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The Photolysis of the Alphatic Aldehydes. XIV. The Butyraldehydes[1]

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New analysis data, product identification and quantum yield determinations from vapor phase photolyses of the butyraldehydes are presented in this paper. These data provide new evidence concerning the primary processes proposed by Leighton, Levanas, Blacet and Rowe[2] and indicate the occurrence of another mode of decomposition following the absorption of light. New evidence regarding the nature of secondary reactions of radicals produced in the primary processes is included.

Experimental Procedure

Photochemical Apparatus.—The apparatus for these photochemical experiments was similar to that used and described by Blacet and Heldman.[3] A direct current mercury arc and a crystal quartz monochromator system provided the means of selective radiation. The photolysis cell was made of fused quartz tubing, 30 mm. inside diameter and 20 cm. in length, with plane quartz windows fused on the ends. The cell, glass circulating pump, trap, and connecting tubing were suspended in an air thermostat maintained at a desired temperature by a system of heaters, Fenwal regulator and circulating fan. The large air thermostat (plywood-asbestos construction) surrounding the photolysis system could not be heated safely to temperatures above 150°, so an additional heating unit was used to obtain cell temperatures from 200-350°. The photolysis cell was surrounded by a cylindrical electrically heated furnace, open at each end; it was similar to that used by Leighton and co-workers[2] and was constructed and described by Blacet and LuValle.[4]

Quantum Yield Determinations.—In experiments where quantum yields were determined directly, the light energy was measured quantitatively by means of a thermopile-galvanometer system. The thermopile was designed and constructed by R. A. Crane[5]; it could not be used at elevated temperatures so absorption coefficients were determined only at room temperature. The light energy passing through the empty cell was measured before and after each run. There was little decrease in intensity due to aging of the arc or to polymer formation during a run (usually less than 5%). Quantum yields were calculated as described by Leighton and Blacet[6]; temperature independence of the absorption coefficient and linear aging of the arc were assumed.

Some experiments were made duplicating the photolysis conditions used by Leighton, *et al.*[2] In these runs the quantum yields of carbon monoxide reported by them and the product analysis of the present work were utilized to calculate quantum yields of other products. That this procedure was justified may be seen from the data of Table I. The quantum yields of runs 1 and 2 of this table are results from direct determinations and those of run 3 were calculated from the quantum yields of carbon monoxide reported by Leighton and co-workers and new analysis data. The degree of agreement between the quantum yields of various products indicates the reliability of the quantum yields which have been determined indirectly.

Aldehyde Purification.—The butyraldehyde samples for this work were prepared by fractionation at atmospheric pressure of Eastman Kodak Co. White Label aldehydes which had been dried over anhydrous calcium sulfate. A constant boiling fraction was further fractionated in a system of evacuated bulbs, and the center fraction was stored over anhydrous calcium sulfate and used as the aldehyde supply.

Product Analysis.—In the usual photochemical experiment about 1 to 2% of the aldehyde was decomposed. The products were divided into two fractions following photolysis. The excess aldehyde and condensable products were condensed in a trap at Dry Ice temperature, and the non-condensable products were removed with a Toepler pump and collected in a gas holder over mercury. The non-condensable fraction was treated with potassium hydroxide to remove traces of aldehyde. In most experiments this fraction was then analyzed for carbon monoxide by the Blacet-Leighton gas analysis method,[7] and the remaining non-condensable gases were analyzed by a Westinghouse (Type LV) mass spectrometer.

The identification of hexanes was accomplished by mass spectrometer analysis of the condensable products after removal of excess aldehyde. In several experiments the condensable fraction was distilled into one arm of a U-tube and then isolated from the vacuum system by a stopcock. The sample was warmed and allowed to vaporize from one side arm and contact solid potassium hydroxide pellets contained in the other arm. The polymerization of the butyraldehydes on the base was practically complete after 4 hours with *n*-butyraldehyde and 48 hours with isobutyraldehyde. The unpolymerized portion of the condensable fraction was then analyzed by the mass spectrometer.

A procedure which utilized a modified Schiff reagent was employed in a few experiments to identify formaldehyde in the products of *n*-butyraldehyde photolysis. The procedure was based on the method of Blaedel and Blacet.[8] The visible absorption spectra of known formaldehyde-butyraldehyde-acetaldehyde mixtures in Schiff reagent were compared with that of photolysis products in Schiff reagent on a Beckman spectrophotometer. A sharp maximum in the absorption spectrum of known formaldehyde solutions occurs near 6000 Å., and the solution follows Beer's law.

Experimental Results

Products of *n*-Butyraldehyde Photolysis. (a) Non-condensable Products.—The major non-condensable products of the photolysis of *n*-butyraldehyde have been identified as propane, carbon monoxide and ethylene. The minor products are hydrogen, propylene and methane. The quantum yields of these products at various wave lengths are summarized in Table I. The temperature independence of ethylene quantum yields (see runs 1, 2, 4, 5 and 6 of Table I) was utilized together with analysis data to calculate the quantum yields of other products in runs 10 and 11 of Table I. The quantum yields of hydrogen given in Table II were determined directly in experiments at temperatures up to 175°. The high temperature values were calculated from carbon monoxide quantum yields reported by Leighton, *et al.*,[1] together with recent analysis data for hydrogen (analyzed by mass spectrometer) and carbon monoxide (analyzed by micro gas analysis) in products from photolysis with experimental conditions very similar to those of Leighton and co-workers.

