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

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

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

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.

LOS ANGELES, CALIF. RECEIVED JULY 5, 1950

[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 aldehyde, 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).

TABLE I

QUANTUM YIELDS OF PRODUCTS FROM PHOTOLYSIS OF *n*-BUTYRALDEHYDE–IODINE MIXTURES AT WAVE LENGTH 3130 Å.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13
Temperature, °C.	102	101	63	65	150	60	82	80	100	100	100	100	150
n-C_3H_7CHO pressure, mm.	42	99.5	57.5	53.5	60.5	40	42	46	40	45	44	43	43
I_2 pressure, mm.	5.0	6.5	2.5	3.2	3.0	1.6	1.1	1.4	3.0	2.2	5.3	4.0	4.0
I_a, quanta/sec.-ccm. × 10^{-12}	4.9	7.8	5.0	6.2	5.0	0.67	4.2	4.4	3.7	5.1	3.9	4.5	4.0
Quantum yields													
CO	0.35	0.35	0.44	0.42	0.36	0.50	0.44	0.39	0.38	0.34	0.39	0.40	0.31
Alkyl iodides	.....	0.36	...	....	.34	.....	.....	.....	......	.35	......	.39	...
C_3H_8	0.016	.016	...	.005	.011	.024	.021	.018	.014	.020	.019	.024	.016
C_2H_4	.157	.158	...	.142	.170	(.164)	(.164)	(1.64)	(.164)	(.164)	(.164)	(.164)	(.164)
H_2	.004	.....	...	....	.010	.00	.....	.00	.005	.005	.005	.004	.0065

TABLE II

AVERAGE QUANTUM YIELDS OF PRODUCTS OF IODINE INHIBITED PHOTOLYSES OF *n*-BUTYRALDEHYDE AT VARIOUS WAVE LENGTHS

Temperature, 100°; pressure of iodine, 4 mm.; pressure of *n*-butyraldedyde about 50 mm.

Wave length, Å.	3130	2804	2654	2537
Quantum yield:				
(a) CO	0.37	0.39	0.52	0.63
(b) C_3H_8	.017	.11	.25	.33
(c) C_3H_7I	.35	.27	.30	.32
(d) C_2H_4	.164	.27	.38	.30
(e) H_2	.005	.01	.04	.09
(f) CH_4	.00	.00	.00	.00
(g) CH_3I	.003	..	..	.014

gases by a modified Westinghouse type LV mass spectrometer. The condensable fraction of the products was analyzed for iodides by an analysis procedure which will be described in detail elsewhere. The analysis was based on the iodide titration of water and carbon tetrachloride fractions which had been equilibrated with the condensable products after the removal of excess iodine. The iodide analysis of the carbon tetrachloride layer provided an estimate of the total alkyl iodides produced; the analysis of the basic water fraction gave an estimate of such compounds as hydrogen iodide in the condensable products. The nature of the iodides was determined by combination of mass spectrometric and chemical analysis data.

Quantum Yields Determinations.—Quantum yields were obtained in the manner described before.[2] Direct quantum yield determinations indicate that the quantum yields of ethylene from *n*-butyraldehyde photolyses at a given wave length are independent of variation in temperature or aldehyde and iodine pressures within the experimental error. These results made possible some rapid indirect determinations of quantum yields of other products from iodine-*n*-butyraldehyde photolyses by use of the average quantum yields of ethylene as found in direct experiments and analysis data from experiments in which the light intensity was not measured.

Experimental Results

Products of *n*-Butyraldehyde–Iodine Photolysis

(a) Non-condensable Products.—The results of quantum yield determinations at wave length 3130 Å. are summarized in Table I. At this wave length the major non-condensable products are carbon monoxide and ethylene. Average results of *n*-butyraldehyde–iodine mixture photolyses at various wave lengths are given in Table II. It is seen that propane also becomes an important product at the shorter wave lengths of absorbed light. Propylene and methane were not found in the products from any of the iodine inhibited photolyses.

The average value of the quantum yield of ethylene from the direct determinations of runs 1–5 of Table I and the values from uninhibited photolyses reported previously[2] is 0.164 at wave length 3130 Å. This value and analysis results were used to calculate the quantum yields of other compounds of runs 6–13 of Table I. The average quantum yields of ethylene at various wave lengths as reported previously[2] and present analysis results from iodine inhibited photolyses were used to calculate the quantum yields of Table II.

