The Photolysis of the Aliphatic Aldehydes. VIII. Acetaldehyde

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

In this paper are reported results which were obtained in further study of the photolysis products of acetaldehyde. Data on the non-condensable gas products have been extended beyond those previously given,[1] and, in addition, an investigation of the condensable or so-called polymerization products, has been made.

The Non-condensable Products.—The experimental methods used in this part of the work were essentially the same as those described before by Blacet and Volman.[1] A repetition of the H_2/CO vs. temperature study at λ 2654 again gave a maximum hydrogen to carbon monoxide ratio at approximately 30°. By extending the study below 0° it was found that this ratio did not rapidly approach a zero value as the first study indicated, but decreases slowly much in the same way that it does above the maximum.

Determinations of the methane to carbon monoxide ratios under varying conditions of temperature and wave length are given in Tables I and II and in Fig. 2. Each mole ratio given for the gases is the average obtained from between two and four separate analyses. The pressure curve in Fig. 2 was obtained from data of Blacet

TABLE I

VARIATION WITH TEMPERATURE OF HYDROGEN AND METHANE PRODUCED PER MOLE OF CARBON MONOXIDE

Concentration of acetaldehyde 0.00376 M = 70 mm. at 25°; wave length 2654 Å.

Temp., °C.	H₂, moles	CH₄, moles	Temp., °C.	H₂, moles	CH₄, moles
−40		0.74	25ᵃ	0.15	0.93
−30	0.040	.84	35	.14	
−20		.84	50	.098	.95
0	.068	.91	98	.041	.95
13	.095	.92			

ᵃ From data of Blacet and Volman.[1]

TABLE II

VARIATION WITH WAVE LENGTH OF MOLES OF METHANE PER MOLE OF CARBON MONOXIDE

Concn. of acetaldehyde 0.00376 M = 70 mm. at 25°; temp., 25°.

Wave length, Å.	CH₄, moles	Wave length, Å.	CH₄, moles
3340	0.94	2537	0.89
3130	.96	2380	.78
2804	.95	2380	.74
2654	.94	2380	.74

and Volman.[1] Especial attempts to detect ethane in the gas produced at low temperatures gave negative results in every case.

The Condensable Products.—In order to obtain sufficient condensable photolysis products for study in a reasonable length of time direct radiation from a high pressure mercury arc was used. With the aid of a collimating lens the light was passed lengthwise through a 3 by 40 cm. fused quartz absorption tube. This cell was connected to a glass system containing a freeze-out trap, a reserve supply of acetaldehyde and a Toepler pump. The initial aldehyde pressure was about 400 mm. and the exposure time, which was dependent upon the temperature, varied from four to twenty-four hours. Considerable resinous material collected on the walls of the tube during exposure. When the pressure had dropped approximately 100 mm., the condensable material remaining in the vapor phase was collected in a dry-ice trap and the gas which had been produced was collected for measurement and analysis. A new supply of acetaldehyde was then introduced and the process repeated. This was continued until it was considered that enough condensate had been accumulated for study—about one gram in all.

The cell and trap were rinsed successively with three 15-cc. portions of cold water, then with three 15-cc. portions of hot water and the total made up to 100 cc. Remaining after this treatment was considerable residue which reasonably can be assumed to have been polymerized acetaldehyde since the polymers of the other possible products are at least partially water soluble and will respond to the corresponding aldehyde tests. Portions of the water solution were treated for the following substances in the manner indicated in each case.

Diacetyl.—The presence of diacetyl was proved by conversion to the 2,4-dinitrophenylhydrazone and to the dioxime.

The 2,4-dinitrophenylhydrazones of the condensate were prepared by the method outlined by Strain,[2] and fractionally crystallized from nitrobenzene. A drop of the solution was placed on a microscope slide and the solvent allowed to evaporate slowly. At first, large (0.01 mm.) yellow orange, rectangular parallelopiped crystals appeared. These had the same crystalline form as the 2,4-dinitrophenylhydrazone of authentic diacetyl, which in turn has a decidedly different appearance from known needle-like crystals of acetaldehyde, glyoxal and methyl glyoxal derivatives. When washed with ethanol and dried these crystals melted at 313–318°, whereas the accepted melting point of diacetyl 2,4-dinitrophenylhydrazone is 314–315°. After the derivative of diacetyl, large amounts of the acetaldehyde derivative separated from the solution, making it impossible to test in this way for other postulated photolysis products.

To prepare the dioxime, solutions of hydroxylamine hy-

(1) Blacet and Volman. THIS JOURNAL, **60**, 1243 (1938).

