THE PHOTOCHEMISTRY OF ALDEHYDES
IN THE GASEOUS PHASE

by

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ABSTRACT

The object of the present work was the investigation of two separate topics, the investigation of the radical-radical termination step in the photochemical oxidation of acetaldehyde and the investigation of the photolysis of crotonaldehyde, both in the gas phase and at room temperature. A third topic, the photolysis of 3-butene-1-al, was investigated in the course of the work, in order to provide evidence in favour of the mechanism proposed for the photolysis of crotonaldehyde.

In the first part of the work, mixtures of acetaldehyde and isotopically enriched oxygen containing argon as a reference gas were irradiated at 25°C with light at a wavelength of 3130 Å and the reaction products were analyzed by gas chromatography and mass spectrometry. The major products were found to be peracetic acid and diacetyl peroxide. By following the rate of formation of these products, as well as the concentrations of the three possible kinds of oxygen in the reaction mixture, it was possible to verify McDowell and Farmer's mechanism for the photooxidation of acetaldehyde and establish a satisfactory mechanism for the chain terminating step of the reaction.

In the second part of the work, crotonaldehyde was irradiated at 30°C with light at a wavelength of 2450-4000 Å, and the products analyzed by gas chromatography and
infra-red spectroscopy. The only product in experiments of short duration was found to be 3-butene-1-al, thus establishing isomerization as the primary process of the reaction. In later stages CO, propylene and 1,5-hexadiene were formed. The following experimental laws were found to hold for the rate of formation of these products:

\[
\frac{d(3\text{-butene-1-al})}{dt} = \Phi \, I_{\text{abs}}, \quad \Phi = 0.095 \pm 0.005 \\
\frac{d(1,5\text{-hexadiene})}{dt} \sim \frac{I_{\text{abs}}}{(\text{crotonaldehyde})} \\
\frac{d(\text{propylene})}{dt} \sim \left( \frac{I_{\text{abs}}}{(\text{crotonaldehyde})} \right)^{1.3-1.5}
\]

No detailed law was established for the rate of formation of CO, but whenever measured, it was found to follow closely the propylene formation.

These experimental laws were interpreted by means of a mechanism, in which crotonaldehyde participates in so far as it isomerizes to 3-butene-1-al. The latter was assumed to yield the three other products of the reaction through a mixed radical-molecular photochemical dissociation.

Evidence was provided in favour of the proposed mechanism by studying the photolysis of 3-butene-1-al at 30°C and a wavelength of 2450-4000 Å. The products of the reaction were found to be propylene, 1,5-hexadiene and CO, with their rates of formation obeying the following laws:

\[
\frac{d(1,5\text{-hexadiene})}{dt} = \Phi_{\text{hexad}} \cdot I_{\text{abs}}, \quad \Phi_{\text{hexad}} = 0.135 \pm 0.028
\]
\[
\frac{d(\text{propylene})}{dt} = \Phi_{\text{prop}} \cdot I_{\text{abs}} \quad , \quad \Phi_{\text{prop}} = 0.79 \pm 0.05
\]

CO formation was found to be approximately equal to propylene formation.

These experimental laws were interpreted by means of a mixed radical-molecular photochemical dissociation of 3-butene-1-al, thus justifying the mechanism proposed for the photolysis of crotonaldehyde.
The present work has been conducted under the supervision of Professor C.A. McDowell to whom I wish to express my gratitude for his lasting interest and enlightening discussions throughout the course of the work. I also wish to thank Dr. D.C. Frost for his helpful guidance in the part of this work connected with mass spectrometry.

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CHAPTER I.

INTRODUCTION
I. INTRODUCTION

1. PHOTOCHEMICAL OXIDATION OF ACETALDEHYDE

The interest of the research workers in the oxidation of lower aliphatic aldehydes is well understood if one remembers that they are among the most easily oxidized organic compounds known. This property makes their oxidation a reaction easily followed at comparatively low temperatures, where techniques are simple and side reactions easy to control.

It is important to investigate the mode of oxidation of aldehydes because there is strong evidence that they are formed as intermediates during the oxidation of hydrocarbons. Therefore an understanding of the elementary processes which occur in aldehyde oxidations will probably make possible an interpretation of the results in the more complicated hydrocarbon oxidations.

That aldehydes play a part during hydrocarbon oxidations was noticed as early as 1930 by Bone et al (1,2) and Naylor and Wheeler (3). Their effect of reducing the induction period of these reactions was studied and many imaginative mechanisms were postulated over the years to explain this effect as well as their formation during the reaction. Norrish (4) postulated that aldehydes arise
through -OH attack on the hydrocarbons, although he did not propose a precise mechanism for their participation in the reaction.

Even if the part played by aldehydes in hydrocarbon oxidations is not completely understood, it is clear that investigation of aldehyde oxidations may be proved helpful in elucidating certain aspects of these complicated reactions, e.g. by evaluating rate constants and activation energies of elementary processes. The easiest way to obtain reliable data of this nature is by running the oxidation in the gas phase, and at low temperatures, where complicating factors such as uneven distribution of oxygen, and reactions between products and first material are minimized. The aldehyde most thoroughly investigated in this respect is acetaldehyde. A low boiling liquid, it can attain considerable pressure at room temperature, a fact which is a distinct advantage in relation with the high boiling aldehydes. Moreover, it can undergo oxidation without polymerizing, as the case is with formaldehyde. These merits have been fully recognized by research workers, as a short review of the work done on acetaldehyde oxidation will show.

In 1930, Bowen and Teitz (5) studied the photochemically initiated oxidation at 20°C. They found peroxides to be the main reaction products and measured the rate of the reaction by iodometrically estimating them. Their data
showed that the rate was directly proportional to the aldehyde concentration and square root of the absorbed illumination, and independent of the oxygen concentration. However the study was not a rigorous one, because no correction was made for the variation of the absorbed light at different aldehyde pressures and the lowest oxygen pressure used was approximately one quarter of an atmosphere. They presented evidence that diacetyl peroxide was the major peroxide formed, along with some peracetic acid, and interpreted their results by means of a mechanism involving activated molecules.

In 1931, Bodenstein (6) investigated the thermal oxidation at 60-90°C and found peracetic acid as the principal product. Its rate of formation was proportional to the square of the aldehyde concentration and inversely proportional to the oxygen concentration. He suggested a mechanism based on activated molecules. Later, Hatcher et al (7) and Pease (8) showed again that peracetic acid was the primary product, but that the rate was proportional to the square of the aldehyde concentration and independent of the oxygen concentration. They proposed various activated molecule mechanisms to explain the results. At about the same time, Semenoff (9) reviewed the reaction and showed that the experimental facts could be explained if it was assumed that an initial reaction product decomposed to give chain branching and that termination was due to interaction
of two chain propagating radicals.

In 1936, Carruthers and Norrish (10) made a brief study of the photochemical oxidation at 30°C. The oxidation was taken to completion. The gaseous products were CO, CH₄, H₂ and C₂H₄ and condensed products were mainly peroxides. The peroxide was assumed to be diacetyl peroxide because the ratio of aldehyde to oxygen used up was 1:0.7. The rate of the reaction was measured by oxygen uptake. No mechanism was proposed.

In 1941, Mignolet (11) studied the photochemical oxidation at 35°C and measured the rate by following overall pressure change. He found that the rate was proportional to \( I_{\text{abs}}^{\frac{1}{2}} \), \( \text{Ald}^2 \) and \( O_2 \) and concluded that the primary oxidation product was diacetyl peroxide.

It was not until McDowell and co-workers reinvestigated both the thermal and photochemical oxidation that a satisfactory mechanism was postulated. In 1949, McDowell and Thomas (12) made a rigorous investigation of the thermal oxidation and proved unambiguously what earlier workers had observed, namely, that peracid was formed via a chain at a rate independent of oxygen concentration and proportional to the square of the aldehyde concentration. For the first time a radical chain mechanism was proposed to interpret the results. The mechanism was as follows:
This mechanism explained most of the experimental results, but it was still not quite satisfactory, due to the unlikely termination step. Also, it did not quite explain why the rate of the aldehyde oxidation remains almost constant after a considerable amount of it was already consumed. Niclaeuse (13) suggested a branching chain step, but it did not agree with the experimental results.

Finally, McDowell and Farmer (14) explained the data convincingly by suggesting that the branching step was unimolecular decomposition of peracetic acid and chain termination was by radical-radical disproportionation, as follows:

\[
\begin{align*}
\text{CH}_3\text{CHO} + O_2 & \rightarrow \text{CH}_3\text{CO}^\cdot + \text{HO}_2^\cdot \\
\text{CH}_3\text{CO}^\cdot + O_2 & \rightarrow \text{CH}_3\text{CO}_2^* \\
\text{CH}_3\text{CO}_2^* + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}^\cdot \\
\text{CH}_3\text{CO}_2\text{H} & \rightarrow \text{CH}_3\text{CO}_2^* + \text{OH}^* \\
2\text{CH}_3\text{CO}_2^* & \rightarrow (\text{CH}_3\text{CO})_2\text{O}_2 + O_2
\end{align*}
\]

This mechanism explained fully the results and agreed with the views that Semenoff (9) had expressed many years earlier. In the same work (14) they investigated the photochemical oxidation using modern techniques at 20°C. Peracetic acid was measured by the ferrous thiocyanate method, and the rate, when only a small percentage of the reactants was consumed,
was found to be accurately proportional to the concentration of the aldehyde and the square root of the intensity of the absorbed illumination, being independent of the oxygen concentration. Essentially the same mechanism proposed for the thermal oxidation was used to explain the results, except that the initiation step was altered to take account of the illumination and the branching step omitted because the experimental conditions rendered it negligible. The whole mechanism was as follows:

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{hv} & \rightarrow \text{CH}_3\cdot + \text{CHO}\cdot \\
\text{CH}_3\cdot + \text{O}_2 & \rightarrow \text{R}.
\end{align*}
\]

\[
\begin{align*}
\text{CHO}\cdot + \text{O}_2 & \rightarrow \text{R}.
\end{align*}
\]

\[
\begin{align*}
\text{R} \cdot + \text{CH}_3\text{CHO} & \rightarrow \text{RH} + \text{CH}_3\text{CO}.
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CO} \cdot + \text{O}_2 & \rightarrow \text{CH}_3\text{CO}_2\cdot
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CO}_2\cdot + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}.
\end{align*}
\]

\[
\begin{align*}
2 \text{CH}_3\text{CO}_3\cdot & \rightarrow (\text{CH}_3\text{CO})_2\text{O}_2 + \text{O}_2
\end{align*}
\]

Application of the stationary state hypothesis to the above scheme gave the expression

\[
\frac{d(\text{CH}_3\text{CO}_3\text{H})}{dt} = \frac{K_{III}}{K_{IV}}(\Phi_{IL})^{1/2}(\text{CH}_3\text{CHO})
\]

which agreed well with the experimental results.

McDowell and Farmer's conclusions were substantiated by subsequent work. Hanst et al (15) provided favorable evidence by studying the ozone initiated oxidation of acetaldehyde. And McDowell and Sherples (16,17,18,19) investigated once more the photochemical reaction, along with that of prop-
ionaldehyde and confirmed the results over a wide range of experimental conditions. By using the intermittent illumination technique, they were able to estimate the absolute values for the propagating and terminating steps in the photooxidation for both aldehydes. They also computed the activation energy for the propagation step.

The above review on the gas phase oxidation of acetalddehyde shows quite well that the reaction was almost completely understood when the present research was undertaken. McDowell and Farmer's mechanism had been repeatedly tested and proved correct. There were, however, some aspects of this mechanism which needed further elucidation. One was due to the fact that the two peroxides formed in the reaction, peracetic acid and diacetyl peroxide, could not be characterized and determined with accuracy in presence of each other with the analytical means available at the time. Earlier workers relied on simple titrations to estimate the amount of each peroxide. This led, for a time, to confusion, as it can be seen from the fact that half of the early workers maintained that peracetic acid was the main peroxide while the other half maintained that diacetyl peroxide was. McDowell and Farmer's mechanism showed how both the peroxides could be formed and implied that the ratio (diacetyl peroxide/peracetic acid) would be directly proportional to the square root of the intensity of the absorbed illumination.

The presence of diacetyl peroxide in the reaction products
was confirmed by paper chromatographic methods. However, no unambiguous proof of the postulate was possible because of the uncertainty inherent in the analytical method.

It was, therefore, an object of the present work to reinvestigate the low temperature photochemical oxidation of acetaldehyde and estimate the rate of formation of both peroxides. It was hoped that modern techniques of analysis, especially gas chromatography, would make the fulfilment of this aim possible.

Another aspect of McDowell and Farmer's mechanism which needed further investigation was the radical-radical termination step. It will be recalled that this step is the following:

\[
2\text{CH}_3\text{CO}_3^- \rightarrow (\text{CH}_3\text{CO})_2\text{O}_2 + \text{O}_2
\]

There are two obvious ways by which this reaction can take place. One possibility is that the oxygen molecule which is formed is produced by elimination of an oxygen atom from each of the interacting radicals, according to the scheme:

\[
2\text{CH}_3\text{CO}_3^- \rightarrow \text{CH}_3\text{C}_2\text{O}_3^- \rightarrow \text{CH}_3\text{C}_3\text{O}_2 + \text{O}_2
\]

The other possibility is that the oxygen atom which is eliminated comes wholly from one of the interacting radicals. This could be understood if the mechanism were the following:

\[
2\text{CH}_3\text{CO}_3^- \rightarrow \text{CH}_3\text{C}_2\text{O}_3^- \rightarrow \text{CH}_3\text{C}_3\text{O}_2 + \text{O}_2
\]
McDowell and Sharples (18) envisioned these two possibilities and suggested that use of isotopically enriched oxygen might enable the chemistry of the process to be elucidated.

It was another object of the work described here to carry out such experiments, in the hope that these fine details of a well established mechanism would be understood.

2. PHOTOLYSIS OF CROTONALDEHYDE

Whereas acetaldehyde oxidation in the gas phase has been so widely investigated, very little work has been done on higher aldehydes, with the exception of propionaldehyde. This is due mainly to the fact that higher aldehydes have too small vapour pressures to be studied conveniently at lower temperatures. However such studies could be of value in understanding certain aspects of hydrocarbon oxidation, because there is evidence of the existence of higher aldehydes in the cool flames in the ignition of higher hydrocarbons. Crotonaldehyde in particular has been detected in the cool flames of butene (20), pentane (21), and four isomeric hexanes (22). Various imaginative mechanisms have been proposed for its appearance but without real substantiation.

The work done on gaseous crotonaldehyde oxidation and decomposition, both photochemical and thermal, can be summarized as follows.
In 1936, Blacet and Roof (23) studied the photolysis of gaseous crotonaldehyde at 30°C at seven wavelengths, ranging from 3660 to 2399 Å and found no detectable decomposition. The only alteration which they were able to observe was polymerization at 3660 Å with a quantum yield 0.02 based on the number of molecules disappearing from the gaseous phase per quantum of light absorbed. They proposed a predominating reverse reaction of the type

$$\text{CH}_3\text{CH:CHCHO} \rightleftharpoons \text{CH}_3\text{CH:CH- + CHO}.$$ 

to account for the fact that no products were detected even in the region of the light where absorption of illumination by crotonaldehyde is apparently continuous. In the same work they recorded briefly that oxidation of crotonaldehyde by oxygen does not proceed at a measurable rate in the dark, but it is accelerated by light.

At the same time, DeLisle et al (24) studied the thermal decomposition at 430-482°C and found 60 and a mixture of hydrocarbons, mostly propylene, to be the main products. The reaction was heterogeneous and in general of the second order. No mechanism was proposed.

Three years later Blacet and his co-workers studied the photolysis at elevated temperatures (25) and the photochemical oxidation at 30°C (26). In the photolysis at 150-400°C the main products were found to be 60% CO, 27% unsaturated hydrocarbons, 6% hydrogen and 7% methane. The rate of decomposition increased with increase in temperature and decrease
in wavelength. No mechanism was proposed. In the same work they studied briefly the thermal decomposition and found that it is not appreciable below 150°C and very slow below 275°C. At higher temperatures they confirmed the results found by DeLisle et al (24). In the photochemical oxidation at 30°C they followed the course of the reaction by recording pressure decrease and postulated that the solid accumulated in the cell during reaction was crotonic acid. They suggested that the overall reaction is

$$2\text{CH}_3\text{CH:CH:CHO} + \text{O}_2 \rightarrow 2\text{CH}_3\text{CH:CHCOOH}$$

but also noticed the possibility of a chain mechanism, because the quantum yield could be as high as 3.2 under certain circumstances. Introduction of nitrogen caused a marked decrease of quantum yield, therefore they concluded that reaction takes place mainly through activated molecules. Later Volman et al (27) used the mirror technique and detected free radicals in illuminated crotonaldehyde. They suggested that a rupture of the type

$$\text{(CH}_3\text{CH:CHCHO) +} \rightarrow \text{CH}_3\text{CH:CH· CHO·}$$

must occur too.

