[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Photolysis of Acetaldehyde and Ethyl Bromide Mixtures at 310°

BY JACK G. ROOF AND FARRINGTON DANIELS

Many gas-phase reactions of organic compounds at elevated temperatures are known to be chain reactions involving free radicals. One of the best means of studying chain reactions lies in the quantitative determination of the quantum yield in the photochemical reaction. Only a few photochemical reactions have been studied quantitatively at temperatures above 100°.

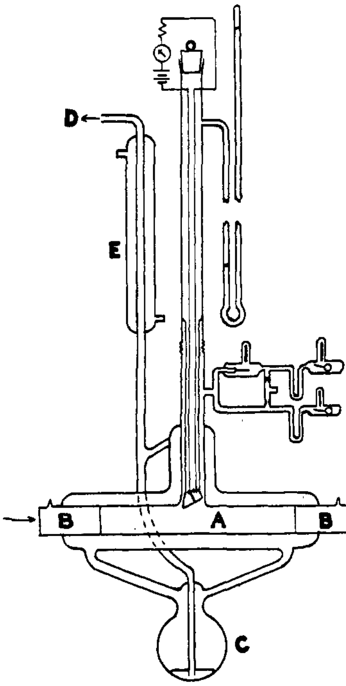

Fig. 1.—Reaction cell surrounded by mercury vapor for measuring pressure changes in photochemical reactions at high temperatures.

The present apparatus was designed to make possible direct, quantitative measurements at high temperatures of photochemical reactions which can be followed by a change in pressure. It has been used to study the photolysis of acetaldehyde which gives a quantum yield of 0.2 to 0.3 at room temperature[1] and several hundred molecules per quantum at 300°.[2] Mixtures of acetaldehyde and ethyl bromide were studied in order to test the theory that ethyl bromide decomposing at this temperature gives free ethyl radicals which can be identified by the initiation of a chain-decomposition of acetaldehyde.

Experimental

Apparatus.—The water-cooled mercury vapor arc and the large quartz monochromator have been described before.[3a,b] A parallel beam of monochromatic light passed through the reaction cell and a thick layer of water H onto a large-area thermopile G as shown in Fig. 1. The water protected the thermopile from the intense infrared radiation emitted by the hot cell. The reaction cell was a double walled all-quartz vessel with an empty cell at each end. The purpose of these evacuated end-chambers B was to provide thermal insulation for the windows and thus help prevent condensation on them. Mercury vapor from the electrically heated boiler C surrounded the reaction chamber A and was condensed and returned at E. The temperature was controlled closely by a barostat indicated at D constructed according to the specifications of Coffin.[4] The vessel was evacuated while hot and the gases were introduced with magnetic hammers at F.

A small part of the reaction vessel (less than 10% of the volume) was heated by a separate air oven the temperature of which was controlled by a bimetallic thermostat regulator. Pressures of the gases were determined through a thin glass diaphragm[5] used as a null-point instrument in an electrical circuit.

Analyses of the gaseous products were made on a microapparatus similar to that of Blacet and Leighton.[6] It has been shown that the amount of carbon monoxide produced is a close measure of the amount of acetaldehyde photolyzed and that the amount of ethylene produced is almost quantitatively equal to the ethyl bromide decomposed. The gaseous product was passed through a trap immersed in a solid-liquid ethyl ether-bath, which gave the lowest, conveniently-attained temperature (−118°) that would remove ethyl bromide, acetaldehyde and hydrobromic acid but would not interfere with the collection of either carbon monoxide or ethylene.

Optical Corrections.—A certain fraction of the light entering the cell is lost due to reflection and scattering and to imperfections in the optical train. This fact tends to complicate the calculation of the energy absorbed by a substance in the cell. A method of approximating the true absorption has been previously worked out[7a,b] for the common cell having only two windows in the light path. This calculation involves the assumption that the light failing to reach the rear window is taken up by absorbing ma-

---

[1] Leighton and Blacet, THIS JOURNAL, **55**, 1766 (1933).

[2] Leermakers, *ibid.*, **56**, 1537 (1934).

[3] (a) Daniels and Heidt, *ibid.*, **54**, 2381 (1932); (b) Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

[4] Coffin, *ibid.*, **55**, 3646 (1933).

[5] Daniels, *ibid.*, **50**, 1115 (1928).