(b) Condensable Products (1) *n*-Propyl Iodide.—A comparison was made between the mass spectra ratios of pure iodides and several photolysis samples obtained from condensable products after separation of excess iodine and aldehyde.[8] There was no indication of parent 86 peak of the hexanes (major product of the uninhibited photolyses) in the spectra of the photolysis samples, but peaks 170 (parent propyl iodide peak) and 142 (parent methyl iodide) were present. Ethyl iodide (parent mass 156) was not detected in the products. The only significant differences between the mass spectra ratios of the two pure propyl iodides occur below mass peak 43.[8] This lower region of the mass spectra of photochemical samples had unpredictable small contributions due to compounds introduced or not removed in the polymerization procedure used to remove excess aldehyde. The uncertainty in the contribution of the iodide in the photolysis samples to the lower characteristic peaks made impossible the identification of the iodide by the simple comparison procedure used to identify the hexanes in uninhibited butyraldehyde photolyses.[2] However, for a given number of moles of propyl iodides introduced into the mass spectrometer, the intensity of the parent mass peak from *n*-propyl iodide is about twice as large as that from isopropyl iodide. Thus if the spectra of known propyl iodides and unknown propyl iodides are determined and the quantity of iodide producing these intensities is then found by chemical analysis, it is possible to identify the unknown iodides even in the presence of unknown non-iodine containing compounds. The data of Table III summarize the intensities per mole of a few of the important peaks in the mass spectra of the pure propyl iodides and samples from *n*-butyraldehyde–iodine photolyses at wave length 3130 Å. The measured intensities of peak 142 were assumed to indicate the presence of methyl iodide, and small contributions due to this iodide have been subtracted to obtain the corrected intensities per mole of propyl iodide given in runs 1,

[8] For mass spectrometric data order Document 2932A 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.

TABLE III

COMPARISON OF INTENSITY (VOLTS) OF THE UPPER MASS SPECTRA PER MOLE OF PURE IODIDES WITH PHOTOLYSIS PRODUCTS

Mass charge	Isopropyl iodide	*n*-Propyl iodide	Products from *n*-Butyraldehyde-iodine photolysis (1)	(2)	(3)	Products from Isobutyraldehyde-iodine photolysis (4)	(5)
170	1.02	1.96	1.9	1.7	2.1	1.02	0.97
155	0.02	0.06	0.05	0.05	0.06	[a]	[a]
141	.01	.08	.08	.08	.09	[a]	[a]
127	.19	.35	.34	.32	.38	[a]	[a]

[a] Indicates that the peak was not measured.

2 and 3 of Table III. The comparison of the data of these runs with that for pure propyl iodides indicates strongly that the *n*-butyraldehyde–iodine photolysis product is *n*-propyl iodide.

The quantum yields of total alkyl iodides from photolyses at wave length 3130 Å. are given in Table I; no estimate of this quantum yield is given for several experiments which were made prior to the development of a successful alkyl iodide analysis method.

(2) **Methyl Iodide.**—The mass spectra of the condensable products contained small 142 peaks which were explained best by assuming the presence of methyl iodide in the photolysis products. The quantum yields of *n*-propyl and methyl iodides were calculated from the ratio of methyl iodide to propyl iodide as determined by mass spectrometric analysis and the quantum yield of total alkyl iodides as found by chemical analysis. The average values of these quantum yields are given in Table II.

(3) **Other Condensable Products.**—Although acetaldehyde, previously reported,[2] and hydrogen iodide are expected to be other major products of the iodine inhibited photolyses of *n*-butyraldehyde, no identification of these compounds was made in the present work. There was no indication of butyryl iodide in the mass spectrum of the condensable products, and only traces of a base soluble iodide (presumably hydrogen iodide) were found in the water soluble fraction of the condensable products.

Products of Isobutyraldehyde–Iodine Photolysis (a) Non-condensable Products.—The quantum yields of products are summarized in Table IV. Carbon monoxide is the only major non-condensable product at wave length 3130 Å.; propane is a minor product. Propane, in addition to carbon monoxide, becomes a major product at higher energies of absorbed light. Very small amounts of hydrogen were found in the products from photolysis at all of the wave lengths used in this work, while propylene and methane were not detectable in the products from any of the photolyses.

Analysis data alone were obtained from one photolysis of isobutyraldehyde and iodine at 2537 Å. The other experimental conditions were: temperature, 100°; isobutyraldehyde pressure, 97 mm.; iodine pressure, 3.5 mm. The following volumes of products in microliters were found by analysis: carbon monoxide, 170.2; propane, 97.9; hydrogen, 2.5.

(b) Condensable Products (1) Isopropyl Iodide.—Runs 4 and 5 of Table III were obtained from products of isobutyraldehyde–iodine photolysis at 3130 and 2537 Å., respectively. The value for run 5 has been corrected for the presence of a small amount of methyl iodide in these products. Comparison of the measured intensities of runs 4 and 5 with those for the pure propyl iodides indicates strongly that the photochemically produced iodide of parent mass 170, resulting from iodine inhibited photolyses of isobutyraldehyde, is isopropyl iodide. The results of the alkyl iodide quantum yield determinations are listed in Table IV.

(2) **Methyl Iodide.**—Quantitative analysis data for methyl iodide were not obtained in this work; however, the qualitative observations based on mass spectra of condensable products indicate that methyl iodide is not detectable in the products from the photolysis of isobutyraldehyde at wave length 3130 Å., while a small but definite amount is produced at 2537 Å. From the results of one analysis of products from photolysis at 2537 Å. the ratio of methyl iodide to isopropyl iodide was estimated to be 0.024.

