

OXIDATION OF
GASEOUS PROPIONALDEHYDE

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THE KINETICS OF THE OXIDATION OF GASEOUS PROPIONALDEHYDE.

A T H E S I S

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
AND RESEARCH OF MCGILL UNIVERSITY.

B Y

Solomon Rosenberg B. Sc.

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THE DEGREE OF MASTER OF SCIENCE.

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Montreal, Canada.

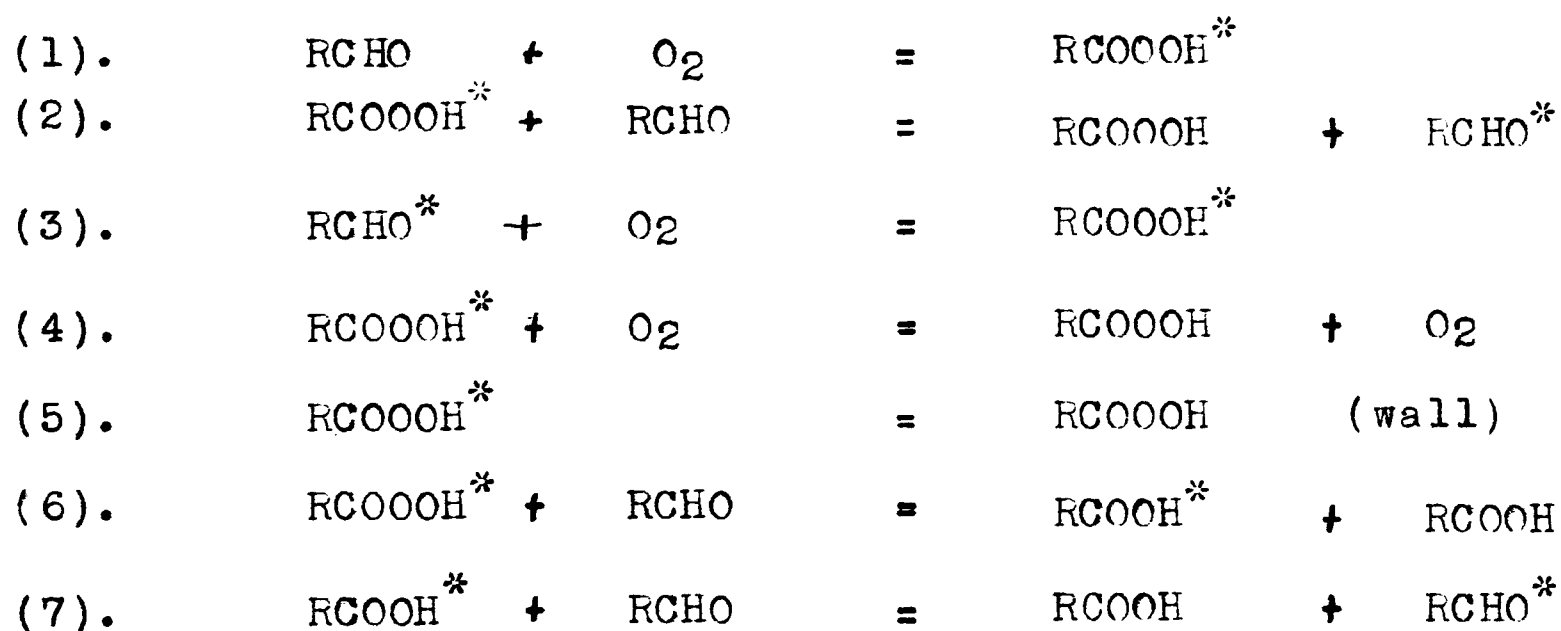
April, 1934

S O L O M O N R O S E N B E R G

Kinetics of the Oxidation of Gaseous Propionaldehyde.

The kinetics of the oxidation of gaseous propionaldehyde have been investigated from 120 to 170°C by a static method. The reaction is a chain process and is similar to the oxidation of acetaldehyde. The rate is proportional to the square of the aldehyde concentration, and independent of that of oxygen. The apparent heat of activation is 15,400 calories per gram molecule.

The following mechanism is suggested for the oxidation of aldehydes:



In the absence of deactivation at the wall, this leads to

$$-\frac{d}{dt}(\text{RCHO}) = \frac{2 K_1 K_6 (\text{RCHO})^2}{K_4}$$

in agreement with experiment.

This work was carried out during the tenure of a graduate assistantship at McGill University. The author takes this opportunity to very gratefully acknowledge the kind assistance and advice of Dr. E. W. R. Steacie and Dr. W. H. Hatcher, who supervised this research.

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INTRODUCTION (1)

The slow oxidation of hydrocarbons has, of late, become of considerable interest, both theoretically and industrially. Reactions which have been investigated are the oxidation of methane, propane, butane, ethylene, acetylene, benzene, methyl alcohol, acetaldehyde and benzaldehyde. These have yielded the generalizations which follow:

The reactions occur through chain mechanisms. The chain length, and how and where the chain is initiated and broken, are specific for each reaction. For example, in the methyl alcohol oxidation, increase in the volume of the reaction vessel increases the rate far more than a similar change does in the benzene oxidation; so that in the first case, the chains are mostly broken at the wall, while in the second, chain breakage occurs more in the gas phase.

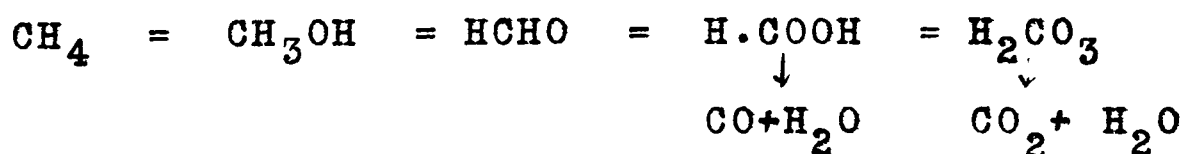
The rate is little affected by oxygen concentration, but sometimes varies as the square or the cube of the hydrocarbon concentration. This seems to indicate that the chains are started when an activated molecule (whose nature is not yet settled) collides with the hydrocarbon in the gas mixture. Oxygen, however, sometimes reflects the chains elastically, and sometimes destroys them, and accelerates or retards the reaction slightly, according as to which of these effects predominates.

Filling the bulb with the material, finely ground, of which the bulb is made, inhibits, or strongly retards the reaction. In the oxidation of benzene, however, it has been shown that a heterogeneous reaction also occurs, yielding products different from the homogeneous one. It seems, however, that the wall has

an effect, different from its chain breaking action. Pease, by covering the wall with KCL, caused the reaction to proceed at a definitely higher temperature. Then there is the phenomenon of bulb ^{aging} aging, a progressive change in reaction velocity, until finally, a steady state is reached, where reproducible results may be obtained. In this connection, it is important that in the experiments under consideration, the order of admission of O_2 and the combustible gas, has, in general, no effect.

In all these reactions, the oxidation of hydrocarbons as well as of substances containing oxygen, there is an induction period, during which very small pressure changes occur, although oxygen, as such, disappears from the system. This induction period is thought to be due, either to a time interval during which the formation of chain carriers is small, or to the presence of an impurity which destroys the spontaneously formed chain carriers, and is itself destroyed in the process. Examples of both causes are known.

