[Contribution from the Chemistry Department, University of California, Los Angeles]

The Photolysis of the Aliphatic Aldehydes. XVI. Propionaldehyde and Propionaldehyde–Iodine Mixtures[1,2]

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A mechanism is presented for the vapor phase photolysis of propionaldehyde and propionaldehyde–iodine mixtures, which includes the following primary processes: (I), dissociation into ethyl and formyl radicals; (II), formation of ethane and carbon monoxide in an intramolecular process; (III), decomposition into ethylene and formaldehyde; and (IV), dissociation into methyl and CH_2CHO radicals. At 3130 Å. (I) is highly favored, but at 2654 Å. (I) and (II) are equally probable. Process (IV) is negligible at 3130 Å. but not at 2380 Å., whereas (III) is minor at all wave lengths. The gaseous products of unhibited photolyses, carbon monoxide, ethane, butane, methane, propane, ethylene and hydrogen, are explained on the basis of the four primary processes, and subsequent secondary reactions of the free radicals formed by those processes. Values of 13, and 8.1 kcal./mole, are found for the over-all activation energies of formyl radical decomposition and of carbon monoxide formation, respectively. Butane formation by ethyl radicals is about nine times as probable as the disproportionation reaction giving ethylene and ethane.

The vapor-phase photolysis of propionaldehyde has been the subject of several previous investigations,[3–7] however, some fundamental questions have continued to exist concerning the nature and extent of the primary and secondary processes. In the present work, the use of iodine vapor to trap free radicals, a technique employed successfully with other aldehydes,[8–11] led to the establishment of four primary modes of photodecomposition. A quantitative study of the reaction products from the non-inhibited processes has shown that propionaldehyde free radical reactions are similar to those postulated for other aldehydes.

Experimental

Photochemical Apparatus.—All photolyses were carried out by a procedure similar to that developed by Blacet and Heldman[9] and recently employed by Blacet and Calvert.[11,12] A direct current mercury arc operating at atmospheric pressure, and a crystal quartz monochromator provided selective radiation in the region 2380–3340 Å. The cylindrical quartz reaction cell was 20 cm. long, had an inside diameter of 30 mm., and a volume of about 140 cc. The cell was completely filled with a parallel light beam. The reaction system was composed of the cell, a glass circulating pump, and a trap, all of which were contained in an air-thermostated chamber which could be maintained at constant temperatures up to 180°. The reaction system was joined to a conventional gas train utilized to introduce the aldehyde at the start of photolysis and to remove the gaseous products at the end of the run. Quantitative measurements of radiant energy were made with a thermopile–galvanometer system calibrated against Bureau of Standards lamps. The thermopile was designed and constructed by Crane.[13]

Purification of Propionaldehyde.—Eastman Kodak Co. white label propionaldehyde was dried over anhydrous calcium sulfate and fractionated in an atmosphere of dry nitrogen. A trace of hydroquinone was added to the pot liquid prior to distillation in order to retard possible oxidation reactions. The middle fraction (48.5–48.7°) was retained and subjected to repeated vacuum distillations until a cut was obtained in which no solid polymer was observed when the sample was cooled to −80°. This fraction, stored over anhydrous calcium sulfate, served as the aldehyde supply.

Quantum Yield Determinations.—Quantum yields for photolyses at room temperature were determined by the method described previously.[13] Since it was impractical to heat the thermopile above 40°, in the runs at elevated temperatures the fraction of light absorbed by the propionaldehyde could not be determined directly. Therefore, in the manner of Blacet and Heldman,[9] curves were obtained at room temperature, giving the fraction of light absorbed *vs.* concentration and the assumption was made that the absorption coefficients were temperature independent in the range from 25 to 175°. In all quantum yield runs, not more than 1 or 2% of the aldehyde was decomposed.

No appreciable reaction was observed when dry propionaldehyde vapor was added slowly to iodine vapor and the mixture allowed to stand at 100° in the dark for nine hours in a clean dry reaction system. Considerable care had to be taken to ensure that the gases and reaction system were anhydrous, for traces of moisture caused the iodine to deposit in the reaction cell. The procedure for the photolysis of propionaldehyde–iodine mixtures was essentially the same as that described before.[11]

Product Analysis.—The non-condensable products were separated with the aid of a Toepler pump from the remaining products and the unreacted aldehyde condensed at −80°. The gaseous products were treated with a potassium hydroxide bead to polymerize traces of propionaldehyde, and then analyzed for carbon monoxide by micromethods using silver oxide as the absorbing agent. The residual gas was then analyzed with a modified Westinghouse Type LV Mass spectrometer.

The entire condensed phase from several uninhibited runs was introduced into the mass spectrometer and the mass spectrum observed from m./e. 180 to m./e. 59. The sample was then removed from the gas train of the spectrometer, treated with solid potassium hydroxide to remove the excess propionaldehyde, and the cracking pattern again determined. In two runs, in which liquid nitrogen was the refrigerant, the sample remaining after the potassium hydroxide polymerization treatment was exposed to cold concentrated sulfuric acid to remove oxygenated compounds. A spectrum having mass peaks of considerable intensity remained and it was conclusively proved to be due to normal butane.