(3) **Hydrogen Iodide.**—The iodide analyses of the water fractions obtained by the extraction procedure generally corresponded to a very small fraction (few per cent.) of the hydrogen iodide expected from proposed mechanisms. No indication of iodide was obtained in the analysis of the potassium hydroxide beads used to polymerize the excess aldehyde in the non-condensable fraction of the iodine inhibited photolysis products. Following each of several photochemical experiments the entire glass system inside the thermostat was removed and rinsed with a measured quantity of 0.2 *N* base and then with several small portions of distilled water. The wash solutions were all

TABLE IV

QUANTUM YIELDS OF PRODUCTS FROM PHOTOLYSIS OF ISOBUTYRALDEHYDE–IODINE MIXTURES

Run		1	2	3	4	5	6	7	8	9
Wave length, Å.		3130	3130	3130	3130	3130	3130	3130	3130	2654
Temperature, °C.		60	102	102	100	100	102	104	150	100
Aldehyde pressure, mm.		118	125	122	119	121	121	124	142	125
Iodine pressure, mm.		1.5	2.0	3.2	4.0	4.8	5.4	6.3	4.7	4.0
I_a, quanta/sec.-ccm. × 10^{-12}		6.1	13.0	12.5	4.1	7.2	13.5	11.0	6.4	4.2
Quantum yields	CO	0.82	0.77	.....	0.73	0.71	0.80	0.68	0.74	0.85
	C_3H_8	0.056	.033	.....	.013	.016	.027	.011	.045	.40
	Alkyl iodides	0.77	.72	.64	.78	.82	......	.56	.74	.40
	HI	......	......	0.65	......	......	.60	.71	......	.....
	H_2	0.00	.007	.....	.006	.014	.016	.005	.00	.02

combined, acidified and analyzed for iodide. Following these operations it was found that the quantity of base soluble iodide on the cell and tubing walls and in the trap products was approximately the same as the alkyl iodide produced in the same experiment. These analyses were used to obtain the estimates of quantum yields of hydrogen iodide listed in Table IV.

An apparent reaction between hydrogen iodide and acetaldehyde vapor was reported by Blacet, Heldman[4] and Loeffler[5]; the results of the present work suggest the occurrence of a reaction between hydrogen iodide and the butyraldehydes. All of the evidence seems to indicate that an iodide containing compound is formed by the action of photochemically produced hydrogen iodide on the aldehyde vapor, inducing polymerization or forming a non-volatile addition compound with the aldehyde which condenses on the walls of the photolysis system. On treatment with dilute alkaline solution, this substance releases the iodide ion.

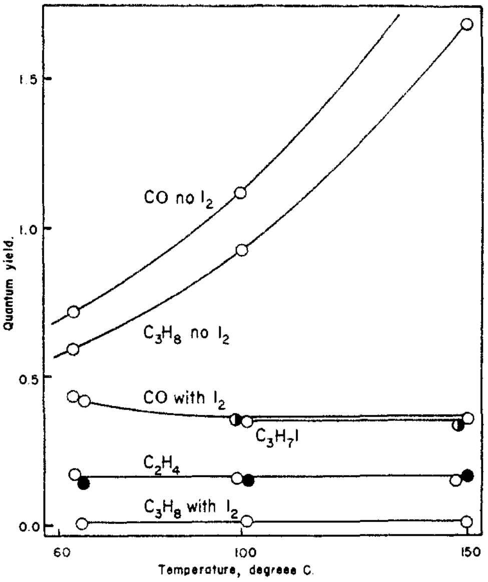

Fig. 1.—Quantum yields of major products of *n*-butyraldehyde–iodine photolyses *vs.* temperature: wave length, 3130 Å.; *n*-butyraldehyde pressure, about 43 and 100 mm. in inhibited and uninhibited reactions, respectively; iodine pressure in inhibited reactions, greater than 2 mm. Quantum yields of ethylene from uninhibited and inhibited photolyses are represented by open circles and closed circles, respectively. Quantum yields of *n*-propyl iodide are represented by half-closed circles.

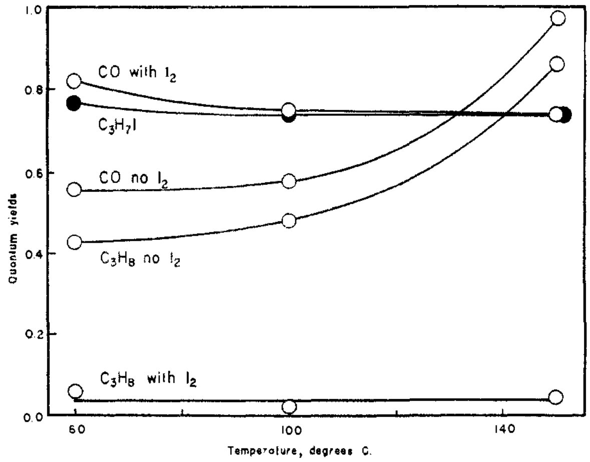

Fig. 2.—Quantum yields of major products of isobutyraldehyde–iodine photolyses *vs.* temperature: wave length, 3130 Å.; isobutyraldehyde concentration constant, 100 mm. pressure at 25°; iodine pressure in the inhibited photolyses, greater than 1.5 mm.