In recent years Tosberg and Pitts (28) reinvestigated the high temperature photolysis of crotonaldehyde and in general confirmed the results found by Blacer et al (25). They identified the unsaturated hydrocarbon as being mainly but-2-ene and suggested that it was formed through a radical
displacement process:

\[ \text{CH}_3^+ + \text{CH}_3\text{CH:CHCHO} \rightarrow \text{CH}_3\text{CH:CHCH}_3 + \text{CHO}^+ \]

Harrison and Lossing (29) studied the mercury-photosensitized low temperature decomposition, in an effort to define the primary process taking place in crotonaldehyde photolysis. They used a mass spectrometer to follow the reaction products which were mainly CO and propylene. Added methyl radicals, CH\(_3^+\), showed that a radical splitting was not sufficient to account for the amount of products formed. They concluded that the main process taking place was molecular rearrangement to CO and propylene, accompanied by some radical splitting, as follows:

\[ \begin{align*}
\text{CH}_3\text{CH:CH}_2 + \text{CO} + \text{Hg} & : \text{main process} \\
\text{CH}_2\text{CH:CHCHO} + \text{Hg}^* & \rightarrow \text{CH}_3\text{CH:CH}^+ + \text{CHO}^+ + \text{Hg} \quad \text{minor} \\
& \rightarrow \text{CH CH:CHCO}^+ + \text{H}^+ + \text{Hg} \quad \text{processes}
\end{align*} \]

Recently Osborne and Skirrow (30) reinvestigated the thermal oxidation using modern techniques of analysis to identify and determine the products. They found peroxycrotonic acid to be the main product at 166°C and adopted McDowell and Farmer's mechanism for the oxidation of acetaldehyde to explain the results. Above 200°C the peracid was quickly decomposing and only low molecular weight fragments could be detected.

From the preceding survey it can be seen that the reactions taking place when crotonaldehyde, alone or in mixture with oxygen, is heated or illuminated, are far from
being unambiguously understood. The low temperature photolysis, which could provide information about the primary processes taking place without the latter being masked by secondary reactions, was abandoned early because the analytical tools available at the time made detection and determination of any products impossible. In Harrison and Lossing's work (29) it was possible to gather evidence in favour of a primary process, but, unfortunately, no kinetic study of the reaction was undertaken to confirm the proposed scheme.

It was, therefore, an object of the present work to reinvestigate the low temperature photolysis of crotonaldehyde, with the hope that modern techniques of analysis would make it possible to gather evidence for a convincing primary process.
CHAPTER II.

PREPARATION OF MATERIALS
II PREPARATION OF MATERIALS

1. ACETALDEHYDE

Acetaldehyde was purified gas-chromatographically by passing the commercial material through a 5 foot long column packed with dinonyl phthalate on firebrick. The carrier gas was helium. The apparatus was the same gas-chromatography unit used for the analysis of reaction mixture in the photo-chemical oxidation of acetaldehyde and it is described on page 26. A diagram is shown in Figure 2.

Before a run, the trap F, in which the purified acetaldehyde would be collected, was flamed and evacuated to better than $10^{-4}$ mm Hg for several hours. At the same time helium was passing at a slow rate through the dinonyl phthalate column, which was heated at 40°C, to ensure that no impurities from previous runs remained in the system. After this treatment the stopcocks leading to the vent and the vacuum line were both closed and the helium was allowed to pass through the trap F, which was at room temperature, and the bubbler to the atmosphere for one more hour. This ensured that no traces of oxygen were left in the trap. Then the flow of helium was adjusted by increasing the pressure to 4 psi and the current of the gas directed to the vent, after the trap was cut by means of the stopcock. The trap was then cooled to -78°C with dry ice and acetone.
Acetaldehyde was distilled into the cooled sampling trap D with the aid of the vacuum line. When approximately 2 ml were collected, the connection with the vacuum was closed, the trap surrounded with water at the temperature of 35°C and helium allowed to pass through it. It took less than half a minute for the acetaldehyde to evaporate completely. The recorder of the apparatus was watched, and when the peak corresponding to acetaldehyde appeared, the current of the gases was directed to the cooled trap F, where the aldehyde was retained. It was degassed by distilling it into trap G and back into trap F, each time rejecting approximately the first one tenth of the sample. The acetaldehyde purified in this way was kept at -78°C in trap F. It lasted, usually, for 5-6 experiments, then another sample was prepared.

To check for impurities, especially diacetyl peroxide which was found to occur in the commercial product, a small portion of each sample was analyzed by passing it through the analytical dinonyl phthalate column. No impurities were ever detected using the thermoconductivity detector of the apparatus.

2. OXYGEN

Cylinder oxygen was purified by liquifying and distilling it four times, each time rejecting approximately the last one tenth of the sample, and then distilling it into a 5
litre receiving flask.

3. OXYGEN-18

O\textsuperscript{18}, in the form of molecular oxygen, of 98.35 per cent purity was obtained from the Isotope Department, Weizmann Institute of Science, Rehovoth, Israel.

4. ARGON

Cylinder argon was used without further purification. No impurities could be detected in a mass spectogram.

5. OXYGEN-ARGON MIXTURE

Isotopically enriched oxygen was needed in order to study the radical-radical termination step in the photochemical oxidation of acetaldehyde. Argon was added to it so as to give a reference peak in the mass spectrometer. This mixture was prepared by allowing oxygen-18, argon and purified natural oxygen to expand successively in a 5 litre bulb measuring the total pressure after each gas entered the bulb. The pressures were 6.13, 11.13 and 117.5 mmHg respectively. Therefore the composition of the gas was \( O_{2}^{32} : O_{2}^{36} : \text{Argon} = 106.4 : 6.13 : 5.00 \).

Taking into account the fact that the \( O_{2}^{36} \) was 98.35\% pure and contained 0.497\% \( O^{17} \), and that the natural abundance of \( O^{18} \) in ordinary oxygen is 0.204\% (31), it can be
calculated that the real composition of the oxygen-argon mixture was $^{32}O_2 : ^{34}O_2 : ^{36}O_2 : \text{Argon} = 106 : 0.443 : 6.03 : 5.00$.

In deriving these numbers it was assumed that $^{18}O$ is statistically distributed with the other species in natural oxygen. The same assumption was made for $^{17}O$ in $^{36}O_2$.

6. PERACETIC ACID

Peracetic acid was prepared by the method of D'Ans and Frey (32) as modified by Greenspan (33). To 10 ml of glacial acetic acid, 0.11 ml of sulphuric acid were added under cooling with water at 20°C. After standing for 12 hours at 20°C the mixture contained 40-50% peracetic acid (33). A small amount of it, used for calibration of the chromatography apparatus, was purified gas chromatographically using a 2 foot long dinonyl phthalate column at 0°C. In order to inject the raw peroxide into the system, the heated sampler (D1) of the apparatus was used (Figure 2), which was suited for high boiling materials. In this case the sampler could not be heated higher than 35°C because of danger of explosion of the peracid, but even under these conditions enough peracid for calibration was prepared after two runs.

7. DIACETYL PEROXIDE

Diacetyl peroxide, in the form of 25 per cent solution in dimethyl phthalate, was obtained from Wallace and Tiernan Inc., Lucidol Division.
Small amounts of it, used for quantitative calibration of the gas chromatography system, were freed from the solvent by passing through the 2 foot dinonyl phthalate column at 0°C. In this case, too, the heated sampler D₁ was used.

8. LIGHT FILTER SOLUTIONS

The two light filter solutions used in the photooxidation of acetaldehyde were those recommended by Bäckström (34) to isolate a fairly narrow wavelength band close to 3130 Å mercury line.

Filter solution I comprised 46 grams of analytical reagent grade NiSO₄·6H₂O and 14 grams of analytical reagent grade CoSO₄·7H₂O dissolved in 100 ml of distilled water. This solution was stable to the action of light.

Filter solution II comprised 25 grams of analytical reagent grade potassium hydrogen phthalate dissolved in 500 ml of distilled water. This solution was not stable to the action of light.

9. CROTONALDEHYDE

Analytical reagent grade crotonaldehyde was purified gas chromatographically. Since the sample prepared in each run was enough for approximately fifteen experiments only, a comparatively large quantity (≈10 ml) was introduced into the sampler D₁. This amount lasted for 5-6 purifications. The same procedure was followed as in the preparation of
acetaldehyde, except that the dinonyl phthalate column was heated to 55°C. Under these conditions the purified crotonaldehyde showed only infinitesimal amounts of impurities (less than 0.02%) when analyzed gas-chromatographically using the ionization detector of the apparatus.

10. 3-BUTENE-1-AL

This isomer of crotonaldehyde was prepared by oxidizing the corresponding alcohol, 3-butene-1-ol, by chromic acid at low temperature. This method of oxidation is generally recommended when an unsaturated aldehyde is going to be prepared from the alcohol (35). The experimental details were the following: In a triple-necked 500 ml flask immersed in ice and salt, and equipped with thermometer, drop funnel and capillary, and connected to the vacuum line through a trap cooled at -78°C, a mixture of 12 ml H₂SO₄ and 40 ml distilled water was placed. After cooling to 0°C, 16 ml of 3-butene-1-ol were added. Then the pressure was reduced to 30-40 mmHg and a solution of 10.8 grams CrO₃ and 12 ml H₂SO₄ in 40 ml distilled water was added drop by drop in such a way that the temperature in the flask was maintained between 2° and 10°C. When all the chromic acid had been added (in about 25 minutes) the pressure was lowered to 10 mm Hg and the flask allowed to reach room temperature. The substance collected in the trap separated into two layers after being allowed to thaw. The upper layer was introduced
in the sampler $D_1$ and the mixture separated gas-chromatographically using the same 5 foot long dinonyl phthalate column as for crotonaldehyde but at 2 psi pressure and 40°C.

The main impurities in the reaction mixture were crotonaldehyde and acrolein. After passing through the column, acrolein was almost completely eliminated, but crotonaldehyde persisted. It seems that 3-butene-1-al cannot be freed completely from crotonaldehyde, because it isomerizes very easily to this aldehyde with the conjugated double bonds. Hoaglin et al. (36) noticed this instability when they tried to prepare 3-butene-1-al by hydrolyzing its ethyl acetal; they obtained crotonaldehyde instead. Also in the present work it was attempted at the beginning to oxidize 3-butene-1-ol to the aldehyde by the Oppenauer method using cinnamaldehyde as the oxygen donor. The final stage of this method involves heating to 130-140°C to decompose the aluminium alcoholate formed in earlier stages and distill the formed aldehyde. Again crotonaldehyde was obtained instead of 3-butene-1-al.

Therefore it is understandable that any method used for purification of 3-butene-1-al will fail to free it from a small amount of crotonaldehyde, unless it operates at very low temperature. Use of the dinonyl phthalate column for preparative purposes proved to be intolerably inefficient below 40°C. Analysis of the product purified under these conditions showed that it contained still 1% crotonaldehyde.
The 2,4-dinitrophenylhydrazone of the purified compound, after recrystallizing twice from alcohol, had a melting point of 175°C, in good agreement with the 177°C found by Shostakovskii et al (37).

11. PROPYLENE, CO and 1,5-HEXADIENE

These substances were needed for calibration of the chromatography system. Analytical reagent grade materials were used for this purpose without further purification.

12. SILVERING SOLUTIONS

Silvering solutions, used for preparation of neutral density filters, were prepared according to the procedure described by Strong (38) as follows:

Solution A was made by dissolving 5 grams of silver nitrate in 300 ml of water and adding ammonia until the silver oxide, precipitated at the beginning, had almost, but not completely, disappeared. The liquid was filtered and diluted with water up to 500 ml.

Solution B was made by dissolving 1 gram of silver nitrate in water, boiling the solution and then adding 0.83 grams of Rochelle salt. The boiling was continued until a gray precipitate was deposited. The solution was then filtered hot and diluted to 500 ml.

These solutions were stored in a dark place and used
whenever neutral density filters were needed. They could be used for one month.

13. ACTINOMETRIC SOLUTIONS

The only solution which needed special care in preparation was that of potassium ferrioxalate. Crystals of this complex salt were first prepared by mixing under vigorous stirring 3 volumes of 1.5 M $K_2C_2O_4$ and 1 volume of 1.5 M $FeCl_3$. The resulting salt was recrystallized three times from warm water and dried at 45°C. Under these conditions its composition was $K_3Fe(C_2O_4)_3\cdot3H_2O$ (39). A 6.006 M solution of the salt was prepared and stored in a dark-coloured bottle.

The other solutions used in actinometry were prepared by dissolving the analytical grade compounds in distilled water. They are described under "Actinometry" on page 71.
CHAPTER III.

MECHANISM OF THE TERMINATION STEP IN THE PHOTOOXIDATION
OF GASEOUS ACETALDEHYDE AT 25°C
III MECHANISM OF THE TERMINATION STEP IN THE
PHOTOOXIDATION OF GASEOUS ACETALDEHYDE AT 25°C.

1. APPARATUS

The Vacuum System

The vacuum system is shown in Figure 1. It was constructed of pyrex, apart from the reaction vessel which was constructed of quartz. All the stopcocks were lubricated with Apézon N grease.

The apparatus was evacuated to a one-stage mercury diffusion pump of conventional design, backed by a "Hyvac" rotary oil pump (not shown). A $P_2O_5$ trap was included.

The cold trap was demountable and liquid nitrogen was used always as refrigerant. Using this trap, the system could be evacuated to better than $10^{-4}$ mm Hg, as recorded by a McLeod manometer (not shown).

The quartz reaction vessel (A) was cylindrical with flat optical ends and was connected to the vacuum system by a quartz-to-pyrex graded seal. It was 10 cm long and had an illuminated volume of 73 ml. The narrow tubing between the cell and the stopcock had a volume of 2 ml and was not illuminated. The cell was in an alluminium-block furnace with quartz windows to permit the passage of ultra-violet light. The furnace was electrically heated by means of a coil.
Figure 1. High Vacuum Apparatus

Figure 1α. Spiral Gauge
supplied by a manually regulated "Variaoc" transformer. The temperature could be kept constant within 0.2°C.

The pressure of reactants to enter into the reaction vessel, if not greater than 89 mm Hg, was measured by means of a spiral gauge (B) linked with an optical lever system as shown in Figure 1a. With the gauge, pressures could be readily measured with 0.2 mm Hg accuracy. When a reactant pressure greater than 80 mm Hg was required, the spiral gauge was zeroed and the pressure was measured with the Hg manometer.

(C) was a five lt. bulb where oxygen was kept, (F) was a spiral trap where acetaldehyde was kept at -78°C. In the other trap, (G), various products could be isolated after being separated gas-chromatographically from the reaction mixture. Also it was used in pair with (F) to degas a sample of material purified gas-chromatographically.

After an experiment had been carried out, the products were allowed to expand into trap (D), which was cooled with liquid nitrogen. The condensable products were retained there and the gases toeplered tinto the calibrated volume (H). The condensable products could be analyzed at once, because trap (D) was, at the same time, the sampler of the gas chromatography apparatus. The gases could be compressed from (H) to either the gas chromatography sampler or a previously evacuated collecting bulb, fitted at (I), for further analysis.
The Gas Chromatography Apparatus

The gas chromatography apparatus was incorporated to the vacuum system and was constructed of pyrex, except for the metallic parts of the detector.

The carrier gas was helium. Before entering the system, it was freed from condensible impurities, mainly water, by passing through two cold traps. When the apparatus was used for analytical purposes, the traps were cooled with dry ice and acetone. Under these conditions small traces of water could be detected in the passing helium, which did not affect the analysis. When the apparatus was used to purify substances, e.g. acetaldehyde, the traps were cooled with liquid nitrogen. In this way no traces of water could be detected in the purified material. The pressure of helium was regulated by means of a pressure regulator (A) and its flow rate was read on the fluometer (B).

The sampler (D) of the apparatus was connected to the vacuum system through two taps. It was shaped in such a way, that it could be used as a trap for condensible materials. Also, it could be fed with gases by means of the Toepler pump. It was used in all the analytical uses of the apparatus, as well as when acetaldehyde was purified. For purification of high boiling materials, e.g. diacetyl peroxide, the sampler (D₁) was used. This sampler could be fed either by distilling into it the substance to be purified, or by means of a removable stopper. It was shaped in such a way, that
HEATING TAPE

Figure 2. Gas Chromatography Apparatus
the sample was subjected to heating only when it was forced
to the heated part of the sampler by helium bubbling through
it, retreating to the cold part below when helium stopped
passing.

The furnace (E) contained the chromatography column. It
was constructed of two pyrex tubes with internal diameters
3 and 5 cm. The thinner tube was fitted into the larger one
and it was wound with an electrically heated coil. The two
ends of the furnace were packed with glass wool. The temp-
erature was regulated by means of a "Variac" transformer
operated manually, and it could remain constant within 0.2°C.
The furnace was removable and could be replaced by a cooling
system (a one litre Dewar filled with ice). The column was
also removable.

Two columns were used regularly in this part of the
work. Both of them were packed with dinonyl phthalate coated
on firebrick, but they were differing in dimensions and
operating conditions. One was 2-foot long with internal diam-
eter of 3 mm. It was operated at 0°C and under a pressure
of 8 psi. The other was 5-foot long with internal diameter
of 6 mm and was used only for purifying materials. Its oper-
ating conditions varied according to the material to be
purified.

The detector (C) of the apparatus was a thermoconductiv-
ity detector. It was surrounded by electrically heated tape
supplied by a manually adjusted "Variac" transformer, and
was kept always at 40°C within 0.2°C. The electrical potential difference at the two resistors of the detector was recorded by the autographic recorder (H).

When the apparatus was used for analysis, the helium, after the detector, was driven to a vent through a restriction. In this way it was ensured that the pressure in the system was always greater than the atmospheric pressure and no back-diffusion of air was possible.

When a component of the reaction mixture was to be collected, or when a substance was to be purified, the vent was closed at the moment in which the peak corresponding to this substance was appearing and the stream directed through the cold traps (F) or (G).

The Optical System

The optical system is shown in Figure 3. The lamp (A) was a General Electric, water cooled, AH6 high pressure mercury arc with a housing designed to give a 3 mm diameter source. The position of lamp and quartz lenses was adjusted in such a way that a parallel light beam completely filled the reaction vessel. The quartz lenses after the cell, focussed the light onto the photocell (D).