The condensable fractions from the aldehyde–iodine runs were dissolved in several ml. of carbon tetrachloride and the solution equilibrated with mercury. The volatile materials were then distilled from the mercury–mercuric iodide residue and equilibrated with 0.001 *N* aqueous potassium hydroxide. Analysis of the organic phase for iodide by a modified Vieböck procedure provided an estimate of the total alkyl iodide yield, and the iodide titer of the aqueous solution was taken to represent the hydrogen iodide that had condensed in the cell trap. As an additional check on the distribution of hydrogen iodide, the interior of the reaction system was washed with dilute base and analyzed for total

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(1) Presented at the San Francisco Meeting of the American Chemical Society, April, 1949.

(2) Taken from the doctoral dissertation of J. N. Pitts, Jr., University of California, Los Angeles, 1949.

(3) P. A. Leighton and F. E. Blacet, This Journal, **54**, 3165 (1932).

(4) J. A. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A159**, 32 (1937).

(5) L. May, H. A. Taylor and M. Burton, This Journal, **63**, 249 (1941).

(6) W. M. Garrison and M. Burton, *J. Chem. Phys.*, **10**, 730 (1942).

(7) W. J. Blaedel and F. E. Blacet, This Journal, **67**, 1283 (1945).

(8) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

(9) F. E. Blacet and J. D. Heldman, This Journal, **64**, 889 (1942).

(10) F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

(11) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 667 (1951).

(12) F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 661 (1951).

(13) R. A. Crane and F. E. Blacet, *Rev. Sci. Instruments*, **21**, 259 (1950).

iodide ion. Practically all of the water-soluble iodide was found on the walls of the reaction system. The deposit probably was a non-volatile addition compound of hydrogen iodide and propionaldehyde.[11]

Experimental Results

I. The Non-inhibited Photolysis of Propionaldehyde. The Non-condensable Products.—The major products of the photolysis of propionaldehyde in its first electronic absorption band are carbon monoxide and ethane. In addition, *n*-butane, ethylene, methane, hydrogen and propane are produced in small but significant amounts. The quantum yields of the latter three compounds increase materially on going to the shorter wave lengths.

(a) Composition *vs.* **Wave Length.**—The original work of Leighton and Blacet[3] on the photolysis of propionaldehyde furnished values for the quantum yield of carbon monoxide production over the region from 3130 to 2537 Å. In the present study the wave length range was extended to include 3340 and 2380 Å., and values for the quantum yields of carbon monoxide at these wave lengths, as well as some check values run at 3130 and 2537 Å., are presented in Table I. In addition to determining the quantum yields of carbon monoxide, the quantum yields of hydrocarbons and hydrogen were determined over the entire wave length range from 3340 to 2380 Å. These results are given in Table II. The quantum yields were obtained by multiplying the mole per cent. of each constituent as determined with the mass spectrometer, by the ratio (average quantum yield of CO)/(mole per cent. CO).

TABLE I

QUANTUM YIELDS OF CARBON MONOXIDE PRODUCTION AS A FUNCTION OF WAVE LENGTH AT 30° AND 200 MM. PRESSURE

Wave length, Å.	3340	3130	3130	3130	2537	2380	2380
Experiment	30	10	12	21	32	29	31
I_a (quanta/sec.-ccm.) $\times 10^{-12}$	2.07	11.2	7.23	8.85	6.24	1.45	1.15
Quantum yield of CO, Φ	0.43	0.53	0.49	0.51	0.78	1.00	0.94

TABLE II

QUANTUM YIELDS OF NON-CONDENSABLE PRODUCTS AS A FUNCTION OF WAVE LENGTH AT 200 MM. PRESSURE

Wave length, Å.	3340	3340	3130	3130	3130	2804	2804	2654	2537	2537	2380	2380	2380
Experiment	9	30	6	21	22	5	46	8	5	32	7	29	31
Temp., °C.	21	23	21	30	30	23	24	22	22	30	21	24	30
Time, sec. $\times 10^{-4}$	19.3	3.04	11.3	0.852	3.19	15.7	15.4	19.0	8.28	1.96	23.0	3.27	2.74
Volume gases, ml., p = 1 atm., T = 25°	1.9	0.26	2.1	0.38	1.6	4.0	5.1	0.67	1.1	1.1	1.1	0.52	0.32
Quantum yields, Φ													
CO	0.43	0.43	0.51	0.51	0.51	0.70[a]	0.70[a]	0.76[a]	0.88[b]	0.88[b]	0.97	0.97	0.97
C_4H_{10}	.053	.013	.098	.033	.061	[c]	.063	.019	.003	.014	.004	.011	.004
C_3H_8	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	[c]	.012	.015
C_2H_6	.28	.26	.29	.29	.27	.49	.50	.62	.67	.71	.77	.71	.65
C_2H_4	.011	.008	.018	.011	.009	.020	.013	.006	.023	.000	.020	.000	.010
CH_4	.000	.000	.000	.000	.000	.003	.011	.012	.040	.038	.084	.080	.0075
H_2	.009	.015	[c]	.012	.012	.017	[c]	.027	.043	.053	.072	.073	.071

[a] Data of Leighton and Blacet. [b] Average of results of Leighton and Blacet and the authors. [c] Not determined.

TABLE III

THE EFFECT OF TEMPERATURE ON THE QUANTUM YIELDS OF THE GASEOUS PRODUCTS OF THE UNINHIBITED PHOTOLYSIS AT 3130 AND 2537 Å.

