THE PHOTOCHEMICAL OXIDATION OF ALDEHYDES IN THE GASEOUS PHASE

PART II. THE KINETICS OF THE PHOTOCHEMICAL OXIDATION OF PROPIONALDEHYDE[1]

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ABSTRACT

The photochemical oxidation of propionaldehyde has been studied in the gaseous phase at 23° C. and a wavelength of 3130 Å. With pressures of oxygen varying from 0.3 mm. to 100 mm. Hg it has been established that the reaction obeys the same kinetic law as that found for the corresponding reaction with acetaldehyde, namely:

$$d[C_2H_5CO_3H]/dt = (k_3/k_6^{\frac{1}{2}})\ (\phi_2 I_a)^{\frac{1}{2}}[C_2H_5CHO],$$

where k_3 is the velocity constant for the propagating reaction [3]:

$$C_2H_5CO_3 + C_2H_5CHO = C_2H_5CO_3H + CH_3CO \qquad [3]$$

and k_6 is the velocity constant for the terminating reaction [6]:

$$2C_2H_5CO_3 = (C_2H_5CO)_2O_2 + O_2. \qquad [6]$$

$\phi_2 I_a$ is the rate of initiation and it is regarded as being a composite quantity representing the rate of formation of propionyl radicals, which are thought to be the initiators of the oxidation chain. The propionyl radicals are thought to be formed by two processes: (*a*) from the subsequent reactions of free radicals produced in the primary free radical process which occurs when propionaldehyde absorbs a quantum of radiation at 3130 Å, and (*b*) from the subsequent reactions, with oxygen, of excited states of propionaldehyde, which are also thought to be formed by the absorption of light of wavelength 3130 Å.

INTRODUCTION

Following the study of the photooxidation of acetaldehyde (Part I) reported in the preceding paper, it seemed desirable to study other higher aldehydes. It is important to know if the derived mechanism was of general application. It was also necessary to establish this mechanism for several aldehydes, for one of our main aims was to determine the absolute values for the propagating and terminating steps in the oxidation chain. A knowledge of the velocity constant for these oxygen-containing radicals is most important if the general features of the rates of combustion processes of hydrocarbons and other organic compounds are to be understood. Such results would also add to our available information of the factors influencing the interactions of large radicals in the gaseous phase.

Few studies have been made of the kinetics of the oxidation of aldehydes higher than acetaldehyde. Steacie *et al.* (8) investigated the gas phase thermal oxidation of propionaldehyde and showed that its kinetics were similar to those found for acetaldehyde. More recently a similar investigation (4) has largely substantiated the earlier work. Both of these studies were carried out at temperatures between 100° and 200° C. and the rates were determined by measuring pressure–time curves. It was found that the main product was perpropionic acid. Blacet and Volman (2) reported a study of the photooxidation of crotonaldehyde, but their results were not detailed enough to yield much information about the mechanism and kinetics of the reaction.

EXPERIMENTAL

Eastman-Kodak white label propionaldehyde was dried three times over anhydrous $CaSO_4$ and distilled, at a reflux ratio of 20: 1, through an efficient column in an atmosphere

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of cylinder "purified" grade nitrogen. A fraction boiling at 47.9° C., comprising half of the sample, was collected. This sample was redistilled and finally bulb-to-bulb distilled 10 times on the vacuum line, each time a middle fraction being taken.

Oxygen was prepared by heating A.R. grade potassium permanganate. A trap plugged with glass wool and immersed in liquid oxygen was interposed between the oxygen reservoir and the potassium permanganate.

A sample of ethanol from a freshly opened can of "absolute" was dried over anhydrous magnesium sulphate and bulb-to-bulb distilled on the vacuum line. A sample of A.R. isopropyl alcohol was similarly purified.

A sample of A.R. acetone was dried over anhydrous potassium carbonate, refluxed with potassium permanganate, and bulb-to-bulb distilled on the vacuum line.

