

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Chain Photolysis of Gaseous Acetaldehyde

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Recently F. O. Rice and Herzfeld<sup>2</sup> have proposed chain mechanisms for the thermal decompositions of a number of organic compounds; among these was a mechanism for the decomposition of acetaldehyde. Until the work of Allen and Sickman<sup>3</sup> there had been no direct kinetic experimental support of any of these mechanisms. These authors, however, found that by introducing methyl radicals into acetaldehyde the latter could be caused to decompose at temperatures where the normal thermal decomposition did not proceed. They established the existence of chains in the decomposition when methyl radicals were present.

It seemed likely that chains might also be initiated in the acetaldehyde decomposition by radicals liberated during the photolysis of the aldehyde. Although there has been some question as to whether radicals are actually formed in this photolysis,<sup>4</sup> the results of the present experiments establish unambiguously that they are produced. None of the many researches on the photodecomposition of acetaldehyde<sup>5</sup> has given indication of its chain character.

It has been found that the photolysis of acetaldehyde at temperatures as low as 100° results in the establishment of chains, and that at 310° the chain length, under certain of our conditions, is as great as 300. The over-all activation energy of the thermal reactions taking part in the chains has been determined over a 230° temperature range and the data have been found to lead to a satisfactory kinetic expression for the decomposition. The results substantiate markedly the general predictions of Rice and Herzfeld for this particular reaction.

## Experimental

The procedure has been to illuminate acetaldehyde with approximately monochromatic light of wave length 3130 Å. at temperatures from 25 to 310°. In most of the experiments only 2% of the aldehyde was decomposed. This was done to avoid possible side reactions with the

products and to ensure that during the course of an experiment conditions of light absorption and concentration would be constant. The amount of decomposition was quite accurately measured by determining the volume of carbon monoxide resulting from the reaction.

Apparatus.—The apparatus is sketched in Fig. 1. The quartz reaction cell, A, 2.5 cm. in diameter and 9.0 cm. between the plane windows, was contained in the furnace B. This was fitted with two quartz windows C and C' to allow the light to pass through the cell. Suitable diaphragms immediately in contact with the windows of the cell prevented distortion of the light where the windows were sealed to the cell. The furnace temperature was read directly on a thermometer, and was manually controlled and held constant to at least one degree during the course of an experiment.

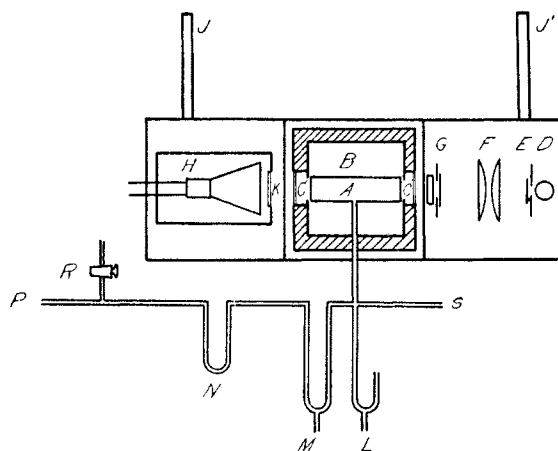


Fig. 1.—Diagram of apparatus.

The rest of the optical system was mounted on a movable stage which slid on the grooved tracks J and J'. When the stage was moved outward from the furnace, the latter was completely out of the light path. The position of the stage at each end of the tracks was accurately reproducible. The light source D was a Cooper-Hewitt, vertical type, quartz mercury arc. It was usually run at 3.5 amperes and 70 volts. E is a diaphragm, 0.6 cm. in diameter, to which was attached a shutter which was operated by remote control. F is a quartz condensing lens whose focus was about the rear window of the reaction cell. G is a diaphragm which also supports the filters. These consisted of a 0.001 N solution of potassium chromate contained in a quartz cell with plane windows, and a section of Corning glass red-purple Corex A. This combination was found by spectrographic examination to transmit almost all of the 3130 Å. line and little of the 3022 and 3342 Å. lines. It did not transmit the other lines in the visible or ultraviolet. Probably 90% of the total light transmitted was 3130 Å. H is a Moll surface thermopile, equipped with horn.