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

[7] (a) Luther and Forbes, THIS JOURNAL, **31**, 779 (1909); (b) Leighton and Blacet, *ibid.*, **54**, 3170 (1932).

terial in the reaction cell. The four windows in the cell with eight reflecting surfaces complicate the derivation and the final correction to be made upon the apparent absorption is the product of several factors which must be determined experimentally for the particular cell.[8]

Preparation of Materials.—Of the various materials used in this work those that had boiling points above 20° were handled as liquids in glass bulblets, which were broken in the sealed-off system by a magnetic hammer. The reagents were purified in an all-glass system and deoxygenated by repeatedly freezing, evacuating and thawing, and then forced into the bulblets with dry carbon dioxide. The contents of each bulblet was partially evaporated under vacuum and cooled before the capillary neck was sealed off in a flash with a hot microflame.

The acetaldehyde was dried over copper sulfate and distilled once or twice at temperatures below 0°. The ethyl bromide was prepared by Timmermans for the U. S. Bureau of Standards. Ethyl iodide was prepared by P. L. Veltman of this Laboratory by the reaction of sodium iodide on ethyl sulfate. Heptane was from a sample prepared by distillation of the Jeffrey pine and purified to give a boiling range from 98.56 to 98.57°. Ethylene was a commercial grade prepared by the Puritan Compressed Gas Corp. It was fractionated near liquid air temperatures. Commercial hydrogen was dried before using.

Results

Photolysis of Acetaldehyde.—In experiments where the acetaldehyde was introduced first it was possible to get the quantum yield of its photolysis at 3130 Å. assuming that the reaction gives two molecules for each one decomposing, mostly methane and carbon monoxide. The results are shown in Table I.

TABLE I

PHOTOLYSIS OF ACETALDEHYDE: CELL 20 CM. LONG, LIGHT 3130 Å.

Temp., °C.	Press., mm.	Absorption, %	Quanta absorbed per sec. $\times 10^{14}$	Molecules decomp. per quantum	Φ, Mitchell and Hinshelwood
311	68	45.1	5.9	102	86
311	112	61.0	4.3	184	166
357	92	52.1	5.1	238	214
357	109	56.9	6.7	250	227

Mitchell and Hinshelwood[9] determined the quantum yield of pure acetaldehyde over a wide range of experimental conditions. Compared to values interpolated from their data, as shown in the last column of Table I, our values are high by a factor of about 1.1 with a mean deviation of approximately 2.4%. Since Mitchell and Hinshelwood have shown that the quantum yield varies inversely as the square root of the absorbed light intensity and since the quantum yield depends on the dimensions of the containing vessel, the difference can be explained on the basis of differences in size and shape of the reaction cells.

Acetaldehyde and Products.—The gaseous products of acetaldehyde decomposition are carbon monoxide, ethane and perhaps methane and hydrogen. Measurements were made on the photolysis of acetaldehyde in the presence of carbon monoxide, of hydrogen and of heptane. In each case the photochemical rate was determined for the aldehyde alone and then the "product" was introduced and the rate redetermined. Only in the case of the hydrogen did the product give a definite change in the quantum yield—a 15% increase when the hydrogen pressure was about 300 mm. and the aldehyde pressure was about 90 mm. Apparent increases of 5 and 3% with heptane and carbon monoxide based on pressure measurements were within the limit of experimental error.

Ethyl Bromide and Acetaldehyde.—A typical pressure curve at 311° is shown in Fig. 2. The acetaldehyde at 223 mm. pressure alone in the dark at A shows no appreciable change in pressure.

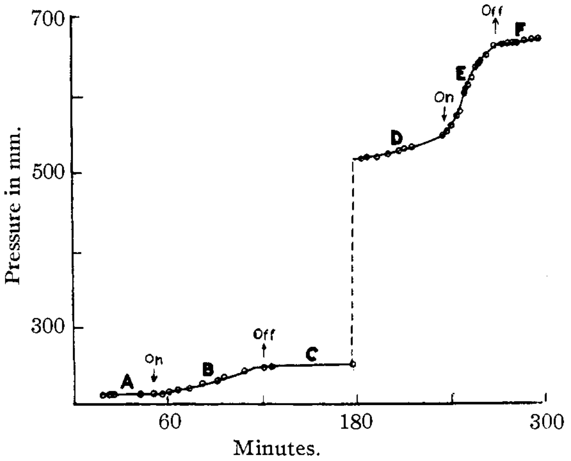

Fig. 2.—Decomposition of acetaldehyde: A, dark; B, light. Decomposition of a mixture of acetaldehyde and ethyl bromide: D, dark; E, light; F, dark.