The apparatus was a conventional high vacuum system utilizing stopcocks lubricated with Apiezon L grease. A cylindrical quartz reaction vessel (volume 76 ml., 4 ml. of which was dead space) having optically flat ends was housed in a block aluminum furnace, the temperature of which could be readily adjusted and accurately maintained. The gases were metered into the vessel using either a calibrated, sensitive spiral gauge, or, for lower pressures, the same gauge in conjunction with a calibrated expansion volume. The reaction products were trapped in a series of cold traps, which could be plugged with glass wool, the last of which was removable to facilitate analysis of the normally liquid reaction products. A copper oxide furnace was incorporated to analyze for CO and H_2, and means was incorporated for measuring small quantities of gas, and for collecting small samples of gaseous products for analysis by mass spectrometry.

A water-cooled, General Electric AH6 mercury arc, housed in a small, water-cooled box with a 3 mm. diameter hole in one side, gave a "point" source of illumination. The input voltage to the 1000 volt transformer for the arc was stabilized at 100 volts by a Sorensen a-c. voltage regulator. The arc had a short-term stability within 5%. Liquid filters were used to isolate a fairly narrow wavelength band in the 3200 Å region. Neutral density filters made by evaporating aluminum on quartz plates were used to vary the intensity incident upon the reaction vessel. Quartz lenses were arranged so that light from the "point" source was collimated through a 5 mm. diameter hole and then into a 50 mm. diameter, very nearly parallel, beam which uniformly filled the reaction vessel. The intensity of the radiation was monitored by an electronic photometer unit utilizing a QVA39 quartz photocell as a light detector. The linearity of the response of this unit was checked occasionally and found to be good.

Perpropionic acid was estimated by the ferrous thiocyanate method, a Bausch and Lomb "Spectronic 20" absorptiometer being used to assess the intensity of the color developed by the various concentrations of peroxide. The absorptiometer was calibrated using a solution of perpropionic acid, the actual strength of which was determined iodometrically by the method of Sully (9).

The light intensity was estimated by measuring the amount of CO formed when gaseous acetone was illuminated under identical conditions to those prevailing during runs, at temperatures from 100° to 120° C. for a given length of time. The quantum yield of CO formation was found to be very nearly constant over the region 100–120° C. In calculating the intensity of our source, the quantum yield of CO from acetone was taken as being 1 (7). The estimated intensity may be in error owing to the fact that an unknown, but presumably appreciable, fraction of the light used was in the 3130–3300 Å region of the spectrum (owing to lack of sharpness of the filters and the continuous background delivered by the arc) and the precise CO quantum yield in this region is not known.

RESULTS

Initial runs showed that the main product of the reaction was perpropionic acid, with a quantum yield proportional to the square root of the absorbed intensity, $I_a^{\frac{1}{2}}$, and of the order of 50 for a medium intensity. The oxygen uptake was found to be equal to the perpropionic acid formation within experimental error. A complete analysis of the products was not carried out, but CO_2 and CO were formed in approximately equal amounts with a quantum yield of the order of 1. A very small quantity of ethane was formed, but the quantum yield was not estimated.

The reaction rate was estimated by measuring the amount of peracid formed in a given time. In all runs, except those for the determination of CO_2 and CO formation and O_2 uptake, the reaction was confined to $<0.5\%$ conversion of aldehyde.

There was found to be no measurable thermal reaction at all in a range from 20° to 40° C. and the absence of this was frequently checked. However, after about 70 runs, quite suddenly an appreciable thermal reaction became apparent and built up to a rate which was about 2% of the photochemical rate. This was only appreciable because the reactants were allowed to mix for 1 hour prior to photolysis. When the cell was removed, cleaned, and replaced, no thermal reaction took place.

No cell aging effect was noticed and runs were generally reproducible within $\pm 7\%$. A colorless, transparent polymeric substance of unknown composition was gradually deposited upon the cell walls. On being heated to 300° C. the polymer did not simply decompose and evaporate, but charred. When propionaldehyde is photolyzed, a certain amount of polymerization does take place (6); hence the polymer on the wall may be polypropionaldehyde with physically absorbed reaction products, or a polyoxypolymer formed by reaction of polypropionaldehyde with perpropionyl radicals.

