The quantum efficiency was found to increase regularly with the concentration of the metal, but remained considerably smaller than unity at all concentrations studied. A distinct long wave length threshold was found for the quantum efficiency, and a maximum at around 2300 Å. Pure liquid ammonia was found to absorb light to considerably longer wave lengths than the gas, while solutions of metals and of metal amides show continuous absorption throughout the ultraviolet. The significance of these findings with respect to the photodecomposition of gaseous ammonia is discussed.

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The Photolysis of the Aliphatic Aldehydes.
II. Acetaldehyde

BY PHILIP A. LEIGHTON AND FRANCIS E. BLACET

In an earlier paper[1] the authors have summarized the general features of the photochemical decomposition and polymerization of the aliphatic aldehydes together with the results of a quantitative study of these reactions in the case of propionaldehyde. It was pointed out that the aldehydes present a favorable class of compounds for the study of the relations existing between absorption spectra and photochemical activity. In the aldehydes, three distinct absorption regions have been observed; bands with fine structure, diffuse bands or predissociation, and continuous absorption. These are more differentiated for acetaldehyde than for propionaldehyde, and this paper is concerned with a study of the photochemical reactions produced in acetaldehyde vapor by wave lengths falling in these different regions.

1. **The Absorption Spectrum of Acetaldehyde.**—The absorption band of acetaldehyde vapor which shows the phenomenon of predissociation extends from approximately 3480 to 2300 Å., with a maximum at about 2890 Å. The absorption coefficients have been determined by Smith,[2] and show a nearly symmetrical falling off on both sides of this maximum. Schou and Henri,[3] using a Hilger spectrograph, found that the region of absorption bands with distinct structure sets in, very faintly, at 3484 Å. and extends to the neighborhood of 3300 Å. Below 3300 Å. the structure grows gradually more diffuse and disappears entirely around 3080 Å. The diffuse bands were reported to continue to 2820 Å.

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

(2) Smith, Carnegie Inst. Reports, **27**, 178 (1928).

(3) Schou, Doctorate Thesis, Les Presses Universitaires de France, Paris, 1928; Henri and Schou, *Z. Physik*, **49**, 774 (1928); Henri, *Trans. Faraday Soc.*, **25**, 765 (1929).

In the present work, peculiarities in the photochemical results obtained led the authors to rephotograph the absorption spectrum of acetaldehyde vapor, with particular reference to the positions of the mercury arc lines used in the photochemical study.

For this purpose a 21-foot focus concave grating was employed, giving a dispersion of 2.7 Å./mm. in the first order. Continuous illumination was obtained from a hydrogen discharge tube. The acetaldehyde vapor was contained in a silica tube 40 cm. in length and 3 cm. in diameter, with plane windows fused on the ends. A mercury manometer and a cooling bulb were connected to the tube by means of Pyrex to silica seals. The aldehyde was distilled into the system in an atmosphere of nitrogen, frozen in the cooling bulb with liquid air, the nitrogen removed by evacuation, and the tube sealed off. The desired pressure of vapor in the absorption tube could then be obtained by controlling the temperature of the cooling bulb.

The wave length limits found for the region of distinct structure, and the merging of this into the region of diffuse bands, agree closely with those given by Schou and Henri, but the diffuse bands are found to extend to shorter wave lengths than the limit of 2820 Å. which they observed. These bands extend at least to 2730 Å., with a trace of banded structure appearing down to 2660 Å. The bands show a distinct periodicity in intensity in the diffuse region, with maxima at approximately 3060, 2984, 2905, 2825, 2747, and 2666 Å., respectively, the last named being very faint.

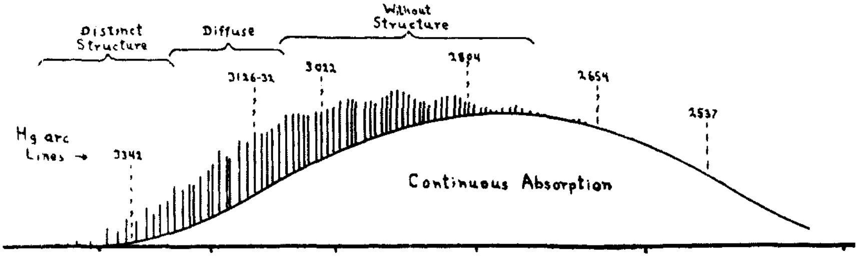

Fig. 1.—Diagrammatic representation of the absorption spectrum of acetaldehyde vapor, showing how the region of bands is underlaid by a gradually increasing continuous absorption.

