

phthalide<sup>15</sup> dissolved in 50 cc. of benzene. The mixture was heated for two hours, decomposed with ice and ammonium chloride and the colorless benzene layer separated; the latter rapidly turned yellow and acquired a green fluorescence due to the formation of the furan. The benzene was removed under diminished pressure and the green, gummy furan oxidized with sodium dichromate; the ketone melted at 109–110°.

In order to obtain the di-(*p*-bromophenyl)-hydrazone 1.7 g. of the ketone, 50 cc. of alcohol, 5.4 g. of *p*-bromophenylhydrazine and two drops of acetic acid were refluxed for twenty-four hours; the crystalline precipitate was boiled with 150 cc. of methyl alcohol to remove impurities, then washed three times with small amounts of cold acetic acid and recrystallized from a mixture of methyl alcohol and ethyl acetate; m. p. 163–165° with decomposition.

(15) Nourisson, *Ber.*, **19**, 2105 (1886).

*Anal.* Calcd. for C<sub>34</sub>H<sub>22</sub>O<sub>2</sub>N<sub>4</sub>Br<sub>2</sub>: Br, 23.59. Found: Br, 23.41.

**Oxidation of 2,5-Di-(*p*-hydroxyphenyl)-3,4-benzofuran with Potassium Ferricyanide.**—The gummy benzofuran obtained from 9.6 g. of phenolphthalin was dissolved in 100 cc. of 10% sodium hydroxide solution and treated with 22 g. of potassium ferricyanide, dissolved in 100 cc. of water. After five minutes the clear solution was acidified, whereupon 5 g. of 2-(4"-hydroxybenzoyl)-4'-hydroxybenzophenone precipitated; m. p. 225–226°.

### Summary

Tetrabromophenolphthalin and 2',4"-dimethoxydiphenylphthalin, when treated with sulfuric acid, yield 2,5-diaryl-3,4-benzofurans which upon oxidation are converted into 2-benzoylbenzophenones.

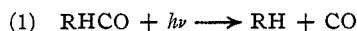
ANN ARBOR, MICHIGAN RECEIVED NOVEMBER 22, 1935

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

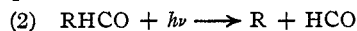
## The Photolysis of the Aliphatic Aldehydes. III. Hydrogen from Acetaldehyde

BY FRANCIS E. BLACET AND JACK G. ROOF

The primary process in the photochemical decomposition of the aliphatic aldehydes in the vapor phase has been assumed by Norrish<sup>1</sup> and others to be represented principally by



Pearson considers this to be the initial act even though he has shown recently<sup>2</sup> that free radicals are produced in acetaldehyde photolysis. If this is the initial process, no subsequent reactions are probable and in the continuous region of absorption a quantum yield of unity is to be expected. Leighton and Blacet have shown that the quantum yield of decomposition is not always unity in this region.<sup>3</sup> In the case of propionaldehyde, they found hydrogen among the decomposition products. These facts along with the work of Herzberg on formaldehyde<sup>4</sup> led them to postulate the initial process to be



The free radicals thus liberated enter into secondary reactions in which R<sub>2</sub> and H<sub>2</sub> are probable products as well as RH. However, because of experimental difficulties they were not able to

confirm the presence of hydrogen in the photolytic products of acetaldehyde.<sup>5b</sup> This fact has been taken by Norrish<sup>1</sup> as added proof of his primary mechanism. Leermakers,<sup>5</sup> however, studying the photolysis of this compound at elevated temperatures obtained results in agreement with Reaction 2. Since the results of Leighton and Blacet on acetaldehyde were published, a method of microanalysis for hydrogen has been developed which permits the analysis for this gas in the presence of a mixture of saturated hydrocarbons.<sup>6</sup> This development has permitted a re-examination of the products of photolysis of acetaldehyde with the object in view of determining which of the primary processes postulated above is correct.

### Experimental Method and Results

The apparatus used for the photolysis was essentially the same type as that previously described.<sup>3</sup> The light sources were the λ 3130, 2804 and 2537 lines of mercury, obtained from a high pressure mercury arc and a crystal quartz monochromator. The absorption of radiant energy took place in an all fused silica cell and the aldehyde vapor was not allowed to contact any substances except fused silica, Pyrex glass and mercury. The average pressure in the cell dur-

(1) (a) Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934); (b) Kirkbride and Norrish, *ibid.*, **27**, 404 (1931); (c) W. West, *THIS JOURNAL*, **57**, 1931 (1935).

(2) Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935).

(3) (a) Leighton and Blacet, *THIS JOURNAL*, **54**, 3165 (1932); (b) *ibid.*, **55**, 1766 (1933).

(4) Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

(5) Leermakers, *THIS JOURNAL*, **56**, 1537 (1934).

