culated from equations 14 and 15 and indicate that at 2654 Å., and probably at 3130 Å., the primary quantum yield is independent of temperature. It should be noted that it is necessary to specify the approximate biacetyl concentrations, for it appears that increasing the concentration decreases the ethane quantum yield (see 3130 Å., Table II).

In Table V, primary quantum yields, calculated from equations 14 and 20 at various wave lengths, are compared. All the values are less than unity. This indicates that part of the activated biacetyl molecules lose their energy without dissociating.

TABLE V

EFFECT OF WAVE LENGTH ON PRIMARY QUANTUM YIELDS CALCULATED FROM EQUATIONS 14 AND 15

Biacetyl concn., about 1.8 mmoles/l.

Wave length, Å.	ϕ, uninhibited	ϕ, iodine inhibited
2380	0.25	0.50
2537	.33	.44
2654	.39	.36
2804	.27	.22
3130	,074	.10

Evidence for collisional deactivation is furnished by the fact that primary decomposition at 3130 Å. decreases with increasing biacetyl concentration. No visible fluorescence was noted in any of these experiments.

At wave lengths 3130, 2804 and 2654 Å., the quantum yields of primary decomposition for both uninhibited and inhibited photolyses are almost equivalent. This was expected to be the case at all wave lengths. However, at 2537 and 2380 Å. more dissociation appears to occur in the presence of iodine than without it. Possibly at these wave lengths iodine begins to react directly with the highly excited molecules.

Acknowledgment.—The mass spectrometer used in this work was donated to the University of California, Los Angeles, by the Signal Oil and Gas Company of Los Angeles. The Signal Oil and Gas Company also established the H. M. Mosher Fellowship which was held by the first-named author during the 1951–1952 academic year. A portion of this research was carried out under contract with the Office of Ordnance Research.

LOS ANGELES, CALIFORNIA

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

The Photolysis of the Aliphatic Aldehydes. XVII. Propionaldehyde, *n*-Butyraldehyde and Isobutyraldehyde at 2380 and 1870 Å.

BY F. E. BLACET AND ROBERT A. CRANE[1]

RECEIVED MAY 11, 1954

Photochemical studies of the decomposition of propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were made at 2380 Å. in their first ultraviolet absorption region and at 1870 Å. in their second ultraviolet absorption region. Room temperature quantum yields for the non-condensable products were obtained at both wave lengths. Marked changes at the shorter wave lengths were observed in the quantum yields for the products and some new products were identified. Although a different electronic excitation state doubtless is involved at 1870 Å., the experimental results indicate that in determining the mode of decomposition, the increased energy of the quanta at the shorter wave lengths is more important than the electronic state, since results for the most part are a logical extrapolation of trends found down to 2380 Å. in the first ultraviolet absorption region. The quantum yield for carbon monoxide becomes greater than unity at 1870 Å. for all of these aldehydes. The quantum yields for methane, hydrogen and unsaturated compounds were large at 1870 Å. compared to those obtained at 2380 Å. Propane from the photolysis of propionaldehyde and butane from the photolysis of the butyraldehydes were identified for the first time in these studies. More polymerization was observed at the shorter wave length. Even though no work was done with free radical traps, it was possible, by making reasonable assumptions, to estimate the relative importance of the several primary processes that occur.

The photochemical decomposition of the aliphatic aldehydes has been studied in considerable detail in the easily accessible quartz region of the ultraviolet spectrum, and several primary processes have been established.[2,3] It has been possible to extend these photochemical decomposition studies into their second absorption region to 1870 Å. by developing new experimental equipment. Acetaldehyde was not investigated since it is highly transparent at this wave length.

Experimental Procedure

Monochromator.—A prism monochromator was designed and constructed using synthetic fluoride optics suitable for providing monochromatic light for photochemical studies in the short wave length ultraviolet to 1300 Å. The 60 degree fluorite prism was 30 mm. high and 40 mm. on its face. Two fluorite lenses 30 mm. in diameter were used. The radii of curvature for the two surfaces of the lens were chosen to minimize spherical aberration. Relatively short focal lengths (100 mm. at 2537 Å.) and wide apertures (1 mm.) were used to ensure maximum light intensities. The prism was moved mechanically in such a manner that minimum deviation of the light beam was maintained through the prism at all wave lengths. The resolution of the monochromator was such that the 2537 and 1849 Å. mercury resonance lines were separated by 7 mm. at its exit slit. A sealed case was provided so that an inert oxygen-free atmosphere could be maintained, if desired, for studies between 1800 and 1300 Å. Gas-tight seals on the control shafts allowed lens focusing and wave length and thermopile adjustments to be made without allowing air to enter the case.