(2) Strain. ibid., **57**, 758 (1935).

drochloride and sodium hydroxide were added to a portion of the aqueous extract. On heating this mixture almost to boiling and neutralizing the resulting solution a white crystalline solid was precipitated. This solid melted with partial sublimation at 230°, whereas a sample of Eastman Kodak Co. C. P. dimethylglyoxime melted with partial sublimation at 232°. An alcoholic solution of this solid gave the characteristic red nickel precipitate of dimethylglyoxime when added to an aqueous solution of nickel sulfate in ammonium hydroxide buffered with ammonium chloride. The total amount of diacetyl was estimated by weighing this nickel salt. Acetaldehyde oxime and oximes of the other theoretically possible photolysis products are fairly soluble in this slightly basic solution and do not give colored nickel precipitates under these experimental conditions.

Glyoxal.—On treating portions of the aqueous solution with 3-nitrobenzohydrazide, in the manner described by Strain,[2] and allowing them to stand for a week or more, small white crystals were formed. After washing with alcohol and drying, these crystals melted in the range 335–345°, with some decomposition taking place. They were only very slightly soluble in hot nitrobenzene. Strain reports the glyoxal derivative of 3-nitrobenzohydrazide to be slightly soluble in hot nitrobenzene and to melt at 339.5–340.5°. The other carbonyl compounds which were, or might have been, in the solution either do not give precipitates with this reagent or give derivatives with distinctly different properties.[2] The quantity of glyoxal produced in photolysis was estimated by weighing the 3-nitrobenzohydrazone.

Methyl Glyoxal.—This compound will form a water insoluble 3-nitrobenzohydrazone (m. p. 288.5°) which is appreciably soluble in hot nitrobenzene. Since, within the limits of experimental error, there was no decrease in weight of the 3-nitrobenzohydrazide precipitate when it was treated with hot nitrobenzene, it may be considered that no methylglyoxal was produced in photolysis.

Formaldehyde.—By a modification of the Schiff test this substance was shown to be present in the condensate. The method, which makes use of a colorimeter, is semi-quantitative in character and will determine formaldehyde and its polymer, trioxymethylene, in the presence of the higher aldehydes of the series, and in the presence of diacetyl and glyoxal. A careful study of the photolysis residue which did not dissolve in hot water showed that it contained no trace of formaldehyde polymer. Details of the analytical method will be published elsewhere.

Acetone.—The first drop of liquid obtained from direct micro fractionation[3] of the yellow photolysis product obtained at room temperature had a boiling range of 86.5–87° (b. p. of diacetyl, 87.5–88.0°). Experimenting with pure substances it was found that a mixture of 10% acetone and 90% diacetyl in microfractionation gives a first drop boiling at 72–73°, while 5% acetone and 95% diacetyl gives a first drop which boils at 78–79°. From this evidence it can be stated with reasonable assurance that in these experiments acetone was not a photolysis product of acetaldehyde.
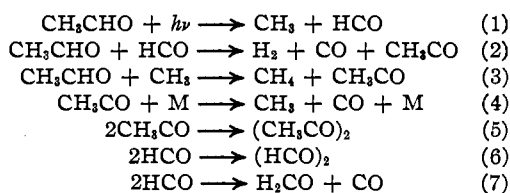
In Table III is given the relative number of moles of each product which has been found to result from acetaldehyde photolysis at three temperatures and using the full radiation from a high pressure mercury arc. One mole of carbon monoxide is used as a standard of comparison in each case.

TABLE III

RELATIVE NUMBER OF MOLES OF ACETALDEHYDE PHOTOLYSIS PRODUCTS BASED ON UNIT CARBON MONOXIDE AS A STANDARD OF COMPARISON

Temp., °C.	Carbon monoxide	Hydrogen	Methane	Diacetyl	Glyoxal	Formaldehyde
25	1.00	0.063	0.87	0.084	0.014	0.018
60	1.00	.049	.92	.012	.0076	.0022
102	1.00	.033	.94	.007	.000	< .0015

Discussion of Results

For the purposes of discussion it may be stated that the following reactions appear important in explaining the experimental results which we have obtained

$$CH_3CHO + h\nu \longrightarrow CH_3 + HCO \qquad (1)$$
$$CH_3CHO + HCO \longrightarrow H_2 + CO + CH_3CO \qquad (2)$$
$$CH_3CHO + CH_3 \longrightarrow CH_4 + CH_3CO \qquad (3)$$
$$CH_3CO + M \longrightarrow CH_3 + CO + M \qquad (4)$$
$$2CH_3CO \longrightarrow (CH_3CO)_2 \qquad (5)$$
$$2HCO \longrightarrow (HCO)_2 \qquad (6)$$
$$2HCO \longrightarrow H_2CO + CO \qquad (7)$$

Under the experimental conditions employed, M of reaction 4 may be regarded as an acetaldehyde molecule. Particularly because of the work of Gorin[4] on acetaldehyde, one is inclined to add the primary process

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad (1a)$$
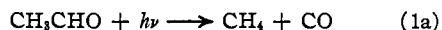
to the above list of reactions but since it contributes nothing to the secondary reactions it seems profitable to concentrate on the processes involving free radicals and see how well they may explain the experimental results given herewith.