Dependence of Rate of Reaction on Time

The rate of reaction remained constant up to a conversion of 0.7% of the aldehyde during a 10 minute run, indicating that there was no induction period or photochemical growth effect and no autocatalysis. See Fig. 1.

Later on in this study the apparent rate for certain runs of $<0.5\%$ conversion, but of longer duration than usual, was lower than had been anticipated. This was due to the slow decomposition or removal of perpropionic acid, and the rate of this reaction was therefore investigated.

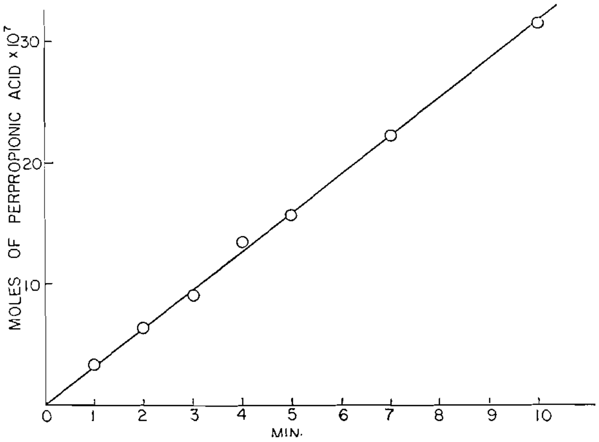

FIG. 1. Dependence of rate of photochemical oxidation of propionaldehyde on time.

Effect of Decomposition of Perpropionic Acid on Rate

The rate of peracid decomposition was not very reproducible, but it was found to be proportional to the concentration of the peracid within experimental error and roughly proportional to the reciprocal of the aldehyde pressure. It was initially thought that removal of peracid may have been due to the reaction

$$C_2H_5CO_3H + C_2H_5CHO = 2C_2H_5COOH$$

either homogeneously or at the wall, but this was obviated by the 1/[aldehyde] dependence of the rate. The rate is too slow for diffusion to be the rate-controlling step. A possible explanation is that the peracid is removed by physical absorption at the wall and the aldehyde deactivates absorption sites.

In a system where peracid is formed at a constant rate and is removed at a rate proportional to [peracid], then if P is the amount of peracid measured after t seconds, and P_1 is the amount of peracid that would have been formed in t seconds if the peracid was not being removed at all, then $P/P_1 = 1-e^{-k_p t}/k_p t$ where k_p is the rate constant of the removal step; hence the ratio of the measured rate of formation of peracid to the real rate of formation is a function of time only for a given k_p. The values of k_p were calculated for 100 mm. Hg and 35 mm. Hg of aldehyde, and the ratios P/P_1 were calculated for various times. The results are shown in Table I. The results are probably correct within ±20%.

TABLE I

EFFECT OF TIME ON RATIO OF OBSERVED RATE TO ACTUAL RATE

Time, min.	k_p, sec.$^{-1}$	P/P_1
1	0.0011	1.00
10	0.0011	0.97
30	0.0011	0.91
60	0.0011	0.80
1	0.0023	0.99
10	0.0023	0.92
30	0.0023	0.79
60	0.0023	0.68

It is seen that the error, due to removal of peracid, in the measured rate for a 10 minute run with 100 mm. aldehyde, is about 2%; hence the only runs in this study which require correction in this respect are runs 53, 54, and 60.

Dependence of Rate of Reaction on Intensity of Absorbed Radiation

The dependence of the rate of oxidation on the light intensity was studied over a 10,000-fold range of absorbed intensity for a mixture of 100 mm. Hg of propionaldehyde and 3 mm. of O_2. It was found that over a range of I_a from 10^{-10} to 2.5×10^{-8} einstein l.$^{-1}$ sec.$^{-1}$ the rate was accurately proportional to $I_a^{\frac{1}{2}}$, but at $I_a < 10^{-10}$ einstein l.$^{-1}$ sec.$^{-1}$ this $I_a^{\frac{1}{2}}$ dependence falls off. The results are shown in Fig. 2 and Table II.

