THE VAPOR PHASE PHOTOLYSIS

OF (†)2-METHYLBUTANAL

DISSertation
Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State
University

By
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*****

The Ohio State University
1957

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Adviser
Department of Chemistry
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I. INTRODUCTION

The photolysis of the lower molecular weight aliphatic aldehydes have been well investigated. The present work, the photolysis of (t)2-methylbutanal was undertaken for a number of reasons.

(1) The first objective was to investigate the primary processes which occur when an aldehyde molecule absorbs light energy. These processes would be expected to be similar to those found for n-butyraldehyde by Blacet and Calvert² since the molecular structure has been altered

\[ n-C_3H_7CHO + h\nu \rightarrow C_3H_7 + HCO \quad \text{I} \]
\[ \rightarrow C_3H_8 + CO \quad \text{II} \]
\[ \rightarrow C_2H_4 + CH_3CHO \quad \text{III} \]
\[ \rightarrow CH_3 + C_2H_4CHO \quad \text{IV} \]

only by addition of a methyl group on the carbon alpha to the carbonyl carbon.

(2) Primary process III'

\[ CH_3CH_2CH_2COR + h\nu \rightarrow C_2H_4 + CH_3COR \quad \text{III'} \]

has been observed in a number of cases²,³,⁴ which involve

---

a normal propyl group adjacent to the carbonyl group. It was therefore desired to learn what effect the alpha methyl group would have on the intramolecular ethylene-forming primary process III.

(3) The secondary thermal reactions of photochemically produced methyl, ethyl, n-propyl, and isopropyl radicals have been investigated. It was felt that (†)2-methylbutanal would be a good source of sec-butyl radicals. Therefore the possible secondary thermal reactions of the sec-butyl radical, hydrogen abstraction, disproportionation, combination, and decomposition, could be identified and studied.

(4) Many investigators have been interested in recent years in the configuration of alkyl free radicals, that is, whether they retain a tetrahedral configuration or flatten out into a planar form or are perhaps in some intermediate form. The aldehyde, (†)2-methylbutanal, used in this work contains an asymmetric center and if primary process I

\[ \text{C}_2\text{H}_5\text{CH(CH}_3\text{)CHO} + \text{hv} \rightarrow \text{C}_2\text{H}_5\text{CH(CH}_3\text{)CHO} + \text{HCO} \]

occurs on photolysis, it is possible that a sec-butyl radical could be formed that is optically active, that is,

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retains its pyramidal structure. This would be the simplest alkyl free radical that could contain an asymmetric carbon atom, except for CH₃CH(D). If iodine vapor is present in the vapor phase photolysis of (+)2-methylbutanal, a rapid secondary reaction (1)

C₂H₅CH(CH₃) + I₂ → C₂H₅CH(CH₃)I + I

(1)
to form 2-iodobutane would be expected. Therefore from the iodine-inhibited photolysis of (+)2-methylbutanal it was felt that some knowledge of the configuration of a gaseous alkyl free radical could be gained by observing the optical activity of the 2-iodobutane formed as a condensable product.
II. EXPERIMENTAL PROCEDURE

A. Photolysis Apparatus for Uninhibited Iodine Runs

1. The Mercury Arc and Optical System

The source used is a Hanovia S-500 Type A burner mounted in a brass cylinder and cooled by circulating water through copper tubing soldered to the outside of the cylinder. A stable 250 volt potential is obtained for the arc circuit by connecting the 110 volt line voltage through a Sorenson A. C. Voltage Regulator to a Model 20651 transformer. The output of the arc is controlled with a series 50-ohm, 500 watt Ohmite Variable resistor. The current is adjusted to 3 amperes in all runs, by use of the resistor, with a potential of about 145 volts.

The arc radiation is passed through a filter system described by Hunt and Davis\(^e\) which isolates 3130 Å light with less than 0.01% extraneous light. Light from the arc F (Figure I) is collimated with a quartz lens G, and passed through the all quartz cell H, which is divided into three parts. In the two larger divisions (diameter 50 mm., length 50 mm.) are nickel chloride and potassium chromate respectively, and the third (length 10 mm.) contains potassium acid phthalate. The light then is passed

Fig. 1. - The photolysis system.

A. Sample tube  
B. Sample tube  
C. Circulating pump  
D. Trap  
E. Cell  
F. Mercury arc  
G. Lens  
H. Filter cell  
I. Corning filter No. 9863  
J. Lens  
K. Stop  
L. Quartz plate  
M. Filter cell  
N. Photomultiplier microphotometer  
P. Mercury valve  
Q. Mercury valve  
R. Mercury valve  
S. Toepler pump  
T. Mercury reservoir  
V. Low-vacuum stopcocks
through filter I (Corning Red Purple Corex No. 9863) and is further collimated by quartz lens J, and then is passed through stop K (25 mm. diameter) which decreases the beam cross section to about the area of the cell, a quartz window L, the quartz reaction cell E, and another quartz window L. The amount of light transmitted is measured by use of a No. 10-210 Aminco Photomultiplier Microphotometer (N). To obtain conditions giving linear response, the intensity was reduced by placing cell M, which contained potassium chromate, in front of the microphotometer.

2. The Temperature Control System

The reaction cell is inclosed in an oven, which is made up of two identical halves for easy access to the cell. The oven consists of an inner aluminum cylinder (9.5 cm. outer diameter, 4.4 cm. inner diameter), which is wrapped in a mica sheet for electrical insulation and the mica is wrapped with resistance wire. The wire is covered with a layer of asbestos which has a sheet-metal jacket. The oven's overall dimensions are 21.6 cm. in length and 14.6 cm. in diameter. The distance from the quartz window L to the cell is therefore about 8 cm. which insures minimum temperature fluctuations.

The voltage is regulated by a Sorenson A. C. Voltage Regulator, Model 1000-S connected through a powerstat. The stabilized voltage to the oven has a 0-110 volt range.
and the temperature can be controlled to within ±1° with normal room conditions.

3. The Photolysis System

The photolysis system (Figure I) consists of a 50 mm. all-quartz cell E, a trap D, an all-glass circulating pump C and 8 mm. Pyrex tubing having a total volume of approximately 280 cc. The circulating pump consists of a soft iron bar sealed in a Pyrex glass piston which fits snugly in 22 mm. Pyrex tubing. At the lower end of the vertical pump is a ground glass valve. The piston is lifted by activation with a solenoid positioned around the pump. By use of an electronic timer, intermittent current is supplied to the solenoid. When the solenoid is actuated the resulting pressure differential caused by the rising piston opens the valve and the gases enter the cylinder. When the circuit is broken the piston falls, slowly closing the valve, and the gases leak between the piston and the pump walls. The trap D is 17 cm. in length and 2.5 cm. in diameter. Cell E has planar quartz windows, an all-quartz body and is 5 cm. in length, 3 cm. in diameter.

4. The High-Vacuum System

The high-vacuum system consists of a Welch Duo-Seal Oil Pump Model 1400-B, a three-stage mercury diffusion

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-9-
pump, a 20 mm. hollow bore stopcock, a main high vacuum line of 25 mm. diameter and a McLeod gauge with a gas trap volume of 500 cc. and a 1.0 mm. diameter capillary.

B. Photolysis Apparatus for Iodine-Inhibited Runs

1. The Mercury Arc and Optical System

This system was the same as in II-A-1 except for the following changes. lens G was omitted, filter cell M and the microphotometer, N, were removed, stop K was omitted and cell E was replaced by a 150 mm. cell (E) as shown in Figure 4.

2. The Temperature Control System

The entire photolysis system was enclosed in a specially made furnace (Figure 4) or "black box" which measured 86 mm. long, 56 mm. wide and 76 mm. in height, outside dimensions. The box was made of Transite, inner surface, and black painted 3/16 in. plywood outer surface which was separated by about a 1 in. dead space. The box was made with the front and top removable to facilitate easy access to the component parts of the system. The box was heated with two 500 watt fin heaters (I) which were operated off the 115 volt line voltage through a powerstat. The desired temperature was maintained by use of a cone

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Fig. 2 - System for product transfer
Fig. 3 - The polymerization tube
Fig. 4. - The optical and temperature control systems for the iodine-inhibited photolysis of 2-methylbutanal.

| A.         | Mercury arc                  |
| B.         | Filter cell                  |
| C.         | Corning filter No. 9863      |
| D.         | Lens                         |
| E.         | Cell                         |
| F.         | Trap                         |
| H.         | Ground glass valve           |
| I.         | Fin heaters                  |
| J.         | Blower                       |
| K.         | Cone heater                  |
| L.         | Thermoswitch                 |
| M.         | Quartz plate                 |
heater (K) in series with a thermostwitch (L) which was set to switch the cone heater on if the temperature fell, and switch off when the right temperature was again reached. The air was well circulated by use of a blower (J) so that all parts of the furnace were at the same temperature. All pieces were clamped in place, by wrapping lead foil around them to avoid "cold spots." In this manner temperatures were controlled to ±1°, with normal room conditions.

3. The Photolysis System

The photolysis system (Figure 4) consisted of a 150 mm. all-quartz cell E, a trap F, all ground glass valve G and 7 mm. Pyrex tubing. The system had a total volume of 235 ml. The glass valve consisted of a soft iron bar sealed in a Pyrex glass piston and ground to fit the opening at the bottom of a 20 mm. Pyrex tube. The valve was opened by activation with a solenoid positioned around the valve. The trap was 18 cm. long and 2.5 cm. in diameter. The cell E has planar quartz windows, a quartz body, and was 15.0 cm. long and 3.1 cm. in diameter.

C. Preparation of (+)2-Methylbutanal

By oxidation of (+)2-methylbutanol ([α]D20 = +5.75°) with a chromic oxide-pyridine mixture (†)2-methylbutanal

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9 Obtained from Harold Shechter and D. K. Brain of The Ohio State University.
was prepared. To 50 gm. (0.57 moles) of 2-methylbutanol in 200 ml. pyridine was added dropwise 45 gm. (0.45 moles, 15 excess) chromic oxide in 200 ml. pyridine at 15°. The chromic oxide was added to the pyridine over a 1/2 hour period at 5°-10° through a Gooch sleeve. On addition of the alcohol the yellow complex solution turned dark at once. The mixture was allowed to stand 16-24 hours and then was fractionally distilled, after the column came to equilibrium. At a high reflux ratio the distillate was removed at 75°. The azeotrope was separated into two layers, the lighter was mainly aldehyde, the heavier, water and pyridine. The aldehyde layer was washed twice with a 2 N. H₂SO₄ solution saturated with Na₂SO₄, and then with a saturated solution of Na₂CO₃. The aldehyde was then added to a saturated solution of NaHSO₃ and the white bisulfite adduct was filtered, washed with ether and dried for 24 hours on a porous plate. The adduct was then decomposed with a saturated solution of Na₂CO₃ and the aldehyde layer separated, dried over CaCl₂ and distilled, b.p. 90°-92° (750 mm.); lit. 90°-92° (760 mm.) \(^{11}\) \([\alpha]_D^0 = 4.49°,\) 2,4-dinitrophenylhydrazone, recrystallized from ethyl alcohol, m.p. 123.5°-124.7°). A middle cut was used as the photolysis sample. The aldehyde was further purified

\(^{11}\) Erhlich, F., Ber., 40, 2538 (1907).
in the photolysis system by bulb-to-bulb distillation (A to B, Figure I) and bulb A was then pulled off.