In no case is the exact mechanism of reaction, or the nature of the chain carriers and chain starters, definitely agreed upon. Where the reaction is carried out in a closed vessel, the main final products are CO , CO_2 and water. However, in industrial processes, where the combustible mixture is allowed to flow through tubes kept at a temperature appropriate for reaction, as high as fifty per cent. of the hydrocarbon used is changed to aldehyde, acetylene yielding glyoxal. This would seem to favour the Bone oxidation scheme:



Bodenstein has put forward a more general oxidation mechanism.

Let. A = aldehyde molecule

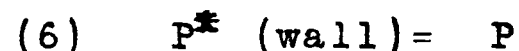
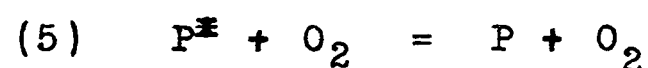
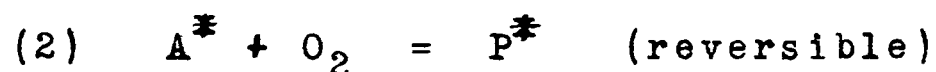
A^* = activated aldehyde molecule

P = product molecule

P^* = activated product molecule

K = negative catalyst

Then Bodenstein suggests the following reaction steps:



Reaction (1) shows the spontaneous formation of A^* from A.

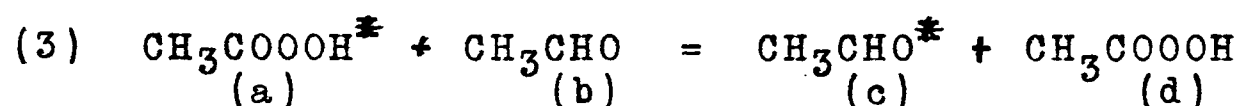
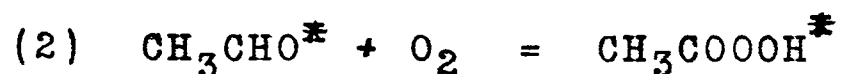
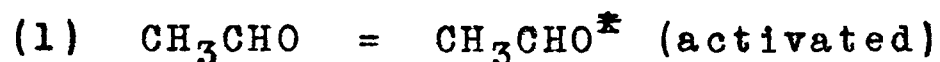
Reaction (2) shows the formation of P^* , and the reversibility of this step. Reaction (3) denotes the propagation of the chain and must occur readily for a chain reaction mechanism.

Reactions (4), (5) and (6) denote the breaking of the chain by the negative catalyst, oxygen, or the wall. Where the negative catalyst is absent, this scheme leads to the following reaction rate expression:-

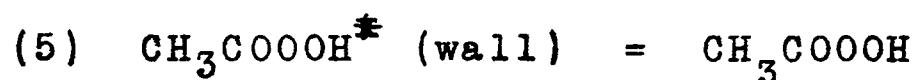
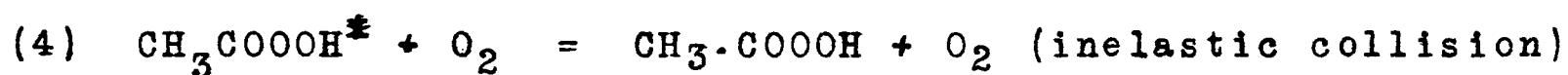
$$\frac{d(P)}{dt} = \frac{K_1 K_3 (A)^2}{K_5 (O_2) + K_6 K_5}$$

This, on the whole, is in fair agreement with experimental results.

Applied to acetaldehyde, this scheme indicates the following reaction steps:



(a) yields (c), oxidizing (b) to (d)



Bodenstein's scheme will fit other hydrocarbon oxidations, where double or triple bonds exist in the hydrocarbon; but unless modified, it does not fit the oxidation of saturated hydrocarbons. Furthermore, the induction period which exists in practically all of these oxidations, can only be explained, according to this scheme, by reaction (4); and since considerable quantities of reactants are used up during this period, it does not seem justifiable to attribute it to traces of a negative catalyst.

It is thought that the oxidation of acetaldehyde is one of the steps, and an important one, through which the oxidation of non-oxygen hydrocarbons proceeds. Three investigations of the acetaldehyde oxidation have been carried out (2), but its mechanism is still not clear.

It was in the hope of shedding light on this mechanism, and so helping to establish a general theory for organic chain oxidations, that this investigation was undertaken.

APPARATUS

The reaction was investigated by mixing propionaldehyde with oxygen in a heated Pyrex bulb, and measuring the rate of pressure change as the reaction proceeded.

The apparatus employed was a modification of that used previously for the oxidation of acetone, (3). and is illustrated in Figure A. The reaction bulb A was packed into the electric furnace B with iron filings. The temperature was measured with a standardized thermometer D, and could be maintained constant to within 1°C by hand regulation of a rheostat. Nichrome wire was wound, as indicated, on the connecting capillary tubing, which was kept at about 100°C , sufficient to prevent any condensation. Stopcock (1) kept the reacting mixture out of contact with mercury, which was found necessary. The mercury was protected by an air buffer, when pressure readings were made. The bulb G was used as a mercury reservoir, to give a practically constant head of mercury.

Oxygen was stored in F, and liquid propionaldehyde in K. The bulb E could be used as a mixing bulb if desired, with the manometer L to measure the partial pressures of the constituents of the mixture.

The oxygen used was obtained from cylinders, and was dried over phosphorus pentoxide. It contained 6.4 ~~9~~ % N_2 . Propionaldehyde from three sources, Eastman Kodak, Kahlbaum and Eimer and Amend, was used. It was purified by fractional distillation.

