The anilinium salt shows no significant absorption at 400 mμ or above in 60% aqueous perchloric acid. The concentration of unprotonated aniline was therefore determined from the optical densities at 460, 440, 420 and 400 mμ, and averaged. The average deviation from the mean was less than 1%. The ratio $(BH^+)/(B)$ was then calculated from the known total indicator concentration.

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SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA]

The Primary Quantum Efficiency of Free Radical Formation in Acetaldehyde Photolysis at 3130 Å.

BY JACK G. CALVERT,[1] JAMES N. PITTS, JR., AND DONALD D. THOMPSON

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The quantum yields of hydrogen and carbon monoxide are determined in acetaldehyde vapor photolyses at low intensities of 3130 Å. light and at temperatures up to 350°. The data are consistent with hydrogen formation in a non-chain process: $CH_3CHO + h\nu \rightarrow CH_3 + CHO$ (I): $HCO + M \rightarrow H + CO + M$ (1): $H + CH_3CHO \rightarrow H_2 + CH_3CO$ (2): $HCO + \text{Wall} \rightarrow$ Products not H_2 (3). In the experiments at the highest temperatures, reactions 1 and 2 dominate over 3, and under these conditions $\Phi_{H_2} = 0.8_1 \cong \phi_I$. It is estimated that $E_1 - E_3 = 13 \pm 2$ kcal./mole. This work suggests that deactivation of an appreciable fraction of light-activated acetaldehyde molecules occurs in iodine-inhibited acetaldehyde photolyses at 3130 Å.

The many quantitative studies of acetaldehyde photolysis have demonstrated the occurrence of two primary processes

$$CH_3CHO + h\nu \longrightarrow \begin{cases} CH_3 + CHO & \text{(I)} \\ CH_4 + CO & \text{(II)} \end{cases}$$

Estimates of the primary quantum efficiencies (ϕ_I and ϕ_{II}) have been made from iodine inhibited photolyses at several wave lengths.[2,3] In the studies of Blacet and co-workers Φ_{CH_3I} and Φ_{CH_4} were about 0.20 and 0.01_3, respectively, at 3130 Å. The insensitivity of these yields to iodine concentration (at $P_{I_2} > 1$ mm.) and temperature (60–170°) suggested that in these experiments $\Phi_{CH_3I} = \phi_I$ and $\Phi_{CH_4} = \phi_{II}$. One might question this interpretation in view of the demonstrated influence of iodine on acetone photodecomposition. Pitts and Blacet[4] and Martin and Sutton[5] found that a significant fraction (0.88 at 100° and 0.72 at 177°)[4] of the 3130 Å. light activated acetone molecules which normally decompose in the uninhibited photolyses are deactivated in the photolyses with added iodine. Buchanan[6] has compared the rate of formation of CH_3I in iodine inhibited acetaldehyde photolyses with the rate of C_2H_6 formation in similar but uninhibited photolyses. Providing certain assumptions are made concerning the reaction mechanism, the results are consistent with the unimportance of excited molecule deactivation by iodine. However, the opposite view that these results indicate deactivation by iodine can also be supported.[7] On the basis of existing data it is difficult to establish unambiguously the role of excited molecule deactivation in the acetaldehyde–iodine mixture photolyses.

The present work was initiated to provide an independent estimate of the primary efficiency of radical formation in acetaldehyde photolysis at 3130 Å. The method involves the determination of the quantum yields of hydrogen formation at high temperatures and low light intensities. Under these conditions one expects practically complete decomposition of the CHO radicals formed in primary process I. Provided that hydrogen is not formed in some chain reaction, then the limiting Φ_{H_2} at high temperatures may be taken as an estimate of ϕ_I. Some justification for this technique may be obtained from the studies of the photolysis of the butyraldehydes.[8] In these cases deactivation of excited molecules by iodine appears to be unimportant since the limiting value of Φ_{H_2} at high temperature is approximately equal to the primary efficiency of CHO formation as estimated by the iodine inhibition technique.

The only extensive hydrogen quantum yield data for CH_3CHO at elevated temperatures are those of Dodd.[9] However, these are not suitable for the application of this technique since all of the experiments were carried out at temperatures below 207° and at relatively high light intensities, conditions which do not favor complete decomposition of CHO radicals.

