OXIDATION OF LIQUID ALDEHYDES BY MOLECULAR OXYGEN

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CONTENTS

I. INTRODUCTION

When exposed to oxygen or air, an aldehyde is slowly oxidized to the corresponding peracid, which further reacts with the aldehyde to form the normal acid. The rate of oxidation is decreased by a long list of inhibitors and is increased by light and certain catalysts. Backstrom (4) in 1927 carried out the photoöxidation of benzaldehyde and heptaldehyde and discovered quantum yields from 560 to 15,000. Since each photon would be absorbed by only one molecule, it was necessary to postulate a chain mechanism such as had been outlined by Bodenstein (10) and Christiansen (19).

Since then, this reaction has been studied by a large number of workers, so that at present some fairly detailed mechanisms have been formulated. It is the purpose of this article to show the areas of agreement and disagreement of the various workers and to point out how some disagreements may be resolved.

As the title indicates, the subject has been limited to the reaction of liquid aldehydes, or solutions thereof, with dissolved oxygen. Only those papers written since 1926 have been interesting enough from the point of view of reaction mechanism to warrant inclusion in this review.

II. Experimental Techniques

A. PURITY OF REACTANTS

1. Aldehyde

Almost everyone who has attempted to study the kinetics of the liquid-phase oxidation of aldehydes has experienced difficulty in reproducing the rate of absorption of oxygen from one experiment to another, even when using the same batch of aldehyde. In fact, this difficulty is largely responsible for the slowness of progress and lack of agreement among various workers in the field of aldehyde oxidation. Haber and Willstätter (24) first pointed out that trace amounts of such ions as ferric ion could trigger aldehyde oxidation by the reaction

$$Fe^{+++} + RCHO \rightarrow RCO\cdot + H^+ + Fe^{++}$$

When Backstrom showed that aldehyde oxidations were chain reactions, the Haber and Willstätter mechanism became popular as a reasonable explanation for the general failure to reproduce the rate of oxidation in the dark. However, even after care had been taken to remove such ions as ferric ion from the aldehyde, difficulty was still encountered. Mulcahy and Watt (37) have shown that the rate is decreased by contaminating the aldehyde with oxygen during storage, while if oxygen is admitted during distillation, an increased rate is observed. It would seem, therefore, that in order to measure a purely thermal rate of oxidation, care must be taken to purify the aldehyde in the absence of air and to remove both catalysts and inhibitors. Most workers (16, 17, 29, 33, 39) have found that the purification of the aldehyde decreases the rate of the dark reaction, that is, removes catalysts, while Cooper and Melville (21) found the rate of oxidation of decanal to increase with successive distillation, presumably owing to removal of inhibitor. Mulcahy and Watt (37) observed both effects in several purifications of benzaldehyde when starting with different samples of impure aldehyde.

2. Oxygen

The influence of ozone in minute concentrations upon the rate of oxidation has been very thoroughly studied (12–18). It appears that in order to measure a purely thermal reaction rate it is necessary to reduce the ozone concentration to less than 1 part in 10^9 (17). The fact that a number of workers have obtained very small dark-reaction rates without attempting to remove ozone from oxygen may be attributed to the oxygen source being fractionated liquid air. The oxygen should also be dust-free, since dust could be a catalyst for aldehyde oxidation.

3. Contamination

The fact that aldehyde oxidation is very sensitive to traces of metal ions and a large number of other substances makes it imperative that the apparatus for the purification of aldehyde and the vessel in which the reaction is to be carried out be scrupulously clean. It has been observed (33) that cleaning a fused silica vessel with hot chromic acid and subsequently rinsing several times with redistilled water results in irreproducibly large dark-reaction rates for the oxidation of *n*-heptaldehyde. However, if the rinsing is carried out about thirty times, the rate of reaction is reduced to about 1 per cent of the former value. It has been observed (37) that cleaning with a mixture of nitric acid and sulfuric acid and washing twice with distilled water produces a constant reaction rate for several-times distilled benzaldehyde.

B. DISSOLUTION RATE

Since the reaction takes place between aldehyde and dissolved oxygen, it is evident that a quiescent volume of aldehyde may quickly exhaust the dissolved oxygen, and the rate of absorption of the oxygen from the gas phase becomes controlled by the rate of diffusion of the oxygen from the surface into the volume of aldehyde. It becomes apparent that if the rate of reaction is to be measured, the aldehyde must be kept physically saturated with oxygen. The rate of oxidation has been shown to be a function of the rate of agitation (21, 33, 37, 39). The amount of agitation to maintain saturation depends largely upon the volume employed (39), the means of agitation, and the rate of reaction as controlled by catalysts and light. Mulcahy and Watt (37), working on the oxidation of benzaldehyde, have made the most thorough study thus far of the effect of agitation. When 20 ml. of a solution of benzaldehyde in benzene was employed, the plateau rate of 9 S.T.P. ml. O_2/min. was obtained using a minimum stirring rate of 1200 R.P.M. at an oxygen pressure of 523 mm. At a lower pressure, 71 mm., 1400 R.P.M. was required. The oxidation rate was 5 ml./min. at the second pressure. This observation is understandable on the basis that the rate of solution of oxygen changes more rapidly with pressure than does the reaction rate.

In the photochemical oxidation of heptaldehyde (33) it was shown that a shaking speed of 350 R.P.M. was sufficient to insure saturation of 2 ml. of aldehyde during photoöxidation at a rate of oxygen uptake of about 8 ml. per minute. It is evident that the average surface: volume ratio when 2 ml. of aldehyde is shaken is far greater than when 20 ml. is stirred. Hence a shaking technique using small volumes of liquid appears to insure rapid saturation of aldehyde with oxygen more efficiently and conveniently than does rapid stirring of large volumes of aldehyde.

III. Analysis of Products

A. PEROXY COMPOUNDS

The first product of oxidation appears to be the peracid, which is rather difficult to determine as such in a mixture of aldehyde and the final normal acid product. The oxygen balance permits one to write the equation

$$RCO_3H + RCHO \rightarrow 2RCO_2H \qquad (1)$$

to account for the disappearance of peracid. This reaction can be very slow, since some studies of the peroxide formed show that its rate of formation equals the rate of oxygen uptake for some time (1, 38, 46), i.e., no normal acid is formed in the early reaction. Bowen and Tietz (11) thought that the intermediate of reaction 1 was acetyl peroxide but did not identify this substance.

It was found (1, 38) that eventually the rate of formation of peroxide fell below the rate of oxygen uptake and that normal acid appeared. An explanation for reaction 1 postulated a complex between normal acid and peroxide whereby the acid catalyzed reaction 1.

Kagan and Lubarsky (28) were the first to isolate a complex, using acetaldehyde and peracetic acid. Their complex was stable at $-30°C.$ and decomposed to normal acid on heating or on treatment with manganous-ion catalysts. Thus,

$$CH_3CO_3H + CH_3CHO \rightleftarrows X \qquad E_A = 7 \text{ kcal./mole} \qquad (2)$$

$$X \rightarrow 2CH_3CO_2H \qquad E_A = 15\text{–}16 \text{ kcal./mole} \qquad (3)$$

To differentiate X from the peracid they used a 10 per cent potassium iodide solution to which 0.1-ml. samples were added. The liberated iodine was rapidly titrated with sodium thiosulfate solution. This presumably measured only peracid and not X.