Wave length, Å.	3130	3130	3130	3130	3130	2537	2537
Temp., °C.	30	60	100	140	175	30	100
Average quantum yields, Φ							
CO	0.51	0.65	0.96	1.57	3.04	0.88	1.70
C_2H_6	.28	.41	.77	1.20	2.62	.69	1.24
C_4H_{10}	.098	.045	.047	.016	.026	.014	0.006
C_2H_4	.013	.011	.012	.010	.020	.012	.005
CH_4	.000	.001	.001	.005	.022	.039	.052
H_2	.012	.016	.030	.072	.184	.048	.085

The reported quantum yields of butane represent *minimum values* which may be considerably low in these photolyses carried out for a very short time, for butane is somewhat soluble in propionaldehyde at −80° and it is difficult to make a quantitative separation from the condensable fraction. This difficulty was minimized by carrying out at least one long run at each of the wave lengths 3340, 3130 and 2804 Å. (runs 9, 6, 46). Larger amounts of butane were formed in these longer runs and in each case the amount of butane retained with the condensable fraction was small compared with that collected in the non-condensable portion.

(b) Composition of Gaseous Products *vs.* **Temperature.**—In Table III are presented the average values obtained for the quantum yields of the gaseous products as a function of temperature at 3130 and 2537 Å.

(c) Composition of Gaseous Products *vs.* **Intensity.**—In one series of room temperature runs at 3130 Å. the intensity was varied while the other variables were held constant. The fact that intensity plays an important role in determining the nature of the gaseous products is illustrated by the results of these runs presented in Table IV. In each run the photochemical reaction was allowed to proceed until at least 2 ml. of gaseous product was obtained, thus giving better accuracy in the determination of butane. The intensity was varied by placing different thicknesses of Pyrex glass in front of the collimating slit.

The Condensable Products.—The results of a series of chemical and mass spectrometric tests upon the condensable fractions from photolyses of propionaldehyde at several wave lengths and 25° show that a compound with an apparent molecular weight of 86 ± 1 is formed in photolyses at 3130 and 2804 Å. The behavior of this compound toward potassium hydroxide and sulfuric acid indicates that it may be diethyl ketone, although further experiments are necessary to establish its identity unequivocally. No parent peak corresponding to dipropionyl was observed at any wave length. Blaedel and Blacet[8] had identified formaldehyde and glyoxal as products of the photolysis of propionaldehyde and no further attempt was made to identify these compounds in this research.

TABLE IV

COMPOSITION OF THE GASEOUS PRODUCTS AS A FUNCTION OF INTENSITY AT 3130 Å. AND 25°

I_a (quanta/sec. ccm.) $\times 10^{-12}$	6.5	3.1	0.86
Experiment	6	34	28
% ethane	31.3	33.5	38.4
n-Butane	10.6	6.7	2.7
Ethylene	1.9	1.2	1.2
Hydrogen	1.3	0.5	1.6
Carbon monoxide	55.4	58.1	56.1
%ethane/%CO	0.56	0.58	0.68
%ethane/%butane	2.95	5.00	14.2

II. Propionaldehyde-Iodine Photolysis.—The photolysis of propionaldehyde–iodine mixtures was studied over a range of temperatures, wave lengths and pressures of iodine. The products are carbon monoxide, ethane, ethylene and a trace of hydrogen in the gaseous fraction, and ethyl iodide and hydrogen iodide in the condensed phase. Carbon monoxide was the only major noncondensable product at 3130 Å., but at higher quantum energies, the yield of ethane also became important. The yields of ethylene and hydrogen were very small under all experimental conditions investigated.

(a) **Quantum Yields** *vs.* **Temperature.**—Quantum yields of the products of propionaldehyde–iodine photolyses at 3130 Å. and several temperatures ranging from 73 to 175° are given in Table V. Most of the photolyses were carried out before a suitable method of analysis for hydrogen iodide was available and data for that compound were obtained for runs 47 and 48 only.

Table V

Quantum Yields of Products from the Photolysis of Propionaldehyde–Iodine Mixtures at 3130Å. and Several Temperatures

Temperature, °C.	73	100	100	140	175
Experiment	48	47	35	36	45
C_3H_6O pressure, mm.	110	201	211	224	237
I_2 pressure, mm.	1.7	2.2	4.0	4.2	4.9
I_a, (quanta abs./ sec. ccm.) $\times 10^{-12}$	13.0	12.9	15.3	13.2	14.0
Quantum yields, Φ					
CO	0.56	0.45	0.50	0.56	0.68
C_2H_5I	.45	.44	.41	.46	.65
HI	.43	.49	...	...	...
C_2H_6	.014	.009	.026	.029	.026
H_2	...	.004	...	.006	.011
C_2H_4	...	.004	...	.002	.004

(b) **Quantum Yields** *vs.* **Wave Length.**—In Table VI are the results of a series of photolyses carried out at 100°, about 4 mm. iodine pressure, and wave lengths 3130, 2804, 2654 and 2537 Å. No analyses for HI were made in these runs.

Table VI

Quantum Yields of the Products of Propionaldehyde–Iodine Photolyses at 100° and Several Wave Lengths

Wave length, Å.	3130	2804	2804	2654	2537
Experiment	[a]	42	49	43	40
C_3H_6O pressure, mm.	...	210	138	218	207
I_2 pressure, mm.	...	4.2	3.2	3.5	4.0
I_a (quanta abs./ sec. ccm.) $\times 10^{-12}$	...	5.53	3.79	6.38	3.24
Quantum yields of					
CO	0.48	0.59	0.69	0.66	0.66
C_2H_5I	.43	.57	.51	.25	.26
C_2H_6	.018	.098	.15	.34	.37
H_2	.004	...	...	.021	.075
C_2H_4	.004	...	.011	.013	.014

[a] Average of runs 47 and 35.