Discussion of Results

The following primary processes best explain the results obtained in this study of the butyraldehyde–iodine photolyses.

$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \left[\begin{array}{ll} \longrightarrow \mathrm{CH_3CH_2CH_2 + HCO} & \text{(I)} \\ \longrightarrow \mathrm{C_3H_8 + CO} & \text{(II)} \\ \longrightarrow \mathrm{CH_2CH_2 + CH_3CHO} & \text{(III)} \\ \longrightarrow \mathrm{CH_3 + CH_2CH_2CHO} & \text{(IV)} \end{array}\right.$$

$$\mathrm{(CH_3)_2CHCHO} + h\nu \left[\begin{array}{ll} \longrightarrow \mathrm{(CH_3)_2CH + HCO} & \text{(i-I)} \\ \longrightarrow \mathrm{C_3H_8 + CO} & \text{(i-II)} \\ \longrightarrow \mathrm{CH_3 + CH_3CHCHO} & \text{(i-IV)} \end{array}\right.$$

The following secondary reactions are suggested in explanation of the results. C_3H_7 represents the normal and isopropyl radical from *n*-butyraldehyde and isobutyraldehyde, respectively.

$$\mathrm{C_3H_7 + I_2 \longrightarrow C_3H_7I + I} \qquad (1)$$

$$\mathrm{HCO + I_2 \longrightarrow CO + HI + I} \qquad (2)$$

$$\mathrm{CH_3 + I_2 \longrightarrow CH_3I + I} \qquad (3)$$

$$\mathrm{C_2H_4CHO + I_2 \longrightarrow IC_2H_4CHO + I} \qquad (4)$$

Reactions (5), (6) and (7) are of minor importance.

$$\mathrm{HCO \longrightarrow H + CO} \qquad (5)$$

$$\mathrm{H + I_2 \longrightarrow HI + I} \qquad (6)$$

$$\mathrm{H + C_3H_7CHO \longrightarrow H_2 + C_3H_7CO} \qquad (7)$$

Primary Processes (I) **and** (i-I).—These processes were first proposed by Leighton and coworkers[1] and recently confirmed by the experimental results reported by Blacet and Calvert.[2] The results obtained in this work provide additional evidence for their occurrence.

(a) The identification of *n*-propyl and isopropyl iodides in the iodine inhibited photolysis products of *n*-butyraldehyde and isobutyraldehyde, respectively, is conclusive evidence for the occurrence of processes (I) and (i-I) which are followed by reaction (1).

(b) The temperature independence of quantum yields of the propyl iodides (Figs. 1 and 2) indicates that the iodides are formed in a rapid secondary reaction (1) of low activation energy following the primary process in which a propyl radical is formed.

(c) It is apparent from the data of Fig. 3 that within the experimental error the propyl iodide quantum yields are independent of iodine pressure in the range from 2 to 6 mm. pressure of iodine. The average value of the quantum yields of *n*-propyl iodide from *n*-butyraldehyde–iodine photolysis is about 0.35; the average quantum yield of isopropyl iodide from isobutyraldehyde–iodine photolysis is about 0.72. These data provide evidence against propyl iodide formation by reaction between iodine and activated aldehyde molecules, because if such a reaction did occur the quantum yield of propyl iodide would be expected to increase with increasing iodine pressure.

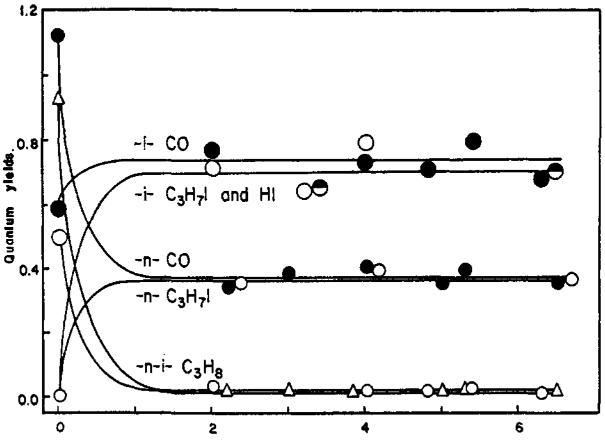

Fig. 3.—Quantum yields of major products of butyraldehyde–iodine photolyses *vs.* iodine pressure: wave length, 3130 Å.; temperature, 100°; *n*-butyraldehyde pressure, about 43 mm.; isobutyraldehyde pressure, 122 mm. The prefixes *-i-* and *-n-* indicate products of isobutyraldehyde and *n*-butyraldehyde, respectively. The quantum yield data for carbon monoxide are represented by closed circles, propyl iodides by open circles, hydrogen iodide by half-closed circles, propane from isobutyraldehyde and *n*-butyraldehyde by open circles and triangles, respectively.

