ring. It seems probable that the structure of the anhydro-form that *d*-altrose generates in acid solution is analogous to that of sedoheptulosan and may be written as (X), the substance being a D-altrosan.[14]

It is not possible on present evidence to decide whether either the ethylene oxide or the septanoid ring is present in the reducing form of sedoheptulose or of altrose. The pyranoid or furanoid ring is not excluded in the reducing structure, but it is certainly questionable whether crystalline *d*-altrose, of $[\alpha]_D$ +33°, with no mutarotation, is of either the pyranose type or the furanose. Altrose and sedoheptulose are different in behavior in certain fundamental aspects from the sugars that have given rise to most of our generalizations in sugar chemistry. Various extensions of these views to give speculative explanations of some of the anomalies that have been observed with certain of the sugars, the lack of mutarotation in some reducing sugars and its complex character in some others, the agreement of rotations with the isorotation rules in some cases and a failure in others, are obviously possible, but it is too early now to discuss them. New experimental data must first be obtained. Possibly such anhydride formation may be found to occur with sugars of configurations different from that of altrose.

Summary

It is shown that sedoheptulosan possesses an unusual structure, one of its rings being an ethylene oxide form and the other a septanoid ring. This result is extended by analogy to the anhydro-form of altrose. Our present generalizations regarding the ring structures of sugars do not apply to sedoheptulose and altrose; their behavior is exceptional and appears to be due to their tendency to form types of rings that play little or no role in the case of the more common sugars.

WASHINGTON, D. C. RECEIVED APRIL 18, 1938

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[14] It is emphasized that at the present time the formula (X) for D-altrosan rests solely upon the apparent analogy to sedoheptulosan (IX). The article by Robertson and Griffith (*J. Chem. Soc.*, 1193 (1935)), furnishes observations in the altrose series which seem difficult to interpret on the basis of (X), but I hope that the questions may soon be answered through additional experimental data.

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

The Photolysis of the Aliphatic Aldehydes. VI. Acetaldehyde

BY FRANCIS E. BLACET AND DAVID VOLMAN

The discussion of the photochemistry of the aldehydes by Rollefson[1] and Burton[2] has served to emphasize the fact that additional experimental data, especially in regard to decomposition products, must be obtained before the mechanism of decomposition of these compounds can be fully appreciated. The experimental results reported in this paper appear to settle certain of the questions which have been raised concerning the gaseous decomposition products of acetaldehyde. In addition, other information has been obtained which must be considered in the study of this reaction mechanism.

Experimental Method

The aldehyde was studied in the vapor phase in an apparatus essentially the same as that previously described[3] with the exception that since the object of the study was to determine the nature of the gaseous decomposition products, no provision was made to measure quantum yields. The source of radiation was a high pressure mercury arc used in conjunction with a crystal quartz monochromator. In order to vary the reaction temperature the silica reaction cell was submerged in a water thermostat. The cell was recessed from the wall of the thermostat with the aid of a metal tube of the same diameter. This tube was soldered to the inner wall of the thermostat and connected to the reaction cell by means of a rubber sleeve. Monochromatic light entered the system through a slit placed at the outer end of the metal tube. In experiments carried out below room temperature moisture was prevented from condensing on the front window of the cell by having a drawn-out glass tube carrying a slow stream of nitrogen enter one end of the slit.

After irradiation, the excess acetaldehyde was liquefied by means of a carbon dioxide–alcohol refrigerant and the non-condensable gas removed by means of a Toepler pump. In order to avoid the possibility of differential absorption of the gas by the liquid aldehyde, the condensation trap was warmed and cooled several times with additional pumping carried out after each cooling operation. Some liquid aldehyde collected in the gas holder of the analytical apparatus but this was removed by the introduction of successive potassium hydroxide beads in the sample. The micro methods of analysis which were used have been described elsewhere.[4-7]

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[1] Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

[2] Burton, *ibid.*, **41**, 322 (1937).

[3] Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932).

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

[5] Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933).

[6] Blacet and MacDonald, *ibid.*, **6**, 334 (1934).

[7] Blacet and Volman, *ibid.*, **9**, 44 (1937).