Bawn and Williamson (8) were able to differentiate two peroxides by using five different methods of analysis, two giving a high value and three a low value. Assuming the high value as total peroxide and the low as peracid, they were able to plot concentrations of peracid, peroxide X, acetic acid, and residual aldehyde. This permitted calculation of the equilibrium constant for reactions 2 and 2′. They were able to freeze out the peroxide X and compare it with a similar compound reported by Losch (30). They report Losch's compound as a white crystalline solid, melting with decomposition at 20°C., having a molecular weight of 105, and containing 14–15 per cent active oxygen. Both compounds decomposed to acetic acid and/or to acetic acid and aldehyde. The formula finally proposed (8) is

$$(RCO_3H \cdot RCHO) \cdot RCHO$$

The second molecule comes off readily as aldehyde, while the first is oxidized to acetic acid.

Wittig and Pieper (46) tried to analyze for the complex between perbenzoic acid and benzaldehyde which their kinetic data indicated was formed rapidly and decomposed slowly at room temperature, but were not successful. They suggested two possible structures (46). Bawn (7) has looked, without success, for a similar complex in the oxidation of benzaldehyde.

B. OTHER PRODUCTS

The major product besides the peracid and the peracid–aldehyde complex is the normal acid of the particular aldehyde used. Under various conditions other products can be formed. Carbon dioxide has been reported (33) as a product of the oxidation of heptaldehyde, and has been observed as a decomposition product of peracids (28). A yellow coloration and precipitated solid corresponding to an oxygen discrepancy in the peracid plus acid products has been reported without analysis (1). Oxygen has been detected when peracid and aldehyde are mixed (28).

With inhibitors added there have been found a variety of primary and secondary products. Anthracene is oxidized to anthranol, which is further oxidized to anthraquinone (6). Dibiphenylethylene is oxidized to two molecules of fluorenone. *p*-Cresol gives a small yield of quinones, while *m*-2-xylenol forms a dimer, 3,5,3′,5′-tetramethyl-4,4′-diphenoquinone. This quinone is also oxidized, yielding partially the corresponding dibenzoate (5 per cent). A yellow amorphous solid also appeared when these inhibitors were used (22, 34, 43, 44).

IV. KINETICS

In aldehyde oxidations, the order of the reaction has generally been found by the method of measuring the change of initial rate due to change of the initial concentrations rather than by studying the change of rate during a single reaction. Self-inhibition and catalysis have made the second method difficult to use. The order of reaction can be determined for the aldehyde, the oxygen, the catalyst, the initiating light or radical source, and the inhibitor. Different orders are found depending upon the conditions of the experiment. Here the details of the various experimental findings will be given; in Section V the suggested explanations for the variations in order, under different experimental conditions, will be discussed.

A. INITIATION

The kinetic order with respect to the initiating molecule, radical, or quantum depends mainly upon the chain-ending step. Pure reactants give a half-order reaction, while added inhibitors give a reaction of the first order. Examples of half-order kinetics are found for initiation by photolysis (11, 21, 23, 26, 33), radical sources (36, 37, 38, 44), ozone (16), and metal catalysts (7, 8). The data in reference 16 had to be plotted by the authors to obtain the order. In the only case of disagreement (8), where the order was given as unity, a replotting of the data on a log concentration *versus* log rate basis gave an order of 0.4.

For the thermal reaction one cannot tell what to consider the initiator. The unraveling of the initiation from the subsequent reactions depends upon the mechanism, which will be considered later.

B. ORDER IN ALDEHYDE

Bowen and Tietz (11) reported that the photoöxidation of acetaldehyde is of the first order in aldehyde. However, the rates are reported ambiguously and it is impossible to tell whether they are reported per unit volume of solution or per unit volume of aldehyde. Neither interpretation reveals a first-order relationship. The order of the benzaldehyde photoöxidation has been reported by Raymond (9) to be 2. Although he determined the order by measuring rates at various initial concentrations of aldehyde in methylcyclohexane, his data are not sufficiently precise to establish a second-order relation. The oxidation of decanal was found to be of the 3/2 order for the thermal rate and of the first order for the photo rate (82) when the reaction was carried out in decane solution. The oxidation of benzaldehyde in benzene solution (36) with benzoyl peroxide as initiator was found to be of the first order in aldehyde, while the order of the thermal reaction was observed to be between 2 and 2.5. Later work (38) indicated that the thermal reaction was of the second order in aldehyde at high pressures of oxygen. Over the range of oxygen pressure studied, the order in benzaldehyde was complex for the thermal reaction, the rate being given by the expression:

$$R = k(\mathrm{A})^2/(b\mathrm{A} + C) \qquad \text{(I)}$$

The benzoyl peroxide-catalyzed oxidation of benzaldehyde in the presence of *p*-cresol or *m*-2-xylenol was found to obey a rate expression of the same form (43), although the mechanisms are not the same. The cobalt ion-catalyzed oxidation of solutions of acetaldehyde in acetic acid (8) was found to be of the first order in acetaldehyde. A later paper by Ingles and Melville (26) states that the oxidation of benzaldehyde in decane is of the first order in benzaldehyde, but the authors give no data in support of this statement. The photoöxidation of heptaldehyde in cyclohexane solution has been reported (33) as of the first order in aldehyde.

While there is a certain amount of conflict in the order in aldehyde, certain general consistencies emerge from the reported experimental information: (*1*) When the oxidation is initiated by a process whose rate is independent of aldehyde concentration, the reaction is usually of the first order in aldehyde. Thus, initiation by light and initiation by benzoyl peroxide both produce reactions of the first order in aldehyde. (*2*) The thermal reaction is of the form of equation I.

C. ORDER IN OXYGEN

Until recently almost nothing had been reported on the order in oxygen for the oxidation of liquid aldehydes. Almquist and Branch in 1932 found that the thermal oxidation of benzaldehyde is of the first order in oxygen. It was not until 1951 that anything further was published regarding the order in oxygen for the oxidation of liquid aldehydes. The thermal oxidation of decanal (21) in decane solution was found to be of the 0.5 order in oxygen between 350 and 700 mm. pressure, while the photochemical reaction was reported as of zero order. The hydroquinone-inhibited photoöxidation was also reported to be of zero order in oxygen. The cobalt-catalyzed oxidation of acetaldehyde (8) in acetic acid solution was found to be a zero-order reaction in oxygen from 550 to 950 mm. pressure. The photoöxidation of heptaldehyde (33) was found to be a zero-order reaction in oxygen between 250 and 400 mm. and a first-order reaction above 400 mm. The thermal oxidation of benzaldehyde was found not to depend on oxygen in a simple way (37). However, as the benzaldehyde–benzene solutions were made more concentrated, the order in oxygen more and more closely approached unity. At the highest aldehyde concentration reported, 0.343 mole fraction, the reaction was virtually of the first order in oxygen from about 40 to 400 mm. In general, the rate was given by the expression:

$$R = \frac{a(O_2)}{b + c(O_2)} \tag{II}$$

The benzoyl peroxide-catalyzed, *p*-cresol-inhibited oxidation of benzaldehyde similarly conforms to such an expression (43). The photoöxidation of liquid acetaldehyde appears to be of the first order at low oxygen pressures and approaches zero order at about 0.5 atm. (23), in qualitative agreement with equation II.

At 16°C. the thermal oxidation of benzaldehyde was of zero order in oxygen over a large pressure range with 0.179 mole fraction of aldehyde (37). As the temperature was raised, the reaction approached a first-order relation. Apparently as the aldehyde:oxygen ratio increases, as it does with increased temperature and increased aldehyde concentration, the reaction proceeds gradually from zero to first order in oxygen.