(d) The identification of a water soluble iodide, presumably hydrogen iodide, in the products of the iodine inhibited photolyses of isobutyraldehyde in amounts nearly equivalent to isopropyl iodide (the average quantum yields of propyl iodide and hydrogen iodide are 0.72 and 0.65, respectively) provides evidence for the formation of formyl radicals in a primary process in amounts equivalent to those of propyl radicals and indicates that formyl radicals produced react in the rapid secondary reaction (2). The results indicate also that reaction (2) is followed by (2-a), where $n \geqq 1$.

$$HI + n(C_3H_7CHO) \longrightarrow \text{(non-volatile substance)} \quad (2\text{-a})$$

Primary Processes (II) and (i-II).—These processes which were first proposed by Leighton and co-workers[1] are confirmed by the experimental data obtained in this work.

(a) The quantum yields of propane from butyraldehyde photolyses with varied iodine pressure are represented in Fig. 3. These quantum yields are seen to decrease rapidly to a small but constant value which is unaffected by further increase in iodine pressure. The explanation of these data and the large quantum yields of propane in the iodine inhibited photolyses at the shorter wave lengths (see data of Tables II and IV and Fig. 4) necessitates the proposal of the intramolecular processes (II) and (i-II).

(b) The temperature independence of the quantum yield of propane from iodine inhibited photolyses, Figs. 1 and 2, is strong evidence for propane formation in a primary process. If propane produced in these experiments were formed by propyl radicals abstracting hydrogen atoms from aldehyde, a definite increase in efficiency of propane production would be expected as temperature is increased.

Within the experimental error the data from inhibited photolyses of both butyraldehydes at each wave length follow relation (8).

$$\Phi_{CO} = \Phi_{C_3H_8} + \Phi_{C_3H_7I} \quad (8)$$

The agreement of the data with this relation points to the occurrence of primary processes (I), (II), (i-I) and (i-II) together with the rapid secondary reactions (1) and (2).

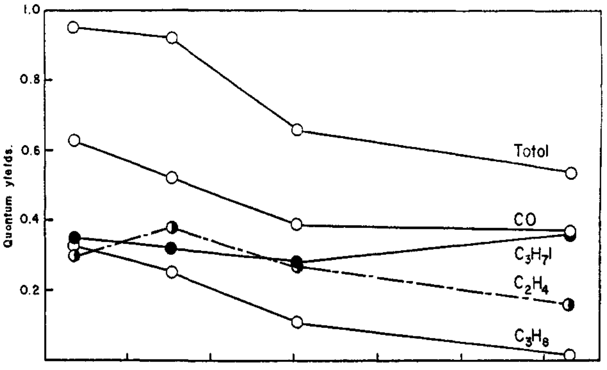

Fig. 4.—Quantum yields of major products of *n*-butyraldehyde–iodine photolyses *vs.* wave length: temperature, 100°; pressure *n*-butyraldehyde, about 50 mm.; pressure iodine, about 3 mm.

Primary processes (II) and (i-II) are analogous to the intramolecular rearrangement of acetaldehyde to form carbon monoxide and methane which has been suggested by Gorin[3] and Blacet and Loeffler[5] to explain their results from acetaldehyde–iodine photolysis. Apparently, the aldehydes undergo this intramolecular rearrangement with increasing efficiency as the energy of absorbed quanta increases. There is a striking correlation between the relative efficiencies of analogous primary processes (I), alkyl and formyl radical formation and (II), intramolecular formation of carbon monoxide and hydrocarbon, in the photolysis of acetaldehyde and the butyraldehydes at different wave lengths. Relative efficiencies of processes (I) and (II) calculated from the data of Blacet, Heldman[4] and Loeffler[5] from acetaldehyde–iodine photolyses and the present data from butyraldehyde–iodine photolyses are compared in Table V. Presumably the carbonyl group is responsible for the absorption of light in each aldehyde and completely analogous bonds are broken and made in the primary processes (I) and (II), so it is not surprising that the relative efficiencies of these processes are very similar for the different aldehydes at a given energy of adsorbed quanta.

TABLE V

COMPARISON OF THE RATIOS OF PRIMARY PROCESS (II) TO PRIMARY PROCESS (I) IN THE PHOTOLYSIS OF ACETALDEHYDE AND THE BUTYRALDEHYDES

Wave length, Å.	2380	2537	2654	2804	3103
Energy, kcal./mole	120	113	108	102	91
(1) Acetaldehyde	1.19	..	0.78	0.39	0.065
(2) *n*-Butyraldehyde	..	1.06	.89	.39	.049
(3) Isobutyraldehyde	..	1.35	.93	..	.042

Primary Process (III).—This process was proposed by Leighton and co-workers[1] and Bamford and Norrish[9] and recently confirmed by experimental results reported by Blacet and Calvert.[2] The results of the present work also confirm its occurrence. From the data of Fig. 1 it may be seen that the quantum yields of ethylene from iodine inhibited photolyses remain constant with increase in temperature and equal to the quantum yields of ethylene from uninhibited photolyses within the experimental error. This study presents abundant evidence that the dissociation of propyl radicals by reaction (9) could not have been an important factor in the production of ethylene.