A graphical representation of the different absorption regions, together with the positions of the mercury arc lines used in this research, is given in Fig. 1. The amount of apparently continuous absorption is represented by the lower curve; the positions and heights of the lines above the continuum curve represent the positions and approximate intensities of the band maxima. As this diagram indicates, the regions of distinct and diffuse bands are underlaid by continuous absorption, very faint at first, but increasing in intensity with decreasing wave length until below 2730 Å. the absorption becomes entirely continuous. There appears to be no break in this continuous absorption curve, as measured at the absorption minima between bands, and its maximum lies close to 2750 Å. The maximum band intensities, as shown by the greatest variations between absorption maxima and minima, are found at about 3100 Å., while the maximum of observed absorption (bands plus continuum) occurs at 2890 Å.

A more detailed study of the acetaldehyde bands will require a higher dispersion, such as has been recently applied to formaldehyde by Dieke and Kistiakowsky.[4]

2. Photochemical Reactions of Acetaldehyde.—The absorption of light by the absorption band just discussed produces two reactions, a decomposition, which has been shown to result principally in carbon monoxide and the corresponding hydrocarbon,[5] and a polymerization into complex products. The rates of these two reactions have been studied by Smith,[2] who, using the total radiation from a quartz mercury arc, found that the rate of decomposition was directly proportional to the incident light intensity and independent of the pressure (after correction for change in absorption with pressure), while the rate of polymerization was proportional to the logarithm of the light intensity and directly proportional to the pressure. Polymerization was found to be produced by wave lengths throughout the absorption band, while decomposition was produced chiefly by the shorter wave lengths in the band.

Smith estimated an approximate value of 0.04 for the quantum yield of decomposition for an average wave length of 2650 Å. obtained by use of a chlorine filter. Using unfiltered ultraviolet light, Bowen and Watts[5] obtained a net quantum yield of approximately two molecules of aldehyde disappearing per quantum absorbed, for an average wave length of 3130 Å., which was divided into 1.6 for polymerization and 0.4 for decomposition. This value was obtained by comparison with a uranyl oxalate actinometer, for which a quantum yield of unity was assumed. If the more accurate value of 0.55 be taken for the quantum yield of the uranyl oxalate actinometer for this average wave length,[6] Bowen and Watts' values for acetaldehyde become 0.88 for the quantum yield of polymerization and 0.22 for that of decomposition.

The need of further measurements is obvious, and in the present paper the quantum yields for the two reactions, and their variations with wave length and pressure, have been redetermined. The monochromator, gas

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[4] Dieke and Kistiakowsky, *Proc. Nat. Acad. Sci.*, **18,** 367 (1932).

[5] Berthelot and Gaudechon, *Compt. rend.*, **151,** 478 (1910); **156,** 68 (1915); 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).

[6] Leighton and Forbes, THIS JOURNAL, **52,** 3139 (1930).

train and absorption cell, pressure gage and method of analysis and measurement were as previously described.[1]

The acetaldehyde sample was prepared from paraldehyde. After shaking with sodium carbonate, the paraldehyde was distilled and the fraction collected which came over between 123.2 and 123.3°. Two drops of concentrated sulfuric acid were added to this distillate and a second distillation carried out over a water-bath at 40–50°. The middle fraction obtained in this process was used in the studies reported. The vapor pressure of this acetaldehyde was found to be 337 mm. at 0°. This is in excellent agreement with the values calculated from the data of Emeleus.[7]

Six different lines of the mercury arc were used as sources of monochromatic radiation in this study. These lines ranged from 2537 to 3342 Å. and as shown in Fig. 1 at least one line falls in each different region of the absorption band.

The quantum yields of both decomposition (Φ_d) and of apparent polymerization (Φ_p) obtained under various conditions of pressure, wave length and intensity of illumination are given in Table I. A constant temperature of 30° was used for all determinations.

