THE PHOTOLYSIS OF THE ALIPHATIC ALDEHYDES. I. PROPIONALDEHYDE

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The application of atomic mechanics to the processes following upon the absorption of light has met with some success in the case of diatomic molecules, in elucidating the nature of photochemical activation and reaction mechanism. In applying to polyatomic molecules some of the principles of photochemical activation and reaction mechanism which have arisen from the study of diatomic molecules, one of the most promising fields is offered by the aliphatic aldehydes, which, starting with formaldehyde, are only a step more complicated than a diatomic molecule of the oxygen type.

The absorption spectra of the aldehydes in the region 2500–3500 Å. have been studied by Victor Henri and his collaborators[1] who have shown that in every case the three typical regions of absorption; bands with fine structure, diffuse bands or predissociation, and continuous absorption, are found as one goes from long to short wave lengths. The different regions merge into each other, and the first two are overlaid with a faint continuous absorption.

The work of a number of observers[2] has shown that the simpler aldehydes are all decomposed by the absorption of light in this region. The reaction proceeds principally in two ways: first, a direct decomposition into carbon monoxide and the corresponding hydrocarbon, $RHCO = RH + CO$; and second, a polymerization into complex solid products. Attempts to detect the presence of other gases, such as hydrogen, carbon dioxide, oxygen or water vapor in the products of decomposition have shown that they are either totally absent or, if present, are found in only very small amounts.

An investigation by J. H. C. Smith and Victor Henri[3] into the kinetics of the reactions has shown in the case of acetaldehyde that the governing rate of the decomposition is unimolecular, while the governing rate of the polymerization is bimolecular.

It is a matter of interest, in view of recent interpretations of the phenome-

[1] Henri, *Trans. Faraday Soc.*, **25**, 765 (1929); Henri and Schou, *Z. Physik*, **49**, 774 (1928); de Hemptinne, *J. phys. radium*, [VI] **9**, 357 (1928).

[2] Berthelot and Gaudechon, *Compt. rend.*, **151**, 478 (1910); **156**, 68 (1913); Bredig and Goldberger, *Z. physik. Chem.*, **110**, 532 (1924); Bowen and Watts, *J. Chem. Soc.*, **129**, 1607 (1926); Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913); *J. phys. radium*, [VI] **8**, 289 (1927); Volmer, *Compt. rend.*, **178**, 697 (1924); Norrish and Griffiths, *J. Chem. Soc.*, 2829 (1928); Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

[3] Smith, *Carnegie Inst. Reports*, **27**, 178 (1928).

non of predissociation,[4] to correlate, as far as is possible, the spectroscopic data with the photochemical reactions produced. In particular the influence of wave length changes on the two reactions should be investigated. Several approximate measurements of the influence of wave length have been made. De Hemptinne,[1] working on benzaldehyde, found that the decomposition into benzene and carbon monoxide did not occur at wave lengths longer than the limit of the diffuse spectrum. Kirkbride and Norrish[2] have recently made similar tests on formaldehyde, and have reached the same conclusion regarding its decomposition. Smith[3] studied the effect of wave length on both the decomposition and polymerization of acetaldehyde vapor. He found that polymerization was effected by light throughout the absorption region, but that the decomposition proceeded rapidly only in the region of continuous absorption.

Since these measurements were all made with the use of light filters, which can give only an approximate separation of the different regions, and since none involved an accurate measurement of quantum yields, the authors have undertaken a series of quantitative measurements in monochromatic light on a number of the aldehydes. The present paper describes the experimental method, and the results on propionaldehyde. In a subsequent paper, a study on acetaldehyde will be reported, and a correlation between spectroscopic and photochemical data proposed.

2. Apparatus and Method

(a) **Monochromator.**—The ultraviolet radiation was obtained from a high pressure quartz mercury arc of the type perfected by Forbes, Harrison, P. A. Leighton and W. G. Leighton.[5] These arcs give very constant and intense illumination. The one employed in this research has been used frequently for runs of over twelve hours duration without appreciable fluctuation of intensity although no adjustments of any kind were made during this time.

Monochromatic light was obtained by means of a fused quartz prism and lenses, as shown diagrammatically in Fig. 1. Section A outlines the box, drawn to scale, which housed the arc and monochromator. Light from the arc entered the collimating slit S and, after passing through the prism and lenses, had its various components focused along the dotted line F. The entire box A was movable so that any desired line of the mercury spectrum could be brought to a focus upon the second slit S'. This was facilitated by pivoting the box beneath the lens L'. The pivot pin fitted in a channel which was in direct line with S'. This made it certain that the light entering section B was always traveling in the same direction.

