a trace of hydrogen is formed, (2) that acetyl iodide is not formed, and (3) that hydrogen iodide is produced in considerable quantity.

6. These results are interpreted to mean that, at λ3130: (1) the formation of free methyl and formyl groups is the only important primary dissociation process, (2) iodine reacts readily with both methyl and formyl radicals, thus stopping all normal secondary processes, (3) iodine does not react readily with activated acetaldehyde molecules, (4) the recombination of methyl and formyl radicals in normal photolysis does not occur to any great extent, (5) the primary dissociation quantum yield, ϕ, equals Φ_{CO} and Φ_{CH_3I}, and is approximately 0.20, and (6) collisional deactivation accounts for a large portion of the total absorbed radiant energy.

LOS ANGELES, CALIF. RECEIVED JANUARY 2, 1942

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

The Photolysis of the Aliphatic Aldehydes. XI. Acetaldehyde and Iodine Mixtures

BY F. E. BLACET AND DONALD E. LOEFFLER

This article pertains to photolysis experiments on acetaldehyde and iodine mixtures in which wave length, temperature and iodine concentration were varied one at a time while other conditions remained constant. The major portion of this work was done at λ2654. Except for a few minor differences, the apparatus and experimental methods employed in the work were the same as given in the preceding article of this series[1] and need not be described here.

Experimental Results

In Tables I and II are given quantum yields of carbon monoxide, methane and methyl iodide production obtained under various conditions. In all runs the acetaldehyde concentration was approximately 1.00×10^{-2} mole per liter and the incident intensity was about 7.0×10^3 ergs per second.

In the presence of 1 mm. or more of iodine vapor the average quantum yield of hydrogen formation was 0.02. It is doubtful if this value is outside the limits of experimental error. Hydrogen iodide was qualitatively detected to be a photolysis product of the mixture. A small amount of condensed material was observed to form in the reaction cell during the photochemical process. This polymer-like material was found to give a positive test for free iodine and for a trace of iodide ion. The amount of free iodine in this substance was small compared to the total amount added to the system and the iodide present probably accounts for the failure to get reproducible results for hydrogen iodide in the condensed vapors. Dark runs at 60° showed no reaction between acetaldehyde and iodine when both substances were in the vapor phase.

In the study of acetaldehyde and iodine mixtures experimental errors were somewhat larger than those obtained in the study of pure acetaldehyde. However, as shown in the accompanying figures, by averaging results obtained for each set

TABLE I

VARIATIONS OF QUANTUM YIELDS WITH IODINE PRESSURE WITH TEMPERATURE AT WAVE LENGTH 2654 Å.

Run	Temp., °C.	Pressure of iodine, mm.	Φ_{CO}	Φ_{CH_4}	Φ_{CH_3I}
1	58	0.24	0.60	0.56	
2	58	.26	.73		0.32
3	58	.30	.60	.35	.22
4	60	.43	.63	.21	
5	58	.43	.70	.41	.07
6	57	.87	.38		.35
7	61	.89	.66	.25	
8	58	1.02	.67	.37	.27
9	57	1.4	.58	.26	.35
10	57	1.7	.52		.20
11	57	1.7	.78	.25	
12	61	1.9	.77	.29	.44
13	57	2.0	.64	.28	
14	58	2.2	.74		.44
15	61	2.4	.68	.24	.43
16	58	2.4	.55	.22	.31
17	60	2.5	.70	.32	
18	100	1.7	.75	.31	.31
19	100	1.6	.61	.28	.18
20	100	1.6	.42	.28	.38
21	125	1.4	.74	.34	.34
22	125	1.8	.71	.30	.49
23	150	1.9	.64	.29	.44
24	150	1.9	.79	.27	.53
25	57	0.0	.78	.79	
26	100	.0	1.25	1.00	
27	125	.0	3.20	2.69	
28	150	.0	5.85	4.53	

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[1] Blacet and Heldman, THIS JOURNAL, 64, 889 (1942).

TABLE II

VARIATION OF QUANTUM YIELDS WITH WAVE LENGTH AT 60°

Run	Wave length, Å.	Pressure of iodine, mm.	Φ_{CO}	Φ_{CH_4}	Φ_{CH_3I}
29	3130	2.2	0.26	0.02	0.19
30	3130	2.7	.19	.01	.27
31	3130	2.1	.25	.02	.27
32	2804	1.5	.46	.13	.44
33	2804	1.2	.54	.17	.43
34	2804	1.3			.43
35	2380	1.3	.68	.39	.41
36	2380	1.5	.56	.35	.37
37	2380	0.0	2.41	2.26	
38	2380	0.0	1.69	1.84	

of experimental conditions curves of considerable significance have been obtained.