The photochemical oxidation of liquid acetaldehyde (23) was reported to be of zero order in oxygen above 0.5 atm. The photoöxidation of benzaldehyde in decane (26) solution has been reported as of zero order in oxygen from 460 to 700 mm., but inspection of the data shows the deviation from zero order to be considerably larger than the experimental error claimed. All of the reported work is in harmony with equation II, which gives orders between zero and unity depending upon the values of a, b, and c.

D. INHIBITORS

Backstrom (5) showed that the order of oxidation of benzaldehyde with respect to light intensity depended upon the nature of the inhibitor employed. Pure benzaldehyde gives an order of 0.5 in light intensity, while values for other inhibitors are as follows: anthracene, 0.65; benzyl alcohol, 0.5; diphenylamine and hydroquinone, 0.9. Ethanol changed the order of oxidation of acetaldehyde from 0.5 to 1 in light intensity (11). It has been proposed (43, 44) that these differences are due to two different mechanisms involved. Adducts changing the initiator order to 1 are chain-ending inhibitors; those in whose presence the order remains 0.5 are chain-transfer retarders. Intermediate orders are due to both mechanisms operating simultaneously. Several (5, 11) authors have noted this effect of inhibitors on order with respect to light intensity.

The order with respect to the inhibitor itself has not often been reported, probably because it is complex. Dibiphenylethylene represses the rate at a ratio of 1:150 but accelerates the rate at a ratio of 1:15 (46). Furthermore, the product found when large amounts are added is benzoic acid rather than the peracid. Waters and Wickham-Jones (43) found the rate of benzaldehyde oxidation initiated by benzoyl peroxide to be inversely proportional to the concentration of *p*-cresol, while Cooper and Melville (21) found the photooxidation of decanal to be inversely proportional to the concentration of hydroquinone. Ingles and Melville (25) give data for initial rates of benzaldehyde oxidation and concentrations of hydroquinone which show the rate to be inversely proportional to some power between 0.7 and 2.0 of the concentration of the inhibitor.

Another distinction between inhibitors and retarders has been made by their effect on the shape of the curve of oxygen uptake. Inhibitors cause an induction period of nearly zero rate and when used up give a normal and uninhibited rate (35, 43). Retarders reduce the rate to several per cent of the unretarded rate and are not consumed during reaction. They might be considered as negative catalysts.

E. TEMPERATURE COEFFICIENT AND ACTIVATION ENERGY

In determining the overall activation energy for reactions between dissolved gas and liquid it is not sufficient simply to measure the rate as a function of temperature, unless it is certain that the reaction is of zero order in dissolved gas. If the rate depends upon the concentration of dissolved gas, a change in rate with temperature will reflect not only the activation energy but also the effect of temperature on the gas solubility. That is, the apparent activation energy will consist of two parts, one a chemical rate term and one a physical equilibrium term. If the reaction is of order n in dissolved gas,

$$R = \text{reaction rate} = k(O_2)^n f(C) = \alpha e^{-E/RT} f(C)(O_2)^n \tag{III}$$

where $f(C)$ is the factor representing the effect of concentration of other reactants upon the rate and α is the preëxponential factor in the Arrhenius equation. If Henry's law is obeyed,

$$K = (O_2)/P_{O_2} \text{ and } \ln K = \ln (O_2) - \ln P_{O_2} \tag{IV}$$

At constant pressure

$$d \ln K/d(1/T) = d \ln (O_2)/d(1/T) = \Delta H/R \tag{V}$$

where ΔH is the differential heat of solution of oxygen in aldehyde. From equation III,

$$\ln R = \ln f(C) + n \ln O_2 + \ln k$$

Therefore

$$\begin{aligned} d \ln R/d(1/T) &= n\Delta H/R - E/R \\ &= -(E - n\Delta H)/R = -E \text{ (experimental)}/R \end{aligned} \tag{VI}$$

TABLE 1

Experimental activation energies

ALDEHYDE	INITIATION	OXYGEN ORDER	E_A (EXPERIMENTAL)	REFERENCE
			kcal.	
Decanal	Photo	0	3.7	(21)
Decanal	Thermal	0.5	11.5	(21)
Heptanal	Photo	1	3.9	(33)
Benzaldehyde	Photo	0	1.8	(26)
Benzaldehyde	Thermal	0	7.6	(26)
Benzaldehyde	Thermal	0–1	17.7	(38)
Acetaldehyde	Photochemical	0–1	3.5	(23)
Benzaldehyde	Photochemical		5.	(39)

Thus E (experimental) $= E - n\Delta H$. Thus, in order to obtain the activation energy from an Arrhenius plot of the reaction rate data, $n\Delta H$ must be added to the apparent energy of the activation. It is unfortunate that no data exist for the solubility of oxygen in aldehydes at different temperatures. For this reason recourse must be had to intelligent guesses as to ΔH on the basis of similar systems whose behavior is known.

The heat of solution of most gases in organic liquids is from 0.5 to 5 kcal./mole. We can arbitrarily choose 2 kcal./mole as the heat of solution of oxygen in aldehydes in the absence of the requisite data. If the aldehyde oxidation were of zero order in oxygen, the apparent activation energy would be equal to the true activation energy.

F. QUANTUM EFFICIENCY AND CHAIN LENGTH

Backstrom (4) in 1927, carrying out the photoöxidation of benzaldehyde and heptaldehyde using ultraviolet light of various wave lengths, discovered quantum yields of from 560 to 15,000. These results lent strong support to the concept of chain reactions. McNesby (33) found chain lengths of the order of 4000 in the photoöxidation of heptaldehyde at 2537 Å. for rates of light absorption of the order of 10^{14} quanta per second, while the photoöxidation of acetaldehyde (23) in the temperature range −90° to −40°C. gave a quantum yield of 1000. The comparison of quantum yields for photoöxidation of various aldehydes has little meaning unless the light intensity is specified, since the quantum yield is inversely proportional to the square root of the rate of light absorption. Nevertheless the order of magnitude of the quantum yields reported shows quite conclusively that the reaction chains are very long.

Briner and Papazian (16) showed that chain lengths as high as 50,000 for benzaldehyde and 200,000 for butyraldehyde existed for the ozone-initiated oxidations in carbon tetrachloride solution.

Backstrom and Beatty (6) approached the problem of measurement of chain length in a novel way. The number of chains started in a chain reaction must equal the number ended under steady-state conditions. They assumed that each molecule of the inhibitor molecule anthracene, oxidized in the process of benzaldehyde oxidation, corresponded to one chain ended and that the number of chains started could be obtained by measuring the number of molecules of anthracene destroyed. The number of molecules of aldehyde oxidized, as measured by the amount of oxygen absorbed, divided by the number of chains started gave the average chain length for the oxidation. The values obtained, while not quantitatively significant, were nevertheless so large that no doubt remains as to the chain character of the oxidation of benzaldehyde.

The calculation of the chain length in the benzaldehyde oxidation inhibited by anthracene can be calculated from other data (2) in the above manner. Since 0.000125 mole of anthracene is consumed, while 0.0182 mole of benzoic acid is formed, the chain length is at least seventy, the benzoic acid being equivalent to 0.0091 mole of peracid.