Photolysis System.—This system consisted of a photolysis cell separated by two mercury valves from the aldehyde supply and the Toepler pump which was used to collect the non-condensable products. The photolysis cell was made by cementing two polished fluorite plates to the ends of a Pyrex tube 30 mm. in diameter and 40 mm. long. Glyptal lacquer was used for the cement. Windows clouded with

---

(1) Dow Chemical Company, Pittsburg, California.

(2) F. E. Blacet and J. N. Pitts, Jr., THIS JOURNAL, **74**, 3382 (1952).

(3) F. E. Blacet and J. Calvert, *ibid.*, **73**, 661, 667 (1951).

photochemically induced films could be removed for cleaning by soaking overnight in acetone. Aldehyde pressures of from 100 to 200 mm. of mercury were used in all photolyses.

Light Source.—A small atmospheric pressure, water-cooled mercury arc in a quartz tube provided a satisfactory source of ultraviolet radiation in the range of 2380 to 1850 Å. The quartz tube was specially thinned at the surface from which the radiation was taken to allow maximum transmission of the short wave ultraviolet. Under its normal operating conditions this arc has pronounced pressure broadening of the 1849 Å. line into a comparatively intense emission band between 1850 and 1900 Å. This band was used as a radiation source and for convenience in calculations is referred to in this paper as wave length 1870 Å. Due to rapid aging of the quartz, a new arc was constructed for almost every photolysis.

Measurement of Light Intensities.—Absolute light intensity measurements were made using a series parallel thermopile previously described.[4] Quantum yield calculations were made as described earlier,[5] with the substitution of appropriate experimentally determined values to correct for the fact that fluorite windows were used for the reaction cell and thermopile. The light energy passing through the cell was measured before and after each photolysis and a linear rate of aging of the light source and of polymer film formation was assumed in quantum yield calculations. Absorbed intensities were low in all experiments, being of the order of 1 to 5 × 10^{13} quanta per second in the total cell volume.

Purification of the Aldehydes.—Eastman Kodak Co. white label aldehydes were distilled at atmospheric pressure through a Tru Bore column maintaining a reflux ratio of about 10 to 1. The center fraction was then vacuum distilled into a reservoir trap attached to the photolysis system and stored over anhydrous calcium sulfate.

Analysis of Photolysis Products.—At the conclusion of a photolysis, the excess aldehyde and condensable products were condensed in a trap at −80° while the non-condensable products were removed by a Toepler pump. Unreacted aldehyde vapor in the non-condensable products was polymerized on the surface of a potassium hydroxide bead. The analysis for carbon monoxide in the gaseous products was made using solid silver oxide.[6] The other products were analyzed and identified with a Westinghouse Type LV Mass Spectrometer.

Experimental Results

Extinction Coefficients.—The extinction coefficients for propionaldehyde, *n*-butyraldehyde and isobutyraldehyde in the gas phase listed in Table I were calculated from the experimental data for wave lengths 2380 to 1870 Å. Data taken from earlier work[7] were used to determine the coefficients for these aldehydes for the wave lengths 3130 to 2380 Å.

Table I

Aldehyde Extinction Coefficients, Cm.$^{-1}$ Hg Mm.$^{-1}$; 25°. Pressure Range, 100 to 200 Mm.

