847. *The Thermal Decomposition of Acetaldehyde: The Formation of Hydrogen.*

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In the pyrolysis of acetaldehyde the primary splitting of an acetaldehyde molecule yields methyl and formyl radicals, and the subsequent decomposition of the latter leads to the formation of hydrogen. The amounts of hydrogen produced at temperatures between 502° and 536° and acetaldehyde pressures of 100—400 mm. have been measured. After a short induction period, which varied with the temperature and surface area of the reaction vessel but was independent of the acetaldehyde pressure, hydrogen was produced at an initial rate which depended on the square of the acetaldehyde pressure. Values for the rate constant of the reaction $2CH_3{\cdot}CHO \longrightarrow {\cdot}CH_3 + {\cdot}CHO + CH_3{\cdot}CHO$ have been determined and, from lengths of induction periods, approximate values have been derived for the rate constant of the wall-reaction ${\cdot}CHO \longrightarrow CO + {\cdot}H$.

Thermal decomposition of acetaldehyde has been the subject of numerous investigations which have been adequately reviewed elsewhere.[1,2] The Rice–Herzfeld mechanism, which can be written as:

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\begin{aligned}
CH_3{\cdot}CHO &\longrightarrow {\cdot}CH_3 + {\cdot}CHO && (1)\\
{\cdot}CHO &\longrightarrow CO + {\cdot}H && (2)\\
{\cdot}H + CH_3{\cdot}CHO &\longrightarrow H_2 + {\cdot}CO{\cdot}CH_3 && (3)\\
{\cdot}CH_3 + CH_3{\cdot}CHO &\longrightarrow CH_4 + {\cdot}CO{\cdot}CH_3 && (4)\\
{\cdot}CO{\cdot}CH_3 &\longrightarrow {\cdot}CH_3 + CO && (5)\\
{\cdot}CH_3 + {\cdot}CH_3 &\longrightarrow C_2H_6 && (6)
\end{aligned}
$$

accounts for the majority of the experimental observations, although there remains some doubt as to the orders of the chain-initiating and -terminating steps.[3] Although the mechanism predicts that small amounts of hydrogen and ethane will be produced, these minor products have only recently been detected and estimated.[4] A more detailed

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[1] Friess and Weissberger, " Investigation of Rates and Mechanisms of Reactions," Interscience Publishers, Inc., New York, 1953, p. 291.

[2] Benson, " The Foundations of Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, 1960, p. 379.

[3] Bril, Goldfinger, Letort, Mattys, and Niclause, *Bull. Soc. chim. belges*, 1950, **59**, 263.

[4] Freeman, Danby, and Hinshelwood, *Proc. Roy. Soc.*, 1958, *A*, **245**, 456.

investigation of the factors governing hydrogen formation is described in this paper. The results show that the chain-initiating step is of second order, and further information has been obtained on the decomposition of the formyl radical.

EXPERIMENTAL

Materials.—Commercial acetaldehyde was purified by distillation over anhydrous sodium sulphate, a middle fraction, b. p. 21°, being collected and stored in the absence of air at −78°.

Apparatus.—This was essentially the same as that described previously.[5] Two cylindrical silica reaction vessels were used, one empty, 15 × 4·5 cm., of 183 ml. volume and 219 sq. cm. surface area, and the other, 17 × 4·5 cm., packed with silica tubing, with a volume of 163 ml. and 1140 sq. cm. surface area. A series of four traps was used to collect the products; the first three were empty and the last contained activated charcoal. The last trap was connected to a Töpler–McLeod gauge; a two-way tap at the top of the gauge allowed it to be connected either to a Töpler pump, through a small trap, or to a gas-sample vessel by means of which the gas to be analysed could be introduced into the flow stream of a Perkin-Elmer gas-chromatography apparatus having a thermal conductivity detector. The hydrogen analyses were performed with this instrument, which was fitted with a 3·6 m. column of active carbon (40—70 B.S.S.) at 50°, nitrogen being used as carrier gas. A cartesian manostat (Edwards High Vacuum Limited) was incorporated to ensure uniform flow rates, which were measured by means of a capillary flowmeter. A calibration was performed by measuring peak areas obtained with known volumes of hydrogen, and this was checked frequently.

Operation.—On introduction of a prearranged pressure of acetaldehyde, from a sampling bulb, into the reaction vessel the progress of the reaction was followed by making pressure–time measurements. After the required heating time the products were transferred, as rapidly as possible (15—30 sec.), to the collecting traps (cooled to −197°). The reaction vessel was then closed from the rest of the system and kept so until the apparatus had been prepared for the succeeding run; then it was kept under a vacuum for 5 min.