Dependence of Rate of Reaction on Pressure of Propionaldehyde

The dependence of the rate on the aldehyde pressure was studied by maintaining the oxygen pressure at 3 mm. Hg and varying the aldehyde pressure from 10 to 200 mm. Hg. As the aldehyde pressure was varied, the absorbed intensity also varied, so all these runs were carried out in the intensity region where rate is accurately proportional to $I_a^{\frac{1}{2}}$, and the tabulated results are corrected to 100% absorption of a given constant intensity (Table III). The plot of rate against aldehyde pressure was a straight line passing through

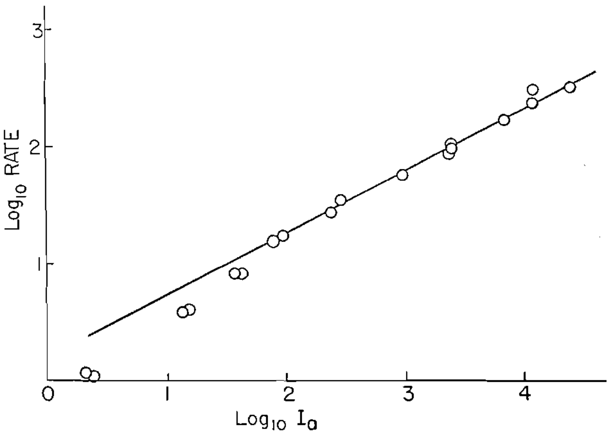

FIG. 2. Dependence of rate of photochemical oxidation of propionaldehyde on intensity of absorbed radiation.

TABLE II

DEPENDENCE OF RATE ON ABSORBED INTENSITY

These experiments were all carried out with a mixture of 100 mm. Hg of propionaldehyde, 3 mm. Hg oxygen, and at 23° C.

Run No.	I_a, ein. $l.^{-1}$ $sec.^{-1}$ $\times 10^{+12}$	Rate, mole $l.^{-1}$ $sec.^{-1}$ $\times 10^{+9}$
32	2.39×10^3	8.32×10
33	2.42×10^4	2.50×10^2
34	9.34×10^2	4.48×10
35	2.32×10^2	2.14×10
36	4.20×10	6.40
37	1.35×10	3.07
38	1.18×10^4	2.40×10^2
39	2.37×10^3	7.68×10
40	6.76×10^3	1.31×10^2
41	2.35×10^3	7.04×10
42	2.82×10^2	2.78×10
43	8.01×10	1.25×10
44	2.06	0.93
45	1.53×10	3.20
46	2.32	0.82
47	9.25×10	1.34×10
48	3.73×10	6.60
49	1.18×10^4	1.86×10^2
50	2.29×10^3	8.00×10

the origin, Fig. 3, but the apparent rates for low aldehyde pressure runs fall well below the straight line. This is probably due to the peracid removal step mentioned earlier, and if a correction is applied, these points fit more closely to the line.

Dependence of the Rate of Reaction on Pressure of Oxygen

The rate of oxidation was found to be independent of oxygen pressure over a range of 0.3–100 mm. Hg, in a system in which the aldehyde pressure and I_a were maintained constant. The results are shown in Table IV.