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(2) Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).(3) Sickman and Allen, *ibid.*, **56**, 1251 (1934).(4) See Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934), for a discussion of the evidence.(5) For leading references, see Leighton and Blacet, *THIS JOURNAL*, **55**, 1788 (1933).

which collected all of the light passing through the cell. It was contained in a wooden box fitted with a quartz window K. The thermopile was connected to a Leeds and Northrup high sensitivity galvanometer with scale at 1 meter distance. The galvanometer deflections were from 10 to 50 cm. in almost all of the measurements.

The reaction cell A led to a quartz spiral manometer of the Bodenstein type at S, to the mercury cut-off L which was connected to the acetaldehyde supply, and to the cut-off M. Beyond M was a liquid air trap N which led to a Toepler pump at P and to the stopcock R which opened to the usual high vacuum line. Pressures in the cell were read through the quartz gage on an accurate mercury manometer.

The gases not condensed in liquid air were analyzed by means of a micro gas-analysis apparatus described by Blacet and Leighton.<sup>6</sup>

**Procedure.**—The purpose of the sliding optical system was to provide a means of determining the intensity of light entering the cell at any desired time. The stage was moved out from the furnace and the intensity measured in terms of the galvanometer deflection. The intensity was then measured with the stage in its normal position and with the cell evacuated. The ratio of these two galvanometer deflections was found to be 0.475 and remained constant within one per cent. during all of the measurements here reported. This latter fact is evidence that no solid products condensed on the windows of the cell during the measurements. When the incident intensity was desired it was only necessary to measure the intensity with the stage pushed out, and to multiply this by 0.475. In conjunction with the measurement obtained with the stage in place and the cell filled with acetaldehyde, the amount of light absorbed could be calculated. The mercury arc was always run for an hour before measurements were made and after this period of time was found to hold very constant.

It was found that at temperatures above 200° the amount of infra-red radiating from the furnace was so great that the thermopile could not be used with the stage in its normal position. The intensity of light entering the cell was therefore determined as outlined above, and the amount of light absorbed by the acetaldehyde was calculated on the assumption that the molal absorption coefficient of acetaldehyde was independent of temperature. This was found to be true between 20 and 200°, where the absorption could be measured.

In making an experiment, the cell was evacuated and the furnace brought to the desired temperature. The incident intensity was measured, the mercury let into the cut-off M and acetaldehyde introduced into the cell at the desired pressure. The absorption was measured and the illumination started. After irradiation the stopcock R was closed and liquid air placed around the trap N. Upon lowering the mercury in M, the vapors condensed in the cold trap and the non-condensed gases were pumped by means of the Toepler pump into a capsule in the gas analyzer. The gases were freed of acetaldehyde by means of a bead of fused potash and then analyzed for carbon monoxide by using solid silver oxide as reagent.

(6) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931); **5**, 272 (1933).

**Calibration of the Apparatus.**—The absolute intensity of light, and the total number of einsteins per second (assuming for simplification that all of the light was 3130 Å.) passing through the cell was determined in terms of cm. galvanometer deflection by decomposing acetaldehyde at 200 mm. pressure at 30°. Leighton and Blacet<sup>5</sup> have found the quantum yield of this photolysis under these conditions to have an average value of 0.208. Since by coincidence the absolute intensity of light entering the cell was within 20% of that employed by them, this choice of actinometer seems justified. It was found that 1 cm. deflection of the galvanometer was equivalent to  $2.9 \times 10^{-10}$  einsteins per sec. entering the cell. Assuming a uniform beam of light, this is equal to  $7.12 \times 10^{-12}$  einsteins per cc. per sec. entering the cell for each cm. of galvanometer deflection. The volume of the cell was 40.7 cc. It should be pointed out that this means of calibration of the system eliminates all corrections for reflection, etc. Since the entire system was unchanged during the course of the work, the absolute values found for different experiments should be strictly comparable.