(6) Blacet and MacDonald, *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934).

ing exposure was approximately 300 mm. The temperature was maintained at 30°.

After irradiation, the excess aldehyde was condensed and the residual gases were collected in the gas holders of the micro gas analysis apparatus.<sup>7</sup> The last traces of aldehyde vapor were removed by means of potassium hydroxide and the amount of carbon monoxide determined by the use of solid silver oxide.<sup>3,7</sup>

The percentage of hydrogen was determined by the use of copper oxide and potassium hydroxide.<sup>6</sup> Duplicate analyses of the hydrogen were made for each of the wave lengths,  $\lambda$  3130, 2803 and 2537. The number of molecules of carbon monoxide produced represents the molecules of aldehyde which decomposed. The ratios of molecules of H<sub>2</sub> to CO experimentally determined are

Wave length, Å.	3130	2804	2537
Ratio 1, H <sub>2</sub> /CO	0.049	0.092	0.158
Ratio 2, H <sub>2</sub> /CO	0.050	0.108	0.152

#### Discussion of Results

The secondary processes which have been postulated<sup>3</sup> to follow the primary dissociation into the free radicals R and HCO are

- (3)  $R + HCO \longrightarrow RH + CO$
- (4)  $R + R + M \longrightarrow R_2 + M$
- (5)  $HCO + HCO \longrightarrow H_2 + 2CO$
- (6)  $R + HCO + M \longrightarrow RHCO + M$

The energy required to disrupt the C—C bond is approximately 85 cal. Since  $Nh\nu$  for  $\lambda$  3130 represents 91 cal. the kinetic energy imparted to R and HCO at this wave length on dissociation of the molecule would be small. This means that the free radicals would not rapidly depart from their mutual field of influence and, therefore, Reactions 3 and 6 may well predominate over 4 and 5. Hence, at  $\lambda$  3130 a low percentage of hydrogen would be expected in the products of decomposition and the quantum yield should be relatively small because of the reversal process 6. As shorter wave lengths are used the free radicals separate with greater kinetic energy and the chances for Reactions 4 and 5 become greater. This accounts in part for the increase in decomposition quantum yield which has been found as the quantum energy is increased<sup>3</sup> and for the increase in the hydrogen content of the decomposition products.

These relationships are brought out in Fig. 1 where the average percentages of decomposing

(7) Blacet, MacDonald and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

acetaldehyde molecules which yield hydrogen are shown as a function of the energy absorbed. The average quantum yields of polymerization and of decomposition obtained at 200 mm. pressure,<sup>3b</sup> are also given for the corresponding wave lengths. It will be observed that the percentage of acetaldehyde molecules which yield hydrogen increases almost in a linear manner from 10% at  $\lambda$  3130 to 31% at  $\lambda$  2537. Unfortunately, because of the limit of absorption the maximum value of this curve cannot be obtained. It is probable, however, that with increased energy the point would soon be reached at which the fragments R and HCO would depart completely from their sphere of influence in every act of absorption and that thereafter the secondary processes would be nearly independent of  $h\nu$ .

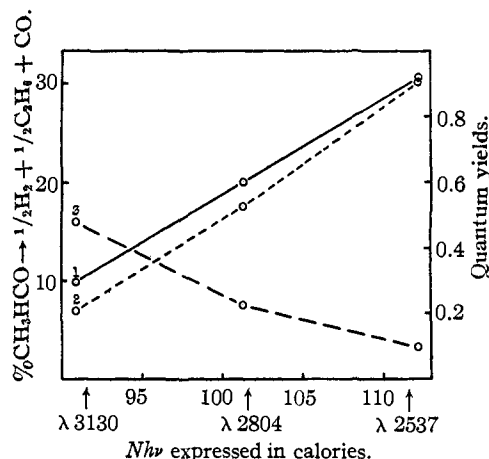


Fig. 1.—Curve 1, variation of acetaldehyde molecules which yield hydrogen gas with the quantum energy. Curves 2 and 3, quantum yields of decomposition and polymerization, respectively.

It has been suggested<sup>1a</sup> that the small percentage of hydrogen previously reported<sup>3</sup> may result from the absorption of light by the polymer which is formed concomitantly with photodecomposition. The fact that the greatest percentage of hydrogen occurs at the wave length where the amount of polymerization is very small (see Fig. 1) appears to render this concept untenable.

The writers are indebted to the National Research Council for a Grant-in-Aid which helped to make this study possible.

#### Summary

Hydrogen has been found in the photochemical decomposition products of acetaldehyde. The

fraction of decomposing aldehyde molecules which produce hydrogen gas increases linearly from 10% at  $\lambda$  3130 to 31% at  $\lambda$  2537.