(b) Condensable Products. (1) *n*-Hexane.—The mass spectrum of the fraction of the con-

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(1) For tables supplementary to this article order Document 2918 from American Documentation Institute, 1719 N Street N.W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

(2) Leighton, Levanas, Blacet and Rowe, THIS JOURNAL, **59**, 1843 (1937).

(3) Blacet and Heldman, *ibid.*, **64**, 889 (1942).

(4) Blacet and LuValle, *ibid.*, **61**, 273 (1939).

(5) Crane and Blacet, *Rev. Sci. Instruments*, **21**, 259 (1950).

(6) Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932).

(7) Blacet, MacDonald and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

(8) Blaedel and Blacet, *ibid.*, **13**, 449 (1941).

TABLE I

QUANTUM YIELDS OF PRODUCTS IN *n*-BUTYRALDEHYDE PHOTOLYSES

Experiment	1	2	3	4	5	6	7	8	9	10	11
Wave length, Å.	3130	3130	3130	3130	3130	3130	2804	2654	2537	2537	2537
Temperature, °C.	25	25	25	63	100	150	25	25	25	100	175
Pressure, mm.	101	97	100	100	104	103	100	100	100	80	90
Quanta absorbed. (sec.-cc.)$^{-1}$ × 10^{-12}	9.2	8.6	5.0	9.4	9.2	8.6	1.9	2.4	0.93	1.3	0.50
Quantum yield:											
CO	0.50	0.49	0.44[a]	0.72	1.12	2.03	0.44[a]	0.48[a]	0.75[a]	1.77	4.31
C_3H_8	.30	.30	.30	.59	0.93	1.69	.30	.35	.75	1.63	3.76
C_3H_6	.009	.012	.017	...	...	...	.0068	.0047	.00	...	...
C_2H_4	.178	.188	.164	.176	0.153	0.153	.27	.38	.30	(0.30)	(0.30)
CH_4	...	...	.005	...	...	...	.006	.010	.015	0.015	0.017
H_2	.015	.013	.016	.019	0.028	0.073	.025	.023	.037	0.064	0.155
n-C_6H_{14}	...	...	.13	...	...	...	.053	.048	.04	...	...

[a] Data of Leighton, Levanas, Blacet and Rowe.[2]

TABLE II

QUANTUM YIELDS OF HYDROGEN IN PHOTOLYSES OF THE BUTYRALDEHYDES (WAVE LENGTH, 3130 Å.; PRESSURE, 100 MM.)

Temperature, °C.	25	63	100	150	175	200	250	275	300	350
Φ_{H_2} from										
n-Butyraldehyde	0.014	0.019	0.028	0.073	0.13	....	0.36	0.39	0.35	....
Isobutyraldehyde	.030	....	.041	.11	....	0.42	.55	....	.70	0.76

densable products remaining after separation of the excess butyraldehyde (by either fractional distillation or polymerization) was determined. A comparison of characteristic peaks of the various possible hexanes and the photolysis samples indicated clearly that the photochemical product was *n*-hexane.[9]

(2) **Acetaldehyde.**—A low boiling fraction of the condensable products from *n*-butyraldehyde photolysis at room temperature and wave length 2537 Å. was analyzed by the mass spectrometer. The peaks of the mass spectrum remaining after subtraction of hexane and butyraldehyde contributions correlated well with those of pure acetaldehyde.[9] During the course of the experiments, that portion of the low boiling fraction which compared well with acetaldehyde in mass spectrum indicated a vapor pressure and an ease of polymerization on treatment with potassium hydroxide which are characteristic of acetaldehyde.

The 2,4-dinitrophenylhydrazones of butyraldehyde and acetaldehyde can be separated chromatographically. Following the procedure of Roberts and Green[10] the hydrazones of known mixtures of pure butyraldehyde and acetaldehyde and the aldehydes in the photolysis condensable fractions were prepared. Known mixtures of aldehydes of the composition expected from photochemical products (acetaldehyde equivalent to ethylene) gave column bands identical in appearance to those obtained from photolysis samples. Attempts to further characterize the small bands and to obtain quantitative data were unsuccessful.

(3) **Formaldehyde.**—The products from photolysis at wave length 3130 Å., temperature 25° and *n*-butyraldehyde pressure of 100 mm., were treated as described in the preceding section. The absorption band characteristic of formaldehyde in Schiff reagent was found. Comparison with known mixtures indicated that about 1.4 × 10^{-5} mole of formaldehyde was formed per 3.5 ml. of non-condensable products. The quantum yield of formaldehyde under these conditions is about 0.09.