G. THE PERACID–ALDEHYDE REACTION

As stated above, the first product formed in most aldehyde oxidations is the peracid, which then forms the acid. The reaction by which the peracid goes to acid has been studied rather extensively (1, 3, 28). It is of the first order with respect to both peracid (3, 28) and aldehyde (28). Actually, one peracid and one aldehyde molecule react to form a complex which decomposes into two acid molecules (28, 46). The combination is apparently more rapid than the decomposition. For acetaldehyde and peracetic acid the combination has an activation energy of 7 kcal., while the decomposition has an activation energy of 15–16 kcal. (28). Either one or both of the reactions are catalyzed by acid (28). Bawn (7) has stated that no complex is formed between benzoic acid and benzaldehyde.

Both the peracid and the peracid–aldehyde complex can decompose above −30°C. to give other products than acid, and these reactions are both photosensitive (3) and catalyzed by metal ions (28). One of the products is a gas: either oxygen for the reaction in water solution, or carbon dioxide in acetic acid solution (38). Radicals which can initiate new chains can also be formed from the peroxy compounds (1).

Although kinetic evidence has been presented (2) to show that perbenzoic acid oxidizes anthracene directly, the experimental facts show that it does not (6).

V. REACTION MECHANISM

Mechanisms proposed for reactions must agree with the kinetic data obtained. If a reaction proceeds via a molecular mechanism involving stable molecules, the rate as a function of the concentrations of the various molecules present quickly gives the mechanism. In recent years many reactions have been shown to proceed via a free-radical mechanism. In order to deduce the mechanism from kinetic data, it is necessary to know the concentrations of the radicals involved. Up to the present time no satisfactory method has been developed to measure radical concentrations, and recourse has been had to the steady-state method. In this method a plausible mechanism is assumed and the differential equation for the rate of change in concentration of each of the radical species is written. It is assumed that when the rate is measured, the concentrations of free radicals are constant, i.e., a steady state has been reached, in which the rate of appearance of a particular species is equal to its rate of disappearance. With this assumption it is permissible to set each of the differential equations equal to zero. Since there are as many differential equations as there are radical species, a set of n algebraic equations in n variables is obtained and can be solved simultaneously for each of the radical concentrations in terms of elementary rate constants and concentrations of stable molecules. This method tells how the radical concentration varies with concentration of reactant molecules but gives the radical concentration only in units of rate constants for elementary reactions. These rate constants can only be determined by a knowledge of radical concentrations. A dilemma thus appears from which the only apparent hope for escape is the measurement of absolute concentrations of radicals. However, the radical concentrations in terms of rate constants can be very useful in deciding whether a proposed mechanism is a possible one. The method can be clarified by means of the following illustration:

Suppose that the photoöxidation of an aldehyde is found to be of 0.5 order in light intensity, of first order in aldehyde, and of zero order in oxygen. A plausible mechanism would be:

$$\mathrm{RCHO} \xrightarrow{h\nu} \mathrm{R\cdot} + \mathrm{CHO\cdot} \qquad (4)$$

$$\mathrm{R\cdot} + \mathrm{O_2} \rightarrow \mathrm{RO_2\cdot} \qquad (5)$$

$$\mathrm{RO_2\cdot} + \mathrm{RCHO} \rightarrow \mathrm{RO_2H} + \mathrm{RCO\cdot} \qquad (6)$$

$$\mathrm{RCO\cdot} + \mathrm{O_2} \rightarrow \mathrm{RCO_3\cdot} \qquad (7)$$

$$\mathrm{RCO_3\cdot} + \mathrm{RCHO} \rightarrow \mathrm{RCO_3H} + \mathrm{RCO\cdot} \qquad (8)$$

$$2\mathrm{RCO_3\cdot} \rightarrow (\mathrm{RCO_3})_2 \qquad (9)$$

To test the mechanism we set up the differential equations for the rate of change in concentration of $\mathrm{R\cdot}$, $\mathrm{RO_2\cdot}$, $\mathrm{RCO\cdot}$, and $\mathrm{RCO_3\cdot}$.

$$\mathrm{d}(\mathrm{R\cdot})/\mathrm{d}t = k_4\mathrm{I} - k_5(\mathrm{R\cdot})(\mathrm{O_2}) = 0 \qquad (\mathrm{VII})$$

$$\mathrm{d}(\mathrm{RO_2\cdot})/\mathrm{d}t = k_5(\mathrm{R\cdot})(\mathrm{O_2}) - k_6(\mathrm{RO_2\cdot})(\mathrm{A}) = 0 \qquad (\mathrm{VIII})$$

$$\mathrm{d}(\mathrm{RCO\cdot})/\mathrm{d}t = k_6(\mathrm{RO_2\cdot})(\mathrm{A}) - k_7(\mathrm{RCO\cdot})(\mathrm{O_2}) + k_8(\mathrm{RCO_3\cdot})(\mathrm{A}) = 0 \qquad (\mathrm{IX})$$

$$\mathrm{d}(\mathrm{RCO_3\cdot})/\mathrm{d}t = k_7(\mathrm{RCO\cdot})(\mathrm{O_2}) - k_8(\mathrm{RCO_3\cdot})(\mathrm{A}) - k_9(\mathrm{RCO_3\cdot})^2 = 0 \qquad (\mathrm{X})$$

Adding equations VII, VIII, IX, and X we get:

$$(\mathrm{RCO_3\cdot})^2 = (k_4/k_9)\mathrm{I} \qquad (\mathrm{XI})$$

whence

$$(\mathrm{RCO\cdot}) = \frac{k_4\mathrm{I} + k_8(\mathrm{A})[(k_4/k_9)(\mathrm{I})]^{1/2}}{k_7(\mathrm{O_2})} \qquad (\mathrm{XII})$$

$$(\mathrm{R\cdot}) = k_4\mathrm{I}/k_5(\mathrm{O_2}) \qquad (\mathrm{XIII})$$

The rate of oxygen disappearance is then

$$\text{Rate} = k_5(\text{R}\cdot)(\text{O}_2) + k_7(\text{RCO}\cdot)(\text{O}_2) \quad \text{(XIV)}$$

$$\text{Rate} = k_4\text{I} + k_4\text{I} + k_8(\text{A})[(k_4/k_9)(\text{I})]^{1/2} \quad \text{(XV)}$$

$$\text{Rate} = 2k_4\text{I} + k_8(\text{A})[(k_4/k_9)(\text{I})]^{1/2} \quad \text{(XVI)}$$

If the chains are long, $2k_4\text{I}$ is negligibly small and

$$\text{Rate} = k_8(\text{A})[(k_4/k_9)(\text{I})]^{1/2} \quad \text{(XVII)}$$

The result agrees with experiment and the mechanism is therefore a possible one. It is to be emphasized that such agreement is only a necessary but not a sufficient condition for proof of mechanism. The situation is not always as simple as that outlined in the above illustration. In discussing reaction mechanisms the steady-state method will be referred to frequently.

A. INITIATION REACTION

1. Radical primary process

The introduction of alkyl or aryl peroxides, metal-ion catalysts, ultraviolet light, or ozone into an aldehyde–oxygen system can produce free radicals, the effect of which is to initiate reaction chains. The high quantum yields and ozone yields prove the existence of a chain mechanism. The primary processes by which the radicals are formed is of great importance in understanding the mechanism of photoöxidation.