### Experimental Results

**Products of the Reaction.**—At 309°, under conditions of high and low light intensity, and high and low pressure of acetaldehyde, the percentage of carbon monoxide in the gaseous products was  $48.5 \pm 0.1$ . This percentage remained the same even after long contact of the gas with silver oxide. At 83° the apparent percentage of carbon monoxide was 52.9 after long contact of the products with the silver oxide. Since silver oxide adsorbs hydrogen slowly, and since 50% is the maximum amount of carbon monoxide whether the decomposition yields methane or ethane and hydrogen, it seems safe to conclude that the added 3% is hydrogen. This is in accordance with the results of Leighton and Blacet,<sup>7</sup> who found about 5% of hydrogen among the products of the photolysis of propionaldehyde at 30°. It can be concluded that for large chain lengths the products are almost entirely carbon monoxide and methane, while for very short chains (around 2) there is a small amount of hydrogen formed.

**Kinetics of the Reaction.**—The experimental data are collected in Table I. Every experiment performed except the first, where the temperature varied by 4° during the run, has been included in the table. Since the experiments at 25° were used to calibrate the apparatus, and consequently are not independent of the rest, they have been excluded.

The first column gives the pressure of acetaldehyde in the cell; the second, the temperature;

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

TABLE I.

$P$ , mm.	$T$ , °	$l$ , sec.	CO, cc.	$I_0$	$A$	$k' \times 10^6$	$k$
23.0	310	592	0.1945	20.20	0.0615	12.9	179
12.7	309.5	1050	.1448	19.85	.0337	13.2	183
81.4	308	133	.2870	19.65	.198	13.5	187
177.5	309.5	50	.3145	19.65	.381	12.9	179
147.2	309.5	51	.2463	18.82	.329	13.1	181
49.0	309.5	185	.1938	18.82	.1245	13.9	192
105.9	309.5	213	.2062	1.65	.250	14.2	196
102.1	309	121	.1922	5.11	.242	14.0	194
113.0	309.5	100	.2315	9.21	.264	13.1	181
103.5	309.5	89	.2595	20.05	.245	12.7	176
100.6	286	115	.2395	19.50	.248	9.42	126
104.9	286	96	.2120	19.50	.258	9.29	124
104.0	263	167	.2685	20.00	.265	6.70	85.3
103.6	263	170	.2660	20.00	.264	6.59	83.9
96.5	239.5	255	.2515	19.15	.257	4.61	56.1
102.8	240	250	.2650	19.15	.271	4.54	55.3
103.4	218	241	.1768	18.81	.284	3.16	36.8
105.2	218	265	.1968	18.81	.289	3.02	35.2
100.7	190	525	.2235	20.22	.291	1.74	19.2
98.0	191	420	.1710	20.22	.285	1.73	19.1
93.1	162.5	750	.1642	19.35	.287	0.995	9.75
97.8	162.5	790	.1840	19.35	.300	.986	9.73
100.5	126.5	1875	.2148	19.25	.314	.441	3.70
92.9	117	2569	.2080	18.25	.315	.363	2.75
93.4	83	4625	.1658	19.00	.334	.153	0.83
96.0	83	4760	.1682	19.79	.338	.143	.73

the third, the exposure time; the fourth, the cc. of carbon monoxide measured at room temperature and atmospheric pressure; the fifth, the incident light intensity in cm. galvanometer deflection; the sixth, the fraction of light absorbed by the acetaldehyde. The last quantity was either measured directly or was calculated for temperatures above 200°.

An examination of the data for the experiments at 309.5° indicated that the results could be represented by the equation

$$\frac{d(\text{CO})}{dt} = k' \sqrt{I_{\text{abs.}}} (\text{CH}_3\text{CHO})$$

where  $I_{\text{abs.}}$  is the product of the quantities given in columns 5 and 6. Column 7 gives the values of  $k'$  so calculated, where the units are those given in the first six columns. In order to convert these constants to those having the more fundamental units moles per cc. and einsteins per cc. per sec., the following relationships were employed: no. of moles per cc. of acetaldehyde =  $P_{\text{mm.}}/T \times 1.602 \times 10^{-6}$ ; one cc. CO as measured =  $1.019 \times 10^{-6}$  mole per cc. in reaction cell;  $I_{\text{abs.}}$  in einsteins per liter per sec. =  $7.12 \times 10^{-12} \times I_0 \times A$ . From these,  $k$ , sec.<sup>-1/2</sup>, cc.<sup>1/2</sup>, einst.<sup>-1/2</sup> =  $k' \times 2.375 \times 10^4 \times T$ , where  $T$  is the absolute temperature. Column 8 gives the values so calcu-

lated for the experiments above 162.5°. The experiments below 191° will be discussed later.

