$ may form a complex with the catalyst[57], and thus react more readily with oxygen than it decomposes into $R\cdot + CO$. As a consequence, use of a catalyst leads to a decrease in the quantity of carbon monoxide among the reaction products. A decrease in the yield of carbon dioxide in the oxidation of acetaldehyde has been observed in the presence of silver oxide[101]. The probable reason is that radicals attached to a heterogeneous catalyst are unlikely to break down with the formation of carbon dioxide.

The equilibrium constant of adduct formation K_9 is unaffected by the catalyst[58,60]. No data have appeared on the effect of the catalyst on decomposition of the adduct into carboxylic acids ($k_{9'}$). However, it is known that ions of metals of variable valency may take part in the decomposition of carboxylic acids. Thus Mn^{3+}, Co^{3+}, and Ce^{4+} ions react at 50–100°C with carboxylic acids[102–105]:

$$RCOOH + M^{(n+1)+} \rightarrow M^{n+} + \dot{R} + CO_2 + H^+ . \quad (25)$$

Another possible reaction is[106–108]

$$CH_3COOH + M^{(n+1)+} \rightarrow M^{n+} + \dot{C}H_2COOH + H^+. \quad (26)$$

Intermediate formation of an adduct and its decomposition

$$Co^{3+} + 2C_6H_5COOH \overset{K_{11}}{\rightleftharpoons} [Co^{3+} \cdots 2C_6H_5COOOH] \overset{k_{11}}{\rightarrow} Co^{2+} + C_6H_5COO\cdot + C_6H_5COOH + H^+ \quad (27)$$

have been discussed[37]. A peculiar feature of the action of salts of metals of variable valency in oxidising processes is the dual function of the catalyst—accelerating at low concentrations of the metal salt in the reaction mixture, and inhibiting at high concentrations.

Chain Termination

Since it was first shown that the catalyst may be involved in the termination of chains [109,110], there are indications that this occurs also in the oxidation of aldehydes. Thus the oxidation of benzaldehyde [84] in the presence of a sufficiently high concentration ($\sim 10^{-3}$ M) of cobalt(II) acetate as catalyst has an induction period directly proportional to the catalyst concentration and inversely proportional to the initial aldehyde concentration. Completion of the induction period coincides with complete conversion of cobalt(II) into cobalt(III). This was explained by the presence of an unpaired electron in cobalt(II) compounds, which (at high concentrations) play a considerable part in the destruction of radicals, whereas cobalt(III) contains no unpaired electrons and does not interact with free radicals.

Chains may be terminated by interaction of the benzoylperoxy-radical $C_6H_5COOO\cdot$ with cobalt(II) acetate or its dimer. However, data given [84] on the inhibiting action of ions of other metals are fairly contradictory and require further refinement. It was stated [84] in particular that copper(II) even in high concentrations does not bring about an induction period in the oxidation of benzaldehyde. Yet copper(II) at concentrations of ~0.05 M strongly inhibits the oxidation of hydrocarbons [110].

Experimental results on the oxidation of *p*-tolualdehyde in the presence of cobalt salts [85] are reported on the hypothesis that chain termination takes place on acyl radicals $RCO\cdot$. Similarly [54] chain termination by reaction (10) with the formation of butane-2,3-dione has been established in the oxidation of acetaldehyde catalysed by cobalt acetate. The formation of considerable quantities of this dione (up to 10% on the acetic acid formed) may indicate that the catalyst accelerates recombination of acyl radicals, making it competitive with the chain-propagating reaction (5). Nevertheless, reaction (10) does not strictly involve termination, since the butanedione formed can itself undergo further oxidation by a radical-chain mechanism [112]. The ratio of the rate of accumulation of carbon dioxide to that of acetic acid in the oxidation of butane-2,3-dione is respectively 0.3 and 0.5 in the presence and in the absence of a catalyst [54,112]. This indicates that the catalyst enhances the selectivity of oxidation of the dione to acetic acid.