Experimental Results

Decomposition Products.—Studied over a considerable range of experimental conditions the gases collected consisted of only carbon monoxide, hydrogen and methane. Treatment of the gas with fuming sulfuric acid and then potassium hydroxide[3] gave volume reductions of approximately 0.5%. Blank runs demonstrated that this slight reduction is to be expected due to the solubility in the acid of the gases known to be present and hence it appears certain that no unsaturated hydrocarbons are produced in the photolysis.

Carbon monoxide was removed by solid silver oxide,[5] hydrogen by copper oxide and potassium hydroxide,[6] and saturated hydrocarbons by combustion over a hot platinum coil.[7] In Table I the results are given of duplicate analyses for hydrocarbons produced in four experiments carried out at λ 2654 and 25° and over a pressure range of from 39 to 279 mm. Volumes are expressed in cubic millimeters. The samples indicated are the gas which remained after carbon monoxide and hydrogen have been removed and may contain saturated hydrocarbons and residual nitrogen. (a) gives volume decreases after combustion and the removal of water vapor and (b) gives the additional volume decrease due to the removal of carbon dioxide by potassium hydroxide. Since the ratio a/b is equal, within experimental error, to the theoretical value for methane, it follows that there were no other saturated hydrocarbons, such as ethane, in the samples.

TABLE I

Expt.	Sample, cu. mm.	Sample + O_2	After combustion and P_2O_5	(a) Volume decrease	Volume after KOH	(b) Volume decrease	Ratio a/b
1	14.49	113.16	88.44	24.72	76.10	12.34	2.00
	24.70	123.61	80.99	42.62	59.59	21.40	1.99
2	48.58	160.68	104.10	56.58	75.84	28.26	2.00
	48.93	163.77	105.57	58.20	77.75	27.82	2.09
3	40.19	153.75	80.09	73.66	42.55	37.54	1.96
	40.47	157.24	84.31	72.93	48.05	36.26	2.01
4	28.00	135.67	84.09	51.58	58.43	25.66	2.01
	30.01	135.16	79.32	55.84	50.94	28.38	1.97
						Average ratio	2.004
						Methane ratio	2.000

Variation of Reaction Products with Pressure.—After establishing the fact that the volatile decomposition products of acetaldehyde are only carbon monoxide, hydrogen and methane, and since the role played by hydrogen in the photolysis is a matter of considerable speculation, it has been deemed advisable to determine the H_2/CO ratio under a variety of conditions. In Table II are the relative amounts of gaseous products obtained in the experiments given in Table I.

TABLE II

Expt.	Pressure	CO, mols	H_2, mols	CH_4, mols
1	279	100	12.3	91.0
		100	12.8	91.4
2	134	100	13.4	93.0
		100	13.5	90.2
3	92	100	14.3	97.0
		100	14.3	94.2
4	39	100	15.7	90.0
		100	14.8	89.9

Variation of H_2/CO with Wave Length.—This ratio has been studied at four wave lengths in addition to those previously reported.[8] The results obtained are given in Table III along with those of Blacet and Roof. These experiments were done at 25° and with an aldehyde pressure of 300 mm. The result at λ 2000–2100 was obtained by placing the end of the reaction cell in the λ 2000–2100 region of the focal plane of a Hilger E316 spectrograph and focusing the rays from a moderately intense hydrogen discharge for thirty-nine hours on the spectrograph slit. This slit was 1 mm. wide and approximately equal in length to the diameter of the absorption cell.

TABLE III

Wave length, Å.	H_2/CO 1	2	H_2/CO, Average	Experimenters
3340	0.037	0.036	0.037	Authors
3130	.049	.050	.050	B. and R.
2804	.092	.108	.100	B. and R.
2654	.123	.128	.126	Authors
2537	.158	.152	.155	B. and R.
2380	.218	.218	.218	Authors
2100–2000	No decomposition			Authors

Variation of H_2/CO with Intensity of Illumination.—At λ 2654 and with a temperature of 25° and a pressure of 205 mm. in the reaction cell, a series of experiments was made in which the intensity of incident light was varied. This was done by placing a quartz cell of 1 cm. internal thickness in front of the reaction tube. In this small cell were placed solutions of benzoic acid in ethyl alcohol. The relative transmissions of these solutions were determined with the aid of a

TABLE IV

Relative intensities	H_2/CO 1	2	Average
100	0.107	0.099	0.103
52	.085	.078	.082
16	.059	.063	.061

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[8] Blacet and Roof, THIS JOURNAL, **58**, 278 (1936).

thermopile–galvanometer system. Results are given in Table IV.