TABLE I

EXPERIMENTAL DATA FOR QUANTUM YIELDS

Å.	Press., mm.	L_0 erg/sec.	L_m	Quanta absorbed × 10^{18}	Molecules decompd. × 10^{18}	Mol. appar. polymerized × 10^{18}	Φ_d	Φ_p
2537	202	6555	0.741	8.93	8.45	0.80	0.945	0.086
	198	6415	.749	6.93	6.02	.80	.870	.115
	79	6280	.473	6.65	6.01	.63	.905	.095
2654	306	6535	.899	12.58	10.43	4.58	.821	.360
	198	8800	.869	13.24	10.50	1.20	.793	.114
	80	8300	.673	10.40	7.80	1.53	.757	.148
	12	8560	.178	4.12	3.12	0.46	.756	.111
2804	202	3820	.876	8.11	4.02	1.64	.496	.202
	201	4000	.880	10.34	5.85	2.67	.559	.255
3022	207	18200	.904	29.90	8.50	11.17	.284	.373
3130	291	19390	.911	20.95	4.10	13.37	.193	.638
	195	25750	.877	50.35	9.72	22.18	.193	.440
	195	26200	.877	36.80	7.69	17.88	.209	.485
	201	19010	.866	25.80	5.54	13.43	.212	.514
	201	10195	.820	19.29	4.53	9.19	.236	.479
	201	2592	.834	7.51	2.15	4.81	.286	.640
	203	2038	.728	5.16	1.65	3.26	.312	.617
	76	20670	.623	28.80	8.83	7.67	.306	.266
	14	21940	.189	10.37	4.20	−0.11	.396	−0.011
3342	486	1465	.300	3.13	2.56	...	.818	...
	507	1140	.368	2.36	1.69	...	.716	...

The variations in these quantum yields with both pressure and wave length are of interest. At 3130 Å., which is on the long wave length edge

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[7] Emeleus, *J. Chem. Soc.*, 1733 (1929).

of the predissociation region, Φ_p increases, while Φ_d uniformly decreases, with increasing pressure. At 2654 and 2537 Å., which are in the region of continuous absorption, both quantum yields are very nearly independent of pressure, with the exception of a rise in Φ_p at the highest pressure used.

The wave length variations show that, with the exception of 3342 Å. and the lowest pressure at 3130 Å., the apparent polymerization decreases, while the decomposition increases, as the wave length is decreased. Thus, at pressures of approximately 200 mm., Φ_p drops from 0.47 at 3130 Å. to 0.1 at 2537 Å., while Φ_d increases from 0.2 to 0.9 under the same conditions.

In order to ascertain whether the intensity of illumination had an effect upon the quantum efficiencies of the reactions, a number of determinations were made in which the wave length and pressure were kept constant at 3130 Å. and 200 mm., respectively, while the amount of light entering the reaction tube was changed. This variation of intensity was accomplished by placing various combinations of quartz and glass plates directly in front of the tube. The results of this study show that only at very low intensities do the quantum yield values vary beyond the normal limits of experimental error from a constant value. The number of filter plates necessary to give this decrease of intensity, without doubt, increased the scattering of light (see x value of previous article[1]). This means that probably more light entered the reaction chamber than was measured by the thermopile, and this effect might well account for the apparently high quantum yields which have been obtained under these extreme conditions. The fact that both reactions are apparently affected in the same manner lends weight to this argument.

A qualitative study of fluorescence of the aldehyde vapor showed that it occurred at all wave lengths between 3342 and 2804 Å., but that it did not occur at 2654 and 2537 Å.

Blank runs made at various times during this study gave no pressure change and no non-condensable gaseous products, showing that the reactions were not due to other causes than light absorption.

The evidence obtained in regard to the nature of the polymerization products was similar to that given previously for propionaldehyde, namely, (1) after long exposure a very slight cloudiness appeared on the walls of the quartz absorption tube, and (2) the percentage of light absorption did not decrease appreciably during an exposure. This indicates the existence of some polymer in both the solid (or condensed liquid) and vapor phase.

In the study of propionaldehyde it was possible to determine with some success the amount of hydrogen formed in the decomposition reaction. Recent study has shown that it is also produced in the photo-decomposition of *n*-butyraldehyde. In the case of acetaldehyde the high vapor pressure at liquid air temperature of the hydrocarbons, methane and ethane, formed in the decomposition, prevented their partial separation, and the difficulties involved in analyzing for three combustible gases by explosion make it impossible to say with certainty that hydrogen is produced. However, by analogy with the other two aldehydes it seems reasonable to believe that a small amount of hydrogen is produced in this case also.

The use of the 3342 Å. line of the mercury arc was attended by two difficulties: (1) this line is relatively very weak in intensity and (2) the absorption of acetaldehyde in this region is slight (Fig. 2). However, because of the especial theoretical significance to be attached to photolysis in the region of fine structure absorption bands, two quantum yield determinations of decomposition were carried out using this wave length (Table I). In order to obtain sufficient absorption for accurate energy measurements, it was necessary to use pressures of aproximately 500 mm. in the reaction tube. This made it impossible, with the apparatus employed, to get the pressure change in the system and hence no quantum yields of apparent polymerization were obtained. In addition to the data given in Table I, the times of exposure for the two runs were, respectively, 41,820 and 33,180 seconds and the volumes of carbon monoxide products were, respectively, 95.0 and 62.8 cu. mm., at standard conditions. Because of the experimental difficulties involved, it is felt that the quantum yields reported here are by no means final for this wave length.