The light intensity filters were silver semi-mirrors on quartz. They were prepared by a slow silvering process described by Strong (38) as follows. The quartz plate to be silvered was first cleaned by boiling with concentrated nitric acid, then thoroughly rinsed with water and distilled water
Figure 3. Optical System for Acetaldehyde Oxidation
Figure 4. Transmission of Combined Filter Solutions
and immediately covered with 40 ml each of silvering solutions A and B. After 5 to 15 minutes, the time depending on the thickness wished, the mirror was removed from the silvering mixture, washed successively with water, distilled water and acetone and dried.

(B) and (C) were quartz filter cells, 3 cm and 1 cm respectively. The first was containing filter solution I, the second, filter solution II. The spectrum of the filter solutions combination was measured against no blank in an automatic recording spectrophotometer. The spectrum is shown in Figure 4. It is seen that the combination has an absorption minimum at 3160 Å, therefore the wavelength used was the 3130 line.

The Photometer Unit

The circuit diagram of the photometer unit is shown in Figure 5. The photocell was in a quartz envelope designed for work in the ultra violet region. The output of the cell was accurately proportional to the illumination shone into it for the illumination intensities used in the experiments with acetaldehyde. The photocell current passed through the resistor chain $R_{1-4}$ and the required voltage was tapped off by the selector switch $S_1$. An opposing voltage was provided by the potentiometer circuit $B_1$ and $R_{5-12}$. $B_1$ was a 2 volt battery and the voltage tapped from the potentiometer was adjustable to any value between 0 and 2 volts with an ac-
Figure 5. Photometer Unit

**KEY:**

- **R1**: 2 volt accumulator.
- **R2**: 120 volt h.t. battery.
- **G**: Galvanometer.
- **S.C.**: Weston Standard Cell.
- **V**: 6SC7 valve.
- **R1**: 5M : h.s.c. : 1W.
- **R2**: 1.5M : h.s.c. : 1W.
- **R3**: 600k : h.s.c. : 1W.
- **R4**: 150k : h.s.c. : 1W.
- **R5,6**: 10k : dual decade: Muirhead.
- **R7,9**: 1k : " : "
- **R9,10**: 100 ohms : " : "
- **R11,12**: 10 ohms : " : "
- **R13**: 25k : w.w.
- **R14**: 2k : w.w.
- **R15**: 50k : w.w. : 1W.
- **R16**: 50k : w.w. : 1W.
- **R17**: 2.2k : w.w. : 1W.
- **R18**: 1W : w.w.
- **R19**: 100k : w.w. : 1W.
- **R20**: 33k : w.w. : 1W.
- **R21**: 10k : w.w. : 1W.
- **R22**: 3.3k : w.w. : 1W.
- **R23**: 1k : w.w. : 1W.
- **R24**: 330 ohms : w.w. : 1W.
- **R25**: 10k : w.w. : 1W.
accuracy of $2 \times 10^{-4}$ volts. The difference between the voltage tapped from the resistor chain $R_{14}$ and the opposing voltage from the potentiometer was applied to the double-triode amplifier valve $V$. The second triod unit compensated for supply voltage variation. The output of the amplifier was fed into the galvanometer, $G$, through the attenuator $R_{19-24}$. The high intensity for the unit was supplied by a 120 volt battery and the low intensity from a 6 volt transformer.

To take a photometric measurement the following procedure was followed. The circuit was switched on by closing switches $S_2$, $S_3$ and $S_4$ and allowed to warm for 15 minutes. With no light falling on the photocell and with the potentiometer reading zero, dark current from the photocell was balanced by adjusting $R_{13}$ and $R_{14}$ for zero galvanometer current. The circuit had to be rebalanced for each position of the selector switch $S_1$. To ensure that the battery, $B_1$, gave a constant voltage, switch $S_6$ was closed and the voltage from the standard cell (S.C.) was balanced by increasing the voltage of the potentiometer. A reading was taken which was the same every time that the operation was repeated. When the voltage of the battery had decreased, this reading was different and then the battery was recharged. Switch $S_6$ was then opened and light was allowed to fall on the photocell. The photocell current was balanced with the potentiometer and a reading taken. This reading was proportional to the light intensity.
Only position 4 of the switch $S_1$ was used throughout this part of the work. This was the less sensitive position and was quite suited for the light intensities used.

The photometer unit was used for monitoring the output of the mercury arc and measuring the percentage absorption of light by 150 mm Hg of acetaldehyde in the reaction vessel.

2. EXPERIMENTAL

**Determination of Percentage Absorption of Light by 150 mm Hg of Acetaldehyde at 3130 Å**

In all the experiments, 150 mm Hg of acetaldehyde were used; therefore it did not appear necessary to draw an absorption curve for a range of acetaldehyde pressures. Instead, three individual measurements of the light absorbed by 150 mm Hg of acetaldehyde were taken. These measurements were spaced one week apart from each other and all showed that 30 per cent of the light shone into the cell is absorbed by acetaldehyde. The agreement between the measurements was 0.5 per cent.

The following procedure was used. The AH6 lamp was switched on and allowed to warm for a few minutes, so that the variation in intensity was less than 1%. A suitable intensity was then selected and measured in ohms using the photometer unit. 150 mm Hg of acetaldehyde were measured quickly into the cell and the new light intensity measured.
Addition of oxygen had no effect on the absorption of light by acetaldehyde.

**Determination of Reaction Products**

It is well known (6,7,8,12) that peracetic acid is the main reaction product formed in the photochemical oxidation of acetaldehyde. Diacetyl peroxide is another product, which becomes of increasing importance as the intensity of the absorbed illumination increases. Preliminary tests with these two peroxides showed that they could be separated gas chromatographically by a 2 foot long dinonyl phthalate column operated at 0°C and under a pressure of 8 psi. Under these conditions the retention time for diacetyl peroxide was 4 minutes and for peracetic acid, 21 minutes. Acetaldehyde appeared at 1 minute, therefore it was possible to measure the two products in presence of unused aldehyde (Figure 6).

No attempt was made to measure the unused acetaldehyde, because such a measurement would require operation of the chromatography apparatus under various sensitivities in the same analysis. The imperfections of the apparatus did not permit such an operation, because the electrical system required some minutes to come into equilibrium after the sensitivity was changed, and the separation of diacetyl peroxide from acetaldehyde was not long enough to allow for such delay.
Figure 6. Separation Of Peroxides By Dinonyl Phthalate Column
In order to decide about the mechanism of the radical-radical chain termination step (see Discussion) it was important that formation, if any, of $O_2^{34}$ would be fast enough to be followed by a mass spectrometer with some accuracy. This fact implied that diacetyl peroxide should be formed at a reasonable rate. Preliminary experiments showed that when no light intensity filters were used, this peroxide was formed with a rate comparable to that of formation of the main product, peracetic acid. When light intensity filters were inserted before the cell, the rate of formation of diacetyl peroxide was found to decrease with the same percentage as the decrease of illumination. It was decided to work with two light intensities, one with no neutral filter on the path of the light, the other with a neutral filter permitting 34.6 per cent of the light to pass. Therefore, if 100 arbitrary units of illumination were absorbed by acetaldehyde in the first set of experiments, 34.6 arbitrary units were absorbed in the second set.

Calibration of the Chromatography Apparatus for Peracetic Acid and Diacetyl Peroxide.

Calibration curves were constructed by passing a known amount of the pure substance through the chromatography system and then measuring the area of the peak recorded by the autographic recorder. The peroxides could not be measured by means of the gas burette, because the mercury of the Toepler was attacked. Instead, a known pressure of the pure
substance was allowed into the reaction vessel, which had a total volume of 75 ml, and then distilled quantitatively into the sampler of the gas chromatography apparatus.

It was found that for both peroxides, the area of the peak was, within experimental error, proportional to the amount of the substance injected into the apparatus. The areas were measured by means of an "Aristo" planimeter. The proportionality coefficients were $2.1 \times 10^{-7}$ moles of peracetic acid and $1.15 \times 10^{-7}$ moles of diacetyl peroxide per area unit (as measured by the planimeter) of the respective peak, using the maximum sensitivity of the chromatography apparatus. These coefficients were checked for amounts of peroxides up to $6 \times 10^{-5}$ moles.

**Experimental Procedure**

This procedure was followed to study the photochemical oxidation of acetaldehyde. The reaction vessel was evacuated for two hours while heated at 200°C, then allowed to cool to 25°C. This precaution was necessary in order to ensure than no products from a previous reaction were left in the vessel. The lamp and the photometer unit were switched on and allowed to settle down. In one set of experiments a neutral density filter was placed in the light beam. The photometer unit was balanced with no light falling on the photocell and the temperature adjusted if necessary. Then O$_2$-Ar mixture was expanded into the vessel to 60 mm Hg
followed by acetaldehyde until the total pressure was 210 mm Hg. In this way the vessel contained O₂–Ar mixture and acetaldehyde with partial pressure 60 and 150 mm Hg respectively. The reactants were allowed to mix for 15 minutes, then light was shone into the reaction vessel for a given time, measured with a stopwatch, and the intensity measured using the photometer unit. The absorbed intensity could be calculated, knowing that acetaldehyde absorbs 30 per cent of the illumination. The light was cut off and the condensable material was condensed out quickly in the chromatography sampler, which was immersed in liquid nitrogen. The non-condensible gases were then very slowly pumped off using the Toepler pump and driven into the gas burette. The refrigerant was removed from the sampler and a stream of helium allowed to pass through it, which drove the contents into the chromatography column.

The gases in the gas burette were compressed into a demountable bulb equipped with a break-seal. The bulb was sealed and stored until enough similar bulbs were collected to employ the mass spectrometer for one day. In the mass spectrometric analysis, the intensities of the peaks at masses 32, 34, 36 and 40 were recorded. This last peak belonged to the argon and since this gas passed unaltered the reaction it was possible to calculate the amount of the other species, i.e. O₃⁶, O₃⁴, O₃₂, relative to it. The amount of argon, based on the original composition of the oxygen-argon
mixture at 25°C, was $1.01 \times 10^{-5}$ moles; therefore, the absolute amounts of the other species could be calculated.

3. RESULTS

Two sets of experiments were carried out using the same concentrations of reactants (i.e. 60 mm Hg oxygen-argon mixture and 150 mm Hg acetaldehyde) but at different light intensities. In one set, the light intensity was 100; in the other set the light intensity was 34.6 (arbitrary units). The results are given in tables I and II.

### TABLE I

Analysis of Products During the Photochemical Oxidation of 150 mm Hg Acetaldehyde and 60 mm Hg O$_2$-Ar Mixture at 25°C.

$I_{\text{abs}} = 100$ arbitrary units. All data are in units of moles x $10^5$. P = Peracetic Acid, D = Diacetyl Peroxide.

<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>O$_2^{32}$</th>
<th>O$_2^{34}$</th>
<th>O$_2^{36}$</th>
<th>W</th>
<th>$O^{18%}$</th>
<th>P</th>
<th>D</th>
<th>P/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.71</td>
<td>0.123</td>
<td>1.220</td>
<td>23.05</td>
<td>5.55</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>19557</td>
<td>0.230</td>
<td>1.053</td>
<td>20.85</td>
<td>5.60</td>
<td>1.26</td>
<td>1.15</td>
<td>1.095</td>
</tr>
<tr>
<td>180</td>
<td>15.79</td>
<td>0.331</td>
<td>0.764</td>
<td>16.84</td>
<td>5.52</td>
<td>2.86</td>
<td>2.88</td>
<td>0.993</td>
</tr>
<tr>
<td>240</td>
<td>13.10</td>
<td>0.392</td>
<td>0.579</td>
<td>14.07</td>
<td>5.51</td>
<td>4.16</td>
<td>3.82</td>
<td>1.088</td>
</tr>
<tr>
<td>300</td>
<td>12.93</td>
<td>0.407</td>
<td>0.568</td>
<td>13.90</td>
<td>5.55</td>
<td>4.78</td>
<td>4.27</td>
<td>1.094</td>
</tr>
<tr>
<td>360</td>
<td>11.62</td>
<td>0.409</td>
<td>0.505</td>
<td>12.53</td>
<td>5.66</td>
<td>5.58</td>
<td>5.58</td>
<td>1.000</td>
</tr>
</tbody>
</table>

mean value: 1.054 ± 0.052
TABLE II

Analysis of Products During the Photochemical Oxidation of 150 mm Hg Acetaldehyde and 60 mm Hg O₂-Ar Mixture at 25°C. 

Iabs = 346 arbitrary units. All data are in units of moles x 10⁵. P = Peracetic Acid, D = Diacetyl Peroxide.

<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>O₂² (x)</th>
<th>O₂³⁴ (y)</th>
<th>O₂³⁶ (z)</th>
<th>W</th>
<th>O₁⁸%</th>
<th>P</th>
<th>D</th>
<th>P/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.71</td>
<td>0.123</td>
<td>1.220</td>
<td>23.05</td>
<td>5.55</td>
<td>0</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>60</td>
<td>21.12</td>
<td>0.154</td>
<td>1.180</td>
<td>22.44</td>
<td>5.60</td>
<td>0.313</td>
<td>0.161</td>
<td>1.96</td>
</tr>
<tr>
<td>120</td>
<td>20.31</td>
<td>0.184</td>
<td>1.110</td>
<td>21.60</td>
<td>5.57</td>
<td>0.882</td>
<td>0.460</td>
<td>1.92</td>
</tr>
<tr>
<td>180</td>
<td>19.65</td>
<td>0.200</td>
<td>1.048</td>
<td>20.90</td>
<td>5.49</td>
<td>1.345</td>
<td>0.702</td>
<td>1.92</td>
</tr>
<tr>
<td>300</td>
<td>17.68</td>
<td>0.241</td>
<td>0.926</td>
<td>18.85</td>
<td>5.55</td>
<td>2.50</td>
<td>1.473</td>
<td>1.70</td>
</tr>
<tr>
<td>420</td>
<td>15.71</td>
<td>0.288</td>
<td>0.805</td>
<td>16.80</td>
<td>5.60</td>
<td>3.64</td>
<td>2.10</td>
<td>1.73</td>
</tr>
<tr>
<td>600</td>
<td>12.87</td>
<td>0.312</td>
<td>0.617</td>
<td>13.80</td>
<td>5.60</td>
<td>6.25</td>
<td>3.16</td>
<td>1.98</td>
</tr>
</tbody>
</table>

mean value: 21.87 ± 0.12

From these tables it is evident that oxygen-34 appears during the course of the reaction. Also, in the last column of each table the ratio (Peracetic Acid)/(Diacetyl Peroxide) is given, and it is seen that this ratio is constant for a given illumination. These results will be interpreted in the following section.
4. DISCUSSION

It is convenient to write down the complete mechanism for the photochemical oxidation of acetaldehyde as it has been established by previous work (14,16). This mechanism is the following:

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{hv} & \rightarrow \text{CH}_3^\cdot + \text{CHO}^\cdot \quad 1a \\
\text{CH}_3\text{CHO} + \text{hv} & \rightarrow (\text{CH}_3\text{CHO})^* \quad 1b \\
\text{CHO}^\cdot + \text{O}_2 & \rightarrow R^\cdot \quad 1c \\
(\text{CH}_3\text{CHO})^* + \text{O}_2 & \rightarrow \text{CH}_3\text{CO}^* + \text{HO}_2^* \quad 1d \\
\text{CH}_3\text{CO}^* + \text{O}_2 & \rightarrow \text{CH}_3\text{CO}_2^* \quad 2 \\
\text{CH}_3\text{CO}_2^* + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_3\text{CO}_3\text{H} + \text{CH}_3\text{CO}^* \quad 3 \\
2\text{CH}_3\text{CO}^* & \rightarrow (\text{CH}_3\text{CO})_2 \quad 4 \\
\text{CH}_3\text{CO}^* + \text{CH}_3\text{CO}_2^* & \rightarrow (\text{CH}_3\text{CO})_2\text{O}_2 \quad 5 \\
2(\text{CH}_3\text{CO}_2^*) & \rightarrow (\text{CH}_3\text{CO})_2\text{O}_2 + \text{O}_2 \quad 6
\end{align*}
\]

It is believed that reaction (2) is fast and that at the oxygen pressures used in the experiments, reaction (6) is the only important chain terminating step. Therefore, in deriving kinetic expressions for the production of the peroxides in the photochemical oxidation of acetaldehyde, only reaction (2), (3) and (6) should be considered, along with the initiation step. Application of the stationary state hypothesis to this scheme shows that

\[
(\text{CH}_3\text{CO}_3^*) = (\Phi_{2\text{abs}}/k_6)^{1/2}
\]
The rate of formation of peracetic acid is then:

\[ \frac{d(CH_3CO_2H)}{dt} = k_3(CH_3CO_3^-)(CH_3CHO) \]

\[ = k_3(\Phi_2I_{abs})^{\frac{1}{2}}(CH_3CHO)/k_6^{\frac{1}{2}} \]  

(A)

The rate of formation of diacetyl peroxide is:

\[ \frac{d((CH_3CO)_2O_2)}{dt} = k_6(CH_3CO_3^-)^2 \]

\[ = \Phi_2I_{abs} \]  

(B)

Comparison of (A) and (B) shows that the ratio

(Peracetic Acid)/(Diacetyl Peroxide)

at a given time is proportional to the reciprocal of \( I_{abs}^{\frac{1}{2}} \).

An inspection of the mean values of this ratio for the two light intensities studied in this work shows that this relation is obeyed within experimental error. In fact, the values of the ratio are 1.054 ± 0.052 and 1.87 ± 0.12 for the light intensities 100 and 34.6 respectively:

\[ \frac{(1.87 ± 0.12)(1.054 ± 0.052)}{(100/34.6)^{\frac{1}{2}}} = 1.78 ± 0.20 \]

Since peracetic acid is the chain propagation product and diacetyl peroxide the chain termination product, their ratio is equal to the chain length. The values 1.054 and 1.87 for the chain length may appear surprisingly low. It should be noted, however, that chain lengths as low as 2.2 have been observed (40), in experiments with \( I_{abs} \) equal to
6.21% of the output of a B.T.H. lamp at 3130 A. Since the AH6 lamp used in the present work has a greater output, and 10% to 30% of it was absorbed by the reaction mixture, it is clear that the chain length would be shorter.