(c) **Other Information.**—No evidence was obtained which proves the presence of other compounds in the condensable products. However, certain other experimental results are worthy of mention. In one photolysis of *n*-butyraldehyde at wave length, 3130 Å., temperature 25° and pressure 100 mm., 5.4 ml. of non-condensable products was obtained. The entire condensable fraction was vaporized into a large mixing bulb and introduced into the spectrometer without polymerization. The mass spectrum was determined from the region of mass peak 142 to peak 73. No peaks were observed in more than traces at any mass/charge ratio above 87, 86, etc., which are characteristic peaks of hexane. We may conclude therefore that bibutyryl (parent mass 142) and di-*n*-propyl ketone (parent mass 114) were not present in the products.

Small quantities of a solid material were visible on the cell walls after several successive exposures of *n*-butyraldehyde totaling 150 hours. The identification of this substance was not accomplished.

Products of Isobutyraldehyde Photolysis. (a) **Non-condensable Products.**—The major non-condensable products from isobutyraldehyde photolyses are carbon monoxide, propane and propylene. The minor products are hydrogen and methane. The quantum yields of these products are summarized in Table III.

(b) **Condensable Products.** (1) **Bi-isopropyl.**—Mass spectrometric analysis of the condensable products which remained after polymerization of excess isobutyraldehyde proved the presence of bi-isopropyl (2,3-dimethylbutane).[9] Yields of the hexanes and propylene from the butyraldehyde photolyses are given in Table IV.

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(9) These data are available on microfilm from the American Documentation Institute, Washington, D. C., see footnote 1.

(10) Roberts and Green, *ibid.*, **18**, 335 (1946).

TABLE III

QUANTUM YIELDS OF PRODUCTS IN ISOBUTYRALDEHYDE PHOTOLYSES

Experiment	1	2	3	4	5	6	7
Wave length, Å.	3130	3130	3130	3130	2804	2654	2537
Temperature, °C.	25	25	100	150	25	25	25
Pressure, mm.	100	100	124	142	100	100	100
Quanta absorbed (sec.-cc.)$^{-1}$ × 10^{-12}	8.1	9.0	8.9	7.0	1.3	0.92	0.71
Quantum yield:							
CO	0.63[a]	0.56	0.59	0.99	0.72[a]	0.79[a]	0.87[a]
C_3H_8	.46	.41	.49	.86	.58	.65	.72
C_3H_6	.081	.072	.032	.023	.053	.021	.014
C_2H_6	......	......	......	......	< .006	< .017	< .020
CH_4	.006	.005	.005	.007	.012	.036	.072
H_2	.030	.030	.041	.11	.032	.024	.031
C_6H_{14} (biisopropyl)	.15	......	......	......	.17	......	......

[a] Data of Leighton, Levanas, Blacet and Rowe.[2]

TABLE IV

YIELDS OF HEXANE AND PROPYLENE FROM BUTYRALDEHYDE PHOTOLYSES

		n-Butyraldehyde							Isobutyraldehyde		
	Aldehyde	1	2	3	4	5	6	7	8	9	10
1	Temperature, °C.	25	25	25	25	20	60	175	25	25	25
2	Pressure of aldehyde, mm.	100	100	100	100	80	82	87	100	101	100
3	Wave length, Å.	3130	2804	2654	2537	3130	3130	3130	3130	3130	2804
4	Quanta absorbed, (sec.-cc.)$^{-1}$ × 10^{-12}	7.1	2.8	1.4	0.57	4.9	8.2	5.3	9.2	9.2	1.4
		n-Hexane							Bi-isopropyl		
5	Moles hexane × 10^6/cc. of non-cond. gas	5.3	2.1	1.7	1.2	5.8	7.4	0.69	6.0	3.8	5.1
6	Moles propylene × 10^6/cc. of non-cond. gas	0.54	0.27	0.15	0.1	0.74	....	.04	2.7	2.7	1.6
7	Ratio (6)/(5)	0.10	0.13	0.09	.....	0.13	....	.06	0.45	0.71	0.31

(c) **Other Information.**—Experiments to detect formaldehyde in isobutyraldehyde photolysis products were not done. Room temperature photolysis products gave no measurable mass spectrum above that of the hexane parent peaks, so it is improbable that compounds such as diisopropyl ketone and biisobutyryl were formed in more than trace amounts. There was no visible evidence of a solid formation on the walls of the cell following photolyses totaling 50 hours exposure time.

Discussion of Results

The experimental evidence is in accord with the occurrence of the primary processes proposed by Leighton, Levanas, Blacet and Rowe.[2]

$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \left\{\begin{array}{ll} \mathrm{CH_3CH_2CH_2 + CHO} & \text{(I)}\\ \mathrm{C_3H_8 + CO} & \text{(II)}\\ \mathrm{C_2H_4 + CH_3CHO} & \text{(III)}\end{array}\right.$$

$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \left\{\begin{array}{ll} \mathrm{(CH_3)_2CH + CHO} & \text{(i-I)}\\ \mathrm{C_3H_8 + CO} & \text{(i-II)}\end{array}\right.$$

The following secondary reactions are considered in the explanation of the results. C_3H_7 represents an *n*-propyl or isopropyl radical from *n*-butyraldehyde or isobutyraldehyde photolyses, respectively.