3. Discussion. Correlation of Spectroscopic and Photochemical Data.—As pointed out in section 1, the diffuse absorption bands of acetaldehyde are taken by Schou and Henri[3] as a typical example of predissociation. The Auger effect analogy[8] may be applied, but with caution, since in this case light is undoubtedly absorbed in the C═O bond, while probably the C–C bond is broken in the dissociation.

The source of the continuous absorption is not as easily explained. The structural similarity between the aldehydes and molecular oxygen, noted by Herzberg,[8] would suggest that this continuum corresponds to the Schumann–Runge continuum of oxygen, *i. e.*, that it results from excess vibrational energy in the excited state, and hence that the dissociation products would be

$$CH_3CHO + h\nu \longrightarrow CH_3CH + O'$$

which is analogous to the dissociation of oxygen by the Schumann–Runge continuum. That this cannot be the case is indicated by several facts. First, the energy of this dissociation, calculated from thermal data, is of the order of 200,000 cal. The energy corresponding to the maximum of continuous absorption is 103,000 cal., and hence not sufficient. Second, the diffuse bands fade into the continuum at a place where the convergence limit of the series is far from being reached. Third, analysis of the reac-

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(8) V. 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).

tion products shows none of the substances (oxygen, carbon dioxide, organic acids) which one might expect if atomic oxygen were present. In fact, the decomposition products appear to be the same, whether the reaction is produced by diffuse or continuous absorption. This evidence indicates that the same dissociation is produced by absorption in the continuum as is produced by the diffuse bands, and hence that probably the same unstable upper state is concerned in both cases.

At longer wave lengths, in the region of rotational structure, there exists a distinct, although small, probability of direct transfer upon absorption from the normal to this unstable state, as indicated by the weak continuous absorption which underlays the bands (Fig. 1). As the energy of the quantum increases the relative probability of direct transfer to this state increases until at approximately 2730 Å. it becomes equal to unity, and the banded absorption disappears. The maximum probability of excitation to the vibrationally quantized upper state, as determined by the maximum band intensities, occurs at about 3100 Å. This is very close to the wave length at which all rotational structure disappears from the bands, hence coincides with the point of maximum probability of transfer from the quantized to the non-quantized excited states.[8]

The photochemical reactions produced may be explained on this basis, together with a secondary reaction mechanism similar to that suggested for propionaldehyde,[1] *viz.*

A	B
Discontinuous absorption	Continuous absorption
$RCHO + h\nu \longrightarrow RHCO'$	$RHCO + h\nu \longrightarrow R + HCO$
$RHCO' + RHCO \longrightarrow (RHCO)_2$, etc.	$R + HCO \longrightarrow RH + CO$
$RHCO' \longrightarrow RHCO +$ fluorescence	$R + R + M \longrightarrow R_2 + M$
$RHCO' + M \longrightarrow RHCO + M$ (K. E.)	$HCO + HCO \longrightarrow H_2 + 2CO$
$\searrow RH + CO + M$	$R + HCO + M \longrightarrow RHCO + M$
and in region of diffuse bands	
$RHCO' \longrightarrow R + HCO$, etc.	

At 3130 Å. the amount of continuous absorption is small and the bands are not altogether without structure. Therefore reactions A predominate, a considerable fluorescence is observed, the quantum yield of decomposition is small, and that of polymerization relatively large (Table I). Increasing the pressure should increase the amount of polymerization, which it does, and, since this wave length is just on the border between discrete and diffuse bands, increasing the pressure, should, by removing activated molecules, decrease to some extent the amount of predissociation and resultant decomposition. This is observed to be the case.

As the wave length is shortened, the amount of continuous absorption increases while the bands become more diffuse and finally disappear. Dissociation, as by reactions B, becomes the predominant process, fluorescence weakens and disappears entirely between 2800 and 2654 Å., the quantum yield of decomposition increases, while that of polymerization decreases. In the region of pure continuous absorption, below 2730 Å., the quantum yield of decomposition approaches unity and is independent of pressure, which would be expected from the above mechanism. The existence of some polymerization in this region of pure continuum requires the introduction of the additional postulate that the free radicals resulting from dissociation can produce polymerization in other molecules through the formation of intermediate compounds.[1] It is worthy of note that except at higher pressures the amount of polymerization produced by 2654 and 2537 Å. is independent of pressure. The gradual changes in quantum yield with wave length, with no sharp breaks, agree with the gradual transition which is observed between the different absorption regions.