(a) Photochemically produced radicals

Blacet (9) has reviewed this subject adequately and only a brief comment will be made. There are three processes which have been proposed as primary steps:

$$\text{RCHO} \rightarrow \text{RH} + \text{CO} \quad (10)$$

$$\text{RCHO} \rightarrow \text{R}\cdot + \text{HCO}\cdot \quad (4)$$

$$\text{RCHO} \rightarrow \text{RCO}\cdot + \text{H} \quad (11)$$

Reaction 10 alone cannot be responsible for a chain-wise photoöxidation, while reaction 4 or 11 can. Reaction 11 probably does not occur, since attempts to detect hydrogen atoms in acetaldehyde photolysis and to identify acetyl iodide in the products of acetaldehyde–iodine photolysis have failed. Reactions 10 and 4 appear to be the most likely, and if chains are to be explained in photooxidation as well as in aldehyde photolysis, reaction 4 must occur. At 3130 Å. reaction 4 predominates, while reaction 10 becomes important at shorter wave lengths (47).

It is important to understand that in a photoöxidation, reaction 4 can lead to the consumption of many aldehyde molecules by a mechanism illustrated by reactions 5, 6, 7, and subsequent chain propagation through the RCO• radical. Reactions 4, 5, and 6 are kinetically equivalent to reaction 11 for a long chain reaction. Consequently most mechanisms appearing in the literature on aldehyde photoöxidation include reaction 11 as the primary process, since it explains the observed kinetics as well as reactions 4, 5, and 6. We shall refer to this reaction as the initiation reaction with the rate R_i when suggesting mechanisms.

(b) Catalytically produced radicals

Ferric-ion-catalyzed oxidation of aldehydes can occur with the following process (24):

$$Fe^{+++} + RCHO \rightarrow RCO\cdot + H^+ + Fe^{++} \tag{12}$$

The cobaltous-ion-catalyzed acetaldehyde oxidation (8) gave kinetics which suggested

$$Co^{++} + CH_3CO_3H \rightarrow Co^{+++} + CH_3CO_2\cdot + OH^- \tag{13}$$

$$Co^{+++} + CH_3CO_3H \rightarrow Co^{++} + CH_3CO_3\cdot + H^+ \tag{14}$$

as primary processes. Subsequent work (7) with the oxidation of benzaldehyde catalyzed by cobaltous ion indicated that cobaltous ion was immediately oxidized to cobaltic by peracid and that the following primary process ensued:

$$Co^{+++} + C_6H_5CHO \rightarrow Co^{++} + C_6H_5CO\cdot + H^+ \tag{15}$$

It is probable that this reaction also occurs in the oxidation of acetaldehyde. It is thus reasonably well established that reactions of the type

$$M^{n+} + RCHO \rightarrow M^{(n-1)+} + RCO\cdot + H^+ \tag{16}$$

are responsible for initiating aldehyde oxidations catalyzed by metal ions.

Aryl and acyl peroxides are also effective catalysts. As suggested by Mulcahy and Watt (37), the primary process in the benzoyl peroxide-catalyzed oxidation of benzaldehyde is probably

$$C_6H_5CO_4CC_6H_5 \rightarrow C_6H_5CO\cdot + C_6H_5CO_3\cdot \tag{17}$$

2. Thermal initiation

Earlier workers (15, 29, 39) contended that the rate of thermal oxidation of aldehydes was zero and any observed reaction was due to catalysis by trace metals. However, this contention has never been demonstrated, and it appears that the thermal reaction proceeds at a measurable rate at room temperature. One mechanism suggested for the primary process in the thermal oxidation of decanal (21) is as follows:

$$RCHO + O_2 \rightarrow HO_2\cdot + RCO\cdot \tag{18}$$

This implies that the subsequent reactions of the RCO· radical are exactly the same as in the case of the photochemical or catalytic oxidation. In the thermal oxidation of benzaldehyde two views have been set forth (26, 38). Ingles and Melville (26) present evidence that the thermal reaction proceeds by the same mechanism as the photochemical, while Mulcahy and Watt (38) argue for distinct mechanisms for the benzoyl peroxide-catalyzed oxidation and the thermal oxidation. For the latter reaction (38) the following rate expression is obtained:

$$\text{Rate} = (\text{A})^2(\text{O}_2)/[b(\text{A})^2 - c(\text{O}_2)] \qquad \text{(XVIII)}$$

For given oxygen and aldehyde concentrations, the rate of the benzoyl peroxide-catalyzed oxidation (36) is given by the expression:

$$\text{Rate} = \gamma_T + \alpha(\text{Bz}_2\text{O}_2)^{1/2} \qquad \text{(XIX)}$$

If both the thermal and the benzoyl peroxide-catalyzed oxidations proceeded by the same mechanism, the total rate would be of the form

$$\text{Rate} = [\gamma_T^2 + k(\text{Bz}_2\text{O}_2)]^{1/2} \qquad \text{(XX)}$$

where γ_T represents the purely thermal and $k^{1/2}(\text{Bz}_2\text{O}_2)^{1/2}$ the purely catalytic rate. That equation X was not obeyed was very skillfully demonstrated by the careful experimental work of Mulcahy and Watt. Further, the rate expression XIX is incompatible with the concept of identical mechanisms for the thermal and the catalyzed reactions.

The mechanism suggested for the primary step is:

$$\text{RCHO} \rightarrow \text{RCHO}^* \qquad (19)$$

The species RCHO* is capable of reacting with oxygen and propagating chains. The nature of RCHO* is not discussed by Mulcahy and Watt (38).

B. CHAIN PROPAGATION

There is general agreement that the processes which propagate chains are

$$\text{RCO}\cdot + \text{O}_2 \leftrightarrows \text{RCO}_3\cdot \qquad (7)$$

$$\text{RCO}_3\cdot + \text{RCHO} \rightarrow \text{RCO}_3\text{H} + \text{RCO}\cdot \qquad (8)$$

C. CHAIN TERMINATION AND CHAIN TRANSFER

1. Pure aldehydes

For the oxidation of pure aldehydes the chain-ending steps are probably reactions of the chain-carrier radicals with each other. Since there are two radicals, three reactions are possible:

$$2\text{RCO}\cdot \rightarrow \text{RCOCOR} \qquad (20)$$

$$\text{RCO}\cdot + \text{RCO}_3\cdot \rightarrow \text{RCOO}_2\text{COR} \qquad (21)$$

$$2\text{RCO}_3\cdot \rightarrow (\text{RCO}_3)_2 \qquad (9)$$

The kinetics of the reaction are quite sensitive to the chain-ending step, and one can explain most of the observed orders of reaction on the basis of these reactions. At low oxygen pressures the oxidation has been observed to be of the first order in oxygen (23, 33, 38). It is reasonable to assume that the concentration of $\text{RCO}_3\cdot$ is low under these conditions and the chain-ending reaction is 20. Using reactions i, 7, 7′, 8, and 20 one obtains the first order in oxygen.

$$dO_2/dt = [k_7k_8/(k'_{7'} + k_8A)][AO_2(R_i/k_{20})^{1/2}] \qquad (XXI)$$

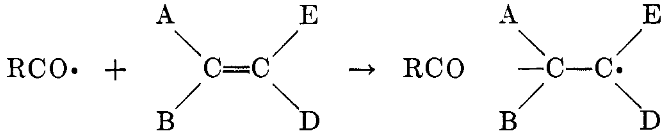
At high oxygen pressures the oxidation changes to zero-order dependence upon oxygen (21, 23, 26, 38). Assuming a large $RCO_3\cdot$ concentration one uses reactions i, 7, 7′, 8, and 9 to obtain zero order in oxygen.