In the experiments at 309.5° the pressure of acetaldehyde was varied 14-fold and the incident light intensity 12-fold. During these variations the value of  $k$  can be seen to remain substantially constant. The 12% drift in  $k$  during the variation of the light intensity is to be compared to the 3.5-fold change which would be expected if the rate were proportional to the first power of the light absorbed. In general, the rate is well represented by the equation. The results indicate that the assumption of uniform light absorption throughout the cell does not introduce appreciable error when the absorption is as low as 30%.

A plot of  $\log k$  against  $1/T$  for the experiments at temperatures above 162.5° gives a very straight line. At temperatures below this, however, the curve bends up in such a way that the calculated constants become increasingly greater with lower temperature than the values extrapolated from that line. At these lower temperatures the chain length is approaching the value unity, and since  $k$  is interpreted as an over-all rate constant for the chain reaction alone, it is necessary to take account of the part of the total photolysis which is not due to the chain. At these lower temperatures the rate becomes

$$\frac{d(\text{CO})}{dt} = 0.3 I_{\text{abs.}} + k \sqrt{I_{\text{abs.}}} (\text{CH}_3\text{CHO})$$

Here, the term  $0.3 I_{\text{abs.}}$  is the amount of carbon monoxide produced per second by the photolysis which is not part of the chain. The factor 0.3 is used since Leighton and Blacet<sup>5</sup> found a quantum yield of about 0.3 for acetaldehyde at 100 mm. and room temperature. It is assumed that this value is independent of temperature. This assumption can be interpreted as stating that about 0.7 of the absorbed light is effectively lost by the known fluorescence and perhaps by some sort of deactivation of the activated acetaldehyde molecules, and that these two factors are independent of temperature. There is no *a priori* reason to doubt that this is true of the fluorescence, since this probably has to do with an electronic transition which would be unaffected by temperature. The values of  $k$  calculated on the assumptions just discussed are given in column 8. A plot of  $\log k$  (where  $k$  is the average for a given temperature) against  $1/T$ , using all of the constants given in column 8, is shown in Fig. 2. The solid circles above the straight line are the values of  $k$  uncor-

rected for the  $0.3 I_{\text{abs.}}$ . The fact that the line passes through all of the points indicates that the assumption of a temperature-independent "fluorescence factor" is justified. The straight line gives an activation energy of 10,000 calories per mole for the over-all chain reaction, and

$$k = 1 \times 10^6 e^{-10,000/RT}$$

An extrapolation to room temperature leads to a value of  $k$  about 0.03.

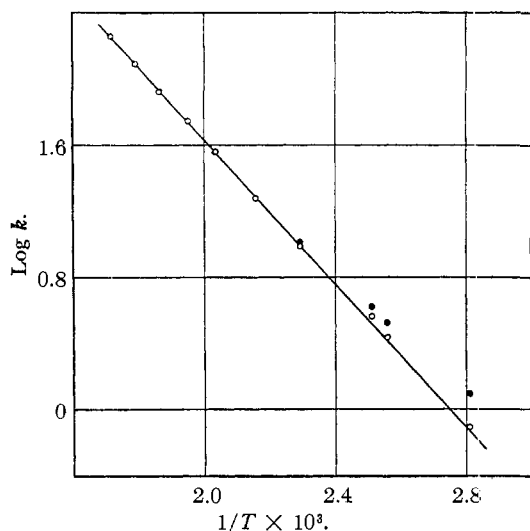


Fig. 2.—Plot of  $\log k$  against  $1/T$ .