$$CH_3CH_2CH_2 \longrightarrow CH_2CH_2 + CH_3 \qquad (9)$$

Bamford and Norrish have suggested the general photochemical reaction (10) as an important primary process in the photolysis of several aldehydes and ketones.[9]

$$RCH_2CH_2CH_2COR' + h\nu \longrightarrow RCHCH_2 + CH_3COR' \qquad (10)$$

R and R′ may be either alkyl groups or hydrogen atoms. They reported that the quantum yields of ethylene from gas phase photolysis of di-*n*-propyl ketone are temperature independent, and in that case the occurrence of reaction (11) is probable.[10]

$$(CH_3CH_2CH)_2CO + h\nu \longrightarrow CH_2CH_2 + CH_3COC_2HC_2HCH_3 \qquad (11)$$

Davis and Noyes[11] have investigated the photolysis of methyl *n*-butyl ketone in some detail and found that propylene and acetone were major products. The quantum yields of these products were equal within the experimental error and appeared to be temperature independent from 25 to 300°. The authors proposed that the primary process (12) is an important mode of decomposition.

$$CH_3COCH_2CH_2CH_2CH_3 + h\nu \longrightarrow C_3H_6 + CH_3COCH_3 \qquad (12)$$

The evidence for the occurrence of reactions of the type represented by reaction (10) is compelling, but Noyes and Davis have pointed out that the mechanism of such processes may proceed by two possible paths.[11] In the case of *n*-butyraldehyde, primary process (III) may occur by the transfer of a γ-hydrogen atom to the oxygen, and an enol-acetaldehyde and ethylene result as the primary products, or the process may be a concerted mechanism involving the transfer of the γ-hydrogen directly to the α-carbon atom as the two stable products form. Because of the uncertain reactivity and stability of the enol form of the carbonyl compounds in the gas phase, definite evidence in favor of either of these mechanisms does not appear to be easily obtained.

Primary Processes (IV) and (i-IV).—The proposal of these primary processes is necessary to explain satisfactorily the results previously reported by Blacet and Calvert[2] as well as certain data presented herewith.

(a) The temperature independent quantum yields of methane from uninhibited butyraldehyde photolyses[2] and the absence of methane in the iodine inhibited photolysis products point to the occurrence of processes (IV) and (i-IV).

(b) The detection of small but definite amounts of methyl iodide in the condensable products of the iodine inhibited photolyses can best be explained by these primary processes followed by reaction (3). There is a good correlation between the quantum yields of methyl iodide from *n*-butyraldehyde–iodine photolysis and the quantum yield of methane from uninhibited photolyses for the two wave lengths where complete analysis data are available.

Wave length, Å.	3130	2537
CH_3I (inhibited photolyses)	0.003	0.014
CH_4 (uninhibited photolyses)	.0047	.015

Qualitatively, it can be seen that the quantum yield of methyl iodide from photolyses of isobutyraldehyde–iodine mixtures at 2537 Å. was much greater than that from photolyses at 3130 Å. This is in agreement with the apparent quantum efficiencies of process (i-IV) as estimated from methane quantum yields from uninhibited photolyses of isobutyraldehyde.[2]

The data indicate that the process (IV) is unimportant at all wave lengths studied, but it appears that (i-IV) cannot be neglected as a mode of decomposition at high energies of absorbed light. Since complete analysis data for methyl iodide from butyraldehyde–iodine photolyses were not determined, the quantum yields of methane from uninhibited photolyses were used as an estimate of the efficiencies of processes (IV) and (i-IV) which are given in Table VI.

Other Possible Primary Decomposition Processes.—The direct formation of hydrogen atoms in a primary process, as first postulated by Noyes and Leighton,[12] is still a possibility. However, at the wave lengths used, this process appears to be no more than a minor one because of the low values of molecular hydrogen quantum yields which have been found at room temperature.[2]

Activation and Deactivation of Aldehyde Molecules.—The data presented in Table VI represent the best estimate of the efficiency of each primary process in the photodecomposition of the butyraldehydes and were obtained from an average of the quantum yield data at each wave length. One may estimate the fraction of molecules of butyraldehyde which decompose on absorption of light of a given wave length by adding the apparent efficiency of each process. The "Total" values given in rows (e) and (i) of Table VI, and represented graphically in Fig. 4, were obtained in this manner. It is apparent from these data that *n*-butyraldehyde molecules absorbing light of long wave length are decomposed with only moderate efficiency, and one must propose, therefore, that activated molecules of relatively long life are formed and are deactivated.

$$CH_3CH_2CH_2CHO + h\nu \longrightarrow CH_3CH_2CH_2CHO^* \qquad (V)$$

$$(CH_3)_2CHCHO + h\nu \longrightarrow (CH_3)_2CHCHO^* \qquad (i\text{-}V)$$

$$C_3H_7CHO^* + M \longrightarrow C_3H_7CHO + M \qquad (13)$$

$$C_3H_7CHO^* \longrightarrow C_3H_7CHO + h\nu' \qquad (14)$$

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(9) Bamford and Norrish, *J. Chem. Soc.*, 1531 (1938).

(10) Bamford and Norrish, *ibid.*, 1544 (1938).

(11) Davis and Noyes, THIS JOURNAL, **69**, 2153 (1947).