[4] Henri, *Nature*, Dec. 20, 1924; *Trans. Faraday Soc.*, **25**, 766 (1929); Born and Franck, *Z. Physik*, **31**, 411 (1925); Franck and Sponer, *Göttinger Nachr.*, 241 (1928); Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1927); Herzberg, *Trans. Faraday Soc.*, **25**, 778 (1929); **27**, 378 (1931); *Z. Physik*, **61**, 604 (1930).

[5] Harrison and Forbes, *J. Opt. Soc. Am.*, **10**, [1] 1 (1925); Forbes and Harrison, *ibid.*, **11**, [2], 99 (1925); Forbes and Leighton, *ibid.*, **12**, [1], 53 (1925); Forbes and Harrison, THIS JOURNAL, **47**, 2449 (1925); W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

The equilateral prism P was of fused silica 6.5 cm. high and 9.5 cm. on a side.   The lenses L and L' were of the same material and 7.5 cm. in diameter.   Their focal lengths were approximately 21 cm. for yellow light.   L was placed 20 cm. from the slit S.   The monochromator had a curved collimator slit, 1.5 mm. by 30 mm. in size, which gave a rectilinear image.

Section B, Fig. 1, was a thermostatically controlled box containing, primarily, the absorption tube R and the thermopile T.   The slit S' was of adjustable knife edges, 3 cm. high.   It was maintained at 1 mm. in width in this work.   A black screen was placed in front of R.   The opening in this was made sufficiently small so that no light could enter directly into the walls of the tube.
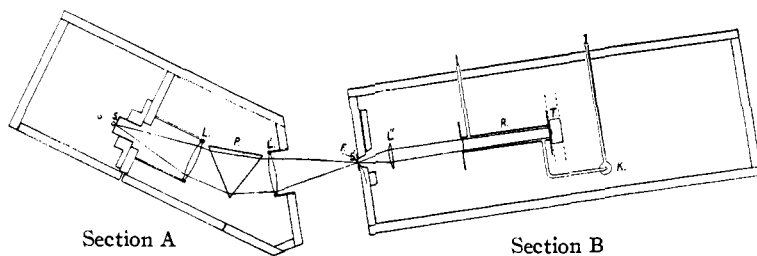

Fig. 1.—Diagram showing the path of monochromatic light.

(b)   **The Gas Train.**—It was found that the common stopcock lubricants cause polymerization of propionaldehyde vapor.   Mercury, on the other hand, in the absence of oxygen has no effect on the aldehydes.   Accordingly, a gas train was constructed in which the aldehyde vapor at no time came in contact with any material except mercury, Pyrex glass and fused silica.   Figure 2 is a diagrammatic sketch of this arrangement.   A was a storage bulb for the substance being investigated.   B and C, with the vertical tubes above, were mercury gas traps.   R represents the absorption chamber.   K was a liquid air trap.   That part of the diagram designated by M, N, O, O', Q, U, Y and W was a gage for measuring small changes in pressure during an exposure.

The operation of the traps B and C is obvious, except that in order to open them it was necessary to have the mercury standing at the same level in the two arms of the U-tube, as vacuum was being applied to the flask.   This was accomplished by using liquid air to reduce the vapor pressure either in A or R as might be required.   The right-hand vertical tube of trap C led to a Toepler pump and the gas analysis apparatus.

The absorption chamber R was 20 cm. long and 3 cm. in diameter.   It was made entirely of fused quartz and was connected to the rest of the apparatus by means of Pyrex-to-silica graded seals.   The ends were of plain quartz fused in place.   An attempt was made to use a glass tube with quartz windows sealed on with chicle cement.   This plan was abandoned, however, when it was found that propionaldehyde vapor condenses rapidly to a liquid upon coming in contact with this cement.

(c)   **The Pressure Gage.**—In order to measure the small changes in pressure during photolysis, the differential pressure gage diagrammed in Fig. 2 was employed.   This was an adaptation of the type described by Pearson.[6]   M was an evacuated bulb, having two sealed-in tungsten electrical contacts.   The tip of the upper one of these was accurately centered in the bulb.   A dry cell and relay completed the circuit.   A condenser was used across the relay terminals to prevent sparking.

N was a tube of uniform bore and 13.1 mm. diameter.   O was a uniform capillary tube having a volume of 0.867 cu. mm. per linear mm.   This was mounted upon a milli-

[6] Pearson, *Z. physik. Chem.*, A156, 86 (1931).