Variation of H_2/CO with Temperature.—A series of runs was made at λ 2654 in which temperature was the variable. By varying the pressure at the different temperatures the acetaldehyde concentration in the reaction cell was maintained at approximately 0.018 mole per liter. The results obtained, together with one value reported by Blacet and Roof, are given in Table V.

TABLE V

Temp., °C.	H_2/CO 1	 2	Average
0	0.058	0.056	0.057
10	.102	.098	.100
25	.123	.128	.128
30 (B. and R.)			.131
35	.117	.115	.116
45	.086	.082	.084
70	.051	.050	.051
92	.037	.034	.035

The information given in the foregoing tables is summarized in Fig. 1 in which the ratio H_2/CO is plotted against the variables wave length, intensity of incident radiation, pressure and temperature.

Discussion of Results

The absence of ethane and unsaturated hydrocarbons in the gaseous products eliminates

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

and

$$CH_3 + CH_3 \longrightarrow C_2H_4 + H_2$$

as reactions in the decomposition mechanism. These facts along with the other information presented here require that the mechanisms for room temperature photolysis which have been proposed in this series of papers, and elsewhere by other investigators, must be considerably modified. It becomes increasingly evident that the so-called polymerization process cannot be divorced from the photodecomposition and that much more must be known concerning the condensable products before any mechanism can be established fully. However, the following series of reactions are helpful and are presented here as a working hypothesis for the explanation of our results.

$$CH_3CHO + h\nu \longrightarrow CH_3 + HCO \quad (1)$$

$$CH_3CHO + HCO \longrightarrow H_2 + CO + CH_3CO \quad (2)$$

$$CH_3CHO + CH_3 \longrightarrow CH_4 + CH_3CO \quad (3)$$

$$CH_3CO + M \longrightarrow CH_3 + CO + M \quad (4)$$

$$2CH_3CO \longrightarrow (CH_3CO)_2 \quad (5)$$

It will be noted that the principal new feature concerning this mechanism is that we are proposing it for room temperature photolysis. Leermakers[9] has given it with minor differences for high temperature photolysis of acetaldehyde, while Rice and Herzfeld[10] have made similar postulations for the thermal decomposition of this compound. The main differences are in the chain breaking steps and it is quite possible that these do vary over a temperature range.

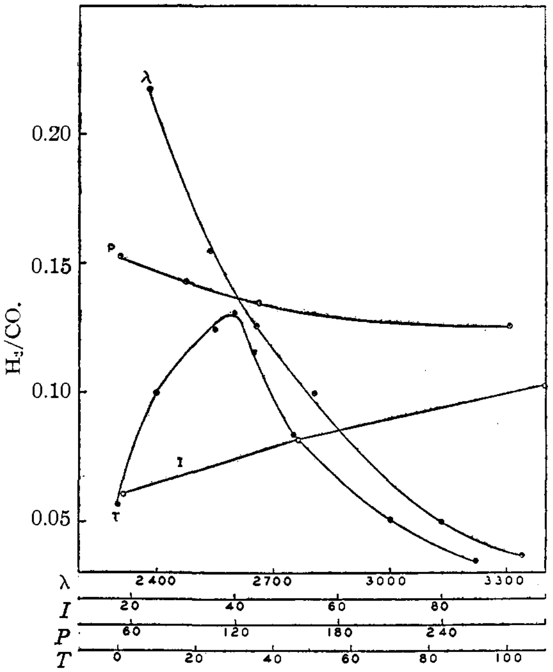

Fig. 1.—Variation of the hydrogen to carbon monoxide ratio in acetaldehyde decomposition with λ, wave length, Å.; with *P*, pressure, mm.; with *I*, relative intensity of incident radiation; and with *T*, temperature, °C.