When weak light of 3130 Å. was admitted at B the pressure increased at the rate of 0.47 mm. per minute due to photolytic decomposition into methane and carbon monoxide. The light was

---

[8] $Q = (1 - L)(1 + 0.1218L)(\log L + 0.146)/\log L$, where Q is the fraction of light entering the reaction cell including the light reflected from the third and fourth windows which is absorbed by the reacting material, and L is the fraction of incident light transmitted after passing once through the gas in the reaction chamber. The details of this and other calculations of the present communication may be found in the Ph.D. thesis of J. G. Roof filed in 1938 in the Library of the University of Wisconsin.

[9] Mitchell and Hinshelwood, *Proc. Roy. Soc.* (London), **A159**, 32 (1937).

turned off at C and 265 mm. of ethyl bromide was added. The pressure rise in the dark at D was 0.9 mm. per minute and on turning on the light at E the rate of pressure increase jumped to 5.5 mm. per minute. At F in the dark the rate of pressure increase was smaller because the materials had undergone considerable decomposition and because there was some polymerization of the product ethylene.

In another similar experiment 95 mm. of acetaldehyde increased at the rate of 1.5 mm. in somewhat more intense light. When 227 mm. of ethyl bromide was added in the dark the pressure rise was 1.1 mm. per minute—and when the light was introduced the pressure increased at the rate of 7.3 mm. per minute.

The fact that the reaction of the mixture in the light was several times as fast as the sum of the acetaldehyde in the light and the mixture in the dark, shows that a new phenomenon is taking place.

When the ethyl bromide was introduced first the decomposition rate was negligible. It was not affected by light because it is transparent in this region.

Similar experiments with acetone and ethyl bromide were unsatisfactory because the effects were small and complicated by polymerization of accumulated ethylene. The photolysis of acetone at high temperatures is not a chain reaction[10] and it was to have been expected that the decomposing ethyl bromide would not affect the decomposition of acetone. The fact that the introduction of free methyl radicals by the photolysis of acetone did not cause a rapid rate of rise in pressure as in the case of acetaldehyde shows that a chain reaction cannot be initiated in ethyl bromide by methyl radicals.

Acetaldehyde and Ethylene.—It has been shown that free radicals from acetone can cause the polymerization of ethylene[11] and so photochemical measurements were made in the present investigation on mixtures of acetaldehyde and ethylene. In one such experiment with a pressure of 60 mm. of acetaldehyde the rate of rise was 0.058 mm. per minute in the dark and 0.22 mm. per minute when light was introduced and back to 0.052 mm. per minute when the light was turned off. When 240 mm. of ethylene was introduced there was a slight decrease in the pressure rise and a marked decrease due to polymerization when the light was introduced. The decrease was such as to indicate an effective decrease of approximately two molecules for each molecule of acetaldehyde decomposing provided that the photolysis of acetaldehyde was proceeding at the same rate as before the ethylene was added. In this experiment the ratio of ethylene to acetaldehyde was 4 to 1 but in the experiments with ethyl bromide such a small fraction of ethyl bromide decomposed that the polymerization of the accumulated ethylene was unimportant in comparison with the decomposition of acetaldehyde and ethyl bromide.

Ethyl Iodide and Acetaldehyde.—Preliminary experiments were made on the reaction of ethyl iodide and acetaldehyde mixtures. Here the dark reaction of the mixture was exceptionally rapid at the lower temperature of 311°. No increase in rate of pressure rise was noted when light of 3130 Å. was used nor when a high intensity Mazda lamp was placed before the cell. A great deal of free iodine was formed during the reaction, as indicated by the increasing violet color of the vapor in the system.

Analyses of Products.—The products from some of the acetaldehyde–ethyl bromide mixtures were collected through a trap at $-118°$ and treated with a potassium hydroxide bead to remove aldehyde. Then analyses were made for ethylene with fuming sulfur trioxide and for carbon monoxide with silver oxide. The accuracy of these particular analyses in the presence of alkanes has been proved in the work of Blacet and Leighton.[6] The average per cent. of carbon monoxide and ethylene in the products is given in Table II.

TABLE II

ANALYSIS OF PHOTOLYSIS PRODUCTS FROM A MIXTURE OF ETHYL BROMIDE AND ACETALDEHYDE AT 355°

	% CO	% C_2H_4
Dark (75 mm. CH_3CHO; 280 mm. C_2H_5Br)	46.8±0.3	5.1±0.5
Light (69 mm. CH_3CHO; 66 mm. C_2H_5Br)	47.1±1.0	2.0±0.1

Discussion

The decomposition of ethyl bromide involves as the first step the formation of an ethyl free-radical and a bromine atom[12a,b] according to the reaction

$$C_2H_5Br \longrightarrow C_2H_5 + Br$$

---

[10] Ackeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

[11] Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

[12] (a) Fugassi and Daniels, THIS JOURNAL, **60**, 771 (1938); (b) Veltman and Daniels, *J. Chem. Phys.*, **7**, 756 (1939).