The non-condensable products were transferred from the charcoal trap to the Töpler–McLeod gauge and their volumes measured. They were then repeatedly passed through the small trap cooled in solid nitrogen. By this means most of the methane and some of the carbon monoxide present were condensed out, and all sample volumes were reduced to *ca.* 1·3 ml. (at s.t.p.). This remaining gas was transferred to the sample vessel and thence to the gas-chromatography apparatus. The gases condensed in the trap were shown to contain no hydrogen.

RESULTS

Experiments were performed at 502°, 512°, 523°, and 536° in the unpacked vessel. Initial pressures of acetaldehyde were estimated by extrapolation of the pressure–time curves to zero time. Repeat runs showed the hydrogen analyses to agree within the limits ±6%. The graphs of hydrogen formed plotted against time for four different initial pressure of acetaldehyde at 536° are shown in Fig. 1. These curves indicate the occurrence of an induction period, the length of which is independent of the initial acetaldehyde concentration. Similar curves were obtained at the other three temperatures, the length of the induction period (Table 1) increasing with decrease in temperature.

TABLE 1.

Variation of induction period with temperature.

Temp. (°c)	502	512	523	536
Induction period (sec.)	122	96	78	58

In experiments with the packed reaction vessel the hydrogen formed in 10 minutes, from the decomposition of approximately 350 mm. of acetaldehyde at 502°, decreased progressively from 0·059 ml., (at s.t.p.) in the first run, to a reproducible value of 0·017 ml. in the seventh, as compared with the 0·014 ml. obtained under similar conditions in the unpacked vessel. Pressure–time curves from these seven runs varied very little; those

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[5] Kenwright, Robinson, and Trenwith, *J.*, 1958, 660.

from subsequent runs showed, by comparison with curves obtained under similar conditions in the unpacked vessel, lower increases in pressure (*ca.* 20%) with time, and correspondingly lower yields of total non-condensable products were obtained. Thus, although during the " seasoning " process the nature of the surface has a marked influence on the hydrogen formed, in " seasoned " vessels surface–area changes only slightly affect the amounts of reaction products. The $[H_2]$–time curves for similar initial pressures of acetaldehyde at 502° in packed and unpacked vessels are shown in Fig. 2. The admission of air into a " seasoned " vessel at the experimental temperature did not influence the amounts of the various products formed in subsequent runs.

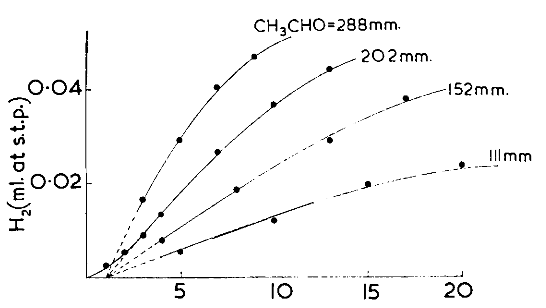

FIG. 1. Hydrogen formed from pyrolysis of acetaldehyde at 536°, for four different initial pressures of acetaldehyde.

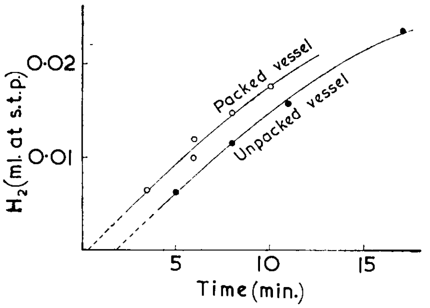

FIG. 2. Hydrogen formed from pyrolysis of 340 mm. of acetaldehyde in packed and unpacked vessels at 502°.

DISCUSSION

According to the Rice–Herzfeld mechanism the initial rate of formation of hydrogen should be proportional to the initial concentration of acetaldehyde. In order to check this, graphs were plotted of $\log_{10}(d[H_2]/dt)$ against $\log_{10}[CH_3{\cdot}CHO]$, values for $(d[H_2]/dt)$ being obtained from the slopes of the $[H_2]$–time graphs at the points of intersection with the time axis. Straight-line plots were obtained for each temperature, the slopes being 1·97 (502°), 2·03 (512°), 2·01 (523°), and 1·99 (536°). These results indicate that the initial rate of formation of hydrogen varies with the square of the initial concentration of acetaldehyde. It follows that, over the experimental pressure range, the chain-initiating step is a second-order reaction, so that reaction (1) must be replaced by

$$CH_3{\cdot}CHO + M \longrightarrow {\cdot}CH_3 + {\cdot}CHO + M \qquad (1a)$$

M initially being entirely $CH_3{\cdot}CHO$.