EXPERIMENTAL PROCEDURE

Prior to each run, the reaction bulb was evacuated

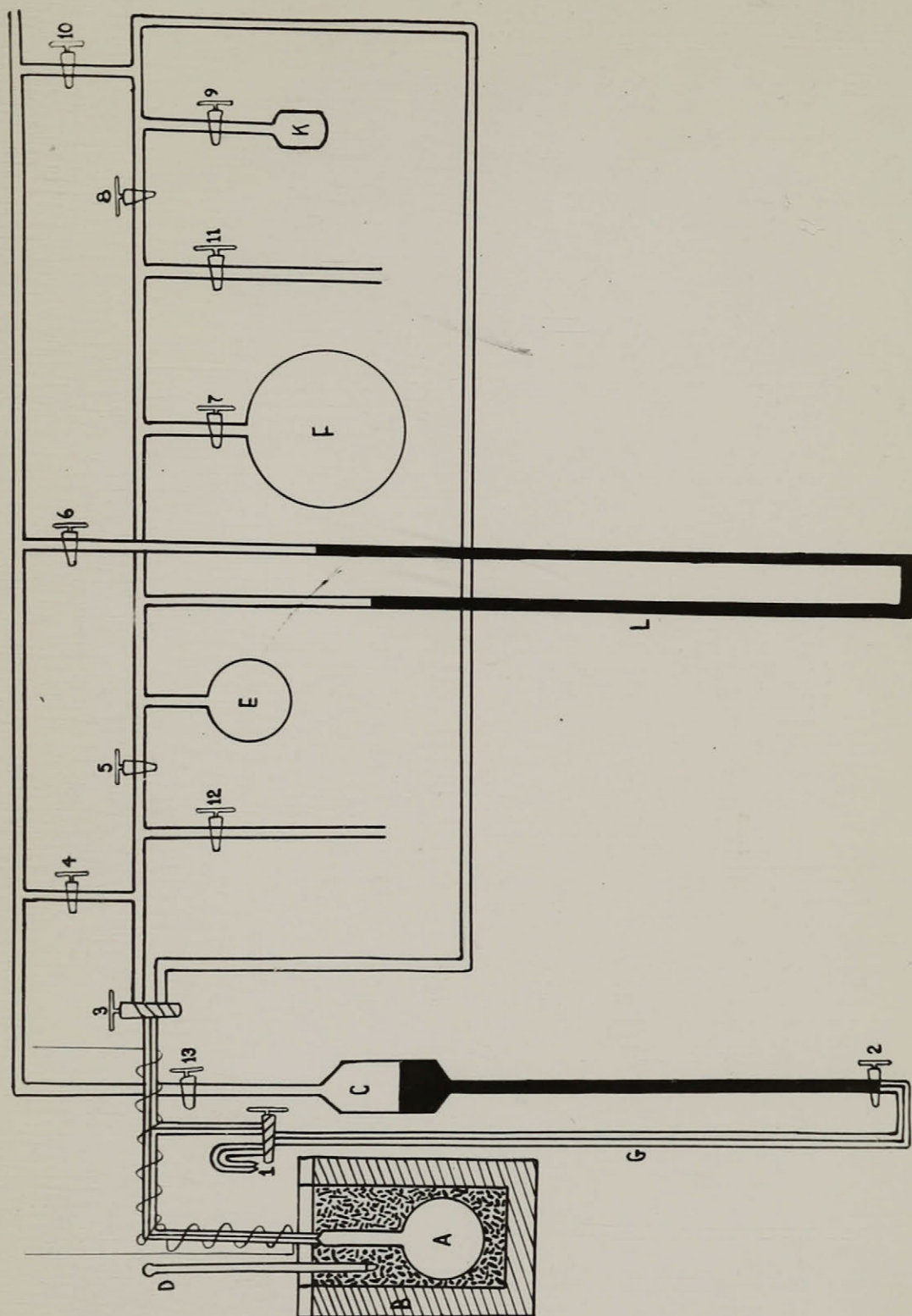


Figure A

EXPERIMENTAL PROCEDURE

Prior to each run, the reaction bulb was evacuated at the reaction temperature to about .02 or .03 mm. pressure. Tap (8) was kept closed unless mixtures were to be made up in bulb E and then admitted to bulb A - kept at reaction temperature. With tap (8) closed, propionaldehyde gas was led into bulb A by suitable opening of taps (9) and (3), its pressure being read on manometer G. When the desired aldehyde pressure in A was attained, the aldehyde was sucked out of manometer G by an auxiliary water pump. The manometer was then buffered. Tap (4) was now closed, and oxygen let into bulb A by suitably opening taps (7), (5) and (3). The pressure of the mixture was read off manometer G by opening tap (1) for a short period at regular time intervals. The correction for capillary depression was made automatically by taking the zero reading of the manometer as the position of the mercury when the system was evacuated.

For the analysis of gaseous products, samples were obtained through tap (12), by means of a gas sampler, with mercury as the confining liquid.

EXPERIMENTAL RESULTS

The reaction was investigated from 120 to 170°C. No appreciable effect due to the aging of the reaction vessel was noticed after the first 10 or 15 runs. It was also found that neither the degree of evacuation nor the temperature at which it was carried out had any appreciable effect on the succeeding run.

In all runs reported here oxygen - aldehyde mixtures were made up by introducing the reactants separately into the reaction bulb. (The order of admission had no effect.) This was done because it was found that the maximum pressure decrease associated with the reaction was diminished about 15 per cent, and the rate of reaction was diminished by about 40 per cent, if the reactants were mixed outside the reaction bulb in the presence of a mercury manometer. Tests showed the presence of peroxides under these conditions.

The Pressure Change Accompanying the Reaction.

As the reaction proceeded the pressure diminished. The maximum decrease amounted to about 73 per cent of the initial partial pressure of the aldehyde. The pressure then slowly rose again. The maximum pressure decreases obtained in a number of typical cases are shown in Table I.

TABLE I.MAXIMUM PRESSURE DECREASE

<u>Temperature °C.</u>	<u>Oxygen- aldehyde ratio.</u>	<u>Initial Partial aldehyde press- ure, cm.</u>	<u>Maximum pressure decrease, per cent.</u>
150.8	2.52	20.00	73
150.8	1.05	20.00	69
150.8	4.39	12.00	74
150.8	1.36	12.00	71
150.8	1.01	8.85	70
150.8	1.06	9.40	68
150.8	0.90	8.85	63
150.8	0.76	8.75	52
150.8	1.23	5.65	63
139.1	2.86	20.00	75
139.1	3.54	12.00	71
125.3	2.87	20.00	74
125.3	1.96	20.00	76

As shown above, the maximum pressure decrease is constant and independent of the experimental conditions, provided that (a) the partial aldehyde pressure is not much below 8 cm., (b) the oxygen - aldehyde ratio is not much below 1.00. Inasmuch as the pressure decrease is followed by a pressure increase, it is evident that the reaction proceeds in stages. Since in most cases the maximum decrease is constant, however, there is no doubt that it is justifiable to use the rate of pressure change as a measure of the rate of reaction. In the cases where the full pressure decrease is not reached, it is probably justifiable to employ the same criterion of reaction if we consider only the early part of the process. In consequence we have used the time for the pressure to change from a 15 per cent decrease to a 30 per cent decrease as a measure of the rate of reaction.

The Rate of Reaction.

Complete data for some typical runs are given in Table II and are plotted in Fig. 1. It will be seen that as is usual in gaseous oxidation reactions, there is a small induction period.

TABLE II

DATA FOR TYPICAL RUNS AT 150.8°C.

$P_{ald.}$	9.70 cm.			20.00 cm.		
$O_2/ald.$	4.00			2.52		
	<u>Time</u> <u>mins.</u>	<u>- $\Delta P,$</u> <u>cms.</u>	<u>%</u> <u>ΔP</u>	<u>Time</u> <u>mins</u>	<u>- $\Delta P,$</u> <u>cms.</u>	<u>%</u> <u>ΔP</u>
	0	0	0	0	0	0
	0.5	0.12	1.2	0.5	0.60	3.0
	1	0.28	2.9	1	1.80	9.0
	1.5	0.45	4.6	1.5	3.85	19.3
	3	1.34	13.8	2	4.60	23.0
	4.5	2.05	21.1	3	6.65	33.3
	7.25	3.24	33.4	4	8.15	40.8
	12.5	4.65	48.0	10	12.00	60.0
	18.5	5.70	58.8	20	14.50	72.5
	28.5	6.50	67.0	30	14.85	74.3
	73.5	7.25	74.8	40	14.96	74.8
	1680	5.05	52.1	50	14.60	73.0

Table III gives values for $T_{30} - T_{15}$ under various conditions.

TABLE III.