Wave length, Å.	Propionaldehyde	*n*-Butyraldehyde	Iso-butyraldehyde
3130	3.5×10^{-4}	4.3×10^{-4}	4.2×10^{-4}
2804		4.8×10^{-4}	
2654	3.2×10^{-4}	3.7×10^{-4}	3.5×10^{-4}
2537	2.2×10^{-4}	2.0×10^{-4}	
2380	0.8×10^{-4}	1.1×10^{-4}	0.7×10^{-4}
2180			8.2×10^{-4}
2150	0.4×10^{-4}	1.2×10^{-4}	13×10^{-4}
1970	7.4×10^{-4}	2.6×10^{-4}	29×10^{-4}
1870	19×10^{-4}	10×10^{-4}	23×10^{-4}

Quantum Yields of Photolysis Products.—The principal non-condensable products were found to be carbon monoxide, *n*-butane, isobutane, propane, propylene, ethane, ethylene, methane and hydrogen. Quantum yields for these products at the wave lengths used are listed in Table II. The values given are the average of two or more determinations in each case.

Table II

Average Quantum Yields, Φ, of Non-condensable Products

Room temperature photolyses, pressure propionaldehyde 200 mm., the butyraldehydes 100 mm.

Φ of	Propion-aldehyde 2380 Å.	Propion-aldehyde 1870 Å.	*n*-Butyr-aldehyde 2380 Å.	*n*-Butyr-aldehyde 1870 Å.	Isobutyr-aldehyde 2380 Å.	Isobutyr-aldehyde 1870 Å.
Carbon monoxide	0.91	1.37	0.70	1.54	0.70	1.22
n-Butane	.02	0.04	.00	0.07	Not found	
Isobutane	Not found		Not found		.02	0.04
Propane	.03	.16	.57	0.77	.40	.28
Propylene	Not found		.01	.04	.02	.23
Ethane	.69	.59	.02	.06	.01	.05
Ethylene	.02	.06	.14	.24		.02
Methane	.09	.46	.01	.18	.04	.25
Hydrogen	.06	.12	.02	.34	.03	.30

Discussion of Results

Examination of the absorption coefficients shows clearly that 1870 Å. is in the second ultraviolet absorption region for these aldehydes. Accordingly, results from photolyses made at this wave length may be regarded as indicative of the decomposition mechanism occurring in this region.

The values for the quantum yields obtained from the photolysis of propionaldehyde at 2380 Å. were in good agreement with those obtained by Pitts,[2] who worked at the same wave length using other experimental equipment for his investigations. The results presented in Table II were obtained from experiments using the fluorite monochromator at both 2380 and 1870 Å., so that the rather significant changes in quantum yields between the two wave lengths can be directly attributed to the wave length change rather than to differences in experimental technique.

Examination of Table II shows that there is an increase in the quantum yield for practically all products given by the photolyses at 1870 Å. above that obtained at 2380 Å. This increase is striking for methane, carbon monoxide and hydrogen. Further consideration of the results shows that the increases in the quantum yields for corresponding products from each aldehyde are similar, indicating that possibly the photochemical decomposition mechanism at 1870 Å. is the same for the aldehydes studied. This was found to be the case for these aldehydes at longer wave lengths by other investigators.[2,3] The major changes observed between the results of the photolyses at 2380 Å. and those at 1870 Å. are listed below.

1. The quantum yield for carbon monoxide production becomes greater than unity at 1870 Å. for all the aldehydes.
2. The quantum yield for methane production

---

[4] R. A. Crane and F. E. Blacet, *Rev. Sci. Instr.*, **21**, 254 (1950).

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

[6] F. E. Blacet, G. D. MacDonald and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

[7] (a) F. E. Blacet, Doctorate Thesis, Stanford University (1931); (b) J. G. Calvert, Doctorate Thesis, University of California, Los Angeles, 1949; (c) J. N. Pitts, Jr., Doctorate Thesis, University of California, Los Angeles (1949); (d) R. D. Rowe, Master's Thesis, Stanford University (1932).

increases by a factor of from five to ten at 1870 Å. above that obtained at 2380 Å. for all the aldehydes studied, being greatest for propionaldehyde and smallest for *n*-butyraldehyde.

3. The quantum yield for hydrogen production increases by a factor of from two to fifteen at 1870 Å. above that obtained at 2380 Å.

4. Propane from the photolysis of propionaldehyde, and butanes from the photolysis of the butyraldehydes have not been previously identified as being present in the photolysis products at the longer wave lengths.

5. The quantum yield for the production of unsaturated compounds has increased at 1870 Å. above that obtained at 2380 Å. with a very pronounced increase in the case of isobutyraldehyde.