The discovery of considerable amounts of diacetyl establishes reaction 5 as an important chain breaker in acetaldehyde photolysis just as it is in the case of acetone.[5] Reactions 6 and 7 are included to account for the glyoxal and formaldehyde which has been found, although it is conceivable that one or both of these compounds may have been formed in a reaction between acetaldehyde and formyl radicals. Reaction 2, involving such a collision, was postulated to account for the hydrogen which is formed in the photolysis,[1] but it must be recognized that in the final analysis we know very little concerning the reactions of the

(3) Benedetti-Pichler and Spikes, "Introduction to the Microtechnique of Inorganic Qualitative Analysis," Microchemical Service, 1935, p. 31.

(4) Gorin, Acta Physicochim. U. R. S. S., 9, 681 (1938).

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

formyl radical. It appears certain that hydrogen, glyoxal and formaldehyde all result from formyl reactions, but what are the processes is an open question. However, by assuming that reactions 2, 6 and 7 consume all the formyl radicals, the data in Table III make it possible to estimate the number of CH_3 and HCO groups formed by reaction 1 for each molecule of carbon monoxide ultimately produced. Such reasoning leads to a chain, involving reactions 3 and 4, of between 5 and 7 cycles at 25°, of about 13 cycles at 60°, and 30 cycles at 100°. It accounts surprisingly well for the amounts of methane and diacetyl which have been found at the various temperatures. It does not require reaction 1a. It does require that the average quantum yield of the *primary process* be much less than has been generally assumed.
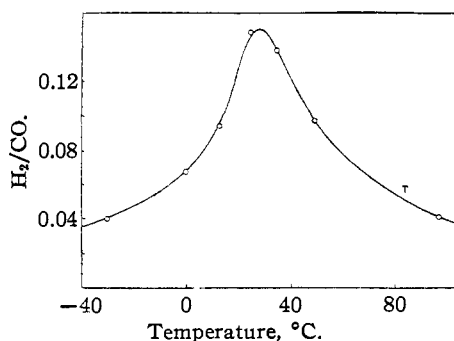

Fig. 1.—Variation of the hydrogen to carbon monoxide ratio in acetaldehyde decomposition with temperature.

The variation of the hydrogen to carbon monoxide ratio with temperature (Fig. 1) is explained by the mechanism given. The rate of reaction 2 increases with temperature but above 30° becomes more and more limited by the primary process. The velocities of reactions 3 and 4, on the other hand, are limited to a large extent at low temperatures by the rate of primary dissociation but become more independent of this factor as temperature is increased and the stability of the acetyl radical decreases. The H_2/CO curve showing a maximum at 30°, represents the net result of these different reactions.

The constancy at 25° of the methane to carbon monoxide ratio with change of pressure (Fig. 2) is to be expected in view of the fact (1) that reactions 2, 3 and 4 each involve a single free radical and one molecule of aldehyde, and (2) reaction 7 only contributes a small fraction of the total carbon monoxide. The decrease of this ratio with temperature below 25° is further indication that

reaction 3 has a high temperature coefficient. Examining only reactions 2, 3 and 4, one can see no reason why both H_2/CO and CH_4/CO should become smaller at lower temperatures since carbon monoxide is affected along with the hydrogen and methane. However, with an increase in free radical stability and hence an increase in radical concentration at the lower temperatures, reaction 7 becomes more important and produces the carbon monoxide necessary to cause the observed drop in the gas ratios. In line with this interpretation is the fact that the formaldehyde to carbon monoxide ratio increases almost ten-fold in the temperature drop from 60 to 25°. It is unfortunate that we do not have this ratio over the range −40° to 25°.
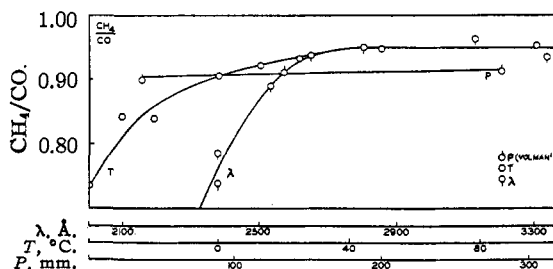

Fig. 2.—Variation of the methane to carbon monoxide ratio in acetaldehyde decomposition with λ, wave length; with T temperature, and with P pressure.