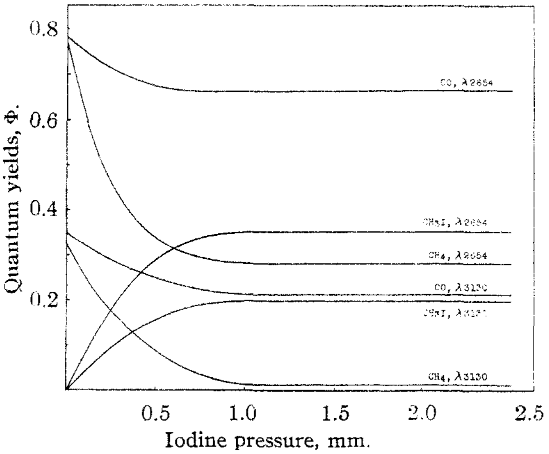

Fig. 1.—Quantum yields *vs.* iodine pressure at λ3130 and λ2654: acetaldehyde pressure, 200 mm.; temperature, 60°.

Discussion

Figure 1 shows the variation at 60° of quantum yields of carbon monoxide, Φ_{CO}, methane, Φ_{CH_4}, and methyl iodide, Φ_{CH_3I}, with initial iodine pressure in the reaction system, for λ2654 and λ3130. The λ3130 values were obtained by Blacet and Heldman.[1] Each curve approximates the best line which can be drawn from the experimental points. The similarities between the curves at the two wave lengths are obvious. The striking differences lie in the facts that at λ2654 with higher concentrations of iodine, Φ_{CH_4} does not become negligibly small, and Φ_{CH_3I} does not become approximately equal to Φ_{CO}. The apparently constant value of all quantum yields above 1 mm. of iodine pressure leads to the conclusions (1) that within the limits of experimental measurements *activated* molecules do not react with iodine vapor, and (2) that all normal secondary reactions are greatly suppressed if not completely stopped. The fact that Φ_{CH_4} drops to a value of 0.28 and remains there with further increase of iodine is strong evidence that at λ2654

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad (1a)$$

is an important primary reaction, accounting for 28% of all quanta absorbed. The results show that in the same experiments the reaction

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

accounts for 35% of the absorbed energy. At λ3130, however, reactions 1a and 1b, respectively, account for only 1.3 and 20% of the total light absorbed. Within the limits of error, it may be observed that for both wave lengths $\Phi_{CH_4} + \Phi_{CH_3I} = \Phi_{CO}$. This may be explained best by assuming that, in addition to the formation of methyl iodide from free methyls, iodine reacts with HCO groups to liberate carbon monoxide and form hydrogen iodide.[1] The qualitative detection of iodide ion in the condensed photolysis products supports this assumption. Little can be said concerning the fate of the iodine atoms formed in the reactions of iodine and formyl and methyl radicals. It is possible that they react with other formyl and methyl radicals, with themselves, or induce resin formation from acetaldehyde. It is not probable that they react with acetaldehyde to form hydrogen iodide and acetyl radicals.

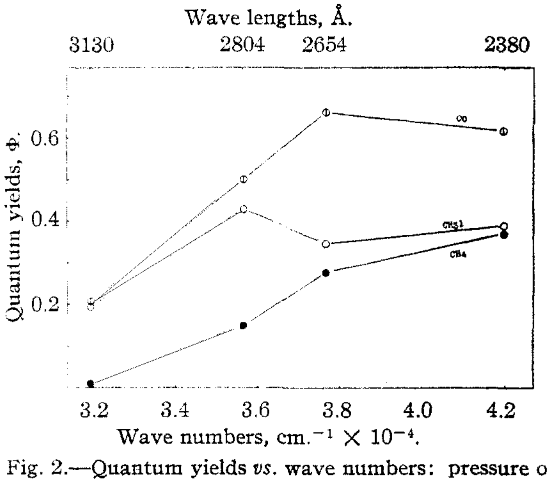

Fig. 2.—Quantum yields *vs.* wave numbers: pressure of acetaldehyde, 200 mm.; iodine pressure between 1 and 2.5 mm.; temperature, 60°. The results of Blacet and Heldman[1] were included in the averages at λ3130.