REACTION RATE DATA

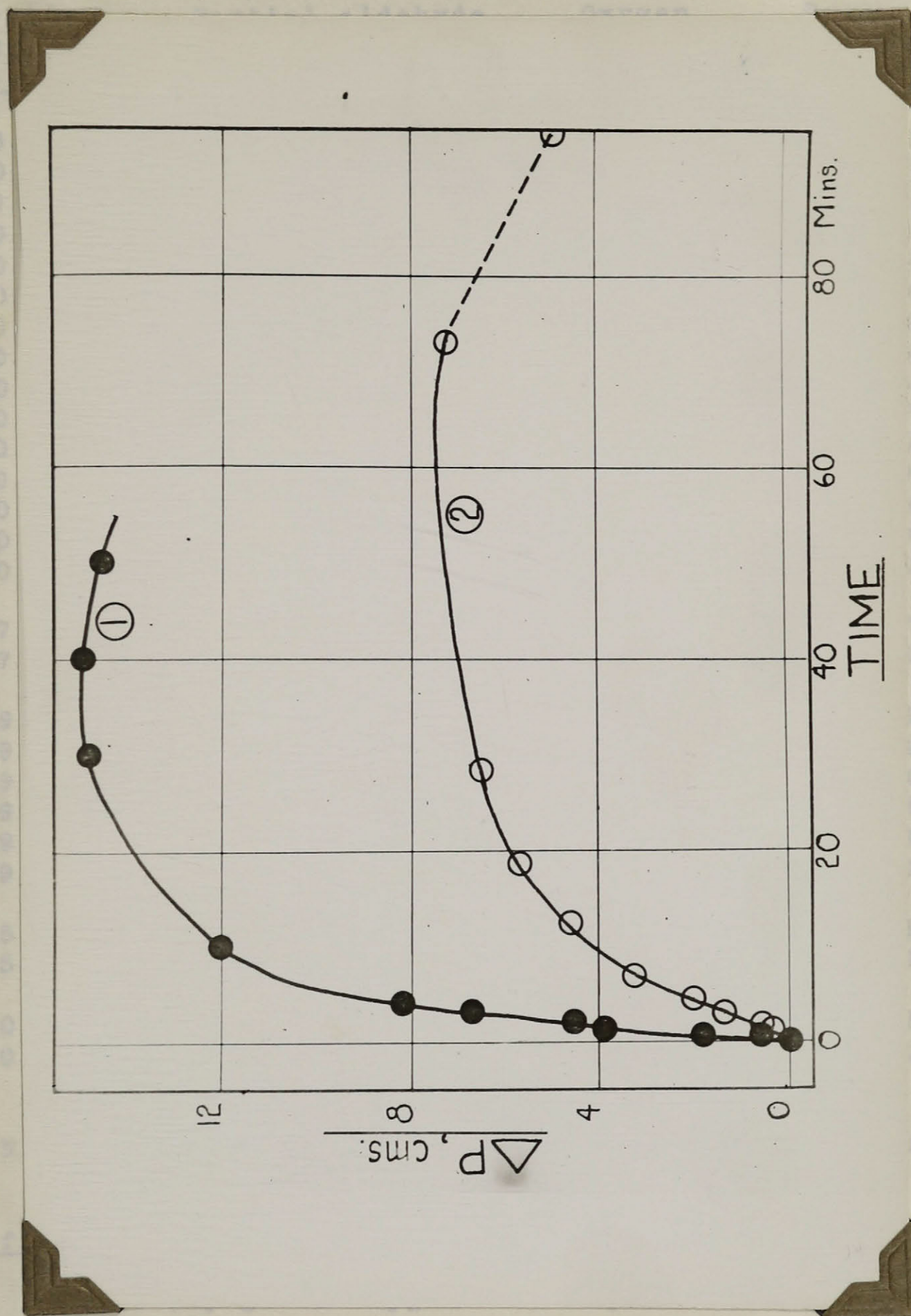


Figure (1)

the total pressure on the rate corresponds to an order of about 2.0. The effect of the oxygen concentration on the rate of the reaction is shown by Fig. 2, in which $T_{30} + T_{15}$ is plotted against the oxygen-aldehyde ratio for various constant initial

TABLE III.

REACTION RATE DATA.

Temperature, °C.	Partial aldehyde pressure, cm.	Oxygen aldehyde	$T_{30} - T_{15}$, secs.
150.8	20.00	2.52	85
150.8	20.00	1.68	80
150.8	20.00	1.05	110
150.8	12.00	4.39	155
150.8	12.00	4.37	156
150.8	12.00	2.58	157
150.8	12.00	1.36	184
150.8	8.00	5.46	260
150.8	8.00	5.75	260
150.8	8.00	3.17	270
150.8	8.00	2.10	256
150.8	8.00	1.32	297
150.8	4.00	5.64	502
150.8	4.00	3.02	502
150.8	4.00	1.86	546
167.4	12.00	3.00	76
167.4	8.00	4.00	128
139.1	20.00	2.86	134
139.1	20.00	1.62	144
139.1	20.00	1.62	142
139.1	12.00	3.54	280
139.1	12.00	2.42	282
139.1	8.00	3.20	508
125.3	20.00	1.96	260
125.3	20.00	2.87	266
150.8	8.00	2.58 *	320
150.8	20.00	1.17 *	111

Nitrogen added in an amount equal to that of the oxygen.

The Effect of Pressure.

For any given oxygen - aldehyde ratio, the effect of the total pressure on the rate corresponds to an order of about 2.0. The effect of the oxygen concentration on the rate of the reaction is shown by Fig. 2, in which $T_{30} - T_{15}$ is plotted against the oxygen-aldehyde ratio for various constant initial