V. EFFECT OF SOLVENT

Studies of the liquid-phase oxidation of aldehydes have hitherto not included a systematic investigation of the influence of the solvent on the elementary stages. Results obtained in individual researches are qualitative in character and relate mainly to the effect on the overall rate of oxidation.

Current views distinguish two types of solvation—non-specific and specific—of reactant species [113]. Non-specific solvation occurs in all solutions and is due to interaction of the solute with the field of the solvent molecules. One of the main forms of non-specific solvation is caused by electrostatic interaction of reactant species with the medium. The relation between the reaction rate constant k and the dielectric constant of the medium ϵ is expressed by Kirkwood's equation

$$\ln k = \ln k_0 - \frac{1}{kT}\frac{\varepsilon - 1}{2\varepsilon + 1}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\neq}^2}{r_{\neq}^3}\right),$$

in which μ is the dipole moment, r is the effective radius of the dipole, and the subscripts A, B, and ≠ denote respectively the starting materials and the activated complex. Plots of ln k against $(\epsilon - 1)/(2\epsilon + 1)$ based on published data for the oxidation of aldehydes [26,69,114,115] either are not linear at all or show many points lying outside a linear relation. They suggest that non-specific solvation is not the main factor governing the effect of the solvent on the oxidation of aldehydes.

Specific solvation is due to the formation of various types of complexes between the reactant species and the solvent, e.g. involving hydrogen bonding and π-complexes. The hydrogen bond between a solvent molecule and a peroxy-acid formed by oxidation of an aldehyde may probably either accelerate or retard decomposition of the acid. The selectivity of oxidation of the aldehyde to the peroxy-acid is correspondingly changed.

An increase in the yield of acrylic acid from the oxidation of acrylaldehyde has been observed when water [76], butyric acid, or valeric acid [69] is used as solvent. Water also increases the yield of carboxylic acids from the oxidation of C_2–C_5 saturated aldehydes [116,64]. In the oxidation of isobutyraldehyde water increases the yield of the acid only when present in quantities exceeding 10%; with about 4% of water the yield of the peroxy-acid is increased [64]. In contrast to the above results, acetic acid lowers the yield of peracetic acid obtained by the oxidation of acetaldehyde [26]. Increase in the yield of peroxy-acids in the presence of compounds capable of forming a hydrogen bond has been observed in the oxidation of butyraldehyde in the presence of chloroform and dichloroethane [115], and in the oxidation of acetaldehyde in water and in acetic acid [117].

When benzene, which is able to form π-complexes [118], is used as solvent, carboxylic acids are obtained as the main product of the uncatalysed oxidation of butyraldehyde [115] and benzaldehyde [65]. However, a benzene medium tends to increase the yield of perbenzoic acid from the catalytic oxidation of benzaldehyde [119] and of peracetic acid from that of acetaldehyde [26].

The dependence of the total rate of oxidation of aldehydes on the nature of the solvent can probably be attributed to the effect of the latter not only on the reactivity of the acylperoxy-radicals $RCOOO\cdot$ in chain propagation but also on chain initiation, as well as on the molecular reactions (16) and (17).

The lower rate of oxidation of acetaldehyde in a carboxylic acid than in acetone can be explained [114] by hydrogen bonding between the acylperoxy-radical and the solvent. The rate of oxidation of benzaldehyde is lower in benzene than in acetone [119], which may be due either to the lower dielectric constant of the solution or to diminished reactivity of peroxy-radicals as a result of "adhering" to the benzene. A similar situation is found [26] for the rate of oxidation of acetaldehyde in various solvents, decreasing in the sequence

$$\text{acetone} > \text{benzene} > \text{acetic acid}\ .$$

The rate of oxidation of acetaldehyde is much lower in cyclohexanone than in other solvents. The solvent effect in this case also may be due to deactivation of peroxy-radicals by hydrogen bonding, since the keto–enol tautomeric equilibrium is displaced considerably further towards the enol with cyclohexanone than with acetone [120]. However, it remains obscure why the decrease in reaction velocity is considerably more marked with cyclohexanone than with other solvents capable of forming hydrogen bonds. The maximum rate of oxidation of acrylaldehyde

was found[57] to decrease in the sequence of solvents

carboxylic acids ≥ aromatic hydrocarbons > aliphatic hydrocarbons > water

The retarding effect of water on the oxidation of aldehydes in the presence of homogeneous catalysts may be due[37] to its ability to form complex hydrates with the catalyst, thereby preventing the latter from taking part in the initiation of chains.