Leermakers has assumed a mechanism for room temperature decomposition different from that which he postulated for high temperatures (1) because the quantum yield reported by Leighton and Blacet[11] was only 0.3 at the wave length employed in his study (λ 3130), and (2) because by introducing a term correcting for low temperature non-chain decomposition a rate expression was found which gave a straight line over a wider temperature range on plotting log *k* against $1/T$. Thus he found a quantum yield for the chain reaction of 0.03 at 25°. However, if one takes his high temperature rate equation without the additional term mentioned above and extrapolates log *k* obtained from his experimental data *vs.*

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[9] Leermakers, THIS JOURNAL, 56, 1537 (1934).

[10] Rice and Herzfeld, *ibid.*, 56, 284 (1934).

[11] Leighton and Blacet, *ibid.*, 55, 1788 (1933).

$1/T$ to 25°, a value of k is obtained which when placed in the equation

$$\Phi = \frac{d(CO)}{dt} \times \frac{1}{I_{abs.}} = \frac{k(CH_3CHO)}{\sqrt{I_{abs.}}}$$

gives a value of the order of 0.2–0.3 for Φ. This is in good agreement with the value of 0.3 previously reported[11] and indicates that the chain mechanism is still in operation at room temperature.

The above equation requires that at low temperatures Φ_d be proportional to $1/\sqrt{I_{abs.}}$ for a given concentration. Leighton and Blacet[11] working with acetaldehyde at 30° obtained data for λ 3130 and approximately 200 mm. pressure from which these values can be calculated over a tenfold variation in I_{abs}. Although it is true that certain experimental errors increase with the lowering of intensity,[11] nevertheless it can be seen from Fig. 2 that, even with liberal allowance for errors, Φ_d appears to be proportional to $1/\sqrt{I_{abs.}}$. It should be noted that the polymerization quantum yield varies in a like manner with intensity.[11]

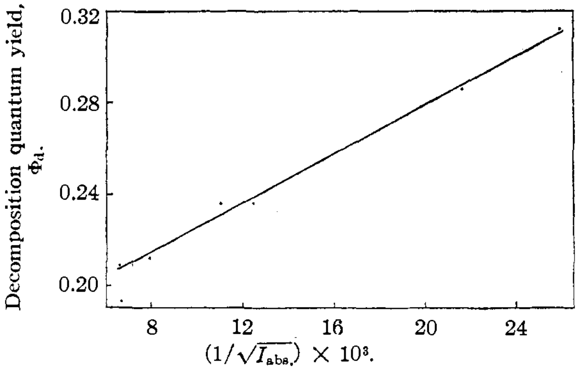

Fig. 2.—Decomposition quantum yields at λ 3130 as a function of absorbed light intensity expressed in ergs per second. Calculations from data obtained at 30° and 200 mm. pressure.

The above mechanism accounts for the formation of hydrogen without the simultaneous formation of either ethane or ethylene. It permits the H_2/CO ratio to vary between the limits 0 and 1 depending upon the length of the chain involving reactions (3) and (4). It suggests that the moles of hydrogen plus methane produced must be equal to or greater than the moles of carbon monoxide. The available data on all the saturated aliphatic aldehydes are in agreement with these restrictions. After making due allowance for both the change in the number of molecular collisions with pressure and the variation of quanta absorbed with pressure the mechanism suggests that with increase in pressure the chain would be lengthened somewhat and hence there would be a decrease in H_2/CO. This is the case as shown in Fig. 1. An increase in the intensity of radiation results in a higher steady state concentration of free radicals and favors the chain breaking reaction 5. The average chain length is diminished and H_2/CO should increase with I_0. Figure 1 shows this to be the case.

The presence of a maximum at 30° in the H_2/CO *vs.* temperature curve indicates that both the hydrogen producing and carbon monoxide producing steps are increasing in velocity with temperature but that the latter reactions are increasing at the greater rate. By isolating diacetyl from the photolysis products of acetone, Spence and Wild[12] have shown that CH_3CO is fairly stable at 0° but with increase in temperature it decomposes rapidly, presumably by reaction 4, and at 60° no diacetyl could be detected. By using the Paneth method for detecting free radicals Glazebrook and Pearson[13] have verified these findings. An effort has been made to include in the above mechanism only reactions which are supported by some experimental evidence or which are necessary postulations to fit the data. However, in addition to the reactions given it is conceivable that reactions resulting in the formation of glyoxal, methylglyoxal and acetone may occur. Proof of the presence or absence of these compounds in the condensed product of photolysis would help in determining how readily reactions 2 and 3 may take place. Although the formulation of rate expressions for reactions 1 to 5 gives results in partial agreement with the curves shown in Fig. 1, it seems best to refrain from a discussion of rates until more information is available.