In Fig. 2 are plotted Φ_{CO}, Φ_{CH_3I} and Φ_{CH_4} as functions of absorbed energy. Wave lengths 3130, 2804, 2654 and 2380 were used in this study.[2] The

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[2] Preliminary results at λ2537 obtained by Volman and reported by Leighton [*J. Chem. Physics*, **7**, 781 (1939)] appear to be inconsistent with this work in that tellurium mirrors were not removed in a Paneth type experiment and no non-condensable gases were obtained.

temperature was maintained near 60° and the iodine pressure for all runs was between 1 and 2.5 mm. Over the wave length range used, Φ_{CH_4}, and consequently reaction 1a, increases almost linearly with the increase of quantum energy. From the Φ_{CO} and Φ_{CH_3I} curves it appears that somewhere in the region 2600 to 2800 Å. predissociation by reaction 1b reaches a maximum probability of occurrence. The relationship $\Phi_{CH_4} + \Phi_{CH_3I} = \Phi_{CO}$ holds well for all wave lengths, except possibly λ2380. This is good evidence that in the presence of iodine two formyl groups do not react to produce a molecule of formaldehyde and a molecule of carbon monoxide,[3] for in that case the quantum yield relationships would have to be $\Phi_{CO} = \Phi_{CH_4} + {}^1/_2\Phi_{CH_3I}$.

The influence of temperature on quantum yields at λ2654 is shown graphically in Fig. 3. Curve 1 indicates that in the absence of iodine the chain mechanism

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

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

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

remains relatively dormant below 60° but has a high acceleration in the range 60 to 100 degrees. There is considerable experimental evidence which shows that this is due to a rapid increase in the rate of reaction 4 with temperature.[4,5,6] Using that portion of Curve 1 which lies above 100°, the activation energy of the over-all chain process was calculated to be 9.6 kcal. per mole. This is in good agreement with 8.3 kcal. obtained by Rollefson and Grahame,[7] 10 kcal. determined by Leermakers,[8] and 9.8 kcal. found by Akeroyd and Norrish.[9] The presence of considerable biacetyl in the reaction products obtained at low temperatures[5] suggests that reaction 4 is the slow step in the chain and the one to which the above activation energy applies. A comparison of Curves 1 and 2, Φ_{CO} with and without iodine, shows the extent to which iodine stops normal secondary photochemical reactions. Within the limits of error it may be noted that with sufficient iodine present Φ_{CO}, Φ_{CH_3I} and Φ_{CH_4} are constant over the temperature range 60 to 150°. Under like conditions, at λ3130 a slight increase of Φ_{CO} and of Φ_{CH_3I} was found over this temperature range.[1] Rollefson and Grahame[7] found that the extinction coefficient has a definite trend upward with temperature at λ3130 but remains constant at λ2654. From this one might infer that the observed increase of quantum yields at λ3130 in the presence of iodine[1] was due to the assumption that Beer's law holds over the temperature range employed.

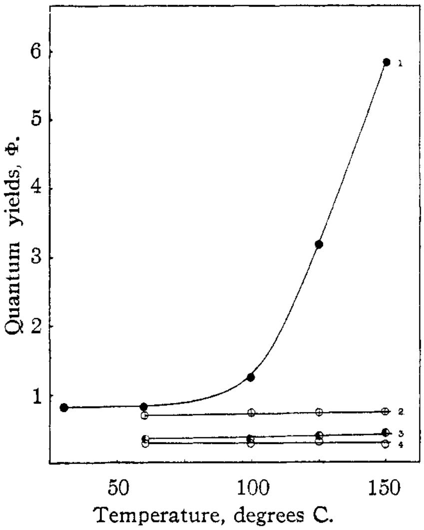

Fig. 3.—Quantum yields *vs.* temperature: 1, quantum yields of carbon monoxide, without iodine; 2, quantum yields of carbon monoxide, with iodine present; 3, quantum yield of methyl iodide; 4, quantum yields of methane, with iodine present, λ2654; acetaldehyde pressure, 200 mm.; iodine pressure, between 1 and 2.5 mm. Value at 30° from Leighton and Blacet (THIS JOURNAL, **55**, 1766 (1933)).

It has been assumed that reactions (1a) and (1b) are the only primary decomposition processes. The experimental evidence obtained in this research does not exclude a dissociation into hydrogen atoms and acetyl radicals, a reaction which was suggested by Noyes and Leighton[10] to account for the increase of molecular hydrogen production with decrease of wave length. However, the failure to detect acetyl iodide as a reaction product both by us in this Laboratory and by Gorin[3] indicates that iodine would have to react with acetyl radical not to give acetyl iodide, but to give methyl iodide and liberate carbon monoxide. Since in a study of acetone photolysis Gorin[6] obtained acetyl iodide, which presumably was a product of a reaction between iodine and the acetyl group, we have indirect evidence against the third primary dissociation process.