D. The Uninhibited Photodecomposition of (+)2-Methylbutanal

The photolysis system is prepared for the photodecomposition by leaking helium into the system and pumping it out over an extended period with the high-vacuum system. The aldehyde is frozen out with a dry ice-acetone bath during the pumping. The oven is allowed to come to equilibrium at the desired temperature and the arc stabilized at 3 amperes. When the system is ready, mercury valve P is opened and the aldehyde sample is warmed to allow the desired pressure to be attained in the system after which valve P is closed. The pressure is measured by reading the difference in height of the arms of mercury valve Q with a cathetometer. At this point the circulation pump C is started and allowed to operate throughout the photolysis. The shutter on arc F is then opened and the photolysis process started. All runs are timed with a Meylan stop watch. At the completion of the run, the arc is shut off and a Dewar containing liquid nitrogen is placed on trap D and all condensable materials are frozen out. All gases not condensable at this temperature are removed by lowering mercury valve R and pumping them out with the Toepler pump. The sample is collected in a sample tube in the mercury reservoir T. The system is pumped on until the remaining
gases collapse to a small bubble at the top of the Toepler pump and no further material can be forced over to the reservoir. The liquid nitrogen is then replaced with a dry ice-acetone mixture and the gases volatile at that temperature (-80.0°C) are removed as before with the Toepler pump. The remaining condensable materials are distilled to the arm A of the polymerization tube shown in Figure 3, which is attached to one of the standard joints shown in Figure 2. The bottom or "larger arm" of the tube contains 50 or 60 pellets of Baker reagent grade KOH. The potassium hydroxide polymerizes almost completely the excess aldehyde which remains after the photolysis. In this manner the products are separated into three fractions.

E. The Photodecomposition of (t)2-Methylbutanal in the Presence of Iodine

In these photolyses, the furnace is allowed to come to approximately the desired temperature, usually over a 10-12 hour period. When this is attained, a nitrogen or helium tank is attached at A, (Figure 2) (with B and C plugged) and the gas leaked in until the inside pressure is slightly higher than atmospheric. The front of the box is then removed and the following operations are completed as soon as possible. The tip of trap F (Figure 4), which has been scratched previously, is broken off, the inert gas flow started again, and a cup, made from a sealed off piece of
3 mm. tubing, which contains a weighed amount of iodine to give the iodine pressure wanted at the given temperature, is dropped into the trap. A Dewar of liquid nitrogen is placed around the trap and the trap is then sealed off, the gas flow is stopped just before sealing is complete, and the box front replaced. The system is then evacuated well with the high-vacuum system. When a good vacuum is attained the valve G is closed and the liquid nitrogen removed from around the trap and the iodine is allowed to warm up. When the box temperature has again reached equilibrium, mercury valve P (Figure I) is lowered and the aldehyde is warmed. When the aldehyde pressure is sufficiently higher than that of the iodine to prevent back diffusion of iodine, valve G (Figure 4) is opened and aldehyde let into the photolysis system. Valve P is closed and the pressure is read on the arms of valve Q as in II-D. Valve G is then closed and the arc shutter is opened to begin the photolysis. A test is made to determine if the iodine in the system is lost due to reaction with water or in some wall reaction with aldehyde (both unlikely unless the technique of induction was bad): white light is shown in window M and the violet iodine color is observed in the cell. No loss of iodine color was observed in any of the photolyses.
At the completion of the photolysis, the arc is closed, the furnace shut off, and the front removed from the box. First a Dewar of liquid nitrogen is placed around trap F, then one of dry ice-acetone and these two fractions are removed as in II-D. The remaining fraction is in trap F.

F. Analyses of the Products

1. The Micro Gas Buret

Both gaseous fractions are measured with a Blacet-Leighton gas analysis system\(^\text{12}\) and the measured volumes corrected to standard temperature and pressure. The first fraction, gases noncondensable at liquid nitrogen temperature, is split into two parts and one part analyzed for CO with the gas buret. This is done by placing a bead of silver oxide (which had been shaven to expose a fresh surface), attached by water glass to a platinum wire, into the sample and CO is removed by adsorption. The sample is measured again with the difference being the amount of CO the sample contained. Repeated additions of the bead are made until no volume change is noted which showed all CO is removed. However the first bead generally removes over 95% of the CO.

2. The Mass Spectrometer

All identifications and measurements of products other than CO are made with a General Electric Analytical Mass

Spectrometer. The products are identified by comparing spectra of unknown composition with spectra of known mixtures and from data of the National Bureau of Standards. Products identified in this manner are H₂ and CH₄ in the first fraction, C₂H₄, C₄H₈ (mixture of 1(and 2)-butene), n-C₄H₁₀, and C₃H₆ (in runs above 150°) in the second fraction. C₆H₁₈ (3,4-dimethylhexane) is found among the condensable products. In the iodine-inhibited runs CO, but no CH₄ is found in the first fraction. H₂ may have been present, but was not analyzed for. Only C₂H₄ and n-C₄H₁₀ are found in the second fraction. 2-Iodobutane is identified in the condensable fraction. Table I shows the manner in which the composition of unknown mixtures is calculated.

The peak intensities of the unknown mixture are measured and compared with the peak intensities of known volumes of standard gases. In the example shown in Table I the peak intensities minus background of the second fraction of run 3 are given in (1). Peaks 44 and 28 are not used because of the large background corrections that are usually necessary. The continuous spectrum starting at 59 indicates the presence of n-butane. (2) gives the intensities for a standard sample of n-butane.

All standard gases used were Phillips Research Grade.
Table 1
Sample Calculation of Mass Spectrometric Analysis (Run 3)

<table>
<thead>
<tr>
<th>m/e</th>
<th>(1) Intensity Run n-Butane (54.7 μl.)</th>
<th>(2) Intensity n-Butane (35.15 μl.)</th>
<th>(3) (2)/(1)</th>
<th>(4) (2)/.759</th>
<th>(5) (1)-(4)</th>
<th>(6) Intensity C₄H₁₀ (33.9 μl.)</th>
<th>(7) (6)/(5)</th>
<th>(8) (6)/17.9</th>
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<tr>
<td>59</td>
<td>7.7</td>
<td>5.1</td>
<td>0.662</td>
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<td>58</td>
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<td>131.8</td>
<td>.745</td>
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<td>57</td>
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<td>55</td>
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<td>10.9</td>
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### Table I (continued)
The Sample Calculation of Mass Spectrometric Analysis (Run 3)

<table>
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<tr>
<th>m/e</th>
<th>(9) (5)-(8)</th>
<th>(10) ( \text{Intensity} ) ( \text{C}_2\text{H}_4 ) ( (35 \mu \text{mol}) )</th>
<th>(11) (\frac{(10)}{(9)})</th>
</tr>
</thead>
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<tr>
<td>26</td>
<td>49.2</td>
<td>316.</td>
<td>6.4</td>
</tr>
</tbody>
</table>

(2) is divided by (1) and the amount of \( n \)-butane present is calculated. The peaks used for this are 59, 58, 57, 43, and 42. These peaks are free from contribution by all other components. If propene were present there would be a contribution by it to the 42 peak, however it can be seen that 42 and 41, another large propene peak, are accounted for in the run without finding propene. A weighted average is calculated and from it the amount of \( n \)-butane present (i.e. \( \frac{35.15}{.759} = 46.3 \mu \text{mol} \) \( n \)-butane). In (4) the remaining butane peaks are divided by the weighted average and these values subtracted from the peak heights of (1) in (5). (6) gives the intensities of 2-butene (Since the butene is present in such a small quantity and is probably a mixture of \( 1 \)-butene and cis(and trans)-2-butene, trans-2-butene was used in all calculations as the most representative. The spectra of these butenes are not greatly different.). (6) is then divided by (5) to give the
values in column (7). A weighted average is again calculated using 56, 55, 41, 40, and 39 and the amount of butene present is found. The remaining peaks to be considered are adjusted by dividing (6) by 17.9 (the weighted average) and subtracting these values from (5) (column (9)). The peak intensities of ethene are given in (10) and (10)/(9) in (11). A weighted average for the ethene is calculated from (11) and the amount of ethene present calculated from peaks 26 and 27. All estimates are made in this manner.

The absence of a 30 peak shows that ethane is not present. In runs where propene was present it was determined in a similar manner as described above. The first fraction containing CH₄, H₂, and CO was split in half. CO is analyzed for on the gas buret and CH₄ and H₂ on the mass spectrograph in the same manner as above.

Table 2 gives the main peaks which are most important in identification and calculation of the products.

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<th>Compound</th>
<th>Main Peaks</th>
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<td>C₂H₄</td>
<td>25, 26, 27</td>
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<tr>
<td>C₃H₆</td>
<td>27, 40, 41, 42</td>
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<tr>
<td>C₄H₈</td>
<td>39, 41, 55, 56</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>41, 43, 57, 58</td>
</tr>
<tr>
<td>C₆H₁₈</td>
<td>114</td>
</tr>
<tr>
<td>C₄H₈I</td>
<td>127, 169, 184</td>
</tr>
</tbody>
</table>
The noncondensable fractions are introduced into the spectrometer by use of a special carrier described by R. M. Smith. The sample is allowed to expand into the spectrometer from this carrier.

3,4-Dimethylhexane is analyzed for in the following manner. When the noncondensable fractions have been removed with the Toepler pump, the remaining condensable materials are distilled to arm A of the polymerization tube (Figure 3), which is attached to arm A of the system shown in Figure 2. The body of the polymerization tube contains 30 or 40 pellets of potassium hydroxide. The stopcock is closed and the condensable material is allowed to warm to room temperature and stand over the potassium hydroxide for 16 to 24 hours. This polymerizes most of the excess 2-methylbutanal. The tube is then placed on the spectrometer and the remaining material allowed to expand into the spectrometer and the spectrum recorded. A quantitative measure of the amount of 3,4-dimethylhexane is made by filling a 1m pipet with pure 3,4-dimethylhexane and placing the entire pipet in the polymerization tube (without the KOH). The tube is placed on the spectrometer and

---

15 Obtained from Kenneth Greenlee of the American Petroleum Institute, Ohio State University.
the spectrum of the known amount of 3,4-dimethylhexane is measured. The amount present in the photolysis sample is found by comparing the peak intensities of the known against the experimental peak intensities. The 114 peak is weighted the most as it is entirely free from the background of unpolymerized aldehyde.