The rapid increase in the H_2/CO ratio with decreasing wave length can be accounted for by several hypotheses. It may be that two primary dissociation processes occur, one to give methane and carbon monoxide directly, the other as indicated here, and that the latter reaction increases as the quantum energy becomes greater. It may be that even in the apparently continuous region of absorption only a fraction of the absorbing molecules dissociates and gives only radicals in this process. Presumably this fraction increases as the energy absorbed increases. It may be that complete dissociation occurs according to reac-

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(12) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

(13) Glazebrook and Pearson, *ibid.*, 567 (1937).

tion 1, but that reaction 2 takes place with difficulty and is aided materially by the excess quantum energy carried off by HCO in the primary process. As the energy in excess of that necessary to break the C–C bond became greater the efficiency of reaction 2 would be increased. The HCO not reacting in this way would go to form some of the condensable molecules mentioned above. Sufficient information is not available at the present time to permit a choice between these alternatives pertaining to the primary process. However, in view of the interest which has been manifest concerning this point, it may be well to point out that although the production of some carbon monoxide and hydrocarbon in the initial act of absorption is not excluded from the possibilities, there appears to be little evidence which requires this reaction.

It should be mentioned that λ 2000–2100 occurs in a second general region of absorption and that the failure to obtain volatile decomposition products in this region is in agreement with the early work of Henri and co-workers.[14]

Summary

1. A study of the volatile decomposition products obtained in the photolysis of acetaldehyde has been made. The products are methane, hydrogen and carbon monoxide *only*.

2. A detailed study of the hydrogen to carbon monoxide ratio has been made in a series of experiments in which pressure, intensity of radiation, temperature and wave length were in turn made the variable. This ratio was found to decrease with increase in pressure; to increase with increase in intensity; to increase with decrease in wave length; and to go through a maximum at about 30° when temperature was varied.

3. A tentative chain mechanism of photolysis similar to that given by Leermakers for elevated temperature decomposition has been proposed.

4. The experimental results indicate that there is a close correlation between the volatile and the so-called polymerization products and that in order to arrive at the correct interpretations of aldehyde photodecomposition more must be known about the resinous material which is formed.

LOS ANGELES, CALIF. RECEIVED MARCH 9, 1938

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[14] Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913); Henri and Bielecki, *ibid.*, **155**, 456 (1912).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Inorganic Phosphors without Metallic Activator

BY WILLIAM H. BYLER

Introduction

The fluorescence of teeth suggests the existence of a type of fluorescent substance differing from the more familiar phosphor resulting from firing a salt with a small amount of foreign metal as activator. Following this suggestion, Glasser and Fonda[1] found that a co-precipitated mixture of calcium phosphate and tartrate developed fluorescence similar to that of teeth upon firing at 400°. This result appears to be particularly significant because it indicates that a foreign anion may serve as activator. Continuing this work, it was found by the writer that a phosphor with luminous intensity about equal to that of the phosphate–tartrate mixture could be made by treating calcium phosphate with phosphoric acid and firing at 400°. An attempt is made in this paper to correlate these types of fluorescent calcium phosphate and to show their relation to phosphors prepared by heat treatment of other salts and salt complexes.

Phosphors from Heat Treatment of Simple Compounds.—Light is thrown on the mechanism of phosphor formation in mixtures of salts by study of phosphors formed from simple compounds. A few compounds which could be expected to produce on heat treatment a complex made up of different compounds or different crystal forms were selected. Most of the products showed fluorescence in the visible region in response to the 3650 Å. line of mercury radiation. The hydrates of zinc sulfate, magnesium sulfate, and strontium chloride developed fluorescence when heated at temperatures which effect partial dehydration. In this type of preparation the fluorescence is reduced by overheating. Barium chloride was made fluorescent by heating it above its transition temperature. The hydroxides of aluminum, calcium, and mag-

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[1] J. Glasser and G. R. Fonda, THIS JOURNAL, **60**, 722 (1938).