meter scale.   O′ was a 300-cc. bulb, which acted as an air cushion and permitted a sensitive adjustment of the mercury height in the capillary O.
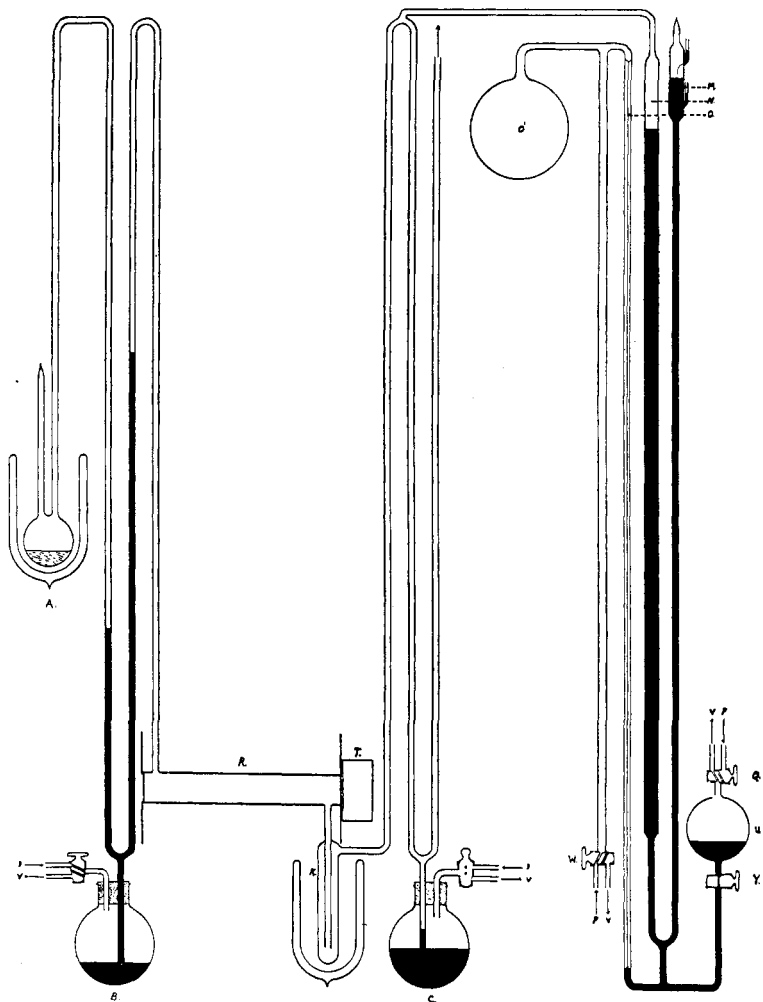

Fig. 2.—Diagram of the essential features of the gas train and the pressure gage.

At the beginning of a run, mercury was brought to a convenient height in the capillary by operating the two-way stopcock W, which was open to the atmosphere and also connected to the vacuum line.   Mercury was then brought just to the point of electrical contact in M by the proper manipulation of stopcocks Q and Y.   Following this, Y was closed, leaving a definite amount of mercury in the system, MNO.   In these adjustments the mercury in N automatically came to a certain level, depending upon the pressure in the absorption tube R.

With the traps B and C closed (but their stopcocks open to the atmosphere), the volume of gas in RKN was fixed.   (Volume change in the small columns of the traps

due to fluctuating atmospheric pressure was negligible with respect to the total volume of the gas.)   Any change in pressure in the system due to a reaction in R caused a variation of the mercury level in N.   Let it be supposed that there was a slight increase in pressure in the system.   Since the space above the mercury in M was evacuated, the system MN acted in the same manner as a barometer and there was a definite completion of the relay circuit.   Now by applying vacuum at W, the mercury level in O was raised, drawing mercury from M until the level there was again just at the point of "make and break."   Since the level in M was back then to the original point, the extra mercury drawn into O came from N.   From the change in height of the column in the capillary and from the volume ratio per unit length of the tubes N and O, the pressure change in the system RKN was calculated.   One mm. change of the mercury height in O was equivalent to 0.00642 mm. pressure change in the reaction system.

In practice, pressure gage readings were taken at frequent intervals during an exposure.   These values were plotted against time and from the curve obtained in this way the total pressure change in the system during an exposure was obtained with a certainty of ± 0.01 mm.

The temperature of the system RKN was controlled to within 0.1 of a degree.   The volume, which varied with the pressure, could always be calculated.   The total pressure in the system was obtained from a metric scale placed between the two arms of the Y tube of trap C.   This was permissible since the tube leading to the Toepler pump was always highly evacuated during an exposure.

(d)   **Energy Measurements.**—The thermopile used in this work was made by one of us.   It contained twenty bismuth to silver "hot" junctions with blackened tin foil radiators.   It was of the line type, having an exposed sensitive surface 3.0 mm. wide and 30.50 mm. high.   A thin crystal quartz window protected the junctions from air currents and dust.   As indicated in Fig. 1, the thermopile could be moved horizontally across the rear window of the absorption tube R.   This movement was effected by means of a machined screw with 1 mm. pitch.   A high sensitivity galvanometer (Leeds-Northrup, type 2285-X) was used with the thermopile.   This was mounted in a heavy Julius suspension and at the center of curvature of a millimeter scale five meters away.