3. Iodide Determination by Titration

A quantitative determination of the amounts of alkyl iodides in the condensable fraction of the iodine-inhibited runs is made. After the noncondensable fractions of the products are removed, the system is filled with nitrogen. The trap F (Figure 4) is then cut out of the system. Two or three drops of mercury and two or three cc. CCl₄ are added to the trap and the trap is sealed and allowed to warm to room temperature. The mercury removes (by formation of iodides) the excess iodine remaining after the run was completed. The trap is then cooled to dry ice temperature, opened, and a 10/30 standard taper joint is sealed to the vertical arm of the trap. The trap is then placed on position A (Figure 2) and a sample tube consisting of a 10/30 standard taper joint sealed to a 15 mm. diameter tube about 5 in. in length is placed at position B. A liquid nitrogen bath is placed around the trap and the system is evacuated. After about 5 minutes the high vacuum is closed and the bath moved to the sample tube.
The volatile contents of the trap are thereby distilled to
the sample tube. On completion of this transfer, the tube
is removed and another one or two cc. CCl₄ and about 5 cc.
acetic acid are added to the tubes and the contents poured
into a 125 ml. standard taper Erlenmeyer flask. The tube
is washed with acetic acid two or three times and the
washings are added to the flask. The total volume is
about 15 ml. About 2 gm. sodium acetate is added and
enough bromine to turn the solution dark orange. The
flask is stoppered and allowed to stand 1 hour to insure
the complete replacement of the iodide and ultimate oxida­
tion to iodate. A carborundum boiling stone is added and
the solution boiled until the vapor is unreactive to
starch-iodide paper and then 15 minutes more to insure
complete removal of bromine. The solution is allowed to
cool to room temperature and is then diluted with distilled
water to about 35 ml. About 1 gm. potassium iodide is
added and the solution is titrated with standard sodium
thiosulfate (0.005 N.).

G. Determination of Optical Activity of 2-Iodobutane
    Formed in Inhibited Runs

The determination of the optical activity of the butyl
iodide formed in the iodine-inhibited photolyses of
2-methylbutanal necessitated the synthesis of sufficient
butyl iodide to give a significant rotation when placed in
the polarimeter. The system in Figure 4 is altered in the following manner to do this. Arc A is replaced with a 1000 watt high-pressure water cooled mercury arc (General Electric AH6), whose housing was constructed by Dr. George Rankin, and is operated through a General Electric Transformer ballast Cat. No. 59G37. Filter B is replaced with a 10 mm. quartz cell which contains a dilute solution of potassium chromate. Cell E is replaced with the cell pictured in Figure 5. This cell has a volume of approximately 23 liters and overall path length of about 25 inches. Iodine and 2-methylbutanal are introduced into the system in the same manner as in the other inhibited runs. The total pressure is again measured by the height differences on the arms of the mercury valves. The photolysis is started by firing the high pressure arc. At various times white light is shown in window M (Figure 4) to observe if the iodine color is maintained. On completion of the photolysis the arc is turned off and a liquid nitrogen bath placed on trap F (Figure 4). The bath is left on the trap for 10-12 hours in order to allow all condensable material to diffuse to trap F, as diffusion is quite slow in this large system. The liquid nitrogen

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The author is indebted to Dr. George Rankin of The Ohio State University for the use of the arc and transformer.
Fig. 5 - The 22-liter photolysis cell
Fig. 6 - The photolysis system
is replaced with dry ice-acetone and the system filled with nitrogen. Trap F is cut out, mercury is added to react with the excess iodine and a 10/30 standard taper joint sealed to the vertical arm of the trap. When all the iodine is reacted with mercury, the trap is placed on arm A of Figure 2 and the volatile material distilled to arm A of the polymerization bulb (Figure 3) which is placed on arm B (Figure 2). The bulb contains 40 or 50 pellets of KOH. When the distillation is complete the bulb is closed and the contents are allowed to stand 16-20 hours over the KOH. After this period the remaining material is distilled to a small sample bulb (a sealed tube with a 10/30 standard taper joint) and transferred from the bulb to a micropolarimeter tube (1 decimeter length, 0.17 mm. diameter). Carbon tetrachloride is added as needed to fill the polarimeter tube. The rotation is then read on a Rudolph Photoelectric Polarimeter, Model 200, with the green line of mercury (5460 Å.) used as a light source (This line gives a higher rotation for (+)2-BuI than the D-line of sodium and is more intense which is of value because of the small cross-sectional area of the tube.). After the rotation is read the tube is emptied into a flask, washed, and total iodide content analyzed for as in II-F-3.
Pure (t)2-iodobutane was prepared from (-)2-butanol\textsuperscript{17} by the method of Berlak and Gerrard\textsuperscript{18} to determine if it would be racemized by the experimental techniques used. No racemization was noted when (t)2-iodobutane was subjected to the experimental method of separating the iodide for analysis. Also (t)2-methylbutanal was run through the procedure to see if any optical activity due to the aldehyde remained after the potassium hydroxide treatment. No activity due to the aldehyde was found in these tests.

H. Calculation of Quantum Yields

To determine the quantum yields of the products formed in the photolyses the number of molecules of each product must be known. The volume at STP of each component is estimated by the mass spectrometric method given in II-F-2. The number of molecules is easily found from this (i.e.

\[
\text{Volume in liters} \times 6.023 \times 10^{23} \text{molecules mole}.
\]

Also needed to calculate quantum yields is an estimate of the light intensity and the amount of absorption of the light in the reaction cell. The light intensity (I\textsubscript{o}) of the mercury arc is calculated by use of an internal actinometer system. At various intervals acetone was photolyzed at temperatures above 100\degree. Since the quantum yield of CO

\textsuperscript{17} Obtained from George Helmkamp, University of California at Riverside.
is unity under these conditions and the absorption coefficient for acetone is known, $I_0$ may be calculated. CO is analyzed for by the gas buret technique. A sample calculation of $I_0$ is given.

\[
\alpha (\text{molar extinction coefficient}) = 3.60 \text{l./mole-cm.} \\
I (\text{pathlength}) = 5 \text{ cm.} \\
c (\text{concentration}) = \frac{P}{RT} = \frac{60.3/(760)(.08205)(377.8)}{\text{moles/l.}} \\
\text{time} = 3.5 \text{ hours} \\
\log \frac{I_t}{I_0} = -\alpha I = \frac{(3.60)(60.3)(5)}{(760)(.08205)(377.8)} = -.0460 \\
= .9540 \\
\frac{I_t}{I_0} = .900, \frac{I_a}{I_0} = .100
\]

Since $I_{CO} = 1.0$

$\frac{I_0}{22.424 \text{l.} \times 6.023 \times 10^{23} \text{ molecules/m.}} = 1.28 \times 10^{15} \text{ quanta/sec.}$

In the iodine-inhibited photolyses the system is cut apart after each run to clean it. A film consisting of some adduct of iodine aldehyde and hydrogen iodide is formed on the cell wall, increasing as the time of photolysis increased. Therefore before each iodide-inhibited photolysis an acetone photolysis is made to determine $I_0$ as the cell position could not be reproduced exactly.

The absorption coefficient for 2-methylbutanal is determined by use of the Aminco Photomultiplier. By use of the photomultiplier the percent of the incident light absorbed is found and $\alpha$ is calculated. Table 3 gives
values over the temperature range used in the experiments.

A sample calculation for the quantum yield of CO from 2-methylbutanal photolysis at 3130 Å in run 3 follows.

\[
\Phi_{CO} = \frac{\text{no. of molecules of CO formed}}{\text{no. of quanta absorbed (I}_a\text{) by 2-methylbutanal}}
\]

\[
\log \frac{I_t}{I_0} = -\frac{(11.6)(5)(46.0)}{(760)(.08205)(469.3)}
\]

\[= 1.9089\]

\[I_t/I_0 = .796, \quad I_a/I_0 = .204\]

\[
\Phi_{CO} = 44.5 \times 10^{-6} \times \frac{1. \times 6.023 \times 10^{23}}{(22.424 \text{ l.})(3120 \text{ sec.})(.204)(1.30 \times 10^{18} \text{ q./sec.})}
\]

\[= 1.44\]

---

**Table 3**

Absorption Coefficients of (†)2-Methylbutanal at Various Temperatures

<table>
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<tr>
<th>Temp., °C.</th>
<th>(\alpha), l./mole-cm.</th>
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<tbody>
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<td>112</td>
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<tr>
<td>312</td>
<td>12.9</td>
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III. EXPERIMENTAL RESULTS

A. Uninhibited Photolyses

The major noncondensable products in low temperature photolysis of 2-methylbutanal at 3130 \AA. are carbon monoxide, ethylene, and n-butane. At high temperatures (above 250°) methane and propene are also major products. Minor products, at both high and low temperatures, are hydrogen and butene (mixture 1(and 2)-butene). The method of calculating the quantum yields of product formed is described in the previous chapter. The only product analyzed among the condensable products is 3,4-dimethylhexane. The photolyses made at full arc (intensity increased by a factor of about 90) give the same major and minor products. The results of the photolyses are given in Tables 4, 5, 6, and 7. Table 4 gives the conditions of the photolyses and the amounts of products formed in microliters at STP. Table 5 gives the quantum yields of the products. Table 6 gives the experimental conditions and microliters of products at STP formed in the full arc photolyses. Table 7 gives the rates of product formation in moles per liter per second. Figure 7 gives a plot of

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19 John Kraus reports this ratio of butenes from 2-methylbutanal photolysis, 1-butene, 49.7\%, trans-2-butene, 32.8\%, cis-2-butene, 17.5\%. Private communication.
20 This was done by removing filter H, Figure 1.
the major products over the temperature range of the
photolyses. Figure 8 gives a plot of the minor products.

B. Iodine-Inhibited Photolyses

In the iodine-inhibited photolyses of 2-methylbutanal
the major noncondensable products identified are carbon
monoxide and ethylene. n-Butane is present as a very
minor product. In the condensable products 2-iodobutane
is identified as a major product. Iodomethane is not iden
tified and if present is in amounts too small to be signif-
icant. Tables 8 and 9 give the results of the inhibited
photolyses. Table 8 gives the experimental conditions and
microliters of product at STP, found in the photolyses.
Table 9 gives the quantum yields. Figure 9 shows the
effect of iodine inhibition by plotting major products
against temperature in both inhibited and uninhibited
photolyses. Figure 10 shows the effect of iodine pressure
on some of the major products.