The quantum yields  $\varphi$  for the chain reaction can be calculated directly from the constants given in Table I.

$$\varphi = \frac{d(\text{CO})}{dt} \times \frac{1}{I_{\text{abs.}}} = \frac{k(\text{CH}_3\text{CHO})}{\sqrt{I_{\text{abs.}}}}$$

where  $(\text{CH}_3\text{CHO})$  and  $\sqrt{I_{\text{abs.}}}$  are in moles per cc. and einsteins per cc. per sec., respectively. Thus, the experiment at  $309.5^\circ$  and the lowest intensity gave a quantum yield of 310. At the intensity used in most of the experiments at  $309.5^\circ$ , the yield was about 90. At  $117^\circ$  the chain quantum yield was 1.5, while at  $25^\circ$  it is calculated to be 0.03. The fact that the chain yield at room temperature is negligible accounts for the failure of other experimenters to recognize the chain nature of this photo-decomposition.

In order to express  $k$  in terms of moles per cc. per sec. of acetaldehyde decomposed in the primary act—that is, in terms of moles per cc. per sec. of methyl or formyl radicals so produced—it is necessary to take account of the factor of 0.7 which represents the fraction of the light absorbed which does not result in decomposition. The

values of  $k''$  will become 1.8 times as great as those given in column 8 of Table I, and

$$k'' = 1.8 \times 10^{-10,000/RT}$$

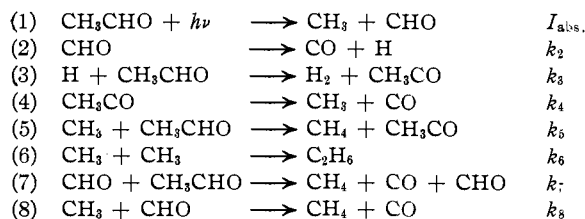
Further, the chain lengths per radical formed (assuming that only one of the radicals carries the chain) will be 3.3 times as great as the quantum yields.

### Discussion

The rate expression found to fit the data is

$$\frac{d(\text{CO})}{dt} = \frac{-d(\text{CH}_3\text{CHO})}{dt} = 0.3 I_{\text{abs.}} + k \sqrt{I_{\text{abs.}}} (\text{CH}_3\text{CHO})$$

It is possible to derive this expression by the combination of a number of plausible reactions. We will write most of the reactions which Rice and Herzfeld<sup>3</sup> postulate for acetaldehyde, and include several others not given by them.



The experiments here reported establish the authenticity of the primary photochemical dissociation into radicals. No other reactions will explain the long chain here observed. Leighton and Blacet<sup>5</sup> postulated reaction 1, while Norrish<sup>4</sup> considers the photolysis of aldehydes to be due to the liberation of carbon monoxide and hydrocarbon without the intermediate existence of the radicals. Leighton and Blacet<sup>7</sup> found that in the photolysis of propionaldehyde there was formed an appreciable amount of hydrogen. This could come from some recombination of HCO radicals. It is possible that there are two modes of decomposition of aldehydes, one resulting in radicals, the other in carbon monoxide and hydrocarbon directly. The fact that the long wave length limit of the predissociation region in acetaldehyde approaches a value of about 80 Cal., which is near the value 77 Cal. for the energy of the carbon-carbon bond,<sup>8</sup> indicates that light absorption in this region causes a rupture of the bond to produce radicals.

Reactions 2, 3, 4, 5 and 6 have been postulated by Rice and Herzfeld. Reaction 7 was suggested by Dr. O. K. Rice of this Laboratory as being a very probable chain carrying step, in order to

(8) Kistiakowsky and Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

explain certain differences between the present results and those found by Sickman and Allen. It is a pseudo Walden inversion which may involve the rupture of the molecule during or immediately following the substitution of CHO for CHO. Another possible mechanism of this step could be the replacement of CHO from the acetaldehyde by the hydrogen in the colliding CHO. Carbon monoxide would be liberated. The heat of the reaction  $\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4$ , calculated from combustion data given in the "International Critical Tables," is zero. Reaction 7 can therefore proceed with an activation energy equal to that of the substitution reaction. There are no data for the activation energies of such reactions in the gas phase, but Bergmann, Polanyi and Szarbo<sup>9</sup> have found a value of 16 Cal. per mole for the conversion of methylbutyl iodide by iodide ion in solution. For lack of more relevant data we will quite arbitrarily assume that reaction 7 has an activation energy of 15 Cal. per mole.