Discussion of Results

The experimental results obtained for the photolysis of propionaldehyde and propionaldehyde–iodine mixtures can be explained logically by assuming the existence of four primary decomposition processes, analogous to those found for the butyraldehydes[11,12]

$$\mathrm{C_2H_5CHO} + h\nu \longrightarrow \left\{\begin{array}{ll} \mathrm{C_2H_5 + CHO} & \mathrm{(I)} \\ \mathrm{C_2H_6 + CO} & \mathrm{(II)} \\ \mathrm{C_2H_4 + H_2CO} & \mathrm{(III)} \\ \mathrm{CH_3 + CH_2CHO} & \mathrm{(IV)} \end{array}\right.$$

The following secondary reactions are postulated to occur in the presence of iodine

$$\mathrm{C_2H_5 + I_2 \longrightarrow C_2H_5I + I} \qquad (1)$$

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

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

$$\mathrm{CH_2CHO + I_2 \longrightarrow ICH_2CHO + I} \qquad (4)$$

$$\mathrm{I + I + M \longrightarrow I_2 + M} \qquad (5)$$

In the absence of iodine vapor the free radicals produced in the several primary processes are believed to react by way of the secondary processes

$$\mathrm{C_2H_5 + C_2H_5CHO \longrightarrow C_2H_6 + C_2H_5CO} \qquad (6)$$

$$\mathrm{CHO \longrightarrow H + CO} \qquad (7)$$

$$\mathrm{H + C_2H_5CHO \longrightarrow H_2 + C_2H_5CO} \qquad (8)$$

$$\mathrm{C_2H_5CO \longrightarrow C_2H_5 + CO} \qquad (9)$$

$$\mathrm{2C_2H_5} \longrightarrow \left\{\begin{array}{ll} \mathrm{C_4H_{10}} & (10) \\ \mathrm{C_2H_6 + C_2H_4} & (11) \end{array}\right.$$

$$\mathrm{C_2H_5 + CHO \longrightarrow C_2H_6 + CO} \qquad (12)$$

$$\mathrm{2CHO} \longrightarrow \left\{\begin{array}{ll} \mathrm{H_2CO + CO} & (13) \\ \mathrm{(CHO)_2} & (14) \end{array}\right.$$

$$\mathrm{CH_3 + C_2H_5CHO \longrightarrow CH_4 + C_2H_5CO} \qquad (15)$$

$$\mathrm{C_2H_5CHO^* + M \longrightarrow C_2H_5CHO + M} \qquad (16)$$

$$\mathrm{C_2H_5CHO^* \longrightarrow C_2H_5CHO} + h\nu' \qquad (17)$$

Primary Processes (a) Primary Process (I).—The following facts substantiate this reaction: 1. The non-inhibited photodecomposition contains the elements of a chain as evidenced by the rise in Φ_{CO} at 3130 Å., from 0.51 at 30° to 3.04 at 175°, while $\Phi_{C_2H_6}$ increased from 0.28 to 2.62 over the same temperature range.

2. The presence of small amounts of iodine vapor suppresses almost completely the secondary reactions which normally produce carbon monoxide, ethane and hydrogen. Within experimental error the quantum yields of carbon monoxide, ethyl iodide and ethane at 3130 Å. were virtually constant at 0.53, 0.45 and 0.02, respectively, over the range from 73 to 140°. This relatively large yield of ethyl iodide in a process independent of temperature, is confirmatory evidence for ethyl radical formation by primary process (I). The presence of butane and to a lesser extent ethylene among the non-condensable products of the uninhibited photolysis is additional evidence for ethyl radical formation by (I).

3. Hydrogen iodide was formed in amounts equivalent to the ethyl iodide in the two experiments in which it was determined. At 3130 Å. the average Φ_{HI} was 0.46 compared to 0.45 for $\Phi_{C_2H_5I}$. Since the yield of hydrogen iodide was equivalent to ethyl iodide, one can conclude that formyl radicals also must be produced in process (I) and that these radicals subsequently react rapidly with iodine by reaction (2). Additional confirmation for (2) is seen in the facts that $\Phi_{CO} = \Phi_{C_2H_5I} + \Phi_{C_2H_6}$ under all experimental conditions employed, and that the hydrogen yields were negligible in iodine runs. Further evidence pointing to the formation of formyl radicals in a primary process is the presence of hydrogen, formaldehyde, and glyoxal among the reaction products[3] from the non-inhibited photolysis.

It should be noted that the quantum yields of carbon monoxide, ethane and ethyl iodide were unchanged when the iodine pressure was increased. This fact is evidence that the reaction responsible for the formation of ethyl iodide is not between molecular iodine and photochemically activated propionaldehyde molecules, but instead the alkyl iodide must be formed by a rapid reaction of low activation energy between ethyl radicals and iodine.

(b) **Primary Process (II).**—In the aldehyde–iodine photolyses the temperature independence of ethane formation at 3130 Å. (*cf.* Table V) and the approximate material balances obtained for carbon monoxide, ethane and ethyl iodide at all wave lengths are evidence for the formation of ethane by (II).