$$\mathrm{C_3H_7 + C_3H_7CHO \longrightarrow C_3H_8 + C_3H_7CO} \tag{1}$$
$$\mathrm{CHO \longrightarrow H + CO} \tag{2}$$
$$\mathrm{H + C_3H_7CHO \longrightarrow H_2 + C_3H_7CO} \tag{3}$$
$$\mathrm{C_3H_7CO \longrightarrow C_3H_7 + CO} \tag{4}$$
$$\mathrm{2C_3H_7} \longrightarrow \left\{\begin{array}{ll} \mathrm{C_6H_{14}} & (5)\\ \mathrm{C_3H_6 + C_3H_8} & (6)\end{array}\right.$$
$$\mathrm{CHO + C_3H_7 \longrightarrow CO + C_3H_8} \tag{7}$$
$$\mathrm{2CHO} \longrightarrow \left\{\begin{array}{ll} \mathrm{CH_2O + CO} & (8)\\ \mathrm{(CHO)_2} & (9)\end{array}\right.$$

Primary Processes (I) and (i-I).—(a) The temperature dependence of quantum yields of carbon monoxide and propane (Fig. 1) indicates the presence of free radicals. Primary processes (I) and (i-I) together with the secondary reactions (1) and (4) best explain these results.[2]

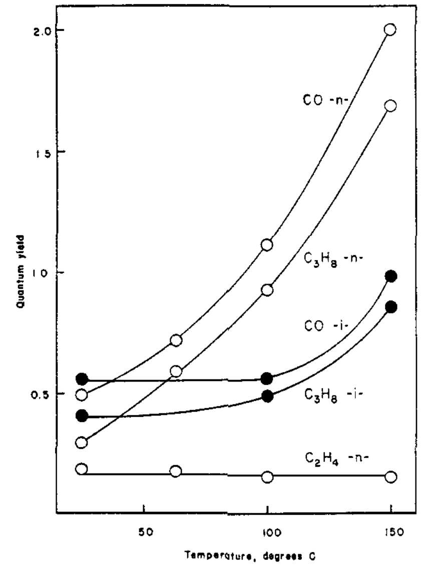

Fig. 1.—Quantum yields of major products *vs.* temperature: *n*-butyraldehyde pressure, 100 mm.; isobutyraldehyde concentration, 0.00538 *M* (100 mm. at 100°); wave length, 3130 Å.; intensity of absorbed light, about 9 × 10^{12} quanta/cc. -sec.;-*n*- and -*i*- refer to products of normal and isobutyraldehyde, respectively.

(b) The identification of hexanes in the products is evidence for the formation of propyl radicals.

(c) The identification of propylene in the products is indirect evidence for the presence of propyl radicals which may react in part to give propylene by reaction (6).

(d) Recognition of formaldehyde in the condensable products of *n*-butyraldehyde photolysis provides indirect evidence for the presence of formyl radicals which may react in part by a reaction such as (8).

(e) The variation in quantum yield of hydrogen with temperature, Fig. 3, is explained best by means of secondary reactions involving formyl radicals and is indirect evidence for the occurrence of processes (I) and (i-I). (See the discussion of hydrogen formation.)

Primary Processes (II) and (i-II).—No new evidence for these processes is presented in this paper. However, studies with iodine vapor, to be discussed in a later publication, indicate that they are important at the shorter wave lengths.

Primary Process (III).—This process, proposed by Leighton and co-workers[1] and Bamford and Norrish,[11] is confirmed by the results obtained in this work.

(a) The large temperature independent quantum yield of ethylene, Fig. 1, is explained satisfactorily only by a primary process such as (III).

(b) The identification of acetaldehyde in the condensable products in amounts approximately equivalent to those of ethylene also provides evidence for the occurrence of process (III).

Other Primary Processes.—The small but definite quantum yields of methane and the temperature independence of these quantum yields (*n*-butyraldehyde runs 9, 10 and 11 of Table I and isobutyraldehyde runs 1, 2, 3 and 4 of Table III) provide evidence for the occurrence of an additional primary process. One might attempt to explain methane formation in *n*-butyraldehyde photolyses by the occurrence of process (I) followed by reactions (10) and (11).

$$CH_3CH_2CH_2 \longrightarrow CH_3 + C_2H_4 \qquad (10)$$

$$CH_3 + C_3H_7CHO \longrightarrow CH_4 + C_3H_7CO \qquad (11)$$

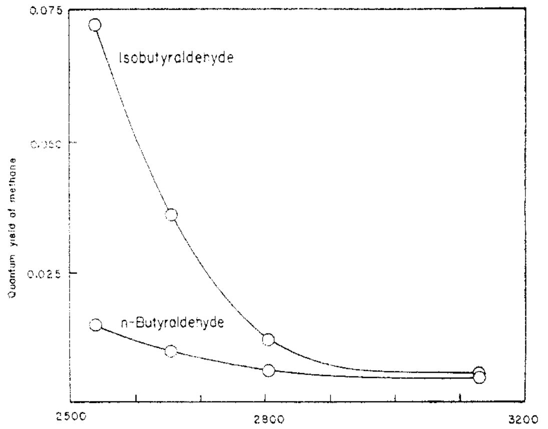

Fig. 2.—Quantum yields of methane *vs.* wave length: butyraldehyde pressures, 100 mm.; temperature, 25°.