6. The material balance between the identified hydrocarbons and carbon monoxide produced is poor at 1870 Å.

The photochemical decomposition of these aldehydes in their first ultraviolet absorption region has been shown[2,3] to occur *via* four primary chemical process. The experimental results obtained by photolyses of these aldehydes at 1870 Å. in their second ultraviolet absorption region can be satisfactorily explained by postulation of similar processes.

Values were obtained for the quantum yields of the primary processes at the longer wave lengths by the use of iodine at moderately elevated temperatures to act as a free radical trap and the subsequent analysis of the alkyl iodides formed. The experimental equipment used for the photolyses at 1870 Å., as well as high absorption by iodine itself, would not permit the use of iodine as a radical trap. However, approximate values for the primary quantum yields of the primary processes postulated still may be obtained from the quantum yields for the products found if certain reasonable assumptions are made. These are discussed for each primary process postulated.

1. Primary Process I

$$\mathrm{CH_3CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3CH_2} + \mathrm{CHO}$$
$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3CH_2CH_2} + \mathrm{CHO}$$
$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \mathrm{(CH_3)_2CH} + \mathrm{CHO}$$

The existence of this process has been well substantiated at the longer wave lengths by the isolation and identification of the alkyl iodides produced.[2,3] The formyl radicals were found to dissociate into hydrogen atoms and carbon monoxide with the dissociation increasing as the temperature was increased. Accepting a value of 13.5 kcal./mole for the activation energy for the dissociation of formyl radicals,[2,3,8] it is reasonable to postulate the immediate dissociation of all formyl radicals at 1870 Å. as they are formed from this primary process. The energy of the quanta absorbed at 1870 Å. is 153 kcal. per mole and a simple calculation shows that the formyl radicals produced by absorption at this wave length possess energy in excess of twice the calculated activation energy for their dissociation. The primary process I quantum yield, ϕ_{I}, is equal to the hydrogen quantum yield, $\Phi_{\mathrm{H_2}}$, if it is assumed that the formyl radicals dissociate immediately upon formation, that the hydrogen atoms thus formed always extract second hydrogen atoms from aldehyde molecules, and that no molecular hydrogen is formed by the direct combination of two hydrogen atoms.

2. Primary Process II

$$\mathrm{CH_3CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3CH_3} + \mathrm{CO}$$
$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{CO}$$
$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{CO}$$

This investigation gave no direct evidence for this process since no free radical traps were used. By including it, however, a closer material balance for the products is obtained. If one postulates the absence of a primary process involving the formation of an activated molecule which becomes deactivated by collision, it is possible to obtain a value for the primary process quantum yield, ϕ_{II}, by subtracting the values found for the other primary processes from unity. Such an assumption may be reasonable since the formation of such an activated molecule has been shown[2,3] to become less important with decreasing wave lengths.

3. Primary Process III

$$\mathrm{CH_3CH_2CHO} + h\nu \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{HCHO}$$
$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_3CHO} \quad \mathrm{IIIa}$$
$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3CH_2{=}CH_2} + \mathrm{HCHO} \quad \mathrm{IIIb}$$
$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \mathrm{CH_3CH{=}CH_2} + \mathrm{HCHO}$$

The production of unsaturated compounds has been variously attributed to both a primary dissociation and to a disproportionation reaction between radicals. In the case of propionaldehyde, ethylene is the only alkene which can be formed. No evidence was obtained to indicate which process is most important at 1870 Å. However, in view of the decreasing importance of the disproportionation reactions with decreasing wave length reported previously,[2] and, in addition, since absorbed intensities were always small, it is reasonable to assume that the contribution of the disproportionation reactions to the total ethylene found is negligible. The primary process III quantum yield, ϕ_{III}, for propionaldehyde is thus nearly equal to the ethylene quantum yield.

Two unsaturated compounds, ethylene and propylene, may be primary dissociation products of *n*-butyraldehyde, while only propylene is possible in the case of isobutyraldehyde. The large increase in the propylene quantum yield observed in the photolysis of isobutyraldehyde is good evidence for a primary process producing propylene and formaldehyde. Propylene has been considered previously to arise exclusively from disproportionation reactions. ϕ_{III} for *n*-butyraldehyde may be regarded to be numerically equal to the sum of $\Phi_{\mathrm{C_2H_4}}$ and $\Phi_{\mathrm{C_3H_6}}$.