It is evident from the quantum yields of ethyl iodide and ethane, 0.45 and 0.02, respectively, that at 3130 Å. the free radical reaction (I) is far more probable than the intramolecular process (II). However, the absorption of the more energetic quanta at shorter wave lengths favors process (II), and in the vicinity of 2700 Å. the two processes are about equally probable and have quantum efficiencies of about 0.3 (*cf.* Table VI).

(c) **Primary Process (III).**—This equation fits a general type first suggested by Norrish and Appleyard[14] and later found by others to apply to a number of ketones and aldehydes.[12,15] It is suggested for propionaldehyde to explain the presence of small quantities of ethylene formed in the propionaldehyde–iodine photolyses (*cf.* Tables V and VI). In those runs ethyl radicals that might otherwise disproportionate to form ethylene are trapped by the iodine. Therefore, the quantum yields of ethylene in Tables V and VI can be taken to represent the magnitude of (III).

(d) **Primary Process (IV).**—Earlier workers on the photolysis of propionaldehyde[3–7] considered the possibility of methyl radicals being formed by (IV), but both Burton and co-workers[5,6] and Blaedel and Blacet[7] presented analytical evidence that ethyl radicals were the only aliphatic radicals formed in the photolysis. However, the use of the mass spectrometer provided a more sensitive analytical method than the chemical tests available to the earlier investigators, and it was found that methane is formed in uninhibited photolyses from 2804 to 2380 Å. The quantum yield at 25° rises from 0.007 at 2804 Å. to 0.080 at 2380 Å.

The evidence is substantial that methane must be formed from methyl radicals produced by primary process (IV). First, the quantum yield of methane is almost temperature independent at 2537 Å. over the range from 30 to 100°; and second, no significant amounts of methane were formed in the iodine inhibited photolyses. The latter evidence rules out the possibility of methane arising from a concerted process giving methane and ketene in one step. If (IV) is the source of methyl radicals, one might expect methyl iodide to be formed in the aldehyde–iodine runs and, indeed, Blacet and Calvert[11] have identified that compound among the photolysis products of *n*-butyraldehyde–iodine photolyses. Further evidence that methyl radicals are formed is the fact that small amounts of propane are formed at 2380 Å. in non-inhibited photolyses. The most logical explanation for its presence has been suggested by Crane; namely, a reaction between methyl and ethyl radicals.

(e) **Other Primary Processes.**—Since the sum of the yields of processes (I) through (IV) is only 0.50 at 3130 Å. and 0.70 at 2537 Å. it is evident that a significant portion of the photoactivated propionaldehyde molecules must fluoresce or be deactivated by collisional processes, thus requiring that reactions (V), (16) and (17) be included in the mechanism.[11]

$$\mathrm{C_2H_5CHO} + h\nu \longrightarrow \mathrm{C_2H_5CHO^*} \quad \text{(V)}$$

Secondary Reactions in the Non-inhibited Photolysis (a) Carbon Monoxide Formation.—The quantum yield of carbon monoxide production shows a pronounced temperature dependence in the region from 30 to 175° (*cf.* Table III), and it is evident that the decomposition contains the elements of a chain process. Reactions (6) and (9) were postulated to account for at least part of the chain character. In the case of acetaldehyde[16,17] and the butyraldehydes[11,12,15c] the analogous reactions seem well established.

An over-all activation energy for the production of carbon monoxide can be obtained by using a rate expression of the type Leermakers[18] and Leighton and co-workers[15c] derived for acetaldehyde and the butyraldehydes, respectively. This equation has the form

$$\mathrm{d(CO)}/\mathrm{d}t = k'I_{\mathrm{abs}} + kI_{\mathrm{abs}}^{1/2}(\mathrm{C_2H_5CHO}) \qquad (18)$$

If I_{abs} is in einsteins absorbed × sec.$^{-1}$ × ccm.$^{-1}$ and k' is taken as 0.51 (the yield of carbon monoxide *not* produced by the chain) the over-all activation energy is 8.1 kcal. in the region from 100 to 175°. This value can be compared with "about 6.5 kcal." reported by Mitchell and Hinshelwood for the region from 300 to 450°.[5] It is difficult to ascribe this activation energy of 8.1 kcal. to any one particular reaction, however, it is interesting to note that in the series of straight-chain aldehydes the over-all activation energies for carbon monoxide production decreased in a regular fashion, 9.8, 8.1 and 5.6 kcal./mole for acetaldehyde,[9] propionaldehyde and *n*-butyraldehyde,[15c] respectively.

It is to be noted that whereas biacetyl is a product of the photolysis of acetone[19] and of acetaldehyde,[17] the analogous compound, bipropionyl, was absent in propionaldehyde photolyses. This fact suggests a greater stability of the acetyl radicals compared to propionyl radicals and may be related to the observed higher activation energy for the formation of carbon monoxide from acetaldehyde compared to propionaldehyde.

(b) **Hydrogen Formation.**—It is evident from Table III that the formation of hydrogen in the non-inhibited photolysis shows a marked tempera-

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[14] R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934).

[15] (a) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1531 (1938); (b) C. H. Bamford and R. G. W. Norrish, *ibid.*, 1544 (1938); (c) P. A. Leighton, L. D. Levanas, F. E. Blacet and R. D. Rowe, THIS JOURNAL, **59**, 1843 (1937); (d) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

[16] F. E. Blacet and D. Volman, THIS JOURNAL, **60**, 1243 (1938).