It is quite clear that solvents have a considerable effect on the oxidation of aldehydes, which comprises the aggregate of its effects on the individual stages in the composite process. In order to elucidate the elementrary mechanism of the solvent effect, therefore, separate investigations are required for every elementary stage.

In the oxidation of aromatic and unsaturated aldehydes the solvent may also have a specific influence depending on the structure of the oxidisable substrates. Thus in the later stages of the oxidation of benzaldehyde[66] the effect of the solvent is largely due to its ability to accelerate the formation of autoinhibitors of chain oxidation that may be formed in the oxidation of benzaldehyde, or on the other hand to prevent their formation. In the oxidation of acrylaldehyde[57] the solvent effect is largely governed by the influence on polymerisation of the initial aldehyde and of the resulting acid. Rates of radical polymerisation are considerably higher in non-polar than in polar media. The resulting polymer is able to deactivate the catalyst, with a consequent decrease in the rate of the process.

VI. USE OF THE OXIDATION OF ALDEHYDES TO OBTAIN CERTAIN OXYGEN-CONTAINING COMPOUNDS

The liquid-phase oxidation of aldehydes forms the basis for the preparation of various oxygen-containing compounds, including processes of industrial value, mainly the oxidation of acetaldehyde. Considerable interest has recently been taken in the liquid-phase oxidation of unsaturated aldehydes—predominantly acrylaldehyde and methacrylaldehyde—and also in the combined (concerted) oxidation of aldehydes and unsaturated compounds as a method for obtaining acids and alkene oxides at the same time.

Preparation of Acids

The liquid-phase oxidation of acetaldehyde is a most important method for the manufacture of acetic acid[121]. The process is usually conducted at about 60°C in the presence of manganese acetate, which is an efficient catalyst also for the preparation of acids by the oxidation of other aldehydes[122,123].

An important problem of chemical technology is to develop an effective method for the direct oxidation of methacrylaldehyde to methacrylic acid in the liquid phase. Large quantities of this acid are required for the production of polyesters, and the existing method of obtaining it from acetone[124] is unable to satisfy the rapidly growing demands of industry.

Several attempts have been made to obtain methacrylic acid from methacrylaldehyde in the presence of homogeneous catalysts, but the results show poor reproducibility and evidently cannot be regarded as reliable. This is indicated also by the fact that manufacture of the acid from the aldehyde has not yet been realised. Thus, when methacrylaldehyde was oxidised with oxygen in benzene medium at 40°C in the presence of copper and nickel acetates as catalysts[125], the selectivity of formation of methacrylic acid was 99% with 60% conversion of the aldehyde. The yield of the acid did not exceed 40%, and a large quantity of polymeric products was formed. However, these results could not be repeated by workers[126] who proposed to obtain methacrylic acid by oxidising the aldehyde in alkaline medium in the presence of silver oxide. Nevertheless, despite the great selectivity of formation of the acid, this process, requiring the use of alkaline solutions, can hardly find industrial application. Conducting the oxidation in the presence of such catalysts as cobalt and manganese acetates and acetylacetonates, as well as vanadium compounds, gave the best results[127] with cobalt acetate (the same catalyst as before[125]), when the yield of methacrylic acid reached 80%.

The above results show that, with the exception of the classic catalyst of liquid-phase oxidation—cobalt acetate—sufficiently effective specific catalysts for the oxidation of methacrylaldehyde are not yet available. A promising approach to the problem is thus to develop new catalytic systems based on heterogeneous catalysts, which possess high selectivity and, in contrast to homogeneous catalysts, do not result in contamination of the product with metal compounds.