This thermopile–galvanometer system was calibrated in the manner previously described.[7]   In addition to the sensitivity of the thermopile as a whole, the integrating ability of aliquot portions of its length was tested in the manner described by W. G. Leighton and G. S. Forbes.[5]   The mean deviation in sensitivity along the sensitive surface was found to be $\pm 4\%$.   Corrections were found for only the first and last thermopile readings, and since these readings were always of small magnitude (being taken on the edge of the beam), the corrections could be neglected without appreciable error.   The sensitive surface of the thermopile was sufficiently long to extend slightly above and below the widest portion of the light beam coming through the absorption tube.   Since the thermopile slit was 3 mm. in width, the total emergent energy, ΣB, was integrated by moving the thermopile across the back of the absorption tube in steps of 3 mm. each.

(e)   **Calibration of the Absorption Tube.**—In order to obtain the amount of energy absorbed by a gas in the reaction chamber, it was not sufficient to calculate the difference between the total radiation passing through the tube when it was full and when it was empty.   A certain fraction, x, of the light entering the tube was lost through the walls because of imperfections in the optical train.   This loss was due principally to the fact that a line source, instead of a point source, of radiation was used.

[7] Leighton and Forbes, THIS JOURNAL. **51.** 3549 (1929).

It can be shown that this fraction x is given for each wave length by the expression

$$x = 1 - \frac{J_t}{b^2 J_0} \qquad (1)$$

in which J_0 is the energy incident on the front window of the cell, J_t is the energy emerging from the rear window, and b is the fraction of incident monochromatic light transmitted by a single quartz window in air. The values for b may be obtained from indices of refraction of the various wave lengths and the application of Fresnel's law. Experimentally, for each of the strong lines of the mercury arc, J_t was obtained in the manner which has been described and J_0 was ascertained by removing the quartz reaction tube and placing the thermopile and its track up so that its window was in the same plane as was previously occupied by the front window of the tube. By integrating the beam which came through the black screen, which was now immediately in front of the thermopile, the correct value of J_0 was secured. Once determined for an experimental set-up, x becomes a constant in the calculation of quantum efficiencies (see equation 2).

(f) **Method of Analysis.**—The method of microanalysis employed has been described in detail elsewhere.[8] In spite of the fact that liquid air was used to condense the surplus aldehyde vapor, a small amount of this substance was always present in the gaseous decomposition products. In order to remove it, a solid potassium hydroxide bead was introduced into the gas by the method previously described. This reagent caused rapid polymerization of the aldehyde to a resin-like substance which adhered to the bead and was removed with it from the gas sample.

The amount of carbon monoxide produced in decomposition was taken as an index of the number of molecules of aldehyde which decomposed. Solid silver oxide was used to absorb the carbon monoxide. A complete description of the use of this absorbent will be given in another article. The volumes of gas used for analysis varied between 50 and 100 cu. mm. Check determinations were made in all cases, and for eighteen consecutive samples from different exposures, the average deviation from the mean per cent. of carbon monoxide for each sample was 0.26% absolute.

In the study of the mechanism of decomposition, it is important to know whether or not hydrogen is produced and, if so, to what extent. The principal hydrocarbon found in the decomposition of propionaldehyde is ethane. If hydrogen is formed there should be an equivalent amount of butane formed also. Since these hydrocarbons are solids at liquid air temperatures, an attempt was made to separate the carbon monoxide and hydrogen from the ethane and butane by thoroughly cooling the trap K (Fig. 2) and pumping off the carbon monoxide and hydrogen in a minimum number of operations of the Toepler pump. Although some of the hydro-

[8] Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

carbons came over in the pumping, there was a sufficient enrichment of the hydrogen content so that an analysis for it could readily be made. The carbon monoxide was first removed and then the residue was analyzed by explosion for hydrogen and ethane, the assumption being made that the butane remained in the liquid air trap.

It is well known that silver oxide reacts with both hydrogen and carbon monoxide and, theoretically, its use as an absorbent introduced an error in the percentages of these gases found to be present. However, dry silver oxide reacts much more slowly with hydrogen than it does with carbon monoxide. By means of a series of experiments with known mixtures of these gases, it was found that in the time necessary to remove all the carbon monoxide in a sample containing 90% CO and 10% H_2, not more than 2.5% of the total amount of hydrogen could be absorbed. Since 10% H_2 is above the maximum amount experimentally found in photolysis (see Table II), it may be reasoned that 0.25% absolute represents the maximum error due to this cause.

(g) **Calculations.**—L_0, the amount of light which entered the absorption tube per second, is given by the equation

$$L_0 = \Sigma B_1 \times \frac{1}{b} \times \frac{1}{1 - x} \tag{2}$$

and L_t, the energy reaching the rear window per second, by

$$L_t = \Sigma B_L \times \frac{1}{b} \tag{3}$$

ΣB_I is the total ergs per sec. emerging from the rear window of the empty tube and ΣB_L is this summation when the tube contains the absorbing gas. In the calculation of each of these quantities a factor was introduced which corrected for the difference in transmission of the quartz thermopile window for the wave length used as compared to its transmission for the mean wave length of the light from the carbon filament standard lamps.