It has been stated earlier (Introduction) that the radical-radical termination step (reaction 6) can take place through two possible mechanisms: (a) when the two peracetyl radicals interact, the oxygen molecule formed is produced by the elimination of an oxygen atom from each radical; (b) the oxygen molecule comes exclusively from one of the interacting radicals by a radical displacement reaction which was previously suggested (18):

\[
\begin{align*}
2\text{CH}_3\text{C}=0 & \rightarrow \text{CH}_3\text{C}=0 + \text{O}_2 \\
& \text{CH}_3\text{C}=0 + \text{O}_2
\end{align*}
\]

When the oxygen used in the photooxidation of acetaldehyde is a mixture of $^{16}\text{O}^{16}$ and $^{18}\text{O}^{18}$, a fraction of the peracetyl radicals will be unlabelled and another fraction labelled with oxygen-18. When a labelled and an unlabelled radical interact according to reaction (6), Mechanism (6a) would allow for an oxygen molecule of mass 34 to be formed, while mechanism (6b) would allow only for expulsion of an oxygen molecule of mass 32 or 36, according to the following scheme:
Therefore, any appearance of oxygen-34 in the reaction mixture would be an evidence in favour of mechanism (6a). This reasoning assumes that no contamination of a mixture or oxygen-32 and -36 with oxygen-34 takes place automatically or in presence of decomposing peroxides. Traylor and Bartlett (41) have shown that no such equilibration takes place: (i) on long standing, (ii) during the photooxidation of rubrene, (iii) from thermal decomposition of rubrene peroxide, or (iv) during the decomposition of unlabelled t-butylhydroperoxide.

From tables I and II, it is seen that oxygen-34 is produced during the reaction. Its appearance is an evidence that reaction (6) takes place by the mechanism (6a). The detailed kinetic analysis of the results given below, is in support of this view.

According to the mechanism given by equations 2, 3 and 6,
for each mole of peracetic acid produced, the equivalent of 
$M_y$ moles of oxygen-34 are consumed. $M_y$ is the mole fraction 
of oxygen-34. For each mole of diacetyl peroxide produced 
via mechanism (6a), $2M_y$ moles of oxygen-34 are consumed and 
$f_y$ moles of oxygen-34 are generated. $f_y$ is the probability 
that a terminating collision will be between a labelled and 
an unlabelled peracetyl radical. It can be written

$$y = y(P,D)$$  \hspace{1cm} (7)

where $y$ is the total amount, in moles, of oxygen-34; $P$ is 
the amount of peracetic acid; and $D$ is the amount of diacetyl 
peroxide produced in the reaction.

Differentiation of equation (7) yields

$$dy = \left(\frac{\partial y}{\partial P}\right)_D dP + \left(\frac{\partial y}{\partial D}\right)_P dD$$  \hspace{1cm} (8)

But $\left(\frac{\partial y}{\partial P}\right)_D = -M_y$ and $\left(\frac{\partial y}{\partial D}\right)_P = -2M_y + f_y$ and substitution 
of these in equation (8) leads to:

$$dy = -M_y dP + (f_y - 2M_y) dD$$  \hspace{1cm} (9)

Under the experimental conditions used, $P/D$ is equal to the 
chain length, $C$, which is constant; therefore it can be 
written $dP = CdD$. Substitution in equation (9) yields:

$$dy = \left[ f_y - (C + 2)M_y \right] dD$$  \hspace{1cm} (10)

$M_y$ is, however, equal to $y/W$, where $W$ is the total oxygen
concentration. This concentration is equal to the initial oxygen concentration, \( W_0 \), minus the oxygen spent. Since one mole of oxygen is spent per mole of peroxide or peracid formed, \( W = W_0 - (P + D) \) and the following equation, in which the substitution \( P = CD \) has been made, can be derived for \( M_y \):

\[
M_y = \frac{y}{W_0 - (C + 1)D} \quad (11)
\]

Substitution of this expression for \( M_y \) into equation (10) yields the following differential equation in \( y \) and \( D \):

\[
dy + \left( \frac{(C + 2)y}{W_0 - (C + 1)D} - fy \right) dD = 0 \quad (12)
\]

This can be readily integrated to the following expression, in which the substitution \( M_y = y/W \) has been made.

\[
f_y - M_y = \left[ f_y - (M_y)_0 \right] \left( \frac{W}{W_0} \right)^{1/(C + 1)} \quad (13)
\]

The symbols with subscript \( 0 \) denote initial concentrations.

On taking logarithms, this equation becomes:

\[
\log \left( f_y - M_y \right) = \log \left[ f_y - (M_y)_0 \right] + \left[ 1/(C + 1) \right] \log \left( \frac{W}{W_0} \right) \quad (14)
\]

A similar expression can be derived relating \( M_z \), the mole fraction of oxygen-36, to chain length \( C \):

\[
\log(M_z - f_z) = \log [(M_z)_0 - f_z] + \left[ 1/(C + 1) \right] \log \left( \frac{W}{W_0} \right) \quad (15)
\]

Here \( f_z \) is the probability that a terminating collision will
take place between two labelled peracetic radicals.

The probabilities $f_y$ and $f_z$ can be related to the atom-fraction of $\text{O}^{18}$ in the total oxygen. If this atom-fraction is $\alpha$, it is clear that the mole-fraction of labelled peracetyl radicals will also be $\alpha$, while the mole fraction of unlabelled radicals will be $1 - \alpha$. Then the probability that two labelled radicals interact is

$$f_z = \alpha^2$$

and the probability that one labelled and one unlabelled radical interact is

$$f_y = 2\alpha(1 - \alpha).$$

The value of $\alpha$ calculated from the composition of the oxygen-argon mixture, taking into account the natural abundance (0.204%) of $\text{O}^{18}$ in ordinary oxygen, is 0.0555. This value is verified by the experimental data, as it can be seen in the sixth column of Tables I and II.

The validity of the mechanism, postulated for the photochemical oxidation of acetaldehyde in general, and for the termination reaction in particular, can be tested now by applying equations (14) and (15) to the experimental results. The values for the various parameters in these equations are outlined in Tables III and IV, as calculated from the experimental data given in Tables I and II.
### TABLE III
Variation of Oxygen Isotopes During Oxidation of Acetaldehyde
Intensity of illumination 100 units (arbitrary).

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$M_y \times 10^2$</th>
<th>$f_y - M_y$</th>
<th>$W/W_0$</th>
<th>$M_z \times 10^2$</th>
<th>$M_z - f_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.533</td>
<td>0.0995</td>
<td>1.000</td>
<td>5.29</td>
<td>0.0498</td>
</tr>
<tr>
<td>90</td>
<td>1.10</td>
<td>0.0938</td>
<td>0.904</td>
<td>5.05</td>
<td>0.0474</td>
</tr>
<tr>
<td>180</td>
<td>1.97</td>
<td>0.0851</td>
<td>0.730</td>
<td>4.54</td>
<td>0.0423</td>
</tr>
<tr>
<td>240</td>
<td>2.79</td>
<td>0.0769</td>
<td>0.610</td>
<td>4.12</td>
<td>0.0381</td>
</tr>
<tr>
<td>300</td>
<td>2.93</td>
<td>0.0755</td>
<td>0.602</td>
<td>4.09</td>
<td>0.0378</td>
</tr>
<tr>
<td>360</td>
<td>3.26</td>
<td>0.0722</td>
<td>0.543</td>
<td>4.03</td>
<td>0.0372</td>
</tr>
</tbody>
</table>

### TABLE IV
Variation of Oxygen Isotopes During Oxidation of Acetaldehyde
Intensity of illumination 34.6 units (arbitrary)

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$M_y \times 10^2$</th>
<th>$f_y - M_y$</th>
<th>$W/W_0$</th>
<th>$M_z \times 10^2$</th>
<th>$M_z - f_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.533</td>
<td>0.0995</td>
<td>1.000</td>
<td>5.29</td>
<td>0.0498</td>
</tr>
<tr>
<td>60</td>
<td>0.686</td>
<td>0.0979</td>
<td>0.975</td>
<td>5.26</td>
<td>0.0495</td>
</tr>
<tr>
<td>120</td>
<td>0.852</td>
<td>0.0963</td>
<td>0.938</td>
<td>5.14</td>
<td>0.0483</td>
</tr>
<tr>
<td>180</td>
<td>0.957</td>
<td>0.0952</td>
<td>0.907</td>
<td>5.01</td>
<td>0.0470</td>
</tr>
<tr>
<td>300</td>
<td>1.28</td>
<td>0.0920</td>
<td>0.817</td>
<td>4.91</td>
<td>0.0460</td>
</tr>
</tbody>
</table>
Figures 7 and 8 show that both equations (14) and (15) are satisfied by the experimental results. Moreover, the chain lengths evaluated from these figures are in agreement with those calculated from the ratio of the peroxides, as it can be seen from Table V, where a concise account of the results is given.

**TABLE V**

Kinetic Analysis of Data in Tables I and II

<table>
<thead>
<tr>
<th></th>
<th>α = 0.0555</th>
<th>( f_y = 0.1048 )</th>
<th>( f_z = 0.0031 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{100} ) from equation 14, figure 7</td>
<td>0.993</td>
<td>( 1.054 \pm 0.052 )</td>
<td></td>
</tr>
<tr>
<td>( C_{100} ) from equation 15, figure 7</td>
<td>0.935</td>
<td>( 1.054 \pm 0.052 )</td>
<td></td>
</tr>
<tr>
<td>( C_{34.6} ) from equation 14, figure 8</td>
<td>1.85</td>
<td>( 1.87 \pm 0.12 )</td>
<td></td>
</tr>
<tr>
<td>( C_{34.6} ) from equation 15, figure 8</td>
<td>1.70</td>
<td>( 1.87 \pm 0.12 )</td>
<td></td>
</tr>
<tr>
<td>( C_{34.6} ) from P/D</td>
<td>( 1.87 \pm 0.12 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 7. VARIATION OF OXYGEN ISOTOPES AT $I_{\text{abs.}} = 100$. 

LEGEND
- $f_y - M_y$
- $M_z - f_z$
Figure 8 Variation of Oxygen Isotopes at $I_{abs.} = 34.6$
The self-consistency of results obtained by using two different analytical methods leaves no doubt about the correctness of the mechanism put forward.

Since it has been shown conclusively that the recombination of peroxyacetic radicals takes place according to equation (6a) with the elimination of one oxygen atom from each reacting peroxyacetyl radical, it remains, now, to suggest a detailed mechanism for this process. A satisfactory reaction scheme is that shown below, which involves a transition state, where a planar four-centered oxygen atomic system is the site of chemical reactivity.

\[
\begin{align*}
\text{CH}_3-\overset{\text{16}}{\text{O}}\overset{\text{16}}{\text{C}}-\overset{\text{18}}{\text{O}}+ \overset{\text{18}}{\text{O}}\overset{\text{18}}{\text{C}}-\text{CH}_3 & \rightarrow \text{CH}_3-\overset{\text{16}}{\text{O}}\overset{\text{16}}{\text{C}}-\overset{\text{18}}{\text{O}}\overset{\text{18}}{\text{C}}-\text{CH}_3 \\
\text{CH}_3-\overset{\text{16}}{\text{O}}\overset{\text{16}}{\text{C}}-\overset{\text{18}}{\text{O}}\overset{\text{18}}{\text{C}}-\text{CH}_3 & + \overset{\text{16}}{\text{O}}\overset{\text{18}}{\text{C}}-\text{CH}_3
\end{align*}
\]
Traylor and Bartlett (41) used isotopically enriched oxygen to elucidate the mechanism of the chain termination step in the autooxidation of cumene in the liquid phase and found that in this case too the oxygen molecule is formed by oxygen atoms coming from two different peroxy-radicals. It seems, therefore, that this mode of radical-radical termination is quite general in reactions involving peroxy radical.
CHAPTER IV.

MECHANISM OF THE PHOTOLYSIS OF GASEOUS CROTONALDEHYDE

AT 30°C AND 2450-4000 Å
IV. MECHANISM OF THE PHOTOLYSIS OF GASEOUS CROTONALDEHYDE at 30°C and 2450-4000 Å.

1. APPARATUS

The apparatus used in the photochemical oxidation of acetaldehyde was used in the photolysis of crotonaldehyde too, with the following alterations.

(i) The AH6 high pressure mercury arc was substituted by a BTH lamp. The output of this lamp (250 Watts) was smaller than that of the one previously used, but it had the advantage that it gave a constant illumination for extended periods of time.

(ii) The light filter solutions were removed from the optical system and a quartz filter permitting passage of light from 2450-4000 Å was used instead.

(iii) It was found that the light falling on the photocell under these conditions was too strong to be measured by the photometer unit. First it was attempted to extend the range of the unit by adding two more resistors to the resistor chain $R_{1-4}$, thus creating two more positions for the selector switch $S_{1}$. It was observed, however, that the photocell did not respond linearly to these high intensities, so it was sought to reduce the light falling on it by placing neutral filters in front of it. This technique gave better results, and in this way it was possible to measure the intensity of the illumination throughout this
part of the work.

(iv) The thermoconductivity detector of the gas chromatography apparatus was supplemented by a Perkin-Elmer flame ionization detector. Using this detector, the sensitivity of the apparatus increased by almost 1000 times and it was possible to detect and measure products in trace quantities. Another advantage of the new detector was that it could be operated at various sensitivities during the same analysis. The greatest sensitivity used was one quarter of the maximum sensitivity of the apparatus. Use of the maximum sensitivity was impractical, because trace impurities in the system were interfering seriously with the analysis. Therefore the effective sensitivity of the apparatus was about 250 times greater than when the thermoconductivity detector was used. This latter detector was kept on the system and it was used for analysis of inorganic gases, for which the flame ionization detector does not give a signal.

2. EXPERIMENTAL

Determination of the Absorption Curve for Crotonaldehyde at a Wavelength 2450-4000 Å.

The percentage absorption of gaseous crotonaldehyde was measured at 30°C for pressures ranging from 3 to 30 mm Hg in the reaction vessel. The results are plotted in Figure 9. This plot was checked at intervals during the work and found to be valid.
Figure 9, Absorption Curve for Crotonaldehyde
The procedure used was the following. The lamp was switched on and allowed to warm for about 40 minutes in order to settle down. When the variation in intensity was less than 0.5% a measurement of the intensity was taken with the reaction vessel completely evacuated. Then 30 mm Hg of crotonaldehyde were let into the vessel and the intensity measured. Crotonaldehyde was pumped out to the next lower pressure required and again the intensity was measured. This process was repeated until the cell was evacuated. The intensity was measured in order to ensure that it was the same as at the beginning. The intensity used throughout the experiment was sufficiently low that no appreciable photolysis of crotonaldehyde occurred.

Determination of Expected Reaction Products.

No products of photolysis of crotonaldehyde at low temperatures had been detected by earlier workers (23), therefore it was difficult to decide what to measure. Since propylene and CO had been detected in the Hg-photosensitized decomposition (29) and they were also products of the thermal decomposition (24,25) it was decided to investigate their formation during the photolysis. Using the flame ionization detector in the chromatography system it was possible to detect propylene in amounts as low as 5.10^{-10} moles and measure it with accuracy when 5.10^{-9} moles were present. For the estimation of CO, the thermoconductivity detector
had to be used, which required amounts of the order of $10^{-6}$ moles to give accurate results.

But-2-ene, methane and hydrogen had been found to be products of the high temperature photolysis of crotonaldehyde (25,28), therefore they had to be considered as possible products of the reaction, along with propylene and CO. It was found that two chromatography columns were needed to separate all these possible products. One was a 10 foot long HMPA column, (for Hexa-Methylphosphor-Amide), the other a 9 foot long molecular sieves column. The first column, when operated at 0°C and 8 psi, could separate efficiently CO$_2$ and all the hydrocarbons from C$_3$ to C$_5$. Even the cis and trans but-2-enes could be separated from each other. The second column could separate H$_2$, O$_2$, N$_2$, CO, CH$_4$ and C$_2$H$_6$ at 80°C and 1.5 psi. The signal for H$_2$, however, was very weak when helium was the carrier gas, because the thermocconductivities of the two gases are very close. For that reason N$_2$ was used as carrier gas whenever H$_2$ detection was attempted.

None of these columns permitted crotonaldehyde, or any other polar compound, to pass. Therefore it was necessary to find another column which would be able to separate the first material from any polar products. A 5 foot long dinonyl phthalate column, operated at 45°C and 8 psi, was found to retain crotonaldehyde for 15 minutes and separate it effic-
iently from various other polar compounds of similar or smaller molecular weight. Also, it could separate higher hydrocarbons if they differed sufficiently in boiling point. Unfortunately, glyoxal, CHOCHO, which could be a possible product of the photolysis, failed to give a peak.

Identification of Reaction Products

Before describing the experimental procedure followed when it was already known what compounds to determine, it is thought necessary to describe how these compounds were established as products of the reaction. The necessity of this way of exposure arises from the fact that some of these products had never been observed or postulated before and therefore they were quite unexpected.

The following preliminary experiments were performed, all of them with 20 mm Hg crotonaldehyde, at 30°C, and using the full intensity of illumination that the B.T.H. lamp could give at 2450-4000 Å.