C. Optical Activity of 2-Iodobutane

The apparatus for producing the large amount of 2-iodo-
butane to test its optical activity has been described
previously. By use of this apparatus, (†)2-methylbutanal
at a pressure of 8 mm. was photolyzed in the presence of
iodine (3 mm. pressure) for nine and one-half hours. The
average of three series of observed readings (mercury
green line used as light source) was +0.639°. The
observed zero point for the polarimeter was +0.623°.
Table 4
Results of the Photolysis of
(t)-2-Methylbutanal at 3130 Å.

<table>
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<tr>
<th>Run</th>
<th>Temp., °C</th>
<th>Temp., sec.</th>
<th>[C₄H₉CHO]</th>
<th>Volume Products, μl. (STP)</th>
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<td>Product Quantum Yields</td>
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<td>-----</td>
<td>-----------</td>
<td>-----</td>
<td>-----</td>
<td>------------------------</td>
</tr>
<tr>
<td>1</td>
<td>24.5</td>
<td>0.352</td>
<td>0.001</td>
<td>0.123</td>
</tr>
<tr>
<td>2</td>
<td>24.5</td>
<td>0.364</td>
<td>0.046</td>
<td>0.121</td>
</tr>
<tr>
<td>3</td>
<td>64.5</td>
<td>0.443</td>
<td>0.024</td>
<td>0.167</td>
</tr>
<tr>
<td>4</td>
<td>97.8</td>
<td>...</td>
<td>0.053</td>
<td>...</td>
</tr>
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<td>112.0</td>
<td>0.605</td>
<td>0.047</td>
<td>0.183</td>
</tr>
<tr>
<td>6</td>
<td>112.3</td>
<td>0.681</td>
<td>0.034</td>
<td>0.216</td>
</tr>
<tr>
<td>7</td>
<td>148.8</td>
<td>...</td>
<td>0.094</td>
<td>...</td>
</tr>
<tr>
<td>8</td>
<td>162.8</td>
<td>1.15</td>
<td>0.073</td>
<td>0.205</td>
</tr>
<tr>
<td>9</td>
<td>196.1</td>
<td>1.44</td>
<td>0.037</td>
<td>0.209</td>
</tr>
<tr>
<td>10</td>
<td>200.5</td>
<td>1.29</td>
<td>0.023</td>
<td>0.172</td>
</tr>
<tr>
<td>11</td>
<td>211.1</td>
<td>...</td>
<td>0.213</td>
<td>...</td>
</tr>
<tr>
<td>12</td>
<td>207.9</td>
<td>1.81</td>
<td>0.157</td>
<td>0.200</td>
</tr>
<tr>
<td>13</td>
<td>228.9</td>
<td>1.95</td>
<td>0.088</td>
<td>0.200</td>
</tr>
<tr>
<td>14</td>
<td>246.4</td>
<td>1.87</td>
<td>0.177</td>
<td>0.27</td>
</tr>
<tr>
<td>15</td>
<td>248.6</td>
<td>1.90</td>
<td>0.268</td>
<td>0.155</td>
</tr>
<tr>
<td>16</td>
<td>248.9</td>
<td>...</td>
<td>0.277</td>
<td>...</td>
</tr>
<tr>
<td>17</td>
<td>249.5</td>
<td>2.42</td>
<td>...</td>
<td>0.112</td>
</tr>
<tr>
<td>18</td>
<td>253.7</td>
<td>2.29</td>
<td>0.316</td>
<td>0.414</td>
</tr>
<tr>
<td>19</td>
<td>271.1</td>
<td>2.30</td>
<td>...</td>
<td>0.390</td>
</tr>
<tr>
<td>20</td>
<td>292.7</td>
<td>2.27</td>
<td>(0.227)</td>
<td>0.366</td>
</tr>
<tr>
<td>21</td>
<td>295.3</td>
<td>...</td>
<td>0.403</td>
<td>...</td>
</tr>
<tr>
<td>22</td>
<td>295.9</td>
<td>2.03</td>
<td>(1.041)</td>
<td>0.658</td>
</tr>
<tr>
<td>23</td>
<td>316.5</td>
<td>3.22</td>
<td>(1.284)</td>
<td>1.72</td>
</tr>
<tr>
<td>24</td>
<td>320.0</td>
<td>3.74</td>
<td>...</td>
<td>1.29</td>
</tr>
<tr>
<td>25</td>
<td>331.5</td>
<td>4.34</td>
<td>(1.189)</td>
<td>3.28</td>
</tr>
<tr>
<td>26</td>
<td>342.2</td>
<td>...</td>
<td>0.606</td>
<td>...</td>
</tr>
<tr>
<td>27</td>
<td>348.7</td>
<td>7.27</td>
<td>0.821</td>
<td>6.99</td>
</tr>
</tbody>
</table>
Table 6
Volume of Products Formed in the Photolysis
of (+)2-Methylbutanal at Full Arc

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °C.</th>
<th>[C₄H₇CHO] M x 10⁻³</th>
<th>Volume of Products, µl. (STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>100.2</td>
<td>1.16</td>
<td>CO: 59.3, CH₄: 1.2, C₂H₄: 30.7, C₃H₈: 0.0, C₄H₆: 6.5, C₄H₁₀: 32.9, C₅H₁₀: 8.8</td>
</tr>
<tr>
<td>28</td>
<td>203.0</td>
<td>1.18</td>
<td>CO: 109.3, CH₄: 8.4, C₂H₄: 34.6, C₃H₈: 0.0, C₄H₆: 4.7, C₄H₁₀: 58.9, C₅H₁₀: 5.4</td>
</tr>
<tr>
<td>32</td>
<td>242.9</td>
<td>1.17</td>
<td>CO: 158.8, CH₄: 7.3, C₂H₄: 43.6, C₃H₈: 3.4, C₄H₆: 6.0, C₄H₁₀: 82.3, C₅H₁₀: 6.4</td>
</tr>
<tr>
<td>29</td>
<td>290.0</td>
<td>1.19</td>
<td>CO: 212.7, CH₄: 28.6, C₂H₄: 32.5, C₃H₈: 17.6, C₄H₆: 5.9, C₄H₁₀: 106.2, C₅H₁₀: 4.8</td>
</tr>
<tr>
<td>31</td>
<td>342.2</td>
<td>1.32</td>
<td>CO: 467.0, CH₄: 188.6, (C₃H₈: 63.9), C₂H₄: 134.1, C₃H₈: 15.8, C₄H₁₀: 162.4, C₅H₁₀: 2.5</td>
</tr>
</tbody>
</table>
Table 7
Rates of Product Formation in the Photolysis of (+)2-Methylbutanal with the Full Arc

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °C</th>
<th>Rates, moles/l.-sec. x 10⁻⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>30</td>
<td>100.2</td>
<td>12.5</td>
</tr>
<tr>
<td>28</td>
<td>203.0</td>
<td>23.1</td>
</tr>
<tr>
<td>32</td>
<td>242.9</td>
<td>33.4</td>
</tr>
<tr>
<td>29</td>
<td>290.0</td>
<td>44.9</td>
</tr>
<tr>
<td>31</td>
<td>342.2</td>
<td>98.5</td>
</tr>
</tbody>
</table>
Table 8
Results of the Iodine-Inhibited Photolysis of (+)2-Methylbutanal at 3130 Å

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp, °C</th>
<th>Time, hrs</th>
<th>P_{total}, mm</th>
<th>P_{ald}, mm</th>
<th>P_{I_2}, mm</th>
<th>I_{o}, 10^{-15} \text{q./sec.}</th>
<th>Volume of Products, µl (STP)</th>
<th>C_4H_{10}</th>
<th>C_2H_4</th>
<th>C_4H_9I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>48.0</td>
<td>1.16</td>
<td>24.3</td>
<td>23.4</td>
<td>0.9</td>
<td>1.27</td>
<td>45.0</td>
<td>0.2</td>
<td>9.8</td>
<td>42.0</td>
</tr>
<tr>
<td>8</td>
<td>61.5</td>
<td>1.35</td>
<td>30.7</td>
<td>27.2</td>
<td>3.5</td>
<td>1.58</td>
<td>60.3</td>
<td>0.3</td>
<td>9.7</td>
<td>49.7</td>
</tr>
<tr>
<td>4</td>
<td>84.0</td>
<td>1.00</td>
<td>29.1</td>
<td>25.7</td>
<td>3.4</td>
<td>1.59</td>
<td>40.2</td>
<td>.5</td>
<td>13.4</td>
<td>34.0</td>
</tr>
<tr>
<td>5</td>
<td>102.0</td>
<td>1.00</td>
<td>30.9</td>
<td>27.9</td>
<td>3.0</td>
<td>1.59</td>
<td>39.2</td>
<td>.4</td>
<td>10.4</td>
<td>33.3</td>
</tr>
<tr>
<td>10</td>
<td>107.1</td>
<td>1.83</td>
<td>59.2</td>
<td>33.3</td>
<td>25.9</td>
<td>0.81</td>
<td>40.4</td>
<td>.1</td>
<td>13.7</td>
<td>37.8</td>
</tr>
<tr>
<td>9</td>
<td>107.4</td>
<td>1.25</td>
<td>42.3</td>
<td>34.3</td>
<td>8.0</td>
<td>1.27</td>
<td>(33.3)</td>
<td>.1</td>
<td>13.1</td>
<td>41.2</td>
</tr>
<tr>
<td>6</td>
<td>127.5</td>
<td>1.00</td>
<td>35.0</td>
<td>32.8</td>
<td>2.2</td>
<td>1.48</td>
<td>45.8</td>
<td>.8</td>
<td>11.7</td>
<td>39.2</td>
</tr>
</tbody>
</table>
Table 9
Quantum Yields of Products in Iodine-Inhibited Photolysis of (+)2-Methylbutanal at 3130 Å.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °C</th>
<th>CO</th>
<th>C₄H₁₀</th>
<th>C₂H₄</th>
<th>C₄H₈I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>48.0</td>
<td>0.655</td>
<td>0.002</td>
<td>0.143</td>
<td>0.611</td>
</tr>
<tr>
<td>2</td>
<td>61.5</td>
<td>0.610</td>
<td>0.002</td>
<td>0.098</td>
<td>0.502</td>
</tr>
<tr>
<td>4</td>
<td>84.0</td>
<td>0.557</td>
<td>0.007</td>
<td>0.186</td>
<td>0.471</td>
</tr>
<tr>
<td>5</td>
<td>102.0</td>
<td>0.525</td>
<td>0.005</td>
<td>0.139</td>
<td>0.447</td>
</tr>
<tr>
<td>10</td>
<td>107.1</td>
<td>0.509</td>
<td>0.001</td>
<td>0.173</td>
<td>0.476</td>
</tr>
<tr>
<td>9</td>
<td>107.4</td>
<td>0.424</td>
<td>0.001</td>
<td>0.167</td>
<td>0.525</td>
</tr>
<tr>
<td>8</td>
<td>109.0</td>
<td>0.687</td>
<td>...</td>
<td>0.213</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>109.5</td>
<td>0.605</td>
<td>0.002</td>
<td>0.145</td>
<td>0.390</td>
</tr>
<tr>
<td>6</td>
<td>127.5</td>
<td>0.610</td>
<td>0.011</td>
<td>0.156</td>
<td>0.525</td>
</tr>
</tbody>
</table>
Fig. 7 - The temperature dependence of the quantum yields of the major products of 2-methylbutanal photolysis at 3130 Å.