The following reaction can take place with only a slight heat effect.

$$CH_3CHO + C_2H_5 \longrightarrow CH_3 + C_2H_6 + CO$$

The free methyl radical formed would then be free to continue the decomposition of the acetaldehyde by the following reaction which is exothermic by 1 kcal. according to calorimetric data.[13]

$$CH_3 + CH_3CHO \longrightarrow CH_3 + CH_4 + CO$$

This reaction may be considered as an ordinary catalytic reaction, the CH_3 free radical being absorbed in a temporary complex by the acetaldehyde which then breaks up with a decrease in free energy liberating the CH_3 radical for further reaction. This reaction can continue a long chain identical with that propagated when acetaldehyde is illuminated with ultraviolet light at a high temperature.

It is possible that the bromine atom may initiate a chain of decomposition in the acetaldehyde by the reaction

$$CH_3CHO + Br \longrightarrow CH_3 + HBr + CO$$

but this mechanism is less likely because it is endothermic to the extent of 20 kcal.

Once the thermal chain is started in acetaldehyde by the liberation of a free methyl radical, the reaction is much more rapid than the decomposition of the ethyl bromide and for each ethylene molecule produced from the decomposition of the ethyl bromide there should be many molecules of carbon monoxide produced from the decomposition of the acetaldehyde. Table II shows that this is the case.

To explain the greatly augmented rate of reaction when ultraviolet light is admitted to the mixture, it should be recalled that the quantum yield of aldehydes is well below unity at room temperatures where chains are not possible. In the case of crotonaldehyde the quantum yield is below 0.02.[14] For acetaldehyde it is of the order of 0.2 to 0.3. The 3130 Å. line falls in the diffuse part of the absorption spectrum of acetaldehyde, the theoretical significance of which has been discussed by Leighton and Blacet.[1] Ethyl bromide is transparent in this region. If it is assumed that the efficiency of the primary process is less than unity for acetaldehyde even at these higher temperatures, the results can be readily explained. Some molecules of aldehyde which absorb a photon with energy equivalent to about 91 kcal. per mole at 3130 Å. decompose but others remain as excited molecules. Before this energy of the excited molecules can be degraded thermally it is transferred to some ethyl bromide molecules. The ethyl bromide needs only 55 kcal. to decompose[12] and in decomposing it furnishes ethyl radicals to start new chains in the aldehyde. The mechanism by which the excited acetaldehyde molecules transfer energy to ethyl bromide molecules is uncertain but it must be emphasized that the ethyl bromide molecules are already at a high temperature, so high that thermal decomposition is actually going on. Furthermore, the temperature is so high that inter-atomic vibrations are partly anharmonic and some quantum restrictions may be inoperative.

One might wish to think of an activated complex of ethyl bromide and acetaldehyde which decomposes directly into final molecules without the formation of free radicals and a chain reaction. This mechanism is rendered unlikely, however, by the fact that the photolysis of the mixture is over ten times as fast as the photolysis of the acetaldehyde alone.

The authors are glad to acknowledge a grant from the Research Committee of the Graduate School for the purchase of the special quartz reaction vessel.

Summary

1. A reaction cell for isothermal photochemical reactions at high temperatures is described, which permits the direct determination of the radiation absorbed.

2. The quantum yield of the photolysis of acetaldehyde at 311° and at 357° indicates a long chain in agreement with the findings of other investigators.

3. The photolysis of acetaldehyde–ethyl bromide mixtures has been studied with light of 3130 Å. Mixtures of the two decompose at a measurable rate in the dark at 357° and at a greatly increased rate when illuminated.

4. The dark reaction is explained as being due to the starting of chains in the aldehyde by the pyrolytic products of the ethyl bromide.

5. The photochemical reaction is thought to be due to the transfer of energy from the excited aldehyde molecules to ethyl bromide molecules which then decompose and start chains in the aldehyde.

6. These experimental facts support the view that free ethyl radicals are formed in the thermal decomposition of ethyl bromide.

MADISON, WISCONSIN RECEIVED JULY 15, 1940

---

[13] Bichowsky and Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[14] Blacet and Roof, THIS JOURNAL, **58**, 73 (1936).