Crotonaldehyde was photolyzed for 30 minutes. The condensable portion of the reaction mixture was frozen with liquid nitrogen into the gas chromatography sampler and the gases teeplered into the gas burette. The condensable material was analyzed using the HMPA column at 0°C and 8 psi and found to contain propylene. No other hydrocarbons were found up to C₅. The gases, 1 ml under pressure of 5-6 mm Hg, were analyzed by the molecular sieves column at 80°C and 1.5
psi. Using the thermoconductivity detector, only CO was found. In a similar experiment the gases were analyzed with the same column as before, but with the flame ionization detector in operation. Using one quarter of the maximum sensitivity of the apparatus, no methane or ethane was detected. In order to test for hydrogen in the reaction products, helium was substituted by nitrogen as a carrier gas. After making sure that no helium remained in the system, the gases from a 30 minute photolysis were analyzed using the molecular sieves column and the thermoconductivity detector. The result was negative, even when the analysis was repeated on gases from a 1 hour photolysis.

It was concluded that the only detectable products in the low temperature photolysis of crotonaldehyde from the domain of lower hydrocarbons and light gases were propylene and CO. This conclusion was supplemented later, when the absence of CO₂ from the reaction products was confirmed by using the HMPA column and the thermoconductivity detector.

In order to test for other products, the condensable material from a 30 minute photolysis was passed through the dinonyl phthalate column at 45°C and 8 psi. Using the flame ionization detector, three peaks appeared on the chromatogram, apart from the peak of crotonaldehyde, at 15 minutes: a large peak at 7 minutes and two smaller ones at 4.5 and 1.5 minutes. The peak at 1.5 minutes was assumed to belong to propylene, because this was the only lower hydrocarbon
detected earlier, and only lower hydrocarbons came so fast out of the dinonyl phthalate column. It was more difficult to identify the peaks at 4.5 and 7 min, because quite a few compounds were found to have these retention times. In order to make separation more efficient, the operating temperature of the column was lowered to 0°C. Under these conditions the two unknown products gave peaks at 16 and 39 min. Tests with various compounds revealed that 16 min was the retention time for hydrocarbons with six carbon atoms, while the only easily available substance with retention time 39 min was found to be butyraldehyde.

It was decided to use the HMPA column in order to gather some more evidence about the identity of the unknown at 16 min. It was found that this column could be extended to separate C_6 hydrocarbons if operated at 20°C. At this temperature it was possible to observe the peaks of two hydrocarbons in the chromatogram of the condensible products, one belonging to propylene. The new peak appeared at 59 min, and it was proved to belong to the same product which appeared at 16 min in the dinonyl phthalate column by trapping the product after the column and checking the retention time in the other column. 1,5-hexadiene was found to have retention time 59 min in the HMPA column at 20°C; it was decided that the unknown product is this hydrocarbon, after the following additional evidence was gathered:

(i) The possibility that the unknown was a saturated hydrocarbon was excluded because its smell, tested at the exit of the chromatography apparatus, was the chara
the chromatography apparatus, was the characteristic smell of an unsaturated hydrocarbon.

(ii) Olefins with 6 carbon atoms were tested and found to have retention times shorter than 59 minutes.

(iii) Of the three dienes with the same number of carbon atoms (not considering dienes of the allene type), only 1,5-hexadiene was available, and it was assumed to be the unknown product. 2,4-hexadiene was excluded as a possibility after an amount of 1,5-hexadiene was passed over alumina at 350°C and the products subjected to gas chromatographic analysis: two peaks appeared in the chromatogram when the dinonyl phthalate column was used at 0°C, one at 16 minutes, the other at 32 minutes. It is known (42,43) that when 1,5-hexadiene is subjected to the treatment described above, it isomerizes to 2,4-hexadiene. It was therefore assumed that the peak at 32°C belonged to this conjugated diene. This assumption was further justified by the fact that when the substance was trapped at the exit of the chromatography system and the ultra violet spectrum taken, it showed a very strong absorption at 2300 A, in agreement with the spectrum of 2,4-hexadiene (44). A final proof that the unknown product of the photolysis of crotonaldehyde is not 2,4-hexadiene was provided when a photolysis was run overnight and the unknown collected in sufficient amount to give an ultra-violet spectrum: it showed a very weak absorption at 2100 A, a fact which excludes the possibility of a
conjugated diene but not of 1,5-hexadiene (45).

(iv) The possibility of the unknown being 1,4-hexadiene was excluded on theoretical grounds, explained in the last section (Discussion) of the present chapter. So was the possibility of dienes of the allene type.

The unknown appearing at 39 min. in the dinonyl phthalate column at 0°C, was thought for a short time to be butyraldehyde, because this aldehyde had the same retention time. In order to gather more information, crotonaldehyde was photolyzed for two hours and the unknown at 39 min. trapped at the exit of the chromatography apparatus and subjected to infrared spectroscopic analysis. The spectrum did not quite agree with that of butyraldehyde, although it showed a strong absorption at 1735 cm⁻¹, the same wavenumber where the carbonyl of butyraldehyde absorbs (Figure 10). It was concluded that the unknown was an aldehyde, but not butyraldehyde. By the same time it had been observed that if crotonaldehyde was illuminated for a short period of time, the only detectable product was the unknown aldehyde appearing at 39 min. Propylene and biallyl were produced in measurable amounts in reaction times longer than 3 min and CO, due to the inferior sensitivity of the thermoconductivity detector, in times longer than 15 min. These facts showed that the unknown aldehyde must derive from crotonaldehyde through a process not involving any fragmentation. Such a process could be only an isomerization reaction.
Figure 10. I.R. Spectra Of Butyraldehyde And 3-Butene-1-Al
This assumption was further substantiated from the observation that the unknown aldehyde gave, among other products, crotonaldehyde, when illuminated or on long standing at room temperature.

There are three conceivable ways in which crotonaldehyde can isomerize to another aldehyde:

(i) By changing geometric configuration i.e. by undergoing a cis-trans isomerization.
(ii) By shifting the double bond to position 3
(iii) By rearranging to 1-methyl-acrolein.

Ordinary crotonaldehyde has the trans-configuration (46). The cis form has never been isolated and all attempts to prepare it resulted in ordinary crotonaldehyde (46, 47). This fact made geometric isomerization an unplausible assumption, because the unknown aldehyde was a reasonably stable compound. Also, if it had a conjugated system of double bonds, the carbonyl absorption in the infrared spectrum would be displaced by 20-40 cm$^{-1}$, as the case is with the spectrum of (trans)-crotonaldehyde. This lack of displacement excluded the possibility for the unknown to be either cis-crotonaldehyde or 1-methyl-acrolein, leaving as the only possibility the product of double bond shift, namely 3-butene-1-al.

This aldehyde was prepared and its infra red spectrum compared with that of the unknown aldehyde (Figure 1D). The two spectra were identical. It was concluded that the
unknown aldehyde was 3-butene-1-al.

Polymer Formation

Another fact, which became obvious while crotonaldehyde was illuminated in order to identify the various products of photolysis, was that a substance was accumulating slowly on the walls of the reaction vessel. Evacuation of the cell for several hours at 30°C did not remove this substance. Heating to 200°C under vacuum simply caused the substance to carbonize partly, thus hindering the passage of light. Only heating with a gas-oxygen flame to white glow completely cleaned the cell. Blacet and Roof (23) have observed that when crotonaldehyde is illuminated at 3660 Å at room temperature, polymerization occurs with a quantum yield of 0.02 based on the number of molecules disappearing per quantum absorbed. Since the illumination used in the present work comprised the wavelength of 3660 Å, it is reasonable to assume that the substance accumulated on the walls of the reaction vessel was a polymer.

Polymer formation was creating some problems of experimental nature in an eventual kinetic study of the photolysis of crotonaldehyde. Cleaning the cell completely before a reaction would require dismantling the furnace, cutting the cell, baking it to white glow and then assembling the whole system back in place. It was thought that all this process could be avoided if the polymer layer on the walls of the reaction vessel could come to a "stationary state";
if, in other words, the cell could attain the condition which is often referred to as "seasoning". Polymer accumulation could be followed by recording the intensity of the light falling on the photocell when the reaction vessel was evacuated. It was found that when the cell was quite clean (i.e. subjected to flaming), the illumination passing through it was appreciably decreasing after each reaction, even when the cell was kept under vacuum for several hours. This decrease of the intensity of passing light was taken as a measure of polymer accumulation. When, however, a certain number of photolyses had been conducted, the cell could be easily made to attain the same condition as before the experiment by evacuating it for one hour, as judged by the fact that the intensity of illumination reaching the photocell was the same as before the experiment. The "seasoned" cell was absorbing about 60% of the illumination falling upon it. The results recorded in the next section were obtained with the cell in this condition.

No detailed kinetic study of the polymer formation was undertaken. Estimation of its extent was attempted by measuring the amount of crotonaldehyde and its photolysis products in the reaction mixture and attributing the deficit of the material balance to polymer formation, but the results were not reproducible, due to the large experimental error inherent in the method.
Determination of Reaction Products

It has been seen in a previous section how 3-butene-1-al was established as the primary product of the photolysis of crotonaldehyde at 30°C, accompanied later by propylene, 1,5-hexadiene and CO. It was decided to follow the rate of formation of all four products; also, the rate of disappearance of crotonaldehyde, for experiments in which sufficient amount of it would be spent. This could be achieved rather easily, because the reaction mixture could be separated into two portions; one non-condensable at liquid nitrogen temperature and containing CO only, the other condensable and containing everything else.

CO was determined gas chromatographically using the molecular sieves column. Measuring the volume of the gases in the gas burette was used as an additional check.

The remaining compounds were determined by using the dinonyl phthalate column at 45°C. It will be recalled that under these conditions the retention times of propylene, 1,5-hexadiene, 3-butene-1-al and crotonaldehyde are 1.5, 4.5, 7, and 15 minutes in the order given. The use of this compact method of analysis was possible only if it was made sure that these were the only substances in the mixture. This was ensured by making additional checks of the identity of the products every time that some alteration was made in the conditions of photolysis.

The two columns were calibrated quantitatively by using measured samples of pure compounds. It was found
that the areas of the peaks are proportional to the amount of the substance injected into the apparatus. This linearity was checked for amounts up to $10^{-3}$ mole. The results are outlined in Table VI.

**TABLE VI**

Calibration of the chromatography system for the components of the reaction mixture in the photolysis of crotonaldehyde. The areas of the peaks are calculated for the maximum sensitivity of the system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>moles/(area unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>crotonaldehyde</td>
<td>$1.67 \times 10^{-10}$</td>
</tr>
<tr>
<td>3-butene-1-al</td>
<td>$1.32 \times 10^{-10}$</td>
</tr>
<tr>
<td>propylene</td>
<td>$1.68 \times 10^{-10}$</td>
</tr>
<tr>
<td>1,5-hexadiene</td>
<td>$6.40 \times 10^{-11}$</td>
</tr>
<tr>
<td>CO</td>
<td>$1.32 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

**Actinometry**

The photometer unit was calibrated by using the potassium ferrioxalate actinometer. The procedure followed was essentially the one described by Hatchard and Parker (39).

1. Calibration graph for ferrous ion. The following reagents were first prepared.
(a) A solution containing $1.0 \times 10^{-6}$ mole/ml of Fe$^{++}$ in 6.1 N $H_2S_4$. This solution was freshly prepared by dilution of standardized 0.1 Fe$S_4$ in 0.1 N $H_2SO_4$.

(b) 0.1% aqueous solution of 1:10 phenanthroline.

(c) A buffer solution prepared by adding 360 ml of 1 N $H_2SO_4$ to 600 ml of 1 N sodium acetate and diluting to 1 litre.

In a series of 50 ml volumetric flasks the following volumes of solution (a) were added:

0, 100, 2.0, 3.0, 4.0, 5.0 ml

Then 0.1 N $H_2SO_4$ was added to make the total volume 10 ml. After adding 5 ml of solution (b) and 5 ml of solution (c), the volume was made up to the mark with distilled water and the flasks were allowed to stand for $\frac{1}{2}$ hour. The optical density relative to that of distilled water was measured in a 1 cm cell at 510 m$. The results appear in Table VII and a graph in Figure 11.

**TABLE VII**

Optical Density of Ferrous Ion Solutions.

<table>
<thead>
<tr>
<th>Moles Fe$^{++}$ x $10^6$/50 ml</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.001</td>
</tr>
<tr>
<td>1.0</td>
<td>0.231</td>
</tr>
<tr>
<td>2.0</td>
<td>0.422</td>
</tr>
<tr>
<td>3.0</td>
<td>0.644</td>
</tr>
<tr>
<td>4.0</td>
<td>0.906</td>
</tr>
<tr>
<td>5.0</td>
<td>1.090</td>
</tr>
</tbody>
</table>
FIGURE 11. CALIBRATION GRAPH FOR FERROUS IONS
From the graph it is seen that the optical density varies linearly with the concentration of the ferrous ion; to optical density "1" there corresponds a concentration of \(4.5 \times 10^6\) moles \(\text{Fe}^{++}\) per 50 ml.

2. Calibration of the photometer unit.

The lamp was switched on and allowed to warm for about 40 minutes. When the lamp output became constant, a reading was taken with the "seasoned" reaction cell evacuated. Then the cell was cut and taken out of the light path and another reading taken. In this way it could be calculated what percentage of illumination was absorbed by the vessel: it was 61.5%. The vessel was put back on the light beam and a 1 cm quartz cell containing approximately 10 ml of a 0.006 M solution of potassium ferrioxalate in 0.1N \(\text{H}_2\text{SO}_4\) was placed behind it and illuminated for a measured time. After photolysis, the contents of the cell were transferred quantitatively into a dark-coloured 50 ml volumetric flask, 5 ml of solution (b) and 5 ml of solution (c) added and the volume was made up to the mark with distilled water. After allowing the flask to stand for \(\frac{1}{2}\) hour in the dark, the optical density of the photolyte was measured relative to that of distilled water in a 1 cm cell at 510 m\(\mu\). Three measurements were made which appear in Table VIII. A solution of potassium ferrioxalate, which was not illuminated, showed, under the same conditions, negligible optical density, thus confirming the purity of the reagents.
TABLE VIII

The intensities of illumination were measured with the "seasoned" reaction vessel on the light path.

<table>
<thead>
<tr>
<th>Intensity of illumination on the photodell</th>
<th>Time (sec.)</th>
<th>Relative optical density</th>
<th>Fe$^{2+}$ moles x 10$^6$</th>
<th>Fe$^{2+}$/sec x Ω moles·sec$^{-1}$·Ω$^{-1}$ x 10$^{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1410</td>
<td>30</td>
<td>0.472</td>
<td>2.12</td>
<td>5.01</td>
</tr>
<tr>
<td>1410</td>
<td>50</td>
<td>0.767</td>
<td>3.45</td>
<td>4.89</td>
</tr>
<tr>
<td>600</td>
<td>60</td>
<td>0.387</td>
<td>1.74</td>
<td>4.84</td>
</tr>
</tbody>
</table>

Mean value: 4.91 ± 0.10

The quantum efficiency for the process at 3000-4000 Å given by Hatchard and Parker (39) is 1.23. The selection filter in the work described here permitted passage of light from 2450-4000 Å. But the BTH lamp is known to produce a very small percentage of its output below 3000 Å, therefore the above factor can be used with a fair degree of approximation. The number of quanta per second per ohm reaching the photocell are thus calculated to be 2.40 (±0.05) x 10$^{13}$. In order to calculate the number of quanta passing through the reaction vessel per second per ohm, it is necessary to take into account the fact that the walls of the vessel were covered with a layer of polymer which absorbed 61.5% of the total illumination. Assuming homogeneous distribution of the polymer on the walls, it can be calculated that each
optical surface of the vessel was absorbing 38% of the illumination reaching it. Therefore the number of quanta reaching the photocell was only 62% of the number of quanta passing the space between the two optical surfaces of the reaction vessel. Therefore, quanta per second per ohm in the vessel

\[
= \frac{2.40(\pm 0.05) \times 10^{13}}{0.62}
\]

\[
= 3.87(\pm 0.08) \times 10^{13}
\]

This number of quanta is absorbed per second and ohm, by any gas in the reaction vessel, which has an illuminated volume of 73 ml. For convenience, all absorbed intensities, \(I_{\text{abs}}\), quoted in this chapter, will have the units einstein*1^{-1}*sec^{-1}.

3. RESULTS

Investigation of the Isomerization Reaction.

It was stated earlier that the only detectable product of the photolysis of crotonaldehyde in experiments of small duration was 3-butene-1-al. This fact showed that the primary process taking place when crotonaldehyde was illuminated at 30°C and 2450-4900 Å was isomerization. A detailed study of this process was undertaken by measuring the rate of formation of the isomer under varying intensity of illumination, crotonaldehyde pressure and temperature. The results are recorded in Tables IX, X and XI.
**TABLE IX**

Dependence of Isomerization of Crotonaldehyde on \( I_{\text{abs}} \)

All experiments were conducted at 30°C with 20 mm Hg of crotonaldehyde.

| \( I_{\text{abs}} \) ein\( \cdot \)l\(^{-1}\)\cdot sec\(^{-1} \) | time sec. | 3-butèneal-al- absorbed \( \text{mole} \cdot \text{l}\(^{-1}\)\cdot 10\(^{7}\) ein\( \cdot \)l\(^{-1}\)\cdot 10\(^{6}\) | Quantum yield \( \text{mole} \cdot \text{ein}\(^{-1}\)\cdot 10\(^{2}\) |
|-----------------|--------|******************************************|------------|
| 31.1            | 50     | 10.1                          | 15.5       | 9.8        |
| 31.1            | 80     | 15.7                          | 24.9       | 9.1        |
| 21.7            | 60     | 8.6                           | 13.0       | 9.5        |
| 21.7            | 120    | 17.0                          | 26.0       | 9.0        |
| 19.2            | 60     | 7.5                           | 11.5       | 9.3        |
| 19.2            | 120    | 14.5                          | 23.0       | 9.8        |
| 12.4            | 100    | 8.4                           | 12.4       | 9.4        |
| 12.4            | 240    | 19.3                          | 29.8       | 9.9        |
| 5.0             | 240    | 7.9                           | 12.0       | 9.3        |
| 3.4             | 300    | 6.4                           | 10.2       | 9.7        |

mean value: \( 9.5 \pm 0.5 \)

From the last column of Table IX it is seen that the quantum yield of isomerization remains constant over a tenfold increase of intensity of the absorbed illumination. This means that isomerization is directly proportional to \( I_{\text{abs}} \).