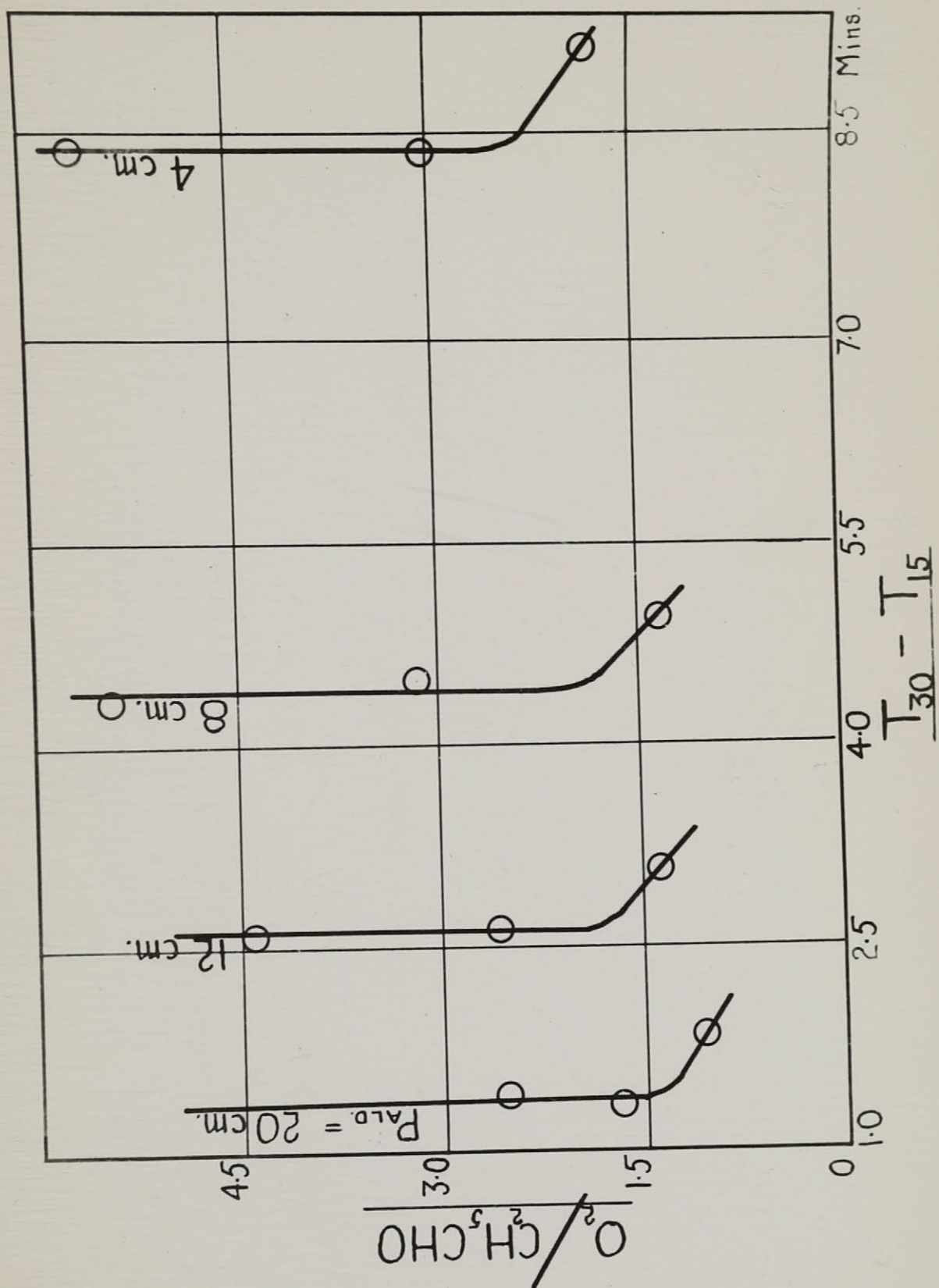


Figure (2)

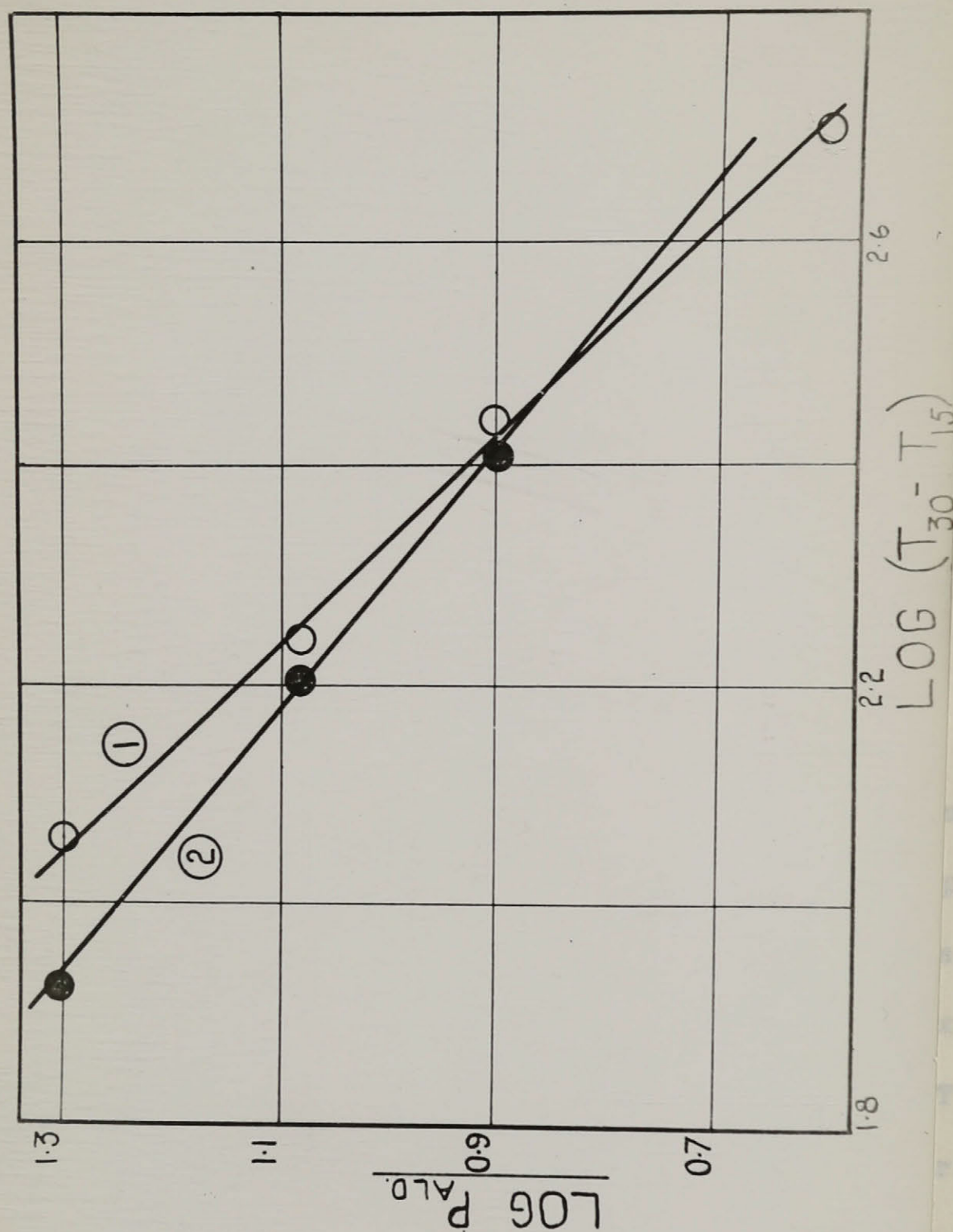


Figure (3)

partial pressures of aldehyde. It will be seen that the rate is virtually independent of the oxygen concentration if the oxygen-aldehyde ratio is above 2.0. When the oxygen concentration is reduced below this value, the rate is somewhat diminished.

Fig. 3 shows the effect of varying the aldehyde concentration while the oxygen concentration is kept constant. The values are given in the form of a log - log plot. From the slopes of the lines the order with respect to aldehyde is found to be between 1.8 and 2.1. Hence, provided the oxygen concentration is not too low, the rate can be approximately expressed by

$$-\frac{d(\text{C}_2\text{H}_5\text{CHO})}{dt} = K (\text{C}_2\text{H}_5\text{CHO})^2 .$$

The Temperature Coefficient.

The temperature coefficient of the reaction has been inferred from 3 series of runs at constant aldehyde pressures of 20, 12, and 8 cms., using oxygen - aldehyde ratios in the region in which the rate is almost independent of oxygen. The results are shown in Fig.4, in which $\log (T_{30} - T_{15})$ is plotted against the reciprocal of the absolute temperature. From the slopes of the lines we obtain the following values for the apparent heat of activation:

$P_{\text{ald.}}$	= 20 cms.	E	= 15,700 cal./gram mol.
	= 12 cms.	E	= 16,200 " " "
	= 8 cms.	E	= 14,400 " " "
<hr/>			
	Mean	= 15,400	" " "