It can be shown that Q and Q', the fraction of L_0 absorbed by the original vapor at the beginning and at the end of an exposure, are given respectively by the expressions[9,7]

$$Q = (1 - L)(1 + rL) \frac{\log L - \log I}{\log L} \tag{4}$$

and

$$Q' = y(1 - L)(1 + rL') \frac{\log L - \log I}{\log L'} \tag{5}$$

in which $L = L_t/L_0$, $I = 1-x$, L' is the fraction of L_0 reaching the rear window at the end of an exposure, r is the fraction of light striking the rear window which is reflected back into the reaction system, and y is the fraction of the original gas remaining in the reaction chamber. In the evaluation of y, the assumption was made that in polymerization a trimer

[9] Luther and Weigert, Z. physik. Chem., **53**, 408 (1905).

was formed which remained in the gaseous state. The error introduced because of this assumption cannot be large, for in all cases y was only slightly less than 1.0.

In this research it was found that L and L' were equal, within about 1%, for all runs. Since this is within the limits of experimental errors

$$Q' = yQ \qquad (6)$$

and from previous study[7] the average fraction of the light entering the tube absorbed during a run

$$Q_m = \sqrt{QQ'} = Q\sqrt{y} \qquad (7)$$

The total quanta absorbed is given by

$$\text{Quanta} = \frac{L_0 S Q_m}{h\nu}$$

in which S represents the time in seconds and $h\nu$, of course, the energy per quantum. Φ_d, the quantum efficiency of decomposition, was taken as the ratio of the molecules decomposed to the total quanta absorbed (*i. e.*, Φ_d = molecules decomposed/quanta absorbed).

It was impossible to determine the polymerization products of photolysis (see experimental results); therefore, in order to obtain some basis for the comparison of the amounts of polymerization at different wave lengths or pressures, a quantum yield of apparent polymerization was adopted. This value was obtained by calculating the decrease in molecular concentration during an exposure which was due to polymerization and dividing this by the number of quanta absorbed. The total molecular change in the system was secured from the pressure gage readings. Each decomposing molecule caused an increase of one molecule in the system. Therefore, molecules apparently polymerized = molecules decomposed − (± total molecular change). From this was calculated the quantum efficiency of *apparent polymerization*.

$$\Phi_p = \frac{\text{molecules apparently polymerized}}{\text{total quanta absorbed}}$$

3. Experimental Results

In the study of propionaldehyde, five lines of the mercury arc, ranging from 2537 to 3130 Å., were used for monochromatic radiation (Table I). As shown in Fig. 3, these lines cover fairly uniformly the region of maximum absorption which is attributed to the carbonyl group. In this graph, the average value of Q_m at 200 mm. pressure is plotted against the wave length of light employed.

The variations of both the decomposition and apparent polymerization quantum yields (Φ_d and Φ_p, respectively) with wave length, are given in Fig. 4. The points shown in each case are the average of two or more values obtained with an approximately constant pressure of 200 mm. in the reaction system.

TABLE I

EXPERIMENTAL DATA FOR QUANTUM YIELDS

λ, Å.	Pressure, mm.	L_0 erg./sec.	Quanta absorbed × 10^18	Molecules decomposed × 10^18	Mol. appar. polymerized × 10^18	Φ_d	Φ_p
2537	203	1860	3.68	3.33	..	0.905	..
	204	1420	3.39	3.76	2.57	1.11	0.758
	196	1469	3.21	3.11	2.43	0.970	.757
	196	4175	8.15	8.86	6.01	1.09	.737
2654	202	2880	4.89	3.84	3.84	0.785	0.785
	203	2600	4.31	3.28	..	.761	..
	204	2251	5.20	3.86	3.91	.742	.751
	89	8235	13.20	10.40	3.49	.787	.264
	33	8560	6.59	4.97	0.58	.754	.086
	14	8565	4.65	3.30	0.04	.723	.066
2804	199	3970	13.15	9.31	8.50	0.708	0.646
	196	4350	11.81	8.22	7.42	.695	.628
3020	196	7800	14.50	7.51	..	0.518	..
	207	7000	14.33	8.09	..	.564	..
	203	5950	10.30	6.11	6.11	.594	0.594
	211	5870	10.50	5.60	5.60	.533	.533
3130	195	13600	29.80	15.71	22.78	0.527	0.764
	92	8485	12.87	6.40	9.80	.497	.763
	74	27500	27.56	14.90	7.32	.540	.266
	36	11620	13.40	7.57	1.80	.565	.134
	13	12340	7.53	4.16	0.26	.552	.034