However, since thermochemical data[12] indicate $\Delta H_{10} = 25 \pm 2$ kcal./mole, and it is probable that E_{10} is about 25–27 kcal./mole, one would expect a strong temperature dependence of methane quantum yield if reactions (10) and (11) were the source of methane. The experimental results show no temperature dependence of this quantum yield. One might suggest also that the methane in *n*-butyraldehyde photolysis products results from the partial photodecomposition of the primary product acetaldehyde; since only 1–2% of the butyraldehyde was decomposed in these experiments this explanation is not adequate.

Two primary processes are possible sources of methane in the products of *n*-butyraldehyde photolysis

$$CH_3CH_2CH_2CHO + h\nu \longrightarrow \begin{cases} CH_3 + CH_2CH_2CHO & \text{(IV)} \\ CH_4 + CH_2CHCHO & \text{(IVa)} \end{cases}$$

Two similar processes may be considered as possible sources of methane from isobutyraldehyde photolysis

$$(CH_3)_2CHCHO + h\nu \longrightarrow \begin{cases} CH_3 + CH_3CHCHO & \text{(i-IV)} \\ CH_4 + CH_2CHCHO & \text{(i-IVa)} \end{cases}$$

If primary processes such as (IV) and (i-IV) are assumed to be the sources of methane, then in order to explain the temperature independence of quantum yield of methane one must postulate that methyl radicals so produced are consumed almost exclusively by reaction (11). Ethane appears to be formed in small quantities (presumably by methyl radical combination) in isobutyraldehyde photolyses at the shorter wave lengths of absorbed light. At these wave lengths the methane quantum yield and presumably the methyl radical concentration are a maximum for the spectral range investigated. This is evidence for the occurrence of (IV) and (i-IV) rather than the intramolecular processes (IVa) and (i-IVa). Recent data from photolysis of butyraldehyde–iodine mixtures provides additional evidence for the occurrence of processes (IV) and (i-IV). Methane is not detectable in the products of these photolyses, but methyl iodide has been identified. Although the process (IV) is unimportant in *n*-butyraldehyde photolysis at all wave lengths, process (i-IV) becomes an important mode of decomposition at high energies of absorbed light (Fig. 2.).

Secondary Reactions. (a) Hydrogen Formation.—It is evident from the data of Fig. 3 that the hydrogen quantum yields from the butyraldehyde photolyses appear to approach a limiting value at high temperatures. This limiting value is in each case in good agreement with recent estimates of the efficiencies of primary processes (I) and (i-I) obtained from the results of photolysis of butyraldehyde–iodine mixtures. In advance of the publication of the detailed results of iodine inhibited butyraldehyde photolyses, it should be stated that these results indicate the average quantum efficiency, ϕ_I, of process (I) to be 0.35 and that of process (i-I) to be 0.72 (photolyses at wave length 3130 Å. and in the temperature range from 60 to 150°). An inspection of Fig. 3 indicates that the limiting values of quantum yield of hydrogen from

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(11) Bamford and Norrish, *J. Chem. Soc.*, 1538 (1938).

(12) Natl. Bur. Standards, "Selected Values of Hydrocarbons," 1947.

TABLE V

CALCULATED VALUES OF THE QUANTUM YIELD FUNCTION AT VARIOUS TEMPERATURES

(1) $10^3/T$	3.35	2.97	2.68	2.36	2.23	2.11	1.91	1.745
(2) $\Phi_{H_2}^{3/2} \times 10^3/(\phi_I - \Phi_{H_2})$								
(a) *n*-Butyraldehyde	4.4	6.8	12.7	61	174	....	5400	4200
(b) Isobutyraldehyde	6.8	..	10.9	54	....	720	1640	5900

n-butyraldehyde and isobutyraldehyde are about 0.40 and 0.80, respectively. In view of the agreement between ϕ_I estimates and the limiting value of Φ_{H_2}, reactions of the formyl radical other than decomposition by reaction (2), or reactions such as

$$CHO + C_3H_7CHO \longrightarrow H_2 + CO + C_3H_7CO \qquad (12)$$

cannot be important at elevated temperatures, since each formyl radical formed in primary process (I) or (i-I) produces one molecule of hydrogen at temperatures above approximately 250°. Since formyl radicals are effectively decomposed at high temperatures, the dominant chain terminating steps must be reactions (5) and (6). This conclusion is in agreement with the high temperature aldehyde photodecomposition mechanism proposed by Leermakers.[13] The assumption of alkyl radical combination as the only important chain terminating reaction leads to the theoretical rate expression which is in agreement with experiment.

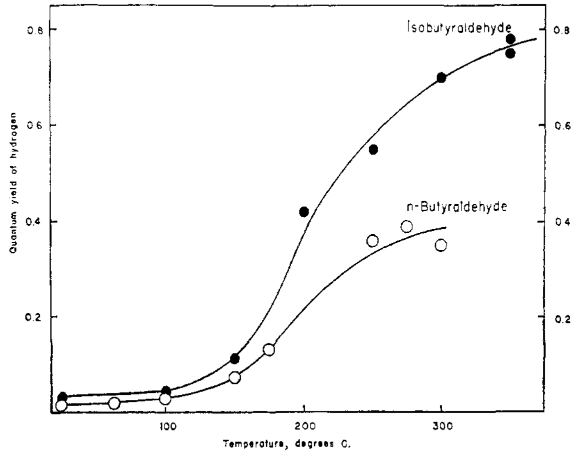

Fig. 3.—Quantum yield of hydrogen *vs.* temperature: butyraldehyde pressures, 100 mm.; wave length, 3130 Å.