Experimental

Apparatus and Photolysis Procedure.—The cylindrical reaction cell was made of fused quartz, 20 cm. long, 30 mm. inside diameter; it had a volume of 140 cc. The cell was filled almost completely with a parallel beam of 3130 Å. radiation isolated from a medium pressure Hg arc spectrum by a Bausch and Lomb 250 mm. focal length grating monochromator. The cell was placed in a metallic block oven with an automatic temperature control. The fraction of

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(1) On leave from the Chemistry Department, The Ohio State University, Columbus 10, Ohio: author to whom communications should be addressed.

(2) (a) E. Gorin, *Acta Physicochim.*, **9**, 681 (1938); (b) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

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(9) R. E. Dodd, *Can. J. Chem.*, **33**, 699 (1955).

TABLE I

QUANTUM YIELDS OF HYDROGEN AND CARBON MONOXIDE FROM THE PHOTOLYSIS OF ACETALDEHYDE AT 3130 Å.

Run	Temp., °C.	$[CH_3CHO]$, $\times 10^3$, M	$Ia \times 10^{-14}$, q./sec.-cell vol.	Φ_{CO}	Φ_{H_2}	$\frac{\Phi_{H_2} \times 10^{-3}}{[CH_3CHO]\,(0.81 - \Phi_{H_2})}$	$\frac{\Phi_{CO} I_a^{1/2} \times 10^{-9}}{[CH_3CHO]}$
1	30	10.1	5.82	0.24_6	0.0025	0.00031	0.58_7
2	109	2.14	2.61	3.7_8	.045	0.027_5	28.5
3	158	2.17	2.75	12.8_5	.18	0.13_2	98.2
4	198	2.16	2.79	32.9	.37	0.38_9	254
5	198	2.21	2.77	33.6	.56	1.01	253
6	198	2.32	0.239	$104._0$	.58	1.0_9	219
7	198	2.25	0.642	71.3	..	..	254
8	199	1.94	1.18	47.7	.47	0.71_2	267
9	201	2.14	2.80	34.9	.52	0.83_8	273
10	253	2.26	3.04	87.5	.73	4.0_4	675
11	253	1.90	2.99	85.5	.70	3.3_5	778
12	275	2.20	3.00	$112._1$	.73	4.1_5	883
13	296	2.23	3.00	160	.77	8.6_3	124_0
14	296	2.25	3.11	162	.84	..	127_0
15	345	2.16	3.17	266	.78	..	219_0

light transmitted by the system was measured with a photomultiplier circuit. The absolute light intensities were determined at four intervals throughout the series of runs using acetone photolysis above 100° as an internal actinometer.[10] The associated equipment for pressure measurement, sample purification and introduction and product removal were of conventional design. Run times were regulated to provide about 1.5 ml. of gaseous products (up to about 5% total decomposition of the original aldehyde).

Materials.—Standard CH_4 and H_2 gases were research grade materials. CO was prepared by the action of H_2SO_4 on NaO_2CH and was purified by chemical and physical treatment to remove CO_2 and H_2O. CH_3CHO used in these experiments was obtained from Eastman White Label product by fractionation in a modified Ward still; it was stored at −78°.

Analytical Methods.—Following photolysis the excess aldehyde and condensable products were frozen at $N_2(l)$ temperature, and CO, CH_4 and H_2 were removed with a Toepler pump. The trace of residual aldehyde pumped off with the products was removed by polymerization with KOH. A small portion of the products was separated from the bulk and analyzed for CO using the Blacet–Leighton gas analysis techniques. The remaining major portion of the products was introduced into a modified Westinghouse LV mass spectrometer, and the mass 2 peak was determined. Since the products contained only 0.15 to 0.83% H_2 in an approximately equimolar mixture of CO and CH_4, analysis for H_2 was very difficult. In the mass spectrometric procedure used, corrections were made for the 2 peak contribution from the large amount of CH_4 product (this was a maximum of 40% of the measured 2 peak in the runs with the smallest concentration of H_2) and for the effect of large CO–CH_4 concentrations on the specific intensity of the H_2 in the mixture (about a 25% reduction in the specific intensity of pure H_2 occurred in the H_2–CO–CH_4 known mixtures with the product composition). Known mixtures similar to the photochemical product compositions were prepared to standardize the analytical procedures. A correction for thermal reactions leading to H_2 formation was important only in a run at 345° where it amounted to 30% of the total rate of H_2 formation. Thus, in view of the complexity of the analysis, the results for Φ_{H_2} are subject to a considerable error.