It still remains to explain the high quantum yield of decomposition found at 3342 Å. An examination of the absorption spectrum (Fig. 1) shows that the mercury arc lines at 3126–3132 Å. and 3022 Å. fall on absorption bands, hence the absorption of these wave lengths is the combined effect of band plus underlaid continuum, and the observed reactions are the resultant of this combined effect. On the other hand, the mercury line at 3342 Å. falls directly between two band maxima. The absorption of this line is then principally due to the underlaid continuum, and we should expect a larger quantum yield of decomposition than was obtained for 3130 Å. This is actually observed, the value of $\Phi_d = 0.76$ being obtained at 3342 Å. as against 0.19 at 3130 Å. However, as pointed out in the preceding section, owing to the small amount of light absorbed together with the weakness of the mercury line, this result at 3342 Å. cannot be accepted as final. The chief significance of this experiment is that decomposition of acetaldehyde has been found in the region of rotationally quantized absorption, in agreement with the recent observations of Norrish and Kirkbride on formaldehyde.[9] The interesting possibility of producing large variations in quantum yields by small variations in incident wave length in this region is being further investigated.

It is worthy of note that the actual production of decomposition as the result of predissociation is indicated by only one observation, namely, the effect of pressure on quantum yield at 3130 Å. All the other experimental data can be explained on the basis of bands underlaid by continuous absorption.

The authors wish to express their appreciation to Mr. R. D. Rowe for his assistance in obtaining the absorption photographs, and to Dr. J. H. C. Smith for his generous coöperation in this work.

Summary

1. A study of the absorption spectrum of acetaldehyde vapor checks the results of Henri and Schou on the wave length region showing distinct

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[9] Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932).

structure and the border between distinct and diffuse bands, and shows that the diffuse bands extend at least to 2730 Å.

2. The quantum yields of polymerization and decomposition, and their variations with wave length, pressure and light intensity, have been determined.

3. Fluorescence is found to extend throughout the regions of distinct and diffuse bands, but to be absent in the continuum.

4. The absorption spectrum is interpreted as consisting of bands underlaid by continuous absorption, and the photochemical reactions produced are explained on this basis.

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Equilibrium in Liquid Systems of Three Components

BY WILLIAM T. REBURN AND WILLIAM N. SHEARER

Equilibrium curves for ternary systems involving polar liquids, water and halogen hydrides were needed. Very few published data on such systems of which the non-aqueous phases are fair conductors of electricity could be found. We were compelled therefore to secure the data in the laboratory. This paper presents data and curves for the equilibrium in a few such systems.

The experimental procedure was as follows. Glass-stoppered bottles containing measured portions of aqueous acid solutions of known concentration were placed in an agitator in a bath maintained at the desired temperature. When bath temperature was attained the organic liquid was delivered from a buret until the first appearance of permanent turbidity indicated saturation. In a few instances only, subsequent agitation caused the solution to clear, whereupon turbidity was restored by addition of a drop or two more. The percentage composition of the phase could then be calculated. Saturation points for the non-aqueous phases were obtained by delivering water from the buret to a solution of aqueous acid in the organic liquid until turbidity developed. End-points were sharper and were satisfactorily duplicated. No appreciable chemical reaction was noticeable during the time required for attainment of physical equilibrium except in the non-aqueous phases involving cyclohexanone with hydrogen bromide and hydrogen iodide.

The materials were obtained from the following sources. The hydrochloric acid was the C. P. product of commerce. The hydrobromic and hydriodic acids were prepared by the usual laboratory process from red phosphorus and bromine and from phosphorus iodide, respectively. These acids were preserved in colored bottles in the dark and remained colorless throughout the course of the experiments. The isoamyl and isobutyl alcohols and the cyclohexanone were of the highest grade furnished by the Eastman Kodak Company. The normal butyl alcohol was C. P. from the J. T. Baker Chemical Company. The liquids were all dried and redistilled and their purity established by boiling point, specific gravity and refractive index determinations.

In some cases tie-lines were determined by agitating, in the thermostat bath, mixtures containing suitable amounts of the three constituents, the two phases then being