The identification of formaldehyde in the products of *n*-butyraldehyde photolyses at room temperature appears to indicate the occurrence of a reaction such as (8). Blacet and Blaedel have carried out a detailed study of the yield of formaldehyde in acetaldehyde photolyses.[14] They report the formation of glyoxal in addition to formaldehyde. On the basis of this work reaction (9) has been included in the secondary reactions given. These authors found that the yield of formaldehyde and glyoxal drops sharply with increase in temperature; formaldehyde and glyoxal were not detectable in the products from photolyses at 100°. If reaction (13) were important in aldehyde photolysis

$$CHO + RCHO \longrightarrow CH_2O + RCO \qquad (13)$$

one would expect a noticeable increase in yield of formaldehyde with increase in temperature; a rapid decrease in formaldehyde production is observed experimentally. The results of Blacet and Blaedel indicate that reaction (13) cannot be important, and reactions (8) and (9) are unimportant at high temperatures. On the basis of this evidence and the evidence for the occurrence of the reaction (7′) in acetaldehyde photolysis,[15,16] one might

$$HCO + CH_3 \longrightarrow CH_4 + CO \qquad (7')$$

choose reaction (7) as the most probable chain terminating reaction involving formyl radicals at temperatures above 100°. (Direct evidence for the occurrence of reaction (7) has been obtained recently from iodine inhibited photolyses of the butyraldehydes.) If one assumes that reactions (2), (3), (4), (5), (6) and (7) are the only important reactions involving propyl and formyl radicals at high temperatures, by the usual steady state methods he obtains relation (14).

$$\frac{\Phi_{H_2}^{3/2}}{\phi_I - \Phi_{H_2}} = \frac{K_2}{K_7}\left(\frac{K_5 + K_6}{2Ia}\right)^{1/2} \qquad (14)$$

If one accepts the limiting values of Φ_{H_2} at high temperatures as estimates of ϕ_I, and this appears to be justified from the results of iodine inhibited photolyses of the butyraldehydes described above, then the experimental values of Table II may be substituted in relation (14), and the function involving the rate constants may be evaluated at several temperatures. Since the intensity of absorbed light was approximately constant in these experiments, the change in the above function with temperature should reflect the change in the rate constants of (14). The values $\Phi_{H_2}^{3/2}/(\phi_I - \Phi_{H_2})$ are given in Table V, and the logarithm of these values is plotted against $1/T$ in Fig. 4.

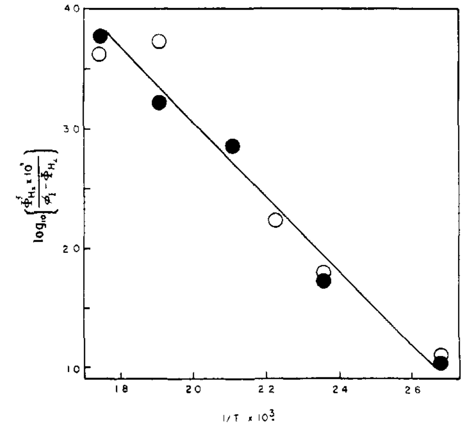

Fig. 4.—Plot of $\log_{10}(\Phi_{H_2}^{3/2} \times 10^3/(\phi_I - \Phi_{H_2}))$ *vs.* $1/T$ for the results of *n*-butyraldehyde, ○, and isobutyraldehyde, ●, photolyses. The slope of the best line through these points (as determined by the method of least squares) corresponds to an apparent activation energy of 14 kcal./mole.

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[13] Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[14] Blacet and Blaedel, *ibid.*, **62**, 3374 (1940).

[15] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[16] Haden and Rice, *ibid.*, **10**, 445 (1942).

The plot of the function of the quantum yields against $1/T$ for both aldehydes appears to determine the same straight line at temperatures of 100° and above. The slope of the best line through these points, as determined by the method of least squares, corresponds to an apparent activation energy of 14 kcal./mole. In terms of the proposed mechanism the apparent activation energy is equal to $E_2 - E_7 + (k_5E_5 + k_6E_6)/2(k_5 + k_6)$. It is probable that E_7, E_5 and E_6 are very small and, therefore, the value of 14 kcal./mole may be taken as an estimate of E_2. This estimate of the activation energy of the decomposition of the formyl radical is in disagreement with the value of 26 kcal./mole reported by Gorin[14] from results of iodine inhibited acetaldehyde photolysis and the value of 19.5 kcal./mole estimated theoretically by Bawn.[17] However, the evidence upon which these estimates are based is not compelling. Recent results (to be published shortly) from a study of formaldehyde photolysis carried out by the second-named author and E. W. R. Steacie at the National Research Council, Canada, indicate that the activation energy of reaction (2) may be as low as 13.5 kcal./mole.