Molar Absorbancy Indices.—The indices, a_M, for acetaldehyde absorption at 3130 Å. at various temperatures are: 6.3_3 (109°); 6.7_0 (158°); 6.8_7 (201°); 7.4_5 (253°); 7.7_1 (296°); 8.0_3 (345°); where $\log_{10}(I_0/I) = a_M bc$; b is the path length in cm., and c is the molar concentration.

Quantum Yield Results.—The quantum yield data are given in Table I. The results for Φ_{H_2} in run 15 at 345° may be in error by as much as ±25%. Agreement between independent check runs at other temperatures indicates that the error in Φ_{H_2} is not greater than ±20% and is probably much less than this in most cases. For some unknown reason Φ_{H_2} from run 4 is in serious disagreement with the very similar check runs 5 and 9. The Φ_{CO} data are probably accurate to ±5% at all temperatures. Most experiments were made at CH_3CHO concentrations of about 0.0021 M. However, experiment 1 was carried out under other conditions which closely duplicated those of Leighton and Blacet[11]; these data serve as a check on the absolute magnitude of the quantum yields reported in this work. The value of $\Phi_{CO} = 0.25$ found in this experiment is in good agreement with 0.24 reported by Leighton and Blacet from an experiment under very similar conditions. In most of the runs the incident light intensity was constant at about 5.8×10^{14} quanta/sec. In runs 6, 7 and 8 the incident intensity was lowered by placing calibrated uniform density filters in the light path.

Discussion

The Mechanism of Hydrogen Formation.—The hydrogen quantum yields from acetaldehyde photolyses are shown as a function of temperature in Fig. 1. The finite limiting value of Φ_{H_2} at high temperatures (about 0.8_1) is consistent with H_2 formation in a non-chain process. Blacet and Brinton[12] have concluded from a study of CH_3CHO photolysis that hydrogen is derived primarily from the acyl end of the acetaldehyde molecule. Danby, *et al.*,[13] Buchanan[14] and Dodd[9] found that the rate of hydrogen formation is equal within the experimental error to the rate of ethane formation at high temperatures. These facts and the present data are consistent with the reaction mechanism

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \qquad (I)$$

$$CHO + M \rightarrow CO + H + M \qquad (1)$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \qquad (2)$$

$$HCO + \text{Wall} \rightarrow \text{Products not } H_2 \qquad (3a)$$

$$HCO + CH_3 \rightarrow CO + CH_4 \ (\text{or } CH_3CHO) \qquad (3b)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad (4)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad (5)$$

$$2CH_3 \rightarrow C_2H_6 \qquad (6)$$

From this mechanism the usual rate law 7 for CO formation is expected at high temperatures where the chains are long.

$$\frac{\Phi_{CO}}{[CH_3CHO]} = \left(\frac{\phi_1}{I_a k_6}\right)^{1/2} k_4 \qquad (7)$$

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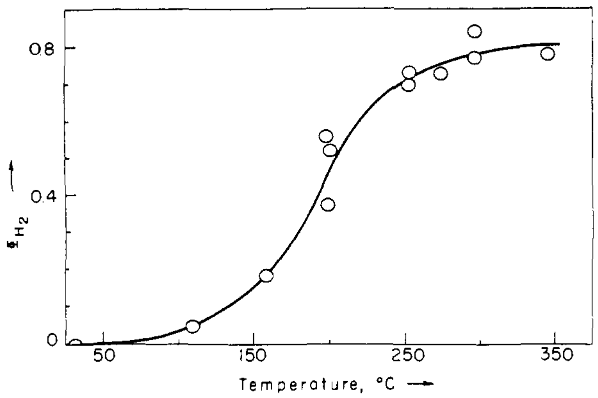

Fig. 1.—The quantum yield of hydrogen from acetaldehyde photolyses at various temperatures: wave length, 3130 Å.; [CH_3CHO], about 0.0021 *M*; I_a, about 2.9 × 10^{14} quanta/sec.-cell volume.

