under the reaction conditions. It is significant to note that much greater amounts of 1,1-dichlorocyclopropane are formed in the photochemical runs than in the thermal experiments. This may be due to inherent thermal instability of the dichloro compound itself or of the 1-chlorocyclopropyl free radical $(CH_2)_2\dot{C}Cl$ which is a probable intermediate in the formation of 1,1-dichlorocyclopropane. Studies of the thermal stability of the cyclopropyl halides should be of considerable aid in deciding this point.

Acknowledgment.—The authors are pleased to acknowledge the aid of Drs. W. G. Young and M. J. Schlatter to this investigation. One of us (P. H. D.) wishes to thank the Dow Chemical Company for a fellowship grant in support of this work.

Summary

1. The photochemical and thermal chlorinations of cyclopropane have been investigated as means for the practical preparation of cyclopropyl chloride.

2. Comparable yields of monohalide are obtained by both methods but the photochemical process is preferred because the product from the thermal reaction is contaminated with considerable amounts of allyl chloride.

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

The Photolysis of the Aliphatic Aldehydes. XII. Propionaldehyde

BY W. J. BLAEDEL AND F. E. BLACET

In the first paper of this series, quantum yields of propionaldehyde photodecomposition and polymerization were reported in considerable detail and a mechanism for the decomposition was proposed based upon limited quantitative data concerning the reaction products.[1] Since that time improvements have been made in analytical techniques which, when applied to acetaldehyde photolysis, have led to considerable change in our conception of aldehyde photochemical processes.[2] These analytical methods now have been applied also to the photolysis products of propionaldehyde.

Experimental Results

The Non-condensable Products.—These were the products which remained in the gaseous phase at Dry Ice temperature. They consisted of hydrogen, carbon monoxide and ethane. No unsaturated hydrocarbons were found although numerous tests were made for them. Proof that the hydrocarbon was pure ethane is given in Table I. It made no difference what the conditions of irradiation were or which gas fraction pumped from the Dry Ice trap was taken for analysis; the ratio a/b obtained from combustion was always equal within experimental error to the theoretical ratio, 1.25, for pure ethane. Before combustion, carbon monoxide was removed by silver oxide and hydrogen by copper oxide and potassium hydroxide.

The number of moles of hydrogen and ethane per mole of carbon monoxide produced under a variety of experimental conditions are given in Table II. Each analytical result given is the average of from two to four determinations. The light source was an intense mercury arc used in conjunction with a crystal quartz monochromator.

TABLE I

COMBUSTION DATA SHOWING ETHANE TO BE THE ONLY HYDROCARBON PRODUCED IN PROPIONALDEHYDE PHOTOLYSIS

Experiment	Vol. sample, cu. mm.	Vol. sample + O_2	Vol. after combustion and P_2O_5	Vol. decrease (a)	Vol. after KOH	Vol. decrease (b)	Ratio a/b
1	26.47	198.43	141.53	56.90	96.83	44.70	1.27
	41.62	244.70	156.60	88.10	86.83	69.77	1.26
	27.04	231.69	176.06	55.63	131.79	44.27	1.26
2	24.62	183.67	126.22	57.45	80.85	45.37	1.26
3	47.04	261.21	155.36	105.85	72.03	83.33	1.27
4	50.06	271.09	162.49	108.60	76.87	85.62	1.27
	47.54	256.73	153.52	103.21	71.89	81.63	1.27
5	48.90	267.92	163.20	104.72	77.99	85.21	1.23
	48.65	266.32	160.46	105.86	74.43	86.03	1.23
6	35.13	219.92	140.09	79.83	76.89	63.20	1.26
7	33.73	247.75	173.96	73.79	113.14	60.82	1.22
	33.21	248.04	174.44	73.60	114.43	60.01	1.23
						Average ratio	1.253
						Ethane ratio	1.250

Figure 1 shows graphically the extent of variation in hydrogen to carbon monoxide and ethane to carbon monoxide mole ratios found when pressure, intensity of radiation, temperature, and wave length in turn were made the variable, keeping the other three constant.

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

[2] (a) Blacet and Volman, *ibid.*, **60**, 1243 (1938); (b) Blacet and Blaedel, *ibid.*, **62**, 3374 (1940).

TABLE II

MOLES OF HYDROGEN AND METHANE PRODUCED PER MOLE OF CARBON MONOXIDE IN THE PHOTOLYSIS OF PROPIONALDEHYDE UNDER VARIOUS EXPERIMENTAL CONDITIONS

Temp., °C.	C_2H_5CHO, moles/liter	Wave length, Å.	Intensity, relative	H_2, moles	C_2H_6, moles
25	0.00376	2380	1.00	0.079	
25	.00376	2537	1.00	.060	
25	.00376	2654	1.00	.056	0.82
25	.00376	2804	1.00	.053	
25	.00376	3130	1.00	.045	
25	.00376	3340	1.00	.039	.83
25	.00376	2654	0.73	.056	
25	.00376	2654	0.44	.056	.83
25	.00169	2654	1.00	.055	
25	.00752	2654	1.00	.054	
25	.0111	2654	1.00	.055	.83
−10	.00376	2654	1.00	.023	
0	.00376	2654	1.00	.044	.82
50	.00376	2654	1.00	.053	
65	.00376	2654	1.00		.83
75	.00376	2654	1.00	.044	
99	.00376	2654	1.00	.022	
110	.00376	2654	1.00	.020	.83
145	.00376	2654	1.00	.011	
180	.00376	2654	1.00	.011	