- $\bigcirc$ = CO
- $\square$ = $C_2H_4$
- $\triangle$ = CH₄
- $\bullet$ = $C_3H_8$
- $\bigtriangledown$ = $n$-$C_4H_{10}$
Fig. 8 - The temperature dependence of the quantum yields of the minor products of 2-methylbutanal photolysis at 3130 Å.
Fig. 9 - Effect of iodine inhibition on major products of photolysis of 2-methylbutanal at 3130 Å.

Uninhibited  Iodine-inhibited

- = CO          O = CO
\( \Delta \) = \( \text{C}_2\text{H}_4 \)     \( \Delta \) = \( \text{C}_2\text{H}_4 \)
\( \Box \) = \( \text{n-C}_4\text{H}_{10} \)     \( \Box \) = \( \text{n-C}_4\text{H}_{10} \)
\( \bigcirc \) = \( \text{C}_4\text{H}_{9}\text{I} \)
Fig. 10 - Effect of iodine pressure on major products
IV. DISCUSSION of EXPERIMENTAL RESULTS

A. Primary Processes

The results are consistent with the occurrence of two major primary processes.

\[ \text{CH}_3\text{CH}_2\text{CHCH}_3 + \text{CHO} \quad \text{(I)} \]

\[ \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)CHO} + h\nu \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CHO} \quad \text{(II)} \]

Two other processes of minor importance are indicated.

\[ \text{CH}_3 + \text{C}_3\text{H}_6\text{CHO} \quad \text{(III)} \]

\[ \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)CHO} + h\nu \rightarrow \text{n-C}_4\text{H}_{10} + \text{CO} \quad \text{(IV)} \]

Process (I) is a type well known in aldehyde photolysis and has been observed in the photolysis of acetaldehyde,\textsuperscript{21} propionaldehyde,\textsuperscript{22} \(n\)-butyraldehyde,\textsuperscript{2} and isobutyraldehyde.\textsuperscript{23} The results which confirm (I) in the present work are summarized in the following.

The rapid increase of the quantum yields of carbon monoxide and \(n\)-butane above unity as the temperature increases (shown in Figure 7) provides evidence that a free radical primary process followed by secondary thermal

\textsuperscript{22}Blacet, F. E., and Pitts, J. N., \textit{ibid.}, 74, 3382 (1952).
\textsuperscript{23}Blacet, F. E., and Calvert, J. G., \textit{ibid.}, 73, 667 (1951).
chain reaction is occurring. The formation of sec-butyl and formyl radicals is the only mechanism that will explain this. Other results that demonstrate the presence of sec-butyl radicals are the following: (1) the identification of 3,4-dimethylhexane in the noncondensable products, (2) the identification of 2-iodobutane in the iodine-inhibited photolyses, (3) the presence of butene in the uninhibited photolysis products and its absence in the inhibited photolyses. The presence of a chain reaction is shown by the temperature independence of carbon monoxide and 2-iodobutane in the inhibited photolyses. Iodobutane, therefore, is formed in a rapid reaction between iodine and a sec-butyl radical formed in a primary process. Further indirect evidence of the presence of the radical is the increasing quantum yield of hydrogen with temperature (Figure 7) indicating a secondary reaction of formyl radicals.

Primary process (II) has been found in photolysis of similar compounds such as n-butyraldehyde, di-n-propyl ketone, and methyl-n-propyl ketone. In every known case of photodecomposition of molecules containing a n-propyl group adjacent to the light-absorbing carbonyl group, a general process (II')

\[ \text{CH}_3\text{CH}_2\text{CHRCOR'} + \hnu \rightarrow \text{C}_2\text{H}_4 + \text{RCH}_2\text{COR'} \]  

(II')

has been observed. The best evidence for this process is
the temperature, intensity, and iodine pressure insensitivity of the quantum yield of ethylene (Table 5, Figures 7 and 9). $\Phi_{C_2H_4}$ is $0.20 \pm 0.03$ (uninhibited) in the temperature range 65°-208°. It is reasonably constant up to 350° although there is considerable experimental error in $\Phi_{C_2H_4}$ introduced at the higher temperatures by the rapid increase in the quantum yields of other products.

Other values are $0.17 \pm 0.02$ (25°-150°) for n-butyraldehyde $^2$ and $0.21 \pm 0.01$ (113°) for di-n-propyl ketone $^3$ for the quantum efficiency of ethylene formation at 3130 Å. in process (II'). It is apparent that minor structural changes in R and R' cause little, if any, change in the primary efficiency of (II').

In the iodine-inhibited photolysis of 2-methylbutanal the quantum yield of ethylene over the temperature range 84°-127.5° is $0.16 \pm 0.03$. This value is in reasonable agreement with the average of those found in the uninhibited photolyses over the temperature range 25°-130° (0.18 ±0.02). There did not appear to be any significant deactivation of excited aldehyde molecules and suppression of process II by increased iodine pressure. Run 10, (Tables 8 and 9) at 25.9 mm. of iodine, nine times the usual pressure of iodine used in these photolyses, did not cause any decrease in ethylene formation. However the average value is a little lower than in the uninhibited
photolyses so there may be a small and constant fraction of excited molecules deactivated by the iodine present over the entire pressure range used.

Process III is indicated by the small, approximately constant quantum yield of methane at temperatures below $200^\circ$ (Table 4, Figure 7). Since no methane was found in the iodine experiments and analysis for this compound is unambiguous the alternate process III'

$$\text{CH}_3\text{CH}_2\text{CH} (\text{CH}_3)\text{CHO} + h\nu \rightarrow \text{CH}_4 + \text{CH}_3\text{CH} = \text{CHCHO} \quad \text{(III') }$$

is unlikely. However no iodomethane is found in the iodine inhibited experiments although it would be expected if process III occurs. Therefore either the methane forming process is eliminated by deactivation in the presence of iodine or the iodomethane was lost in the purification procedure used to isolate the iodides. However the mass spectrometer is very sensitive to iodomethane and the detection of trace quantities should be easily accomplished.

From the inhibited runs (Tables 6 and 7) it can be seen that small amounts of n-butane are formed independent of iodine pressure. The minor occurrence of process IV is suggested to explain this result. A similar intramolecular process of minor importance has been suggested for acetaldehyde, propionaldehyde, n-butyraldehyde, and iso-butyraldehyde photolysis at 3130 Å. It has been
reported that this process becomes a major one at the shorter wavelengths.

The total primary quantum efficiency of decomposition appears to be ~0.8 for 2-methylbutanal photolysis at 3130 Å.

B. Secondary Reactions

The following reactions involving the decomposition and the interactions of sec-butyl and formyl radicals are suggested for the quantitative explanation of the results.

\[ 2\text{C}_3\text{H}_7\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH} (\text{CH}_3 )\text{CH} (\text{CH}_3 )\text{CH}_2\text{CH}_3 \quad (1a) \]
\[ \text{C}_4\text{H}_8 \quad \text{(l)and 2-butene} \quad \text{+} \quad \text{n-C}_4\text{H}_{10} \quad (1b) \]
\[ \text{CH}_3\text{CH}_2\text{CHCH}_3 \rightarrow \text{CH}_3 \quad \text{+} \quad \text{CH}_2=\text{CHCH}_3 \quad (2) \]
\[ \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{+} \quad \text{CH}_3 \text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CHO} \rightarrow \]
\[ \text{n-C}_4\text{H}_{10} \quad \text{+} \quad \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CO} \quad (3) \]
\[ \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{+} \quad \text{CO} \quad (4) \]
\[ \text{M} \quad \text{+} \quad \text{CHO} \rightarrow \text{H} \quad \text{+} \quad \text{CO} \quad \text{+} \quad \text{M} \quad (5) \]
\[ \text{HCO} \quad \text{(t wall)} \rightarrow \text{Products not H}_2 \quad \text{(t wall)} \quad (6) \]
\[ \text{H} \quad \text{+} \quad \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CHO} \rightarrow \text{H}_2 \quad \text{+} \quad \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CO} \quad (7) \]
\[ \text{CH}_3 \quad \text{+} \quad \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CHO} \rightarrow \text{CH}_4 \quad \text{+} \quad \text{CH}_3\text{CH}_2\text{CH(} \text{CH}_3\text{)}\text{CO} \quad (8) \]

1. The Chain Propagation Reactions

It is evident from the data of Table 5 that a chain mechanism is occurring. Steps (3) and (4) are the proposed chain carrying steps. the abstraction of a hydrogen atom from 2-methylbutanal by a sec-butyl radical and the subsequent decomposition of the 2-methylbutyryl radical to
carbon monoxide and another sec-butyl radical. At temperatures greater than 250° there is an increasing importance of reaction (2), the decomposition of sec-butyl radicals to propene and methyl radicals, followed by (8), hydrogen abstraction by the methyl radical, and (4) as a chain carrying reaction sequence. From the inhibited photolysis of 2-methylbutanal the efficiency of primary process I is estimated as about 0.6. From this the chain length can be estimated as about 1.0 at 112°, increasing to about 12 at 349°.