(12) Noyes and Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 349.

Deactivation by collision and fluorescence are represented in (13) and (14), respectively. The fact that the fraction of activated molecules which do not decompose is temperature independent over the range of experimental conditions used in the present work leads one to represent activation of this sort as another independent primary process.

TABLE VI

ESTIMATE OF THE QUANTUM YIELDS OF PRIMARY PROCESSES IN THE PHOTOLYSIS OF THE BUTYRALDEHYDES

$$C_3H_7CHO + h\nu \left[\begin{array}{ll} \longrightarrow C_3H_7 + HCO & \text{(I), (i-I)} \\ \longrightarrow C_3H_8 + CO & \text{(II), (i-II)} \\ \longrightarrow CH_2CH_2 + CH_3CHO & \text{(III)} \\ \longrightarrow CH_3 + C_2H_4CHO & \text{(IV), (i-IV)} \end{array} \right.$$

Wave length, Å.	3130	2804	2654	2537
Energy, kcal./mole	91	102	108	113
n-Butyraldehyde				
(a) Process (I)	0.35	0.28	0.28	0.31
(b) Process (II)	.017	.11	.25	.33
(c) Process (III)	.164	.27	.38	.30
(d) Process (IV)	.005	.006	.010	.015
(e) Total	.54	.67	.92	.96
Isobutyraldehyde				
(f) Process (i-I)	.72	...	.43	...
(g) Process (i-II)	.03	...	.40	...
(h) Process (i-IV)	.006	.012	.036	.072
(i) Total	.72	...	.87	...

One may conclude from the data of Table VI that the fraction of molecules of isobutyraldehyde which take part in reaction (i-V) and subsequently reactions (13) and (14) is small at all wave lengths. However, the analogous activation and deactivation reactions in the photolysis of *n*-butyraldehyde are expected to be important at wave lengths of absorbed light near 3130 Å. These conclusions are in complete agreement with the butyraldehyde fluorescence observations made by Leighton and co-workers[1]; isobutyraldehyde showed no observable fluorescence at any wave length under the experimental conditions used, but *n*-butyraldehyde indicated a weak fluoresence at wave length 3130 Å. and none at shorter wave lengths. The present results are also in agreement with the facts that very little structure is evident in the entire absorption spectrum of isobutyraldehyde and that structure is apparent in the spectrum of *n*-butyraldehyde only at wave lengths greater than 2700 Å.[13] Norrish has suggested that the decrease in structure in the absorption spectra with increasing complexity of aldehyde may reflect the overlapping of the energy levels available to the activated molecules rather than an increased efficiency of molecule disruption.[14] However, the present results lead one to conclude that molecule disruption may be important in determining the extent of structure in the absorption spectra of the butyraldehydes.

Secondary Reactions in Iodine Inhibited Photolyses.—It is clear from the preceding discussion that the results indicate the rapid occurrence of the secondary reactions (1), (2) and (3). No evidence for the occurrence of reaction (4) was obtained, but it appears probable by analogy with the occurrence of reactions (1) and (3).

Secondary Reactions in Uninhibited Photolyses.—Evidence concerning the occurrence of certain secondary reactions in the uninhibited photolysis of the butyraldehydes has been obtained in the present work. It is seen from the data of Fig. 3 that there is a marked difference in the effect of iodine pressure on the quantum yields of products from the butyraldehydes; at the temperature of 100° with increase in the pressure of iodine there is a rapid decrease in the quantum yield of carbon monoxide to a constant value with *n*-butyraldehyde and rapid increase in the quantum yield of carbon monoxide to a constant value with isobutyraldehyde. To explain these results one might suggest that some major reaction of low activation energy which produces condensable products occurs in the low temperature uninhibited photolysis of isobutyraldehyde and accounts for the disappearance of formyl radicals without formation of carbon monoxide. Reactions (15) and (16) appear to be of minor importance, reasoning from the condensable product analysis data reported previously.[2] However, one may account satisfactorily for these experimental results by assuming that the recombination reaction (17) is important in low temperature isobutyraldehyde photolysis.

$$2HCO \left[\begin{array}{ll} \longrightarrow CO + H_2CO & (15) \\ \longrightarrow (HCO)_2 & (16) \end{array} \right.$$

$$CH_3CHCH_3 + HCO \longrightarrow (CH_3)_2CHCHO \quad (17)$$

It has been demonstrated in this work that the primary decomposition of the butyraldehydes at 3130 Å. may be represented almost completely by processes (I), (i-I) and (III), see Fig. 4. Small amounts of formaldehyde and very small amounts of hydrogen are observed in the products of the uninhibited photolyses at room temperature, while carbon monoxide and propane are major products. The chain lengths of carbon monoxide production from uninhibited photolyses of *n*-butyraldehyde and isobutyraldehyde at room temperature are only 1.4 and 0.8, respectively. These results are explained best by a reaction of low activation energy such as (18) which prevents a chain cycle and allows for the transfer of the formyl hydrogen to the propyl radical to form two stable products without the formation of hydrogen or formaldehyde.

$$C_3H_7 + HCO \longrightarrow C_3H_8 + CO \quad (18)$$

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Summary

The gas phase photolysis of butyraldehyde–iodine mixtures has been studied quantitatively using varied experimental conditions. The results indicate that radicals produced by photodecomposition of the butyraldehydes react rapidly with iodine. Quantum yield determinations and mass spectro-

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[13] Blacet, *J. Phys. Colloid Chem.*, **52**, 534 (1948).