(b) **Reaction between Propyl Radicals.**—Reactions (5) and (6) were proposed by Leighton, *et al.*, as possible chain terminating reactions in photolyses of the butyraldehydes.[2] The identification of *n*-hexane from *n*-butyraldehyde photolysis and bi-isopropyl from isobutyraldehyde photolysis is evidence for the occurrence of the reaction (5). The importance of the alkyl radical combination product in aldehyde photolysis varies markedly with the nature of the aldehyde. Hexane is a major product of butyraldehyde photolysis, while Blacet and Brinton[18] find that very small quantities of ethane are formed in acetaldehyde photolysis.

Since di-*n*-propyl and diisopropyl ketones and bibutyryls were not found in the products of photolysis of the butyraldehydes, reaction (4) must be rapid, and it seems unlikely that reactions such as (5′) and (6′) are important sources of hexanes and propylene

$$C_3H_7 + C_3H_7CO \longrightarrow \begin{cases} \longrightarrow C_6H_{14} + CO & (5') \\ \longrightarrow C_3H_6 + C_3H_8 + CO & (6') \end{cases}$$

The correlation between hexane and propylene yields with varied wave length is shown in Table IV. The agreement between the ratio of moles of propylene to moles of *n*-hexane for *n*-butyraldehyde photolyses at room temperature, runs 1, 2, 3 and 5 of Table IV, provides evidence for the formation of hexane and propylene in simultaneous reactions such as (5) and (6). The estimates of moles of bi-isopropyl which are given in runs 8, 9 and 10 of Table IV show considerable variation, but the ratios of row (7) provide an indication of the order of magnitude of the two simultaneous reactions. From the average of the results of Table IV one may estimate the percentage combination by reaction (5) and disproportionation by reaction (6) which occur at room temperature on reaction between two propyl radicals

$$2CH_3CH_2CH_2 \longrightarrow \begin{cases} \xrightarrow{(90\%)} n\text{-}C_6H_{14} & (5a) \\ \xrightarrow[(10\%)]{} C_3H_6 + C_3H_8 & (6a) \end{cases}$$

$$2(CH_3)_2CH \longrightarrow \begin{cases} \xrightarrow{(67\%)} (CH_3)_2CHCH(CH_3)_2 & (5b) \\ \xrightarrow[(33\%)]{} C_3H_6 + C_3H_8 & (6b) \end{cases}$$

The accuracy of the analysis for the very small quantities of propylene decreases greatly at high temperatures since the percentage of propylene in the products decreases rapidly. Thus no estimate of the difference in activation energies of reactions (5) and (6) can be made from the present data. Little information regarding reactions (5a) and (6a) is reported in the literature. Bamford and Norrish[19] reported *n*-hexane (recognized by physical properties) in the products of photolysis of di-*n*-propyl ketone at room temperature. They did not report the presence of propylene in the products; however, ethylene was found to be a major product and the methods of analysis then available would not indicate the presence of small quantities of propylene in large amounts of ethylene.

Several estimates of the relative rates of reactions (5b) and (6b) at room temperature are available in the literature. Bamford and Norrish[20] are reported to have found 56 moles of propylene formed to 44 moles of hexane in the room temperature photolysis of diisopropyl ketone. Moore and Taylor[21] found that 71 moles of hexane were formed to 29 moles of propane in the products of mercury sensitized hydrogenation of propylene at room temperature. It seems probable that each of these experimental results may be considered an estimate of the relative efficiency of reactions (5b) and (6b), and both estimates are in reasonable agreement with the present results. All of the results indicate that the disproportionation reaction is more important relative to combination reaction with isopropyl radicals than with *n*-propyl radicals. In view of the greater steric hindrance of the isopropyl radical, this difference may reflect a lower ratio of steric factors for the reactions of combination and disproportionation of isopropyl radicals relative to this ratio for the reactions of the *n*-propyl radicals.

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Summary

The photodecomposition of the butyraldehydes in the vapor phase has been studied at temperatures from 25 to 300° and at various wave lengths of absorbed light. A mass spectrometer was utilized to identify the main products of the photolysis of

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(17) Bawn, *Trans. Faraday Soc.*, **35**, 899 (1939).

(18) Blacet and Brinton, THIS JOURNAL, **72**, 4715 (1950).

(19) Bamford and Norrish, *J. Chem. Soc.*, 1504 (1935).

(20) Glazebrook and Pearson, *ibid.*, 1777 (1936).