At two different wave lengths (2654 and 3130 Å.) the variations of quantum yields with pressure were determined. In Fig. 5, it may be observed that Φ_d at both wave lengths has a nearly constant value over the pressure range of 13 to 200 mm. Polymerization, on the other hand, increases steadily over this range.
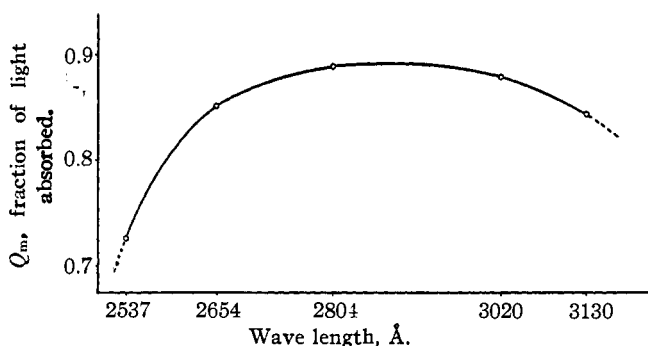

Fig. 3.—Fraction of light absorbed, Q_m vs. wave length, at 200 mm. pressure.

A constant temperature of 30° was used for all determinations of quantum efficiencie:

TABLE II

HYDROGEN FROM PROPIONALDEHYDE DECOMPOSITION

λ, Å.	Pressure, mm.	Analysis	Vol. CO, cu. mm.	Vol. H$_2$, cu. mm.	H$_2$, %	Average % H$_2$	% C$_2$H$_5$CHO molecules yielding H
2537	196	1	328.2	14.1	4.6	4.4	8.8
		2	328.2	13.0	4.2		
2654	89	1	384.8	28.0	7.3	8.8	17.6
		2	384.8	39.6	10.3	.	
3130	14	1	569.2	23.6	4.1	4.2	8.4
		2	569.2	24.5	4.3		

The presence of hydrogen in the decomposition products was confirmed for three different wave lengths as shown in Table II. In calculating the percentage of decomposing propionaldehyde molecules which produced hydrogen, it was assumed that only one hydrogen atom was expelled from each molecule. As shown by Table II, at a pressure of 14 mm. where the polymerization reaction has practically ceased, the amount of hydrogen produced is still comparable with that at higher pressures. Accordingly, it is assumed that the hydrogen production accompanies the decomposition reaction only.
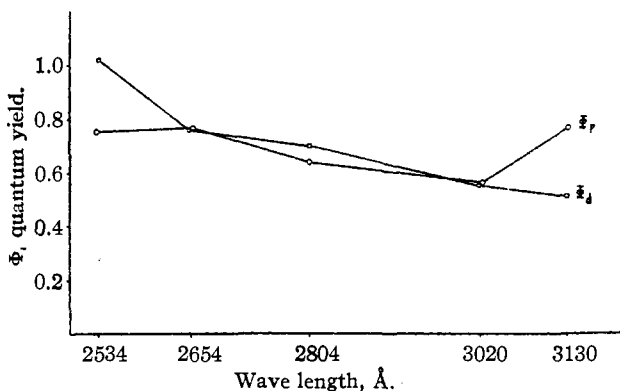

Fig. 4.—Variations of decomposition (Φ_d) and apparent polymerization (Φ_p) quantum yields with wave length, at 200 mm. pressure.

The fluorescence of propionaldehyde vapor could only be studied qualitatively because of the varying intensity of the mercury lines. However, marked fluorescence was present when the vapor was exposed to all wave lengths down to and including the λ2654 Å. line. It apparently decreased in intensity with decreasing wave length, and when the aldehyde was exposed to the λ2537 Å. line it was absent.

The only evidence obtained in regard to the nature of the polymerization products was (1) a very slight cloudiness which appeared on the walls of the quartz absorption tube; and (2) the percentage of light absorption did not

decrease appreciably during an exposure. These observations indicate either that a mixture of different polymers is formed or that if a single substance is the product, it has a high vapor pressure at 30°.

4. Discussion

Upon examination of the curves in Figs. 4 and 5, it is observed that the quantum yield of decomposition, Φ_d, increases with decreasing wave length, from a value of 0.51 at λ3130 to 1.02 at λ2537, with a sharp rise between λ2654 and 2537. The apparent quantum yield of polymerization, Φ_p, shows variable behavior with changing wave length. Between λ3130 and 3020 it drops rapidly, then rises at about the same rate as the decomposition to λ2654, while between λ2654 and 2537 it does not change.
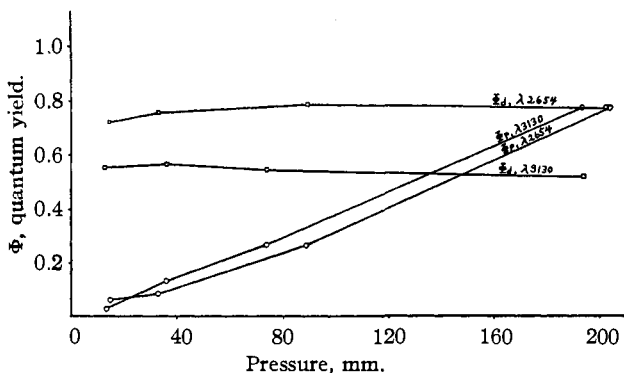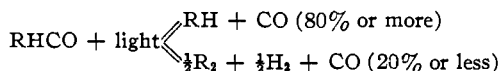