Over-all Activation Energy

In Table V are given the values of the over-all rate of the reaction at observed different temperatures for a mixture containing 3 mm. of oxygen and 5.87×10^{-3} mole $l.^{-1}$ of

TABLE III

DEPENDENCE OF RATE ON PRESSURE OF PROPIONALDEHYDE

These experiments were carried out at 23° C. with a mixture of 3.0 mm. Hg of oxygen, and the rates were corrected to an I_a of 2.14×10^{-9} einstein $l.^{-1}$ $sec.^{-1}$

Run No.	Aldehyde pressure, mm. Hg	Rate, mole $l.^{-1}$ $sec.^{-1}$ $\times 10^{+8}$
51	33	3.68
52	70	8.0
53	22.5	2.24*
54	16.2	1.84*
55	100	13.2
56	200	26.7
57	41.5	5.6
58	100	13.3
59	150	20.3
60	10	1.11*

**These experiments corrected for decomposition of perpropionic acid as they exceeded 12 minutes in duration.*

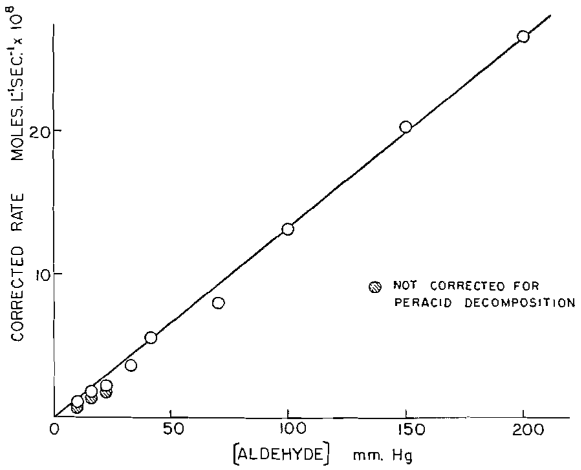

FIG. 3. Dependence of rate of photochemical oxidation of propionaldehyde on pressure of aldehyde.

TABLE IV

DEPENDENCE OF RATE ON OXYGEN PRESSURE

All experiments carried out on a mixture of 100 mm. Hg of aldehyde at 22° C., and at an I_a of 2.14×10^{-9} einstein $l.^{-1}$ $sec.^{-1}$

Run No.	Oxygen, mm. Hg	Rate, mole $l.^{-1}$ $sec.^{-1}$ $\times 10^{8}$
25	10	9.6
26	40	10.4
27	2	12.0
28	0.36	10.9
29	100	9.3
30	5	9.6
31	10	8.5

TABLE V

DEPENDENCE OF RATE ON TEMPERATURE

All experiments carried out with a mixture of 3 mm. Hg of oxygen, 5.87×10^{-3} mole $l.^{-1}$ of propionaldehyde, and at an I_a of 1.11×10^{-9} einstein $l.^{-1}$ $sec.^{-1}$

Run No.	Temp., ° C	Rate, mole $l.^{-1}$ $sec.^{-1}\times10^{8}$
129	19.5	5.28
130	22.6	6.08
131	27.0	8.00
132	37.5	10.6
133	21.3	6.56
134	20.0	5.92
135	39.0	11.7
136	46.5	15.0
137	34.0	9.60
138	19.5	5.75

propionaldehyde. These experiments were performed using a value of I_a of 1.11×10^{-9} einstein $l.^{-1}$ $sec.^{-1}$.

These data have been plotted in Fig. 4. From these data we have calculated by the method of least squares that the activation energy for the photooxidation of propionaldehyde is 6.75 (±0.5) kilocalories $mole^{-1}$.

DISCUSSION

The above experimental results indicate that the gas-phase photooxidation of propionaldehyde at about 23° C. is a chain process and the initial stage is governed by the kinetic equation

$$d[C_2H_5CO_3H]/dt = kI_a^{\frac{1}{2}}[C_2H_5CHO]^1[O_2]^0.$$

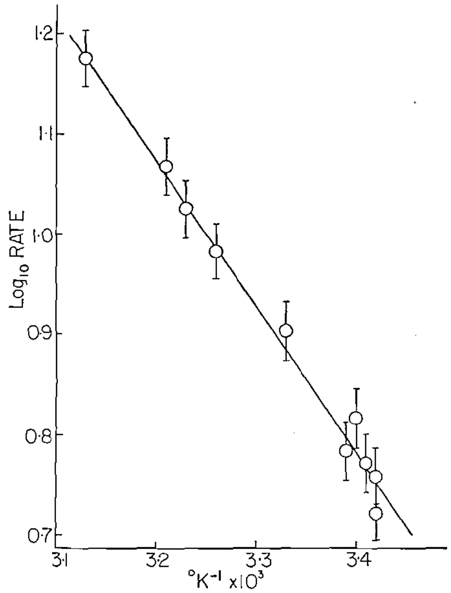

FIG. 4. Activation energy curve for the photochemical oxidation of propionaldehyde.