[17] F. E. Blacet and W. J. Blaedel, *ibid.*, **62**, 3374 (1940).

[18] J. A. Leermakers, *ibid.*, **56**, 1537 (1934).

[19] M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935).

ture dependence in the range from 30 to 175°. In this region Blacet and Calvert[12] found similar results for hydrogen production from the butyraldehydes. However, they extended the range of their studies to include higher temperatures, and found that the hydrogen quantum yields approached limiting values at about 250° which were in excellent agreement with the average primary quantum efficiencies of formyl radical production for each of the butyraldehydes. It seems reasonable that hydrogen production from propionaldehyde would be similar at high temperatures. Therefore reactions (7) and (8) are considered to be the sole source of hydrogen at elevated temperatures. In fact, the evidence assembled to date indicates that this pair of reactions is responsible for hydrogen production in the entire temperature range studied.

At room temperature, hydrogen production increases rapidly with decreasing wave lengths. This suggests that a certain fraction, a, of the formyl radicals formed in (I) simultaneously decompose in the so-called "hot atom" reaction (7′).

$$a\mathrm{CHO}^* \longrightarrow a\mathrm{H} + a\mathrm{CO} \qquad (7')$$

The symbol * represents the energy supplied by the quantum, in excess of that required to break the C–C bond. If the C–C bond strength of the bond broken in reaction (I) is *assumed* to be about 83 kcal.,[20] then the maximum excess energy that could be supplied to the fragments at 3340 Å. would be approximately 3 kcal.; a would be expected to be negligible, and hydrogen production small at room temperature. However, at 2380 A. the ethyl and formyl radicals could share a maximum of approximately 37 kcal. In this case an appreciable fraction of the formyl radicals might be expected to decompose spontaneously and thus produce a relatively larger quantum yield for hydrogen at the short wave length.

Since hydrogen production is a relatively inefficient process at moderate temperatures, it is evident that the formyl radicals must react in some fashion without producing hydrogen as one of the products. Reactions (12), (13) and (14) seem to offer a reasonable explanation of the fate of these radicals for the following reasons: 1. Blaedel and Blacet[7] have identified formaldehyde and glyoxal among the condensable products formed when gaseous propionaldehyde was irradiated at room temperature by the full mercury arc. In similar experiments with acetaldehyde[18] they found that these compounds were also produced in significant amounts at room temperature, but they were absent at 100°.

2. The small values for the quantum yields of hydrogen at 100° and 3130 A. indicates that the formyl radicals are quite stable at that temperature, yet the work of Blaedel and Blacet[17] indicates that formaldehyde and glyoxal are not produced in appreciable amounts at this elevated temperature. Therefore, another reaction must occur in which formyl radicals are destroyed, and reaction (12), originally postulated by Leighton and Blacet,[3] appears to fit the requirements. Further evidence for (12) is the fact that the chain length for carbon monoxide production from uninhibited photolyses is about unity at 25°, hence a chain-terminating reaction involving formyl radicals without the production of hydrogen, formaldehyde or glyoxal must be significant at room temperature.

If one follows the arguments of Blacet and Calvert[12] and assumes that reactions (6)–(12) are the only important reactions involving ethyl and formyl radicals at temperatures above 100°, by the usual steady state methods one can obtain equation (19).

$$\Phi_{\mathrm{H}_2}^{3/2}/(\phi_{\mathrm{I}} - \Phi_{\mathrm{H}_2}) = \frac{K_7}{K_{12}}\left(\frac{K_{10} + K_{11}}{2I_{\mathrm{a}}}\right)^{1/2} \qquad (19)$$

In equation (19), ϕ_{I} revers to the primary quantum efficiency of process (I) and the K's to the rate constants of the reactions indicated. Taking a value of 0.48 for ϕ_{I}, and the results for Φ_{H_2} in Table III, one can evaluate the function $\Phi_{\mathrm{H}_2}^{3/2}/(\varphi_{\mathrm{I}} - \Phi_{\mathrm{H}_2})$ at 100, 140, and 175°. A plot of the log of this function *vs.* $1/T$ gave points which fell along a reasonably straight line. The slope of this line was determined by the method of least squares and it corresponded to an apparent activation energy of 13 kcal./mole. This value is in good agreement with that of 14 kcal./mole obtained by Blacet and Calvert[12] for both of the butyraldehydes, and the value of 13.5 kcal./mole obtained by Calvert and Steacie[21] for the production of hydrogen in the photolysis of formaldehyde. As pointed out by Blacet and Calvert, the apparent activation energy is equal to $E_7 - E_{12} + (k_{10}E_{10} + k_{11}E_{11})/2(k_{10} + k_{11})$. Since doubtless E_{12}, E_{10} and E_{11} are small, 13 kcal./mole may be taken to represent the actual activation energy for the decomposition of formyl radicals. The fact that all four of these aldehydes give within experimental error the same value for E_7 indicates that once the formyl radicals are formed at elevated temperatures, their decomposition and the subsequent formation of molecular hydrogen, presumably by reaction (8), are essentially independent of the nature of the aldehyde present in the system.

(c) Reactions between Ethyl Radicals.—Several investigators[3,6] have included reaction (10) in mechanisms postulated for the photochemical decomposition of propionaldehyde but previous to now there appears to have been no direct experimental proof for the formation of butane. In this research mass spectrometric analyses confirmed the existence of butane as a photolysis product at all temperatures and wave lengths studied.