VII. CONCERTED OXIDATION OF ALDEHYDES WITH OTHER ORGANIC COMPOUNDS

Concerted oxidation provides a highly effective method for obtaining valuable oxygen-containing products, one of which is the carboxylic acid corresponding to the initial aldehyde. The available oxygen of the acylperoxy-radicals and the intermediate products (peroxy-acids) is used to oxidise the second component of the pair. This method was suggested in 1962[2,128,129], when methyloxiran and acetic acid were obtained simultaneously by the concerted oxidation of propene and acetaldehyde. The efficiency of the process has since been improved considerably[101,130] by the use of heterogeneous catalysts, in particular silver oxide. The process is conducted in air compressed to 30–50 atm at 60–100°C.

In the catalytic process the required products are rapidly obtained in high yields—1300 kg of acetic acid and 800 kg of methyloxiran per tonne of acetaldehyde that has reacted—respectively 97 and 60 mole %. The catalytic action of the silver oxide can be explained by involvement of the heterogeneous catalyst in chain propagation[26]:

$$[CH_3COOO \cdots Ag_2O]^{\cdot} + C_3H_6 \rightarrow C_3H_6O + CH_3COO^{\cdot} + Ag_2O \ .$$

Concerted oxidation with aldehydes can be used for the epoxidation not only of propene but also of other unsaturated compounds, e.g. allyl chloride[131,132], as well as for introducing oxygen into other classes of organic compounds, including saturated compounds. Thus amines of the piperidine series can be converted by concerted oxidation with benzaldehyde into the corresponding stable iminoxyl radicals[26].

Acetic Anhydride

An important industrial product of the oxidation of acetaldehyde is acetic anhydride[43,96], for which the best catalyst is a mixture of copper and cobalt acetates. The reason is that Co^{3+} and Cu^{2+} ions react readily with an acyl radical:

$$CH_3CO + Cu^{2+} \rightarrow CH_3\overset{+}{C}O + Cu^{+} \ .$$

This competes with reaction (5) (addition of oxygen to the acyl radical) and ultimately results in formation of an anhydride:

$$CH_3\overset{\cdot}{C}O + CH_3COOH \rightarrow CH_3C(O)O{-}C(O)CH_3 + H^+ . \qquad (28)$$

The chief difficulty in the industrial production of acetic anhydride is its ready hydrolysis. This is prevented by the use of high concentrations of the catalyst, which permit short times of contact and relatively low temperatures (~40°C).

Preparation of Peroxy-acids

Peroxy-acids are formed in the act of chain propagation in the oxidation of aldehydes. In order to diminish their reactivity in subsequent transformations and increase their concentration in the mixture the oxidation is conducted at comparatively low temperatures (0–30°C). Furthermore, many publications, mainly patents, give a selection of solvents and catalysts. Data on the effect of the former is fairly contradictory, and it can be stated with some certainty only that ethyl acetate and benzene are among the best solvents for this purpose. Very many catalysts have been proposed. Thus, in order to obtain peracetic acid, the use has been suggested of cobalt(II) nitrate [133] and acetate [114], a mixture of iron monophenoxide and 2,4,6-trinitroresorcinol, a mixture of the latter and cobalt naphthenate, a mixture of cobalt(II) and iron(III) nitrates with concentrated hydrochloric acid, a mixture of cobalt and iron salts of dicarboxylic acids having pK_a = 4.6, and also additions of 60% nitric acid [134]. Manganese compounds—e.g. manganese salts in the presence of water [117] or manganese naphthenate mixed with selenium dioxide—are used as catalysts. The oxidation of acetaldehyde catalysed by iron citrate and naphthenate yields peracetic acid with nearly 100% selectivity. When malonic acid is used as catalyst, the oxidation of acetaldehyde (at 25–30°C) gives a mixture of peracetic acid and its adduct with the aldehyde, in relative amounts depending on the catalyst concentration. Use of the heterogeneous catalyst Ag_2O produces a considerably higher yield of peracetic acid than obtained in the uncatalysed process [101]. Photochemical initiation is also used to increase the concentration of peroxy-acids.

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