At low intensities this expression ceases to apply because the $I_a^{\frac{1}{2}}$ dependence falls off. Also in later stages of the oxidation, removal of the peracid becomes a significant part of the process. The $I_a^{\frac{1}{2}}$ dependence is undoubtedly due to a radical initiation process which is proportional to I_a and a chain termination process which is bimolecular. Deviation from $I_a^{\frac{1}{2}}$ dependence at low intensities indicates that the termination process is no longer solely bimolecular, but that a first-order termination starts to become important. Such a first order termination could be at the wall; which is inherently feasible, because the concentration of radicals at low I_a is small, and hence the bimolecular termination would be similarly small, thus giving radicals more chance to reach the wall.

The too low rates observed for runs at low aldehyde concentration may be due entirely to the removal of peracid at the wall, but even when a correction is applied, these rates are still somewhat low. There are two possible explanations which could account for this. At low concentrations of aldehyde and consequent low absorbed intensities, the rate of initiation of chain propagating radicals may have an aldehyde pressure dependence if there is a possible fate of the radical R other than reacting with aldehyde to yield C_2H_5CO. The radical R could react at the wall, and if it did, the wall reaction would be favored by low aldehyde pressure and low intensity, and hence under these conditions the rate would be reduced. The other possible explanation is that at low aldehyde pressure and low intensity, first-order termination of propagating radicals at the wall may become appreciable, thus reducing the observed rate.

The photolysis of propionaldehyde at a wavelength of 3130 Å has been studied by several workers (3, 5, 6). A recent detailed investigation has been made by Blacet and Pitts (1). These authors conclude that there are four separate primary processes involved:

$$C_2H_5CHO + h\nu = \left|\begin{array}{ll} \longrightarrow C_2H_5 + CHO & \text{(i)} \\ \longrightarrow C_2H_6 + CO & \text{(ii)} \\ \longrightarrow C_2H_4 + HCHO & \text{(iii)} \\ \longrightarrow CH_3 + CH_2CHO & \text{(iv)} \end{array}\right.$$

From this work it is apparent that the ratio of the primary process (ii) to primary process (i) at 3130 Å is 0.046. This result and most of the conclusions of Blacet and Pitts are based on experiments performed on mixtures of propionaldehyde and iodine. There have been some doubts expressed (see preceding paper, Part I) about the validity of some of the deductions regarding free radical mechanisms based on the use of iodine "to fix" the radical. It is to be expected that at 3130 Å propionaldehyde will form several excited states, and only some of these may dissociate to form free radicals. Further, the presence of iodine will undoubtedly quench some of these excited states of propionaldehyde by energy transfer processes (see Part I).

Our view is that it is best to regard the photolysis of propionaldehyde–oxygen mixtures as following the same processes as suggested in Part I for the case of acetaldehyde–oxygen mixtures. Namely, that the primary process (i) will undoubtedly occur, but that excited states of propionaldehyde will be formed. Some of these will undoubtedly be quenched by the oxygen, but some may react with oxygen molecules to form free radicals which should be capable of initiating the propionaldehyde oxidation chain. Thus we think that the photochemical oxidation of propionaldehyde, since it evidently obeys the same kinetic law as that of acetaldehyde as shown by our experiments, should also follow the same mechanism.