Fig. 5.—The effect of the variation of pressure upon decomposition (Φ_d) and polymerization (Φ_p) quantum yields.

The variations in quantum efficiencies with pressure (Fig. 5) are of especial interest. At two widely different wave lengths, decomposition appears to be a unimolecular process, the quantum yield being independent not only of the pressure but also of the amount of polymerization. The polymerization quantum yield, on the other hand, is zero at zero pressure and increases in direct proportion to the pressure. This suggests that the governing rate of the polymerization is bimolecular, in agreement with the findings of J. H. C. Smith for acetaldehyde.[3] It should be emphasized that the decomposition quantum yields represent the true values, since they maintain their constancy at low pressures, where the rate of polymerization has approached zero.

All of the evidence earlier quoted, together with that found in this Laboratory, indicates that in the decomposition of the aldehydes the principal reactions may be represented by

$$\text{RHCO} + \text{light} \Big\langle \begin{array}{l} \text{RH} + \text{CO (80\% or more)} \\ \tfrac{1}{2}\text{R}_2 + \tfrac{1}{2}\text{H}_2 + \text{CO (20\% or less)} \end{array}$$

In their study of the absorption spectra of the aldehydes, Henri and Schou[10] have found that with increase in molecular weight it becomes more and more difficult to analyze the spectral structure. For propionaldehyde they were able to detect discontinuous absorption only between 3400 and 3250 Å. The bands were faint, very diffuse, close together and became more and more indistinguishable toward shorter wave lengths, merging apparently into a continuum in the neighborhood of 3250 Å.

Herzberg[4] has reviewed the work of Henri and Schou on formaldehyde and on the basis of theoretical reasoning has suggested that the primary product of predissociation is represented thus

$$H_2CO + h\nu = H + CHO$$
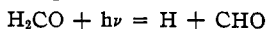
The application of this to the higher aldehydes gives two possibilities

$$RHCO + h\nu = RCO + H$$
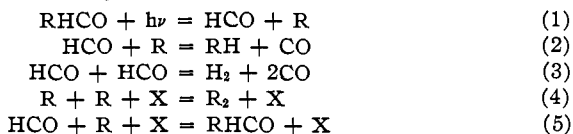$$\text{or } RHCO + h\nu = HCO + R$$
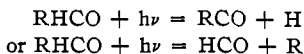
Although studies of the energies of dissociation of the C—H and C—C bonds result in values of 90,000 to 110,000 calories for the former and 70,000 to 90,000 calories for the latter,[11] all measurements agree that the C—C bond energy is about 15,000 to 20,000 calories less than that of the C—H bond. Hence it may be assumed that in the higher aldehydes the C—C bond is broken and the decomposition occurs principally according to the second equation above.

In this regard, it is interesting to observe that, if the dissociation of formaldehyde by light involves the breaking of a C—H bond, while the dissociation of acetaldehyde involves a C—C bond, by the theory of Herzberg the long wave length limit of predissociation in each case should set an upper limit for the energy of dissociation of these bonds. The predissociation limits and corresponding energies in each case are:

	Bond	λ	Upper limit of diss. energy	Thermal bond energy[12]
Formaldehyde	C—H	2750 Å.	103,000 cals.	98,500
Acetaldehyde	C—C	3200 Å.	89,000 cals.	87,600

With regard to the secondary reaction, the simplest course of the decomposition would be represented by

$$RHCO + h\nu = HCO + R \qquad (1)$$
$$HCO + R = RH + CO \qquad (2)$$
$$HCO + HCO = H_2 + 2CO \qquad (3)$$
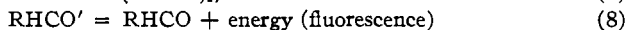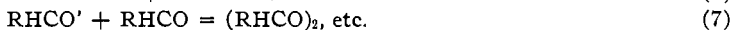$$R + R + X = R_2 + X \qquad (4)$$
$$HCO + R + X = RHCO + X \qquad (5)$$

[10] Schou, Doctorate Thesis, Les Presses Universitaires de France, Paris (1928); Henri and Schou, Z. Physik, **49**, 774 (1928).