In the experiments with variable crotonaldehyde pressure (Table X) the initial intensity of illumination was kept constant. The absorbed intensity, however, was varying,
because of different percentage of absorption by the different aldehyde pressures studied. The absorbed intensity was taken by using the absorption curve for crotonaldehyde (Figure 10).

**TABLE X**

Dependence of Isomerization on the Pressure of Crotonaldehyde

All experiments were conducted at 30°C with $I_{in} = 66.6 \cdot 10^{-8}$ ein·1⁻¹·sec⁻¹ and for 1 minute.

<table>
<thead>
<tr>
<th>Crotonaldehyde mm Hg</th>
<th>$I_{abs}$ ein·1⁻¹·sec⁻¹</th>
<th>3-butene-1-al absorbed yield mole·1⁻¹·10⁷</th>
<th>Total radiation absorbed ein·1⁻¹·10⁶</th>
<th>Quantum yield mole·ein⁻¹ x 10²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>6.0</td>
<td>3.28</td>
<td>3.60</td>
<td>9.1</td>
</tr>
<tr>
<td>8.2</td>
<td>9.6</td>
<td>5.40</td>
<td>5.76</td>
<td>9.4</td>
</tr>
<tr>
<td>16.0</td>
<td>11.6</td>
<td>6.49</td>
<td>6.96</td>
<td>9.3</td>
</tr>
<tr>
<td>15.6</td>
<td>17.4</td>
<td>9.89</td>
<td>10.4</td>
<td>9.5</td>
</tr>
<tr>
<td>20.0</td>
<td>21.7</td>
<td>12.8</td>
<td>13.0</td>
<td>9.5</td>
</tr>
<tr>
<td>24.0</td>
<td>25.3</td>
<td>15.1</td>
<td>15.2</td>
<td>9.6</td>
</tr>
<tr>
<td>26.8</td>
<td>27.6</td>
<td>16.5</td>
<td>16.5</td>
<td>10.0</td>
</tr>
<tr>
<td>30.0</td>
<td>30.0</td>
<td>16.9</td>
<td>18.0</td>
<td>9.4</td>
</tr>
</tbody>
</table>

**mean value :** 9.5 ± 0.5

The constance of the quantum yield over a six-fold variation of aldehyde pressure in the last column of Table X demonstrates the fact that isomerization is independent of the concentration of crotonaldehyde.
In order to study the temperature dependence, 10 mm Hg of crotonaldehyde were photolyzed at temperatures ranging from 20° to 35°C. Higher temperatures were avoided, because 3-butene-1-al underwent a thermal isomerization to crotonaldehyde. From the data on Table XI it is clear that the rate of formation of 3-butene-1-al is independent of temperature.

**TABLE XI**

Dependence of Isomerization on Temperature.

All experiments were conducted with $I_{abs} = 21.7 \text{ ein} \cdot \text{1}^{-1} \cdot \text{sec}^{-1}$ and 10 mm Hg of crotonaldehyde. Time 1 minute.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>3-butene-1-al mole$^{-1}$ 10$^{-7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>6.81</td>
</tr>
<tr>
<td>23.1</td>
<td>6.53</td>
</tr>
<tr>
<td>27.8</td>
<td>6.39</td>
</tr>
<tr>
<td>30.0</td>
<td>6.49</td>
</tr>
<tr>
<td>32.3</td>
<td>6.60</td>
</tr>
<tr>
<td>35.0</td>
<td>6.28</td>
</tr>
</tbody>
</table>

From an inspection of the three Tables it becomes evident that isomerization of crotonaldehyde to 3-butene-1-al is a purely photochemical reaction. The quantum yield of isomerization is 0.095 ± 0.005.
Investigation of the Total Reaction.

Dependence on Time.

When crotonaldehyde was illuminated for a longer period of time, it was possible to determine the rate of formation of the three other products, i.e. propylene, 1,5-hexadiene and CO. The two hydrocarbons could be determined when about $10^{-4}$ ein.l$^{-1}$ of light energy had been absorbed, while CO became measurable only after $5 \times 10^{-4}$ ein.l$^{-1}$.

From preliminary experiments it became obvious that while the formation of 3-butene-1-al varies linearly with time, at least for experiments of short duration, that of propylene, 1,5-hexadiene and CO seems to bear some exponential relation with time. A detailed investigation of the time dependence of all the products was undertaken. The results appear on Table XII and a graph in Figure 12.

From an inspection of both Table XII and Figure 12, it is evident that 3-butene-1-al increases, at the beginning, linearly with time, then the rate of formation decreases and even becomes negative after the isomer reaches a maximum at about 120 minutes. This is an evidence that 3-butene-1-al is consumed during the reaction. The three other products clearly increase exponentially with time. The degree of dependence is seen to be two, from a logarithmic plot in Figure 13. It should also be noticed that propylene and CO are produced in approximately equimolecular amounts.
Figure 12. Photolysis of Crotonaldehyde; Products vs. Time
Figure 13. Photolysis of Crotonaldehyde
Time Dependence

Legend:
- △ propylene
- □ 1,5-hexadiene

$7 + \log_{10}[\text{Product}]$ vs. $\log_{10}[\text{Time}]$

Slope △ : 2.10
□ : 1.91
**TABLE XII**

Analysis of Products During the Photolysis of Crotonaldehyde at 30°C and $I_0 = 66.6 \times 10^{-8}$ ein. l$^{-1}$. sec$^{-1}$.

All data are in units of mole. l$^{-1}$ x 10$^7$. 

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Crotonaldehyde</th>
<th>3-butene-1-al</th>
<th>Propylene</th>
<th>1,5-hexadiene</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10700</td>
<td>18.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>10600</td>
<td>57.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>10600</td>
<td>96.1</td>
<td>1.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>10500</td>
<td>143</td>
<td>4.47</td>
<td>1.41</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>10350</td>
<td>195</td>
<td>9.70</td>
<td>3.35</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>10200</td>
<td>315</td>
<td>29.7</td>
<td>7.78</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>10100</td>
<td>444</td>
<td>70.1</td>
<td>17.4</td>
<td>52.8</td>
</tr>
<tr>
<td>40</td>
<td>9800</td>
<td>520</td>
<td>119</td>
<td>30.4</td>
<td>123</td>
</tr>
<tr>
<td>50</td>
<td>9700</td>
<td>604</td>
<td>184</td>
<td>46.2</td>
<td>123</td>
</tr>
<tr>
<td>65</td>
<td>9500</td>
<td>687</td>
<td>316</td>
<td>75.9</td>
<td>352</td>
</tr>
<tr>
<td>80</td>
<td>9030</td>
<td>722</td>
<td>450</td>
<td>114</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>8420</td>
<td>800</td>
<td>608</td>
<td>151</td>
<td>550</td>
</tr>
<tr>
<td>120</td>
<td>7820</td>
<td>758</td>
<td>849</td>
<td>186</td>
<td>783</td>
</tr>
<tr>
<td>136</td>
<td>8220</td>
<td>825</td>
<td>1066</td>
<td>217</td>
<td>1000</td>
</tr>
<tr>
<td>156</td>
<td>7720</td>
<td>789</td>
<td>1293</td>
<td>259</td>
<td>1120</td>
</tr>
<tr>
<td>170</td>
<td>6390</td>
<td>645</td>
<td>1555</td>
<td>301</td>
<td>1510</td>
</tr>
<tr>
<td>180</td>
<td>6040</td>
<td>660</td>
<td>1646</td>
<td>297</td>
<td>1580</td>
</tr>
<tr>
<td>200</td>
<td>5460</td>
<td>600</td>
<td>1931</td>
<td>337</td>
<td>1720</td>
</tr>
</tbody>
</table>
Dependence on Intensity of Absorbed Illumination.

20 mm Hg crotonaldehyde were illuminated for 30 minutes under variable intensity of absorbed illumination. The amount of absorbed radiation was enough for propylene and 1,5-hexadiene to be produced in measurable amounts, but CO production was not followed. It is probable that its rate of appearance was the same as that of propylene. The results appear in Table XIII.

<table>
<thead>
<tr>
<th>$I_{abs}$ $\times 10^8$, sec$^{-1}$</th>
<th>3-butene-1-al</th>
<th>Propylene</th>
<th>1,5-hexadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.47</td>
<td>84</td>
<td>1.21</td>
<td>-</td>
</tr>
<tr>
<td>6.23</td>
<td>120</td>
<td>3.00</td>
<td>1.01</td>
</tr>
<tr>
<td>10.9</td>
<td>181</td>
<td>4.80</td>
<td>1.32</td>
</tr>
<tr>
<td>10.9</td>
<td>175</td>
<td>4.86</td>
<td>1.35</td>
</tr>
<tr>
<td>17.1</td>
<td>288</td>
<td>25.6</td>
<td>6.77</td>
</tr>
<tr>
<td>21.8</td>
<td>373</td>
<td>34.6</td>
<td>8.96</td>
</tr>
<tr>
<td>31.1</td>
<td>444</td>
<td>70.1</td>
<td>17.4</td>
</tr>
</tbody>
</table>

From an inspection of the data in Table XIII, it is clear that propylene and 1,5-hexadiene increase exponentially with
**Legend**

- △ Propylene
- □ 1,5-Hexadiene

**Figure 14. Photolysis of Crotonaldehyde; Dependence on \( I_{\text{abs}} \).**
the intensity of absorbed illumination. A logarithmic plot in Figure 14 shows that they increase proportionally to $I_{\text{abs}}^2$.

**Dependence on Pressure of Crotonaldehyde.**

A set of experiments with constant amount of absorbed radiation and variable crotonaldehyde pressure was carried out in order to determine the dependence of reaction products on the latter. The total amount of absorbed radiation was kept constant by adjusting the duration of each experiment in such a way, that the product of time to $I_{\text{abs}}$ was always the same. This method is quite legitimate, since it has been established that the products depend on $I_{\text{abs}}^2$ and time with the same degree.

**TABLE XIV**

Dependence of Products on Pressure of Crotonaldehyde.

In all the experiments the total absorbed radiation was $22.4 \times 10^{-5}$ ein.l$^{-1}$. All data are in units of mole.l$^{-1}.10^7$

<table>
<thead>
<tr>
<th>Crotonaldehyde mm Hg</th>
<th>3-butene-1-al</th>
<th>Propylene</th>
<th>1,5-hexadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>111</td>
<td>64.7</td>
<td>12.9</td>
</tr>
<tr>
<td>7.1</td>
<td>153</td>
<td>42.7</td>
<td>9.78</td>
</tr>
<tr>
<td>10.0</td>
<td>160</td>
<td>32.4</td>
<td>7.05</td>
</tr>
<tr>
<td>12.9</td>
<td>176</td>
<td>21.9</td>
<td>5.37</td>
</tr>
<tr>
<td>17.1</td>
<td>196</td>
<td>15.5</td>
<td>4.09</td>
</tr>
<tr>
<td>20.0</td>
<td>195</td>
<td>9.70</td>
<td>3.35</td>
</tr>
</tbody>
</table>
Figure 15. Photolysis of Crotonaldehyde Dependence on Crotonaldehyde Pressure

LEGEND
△ propylene
□ 1,5-hexadiene

Slope △ : -1.30 to 1.50
□ : -1.04

7 + \log_{10} \text{[product]}

4 + \log_{10} \text{[crotonaldehyde]}
The data on Table XIV show that the quantum yields of propylene had 1,5-hexadiene decrease as the pressure of crotonealdehyde increases. A logarithmic plot in Figure 15 shows that 1,5-hexadiene formation is inversely proportional to the crotonealdehyde pressure. For propylene the relation is somewhat more complex; the slope of the curve is -1.3 (full line) to -1.5 (dotted line). A possible explanation will be discussed later in this chapter.

Recapitulation of Results.

It is convenient to outline the results obtained in the photolysis of crotonealdehyde at 30°C and 2450 - 4000 Å. These are the following.

1. For experiments of short duration the only important process taking place is isomerization to 3-butene-1-al. The experimental law was observed

\[
\frac{d(3\text{-butene-1-al})}{dt} = \Phi \times I_{abs}
\]

where \(\Phi = 0.095 \pm 0.005\) is the quantum yield of isomerization.

2. When the photolysis is allowed to proceed further, propylene, 1,5-hexadiene and CO are produced along with 3-butene-
1-al. From the fact that these products increase with the square of time, while 3-butene-1-al starts decreasing after reaching a maximum, it is evidenced that they are formed through decomposition of 3-butene-1-al. The experimental laws were observed:

\[
\frac{d(1,5\text{-hexadiene})}{dt} \sim \frac{I_{\text{abs}} t^2}{(\text{crotonaldehyde})}
\]

and

\[
\frac{d(\text{propylene})}{dt} \sim \frac{I_{\text{abs}} t^2}{(\text{crotonaldehyde})^{1.3-1.5}}
\]

No detailed law was found for CO, because of difficulty in determining it, but it was observed that, whenever measured, it was found to be at approximately the same amount as propylene.

4. DISCUSSION

It is quite clear from the experimental results that the primary process taking place when crotonaldehyde is illuminated at 30°C and a wavelength of 2450-4000 Å is isomerization to 3-butene-1-al. The quantum yield (0.095) of the process does not lead to any definite conclusion, about the activation energy of isomerization, because of the wide range of wavelength used. It could be that only radiation of shorter wavelength, e.g. ≤3130, is effective. This view is supported by the fact that photodecomposition of crotonaldehyde at 150°C increases rapidly with decrease in wavelength, (25). If this is the case, the value 0.095, found for the
quantum yield of isomerization, is too low, given that not all the radiation absorbed was effective. Therefore this value can be considered only as a lower limit.

It is very probable that the upper limit of the quantum yield of isomerization cannot be greater than one. The experimental data show clearly that this reaction is a primary process depending linearly on the amount of absorbed radiation. The process can be simply described by the equation

$$\text{CH}_3\text{CH:CHCHO} + \text{hv} \xrightarrow{\Phi_{\text{abs}}} \text{CH}_2\text{CHCH}_2\text{CHO} \quad (1)$$

If it is assumed that every quantum of radiation absorbed by crotonaldehyde is effective, the quantum yield for (1) will be one. The following possibilities exist for a detailed mechanism of (1).

When crotonaldehyde absorbs one quantum of radiation energy, it is raised to some excited state. Since the radiation used is of a wide wavelength range, it is probable that the excited states will be more than one. Under the experimental conditions studied, most of the excited molecules fall back to their ground state either by emitting fluorescence or by collision with other crotonaldehyde molecules. Unimolecular decomposition may be safely excluded as a possibility, because no low molecular fragments were detected in the first minutes of the reaction. Approximately one out of ten excited molecules was converted to 3-butene-1-al. This fact implies that a fraction of the excited molecules, ranging from 0.095 to 1, must have a structure close to that of 3-butene-1-al. Since a hydrogen atom is transferred from
position (4) to position (2) in the isomerization process, it can be suggested that the structure of an effective activated molecule will be one with a hydrogen atom shared equally between carbon atoms (2) and (4). Then the mechanism of the isomerization reaction (1) would be the following:

\[
\begin{align*}
\text{CH}_2=\text{C} \cdots \text{CHO} + \text{hv} & \xrightarrow{\text{catalyst}} \text{CH}_2=\text{C} \cdots \text{CHO} + \text{CHO}^* \\
\text{CH}_2=\text{C} \cdots \text{CHO} & \rightarrow \text{CH}_2=\text{C} \cdots \text{CHO}
\end{align*}
\]

Once 3-butene-1-al has been formed, it can undergo photolysis by absorbing a portion of the illumination passing through the reaction vessel. Thermal decomposition under the experimental conditions used is not probable, because the only thermal reaction observed in samples of 3-butene-1-al was slow isomerization to crotonaldehyde. The presence of 1,5-hexadiene in the reaction products shows that allyl radicals are present in the reaction cell. This implies that 3-butene-1-al must undergo, at least partly, the radical decomposition

\[
\text{CH}_2=\text{C} \cdots \text{CHO} + \text{hv} \xrightarrow{\text{catalyst}} \text{CH}_2=\text{C} \cdots \text{CHO}^* + \text{CHO}
\]

Then the presence of 1,5-hexadiene could be easily accounted for by a recombination reaction of allyl radicals:

\[
2\text{CH}_2=\text{C} \cdots \text{CHO} \rightarrow \text{CH}_2=\text{C} \cdots \text{CHO} + \text{CH}_2=\text{C} \cdots \text{CHO}
\]

It is important to investigate into which other reactions, apart from recombination, allyl radicals can enter. We will consider first the possibility of a chain mechanism,
similar to the one proposed by Rice and Herzfeld (48) for
the pyrolysis of hydrocarbons. Such a mechanism would involve
abstraction of a hydrogen by the allyl radical to produce
propylene and a new radical, which might be able to con-
tinue the chain. Since crotonaldehyde is the compound with
the highest concentration in the reaction mixture, it would
Have the highest probability to be attacked by radicals. Of
all the hydrogen atoms in the crotonaldehyde molecule the
aldehyde hydrogen is the one with the smallest bond disso-
ciation energy (49). Therefore, if allyl radicals attack,
this hydrogen will be abstracted:
\[
\text{CH}_2:\text{CH}_2\text{CH}_2^\cdot + \text{CH}_3\cdot \text{CH}:\text{CHCHO} \rightarrow \text{CH}_2\cdot \text{CHCH}_3 + \text{CH}_3\cdot \text{CH}:\text{CHCO}^\cdot
\]  (4)

Then the chain could be continued by the crotonoyl radicals
dissociating to CO and propenyl radicals, which could either
abstract a hydrogen from crotonaldehyde, to form propylene
and a crotonoyl radical, or isomerize to allyl radicals, or
dimerize to 2,4-hexadiene.

\[
\text{CH}_3\text{CH}:\text{CHCO}^\cdot \rightarrow \text{CH}_3\text{CH}:\text{CH}^\cdot + \text{CO} \\
\text{CH}_2\text{CH}:\text{CH}^\cdot + \text{CH}_3\cdot \text{CH}:\text{CHCHO} \rightarrow \text{CH}_3\text{CH}:\text{CH}_2 + \text{CH}_2\cdot \text{CH}:\text{CHCO}^\cdot \\
\text{CH}_2\text{CH}:\text{CH}^\cdot \rightarrow \text{CH}_2:\text{CHCH}_2^\cdot \\
2\text{CH}_3\cdot \text{CH}:\text{CH} \rightarrow \text{CH}_3\cdot \text{CH}:\text{CHCH}^\cdot \text{CHCH}_3
\]  (5) (6) (7) (8)

The fact that no 2,4-hexadiene was detected in the reac-
tion products shows that propenyl radicals are not produced
in the reaction, unless it is assumed that the recombination
reaction (8) is too slow compared to (6) and (7). This last
reaction can be very fast, because the allyl radicals formed
In it are stabilized by resonance energy estimated at about 25 kcal/mole by Szwarc et al (50). Then the chain would be propagated by reaction (4), (5), (6) and (7), and terminated by (3) only.