(21) Moore and Taylor, *J. Chem. Phys.*, **8**, 504 (1940).

n-butyraldehyde as carbon monoxide, propane, ethylene, acetaldehyde and *n*-hexane. Propylene, hydrogen, methane and formaldehyde were identified as minor products. Quantum yields of carbon monoxide, propane and hydrogen increase with temperature, while the quantum yields of ethylene and methane are independent of temperature. In the photodecomposition of isobutyraldehyde the main products were identified as carbon monoxide, propane, propylene and biisopropyl and the minor products as methane and hydrogen. Quantum yields of all of the products but methane show a temperature dependence. These experimental results are consistent with the occurrence of the following primary processes

$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \begin{cases} \mathrm{CH_3CH_2CH_2 + CHO} & \text{(I)} \\ \mathrm{C_2H_4 + CH_3CHO} & \text{(III)} \\ \mathrm{CH_3 + CH_2CH_2CHO} & \text{(IV)} \end{cases}$$

$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \begin{cases} \mathrm{(CH_3)_2CH + CHO} & \text{(i-I)} \\ \mathrm{CH_3 + CH_3CHCHO} & \text{(i-IV)} \end{cases}$$

Primary processes (I), (III) and (i-I) are important while process (IV) is unimportant at all wave lengths. Process (i-IV) becomes important at the shorter wave lengths of absorbed light. The data do not exclude the occurrence of intramolecular primary processes producing propane and carbon monoxide, but no evidence for their occurrence was obtained in this work.

A study of the quantum yields of hydrogen as a function of temperature has been made. The hydrogen quantum yields approach limiting values at high temperatures, and the results indicate that these limiting values are equal to the primary quantum yields of processes (I) and (i-I). From the temperature dependence of the quantum yields of hydrogen and an assumed reaction mechanism the activation energy of the formyl radical decomposition is estimated to be about 14 kcal./mole.

The experimental results from room temperature photolyses indicate an increased efficiency of the disproportionation reaction relative to the combination reaction for isopropyl radicals compared to the analogous reactions for *n*-propyl radicals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Photolysis of Aliphatic Aldehydes. XV. The Butyraldehydes with Iodine Vapor

BY F. E. BLACET AND J. G. CALVERT

The first quantitative study of the vapor phase photolysis of the butyraldehydes was carried out by Leighton, Levanas, Blacet and Rowe.[1] Recently the study of the photolysis of these compounds was continued using a mass spectrometer to aid in product analysis, and new evidence concerning the nature of the primary processes has been reported.[2] More direct evidence as to the nature and the importance of the primary processes was deemed necessary for the proper interpretation of the photolyses. Several authors have reported that iodine may be used successfully to inhibit secondary reactions of atoms and free radicals (other than iodide formation) in the photolysis of aldehydes and ketones, and evidence for the occurrence of various primary processes has been obtained from an analysis of the products of these reactions.[3,4,5,6] In the present work the technique of these investigators has been extended to the vapor phase photolysis of butyraldehyde–iodine mixtures; the results provide new evidence concerning the nature and importance of the primary processes in the photolyses of the butyraldehydes.

Experimental Procedure

Photolysis System.—The apparatus and experimental procedure used in these studies were similar to that described by Blacet and Heldman[4] and Blacet and Calvert.[2]

Butyraldehyde and Iodine Purification.—The samples of aldehyde were purified and stored as before.[2] The iodine used was analytical grade which was resublimed at atmospheric pressure. It was stored in a ground glass stoppered bottle placed in a desiccator over anhydrous magnesium perchlorate.

Photolysis Procedure.—The iodine and aldehyde introduction procedure used in this work was based on that described by Blacet and Heldman[6] and need not be given here in detail. However, it should be emphasized that several precautions must be taken to obtain successful photolysis of mixtures of iodine and butyraldehyde vapors. (1) Water must be eliminated from the aldehyde and iodine samples by proper purification and storage. Before each run the photolysis system must be freed from water by evacuation of the system and distillation of water traces to a cold trap (−120°). (2) The entire gas train containing the iodine and aldehyde vapors must be warmed to a temperature at which the vapor pressure of iodine is greater than the partial pressure of iodine in the system. (3) After each iodine–aldehyde photolysis all of the glass tubing and photolysis system parts included in the air thermostat should be removed and freed from aldebyde, aldehyde polymers and hydrogen iodide containing compounds by successive treatment with acetone, hot nitric acid and distilled water. If precautions (1) and (2) are not observed, a rapid heterogeneous reaction between aldehyde and iodine occurs, and all of the iodine is removed from the vapor phase to form with the aldehyde a brown non-volatile substance which deposits on the cell walls and connecting tubing. If procedure (3) is not followed, a polymerization is initiated presumably by traces of hydrogen iodide on the glass tubing.

With proper care to maintain an anhydrous condition of aldehyde and iodine samples and photolysis system and care to prevent the retention of cold spots in the vapor circulating system, there is no measurable occurrence of thermal reaction (on the walls or in the gas phase) between iodine and butyraldehyde vapor in the temperature range from 60 to 150°.

Analysis of Products.—During the usual experiment about 1–2% of the original aldehyde was decomposed. The products were divided into condensable and non-condensable fractions as described previously.[2] In general, the non-condensable gases were analyzed for carbon monoxide by the Blacet–Leighton gas analysis method,[7] and the remaining

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[1] Leighton, Levanas, Blacet and Rowe, THIS JOURNAL, **59**, 1843 (1937).

[2] Blacet and Calvert, *ibid.*, **73**, 661 (1951).

[3] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[4] Blacet and Heldman, THIS JOURNAL, **64**, 889 (1942).

[5] Blacet and Loeffler, *ibid.*, **64**, 893 (1942).

[6] Benson and Forbes, *ibid.*, **65**, 1399 (1943).

[7] Blacet, MacDonald and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).