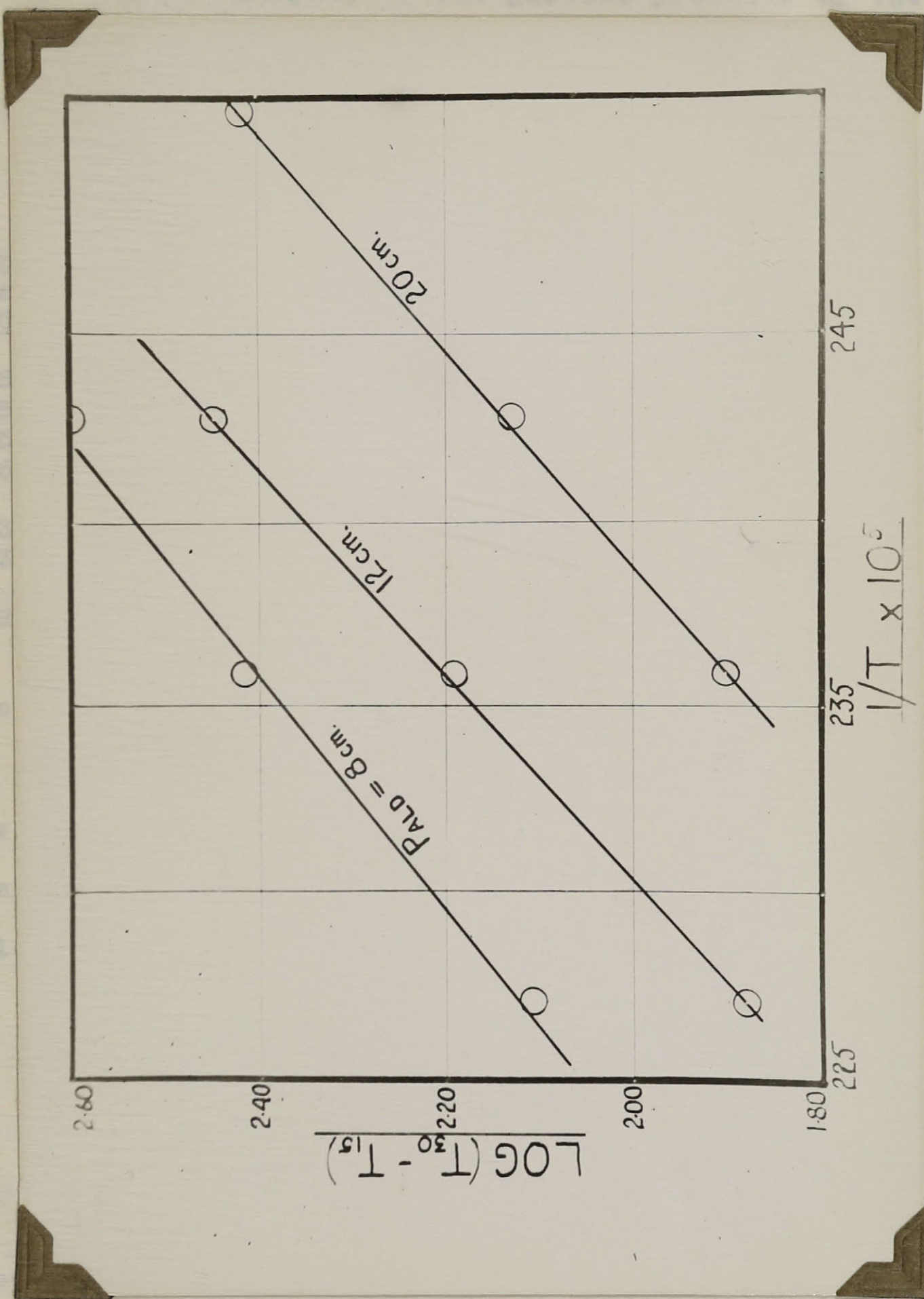


Figure (4)

The Products of the Reaction.

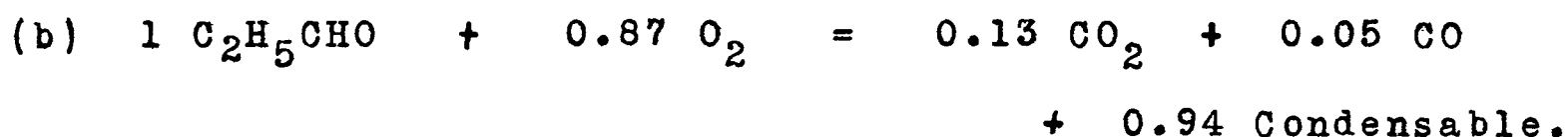
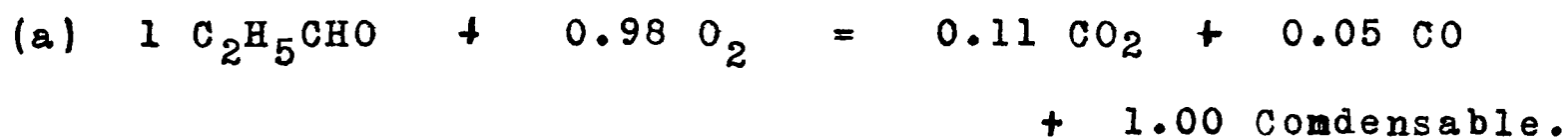
Some analyses of the gaseous products of the reaction are given in Table IV.

TABLE IV
THE GASEOUS PRODUCTS OF THE REACTION

Temper- ature, °C	Aldehyde pressure, cms.	Oxygen- aldehyde ratio.	O ₂ , %	CO ₂ , %	CO, %	CO ₂ CO
152	20.0	1.20	47	27	13	2.1
153	20.0	2.05	78	9	5	1.8
150	20.0	1.16	51	27	13	2.1
151	20.0	1.35	66	17	7	2.4
139	30.2	1.60	73	13	5	2.6
139	30.0	1.54 *	55	34	4	8.5

* Reaction mixture allowed to stand at 139°C for 15 hours.

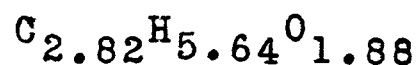
In order to refer the quantities of gaseous products back to the partial pressures which they exerted in the reaction vessel, runs were made with the addition of definite amounts of nitrogen. Thus two runs at 150.8°C with oxygen-aldehyde ratios of 1.16 and 1.35 gave the following results:



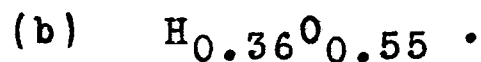
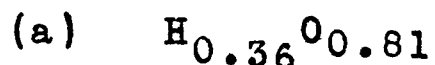
Hence, from a material balance, we find that the condensable products consist of



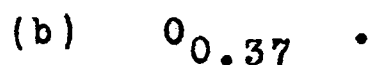
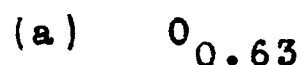
On chemical grounds the most probable product is propionic acid. On the basis of the carbon above, this has the formula



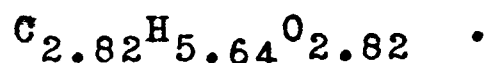
This leaves unaccounted for



If a small amount of complete oxidation occurred, it would result in an amount of water equal to the $\text{CO} + \text{CO}_2$, i.e. 0.16 and 0.18 H_2O respectively. This is in exact agreement with the hydrogen unaccounted for above. We still have unaccounted for



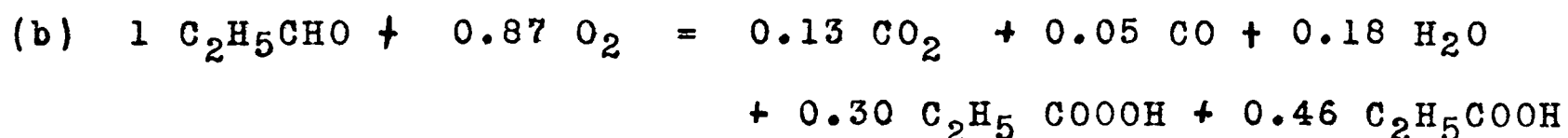
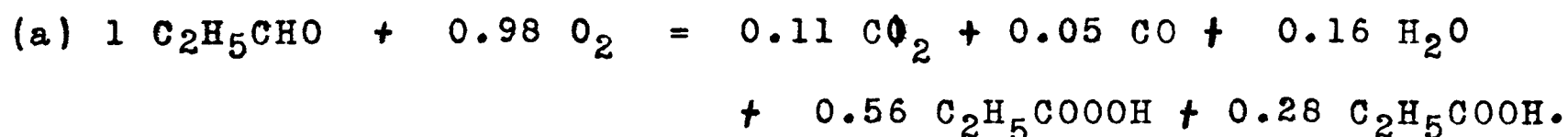
This can obviously be accounted for by assuming the formation of some perpropionic acid. This would have the formula



If the excess oxygen were used in this way, we would have

(a) 67 % perpropionic acid, (b) 40 % perpropionic acid.