It is evident from the data in Table II that the yield of butane decreases markedly at the short wave lengths. This is reasonable since the trend in butane production with wave length should closely follow the relative concentrations of ethyl radicals present at the given wave lengths. At least two factors operated to reduce the concentration of ethyl radicals at that region. First, the intensity of the irradiating light at the shorter wave lengths, was less than it was at 3130 Å. and, second, the photolysis of propionaldehyde–iodine mixtures has shown that the primary quantum effi-

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(20) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 73–80.

(21) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

ciency of reaction (I) producing the ethyl radicals is less at the short wave lengths than it is at 3130 Å.

Two reactions, (III) and (11), have been introduced to explain the presence of small significant amounts of ethylene at all wave lengths and temperatures studied. There is no convenient way to determine the relative efficiencies of these two processes solely on the basis of results from the photolysis of pure propionaldehyde. However, the work on the propionaldehyde–iodine mixtures enables one to estimate the quantum efficiency of ethylene production by process (III) and these values can be subtracted from the total ethylene yield in the uninhibited photolysis to give rough values for the yields of ethylene from the disproportionation reaction (11). These approximations are presented in Table VII.

TABLE VII

QUANTUM YIELDS OF ETHYLENE FORMED BY THE DISPROPORTIONATION REACTION

Wave length, Å.	3130	2804
Average over-all quantum yield of C_2H_4	0.013	0.017
Quantum yield of C_2H_4 by primary process (III)	.008	.011
Net quantum yield of C_2H_4 by disproportionation	.010	.006
Average quantum yield of C_4H_{10}	.098	.063
$\Phi_{\text{disproportionation}}/\Phi_{\text{association}}$	.10	.09

Since the butane from reaction (10) and the ethylene from reaction (11) are both formed by reactions between two ethyl radicals, one might expect to find the relative amounts of these compounds to be independent of the wave length studied, at a given temperature. It is seen from Table VII that at 3130 and 2804 Å. the ratios $\Phi_{\text{disproportionation}}/\Phi_{\text{association}}$ are 0.10 and 0.09, respectively. Unfortunately, as pointed out in the experimental section, in most runs there was a considerable uncertainty in the butane analyses because of the solubility of this compound in propionaldehyde. Thus only these two values for butane are sufficiently accurate to warrant their use in the calculation of ratios. Even in these runs, the good agreement between the ratios is fortuitous because of the small magnitude of the quantities that were measured experimentally. It is interesting to note, however, that Blacet and Calvert[12] found for *n*-propyl radicals a like value of 0.10 for the ratio of $\Phi_{C_3H_6}/\Phi_{C_6H_{14}}$.

(d) **Other Reactions.**—Mass spectrometric studies on the condensable fractions disclosed a compound that apparently had a molecular weight of about 86 and was somewhat reactive toward solid potassium hydroxide but completely removed by concentrated sulfuric acid. The compound had a large m./e. 57 peak. The yield of this compound at room temperature varied with the wave length of the irradiating light in a manner similar to butane, suggesting that intensity factors might be important in its production. Diethyl ketone fits the requirements with regard to molecular weight and mass spectrometric and chemical behavior so reaction (20) is tentatively postulated to account for its formation.

$$C_2H_5CO + C_2H_5 \longrightarrow C_2H_5COC_2H_5 \qquad (20)$$

However, the evidence that the compound is diethyl ketone is not conclusive, and further work is necessary to characterize it unequivocally.

A Comparison of the Photochemical Behavior of the Simple Aliphatic Aldehydes in the First Electronic Region of Absorption.—It seems worthwhile at this time to summarize the significant information, dealing with the photochemistry of acetaldehyde,[9,10,16,17] propionaldehyde,[3,7] and the butyraldehydes[11,12,15c] in the region 3130–2380 Å.

(a) **Primary Processes.**—In Table VIII are summarized the primary quantum yields for the four general processes found to occur in the first electronic absorption band, while Table IX presents a comparison of the ratios of primary processes (II) to (I) for the same region.

The similarity between the values for the ratios of the two major processes of the four aldehydes is obvious. In all cases at 3130 Å. about 95% of the molecules that decompose, dissociate into alkyl and formyl radicals by (I). At 2537 Å., however, the concerted intramolecular process (II) giving "complete molecules" amounts for more than fifty per cent. of the total molecules dissociating by processes (I) and (II).

There appears to be a definite correlation between

TABLE VIII

COMPARISON OF THE PRIMARY PROCESS QUANTUM YIELDS OF SEVERAL ALIPHATIC ALDEHYDES IN THE FIRST ELECTRONIC ABSORPTION REGION

Wave length, Å.	3130	2804	2654	2537	2380
Energy, kcal./mole	91	102	108	113	120
Acetaldehyde[9,10]					
I	0.20	0.39	0.36	...	0.31
II	.013	.15	.28	...	.37
Total	.21	.54	.64	...	.68
Propionaldehyde					
I	0.48	0.53	0.28	0.28	...
II	.022	.125	.34	.37	...
III	.003	.011	.013	.013	...
IV	.000	.007	.012	.039	.080
Total	.51	.67	.64	.70	...
n-Butyraldehyde[12]					
I	0.35	0.28	0.28	0.31	...
II	.017	.11	.25	.33	...
III	.164	.27	.38	.30	...
IV	.005	.006	.010	.015	...
Total	.54	.67	.92	.96	...
Isobutyraldehyde[12]					
I	0.72	...	0.43	...	...
II	.03	...	.40	...	...
IV	.006	0.012	.036	0.072	...
Total	.76	...	.87	...	...