In Fig. 2 the variation of Φ_{CO}/[CH_3CHO] with $I_a^{1/2}$ is shown. At the highest intensities the plot is linear and passes through the origin as required by 7. At the lowest intensity there is a noticeable deviation from linearity, and it is probable that termination of chains at the wall (CH_3 + Wall $\rightarrow$ 1/2 C_2H_6 + Wall) is competing with 6 under these conditions. From the temperature dependence of the function $\Phi_{CO}I_a^{1/2}$/[CH_4CHO], given in column 7 of Table I for runs above 100° it is estimated that $E_4 - E_6/2 = 8.7$ kcal./mole. However, there is some question as to whether this temperature dependence can be attributed to reaction 4.[15,16]

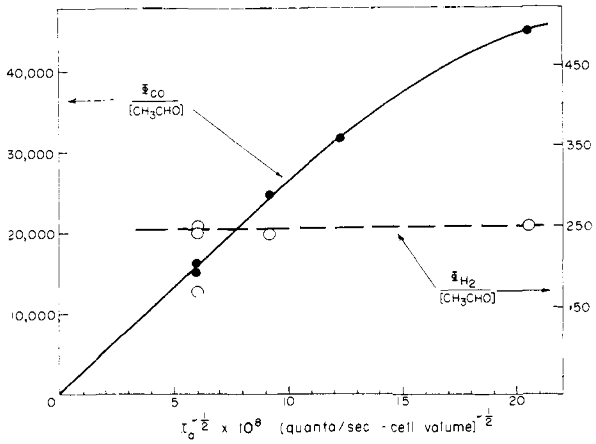

Fig. 2.—The effect of light intensity on the quantum yields of carbon monoxide and hydrogen in the photolysis of acetaldehyde: wave length, 3130 Å.; [CH_3CHO], about 0.0021 *M*; temperature, about 199°.

The proposed mechanism for hydrogen formation is dictated largely by the results of many other investigators. The inclusion of M(CH_3CHO in this case) in reaction 1 is one alternative which may be chosen to explain the observed effect of added gases on the photodecomposition of CH_2O.[19,20] The influence of M on the diffusion of HCO radicals and the rate of reaction 3a is another alternative. It is difficult to choose between these mechanisms, since both give the same over-all effect on the rate. From the standpoint of the conclusions reached in this work, the choice is unimportant. We have adopted the mechanism of Style and Summers,[20] which assumes the influence of M on reaction 1. Depending on the relative importance of reactions 3a and 3b, different rate laws are expected for hydrogen formation. Assuming reactions I, 1, 2, 3a, 4, 5 and 6 one derives relation 8.

$$\frac{\Phi_{H_2}}{[CH_3CHO]\ (\phi_1 - \Phi_{H_2})} = \frac{k_1}{k_{3a}[\text{Wall}]} \qquad (8)$$

If I, 1, 2, 3b, 4, 5 and 6 are assumed, then 9 is expected.

$$\frac{\Phi_{H_2}^{1/2}}{[CH_3CHO]\ (\phi_I - \Phi_{H_2})} = \frac{k_1k_6^{1/2}}{k_{3b}\,I_a^{1/2}}. \qquad (9)$$

In Fig. 2 it is seen that Φ_{H_2}/[CH_3CHO] is relatively insensitive to variation in I_a as is required by 8, so it is likely that reaction 3a rather than 3b is important in these experiments at relatively low intensities. Relations similar to 9 appear to hold for hydrogen formation in aldehyde photolyses at higher light intensities where 3b rather than 3a is expected to predominate.[8,17]

The Activation Energy of Formyl Radical Decomposition.—According to the suggested mechanism the temperature dependence of the function Φ_{H_2}/[CH_3CHO]($\phi_I - \Phi_{H_2}$) should provide an estimate of $E_1 - E_3$. If the suggested reaction scheme is correct than the limiting Φ_{H_2} at high temperatures is equal to ϕ_I. This has been assumed in the calculation of the functions given in column 6 of Table I. In Fig. 3 the logarithm of this function is plotted *versus* $1/T$. The slope of the least squares line through all of the points gives $E_1 - E_3 = 13 \pm 2$ kcal./mole. Since E_3 is probably

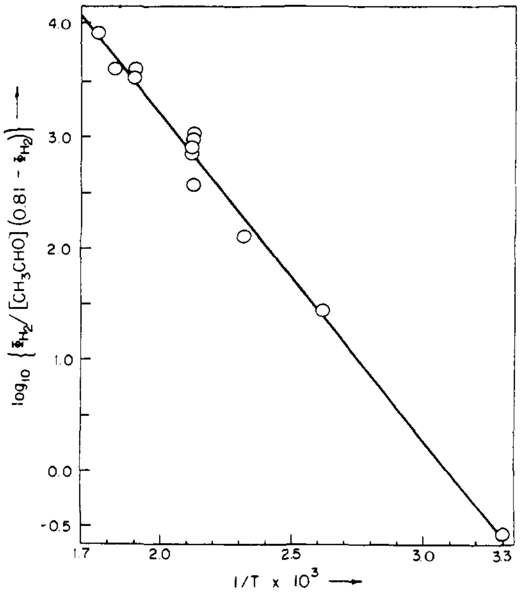

Fig. 3.—Arrhenius plot of a hydrogen quantum yield function from acetaldehyde photolyses at 3130 Å. The slope corresponds to an apparent activation energy of 13 ± 2 kcal./mole.