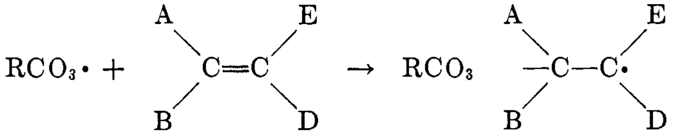
$$dO_2/dt = k_8A(R_ik_9)^{1/2} \qquad (XXII)$$

One case has been observed where the order changes back to 1 again (33) at higher pressures of oxygen. Unfortunately the mechanisms which might explain this kinetic behavior all involve such complicated equations that one cannot obtain solutions.

2. Inhibitor added

The action of rate inhibitors is to react with one of the chain-carrying radicals (and perhaps also with chain-initiating radicals) to shorten the average chain length. The two types of reactions which are likely between one of the chain-carrying radicals and an inhibitor molecule are


(22a)


(22b)

$$RCO\cdot + R'OH \rightarrow RCHO + R'O\cdot \qquad (23a)$$

$$RCO_3\cdot + R'OH \rightarrow RCO_3H + R'O\cdot \qquad (23b)$$

If the new radicals formed in reactions 22 or 23 disappear by a radical–radical reaction, the order in initiating reaction will be 1. This is true even though one of the radicals is a chain-carrying radical. Thus there is a mechanism to explain the kinetic data, which show the order in the initiator changing from 0.5 to 1 when certain inhibitors are added. Intermediate orders would be found depending upon the rates of reactions 20, 21, and 9 relative to the radical–radical terminating reactions involving the radicals formed above.

$$R''^{\cdot} + R'''^{\cdot} \rightarrow R''R''' \qquad (24)$$

The new radicals formed can also react to initiate a chain by abstracting a hydrogen atom from an aldehyde molecule, giving a chain transfer.

$$R''^{\cdot} + RCHO \rightarrow R''H + RCO\cdot \qquad (25)$$

If this is included in a reaction mechanism one gets the overall rate:

$$\text{Rate} = [(k_8A + k_{22}I)/k_{22}I]\cdot[R_i + k_{25}A(R_i/k_{24})^{1/2}] \qquad (XXIII)$$

where A = [aldehyde], I = [inhibitor], R_i = rate of initiation, and k_{23} can replace k_{22}. R_i can be the rate of light absorption, of initiating molecule decomposition, or of ozone–aldehyde reaction. In the latter case it would be of the first order in aldehyde.

It can be seen that the order of reaction with regard to the initiator depends upon the relative values of R_i *versus* $k_{25}A(R_i/k_{24})^{1/2}$. If there is no abstraction of hydrogen atoms by the "inhibitor" radical (i.e., if k_{25} is very small), then the reaction is of the first order in initiator, as shown previously. If k_{25} is large, then the reaction remains of 0.5 order in initiator. Waters and Wickham-Jones have referred to reaction mechanisms where k_{25} is large as chain transfer and the inhibitor as a retarder for such cases. Actually, the behavior of a given inhibitor should change with temperature, as the relative values of k_i, k_{24}, and k_{25} change independently with temperature.

According to this suggested mechanism for an inhibited reaction the order in aldehyde should vary from 2.5 to 1 depending upon the relative values of the rate constants.

Order in the inhibitor also should depend upon the relations of the above elementary rates but should vary from inverse first order to zero order according to the relationship $(k_8A + k_{22}I)/k_{22}I$. Both constants are temperature-dependent.

The suggested mechanism, including reactions 11, 7, 8, 22, 23, 24, and 25, is selected as an example of what has been proposed by various authors. It shows how the temperature, the concentration, the initiation rate, and the particular inhibitor can affect the order of the reaction. Inhibitors which have a labile hydrogen atom and react according to reaction 23 can be seen to regenerate themselves in reaction 25, whereas double-bonded molecules are lost via such reactions as 22 plus 24 or 25. This seems to be the only essential difference for inhibitors which have been termed retarders (43). Inhibitors are used up and the rate returns to normal after an induction period, while retarders continue to repress the rate for a longer period of time for the same initial concentration. Another factor contributing to a long induction period can be the inhibiting action (34, 43) of the molecule formed in reaction 24. It is also possible that the products of inhibitors are too complex to be described completely by the above simple reactions which are, however, valuable in giving an insight into the kinetics.

D. PERACID REACTION

The formation of peroxy compound and of acid has been followed by chemical analysis for the oxidation of benzaldehyde (1, 43). The concentration of peroxy compounds builds up to a maximum, which coincides with the initial appearance of a measurable concentration of benzoic acid. As acid builds up, the concentration of peroxy compound decreases to a small value.

A mechanism suggested by kinetic data is as follows:

$$RCHO + O_2 \rightarrow RCO_3H \qquad (26)$$

$$RCO_3H + RCHO + RCO_2H \rightleftarrows \text{complex X} + RCO_2H \qquad (27)$$

$$X \rightarrow 2RCO_2H \tag{3}$$

$$RCO_3H + RCHO \rightarrow 2RCO_2H \tag{1}$$

These equations can be combined, assuming steady state for the radical and the aldehyde concentrations, to give:

$$dX/dt = k_{27}(\text{peracid})(\text{aldehyde})(\text{acid}) - k_{27'}(\text{acid})X - k_3(X) \tag{XXIV}$$

$$d(\text{acid})/dt = 2k_3(X) + 2k_1(\text{peracid})(\text{aldehyde}) \tag{XXV}$$

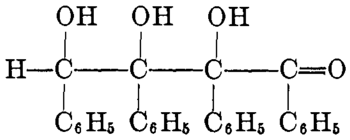
$$\begin{aligned} d(\text{peracid})/dt = R_{26} - k_{27}(\text{peracid})(\text{aldehyde})(\text{acid}) + k_{27'}(\text{acid})(X) \\ - k_1(\text{aldehyde})(\text{peracid}) \end{aligned} \tag{XXVI}$$

These are non-linear differential equations involving five parameters, where R_{26} is the rate of oxygen uptake.

They have not been solved analytically, but the values of peracid + complex X and acid have been traced by an analogue computer. Qualitative agreement with experiment has been obtained in preliminary computations.

E. SELF-INHIBITION

The photochemical oxidation of aldehydes apparently produces products which inhibit the oxidation (37). While the rate of disappearance of aldehyde is of the first order in aldehyde in the early stages of reaction, a pronounced deceleration occurs before 20 per cent of the aldehyde is destroyed. It has been observed (33) that photolysis of a sample of heptaldehyde prior to photoöxidation sharply reduces the rate of the photochemical oxidation. The liquid-phase photolysis of benzaldehyde (20) produces a compound corresponding to the formula



$$\mathrm{H{-}\underset{C_6H_5}{\overset{OH}{C}}{-}\underset{C_6H_5}{\overset{OH}{C}}{-}\underset{C_6H_5}{\overset{OH}{C}}{-}\underset{C_6H_5}{C}{=}O}$$

which contains OH groups characteristic of many well-known inhibitors. Raymond (9) found that benzaldehyde behaved similarly in giving a sharply decreasing rate after a time. He removed oxygen from the system and heated the aldehyde. When oxygen was readmitted to the system, the oxidation rate had returned to its initial value. It seems likely that the heating destroyed the compounds which had caused deceleration of the reaction. Almquist and Branch (1) maintain that an active peroxide formed during oxidation produced inhibition of the reaction.