TABLE IX

COMPARISONS OF RATIOS OF PRIMARY PROCESS II TO PRIMARY PROCESS I, FOR SEVERAL ALIPHATIC ALDEHYDES

Wave length, Å.	3130	2804	2654	2537	2380
Energy, kcal./mole	91	102	108	113	120
Acetaldehyde[9,10]	0.065	0.39	0.78	..	1.19
Propionaldehyde	.046	.24	1.19	1.32	...
n-Butyraldehyde[11]	.049	.39	0.89	1.06	...
Isobutyraldehyde[11]	.042	..	0.93	1.35	..

the character of the absorption spectra of the aldehydes[22] and the total primary process quantum yields of decomposition.

At 3130 Å. the total primary process quantum yields increase in the order of decreasing fine structure and fluorescence of the compounds. The change in the absorption spectrum of each of these aldehydes, from a banded region at 3130 Å., through a region of diffuse bands around 2804 Å. and into an apparent continuum around 2654 Å., is accompanied in each case by an increase in the sum of the primary yields of decomposition.

(b) **Secondary Reactions.**—The uninhibited photolysis of each of these aldehydes has been shown to involve chain processes accompanied by a number of free radical reactions. Of particular interest are the association and disproportionation reactions of alkyl and formyl radicals, and the dissociation of the acyl and formyl radicals in thermal and "hot-atom" processes.

The necessity of including an association reaction between alkyl radicals in the mechanisms for aldehyde photolyses is evident, since the formation of ethane in the photolysis of acetaldehyde was shown by Blacet and Brinton,[23] while butane, hexane, and diisopropyl were identified as products of the photodecomposition of propionaldehyde and the butyraldehydes,[11,12] respectively. Evidence also has been accumulated for disproportionation reactions between the ethyl and propyl radicals.[12] Disproportionation is considerably less probable than the association reaction with the ratio $\Phi_{\text{disproportionation}}/\Phi_{\text{association}}$ being 0.10 for both ethyl and *n*-propyl radicals, and 0.33 for isopropyl radicals.

Studies of the yields of hydrogen *vs.* temperature led to the calculation of activation energies for the decomposition of formyl radicals from the several aldehydes. The value of E was found to be 13 kcal. for propionaldehyde, 14 kcal. for the butyraldehydes,[12] and 13.5 kcal. for formaldehyde.[21] In addition to the dissociation reaction of formyl radicals there is good analytical evidence that these radicals can disproportionate to form formaldehyde and carbon monoxide[7,12,17] or associate to give glyoxal.[7,17]

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[22] F. E. Blacet, *J. Phys. Chem.*, **52**, 534 (1948).

[23] F. E. Blacet and R. K. Brinton, THIS JOURNAL, **72**, 4715 (1950).

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. VII. Complexes Formed between Silver(I) Ions and Triethylenetetramine

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When aqueous or alcoholic solutions of silver(I) nitrate are allowed to react with triethylenetetramine (abbrev. trien) several complexes are formed. Spectrophotometric and conductometric studies of their aqueous and alcoholic solutions indicate that complex ions with the composition [Ag trien]$^+$ and [Ag$_2$ trien]$^{+2}$ are present in both media. Although the complex compound [Ag trien]NO$_3$ has been isolated from alcoholic solutions, it has been impossible to isolate salts of the [Ag trien]$^+$ complex ion present in aqueous solution. Hydrolysis–e.m.f. studies show that the 1:1 complex isolated from alcohol slowly hydrolyzes to that present in water. The observation can be best explained by assuming a coördination number of four for silver(I) complexes.

Introduction

Although many silver(I) complexes containing two, three or four coördinating groups have been reported, investigations have usually been confined to the collection of analytical data. Thus, even when four coördinating groups are present in a complex, it is often impossible to state that they are all coördinated to the silver(I) ion.

The silver(I) complexes containing the polydentate dipyridyl, tripyridyl and tetrapyridyl groups[2–4] have more than two groups available for coördination. In the latter two compounds, however, excessive strain in the coördinating groups would result from the adoption of the tetrahedral structure normally exhibited in four coördinated silver(I) complexes. For this reason Morgan and Burstall[4] believe that these compounds are polynuclear with the coördinating agents acting as bridging units between several metal ions. Only the bis-dipyridyl complex is postulated as a mononuclear four coördinated complex.

It has been claimed in some instances[5] that polydentate groups do not utilize all available coördination positions in complexes with silver(I) even when no steric factors intervene. Job investigated the complexes formed between silver(I) ions and ethylenediamine. Although a stable complex is formed between two molecules of the diamine and one silver(I) ion, the magnitude of the instability constant indicates that the coördination number of silver in the bis-ethylenediamine complex is two rather than four. The fact that one molecule of the amine

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[2] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2594 (1930).

[3] G. T. Morgan and F. H. Burstall, *ibid.*, 1649 (1937).

[4] G. T. Morgan and F. H. Burstall, *ibid.*, 1672 (1938).

[5] P. Job, *Ann. chim.* [10], **9**, 166 (1928).