The overall reaction is therefore



The presence of acids in the condensable products was confirmed by carrying out a run at 150.8°C and removing the reaction bulb. The bulb was then thoroughly washed with distilled water and the washings titrated with 0.05 N NaOH. The results indicated approximately 1 molecule of acid for each molecule of aldehyde disappearing, as required by the above scheme.

A similar experiment was then carried out, the washings

being analysed for peracids using a neutral solution of potassium iodide and titrating the liberated iodine with 0.05 N sodium thiosulphate. Approximately 50 per cent of the total acid was found to be peracid, again confirming the above scheme.

In addition to the above products, traces of esters were detected by their odour. It has previously been shown (4) that ethyl propionate is a product of the decomposition of perpropionic acid. The formation of this compound would be accompanied by the formation of carbon oxides and water in equal quantities, and hence necessitates no modification in the above calculations.

Hence the predominant reaction under investigation is



followed by the formation of propionic acid from the peracid, or from a reaction between the peracid and the aldehyde.

The Effect of Surface.

Runs were also made in a bulb packed with short lengths of pyrex tubing, so as to increase the surface-volume ratio to about 6 times its former value. It was found that the reaction process was completely altered in the packed bulb. Aging effects were noticed, but after the surface had reached a steady condition it was found that the reaction now led to a pressure increase of about 15 per cent. It therefore appears that the chain process in the empty bulb has been wholly or partially replaced by a heterogeneous reaction.

It has previously been shown that in the empty bulb

the pressure after its initial decrease then slowly rose again. As shown by Table IV, this increase in pressure was accompanied by the production of a large amount of carbon dioxide. Analyses of the products from runs in the packed bulb, where there was also a pressure increase, showed the same preponderance of carbon dioxide. It thus appears probable that the secondary process in the empty bulb is also a surface reaction.

Explosions.

There was no evidence of any critical explosion limits. Increased temperature and aldehyde concentration caused a progressive increase in the rate without any sign of a discontinuity.

DISCUSSION.

As shown above, the main reaction is the oxidation of propionaldehyde to the peracid, followed by the formation of propionic acid from the peracid. The formation of the peracid would lead to a pressure decrease of 100 per cent, while the formation of propionic acid would give 50 per cent. Both reactions must thus occur, since the observed pressure decrease is about 75 per cent, but they are not necessarily independent processes. This point will be referred to again later.

There is no doubt that the main process involved is a chain reaction. This is shown by analogy with other gaseous oxidation reactions, and also by the characteristic form of the differential equation expressing the rate.

The heat of activation is 15,400 calories. This is considerably lower than that corresponding to a bimolecular reaction proceeding at an equal rate in the same temperature range.

This, however, is a quite common characteristic of a chain reaction, since the heat of activation is a composite one and includes the temperature coefficient of the chain length.

One common criterion of a chain process is the suppression of the reaction by packing. In this case little information can be obtained from the results in the packed vessel since the course of the reaction is completely altered. It appears, however, that the deactivating effect of the walls is not very pronounced. This is shown by the reproducibility of the results, and by the fact that inert gases, including excess oxygen, have little influence on the rate.

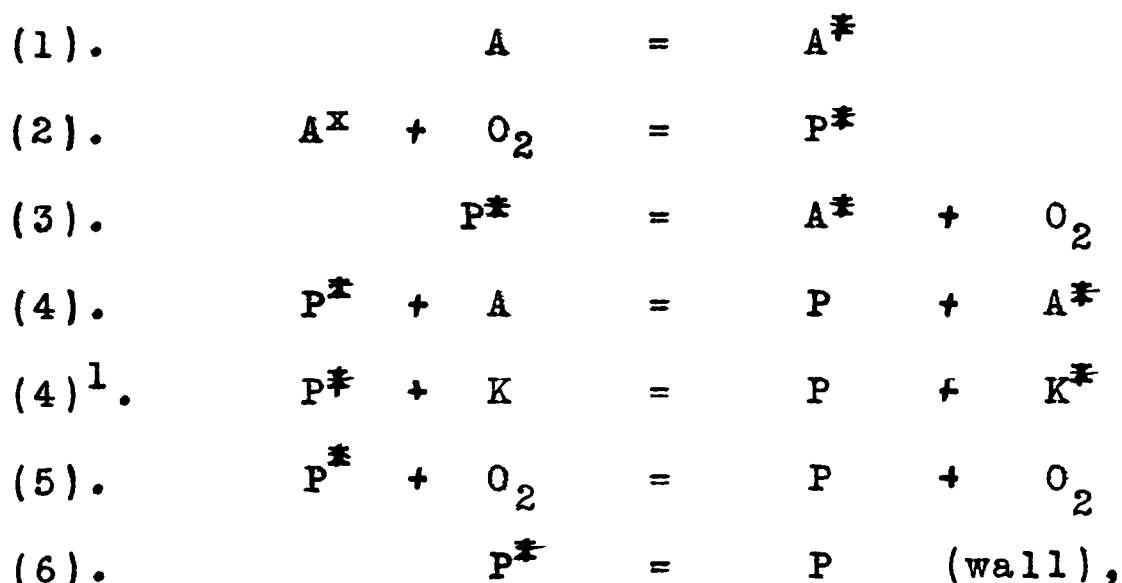
The Mechanism of the Reaction.

As we have seen the rate of the reaction is given by

$$-\frac{d(C_2H_5CHO)}{dt} = K (C_2H_5CHO)^2 .$$

On the basis of the Bodenstein scheme (5)

for the oxidation of acetaldehyde we have



where A represents aldehyde, P peracid, and K a negative catalyst.

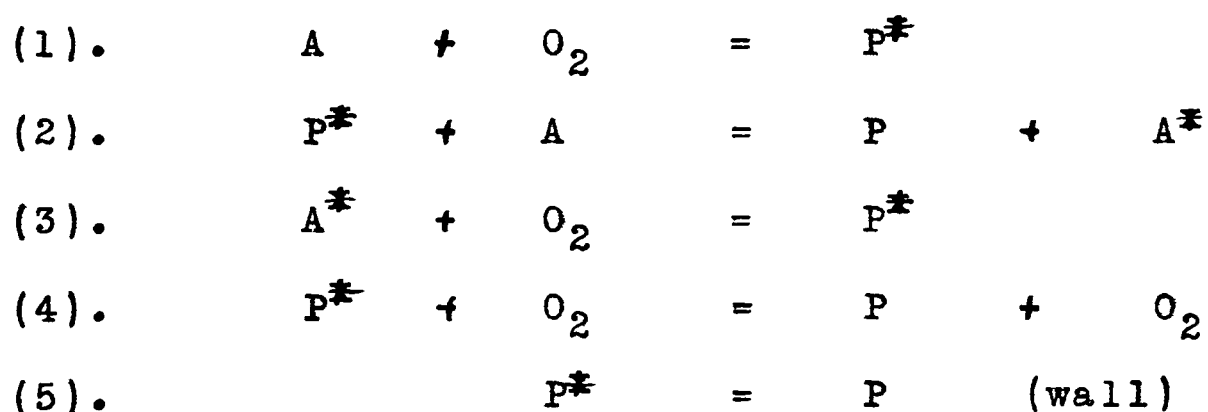
In the absence of a negative catalyst, this leads to

$$-\frac{d(A)}{dt} = \frac{K_1 K_4 (A)^2}{K_5 (O_2) + K_6 K_5^2}$$

This equation disagrees with the experimental results in that it ascribes a retarding effect to oxygen. The only way to avoid this would be to assume that $K_6 K_5^2$ is very much greater than $K_5 (O_2)$. This, however, is not here a valid assumption since it has been found that the wall effect (K_6) is small.