F. ORIGIN OF THE OXIDES OF CARBON

Manganous ion catalyzes the decomposition of peracetic acid (28). The suggested reaction is as follows:

$$\begin{aligned} &5CH_3CO_3H + Mn^{++} \\ &\quad \rightarrow Mn^{++} + CO_2 + H_2O + O_2 + HCO_2H + 4CH_3CO_2H \end{aligned} \tag{28}$$

TABLE 2

Reactions involved in oxidation of aldehydes

REACTION		E_A
		kcal./mole
(3)	$X \longrightarrow 2RCO_2H$	15–16
(4)	$RCHO \xrightarrow{h\nu} R\cdot + CHO\cdot$	0
(5)	$R\cdot + O_2 \longrightarrow RO_2\cdot$	0
(6)	$RO_2\cdot + RCHO \longrightarrow RO_2H + RCO\cdot$	4
(7)	$RCO\cdot + O_2 \longrightarrow RCO_3\cdot$	0
(8)	$RCO_3\cdot + RCHO \longrightarrow RCO_3H + RCO\cdot$	4
(9)	$2RCO_3\cdot \longrightarrow (RCO_3)_2$	1
(12)	$RCO_3\cdot \longrightarrow RCO\cdot + O_2$	—
(16)	$M^{+++} + RCHO \longrightarrow M^{++} + RCO\cdot + H^+$	—
(17)	$RCO_4CR \longrightarrow RCO\cdot + RCO_3\cdot$	—
(18)	$RCHO + O_2 \longrightarrow RCO\cdot + HO_2\cdot$	15.6
(19)	$RCHO \longrightarrow RCHO^*$	13.5
(20)	$2RCO\cdot \longrightarrow (RCO)_2$	1
(21)	$RCO\cdot + RCO_3\cdot \longrightarrow$ products	1
(22a)	$RCO\cdot + I \longrightarrow RCOI\cdot$	—
(22b)	$RCO_3\cdot + I \longrightarrow RCO_3I\cdot$	—
(24)	$R''\cdot + R'''\cdot \longrightarrow R''R'''$	0
(27)	$RCO_3H + RCHO + R\dot{C}O_2H \longrightarrow X + RCO_2H$	7
(29)	$RCHO^* + O_2 \longrightarrow RCHO_3^*$	3.5
(30)	$RCHO_3^* + RCHO \longrightarrow RCO_3H + RCHO^*$	7
(31)	$O_3 + RCHO \longrightarrow RCO\cdot + HO_2\cdot$	4
(32)	$O\cdot + RCHO \longrightarrow OH\cdot + RCO\cdot$	4
(33)	$2RO_2\cdot \longrightarrow$ products	0
(34)	$R\cdot + RO_2\cdot \longrightarrow$ products	0
(35)	$RCHO^* + RCHO \longrightarrow$ inactive products	
(36)	$RCHO_3^* \longrightarrow$ inactive products	

Carbon dioxide was also found among the products of the photoöxidation of heptaldehyde (33). It appears likely that carbon dioxide again has its origin in a reaction similar to reaction 28.

G. RATES AND ACTIVATION ENERGIES FOR INDIVIDUAL REACTIONS

The constants in the Arrhenius equations for elementary processes are just beginning to be evaluated. The assessment of activation energies for the various elementary processes involved in the mechanism of aldehyde oxidation is therefore not easy. Recourse is had to estimates based on reactions of similar molecules or radicals. The activation energies, of course, are functions of the particular reactants involved, and it must be understood that the values given are approximate.

The reactions involved in the variously initiated aldehyde oxidations and their probable activation energies are shown in table 2. The letter I represents an inhibitor, while molecules with an asterisk are some specially active species found in the thermal reaction (38).

The great facility with which oxygen reacts with methyl radicals (32) leads us to suppose that the activation energy for reaction 5 approaches zero, and this is probably the case for reaction 7. Reaction 4 derives its necessary energy from radiation, and can be considered to have an activation energy of zero, unless absorption is temperature-dependent. Mulcahy and Watt (38) contend that the thermal oxidation of benzaldehyde proceeds via reactions 19, 29, 30, 35, and 36, and derive the following information from their data.

$$E_{19} + E_{29} - E_{30} = 6.0 \text{ kcal./mole} \tag{XXVII}$$

$$E_{19} + E_{30} - E_{36} = 17.5 \text{ kcal./mole} \tag{XXVIII}$$

$$(E_{30} - E_{29}) + (E_{35} - E_{36}) = 11.5 \text{ kcal./mole} \tag{XXIX}$$

Since E_{30} is probably 7 ± 2 and E_{36} is 3 ± 1,

$$E_{19} = 13.5 \pm 3 \text{ kcal./mole}$$

If we assume $2 < E_{29} < 5$, from equation XXVII

$$E_{35} = 11 \pm 4.5 \text{ kcal./mole}$$

The fact that the photoöxidation of acetaldehyde proceeds at temperatures from −90° to −60°C. with an activation energy of 3.5 kcal. (23) indicates that $E_8 - \frac{1}{2} E_9 = 3.5$. This result is based on a mechanism using reactions 4, 5, 6, 7, 8, 9 leading to equation XVII. If we assume a reasonable value for E_9 of 1 kcal./mole, $E_8 = 4$ kcal./mole. It is to be emphasized that this calculation is correct only if the reaction is of zero order in oxygen. As has already been discussed, if the reaction is of the first order in oxygen, the differential heat of solution of oxygen in the aldehyde must be added to the apparent activation energy to give the true activation energy.

It is probable that $E_9 \approx E_{20} \approx E_{21}$. Recently (27) the activation energy for reaction 24 for the case of methyl radicals was reported as −2 kcal./mole. Until this is confirmed, zero appears to be a reasonable value for E_{24} as well as for E_{33} and E_{34}. Cooper and Melville (21), assuming a mechanism involving reactions 18, 5, 6, 7, 8, 9, 20, and 21 for the thermal oxidation of decanal, conclude that

$$11.5 = \tfrac{1}{2} E_{18} + E_8 - \tfrac{1}{2} E_9$$

When reaction 4 is substituted for 18, the photochemical rate as a function of temperature gives

$$3.7 = E_8 - \tfrac{1}{2} E_9$$

whence

$$E_{18} = 15.6 \text{ kcal./mole}$$

It is probable that whether the initial process is 18 or 19 for the thermal reaction the activation energy is about 15 kcal., although it has been observed that the activation energy is a function of the oxygen pressure (38). From equation XXVII

$$15 + 3.5 - E_{35} = 6.0$$

$$E_{35} = 12.5 \text{ kcal./mole}$$

TABLE 3

Reaction rates for the oxidation of aldehydes

RATE* $\times 10^5$	ALDEHYDE	INITIATION	OXYGEN PRESSURE	TEMPERATURE	SOLVENT	MOLE FRACTION OF ALDEHYDE	VOLUME	REFERENCE
				°C.			ml.	
7.71	Decanal	Photo	650 mm.	5	None	1	1.7	(21)
1.87	Decanal	Thermal	650 mm.	5	None	1	1.7	(21)
19.	Heptanal	5.9 × 10^{14} quanta/sec. at 2537 Å.	650 mm.	29	None	1	2.0	(33)
0.75	Heptanal	Thermal	650 mm.	29	None	1	2.0	(33)
36.	Benzaldehyde	Photo	1 atm.	Room	None	1	3.0	(39)
0.24	Benzaldehyde	Thermal	1 atm.	Room	None	1	3.0	(39)
2.9	Benzaldehyde	Photo	1 atm.	Room	None	1	4.0	(4)
2.8	Benzaldehyde	Thermal	1 atm.	Room	None	1	4.0	(4)
3.1	Heptanal	Photo	1 atm.	Room	None	1	4.0	(4)
2.4	Heptanal	Thermal	1 atm.	Room	None	1	4.0	(4)
21.5	Benzaldehyde	Photo	650 mm.	5	Decane	0.251	1.7	(26)
2.15	Benzaldehyde	Thermal	650 mm.	5	Decane	0.251	1.7	(26)
4.1	Benzaldehyde	Benzoyl peroxide	523 mm.	24	Benzene	0.224	20	(37)
1.2	Benzaldehyde	Thermal	600 mm.	24	Benzene	0.179	20	(37)
0.027	Butanal	No ozone	130 mm. (air)	0	Carbon tetrachloride	0.25	25	(16)
0.55	Butanal	$10^{-7} O_3/O_2$	130 mm. (air)	0	Carbon tetrachloride	0.25	25	(16)

* The rate is given in moles of oxygen per second per mole of aldehyde.