The Condensable Products.—The photodecomposition of the aldehydes is accompanied by resin formation, or polymerization, for which quantum yields have been reported.[1] The theory of decomposition indicates that several condensable products of lower molecular weight might be formed; and in acetaldehyde photolysis formaldehyde, glyoxal, and diacetyl actually are produced.[2b] An attempt was made to isolate these or analogous compounds from the material which could be condensed in a Dry Ice-bath from propionaldehyde photolysis. In order to obtain sufficient condensate for analysis the quartz reaction chamber was irradiated with the full force of the arc for a total of 190 hours. Periodically the photolysis products were collected and the chamber filled with fresh aldehyde vapor.

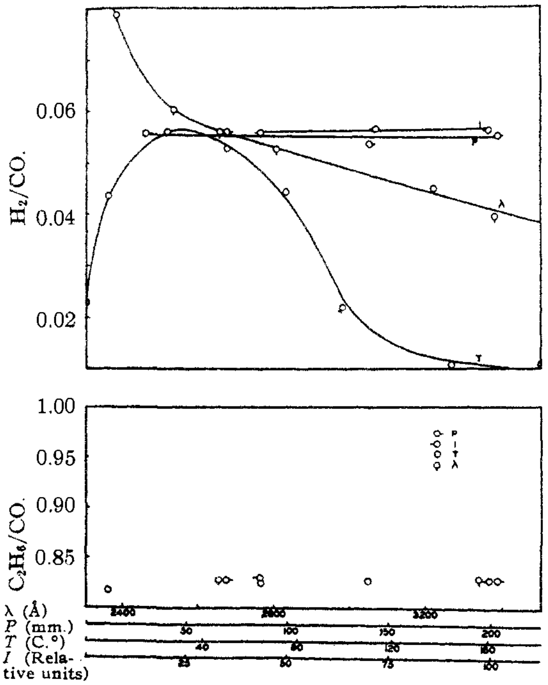

Fig. 1.—Variations of the hydrogen-to-carbon monoxide ratios and the ethane-to-carbon monoxide ratios in propionaldehyde photodecomposition with wave length, λ (Å); pressure, *P* (mm.); temperature, *T* (°C.); and relative intensity of irradiation, *I*.

Formaldehyde was found to be present in the condensate by using a colorimetric method which has been shown to be reliable in the presence of large ratios of propionaldehyde and other aldehydes.[3] Glyoxal was found to be present in small amounts by conversion to the 3-nitrobenzohydrazone by a procedure described previously.[2b] An attempt to determine dipropionyl in the condensate by conversion to the diethylglyoxime in a manner similar to that in which diacetyl is converted to dimethylglyoxime[2b] gave negative results. Subsequent tests have shown, however, that dipropionyl does not behave in a manner similar to diacetyl in this respect, and therefore it cannot be stated at this time that this compound is or is not a propionaldehyde photolysis product. In this experiment the non-condensable products were determined also and all results are summarized in Table III.

TABLE III

SUMMARY OF PHOTODECOMPOSITION PRODUCTS FOUND AFTER EXPOSURE OF PROPIONALDEHYDE VAPOR TO TOTAL RADIATION OF MERCURY ARC FOR A LONG PERIOD OF TIME

Product	Total moles formed	Moles of product per mole of CO
CO	0.00386	1.00
H_2	.00019	0.049
C_2H_6	.00349	.904
H_2CO	.00017	.044
$(HCO)_2$	.00006	.015

Discussion

The above results are similar in many ways to those obtained in a like study of acetaldehyde[2] and indicate that the mechanisms of photodecomposition are the same and differ only in degree for the two aldehydes. However, to establish the mechanism of acetaldehyde decomposition with reasonable certainty it was necessary to study mixtures of the aldehyde vapor with iodine vapor in order to establish the extent of free radical formation as a primary reaction.[4] Until similar studies have been performed with propionaldehyde, and a more exhaustive study of the photolysis condensable products have been made, it is thought best not to give an extensive discussion of the results reported herewith. It is planned to carry out these experiments when conditions again permit this type of research.

Summary

1. A study has been made of the gaseous photolysis products of propionaldehyde. These were found to consist solely of hydrogen, carbon monoxide and ethane.

2. Using λ2654 and keeping other factors constant the H_2/CO mole ratio obtained in photolysis was studied over a temperature range of −10 to 180°. This ratio was 0.023 at −10°, it

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(3) Blaedel and Blacet, *Ind. Eng. Chem., Anal. Ed.*, **13**, 449 (1941).