Any attempt to get over this difficulty by making minor modifications in the scheme is impossible. On the Bodenstein scheme the only fate of A^* is to react with oxygen. Hence oxygen exerts no favourable effect on the chain propagation to balance its deactivating effect, and hence it will always appear in the denominator.

To avoid this difficulty it is necessary to make a fundamental alteration in the initiation step, as follows:



The alteration made here is to abandon the assumption of independent activation of the aldehyde, and substitute the more usual idea of an initial bimolecular step. Whence we have

$$-\frac{d(A)}{dt} = K_1 (A) (O_2) + K_2 (P^*) (A).$$

Evaluating the concentrations of unstable intermediate substances by equating their rates of formation and destruction in the steady state, we obtain

$$-\frac{d(A)}{dt} = K_1(A)(O_2) + \frac{K_1 K_2 (A)^2 (O_2)}{K_4(O_2) + K_5}$$

Neglecting K_5 since the wall effect is small, and dropping the first term since the chain starting step is negligible compared to the chain carrying step, we have finally

$$-\frac{d(A)}{dt} = \frac{K_1 K_2 (A)^2}{K_4},$$

which agrees with the experimental results.

It has been previously mentioned that propionic acid is also formed. If this results from a secondary decomposition of the peracid, the formation of the peracid will be the rate determining step, and the above equation will still hold.

It is, however, possible that propionic acid arises from the reaction of aldehyde and peracid, as an integral part of the chain process. If so, we can account for the observed concentration relationships by the addition to the above scheme of the following steps:



where S represents propionic acid. This leads to the final equation

$$-\frac{d(A)}{dt} = \frac{2 K_1 K_6 (A)^2}{K_4},$$

which is again of the right form. It seems likely that this is the way in which propionic acid arises, since a straight decomposition of perpropionic acid does not normally yield propionic acid. (6).

The Oxidation of Acetaldehyde

As mentioned at the outset, it was hoped that this work might throw some light on the oxidation of acetaldehyde. It turns out in fact that the propionaldehyde oxidation is essentially similar to that of acetaldehyde, but lacks most of its complications. Thus both give peracids as the primary product. Both are accompanied by a pressure decrease, followed by an increase in the later stages. Both reactions have a low apparent activation energy, and there is no doubt that they proceed by chain mechanisms.

In addition the concentration terms in the expression for the rate are strikingly similar for both. Thus the propionaldehyde reaction rate is proportional to the square of the aldehyde concentration and independent of that of oxygen, while the acetaldehyde reaction is proportional to $(\text{aldehyde})^{1.7}$, and independent of oxygen.

The objections to the Bodenstein mechanism outlined above apply with equal force to the acetaldehyde oxidation. In view of the great similarity of the two reactions there is little doubt that they proceed by analogous mechanisms. It is therefore suggested that the scheme outlined above applies also to the main chain process in the acetaldehyde oxidation.

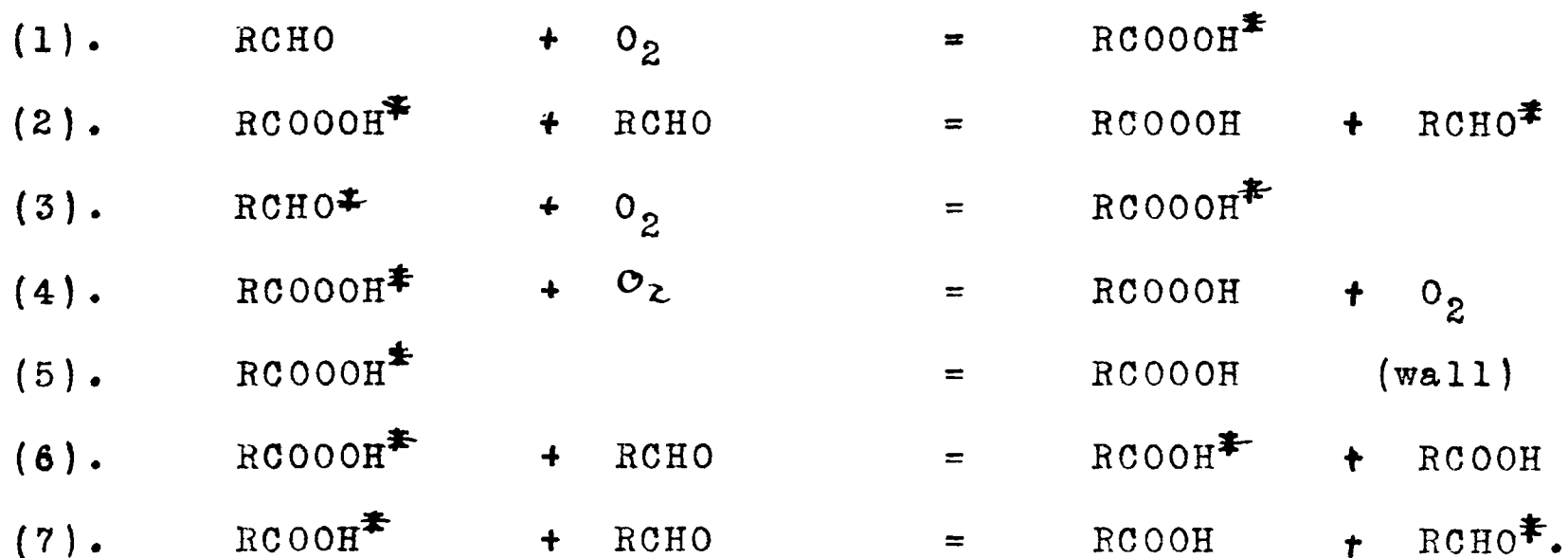
The acetaldehyde oxidation, however, is complicated by a pronounced induction period. A similar effect is noticed in the propionaldehyde oxidation in the first few runs in a new reaction vessel. When the walls have aged (presumably due to

irreversible adsorption of products) the induction period practically disappears. It is apparent therefore that the induction period with acetaldehyde may be explained by assuming that poisoning of the walls is a necessary preliminary to the propagation of chains.

SUMMARY

The kinetics of the oxidation of gaseous propionaldehyde have been investigated from 120 to 170°C by a static method. The reaction is a chain process and is similar to the oxidation of acetaldehyde. The rate is proportional to the square of the aldehyde concentration, and independent of that of oxygen. The apparent heat of activation is 15,400 calories per gram molecule.

The following mechanism is suggested for the oxidation of aldehydes:



In the absence of deactivation at the wall, this leads to

$$-\frac{d}{dt}(\text{RCHO}) = \frac{2 K_1 K_6 (\text{RCHO})^2}{K_4}$$

in agreement with experiment.

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