It is suggested (21) that $E_8 = 4.2 \pm 0.6$ kcal. and that $E_{22a} \approx 0$ for hydroquinone as inhibitor, while E_9 is given as 1 kcal./mole. Since activation energies for radical combination are small, reactions 9, 20, 21, 33, 34 must approach zero. The activation energy for reactions 6, 31, and 32 should be nearly the same as for reaction 8. The activation energies for the subsequent reactions of the peracid E_3 and E_{27} were obtained by measuring the reaction rate between peracid and aldehyde as a function of temperature (28, 31).

VI. SUMMARY

The information available on the oxidation of aldehydes permits one to interpret it as a chain mechanism involving free radicals and yielding a rather reactive peracid. The peracid reacts in turn with aldehyde, producing two acid molecules.

The pronounced effect of small amounts of inhibitors and initiators upon the rate has made quantitative measurement and comparison of rates obtained by different investigators very difficult. Two approaches have been used in studying the oxidation of aldehydes. The reactants have been either highly purified or strongly contaminated with inhibitors and initiators in known amounts. Both techniques have been useful in learning the mechanism of the liquid-phase oxidation of aldehydes.

VII. REFERENCES

(1) ALMQUIST, H. J., AND BRANCH, G. E. K.: J. Am. Chem. Soc. **54,** 2293 (1932).

(2) ALMQUIST, H. J., BRANCH, G. E. K., AND GOLDSWORTHY, E. C.: J. Am. Chem. Soc. **55,** 4052 (1933).

(3) BACKSTROM, H. L. J.: Medd. Vetenskapsakad. Nobelinst. **6,** Nos. 15 and 16 (1927); Chem. Abstracts **22,** 717 (1927).

(4) BACKSTROM, H. L. J.: J. Am. Chem. Soc. **49,** 1460 (1927).

(5) BACKSTROM, H. L. J.: Z. physik. Chem. **B25,** 99 (1934).

(6) BACKSTROM, H. L. J., AND BEATTY, H. A.: J. Phys. Chem. **35,** 2530 (1931).

(7) BAWN, C. E. H.: Discussions Faraday Soc. **No. 14,** 181 (1953).

(8) BAWN, C. E. H., AND WILLIAMSON, J. B.: Trans. Faraday Soc. **47,** 721, 735 (1951).

(9) BLACET, F. E.: J. Phys. & Colloid Chem. **52,** 534 (1948).

(10) BODENSTEIN, M.: Z. Elektrochem. **22,** 53 (1916).

(11) BOWEN, E. J., AND TIETZ, E. L.: J. Chem. Soc. **1930,** 234.

(12) BRINER, E.: Helv. Chim. Acta **23,** 590 (1940).

(13) BRINER, E., AND BIEDERMAN, H.: Helv. Chim. Acta **15,** 1227 (1932).

(14) BRINER, E., DEMOLIS, A., AND PAILLARD, H.: J. chim. phys. **29,** 339 (1932).

(15) BRINER, E., AND PAPAZIAN, G.: Helv. Chim. Acta **23,** 542 (1940).

(16) BRINER, E., AND PAPAZIAN, G.: Helv. Chim. Acta **23,** 497 (1940).

(17) BRINER, E., AND PERROTTET, E.: Helv. Chim. Acta **20,** 458 (1937).

(18) BRINER, E., AND WENGER, P.: Helv. Chim. Acta **26,** 30 (1943).

(19) CHRISTIANSEN, J. A.: J. Phys. Chem. **28,** 145 (1924).

(20) CIAMACIAN, G., AND SILBER, P.: Ber. **33,** 2911 (1900).

(21) COOPER, H. R., AND MELVILLE, H. W.: J. Chem. Soc. **1951,** 1984.

(22) DUNN, J. R., WATERS, W. A., AND WICKHAM-JONES, C.: J. Chem. Soc. **1951,** 2427.

(23) FILLET, P., NICLAUSE, M., AND LETORT, M.: Compt. rend. **236,** 1489 (1953).

(24) HABER, F., AND WILLSTÄTTER, R.: Ber. **64,** 2844 (1931).

(25) INGLES, T. A., AND MELVILLE, H. W.: Proc. Roy. Soc. (London) **218A,** 163 (1953).

(26) INGLES, T. A., AND MELVILLE, H. W.: Proc. Roy. Soc. (London) **218A,** 175 (1953).

(27) INGOLD, K. U., AND LOSSING, F. P.: J. Chem. Phys. **21,** 1135 (1953).

(28) KAGAN, M. J., AND LUBARSKY, G. D.: J. Phys. Chem. **39,** 837 (1935).

(29) KUHN, R., AND MEYER, K.: Naturwissenschaften **35,** 1028 (1928).

(30) LOSCH, H.: *Arbeitsgemeinschaft Methoden der organischen Chemie*, Tagung I, p. 23. Berlin (1941).

(31) LUBARSKY, G. D., AND KAGAN, M. J.: J. Phys. Chem. **39,** 837 (1935).

(32) MARCOTTE, F. B., AND NOYES, W. A., JR.: Discussions Faraday Soc. **No. 10,** 198 (1951).

(33) MCNESBY, J. R.: Dissertation, New York University, 1951.

(34) MOORE, R. F., AND WATERS, W. A.: J. Chem. Soc. **1952,** 2432.

(35) MOUREU, C., AND DUFRAISE, C.: Chem. Revs. **3,** 113 (1926).

(36) MULCAHY, M. F. R., AND WATT, I. C.: Nature **168,** 123 (1951).

(37) MULCAHY, M. F. R., AND WATT, I. C.: Proc. Roy. Soc. (London) **A216,** 10 (1953).

(38) MULCAHY, M. F. R., AND WATT, I. C.: Proc. Roy. Soc. (London) **A216,** 30 (1953).

(39) RAYMOND, E.: J. chim. phys. **28,** 316 (1931).

(40) Raymond, E.: J. chim. phys. **28**, 421 (1931).
(41) Raymond, E.: J. chim. phys. **28**, 440 (1931).
(42) Reiff, O. M.: J. Am. Chem. Soc. **48**, 2893 (1926).
(43) Waters, W. A., and Wickham-Jones, C.: J. Chem. Soc. **1951**, 812.
(44) Waters, W. A., and Wickham-Jones, C.: J. Chem. Soc. **1952**, 2420.
(45) Wieland, H., and Richter, D.: Ann. **486**, 226 (1931).
(46) Wittig, G., and Pieper, G.: Ann. **546**, 142 (1941).
(47) Zemany, P. D., and Burton, M.: J. Am. Chem. Soc. **73**, 499 (1953).