It is, therefore, assumed that the photochemical oxidation of propionaldehyde is initiated by one, or both, of the following processes:

(1) By the absorption of a quantum of radiation of wavelength 3130 Å, the primary process (i) occurs even in the presence of oxygen,

$$C_2H_5CHO \underset{3130\,\text{Å}}{\overset{h\nu}{=}} C_2H_5 + CHO. \qquad [1a]$$

These two radicals can then react with oxygen as follows:

$$\left.\begin{array}{c} C_2H_5 \\ CHO \end{array}\right\} + O_2 = R. \qquad [1d]$$

The radical R can then abstract a hydrogen atom from propionaldehyde to form a propionyl radical, C_2H_5CO, which is regarded as being the initiation of the oxidation chain (4).

(2) Besides primary process (i) occurring, it is possible that excited states are also formed when propionaldehyde absorbs radiation of wavelength 3130 Å (equation [1*c*]). One or more of these excited states may react with oxygen molecules to form propionyl radicals as indicated in equation [1*f*] where in both [1*c*] and [1*f*] the excited states of propionaldehyde are denoted simply as $C_2H_5CHO^*$:

$$C_2H_5CHO \underset{3130\,\text{Å}}{\overset{h\nu}{=}} C_2H_5CHO^*, \qquad [1c]$$

$$C_2H_5CHO^* + O_2 = C_2H_5CO + HO_2. \qquad [1f]$$

The succeeding steps in the mechanism of the photooxidation of propionaldehyde at low temperatures are regarded as being analogous to those shown (Part I) to lead, on the application of the stationary state hypothesis, to a satisfactory explanation of the kinetics of the photochemical oxidation of acetaldehyde:†

$$C_2H_5CO + O_2 = C_2H_5CO_3 \qquad [2]$$

$$C_2H_5CO_3 + C_2H_2CHO = C_2H_5CO_3H + C_2H_5CO \qquad [3]$$

$$2C_2H_5CO = (C_2H_5CO)_2 \qquad [4]$$

$$C_2H_5CO_3 + C_2H_5CO = (C_2H_5CO)_2O_2 \qquad [5]$$

$$2C_2H_5CO_3 = (C_2H_5CO)_2O_2 + O_2 \qquad [6]$$

The application of the stationary state treatment to the above mechanism leads to the equation [A], when it is assumed (see Part I) that $k_3[C_2H_5CHO]/k_2[O_2] \ll 1$, which is likely to be the case in our experiments,

$$d[C_2H_5CO_3H]/dt = (k_3/k_6^{\frac{1}{2}})(\phi_2 I_a)^{\frac{1}{2}}[C_2H_5CHO]. \qquad [A]$$

Equation [A] agrees with the experimentally determined kinetic equation for the photochemical oxidation of propionaldehyde.

It follows from the above results and equation [A] that the over-all activation energy $E = E_3 - \frac{1}{2}E_6$. E_6, which is the activation energy for the mutual interaction of perpropionic radicals, is likely to be zero. Thus the value which we obtained for the over-all activation energy, namely 6.75 (±0.5) kilocalories mole.$^{-1}$, must equal E_3. There are no reliable values for the reaction analogous to [3] but involving the ethyl radical. Comparison of the value of E_3 for the abstraction of a hydrogen atom from propionaldehyde by

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†*From the data given in the following paper (Part III) we calculate* $\phi \approx 1.6$. *Blacet and Pitts (1) found* $\phi_{C_2H_5I}$ *and* ϕ_{HI} *in their experiments on propionaldehyde–iodine mixtures to be* ≈ 0.45. *Since we regard both the* C_2H_5 *and* HCO *radicals as being capable of reacting with oxygen to form a radical which can abstract a hydrogen atom from propionaldehyde to form a propionyl radical it follows that the portion of the quantum yield* ϕ_2 *which arises from the reaction of excited states of propionaldehyde [1f] is approximately 1.6 − 0.9 = 0.7.*

the perpropionic radical with those found for the corresponding metathetical reactions with methyl (7.5±0.3 kilocalories mole^{-1}) and peracetic (7.16±1.0 kilocalories mole^{-1}) radical shows that it is a realistic value.

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