[11] Andrews, Phys. Rev., **36**, 544 (1930); F. O. Rice, Chem. Rev., **10**, 135 (1932); Hogness, paper presented at the Indianapolis meeting of the American Chemical Society, April, 1931; Mecke, Z. physik. Chem., **B7**, 108 (1930).

[12] L. Pauling, personal communication.

Experimental findings on the relative amounts of RH and of H_2 produced would indicate that the probability of reaction 2 occurring is of the order of five to ten times that of reactions 3 and 4. Since the rate of all these reactions is dependent only on the amount of dissociation, the quantum yield of decomposition should be independent of the pressure, as it is.[13] A recombination, as by reaction 5, is indicated by the low decomposition quantum yields at wave lengths between 3020 and 2654 Å.

It is difficult to reconcile the existence of polymerization at all wave lengths, as well as the observation of fluorescence down to λ2654 Å., with a pure dissociation spectrum, as is indicated by the continuous absorption below 3250 Å. It is possible that banded absorption, with the production of activated molecules, extends to much shorter wave lengths than 3250 Å., and is not observable because of the fineness of the bands and the overlaid continuum. The reactions produced by absorption in this banded, overlaid continuum region would be, in addition to the decomposition reactions

$$RHCO + h\nu = RHCO' \tag{6}$$
$$RHCO' + RHCO = (RHCO)_2, \text{ etc.} \tag{7}$$
$$RHCO' = RHCO + \text{energy (fluorescence)} \tag{8}$$

This postulate explains the high polymerization yield at 3130 Å., the existence of fluorescence, and the effects of pressure on polymerization. The drop in polymerization rate between 3130 and 3020 Å. would then be due to a weakening of the bands and a strengthening of the continuum between these two wave lengths. The same postulate does not explain the increase in polymerization quantum yield at still shorter wave lengths. Since the mechanism in reactions 1 to 4 permits of no chain formation, a maximum value of unity is placed on the quantum yield of decomposition. At 2537 Å. the decomposition yield has reached this maximum value, and fluorescence has disappeared, yet polymerization is still produced with an apparent quantum yield of 0.75.

This may only be explained by assuming that the free radicals resulting from the primary dissociation (reaction 1) can produce polymerization in other aldehyde molecules, possibly through the formation of intermediate addition compounds, before combining to give the final decomposition products. Until more evidence is available the authors wish to refrain from undue speculation in this direction.

[13] In view of the number of vibrational degrees of freedom and consequent close spacing of the vibrational energy levels in these molecules, together with the finite width of the energy levels when the total vibrational energy is equal to the energy of dissociation, it may be assumed that in the bimolecular association reactions (4 and 5, above) the product molecule may temporarily accommodate any value of energy. These molecules will, therefore, be sufficiently long-lived to make the rates of association, except at pressures lower than were used here, independent of the concentration of the third body, X. See Kassel, THIS JOURNAL, **53**, 2143 (1931), and Pease, *ibid.*, **54**, 1876 (1932).

The marked rise in decomposition at 2537 Å. cannot be due to activation of mercury vapor in the absorption tube, for spectrum photographs show that with the type of high pressure arc used in this study the 2537 Å. resonance line is completely reversed, only the wings and the continuum to the long wave length side, which are not absorbed by cold mercury vapor, being present.

The authors wish to acknowledge their indebtedness to Dr. J. H. C. Smith for many helpful suggestions made during the course of this work.

Summary

1. The first of a series of articles on the photochemical reactions of the aliphatic aldehydes has been presented. The apparatus and method of study has been described and the experimental results given for propionaldehyde.

2. In the region investigated, $\lambda 2537$ Å. to $\lambda 3130$ Å., photochemical decomposition and polymerization are independent reactions. The quantum yield of decomposition is independent of pressure, while the quantum yield of apparent polymerization is directly proportional to the pressure.

3. The variation of the quantum yields of both reactions with wave length has been studied.

4. The principal products of decomposition were found to be carbon monoxide and ethane. A small amount of hydrogen also was formed in decomposition.

5. Fluorescence was produced by exposure to all wave lengths down to and including $\lambda 2654$ Å.

6. Mechanisms for both photochemical reactions have been proposed.

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DISTRIBUTION OF ACIDS BETWEEN WATER AND SEVERAL IMMISCIBLE SOLVENTS

BY RAYMOND C. ARCHIBALD

Part I. Monocarboxylic Acids

The distribution ratios at 25° of the six straight-chain members of the saturated monocarboxylic acid series from formic acid to caproic acid have been determined between water and the following solvents: ethyl methyl ketone, tertiary amyl alcohol, secondary butyl alcohol, normal butyl alcohol and normal amyl alcohol. Data have also been included from the literature for ratios between ethyl ether and water[1] and between isopropyl

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[1] W. U. Behrens, Z. anal. Chem., 69, 97 (1926).