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small, then this may be taken as an estimate of E_1. The value found is in reasonable agreement with other estimates of E_1 based on photochemical kinetic data: $E_1 = 14$ kcal./mole from n-C_3H_6CHO photolysis[8]; 14 from iso-C_3H_7CHO photolysis,[8] 13 from C_2H_5CHO photolysis[17] $13._4$,[18] $(14._9)$[19]; 12,[20] (15.3)[19]; and $16._2$,[21] $(16._0)$[19] from CH_2O photolysis. The early estimate of Gorin (26 kcal./mole)[2] must be discarded for reasons which have been cited previously.[18] Recently Schoen[22] has demonstrated that DH is formed in CH_2O–D_2 mixture photolyses at 300° temperature and wave lengths $\leq$ 3650 Å. From these observations and thermodynamic data he concludes that $E_1 \geq 27$ kcal./mole. However, this conclusion must be accepted with reservation, since it is probable that light absorption by vibrationally excited CH_2O molecules leads to H atom formation in these experiments. The data of Kistiakowsky and Sternberg[23] suggest that the dissociation of Br_2 is effected at wave length 6800 Å. which provides insufficient energy per quantum (42.0 kcal./mole) to cause dissociation of ground state Br_2 molecules into two normal $Br(^2P_{3/2})$ atoms (45.5 kcal./mole). The temperature dependence of the absorption at 6800 Å. is consistent with the view that vibrationally excited Br_2 molecules are the absorbing species at this wave length. The temperature dependence of the absorption by CH_2O in the "α" band near 3700 Å. indicates that absorption in this region is also by vibrationally excited molecules. The lowest observed fundamental vibration frequency (C–O stretching) in CH_2O is 1167 cm.$^{-1}$ (3.3 kcal./mole), and molecules with this excitation energy may be the light absorbers at 3650 Å.[24] It may be significant that HD formation was reported by Schoen only in experiments at a temperature of 300°. Even under these conditions the photochemical rate was very low, about equal to the rate of the thermal reaction forming HD at this temperature. Although the rate of light absorption is low at this wave length, it seems that the efficiency of H atom formation must be very much lower. It is likely that dissociation following 3650 Å. light absorption occurs only in those molecules which possess considerable vibrational excitation in addition to the demonstrated excitation necessary for absorption; for example, a quantum of excitation in the antisymmetric C–H stretching vibration (2874 cm.$^{-1}$, 8.2 kcal./mole) may be necessary. If this is the case then the E_1 estimate from Schoen's experiments would be in line with the 14 ± 2 kcal./mole found in the other studies: namely, $E_1 \geq 27 - (8.2 + 3.3) = 15.5$ kcal./mole.

In view of all the results probably the best estimate of the activation energy of CHO decomposition is 14 ± 2 kcal./mole, and the agreement of the present estimate with this value lends credence to the interpretation of the mechanism of hydrogen formation.

The Primary Quantum Yield of Free Radical Formation in CH_3CHO Photolysis at 3130 Å.—It has been seen that the quantum yield data form a consistent picture involving hydrogen formation in the non-chain reaction scheme 1, 2 and 3a. One is led to the conclusion that the limiting Φ_{H_2} at high temperatures, about 0.8_1, is an estimate of ϕ_1. Acetone absorption of 3130 Å. radiation leads to the formation of at least two different excited states with very different half-lives.[25] The situation may be similar for acetaldehyde. It may be proposed that acetaldehyde forms one excited state which dissociates in one of its first vibrations. This state could not be quenched by I_2, and the primary quantum efficiency of this process might correspond to the 0.2_0 measured in the iodine inhibited photolyses. Other longer lived states which are formed may suffer deactivation in the presence of I_2 but might dissociate to form free radicals in the normal uninhibited photolysis. In terms of the present work the sum of all the primary efficiencies of free radical formation at 3130 Å. would be equal to 0.8_1. A quantitative study of the fluorescence of acetaldehyde vapor excited by 3130 Å. light absorption would provide an interesting test of this hypothesis.

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RIVERSIDE, CALIFORNIA

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