If propylene were produced by the radical chain reaction described above, its ratio to 1,5-hexadiene would increase with increasing aldehyde concentration and decrease with decreasing \( I_{\text{abs}} \). Inspection of the data in Tables XIII and XIV and plots of the ratio (propylene)/(1,5-hexadiene) against \( I_{\text{abs}} \) (Figure 16) and crotonaldehyde pressure (Figure 17) shows that this is not the case. In fact the opposite tendency is observed, i.e. the ratio (propylene)/(biallyl) decreases with increasing aldehyde concentration and increases with decreasing \( I_{\text{abs}} \). These facts force one to reconsider the possibility of the mechanism represented by reactions (4), (5), (6) and (7).

A reaction similar to (4), studied by Birrel and Trotman-Dickenson (49) is the reaction of methyl radicals with various aldehydes, including crotonaldehyde. They observed that the activation energy for methane formation is almost the same for all aldehydes studied and they concluded that the methyl radicals react by abstracting the aldehydic hydrogen. For the reaction with crotonaldehyde

\[
\text{CH}_3 + \text{CH}_3\text{CH:CHCHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH:CHCHO} \quad (4')
\]

they found \( \log A = 16.3 \) (in units of mole\(^{-1}\).l.sec\(^{-1}\)) and \( E = 10.9 \) kcal/mole. Given that the allyl radical is stabilized
FIGURE 16. DEPENDENCE OF \([\text{propylene}] / [\text{hexadiene}]\) ON \(I_{\text{abs.}}\).
Figure 17. Dependence of $[\text{propylene}] / [\text{1,6-hexadiene}]$ on crotonaldehyde pressure.
by resonance energy, while methyl is not, it is reasonable to assume that reaction (4) would have an activation energy greater than 10.9 kcal/mole. If it is further assumed that the pre-exponential factor for (4) is of the same order of magnitude as for (4'), it can be easily seen that this reaction would be very slow at 30°C. In fact, it can be calculated that at this temperature

$$K_4 < 2.5 \times 10^8 \text{ mole}^{-1}\text{.l. sec}^{-1}$$

The stability of the allyl radical, resulting in preponderance of the radical recombination reaction to hydrogen abstraction from hydrogen donors, has been demonstrated by its inability to react with toluene (50), and by the fact that the main product of the pyrolysis of allyl chloride at 540-550°C is 1,5-hexadiene, propylene being formed at higher temperatures only (51). The mechanism suggested in the latter case is splitting of allyl chloride to allyl radicals and chlorine atoms, followed by recombination of the former to form 1,5-hexadiene. At higher temperature, hydrogen abstraction becomes important, and also 1,5-hexadiene starts decomposing to allyl radicals in a reversal of the radical recombination process. The hydrogen atoms involved in this case are not as mobile as the aldehydic hydrogens involved in reaction (4), but the fact remains that even at 540°C, radical recombination takes preference over the alternative of hydrogen abstraction. It should be very much more so at room temperature.
Since it has been shown that reaction (4) cannot take place under the experimental conditions studied, the whole chain mechanism needs no further consideration.

Some authors (28,52) suggest that the most important reaction of methyl radicals with crotonaldehyde at 120-350°C is the radical displacement

\[
\text{CH}_3^\cdot + \text{CH}_2\text{CH}:\text{CHCHO} \rightarrow \text{CH}_3\text{CH}:\text{CHCH}_3 + \text{HCO}^\cdot
\]

A similar reaction with allyl in place of methyl radical would produce the assymetric diene, 1,4-hexadiene:

\[
\text{CH}_2:\text{CHCH}_2^\cdot + \text{CH}_3\text{CH}:\text{CHCHO} \rightarrow \text{CH}_3\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}_2 + \text{HCO}^\cdot \quad (9)
\]

Considering that reaction (9) would have approximately the same activation energy as reaction (4), it can be safely excluded as a possibility.

The only other reaction into which allyl radicals can enter is abstraction of hydrogen from formyl radicals:

\[
\text{CH}_2:\text{CHCH}_2^\cdot + \text{HCO}^\cdot \rightarrow \text{CH}_2:\text{CHCH}_3 + \text{CO} \quad (10)
\]

Reaction (10) should not have any activation energy, therefore its importance would depend on the concentration of the radicals involved. In this stage it is necessary to investigate what other possibilities are offered for the formyl radical.

It is generally recognized (53) that the formyl radical is stable at room temperature. In fact, the decomposition process

\[
\text{HCO}^\cdot \rightarrow \text{H}^\cdot + \text{CO} \quad (11)
\]

has an activation energy estimated from 14 to 30 kcal/mole
by various authors (54,55,56,57). The fact that no hydrogen was detected among the reaction products confirms the stability of this radical.

Abstraction of hydrogen from crotonaldehyde by the formyl radical should meet with the same unfavourable activation energy as abstraction of hydrogen by the allyl radical.

\[ \text{HCO} + \text{CH}_3\text{CH:CHCHO} \rightarrow \text{HCHO} + \text{CH}_3\text{CH:CHCO}^- \] (12)

In fact, the bond dissociation energy of the hydrogen in formaldehyde, 79.3 kcal/mole (58), is too close to the bond dissociation energy of the allylic hydrogen in propylene, 76.5 (59), to assume that reaction (11) would be possible at room temperature while reaction (4) is completely excluded. The fact that no formaldehyde was detected among the reaction products is in agreement with this view.

There is at least one reaction into which formyl radicals can enter, and this is recombination to glyoxal

\[ 2\text{CHO} \rightarrow \text{CHOCHO} \] (13)

Reaction (13) is quite plausible, although the presence of glyoxal among the reaction products could not be verified by the analytical tools used.

If the formyl and allyl radicals are eliminated only by radical recombination reactions, then reaction (10) is of considerable importance, and it can account for at least part of propylene and CO found in the reaction products. The assumption, however, that all the propylene and CO are produced
by means of reaction (10) comes to complete disagreement with the observation of Harrison and Lossing (29) that these two products of the Hg-photosensitized decomposition of crotonaldehyde arise mainly through a molecular reaction. It is reasonable to assume that such a reaction can take place also in the photolysis of orotonaldehyde (indeed, of 3-butene-1-al) concurrently with (10)

\[
\text{CH}_2\text{CH}_2\text{CH}_0 + \text{hv} \rightarrow \text{CH}_2\text{CH}_2 + \text{CO} \quad (14)
\]

From the above discussion it follows that the experimental data observed in the photolysis of crotonaldehyde should be interpreted by means of a mechanism comprising reactions (1), (2), (3), (10), (13) and (14):

\[
\text{CH}_2\text{CH}_2\text{CHO} + \text{hv} \rightarrow \text{CH}_2\text{CH}_2\text{CHO} \quad (1)
\]

\[
\text{CH}_2\text{CH}_2\text{CHO} + \text{hv} \rightarrow \text{CH}_2\text{CH}_2 + \text{HCO} \quad (2)
\]

\[
2\text{CH}_2\text{CH}_2\rightarrow \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \quad (3)
\]

\[
\text{CH}_2\text{CH}_2\rightarrow + \text{HCO} \rightarrow \text{CH}_2\text{CH}_2\text{CHO} + \text{CO} \quad (10)
\]

\[
2\text{HCO} \rightarrow \text{CH}_2\text{CH}_2\text{CHO} \quad (13)
\]

\[
\text{CH}_2\text{CH}_2\text{CHO} + \text{hv} \rightarrow \text{CH}_2\text{CH}_2\text{CHO} \quad (14)
\]

According to this mechanism, crotonaldehyde participates in the reaction only in so far as it isomerizes to 3-butene-1-al, the secondary products arising only by decomposition of the latter. This view can be tested by plotting the sum of 3-butene-1-al and its fragments against time. Since each 3-butene-1-al molecule yields either one propylene or 1,5-
hexadiene molecule, the sum should be (3-butene-1-al) + (propylene) + \( \frac{1}{2} (1,5\text{-hexadiene}) \). Such a plot appears in Figure 18. The data are taken from Table XII. From Figure 18, it can be seen that this sum varies linearly with time, as expected. Moreover, the quantum yield of the sum is equal to the quantum yield of isomerization.

In order to derive a kinetic expression for the products of the advanced reaction, it is necessary to estimate the intensity of illumination, \( I_{\text{abs}} \), absorbed by 3-butene-1-al. In the reaction mixture, both 3-butene-1-al and crotonaldehyde are present. The other components need not be considered in this context, because they do not absorb at the wavelength used. Application of Beer's law to both aldehydes gives the expression:

\[
\frac{I_{\text{abs}}}{I_{\text{abs}}} = \frac{1 - \exp\left[-\varepsilon \cdot l \cdot (RH)\right]}{1 - \exp\left[-\varepsilon' \cdot l \cdot (R'H)\right]} \tag{15}
\]

where \( (RH) \) and \( (R'H) \) are the concentrations of crotonaldehyde and 3-butene-1-al respectively and \( \varepsilon, \varepsilon' \) their absorption coefficients; \( l \) is the length of the reaction vessel. The exponents in (15) are much smaller than one, therefore the approximation \( \ln(1 + x) = x \) can be applied. This yields the following expression for \( I_{\text{abs}} \):

\[
I_{\text{abs}} = I_{\text{abs}} \frac{\varepsilon'(R'H)}{\varepsilon \cdot (RH)} \tag{16}
\]

In order to obtain an expression for \( (R'H)/(RH) \), account
Figure 18 Variation of Combined Products with Time
should be taken of the facts that (a) crotonaldehyde concentration diminishes during photolysis resulting in decrease of overall absorbed intensity, and (b) the 3-butene-1-al formed photolyzes according to reactions (2) and (14). The rate of disappearance of crotonaldehyde is

\[-\frac{d(RH)}{dt} = \varphi I_{abs},\]  

where  
\[I_{abs} = \frac{\text{int}}{\text{in}}(RH)\]

\(I_{in}\) is the intensity of illumination with empty reaction vessel. Integration of this expression from \(t = 0\) and \((RH) = (RH)_0\) to \(t = t\) and \((RH) = (RH)\) gives the following equation for the concentration of crotonaldehyde at any time:

\[(RH) = (RH)_0 \exp(-\varphi I_{in} t)\]  

(18)

The concentration of 3-butene-1-al varies as follows:

\[\frac{d(R'H)}{dt} = \varphi I_{in} \exp \varphi I_{in} t(RH) - (\varphi_1 + \varphi_2) I_{in} \exp \varphi I_{in} t(R'H)\]  

(19)

Substitution of (18) into (19) yields the following differential equation:

\[y' + by = a \cdot \exp(-cx)\]  

(20)

where  
\[y = (R'H), \quad x = t, \quad a = \varphi I_{in} \exp \varphi I_{in} t(RH)_0, \quad b = (\varphi_1 + \varphi_2) I_{in} \exp \varphi I_{in} t, \quad c = \varphi I_{in} \exp \varphi I_{in} t\]

The general solution of (20) is:
\[ y = \left[ \frac{a}{(b-c)} \right] \exp(-cx) + c \cdot \exp(-bx) \]

Imposing the boundary condition \( y = 0 \) when \( x \to 0 \), \( c \) is found to be \( c = \frac{-a}{(b-c)} \), and the solution of (20):

\[ y = \left[ \frac{a}{(b-c)} \right] \left[ \exp(-cx) - \exp(-bx) \right] \]

or

\[ (R'\text{H}) = \frac{\Phi \cdot (R\text{H})_0}{(\Phi_1 + \Phi_2)\varepsilon - \Phi_\varepsilon} \left\{ \exp(-\Phi I_{\text{in}}\varepsilon t) - \exp\left[-(\Phi_1 + \Phi_2) I_{\text{in}}\varepsilon t\right] \right\} \] (21)

Correlation of this expression with (18) yields:

\[ (R'\text{H})/(R\text{H}) = \frac{\Phi \cdot \Phi_\varepsilon}{(\Phi_1 + \Phi_2)\varepsilon - \Phi_\varepsilon} \left[ 1 - \exp\left[\left(\Phi_1 + \Phi_2\right)\varepsilon - \Phi_\varepsilon \right] \cdot I_{\text{in}}\varepsilon t \right] \] (22)

Two approximate solutions for \( (R'\text{H})/(R\text{H}) \) can be derived from (22): (i) When photolysis has proceeded for a short time, the approximation \( \ln(1 + x) \approx x \) can be applied for the quantity in parentheses, yielding the expression:

\[ (R'\text{H})/(R\text{H}) = \frac{\Phi \cdot I_{\text{abs}}}{(R\text{H})_0} \] (23)

where the substitution \( I_{\text{abs}} = I_{\text{in}}\varepsilon I(R\text{H})_0 \) has been made and \( (R\text{H}) \) put equal to \( (R\text{H})_0 \). (ii) When the reaction time is long, the exponential term becomes insignificant with respect to one and the ratio of the aldehydes tends to a constant value:

\[ (R'\text{H})/(R\text{H}) = \frac{\Phi \cdot \varepsilon}{(\Phi_1 + \Phi_2)\varepsilon - \Phi_\varepsilon} \] (24)

This long time limit is approached in the set of experiments where the time dependence of the products was studied. A graph of the ratio \( (R\text{H})_2/(R'\text{H}) \), calculated from the data on Table XII
Figure 19. Dependence of \([\text{crotonaldehyde}] / [3-\text{butene-1-al}]\) on time.
appears in Figure 19. It is seen that the ratio approaches the constant value 9.10. Since

\[(\frac{R_H}{R_H'}) = \left[\frac{(\varphi + \varphi)}{\varphi - 1}\right] = 9.10\]

and \(\varphi \approx 0.095 \pm 0.005\),

it follows that

\[(\varphi + \varphi') = 10.10 \times (0.095 \pm 0.005)(\varepsilon / \varepsilon')\]

\[= (1.05 \pm 0.05)(\varepsilon / \varepsilon')\] \hspace{1cm} (25)

When the absorption curve of 3-butene-1-al was taken, (chapter V), it was found that its absorption coefficient is very close to that of crotonaldehyde. Therefore the ratio \(\varepsilon / \varepsilon'\) can be taken as equal to one. Then the sum of the quantum yields

\[\varphi + \varphi' = 1.05 \pm 0.05\]

This estimate will be checked later by calculations from other sources.

Substitution of the ratio \((R_H')/(R_H)\) from (23) into (16) yields the following expression for the light intensity absorbed by 3-butene-1-al at the beginning of the photolysis:

\[I_{abs} = \frac{I_{abs}' t}{(RH)}\]

where \(\varepsilon / \varepsilon'\) is taken as equal to one. It is seen that \(I'_{abs}\) increases proportionally to the time. This result was expected because 3-butene-1-al increases by the same way. The increase
of $I_{\text{abs}}$ makes it impossible to calculate stationary state concentrations for the species $\text{CH}_2: \text{CHCH}_2^*$ and $\text{CHO}^*$. In fact, the following differential equations have to be solved:

$$\frac{d(\text{CH}_2: \text{CHCH}_2^*)}{dt} = \left(\frac{I_{\text{abs}}}{\text{RH}}\right) - 2k_3(\text{CH}_2: \text{CHCH}_2^*)^2 - k_{10}(\text{CH}_2: \text{CHCH}_2^*)(\text{CHO}^*)$$

$$\frac{d(\text{CHO}^*)}{dt} = \left(\frac{I_{\text{abs}}}{\text{RH}}\right) - 2k_{13}(\text{CHO}^*)^2 - k_{10}(\text{CH}_2: \text{CHCH}_2^*)(\text{CHO}^*)$$

If it is assumed that $\frac{d(\text{CH}_2: \text{CHCH}_2^*)}{dt} = \frac{d(\text{CHO}^*)}{dt}$, it follows that

$$(\text{CHO}^*) = \left(\frac{k_3}{k_{13}}\right)^{\frac{1}{2}}(\text{CH}_2: \text{CHCH}_2^*)$$

and the previous equations simplify to relations of the form

$$y' + ay^2 = bt$$

(29)

which still has no accurate solution. If the approximation is introduced: $y' = 0$ (which is equivalent to a stationary state hypothesis), the solution of (29) is

$$y = \left[\frac{bt}{a}\right]^{\frac{1}{2}}$$

(30)

and

$$y' = \frac{1}{2} \left(\frac{b}{at}\right)^{\frac{1}{2}}$$

Then

$$y'/y = 1/(2t)$$

If $t > 60$ seconds, as the case is when the secondary products
of the photolysis are measured, it can be seen that the error introduced by the approximation is less than 1%.