2. Hydrogen Abstraction by sec-Butyl Radicals

Assuming that n-butane is formed only in reactions (1b) and (3) and 3,4-dimethylhexane in (1a), information concerning these rate constants can be calculated from the data.

\[
\frac{d}{dt} C_4H_{10} = k_3[sec-Bu][C_4H_9CHO]
\]

\[
\frac{d}{dt} C_4H_{10} = \Phi_{C_4H_{10}} I_a
\]

\[
\Phi_{C_4H_{10}} = (\Phi_{C_4H_{10}}(t) - \Phi_{C_4H_8})
\]

\[
\frac{d}{dt} C_6H_{18} = k_{1a}[sec-Bu]^2
\]

\[
\frac{d}{dt} C_6H_{18} = \Phi_{C_6H_{18}} I_a
\]
\[
\frac{(\Phi_{C_4H_{10}} - \Phi_{C_4H_8})I_a}{\Phi^{1/2}_{C_6H_{18}} I_a^{1/2}} = \frac{k_3[sec-Bu][C_4H_8CHO]}{k_{1a} [sec-Bu]}
\]

For runs made at full mercury arc the development is identical to that given above with rates used instead of quantum yields. The result therefore is

\[
k_{3/2} = \frac{(\Phi_{C_4H_{10}} - \Phi_{C_4H_8})I_a^{1/2}}{k_{1a}^{1/2} \Phi^{1/2}_{C_6H_{18}}[C_4H_8CHO]}
\]

Figure 11 gives an Arrhenius plot of the function A calculated from the quantum yield data (Table 10) of runs at 3130 Å. (open circles) and the rate data (Table 11) from the full arc experiments (black circles). Within the experimental error, the two sets of data obtained at greatly different intensities determine the same straight line, as is required by A. This line was determined by least squares. By use of the values from Tables 10 and 11, Figure 11 was plotted and the slope was calculated to be 4.9 kcal./mole. Therefore \(E_a - E_{1a}/2 = 4.9\) kcal./mole. Since \(E_{1a}/2\) is probably near zero, \(E_a = 4.9\) kcal./mole, the activation energy of hydrogen abstraction by the
Table 10
Calculation of Function Theoretically Equal to $\frac{k_3}{k_{18}}$ (3130 Å data)

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., $1/T$ [°C]</th>
<th>$[\text{C}_4\text{H}_8\text{CHO}]$</th>
<th>$\text{C}<em>4\text{H}</em>{10}$</th>
<th>$\text{C}_4\text{H}_6$</th>
<th>$\text{C}<em>8\text{H}</em>{18}$</th>
<th>$\frac{1}{2}$</th>
<th>$1_{10}^a$ (Ein. / sec.)</th>
<th>$\log (10)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>24.5</td>
<td>3.36</td>
<td>1.39</td>
<td>0.244</td>
<td>0.197</td>
<td>0.262</td>
<td>0.754</td>
<td>8.61</td>
</tr>
<tr>
<td>13</td>
<td>112.0</td>
<td>2.60</td>
<td>1.55</td>
<td>0.388</td>
<td>0.358</td>
<td>0.141</td>
<td>2.55</td>
<td>9.19</td>
</tr>
<tr>
<td>15</td>
<td>200.5</td>
<td>2.11</td>
<td>1.51</td>
<td>1.30</td>
<td>1.28</td>
<td>0.084</td>
<td>15.2</td>
<td>9.44</td>
</tr>
<tr>
<td>14</td>
<td>292.9</td>
<td>1.77</td>
<td>1.40</td>
<td>1.59</td>
<td>1.53</td>
<td>0.063</td>
<td>24.2</td>
<td>9.60</td>
</tr>
</tbody>
</table>
Table 11
Calculation of Function Theoretically Equal to $k_3/k_{18}$ (full arc data)

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °C</th>
<th>$1/T$</th>
<th>[C₆H₅CHO] x 10³</th>
<th>R₄H₁₀⁻</th>
<th>$R_{C₄H₁₀}^{1/2}$</th>
<th>$R_{C₆H₁₈}^{-}$</th>
<th>(6)/(7) x 10⁸</th>
<th>(8)/(4) x 10⁸</th>
<th>log (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>100.2</td>
<td>2.68</td>
<td>1.16</td>
<td>6.94</td>
<td>5.57</td>
<td>1.36</td>
<td>4.10</td>
<td>0.353</td>
<td>-0.452</td>
</tr>
<tr>
<td>28</td>
<td>203.0</td>
<td>2.10</td>
<td>1.18</td>
<td>12.4</td>
<td>11.4</td>
<td>1.07</td>
<td>10.7</td>
<td>0.907</td>
<td>-0.043</td>
</tr>
<tr>
<td>32</td>
<td>242.9</td>
<td>1.94</td>
<td>1.17</td>
<td>17.4</td>
<td>16.1</td>
<td>1.16</td>
<td>13.9</td>
<td>1.18</td>
<td>0.072</td>
</tr>
<tr>
<td>29</td>
<td>290.0</td>
<td>1.78</td>
<td>1.19</td>
<td>22.4</td>
<td>21.2</td>
<td>1.01</td>
<td>20.9</td>
<td>1.76</td>
<td>0.246</td>
</tr>
<tr>
<td>31</td>
<td>342.2</td>
<td>1.63</td>
<td>1.32</td>
<td>34.3</td>
<td>31.0</td>
<td>0.73</td>
<td>42.5</td>
<td>3.22</td>
<td>0.508</td>
</tr>
</tbody>
</table>

Rates in moles/l.-sec.
Fig. 11 - Arrhenius plot of the function theoretically equal to $k_a/k_{1a}$
sec-butyl radical from 2-methylbutanal. From the relation

\[ \frac{k_3}{k_{1a}} = \frac{A_3}{A_{1a}} \frac{1}{\sqrt{RT}} \]

\[ A_3^{1/2} / A_{1a}^{1/2} \] was calculated to be equal to \( 4.8 \times 10^3 \) (cc./moles-sec.)\(^{1/2}\). If we assume \( A_{1a} \) is equal to or less than the collision number, \( Z_{1a} = 2.0 \times 10^{14} \) cc./mole-sec.

\[ Z_{1a} = 4\sqrt{\frac{2}{C_4H_8}} \sqrt{\frac{RT/m_{C_4H_8}}{}} \]

\( \sigma_{C_4H_8} = 5.9 \), \( T = 500^\circ K \), then \( A_3 \sim 6.8 \times 10^{10} \) cc./mole-sec., this corresponds to a collision theory steric factor \( P_3 \approx 3 \times 10^{-4} \), the usual order of magnitude of the \( P \)-factors for the hydrogen abstraction reactions of the other simple alkyl radicals.

3. The Decomposition of the sec-Butyl Radical

In Figure 7 it can be seen that \( \Phi_{CH_4} \) (the blackened circles) and \( \Phi_{C_3H_8} \) (triangles) increase simultaneously at temperatures above 250\(^\circ\). Within the rather large experimental error involved in propene analysis, \( \Phi_{CH_4} = \Phi_{C_3H_8} \). Reaction (2), the decomposition of the sec-butyl radical, accounts best for these results. It is probable that (8) is the major reaction of CH\(_3\) in the system, since the other possible reaction products such as ethane and
2-methylbutane could not be detected in the products. If it is assumed only I, III, (Ia), (2), and (8) are the only steps leading to CH₄ and C₈H₁₈, then the relation (B) is derived.

\[
\frac{d \text{CH}_3}{dt} = k_2[\text{sec-Bu}]
\]

\[
\frac{d \text{CH}_4}{dt} = \Phi_{\text{CH}_4} \text{I}_a
\]

\[
\Phi_{\text{CH}_4}(8) = (\Phi_{\text{CH}_4}(t) - \phi_{\text{III}})
\]

\(\phi_{\text{III}}\) is taken as 0.04, the average \(\Phi_{\text{CH}_4}\) for temperatures less than 200°C.

\[
\Phi_{\text{C}_8\text{H}_{18}I_a} = k_{1a}[\text{sec-Bu}]^2
\]

\[
\frac{(\Phi_{\text{CH}_4} - \phi_{\text{III}})I_a}{\Phi_{\text{C}_8\text{H}_{18}I_a}^{1/2}} = \frac{k_2[\text{sec-Bu}]}{k_{1a}^{1/2}}
\]

\[
\frac{k_2}{k_{1a}} = \frac{(\Phi_{\text{CH}_4} - \phi_{\text{III}})I_a^{1/2}}{\Phi_{\text{C}_8\text{H}_{18}}^{1/2}} \quad (B)
\]

This function is calculated from the data of Table 12. For the runs in which a direct measure of \(\Phi_{\text{C}_8\text{H}_{18}}\) was not available, the value was estimated by interpolation from the data of Figure 8. Function (B') can be derived as
above by use of rate data from the full arc experiments. This data is given in Table 13. \( R_{\text{III}} \) was taken as 0.25 \( \times 10^{-8} \) mole/l.-sec., the rate at 100°.

\[
\frac{k_2}{k_{1a}} = \frac{R_{\text{CH}_4} - R_{\text{III}}}{R_{\text{C}_8\text{H}_{18}}}
\]

An Arrhenius plot of these data is shown in Figure 12. The inaccuracy in the analysis for products results in considerable scattering in the points, but the estimates based on data from the low intensity 3130 \( \bar{R} \) runs (open circles) are in good agreement with those calculated from the runs at the high intensity (90-fold increase) of the full arc (blackened circles). The insensitivity of the function (B) to change in absorbed light intensity supports the proposed mechanism. From the data of Tables 12 and 13, the straight line of Figure 12 was determined by use of the least squares method. This gives an estimate of the activation energy difference \( E_2 - E_{1a}/2 = 24 \) kcal./mole and the pre-exponential factor ratio \( A_2/A_{1a}^{1/2} = 4.6 \times 10^4 \) (mole/cc.-sec.) \( ^{1/2} \). Again \( E_{1a}/2 \) is likely near zero and the activation energy of the sec-butyl radical decomposition, \( E_2 \), equals 24 kcal./mole. This is in good agreement with the value of \( E_2 = 23 \) kcal./mole estimated from the mercury photosensitized decomposition of \( \text{n-butane} \). If it is

Table 12
Calculation of Function Theoretically
Equal to $k_2/k_{18}$ (3130 Å. data)

<table>
<thead>
<tr>
<th></th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
<th>(8)</th>
<th>(9)</th>
<th>(10)</th>
<th>(11)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\mathrm{CH}_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(x 10$^{-3}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.04</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>Temp.,</td>
<td>1/T</td>
<td>$I_0$,</td>
<td>$I_n$,</td>
<td>$\log</td>
<td>$</td>
<td>$\log</td>
<td>$</td>
<td>$\log</td>
<td>$</td>
</tr>
<tr>
<td>°C.</td>
<td>x 10$^3$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>228.9</td>
<td>1.99</td>
<td>10.32</td>
<td>0.088</td>
<td>0.048</td>
<td>0.0052</td>
<td>0.072</td>
<td>0.67</td>
<td>6.91</td>
<td>-4.161</td>
</tr>
<tr>
<td>8</td>
<td>253.7</td>
<td>1.90</td>
<td>10.41</td>
<td>0.414</td>
<td>0.374</td>
<td>0.0044</td>
<td>0.067</td>
<td>5.18</td>
<td>53.92</td>
<td>-3.268</td>
</tr>
<tr>
<td>11</td>
<td>271.1</td>
<td>1.84</td>
<td>10.58</td>
<td>0.344</td>
<td>0.304</td>
<td>0.0043</td>
<td>0.066</td>
<td>4.63</td>
<td>48.99</td>
<td>-3.310</td>
</tr>
<tr>
<td>14</td>
<td>292.9</td>
<td>1.77</td>
<td>9.60</td>
<td>0.366</td>
<td>0.326</td>
<td>0.0040</td>
<td>0.063</td>
<td>5.17</td>
<td>49.60</td>
<td>-3.305</td>
</tr>
<tr>
<td>5</td>
<td>295.9</td>
<td>1.76</td>
<td>10.77</td>
<td>0.658</td>
<td>0.618</td>
<td>0.0040</td>
<td>0.063</td>
<td>7.81</td>
<td>105.65</td>
<td>-2.975</td>
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<tr>
<td>16</td>
<td>316.5</td>
<td>1.70</td>
<td>9.22</td>
<td>1.717</td>
<td>1.677</td>
<td>0.0037</td>
<td>0.061</td>
<td>27.49</td>
<td>253.46</td>
<td>-2.597</td>
</tr>
<tr>
<td>10</td>
<td>320.0</td>
<td>1.69</td>
<td>11.15</td>
<td>1.461</td>
<td>1.421</td>
<td>0.0037</td>
<td>0.061</td>
<td>23.29</td>
<td>259.68</td>
<td>-2.585</td>
</tr>
<tr>
<td>17</td>
<td>331.5</td>
<td>1.65</td>
<td>9.25</td>
<td>2.277</td>
<td>3.237</td>
<td>0.0036</td>
<td>0.060</td>
<td>53.95</td>
<td>499.04</td>
<td>-2.302</td>
</tr>
<tr>
<td>7</td>
<td>348.7</td>
<td>1.61</td>
<td>10.90</td>
<td>6.99</td>
<td>6.95</td>
<td>0.0035</td>
<td>0.059</td>
<td>117.80</td>
<td>1248.0</td>
<td>-1.893</td>
</tr>
</tbody>
</table>
Table 13
Calculation of Function Theoretically
Equal to $k_2/k_{13} \text{ (full arc data)}$