(4) (a) Blacet and Heldman, THIS JOURNAL, **64**, 889 (1942); (b) Blacet and Loeffler, *ibid.*, **64**, 893 (1942).

went through a maximum of 0.056 at 30°, and decreased to approximately 0.01 in the range 145–180°. With wave length as the variable this ratio decreased from 0.079 at λ2380 to 0.039 at λ3340. With variations of intensity of radiation over a 2-fold range and pressure of aldehyde vapor over a 6-fold range, H_2/CO remained substantially constant at 0.055.

3. The C_2H_6/CO ratio was found to remain constant at 0.083 under all the conditions mentioned in (2) above.

4. A preliminary study revealed the presence of formaldehyde and glyoxal in the products of photolysis condensable at −80°.

5. The results indicate a photolysis mechanism for propionaldehyde similar to that postulated previously for acetaldehyde.

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[CONTRIBUTION FROM THE DIVISIONS OF PHYSIOLOGICAL CHEMISTRY AND OF ORGANIC CHEMISTRY, UNIVERSITY OF MINNESOTA]

Spectrophotometric Studies of the Oxidation of Fats. I. Oleic Acid, Ethyl Oleate and Elaidic Acid[1]

BY RALPH T. HOLMAN,[1] WALTER O. LUNDBERG,[2] WALTER M. LAUER AND GEORGE O. BURR

The course of chemical reactions taking place in the oxidation of fats by molecular oxygen has been the subject of much speculation and investigation. Many mechanisms have been proposed for the oxidation, and many substances have been detected in or isolated from oxidized fats which lend support to the various hypotheses, but little is known with certainty concerning the major intermediates and final products of the reactions. To supplement the existing knowledge of fat oxidations a spectrophotometric characterization of some of the possible products of fat oxidation has been attempted and the observations are presented here.

When carefully rendered lard was allowed to oxidize in air it was found that the ultraviolet absorption was increased greatly, and that the absorption in the region near 2700 Å. was roughly proportional to the peroxide value (Figs. 1, 2). However, when the peroxides were decomposed by blowing with superheated steam the absorption in this region showed an added increase. This indicated that the peroxides formed during the oxidation were not responsible for the absorption band appearing at 2700 Å., in agreement with Farmer's[3] observation that peroxides show only a low general absorption in this region. It should be noted that the 2700 Å. band appearing in most of the curves for oxidized fatty material is smooth, lacking the fine structure characteristic of conjugated trienes. However, this band appears as an inflection on the side of the much stronger band at 2300 Å., and much of the fine structure may be masked.

A study of the absorption spectra of the individual unsaturated fatty acids was begun in an effort to ascertain which of these is involved in the change of absorption spectrum seen upon the oxidation of natural fats. In an attempt to determine what structures among the oxidation products were responsible for the observed increased absorption, studies were made of the spectra of compounds whose structures were identical with or related to possible intermediates in the oxidation of fatty acids. Primary attention was given to compounds that are probable or possible intermediates in the oxidation of the monoethenoic acids. Because some of the products of fatty acid oxidation are capable of enolization, the absorption spectra of all substances were also determined in strongly alkaline solution. In subsequent communications experiments with more highly unsaturated fatty acids will be summarized.

Experimental

The instrument used in these studies was a Beckman quartz spectrophotometer. All determinations were made upon alcoholic solutions except in the cases of glycerides, for which peroxide-free ether was used as solvent. For determinations of spectra in alkaline solution the alcoholic solutions of the samples were added to equal volumes of 20% aqueous potassium hydroxide.

The oxidation of the fatty acids was accomplished by exposing them to air in an oven at 68° in the case of oleic acid and ethyl oleate, and at 63° in the case of elaidic acid. The sample vials were stoppered loosely with cotton to prevent the entrance of dust. In the case of lard, the sample was heated in a boiling water-bath and filtered air was bubbled through it at a constant rate. The decomposition of peroxides was accomplished by heating the samples at 110° for several days in vacuum-sealed ampules.

Peroxide determinations to indicate the progress of the oxidations were made according to King's[4] modification of Wheeler's method, and peroxide values are expressed as milliequivalents of peroxide per kilogram of sample.

The oleic acid[5] used in this investigation had a melting point of 12.5° and a peroxide value of zero; the ethyl oleate[5] a boiling point of 150° at 2 mm., $n^{20}D$ 1.4510, and a peroxide value of zero. The elaidic acid was prepared

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(1) This paper represents part of a thesis presented by Ralph T. Holman to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, June, 1944. The work was aided by grants from the Hormel Research Foundation, the National Live Stock and Meat Board, and the National Dairy Council.

(2) Present address: Hormel Institute, Austin, Minnesota.

(3) E. H. Farmer, H. P. Koch and D. A. Sutton, *J. Chem. Soc.*, 541 (1943).

(4) A. E. King, H. L. Roschen and W. H. Irwin, *Oil and Soap*, **10**, 105 (1933).

(5) Prepared by Dr. F. L. Greenwood.