Substitution of the relevant variables in (30) yields the following expressions for the concentrations of species CH$_2$:CHCH$_2$ and CHO at time t:

\[
\text{CH}_2\text{CHCH}_2 = \frac{I_{abs}^2 \Phi t}{A(RH)_0}^{1/2}
\]

\[
\text{CHO} = \left[ \frac{I_{abs}^2 \Phi t}{B(RH)_0} \right]^{1/4}
\]

where \( A = 2k_3 + k_{10}(k_3/k_{13})^{1/2} \)

\( B = 2k_{13} + k_{10}(k_{13}/k_3)^{1/2} \)

Now the rates of formation of 1,5-hexadiene and propylene can be easily calculated:

\[
d(1,5\text{-hexadiene})/dt = k_3 \frac{I_{abs}^2 \Phi t}{A(RH)_0}
\]

\[
d(\text{propylene})/dt = k_{10} \frac{I_{abs}^2 \Phi t}{(AB)^{1/2}(RH)_0} + \frac{I_{abs}^2 \Phi t}{(RH)_0}
\]

The integrated forms of (33) and (34) are:

\[
(1,5\text{-hexadiene}) = \frac{k_3 \Phi \Phi (I_{abs} \cdot t)^2}{A(RH)_0}
\]

\[
(\text{propylene}) = \left[ \frac{k_{10} \Phi \Phi}{2(AB)^{1/2} + \Phi \Phi} \right] (I_{abs} \cdot t)^2 (RH)_0
\]
According to these expressions, the concentration of both hydrocarbons should be proportional to \( (I_{\text{abs}} \cdot t)^2/(R\nu) \). This relation is obeyed quite well by 15-hexadiene. Propylene concentration, however, was found to vary with \( (I_{\text{abs}} \cdot t)^2/(R\nu) \) \( 1.3 \sim 1.5 \). Such a dependence on \( (R\nu)_0 \) could be justified if reaction (14) takes place through an activated complex, which is long-lived enough to undergo collisional deactivation with crotonaldehyde molecules. In this case, reaction (14) would be substituted by the following steps:

\[
\begin{align*}
\text{CH}_2\text{CHCH}_2\text{CHO} + h\nu & \rightarrow (\text{CH}_2\text{CHCH}_2\text{CHO})^+, \Phi'^{\text{abs}} \quad (14a) \\
(\text{CH}_2\text{CHCH}_2\text{CHO})^+ + M & \rightarrow \text{CH}_2\text{CHCH}_2\text{CHO} + M, \quad k_d \quad (14b) \\
(\text{CH}_2\text{CHCH}_2\text{CHO})^+ & \rightarrow \text{CH}_2\text{CHCH}_3 + \text{CO}, \quad k_r \quad (14c)
\end{align*}
\]

This reaction scheme yields the following expression for the rate of formation of propylene:

\[
\begin{align*}
\frac{d(\text{propylene})}{dt} &= \frac{\Phi'^{\text{abs}} I_{\text{abs}}^2 \cdot t}{(AB)^2(R\nu)_0} + \frac{\Phi'^{\text{abs}} I_{\text{abs}}^2 \cdot t}{k_d M + k_r (R\nu)_0} 
\end{align*}
\] (37)

Integration and substitution of \( M \) by \( (R\nu)_0 \) gives the equation

\[
(\text{propylene})^\frac{2}{3} = \left[ \frac{k_{10} \Phi \Phi^t}{2(AB)^2(R\nu)_0} + \frac{k_r \Phi \Phi^t}{k_d (R\nu)_0 + k_r (R\nu)_0} \right] (I_{\text{abs}}^t)^2
\] (38)

which contains the term \( (R\nu)_0^2 \) in the denominator. Inclusion of the deactivation step (14b) is further justified by the fact that the ratio \( \text{propylene}/(1,5\text{-hexadiene}) \) decreases as the crotonaldehyde pressure increases. This can be seen in Figure 17. The fact that the same ratio increases as the reaction proceeds further, as it can be seen in Figures 16 and 20, can be attributed partly to the gradual decrease of
Figure 20. Dependence of [propylene]/[1,5-hexadiene] on time.
crotonaldehyde pressure in the course of the reaction. This factor, however, is not big enough to account for all the increase observed. An additional reaction may be taking place, which involves formation of propylene, e.g. by dissociation of 1,5-hexadiene. This latter hydrocarbon was found to be quite stable, when illuminated alone at 2450-4000 Å, and this result was expected because it does not absorb at this wavelength. It could be, however, that its decomposition is sensitized by the other compounds in the reaction mixture. No further guesses can be made on the subject, because of lack of sufficient data.
CHAPTER V.

MECHANISM OF THE PHOTOLYSIS OF GASEOUS 3-BUTENE-1-AL
AT 30°C AND 2450-4000 Ψ
V. PHOTOLYSIS OF 3-BUTENE-1-AL AT 2450-4000 Å AND 30°C.

1. EXPERIMENTAL

The same experimental technique was used as in the photolysis of crotonaldehyde. The reaction cell was used without removing the layer of polymer deposited on its surface during previous experiments. One hour evacuation, before each experiment, was found an adequate precaution for the results to be reproducible.

The absorbance for each reaction was calculated, as in the case of crotonaldehyde, by measuring the intensity of illumination with the cell evacuated, In, and then evaluating Iabs for a given pressure by using the absorption curve for 3-butene-1-al, Figure 21.

2. RESULTS

Preliminary experiments showed that propylene, 1,5-hexadiene and CO were produced during the photolysis of 3-butene-1-al with a quantum yield several times higher than the one observed in the crotonaldehyde isomerization. Small amounts of crotonaldehyde were detected in each experiment, but the results were not reproducible because 3-butene-1-al in the storage trap contained about 1% crotonaldehyde and also additional amounts were produced during the reaction and the subsequent chromatographic analysis. Therefore no results
**Figure 21. Absorption Curve for 3-Butene-1-AL**
on crotonaldehyde production are recorded in the present work. It can only be noted that the amount of crotonaldehyde observed in a reaction was never larger than 10% of the amount of the other products.

**Dependence on Time**

20 mm Hg of 3-butene-1-al were photolysed for various time intervals using the same light intensity. The results appear on Table XV. The quantum yields of propylene and 1,5-hexadiene are calculated for the first 10 minutes of the reaction. The quantum yield of CO can be taken as equal to that of propylene. From a graph on Figure 22 it is seen that the rate of formation of the products is constant for a fairly long period of time. The reaction time was extended up to 135 minutes in order to study its influence on the ratio propylene/1,5-hexadiene. From Figure 23 it is seen that this ratio increases with time.

**TABLE XV**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Propylene</th>
<th>1,5-hexadiene</th>
<th>CO</th>
<th>prop.</th>
<th>hex.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>16.5</td>
<td>2.99</td>
<td>13.0</td>
<td>0.71</td>
<td>0.128</td>
</tr>
<tr>
<td>3</td>
<td>26.9</td>
<td>5.02</td>
<td>25.1</td>
<td>0.77</td>
<td>0.142</td>
</tr>
<tr>
<td>5</td>
<td>40.0</td>
<td>7.51</td>
<td>45.5</td>
<td>0.68</td>
<td>0.128</td>
</tr>
</tbody>
</table>
Figure 22. Products of photolysis of 3-butene-1-ol.
**LEGEND**

- ○ FROM 3-BUTENE-1-AL PHOTOLYSIS
- □ "CROTONALDEHYDE"

**Figure 23. Dependence of \([\text{propylene}] / [1,5\text{-hexadiene}]\) on Time**
Dependence on $I_{abs}$

20 mm Hg of 3-butene-1-al were illuminated for 10 minutes with variable intensity of illumination. The results appear in Table XVI.

**TABLE XVI**

Dependence of Products on $I_{abs}$.

In all experiments 20 mm Hg 3-butene-1-al were photolyzed for 10 minutes.

All results are in units of mole·l⁻¹·x10⁷.

$I_{abs}$

<table>
<thead>
<tr>
<th>ein·l⁻¹·sec⁻¹ x10⁸</th>
<th>Propylene</th>
<th>1,5-hex.</th>
<th>CO</th>
<th>prop.</th>
<th>hex.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.855</td>
<td>34.2</td>
<td>6.65</td>
<td>-</td>
<td>0.66</td>
<td>0.129</td>
</tr>
</tbody>
</table>
The quantum yield of propylene, 0.71±0.05 and 1,5-hexadiene 0.134±0.018 calculated in Table XVI is in agreement with the quantum yields, 0.73±0.05 and 0.137±0.014 respectively, calculated in Table XV.

**Dependence on Pressure of 3-butene-1-al.**

A set of experiments was carried out in which the 3-butene-1-al pressure was varied from 4-30 mm Hg. The total amount of absorbed radiation was kept constant by adjusting the duration of the experiment in such a way that the product $I_{abs} \times \text{time}$ was constant. From the data on Table XVII it is obvious that the quantum yield of 1,5-hexadiene is independent of the 3-butene-1-al pressure, while that of propylene decreases as the pressure increases. This drift is shown in Figure 24.
Figure 24: Dependence of $P_{\text{propylene}}$ on 3-butene-1-al pressure
Figure 25. Dependence of \([\text{propylene}]/[\text{1,5-hexadiene}]\) on pressure.
TABLE XVII
Dependence on Pressure of 3-butene-1-al.
Absorbed radiation $2.34 \times 10^{-5}$ ein\textit{·}1\textit{-1}

<table>
<thead>
<tr>
<th>3-butene-1-al mm Hg</th>
<th>propylene mole\textit{-1}×10\textit{-6}</th>
<th>1,5-hex mole\textit{-1}×10\textit{-6}</th>
<th>prop</th>
<th>hex</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>18.2</td>
<td>3.06</td>
<td>0.78</td>
<td>0.131</td>
</tr>
<tr>
<td>6.9</td>
<td>18.3</td>
<td>3.50</td>
<td>0.78</td>
<td>0.150</td>
</tr>
<tr>
<td>10.1</td>
<td>17.5</td>
<td>3.30</td>
<td>0.75</td>
<td>0.141</td>
</tr>
<tr>
<td>12.2</td>
<td>18.0</td>
<td>3.02</td>
<td>0.77</td>
<td>0.129</td>
</tr>
<tr>
<td>15.7</td>
<td>17.8</td>
<td>3.18</td>
<td>0.76</td>
<td>0.136</td>
</tr>
<tr>
<td>20.0</td>
<td>16.5</td>
<td>2.99</td>
<td>0.71</td>
<td>0.122</td>
</tr>
<tr>
<td>23.6</td>
<td>17.1</td>
<td>3.06</td>
<td>0.73</td>
<td>0.131</td>
</tr>
<tr>
<td>27.2</td>
<td>16.1</td>
<td>3.26</td>
<td>0.69</td>
<td>0.139</td>
</tr>
<tr>
<td>30.0</td>
<td>16.3</td>
<td>3.19</td>
<td>0.70</td>
<td>0.136</td>
</tr>
</tbody>
</table>

DISCUSSION

From the results shown in the previous section it is clear that 3-butene-1-al, when illuminated at 30°C with light of wavelength 2450-4000 Å, undergoes decomposition to 1,5-hexadiene, propylene and CO. The two last products, in so far that CO was determined, are formed in almost equimolecular amounts.

These results are in agreement with the reaction mechanism proposed for the photolysis of crotonaldehyde. Reactions
(2), (3), (10), (13) and (14a,b,c), of the last chapter explain very well the experimental results.

\[
\text{CH}_2: \text{CHCH}_2\text{CHO} + h\nu \rightarrow \Phi_{\text{abs}} \rightarrow \text{CH}_2: \text{CHCH}_2\cdot + \text{CHO}. \quad (2)
\]

\[
2\text{CH}_2: \text{CHCH}_2\cdot \rightarrow \text{CH}_2: \text{CHCH}_2\text{CH}_2\text{CH}: \text{CH}_2 \quad (3)
\]

\[
\text{CH}_2: \text{CHCH}_2\cdot + \text{CHO} \rightarrow \text{CH}_2: \text{CHCH}_3 + \text{CO} \quad (10)
\]

\[
2\text{CHO} \rightarrow \text{CHOCHO} \quad (13)
\]

\[
\text{CH}_2: \text{CHCH}_2\text{CHO} + h\nu \rightarrow \Phi_{\text{abs}} \rightarrow \left(\text{CH}_2: \text{CHCH}_2\text{CHO}\right)^\dagger \quad (14a)
\]

\[
\left(\text{CH}_2: \text{CHCH}_2\text{CHO}\right)^\dagger + \text{M} \rightarrow \text{CH}_2: \text{CHCH}_2\text{CHO} + \text{M} \quad (14b)
\]

\[
\left(\text{CH}_2: \text{CHCH}_2\text{CHO}\right)^\dagger \rightarrow \text{CH}_2: \text{CHCH}_3 + \text{CO} \quad (14c)
\]

The following kinetic expressions can be derived for propylene and 1,5-hexadiene:

\[
\frac{d (\text{propylene})}{dt} = \left[ \frac{k_{10}\Phi_i}{(AB)^{1/2}} + \frac{k_r\Phi_i}{k_d(RH) + k_r} \right] x_{\text{abs}} \quad (1)
\]

\[
\frac{d (1,5\text{-hexadiene})}{dt} = \frac{(k_3\Phi_i x_{\text{abs}})}{A} \quad (2)
\]

where \( A = 2k_3 + k_{10}(k_3/k_13)^{1/2} \) and \( B = 2k_13 + k_{16}(k_13/k_3)^{1/2} \).

These expressions agree well with the experimental results.

In chapter IV the sum of the quantum yields \((\Phi_i + \Phi_2)\) was estimated to be 1.05±0.05. Now this sum can be calculated directly from the quantum yields of propylene and 1,5-hexadiene. From the mechanism of the photolysis it is seen that the stoichiometry of the overall reaction is:

\[
(m+n) \text{CH}_2: \text{CHCH}_2\text{CHO} + h\nu \Phi_{\text{abs}} \rightarrow m\text{CH}_2: \text{CHCH}_3 + m\text{CO} + n\text{CH}_2: \text{CHCH}_2\text{CH}_2\text{CH}: \text{CH}_2 \quad (3)
\]

Therefore the sum \((\Phi_i + \Phi_2)\) is equal to the quantum yield of
propylene plus twice the quantum yield of 1,5-hexadiene. The latter can be taken, from Tables XV and XVI, as equal to \(6.13 \pm 0.02\). The quantum yield of propylene has been seen to increase with decreasing pressure of 3-butene-1-al. The value at zero pressure, obtained by extrapolation of the curve in Figure 24, is \(0.79 \pm 0.05\). Therefore

\[ \Phi_i + \Phi_2 = (0.79 \pm 0.05) \times 2 \times (0.135 \pm 0.020) = 1.06 \pm 0.09 \]

This value of \((\Phi_i + \Phi_2)\) is in good agreement with the one estimated in chapter IV. It is probable that the lower limit of this value is nearer to the true value of the quantum yield of the overall reaction, because values higher than 1 would imply a chain mechanism.

The fact that the quantum yield \((\Phi_i + \Phi_2)\) calculated in the experiments with crotonaldehyde was verified, is in support of the proposed mechanism for the photolysis of crotonaldehyde. The similarity between the experimental results obtained in the photolysis of the two isomeric aldehydes is further manifested in the fact that the ratio (propylene)/(1,5-hexadiene) varies in a similar way, as seen in Figures 23 and 25. This ratio appears to be higher in the case of 3-butene-1-al, but extrapolation to zero pressure of the curves in Figure 25 shows that probably this ratio is the same in the photolysis of both aldehydes, when no third body interferes.
If the quantum yield of 3-butene-1-al decomposition is taken as one, it means that every quantum of light absorbed by 3-butene-1-al causes it to decompose either to radicals or to propylene and CO. It is not possible to estimate the individual values of $\Phi_1$ and $\Phi_2$. If it is assumed that all the allyl radicals dimerize to 1,5-hexadiene, i.e. that reaction (11) is unimportant, then

$$\Phi_1 = 2\Phi_{\text{hexad}}.$$  

$$= 0.27 \pm 0.04$$

This is a lower limit for $\Phi_1$, leaving an upper limit for $\Phi_2$:

$$\Phi_2 \leq 0.79 \pm 0.05$$

It cannot be considered that the results obtained in the photolysis of crotonaldehyde and 3-butene-1-al are final. There are still some points of the reactions which need further study. One point is the increase of the ratio (propylene)/(1,5-hexadiene) with time in the photolysis of both aldehydes. Another point is the thermal isomerization of 3-butene-1-al to crotonaldehyde, a reaction which can be investigated successfully only if pure 3-butene-1-al is prepared.

Finally, there is much uncertainty about the real quantum yields of crotonaldehyde isomerization and 3-butene-1-al decomposition, due to the fact that illumination of a wide wavelength range was used. The quantum yield of 3-butene-
1-al decomposition, especially, is so high, that it leaves some doubt about the complete absence of chains from the proposed mechanism. A detailed study of the reaction at specific wavelengths would clear this point.
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