<table>
<thead>
<tr>
<th>(1) Run</th>
<th>(2) Temp., °C.</th>
<th>(3) $1/T \times 10^3$</th>
<th>(4) $R_{CH_4}$</th>
<th>(5) $R_{CH_4} - 0.25$</th>
<th>(6) $R_{C_6H_{18}}$</th>
<th>(7) $R_{1/2} G_{CH_4}$</th>
<th>(8) $(5)/(7)$</th>
<th>(9) log (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>290.0</td>
<td>1.78</td>
<td>6.03</td>
<td>5.78</td>
<td>1.010</td>
<td>1.005</td>
<td>5.75</td>
<td>-3.240</td>
</tr>
<tr>
<td>31</td>
<td>342.2</td>
<td>1.63</td>
<td>39.80</td>
<td>39.55</td>
<td>0.53</td>
<td>0.73</td>
<td>54.18</td>
<td>-2.266</td>
</tr>
</tbody>
</table>

Rates in moles/l.-sec.
Fig. 12 - Arrhenius plot of the function theoretically equal to $k_2/k_{1a}$.
assumed that the kinetic estimates of \( E_2 = 24 \text{ kcal./mole} \) and \( E_\theta = 20 \text{ kcal./mole} \) are correct, and that

\[
\text{CH}_3\text{CH}_2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3
\]

(9)

\( E_{-2} = E_{-\theta} \), then from standard enthalpy data \( \Delta H(n-\text{C}_3\text{H}_7-\text{H}) - \Delta H(\text{sec-C}_4\text{H}_9-\text{H}) \) is estimated to be 6 kcal./mole. The kinetic estimates of \( E_2 \) and \( E_\theta \) are reasonably consistent with estimates based on bond strengths and enthalpy data only if the high values of \( \Delta H(n-\text{C}_3\text{H}_7-\text{H}) = 99 \) and \( \Delta H(\text{sec-C}_4\text{H}_9-\text{H}) = 93 \text{ kcal./mole} \) are used together with \( \Delta H(\text{CH}_3-\text{H}) = 102 \text{ kcal./mole} \) and the pertinent enthalpy data. These give \( E_2 = 26 - E_{-2} \) and \( E_\theta = 22 - E_{-\theta} \) kcal./mole. If \( E_{-2} \) and \( E_{-\theta} \) are near zero then these estimates are in fair agreement with the kinetic data for reactions (2) and (9). However there is considerable direct and indirect evidence that supports higher values for the activation energy of radical addition to unsaturated molecules.²⁹ The best

recent estimates of $E_2 = 6$ and $E_g = 7$ kcal./mole lead to estimates of $E_2$ and $E_g$ which are in serious disagreement with the kinetic estimates.\(^{28}\)

The ratio of pre-exponential factors, $A_2/A_{1A} = 4.6 \times 10^4$ (mole/cc.-sec.)\(^{1/2}\), found in this work appears to be inconsistent with the estimate of $A_{1A}$ from the data of Mandelcorn and Steacie.\(^{28}\) If we again assume $A_{1A}$ is equal to or less than the collision number, $Z_{1A} = 2.0 \times 10^{14}$ cc./mole-sec., then $A_2 \approx 6.5 \times 10^{11}$ sec.\(^{-1}\) This is in excellent agreement with the value of $10^{11}$ estimated by Trotman-Dickenson\(^{30}\) from the data of Bywater and Steacie.\(^{24}\) It may be estimated that $\Delta S^0$ for the reaction (2) = 13.8 e.u. with the standard state of 1 mole/cc. ($S^0$ of sec-butyl assumed to be 76.8 e.u. at 1 atm., 25\(^0\) C).\(^{31}\) By equating $\ln(A_2/A_{-2})$ to $\Delta S^0/R$,\(^{32,33}\) we estimate $A_{-2} \approx 6.5 \times 10^8$ cc./mole-sec. The data of Mandelcorn and Steacie give $k_{-2} = 10^8$ at 177\(^0\), if the rate constant for the methyl radical combination is assumed to be $5 \times 10^{13}$. If $E_{2} = 6$ kcal./mole then these data suggest $A_{-2} \approx 10^{11}$ cc./mole-sec. If however $E_{2}$ is actually near zero then $k_{-2} = A_{-2} = 10^8$, in reasonable agreement with the maximum ($6.5 \times 10^8$) estimated

\(^{31}\) Bryant, W. M. D., J. Polymer Sci., 6, 359 (1951).
from the present data. Obviously further experimentation is necessary to establish the origin of the inconsistencies in the estimates of the C₂, E₂, A₂, and A₋₂.

The present data show that the possible rearrangement reaction, sec-butyl → ethyl + ethylene, is an unimportant mode of homogeneous decomposition of the sec-butyl radical at temperatures up to 350°. It is very likely that ethane formation in the mercury-photosensitized decomposition of n-butane originated entirely from the n-butyl radical decomposition, n-butyl → ethyl + ethylene.

The improbability of the homogeneous decomposition of an alkyl radical (to form a smaller radical and an olefin) which requires a simultaneous hydrogen atom shift, suggests that methane formation in the mercury-photosensitized decomposition of butane came from (2) alone. We have assumed this in comparing the present rate data with those obtained in the butane study.

4. Disproportionation and Combination of sec-Butyl Radicals

The ratio of the rate of formation of butene to that of 3,4-dimethylhexane at 25° is essentially independent of the light intensity. 0.68 at the low intensity of 3130 A. radiation and 0.61 at the high intensity of the full arc (obtained by extrapolation of the data of Table 7). The facts are consistent with the formation of butene and
3,4-dimethylhexane in reactions (1a) and (1b). Since these reactions are favored by high radical concentrations provided by high light intensities, the experiments at full arc give the highest rates and thus the most accurate data concerning these reactions. The rate data of runs 30, 28, and 32 of Table 7 and run 12 of Table 5 are considered most reliable and were used to make the Arrhenius plot of $\frac{R_{C_4H_6}}{R_{C_8H_{18}}}$ in Figure 13 (data given in Table 14). From this it is estimated that $E_{1a} - E_{1b} = 0.5$ kcal./mole, and $A_{1a}/A_{1b} = 1.4$. The relatively large ratio of $k_{1a}/k_{1b} = 0.61$ at $25^\circ$ is consistent with the observation that secondary free radicals have a significantly higher ratio of the rate of disproportionation to that of combination than the primary radicals. This may reflect the increased probability of the abstraction reaction for the secondary radicals (there are more hydrogen atoms per radical which can be abstracted and lead to an olefin product), and(or) the decreased rate of combination of the more sterically hindered radical. Kraus found from the photolysis of di-iso-butyl ketone, di-sec-butyl ketone, and di-tert-buty1 ketone that apparently the rate of disproportionation is directly related to the number of abstractable hydrogen

Table 14
Calculation of Function Theoretically Equal to $k_{1b}/k_{1a}$

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp., °C.</th>
<th>$1/T \times 10^3$</th>
<th>$R_{C_4H_8} \times 10^8$</th>
<th>$R_{C_8H_{18}} \times 10^8$</th>
<th>$(4)/(5)$</th>
<th>$\log (6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>24.5</td>
<td>3.36</td>
<td>0.47</td>
<td>0.69</td>
<td>0.681</td>
<td>-0.166</td>
</tr>
<tr>
<td>30</td>
<td>100.2</td>
<td>2.68</td>
<td>1.37</td>
<td>1.86</td>
<td>0.739</td>
<td>-0.131</td>
</tr>
<tr>
<td>28</td>
<td>203.0</td>
<td>2.10</td>
<td>0.97</td>
<td>1.14</td>
<td>0.870</td>
<td>-0.061</td>
</tr>
<tr>
<td>32</td>
<td>242.9</td>
<td>1.94</td>
<td>1.26</td>
<td>1.35</td>
<td>0.938</td>
<td>-0.028</td>
</tr>
</tbody>
</table>

Rates in moles/l.-sec.; values in run 12 are quantum yields.
Fig. 13 - Arrhenius plot of the function theoretically equal to $k_{1b}/k_{1a}$.
atoms of the radical formed. Table 15 gives his results, 
k_2 is the rate of disproportionation, and K_3 is that of 
combination. If k_3 is assumed to be equal in all cases, 
the normalized values of Table 15 give a relative measure 
of k_2. The near equality of columns (2) and (3) for a 

Table 15 
Dependence of k_2 on Number of 
Abstractable Hydrogen Atoms 

<table>
<thead>
<tr>
<th>Radical</th>
<th>(1) k_2/k_3</th>
<th>(2) (k_2/k_3) x (0.418)</th>
<th>(3) Number Abstractable Hydrogen Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-butyl</td>
<td>4.59</td>
<td>11.0</td>
<td>9</td>
</tr>
<tr>
<td>iso-butyl</td>
<td>0.418</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>sec-butyl</td>
<td>2.27</td>
<td>5.4</td>
<td>5</td>
</tr>
</tbody>
</table>

given butyl radical shows the striking correlation between 
the rate of disproportionation and number of abstractable 
hydrogen atoms per radical.