4. Primary Process IV

$$\mathrm{CH_3CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3} + \mathrm{CH_2CHO}$$
$$\mathrm{CH_3CH_2CH_2CHO} + h\nu \longrightarrow \mathrm{CH_3} + \mathrm{CH_2CH_2CHO}$$
$$\mathrm{(CH_3)_2CHCHO} + h\nu \longrightarrow \mathrm{CH_3} + \mathrm{CH_3CHCHO}$$

This process was not found to be very important at longer wave lengths but the large amount of methane found at 1870 Å. can best be explained as

---

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

being due to the increased importance of this process, with the resulting methyl radicals for the most part extracting hydrogen atoms from the excess aldehyde. It is also easier to account for all the carbon monoxide found in the photolysis products if a further postulation is made that the CH_2CHO, CH_2CH_2CHO and CH_3CHCHO radicals produced by Process IV rearrange and then dissociate producing methyl or ethyl radicals and carbon monoxide. Such a process seems energetically possible at 1870 Å. since at this wave length considerable energy may be left with the radicals after the initial photochemically induced dissociation.

An estimate for the primary quantum yield, ϕ_{IV}, for this process can be made if the assumption is made that the only substances produced by the methyl radicals are methane and propane in propionaldehyde photolyses and methane and butane in butyraldehyde photolyses. Allowance must be made for the additional methyl radicals produced in propionaldehyde photolyses by the rearrangement and dissociation of the CH_2CHO radicals. Equation (a) may be used to calculate the primary quantum yield, ϕ_{IV}, for propionaldehyde based on the above assumptions. Equation (b) applies in the butyraldehyde photolyses where additional sources for methyl radicals are not encountered.

$$\phi_{IV} = \frac{\Phi_{CH_4} + \Phi_{C_3H_8}}{2} \qquad \text{(a)}$$

$$\phi_{IV} = \Phi_{CH_4} + \Phi_{C_4H_{10}} \qquad \text{(b)}$$

Values for the estimated quantum yields for the several primary processes at 1870 Å. obtained on the basis of the assumptions stated are presented in Table III.

TABLE III

ESTIMATED PRIMARY QUANTUM YIELDS FOR THE ALDEHYDES AT 1870 Å.

Aldehyde →	Propionaldehyde	*n*-Butyraldehyde	Isobutyraldehyde
Process I	0.12	0.34	0.30
Process II (by diff.)	.51	.13	.18
Process IIIa	.06	.24	.23
IIIb		.04	
Process IV	.31	.25	.29

It is necessary to include secondary reactions of a cyclic nature in order to account for quantum yields greater than one for carbon monoxide. Quantum yields much greater than unity have been observed at elevated temperatures where sufficient energy is added thermally to the systems to sustain the chain.[2,3] The quantum yields determined at room temperature at 1870 Å. are not sufficiently high to necessitate the operation of sustained chains.

The large amount of methane found in the photolyses of these aldehydes at 1870 Å. indicates that an appreciable steady state concentration of methyl radicals may be established during the photolyses. For this reason methyl radical reactions other than the formation of methane must be considered. The existence of a reaction between methyl radicals and the radical produced by primary Process I is supported by the mass spectrometer identification of propane in propionaldehyde photolyses, *n*-butane from *n*-butyraldehyde photolyses, and isobutane from isobutyraldehyde photolyses. The production of these compounds from the interaction of methyl radicals and the corresponding parent aldehyde molecule directly has been assumed not to occur.

The amount of carbon monoxide obtained at 1870 Å. from the photolysis of all the aldehydes was greater than the amount of hydrocarbons produced. Similar lack of material balances has been observed by other workers and was attributed to polymer formation involving the loss of the free radicals in the polymer. Since polymer was found in all the photolyses the occurrence of such a process is plausible.

Acknowledgment.—The second-named author held a Charles A. Coffin Research Fellowship awarded by the General Electric Company in the years 1948–1950 and his research was aided also by a grant-in-aid from the Research Corporation, New York. The mass spectrometer used in this investigation was a gift to the University of California by the Signal Gas and Oil Company.

LOS ANGELES, CALIFORNIA