Gorin[3] has reported unity as the sum of the

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

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

(5) Blacet and Blaedel, THIS JOURNAL, **62**, 3374 (1940).

(6) Gorin, *J. Chem. Physics*, **7**, 256 (1939).

(7) Rollefson and Grahame, *ibid.*, **8**, 98 (1940).

(8) Leermakers, THIS JOURNAL, **56**, 1537 (1934).

(9) Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

(10) Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 341.

methane and methyl iodide quantum yields at both λ3130 and λ2600. Obviously, the results given in this paper and in the preceding one[1] are not in agreement with this. However, in spite of that fact, we concur in one important conclusion reached by him, namely, in the photolysis of acetaldehyde there must be two primary dissociation processes.

Summary

1. At λ2654, with 200 mm. acetaldehyde and with a temperature of 60°, it has been found that over the iodine pressure range of 1 to 2.5 mm., Φ_{CO} is 0.66, Φ_{CH_3I} is 0.35 and Φ_{CH_4} is 0.28.

2. Under similar conditions except for wave length, Φ_{CO} increases from 0.21 at λ3130 to 0.66 at λ2654, then appears to become slightly less at λ2380; Φ_{CH_3I} increases from 0.20 at λ3130 to a maximum at 0.43 at λ2804, decreasing somewhat at shorter wave lengths; and Φ_{CH_4} increases linearly from 0.013 at λ3130 to 0.39 at λ2380.

3. At λ2654, in the absence of iodine, Φ_{CO} increases from 0.78 at 60° to 5.85 at 150°. Over the same temperature range, but with ample iodine present, Φ_{CO}, Φ_{CH_3I} and Φ_{CH_4} remain constant at the values given above.

4. In all experiments having sufficient iodine present to suppress secondary reactions, Φ_{CO} was found to be approximately equal to the sum of Φ_{CH_3I} and Φ_{CH_4}.

5. From the results obtained in the absence of iodine, an activation energy of 9.6 kcal. has been calculated for the photolysis chain process. It is postulated that $CH_3CO + M \rightarrow CH_3 + CO + M$ is the reaction which requires this energy of activation.

6. The conclusions given in the previous paper of this series have been verified. In addition, it has been shown that two primary photodecomposition processes must occur in the region of absorption usually attributed to the carbonyl group. At λ3130 the dissociation is almost entirely into methyl and formyl radicals. With shorter wave lengths a second decomposition, directly into methane and carbon monoxide, becomes increasingly more important, until at λ2380 the two processes have equal probability of occurrence.

LOS ANGELES, CALIF. RECEIVED JANUARY 2, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Five-Membered Rings

BY F. O. RICE AND MARY THOMAS MURPHY[1]

From the point of view of the principle of least motion,[2] ring compounds would be expected to decompose ordinarily through rupture of a C–C bond in the ring; this primary decomposition would then be followed by a very rapid decomposition of the divalent radical directly into molecules. In a recent paper[3] it was shown that cyclohexene undergoes a change of this nature on heating and actually decomposes quantitatively into 1,3-butadiene and ethylene when the pyrolysis is conducted under conditions such that the products do not react with each other or with the substrate.

It seemed worth while to extend this study to other ring systems and accordingly we prepared a number of five-membered ring compounds and made a complete over-all analysis of the products formed on thermal decomposition. We shall discuss the behavior of a group of four acid anhydrides which can conveniently be considered first because the experimental results are readily predictable from the principle of least motion.

In any organic decomposition, the atoms of the original molecule must take up new positions to give products and it is desirable that there be as little motion of the atoms as possible in passing from the old to the new configurations. This is a statement of the first part of the principle of least motion. The second part of the principle states that a reaction will be favored which involves least change of the electronic configuration of the reacting system. It is of course understood that the principle applies only to elementary or single step reactions which from the thermodynamic standpoint are approximately equally probable.

In the light of the preceding paragraph we may now write the products to be expected in the decomposition of the following acid anhydrides

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(1) Present address, College of Chesnut Hill, Philadelphia, Pa.

(2) Rice and Teller, *J. Chem. Physics*, **6**, 489 (1938).

(3) Rice, Ruoff and Rodowskas, THIS JOURNAL, **60**, 955 (1938).