Reaction 8 was suggested by Leighton and Blacet<sup>5</sup> to account for the small fraction of hydrogen formed in the photolysis of propionaldehyde. It might be expected to be a more probable reaction than 6; the collision efficiency of such a simple bimolecular reaction as 8 would probably be greater than that of an association reaction such as the recombination of two methyl radicals.

By using reactions 1, 2, 3, 4, 5 and 6 we follow Rice and Herzfeld and arrive at a rate expression which is entirely in agreement with the experimental findings. However, there is no reason to exclude reaction 7 from the mechanism, and 8 is to be preferred to 6. If we consider reactions 1, 4, 5, 7 and 8, and notice that  $(\text{CH}_3) = (\text{CHO})$  at the steady state, we find

$$-\frac{d(\text{CH}_3\text{CHO})}{dt} = I_{\text{abs.}} + \left[ \frac{k_5 + k_7}{\sqrt{k_8}} \right] \sqrt{I_{\text{abs.}}} (\text{CH}_3\text{CHO})$$

which also agrees with the data. If the activation energy of either reaction 5 or reaction 7 is as little as 3 Cal. greater than the other, and if the two reactions have equal collision efficiencies, the chain will be carried almost entirely by the reaction having the lower activation energy. With the present data it is impossible to decide whether each of the two reactions is equally important, or if one predominates.

(9) Bergmann, Polanyi and Szarbo, *Z. physik. Chem.*, **B20**, 161 (1933).

If we assume with Rice and Herzfeld that  $k_5 = 10^9 e^{-15,000/RT}$  and let  $k_7 = 10^9 e^{-15,000/RT}$  and  $k_8 = 10^9 e^{-8,000/RT}$ , we have  $[(k_5 + k_7)/\sqrt{k_8}] = 6 \times 10^4 e^{-11,000/RT}$  in the units of Rice and Herzfeld. The value of  $k''$ , which is the constant to be compared to  $(k_5 + k_7)/\sqrt{k_8}$ , found in this work is  $1.8 \times 10^8 e^{-10,000/RT}$ . Converting to the units of Rice and Herzfeld this gives  $k'' = 1.2 \times 10^4 e^{-10,000/RT}$ . On the assumption that the collision efficiencies of the bimolecular reactions 5, 7 and 8 are the same, the coefficient of the exponential will be unchanged by a different choice of activation energies. The value of the over-all activation energy, however, is the difference between one-half the reaction energy of reaction 8 and the activation energy of either reaction 5 or 7, depending upon which of these two has the lower value. We can therefore obtain no information as to the absolute values of these activation energies, although it is possible to state that the minimum values for reaction 5 and 7 are 10,000 calories per mole.

I wish to express my thanks to Professor G. B. Kistiakowsky and to Dr. O. K. Rice for the interest they have taken in this work. I have also had the privilege of keeping informed on the experiments of Dr. D. V. Sickman and Mr. A. O. Allen.

### Summary

1. The photolysis of acetaldehyde at temperatures above 80° has been found to be a chain reaction.
2. The rate of the photolysis at wave length 3130 Å. is expressed by the equation  $-d(\text{CH}_3\text{CHO})/dt = 1 \times 10^6 e^{-10,000/RT} \sqrt{I_{\text{abs.}}} (\text{CH}_3\text{CHO})$ , where the units are moles per cc. and einsteins per cc. per sec.
3. Quantum yields as great as 300 have been observed at 309.5°, but at room temperature the quantum yield of the chain reaction is only 0.03.
4. Possible mechanisms of the reaction have been discussed. Direct evidence is offered that the primary act in the photolysis of aldehydes is the production of radicals.
5. The results confirm the predictions of Rice and Herzfeld that the thermal decomposition of acetaldehyde is a chain reaction, and agree in absolute value with the rates predicted by them.