5. The Mechanism of Hydrogen Formation

It is likely that hydrogen is formed only in a non- 
chain sequence I, (5), (6), and (7).

\[
\begin{align*}
C_4H_9CHO + h\nu & \rightarrow C_4H_9 + CHO \quad I \\
M + CHO & \rightarrow M + CO + H \quad (5) \\
HCO (\text{+ wall}) & \rightarrow \text{Products not } H_2 (\text{+ wall}) \quad (6) \\
H + C_4H_9CHO & \rightarrow H_2 + C_4H_8CO \quad (7)
\end{align*}
\]

Since the decomposition reaction (10)
is unimportant up to $400^\circ$, probably the dominant reaction of the formyl radical at $350^\circ$ is (5). For runs at a given temperature $\Phi_{H_2}$ is approximately independent of the absorbed light intensity for consecutive experiments with similar wall conditions (compare $\Phi_{H_2}$ from runs 15 and 18 and 24 and 27 of Table 5). The increase in $\Phi_{H_2}$ with temperature (Figure 8) suggests the increasing importance of formyl radical decomposition at high temperatures. Pronounced variation in $\Phi_{H_2}$ was found in duplicate experiments separated by an extended period of photolysis. All of these facts are consistent with the formation of hydrogen in the sequence I, (5), (6), and (7). It is likely that the effectiveness of the wall for reaction (6) was altered by polymer formation, in general the cleaner the cell walls, the higher was $\Phi_{H_2}$, and presumably the less effective the wall for reaction (6) (compare runs 14, 22, and 5, and 17 and 20 in Table 5). The yields of hydrogen are too variable in this system to provide a meaningful estimate of the activation energy of the hydrogen forming reactions. However the high temperature data are consistent with the limiting value of 0.6 for hydrogen quantum yields. This is the primary efficiency of the formyl formation in the primary process I as estimated in the iodine-inhibited photolyses, and represents the maximum
hydrogen yield expected from the nonchain mechanism suggested in (5) and (7).

6. **Secondary Reactions in the Iodine-Inhibited Photolysis of (+)2-Methylbutanal**

The only secondary reactions of importance in the inhibited photolysis of 2-methylbutanal are (11) and (12).

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCH}_3 + \text{I}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CHICH}_3 + \text{I} \quad (11) \\
\text{HCO} + \text{I}_2 & \rightarrow \text{CO} + \text{HI} + \text{I} \quad (12)
\end{align*}
\]

The formation of 2-iodobutane by (13) and (14)

\[
\begin{align*}
\text{I}_2 + h\nu & \rightarrow 2\text{I} \quad (13) \\
\text{I} + \text{C}_4\text{H}_9\text{CHO} & \rightarrow \text{C}_4\text{H}_9\text{I} + \text{HCO} \text{ (or H} + \text{CO}) \quad (14)
\end{align*}
\]

is ruled out by the facts that within the experimental error, the quantum yield of 2-iodobutane is independent of the iodine pressure (Figure 10). Reaction (15)

\[
\text{C}_4\text{H}_9\text{CHO}^* + \text{I}_2 \rightarrow \text{C}_4\text{H}_9\text{I} + \text{HI} + \text{CO} \quad (15)
\]

is unlikely since the quantum yields of the primary product ethylene are relatively insensitive to the presence of iodine, in fact possibly a small deactivation of excited aldehyde molecules by iodine may occur. The near equality of \( \Phi'_{\text{CO}} \) and \( \Phi'_{\text{C}_4\text{H}_9\text{I}} \) in the iodine-inhibited photolyses suggests reaction (12). It is likely that HI is formed in reaction (12) similar to that reported by Blacet and Calvert\(^2\)\(^{,3} \) in the iodine-inhibited photolysis.
of the butyraldehydes. This would explain the polymer-like substance formed on the cell walls which could result from an interaction of HI with the aldehyde present.

C. The Configuration of Alkyl Free Radicals

An alkyl free radical may exist, in theory, in two molecular configurations: a pyramidal form and a planar form. Early workers concluded, on the basis of quantum mechanics, that a planar configuration was the most favorable for the methyl group. Experimental evidence for the planar configuration of alkyl free radicals in solution has been given by Brown, Kharasch, and Chao. They photochlorinated (+)-1-chloro-2-methylbutane and recovered only inactive 1,2-dichloro-2-methylbutane.

\[
\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}
\]

\[
\text{Cl} + \text{CH}_2\text{Cl}^\prime\text{H(CH}_3\text{)}\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{ClC(CH}_3\text{)}\text{CH}_2\text{CH}_3 + \text{HCl}
\]

\[
\text{Cl}_2 + \text{CH}_2\text{ClC(CH}_3\text{)}\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{ClCCl(CH}_3\text{)}\text{CH}_2\text{CH}_3 + \text{Cl}
\]

However evidence as to the configuration of the gaseous alkyl free radical is limited. Recent investigators have concurred in the conclusion that methyl radicals are planar in the ground state; Walsh reached this conclusion

---

from molecular orbital calculations and Herzberg and Shoosmith\textsuperscript{40} have accepted this model in the explanation of the vacuum ultraviolet absorption spectrum of methyl radicals. However Itoh, Ohno, and Kotani\textsuperscript{41} have made calculations which show the most stable methyl radical configuration may be near tetrahedral.

It was suggested by Dr. M. S. Newman of The Ohio State University that direct experimental evidence of alkyl radical configuration might be obtained in the present work from the iodine-inhibited photolysis of (\textsuperscript{1})2-methyl-butanal. In primary process I,

$$\text{CH}_3\text{CH}_2\text{CH}^\cdot\text{(CH}_3\text{)}\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_3 \rightarrow \text{HCO}$$

the secondary butyl radical is formed by absorption of 3130 Å light, which contains the near minimum energy per quanta (91 kcal./mole) to break the carbon-to-carbon bond without the formation of an activated or "hot" radical. Thus it is likely that the sec-butyl radical is formed in its ground state. When iodine is present in the system, the sec-butyl radical undergoes a rapid reaction to form 2-iodobutane (reaction (11)). If the sec-butyl radical is in a pyramidal form and the inversion rate is slow, the 2-iodobutane formed should be optically active, however if the radical is planar, the 2-iodobutane would be inactive or racemic. Within the experimental accuracy\textsuperscript{~}

of the work, the 2-iodobutane formed in the iodine-inhibited photolysis of $(\dagger)2$-methylbutanal was inactive. Thus this study may lend support to the planar configuration of the gaseous alkyl free radical. However the results can be explained equally well in terms of a pyramidal free radical in which the energy of inversion is very low. A rapid inversion or "umbrellaing" which is faster than the reaction with iodine would lead to an inactive product.

From collision theory the number of collisions of a sec-butyl radical with iodine may be calculated as $3.6 \times 10^7$ sec.$^{-1}$ for an iodine pressure of 3.0 mm. at $335^\circ$K. ($\sigma_{C_4H_9} = 5.9 \AA$, $\sigma_{I_2} = 4.6 \AA$). The reciprocal of this, the time between collisions, is $2.8 \times 10^{-8}$ sec. If it is assumed every collision of sec-butyl and iodine results in the formation of 2-iodobutane and the radical has a pyramidal structure, then its frequency of inversion must be greater than $3.6 \times 10^7$ sec.$^{-1}$ to give a racemic product.

In the case of ammonia the average time between inversions has been calculated to be $2.5 \times 10^{-11}$ sec. By changing the central atom (i.e. PH$_3$, AsH$_3$) the time between

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inversions is much greater than in ammonia ($1.1 \times 10^{-7}$ sec. for PH$_3$, $1.5 \times 10^{-2}$ sec. for AsD$_3$). If we assume that the radical is pyramidal and that a collision must occur to cause inversion of the radical, then with an activation energy as low as 1 kcal./mole, the bulk of the radicals would not be inverted at $60^\circ$ and would lead to an active iodide product in the iodine-inhibited photolysis of (+)2-methylbutanal. However it is very likely that a collision is not necessary to induce inversion. In the study of ammonia it has been shown that collision need not occur for inversion, that interaction of the vibrational modes can cause inversion. From these facts it is difficult to predict an inversion frequency for the sec-butyl radical. Therefore we can only state that if the gaseous sec-butyl radical has a pyramidal configuration the inversion frequency must be greater than $3.6 \times 10^7$ sec.$^{-1}$
V. SUMMARY

The best estimates of the primary quantum efficiencies obtained in the photolysis of (t)2-methylbutanal are given in Table 16 along with those of the simple aliphatic aldehydes. It can be seen that 2-methylbutanal follows the pattern set in these other cases. The total of these efficiencies increases with the complexity of the molecule. Therefore decomposition of a molecule which has been activated by absorption of light energy seems to be more important as a mode of deactivation as molecular weight and branching increase among the simple aliphatic aldehydes.

Table 16
Summary of the Quantum Efficiencies of Primary Processes in the Photolysis of the Simple Aliphatic Aldehydes at 3130 Å.

<table>
<thead>
<tr>
<th>Process</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCHO + hv → R + HCO</td>
<td>I</td>
</tr>
<tr>
<td>→ RH + CO</td>
<td>II</td>
</tr>
<tr>
<td>→ C₂H₄ + RCHO</td>
<td>III</td>
</tr>
<tr>
<td>→ CH₃ + R''CHO</td>
<td>IV</td>
</tr>
</tbody>
</table>

1. Acetaldehyde
   (a) I = 0.20
   (b) II = 0.013
   Total = 0.21

2. Propionaldehyde
   (a) I = 0.48
   (b) II = 0.022
   (c) III = 0.003
   (d) IV = 0.00
   Total = 0.51
3. n-Butyraldehyde
   (a) I = 0.35
   (b) II = 0.017
   (c) III = 0.164
   (d) IV = 0.005
   Total = 0.54

4. Isobutyraldehyde
   (a) I = 0.72
   (b) II = 0.03
   (c) IV = 0.006
   Total = 0.76

5. 2-Methylbutanal
   (a) I = 0.60
   (b) II = 0.004
   (c) III = 0.20
   (d) IV = 0.04
   Total = 0.84

The secondary reactions of the sec-butyl radical are analogous to those of the other simple alkyl free radicals. From the ratio of the rates of disproportionation to combination of n-propyl (0.13), isopropl (0.52), and sec-butyl (0.61) at about 25° it seems that disproportionation is facilitated by the complexity of the radical, that is, the number of abstractable hydrogens available, if it is assumed that the combination reaction is not sterically hindered. The decomposition reaction of the sec-butyl radical forming methyl radicals and propylene is similar to that of the n-propyl radical, the only other radical studied which can give this reaction without a hydrogen shift.
The intramolecular ethylene forming primary process is seemingly little different for 2-methylbutanal, where a methyl group is on the alpha carbon of the n-propyl group adjacent to a carbonyl group, than it is in similar compounds where there is no methyl group.

In the iodine-inhibited photolysis of (t)2-methylbutanal, no optical activity was found in the product, 2-iodobutane. This result is consistent with a planar configuration for a gaseous alkyl free radical, or a frequency of inversion of a sec-butyl radical of non-planar configuration which is rapid compared to the fast reaction of sec-butyl radical with iodine.
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