It should be pointed out that the amounts of formaldehyde from acetaldehyde photolysis reported by Gorin[4] are probably too high since he did not take into account the possibility of diacetyl being present. It has been observed in this Laboratory that diacetyl is only very slowly oxidized by ammoniacal silver nitrate but it reacts rapidly with alkaline permanganate solutions. Since these were the reagents used by Gorin, it seems likely that the greater portion of his diacetyl was reported as formaldehyde.

No acetone was detected in the condensable products which were studied but at low temperatures, where it appears reaction 3 no longer uses all of the methyl radicals, it is conceivable that some acetone or methylglyoxal might be formed. This appears especially probable since the absence of ethane in the gaseous products shows that the combination of two methyl radicals does not take place.

Assuming the mechanism given, the decrease in methane to carbon monoxide ratio with wave length (Fig. 2) is in agreement with the decided increase of H_2/CO with decrease in wave length.[1] As the wave length is diminished the quantum

energy in excess of that necessary for the primary process is used to augment reaction 2. However, reaction 3 is only indirectly influenced by the increase of quantum energy since at room temperature all methyl groups have sufficient thermal energy to react with acetaldehyde.

Summary

1. A detailed study of the gaseous photolysis products of acetaldehyde has been made over the temperature range −40 to +98°. Over this range considerable variation was found in the ratios of the non-condensable products, hydrogen, methane and carbon monoxide.

2. An investigation of the photolysis products which are condensable at the temperature of solid carbon dioxide showed the presence of diacetyl, glyoxal and formaldehyde. With respect to carbon monoxide as a standard of comparison, the quantities of these compounds produced decreased markedly with increase of the temperature from 25 to 100°. Tests for acetone and methylglyoxal gave negative results.

3. A discussion of results is given in which the viewpoint is taken that the only primary dissociation process of acetaldehyde photolysis is one in which methyl and formyl radicals are formed.

The State of Monolayers Adsorbed at the Interface Solid–Aqueous Solution

By Frederick M. Fowkes and William D. Harkins

1. Introduction

While the pressure–area (F–A) relations of insoluble films on water have received much attention, and while a small amount of information is available concerning films formed by adsorption at the surface of a liquid or at an interface between two liquids, nothing has been known of these relations at the interface between a liquid and a solid. The work described in this paper was begun with the idea of determining at least a part of the equation of state of such interfacial films, and in an endeavor to answer the question as to whether such films are solid, liquid, or gaseous in the ordinary pressure–temperature region. Since no method was known for determining the F–A relations of such films the first necessary step was to devise such a method, and this will be described later.

The relations have been determined for films adsorbed upon the surface of a solid from an aqueous solution of the adsorbate. The film forming substances used were n-butyl alcohol, n-butylamine, n-butyric acid, propionic acid, acetic acid, and sodium n-butyrate. The films were adsorbed at the interface with cleaved stibnite, cleaved talc, polished graphite, or solidified paraffin wax. It was assumed that the pressure–area relations obtained with the solid paraffin would not be very different from those at the interface between a liquid paraffin and water, and this assumption was found to be justified.

2. Theory of the Method for the Determination of the Pressure of a Film at the Interface Solid–Liquid

Figure 1 represents a vertical cross section of a system solid–liquid, taken perpendicular to the plane surface, under investigation of the solid, with the contact angle Θ. In accordance with
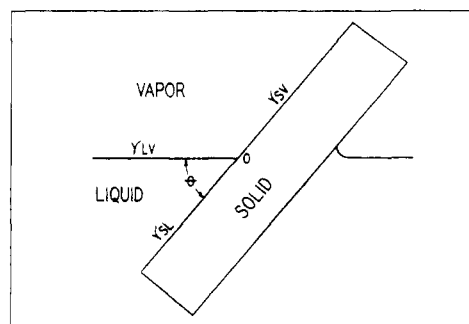

Fig. 1.

the general relations at interfaces it may be assumed that the free energy, γ_{SL}, at the solid–liquid interface is less than that, γ_{SV}, at the phase boundary solid–vapor. Consider that the point O represents the line of contact, perpendicular to the plane of the diagram, between the liquid phase and the solid. If the surface is lowered in its own plane, so that the line O is displaced 1 cm. with respect to the surface of the solid, then the work done by this displacement, neglecting gravita-