Evidence is given which indicates that  $\text{RHCO} + h\nu \rightarrow \text{RH} + \text{CO}$  cannot represent the primary

process in the dissociation of the aliphatic aldehydes, but that  $\text{RHCO} + h\nu \rightarrow \text{R} + \text{HCO}$  is in accord with experimental results.

LOS ANGELES, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## The Activity of Water in Solutions of Barium Chloride<sup>1</sup>

BY ROY F. NEWTON AND EMERSON A. TIPPETTS<sup>2</sup>

### Introduction

Hepburn<sup>3</sup> measured the vapor pressure of barium chloride solutions by a dew point method, and taking as a base the activity coefficient of a 0.5 *M* solution as calculated from the electromotive force determinations of Lucasse<sup>4</sup> he obtained from his measurements the activity coefficients of barium chloride in the more concentrated solutions. His results differed widely from those of Lucasse, and he emphasized a point of inflection in his curve in the neighborhood of the saturated solution, and deplored the fact that Lucasse's results did not extend to saturation. Since the results of our electromotive force measurements<sup>5</sup> at 25° are in close agreement with those of Lucasse, and show no indication of a point of inflection near saturation, it was considered desirable to reinvestigate the vapor pressure of barium chloride solutions.

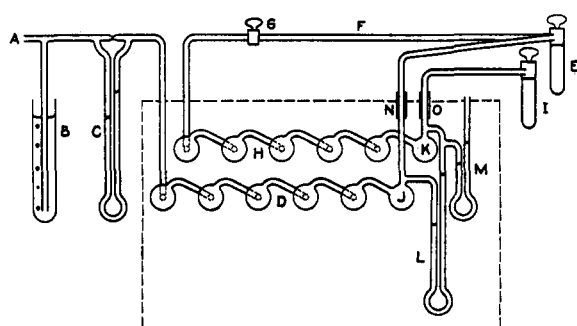


Fig. 1.—Apparatus for determination of vapor pressure.

### Apparatus and Methods

The solutions used were prepared and analyzed as previously described by Tippetts and Newton.<sup>5</sup> The method of determination of vapor pressure was that of

Washburn and Heuse<sup>6</sup> modified by Gibson and Adams<sup>7</sup> with slight further modifications.

Figure 1 shows an end view of the apparatus. The parts of the apparatus enclosed by the broken lines of the figure are surrounded by the water-bath, kept at  $25.00 \pm 0.01^\circ$ . Cleaned air enters at A, at a pressure which is maintained constant by the head of water in B. The air passes through the flowmeter C and into a series of saturators D and J, containing water. The saturated air then passes through absorber E, returns through F and throttling stopcock G, into the saturators H and K containing solution, and thence through absorber I into the atmosphere. Saturators D and H are of the type described by Bichowsky and Storch<sup>8</sup> and are essentially the same as those used by Pearce and Snow.<sup>9</sup> Saturators J and K, which are simply large tubes half filled with liquid, are used to ensure final saturation with no measurable pressure drop in the saturator. Water manometers L and M, together with the barometer, serve to measure the pressure in J and in K. To prevent condensation in the tubes leading from the saturators to the absorbers, the air space surrounding these tubes is maintained two or three degrees warmer than the thermostat, and, in addition, rubber covered electric heating units N and O offset the cooling due to evaporation of water which splashes upon them. The absorbers E and I are U-tubes filled with anhydrous magnesium perchlorate. Each absorber is followed by a similar one to obviate the possibility of absorbing moisture from the solution following it or from the atmosphere.

The various parts of the apparatus were connected to one another in most places by means of ground glass joints; in a few places the connections were made by tightly fitting rubber sleeves within which the glass tubes were butted together so that scarcely any of the rubber was exposed to the saturated air. These were found satisfactory, although slight leakage resulted when the air passed through greater lengths of rubber tubing.

Check runs with varying rates of air flow showed that saturation was attained for rates as high as four liters per hour. The runs usually required about sixteen hours, in which time the gain in weight of the absorbers was approximately 1 g. each. During the runs, the barometer

(1) Presented at the New York meeting of the American Chemical Society, April, 1935.

(2) Present address, du Pont Rayon Co., Buffalo, New York.

(3) Hepburn, *J. Chem. Soc.*, 550 and 1284 (1932).

(4) Lucasse, *THIS JOURNAL*, 47, 743 (1925).

(5) Tippetts and Newton, *ibid.*, 56, 1675 (1934).

(6) Washburn and Heuse, *ibid.*, 37, 309 (1915).

(7) Gibson and Adams, *ibid.*, 55, 2879 (1933).

(8) Bichowsky and Storch, *ibid.*, 37, 2895 (1915).

(9) Pearce and Snow, *J. Phys. Chem.*, 31, 231 (1927).