[14] Norrish, *Trans. Faraday Soc.*, 21, (1939).

metric analyses of the products provide evidence concerning the nature of the primary processes. The results confirm the conclusions of Leighton, *et al.*,[1] and Blacet and Calvert[2] and provide new evidence for the occurrence of several modes of primary photodecomposition: (1) Primary processes producing formyl radicals and *n*-propyl radicals, from *n*-butyraldehyde, and isopropyl radicals, from isobutyraldehyde, are important at wave lengths of absorbed light from 2537 to 3130 Å. (2) Intramolecular primary processes producing carbon monoxide and propane are unimportant in the photolyses of both butyraldehydes at wave length 3130 Å. but increase in importance at the shorter wave lengths. (3) Intramolecular formation of ethylene and acetaldehyde is important in *n*-butyraldehyde photolysis at wave lengths from 2537 to 3130 Å. (4) A primary process in which methyl radicals are formed is of importance in isobutyraldehyde photolysis at wave length 2537 Å.

A correlation between total primary quantum yields of decomposition of the butyraldehydes, fluorescence data and character of the absorption spectra is indicated.

Los Angeles 24, California Received August 14, 1950

[Contribution from the Department of Chemistry, University of Colorado]

Mechanisms of Elimination Reactions. III. The Kinetics of the Alkaline Dehydrochlorination of the Benzene Hexachloride Isomers. II.[1,2,3]

By Stanley J. Cristol, Norman L. Hause and John S. Meek

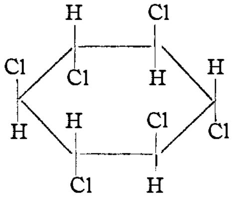
Previous work[1b,4–7] has indicated a stereochemical preference in the E2 (second-order) elimination[8] of the elements of hydrogen halides from alkyl halides, *trans* elements being removed more readily than corresponding *cis* elements. Several suggestions have been made as to the cause of this preference, one[7] involving *cis* repulsions and one[1b] being based on a one-stage mechanism for the *trans* process and a multiple-stage mechanism for the *cis* process.

As it seemed likely that information regarding the importance of these effects on elimination could be gained by a knowledge of the quantities of activation (energy and entropy), we have undertaken a study of alkaline dehydrohalogenation of a number of *cis* and *trans* systems at various temperatures, and this paper considers the first series of such compounds.

The compounds used were four of the five known isomers of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), hereinafter called BHC.

The structures of all of the known isomers have now apparently been established,[9] although dipole moment results are not at all clear.[14] The structures as given by Hassel and co-workers[10] are: alpha, $\frac{124}{356}$; beta, $\frac{135}{246}$; gamma, $\frac{1245}{36}$; delta, $\frac{1235}{46}$; and epsilon, $\frac{123}{456}$, where the numbers above the line indicate the positions of chlorine atoms which lie above a hypothetical planar cyclohexane ring and those below the line lie below the hypothetical planar cyclohexane ring.

For the purpose of this paper, we need be concerned only with the fact that β-BHC has the structure



where no members of a pair of hydrogen and chlorine atoms on adjacent carbon atoms are *trans* to each other, and that in each other isomer, at least one pair comprises *trans* hydrogen and chlorine atoms.

The reaction studied in the present work is the elimination of three moles of hydrogen chloride from each isomer according to equation (1).

$$C_6H_6Cl_6 + 3OH^- \longrightarrow C_6H_3Cl_3 + 3Cl^- + 3H_2O \quad (1)$$

van der Linden[15] has shown that the α-, β- and γ-isomers give slightly different ratios of 1,2,4-, 1,2,3- and 1,3,5-trichlorobenzenes, but that in each case the 1,2,4-isomer is predominant. The present work is restricted to a study of the kinetics of the reaction; except for the test that three moles of chloride ion were formed per mole of BHC, no investigation of the products was made.

Measurement of Reaction Rates and Calculation of Rate Constants.—The reactions were carried out in 76.1% (by wt.) ethanol using

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(1) Previous papers in series: (a) Cristol, This Journal, **67**, 1494 (1945); (b) Cristol, *ibid.*, **69**, 338 (1947).

(2) This work was supported by the Office of Naval Research.

(3) This work was reported in part before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1949.

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(5) Michael, *J. prakt. Chem.*, **52**, 289 (1895).

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(8) Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(9) The structure of the α-isomer has been established by electron diffraction work[10] and by resolution into an optically active form.[11] The structure of the β-isomer has been established by X-ray diffraction,[12] that of the γ-isomer by X-ray analysis[13] and by electron diffraction,[10] and those of the δ and ε isomers by electron diffraction.[10]

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(15) van der Linden, *Ber.*, **45**, 231 (1912).