In order that the theoretical rate equation should have an overall order of 3/2, with respect to acetaldehyde, the chain-ending step (6) must now be replaced by the third-order reaction

$$ {\cdot}CH_3 + {\cdot}CH_3 + M \longrightarrow C_2H_6 + M \qquad (6a)$$

Strong evidence in favour of this reaction has recently been put forward by Laidler and Wojciechowski[6] in connection with the thermal decomposition of ethane. They show that the pressure at which transition of reaction (6*a*) from third to second order occurs, rises markedly with temperature so that, under the experimental conditions employed in this investigation, a third-order reaction is to be expected.

If equations (1*a*) and (6*a*) are taken as the chain-initiating and -ending steps, respectively, the steady-state method gives

$$-d\,[CH_3{\cdot}CHO]/dt = 2k_{1a}/k_4k_{6a}[CH_3{\cdot}CHO]^{3/2},$$

[6] Laidler and Wojciechowski, *Proc. Roy. Soc.*, 1961, *A*, **260**, 91.

which differs from the rate equation from the Rice–Herzfeld mechanism only by the factor 2, and $d[H_2]/dt = k_{1a}[CH_3{\cdot}CHO][M]$, which in the initial stages of the decomposition becomes $d[H_2]/dt = k_{1a}[CH_3{\cdot}CHO]^2$. Values for k_{1a}, obtained from the slopes of the plots of $d[H_2]/dt$ against $[CH_3{\cdot}CHO]^2$ (Fig. 3), are given in Table 2.

TABLE 2.

Variation of rate constant k_{1a} with temperature.

Temp. (°c)	502	512	523	536
10^5k_{1a} (l. mole^{-1} sec.$^{-1}$)	16·20	31·42	61·21	121·23

An Arrhenius plot of these results gives $k_{1a} = 10^{17\cdot0} \exp(-73800/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

The most likely explanation for the sigmoid shape of the $[H_2]$–time curves is that either reaction (2) or (3) has a rate such that a measurable time must elapse before the formyl-radical or hydrogen-atom concentration attains the steady-state value. The time needed to attain equilibrium may be roughly estimated by Howlett's method.[7] If reaction (2) is the slow step then, in the early stages of the reaction, the formyl radical concentration will build up approximately linearly with time (t) according to the equation:

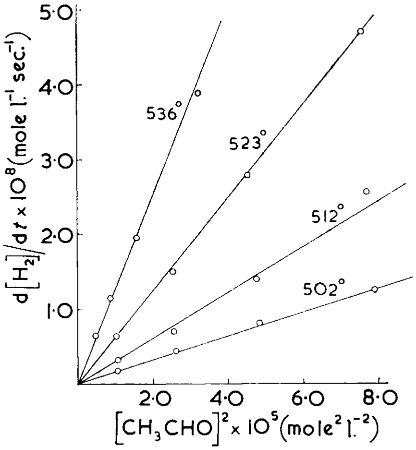

FIG. 3. Graph of $d[H_2]/dt$ against $[CH_3{\cdot}CHO]^2$.

$$[{\cdot}CHO] = k_{1a}[CH_3{\cdot}CHO][M]t$$

When the steady-state concentration is attained, $k_{1a}[CH_3{\cdot}CHO][M] = k_2[{\cdot}CHO]$ so that, by substitution for $[{\cdot}CHO]$, the time needed to attain equilibrium is given by $t = 1/k_2$, and this should correspond to the time at the point of intersection of the smooth curves (Fig. 1) with the time axis.

A similar approach, taking reaction (3) as the slow step, leads to the equation $t = 1/k_3[CH_3{\cdot}CHO]$ and, since the induction period was found to be independent of the acetaldehyde concentration, this alternative can be ruled out. An Arrhenius plot of values for k_2, derived from the figures in Table 1, gives $k_2 = 10^{5\cdot3} \exp(-26{,}300/\boldsymbol{R}T)$sec.$^{-1}$.

Although reaction (2) has been assumed to be of the first order, in accordance with the conclusions of Calvert and Steacie,[8] others [9] have interpreted photochemical results on the basis of a second-order formyl-radical decomposition. This alternative, which appears more likely in view of the simplicity of the radical and of the observed orders of reactions (1*a*) and (6*a*), would again lead to an induction period varying inversely with the acetaldehyde concentration, and is therefore not acceptable.

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[7] Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

[8] Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176.

[9] Horner, Style, and Summers, *Trans. Faraday Soc.*, 1954, **50**, 1201.

Although the Arrhenius parameters derived for k_2 must be only approximate, the following conclusions seem justified:

(i) The activation energy favours the "high" value ($26 \pm l.$ kcal. mole^{-1}) for E_2 obtained from theoretical calculations[10] and electron-impact studies,[11] as opposed to the "low" value (14 ± 2 kcal. mole^{-1}), obtained from kinetic studies of aldehyde photolyses (for a review of relevant data see ref. 12);

(ii) Although a low A-factor for reaction (2) is to be expected (Marcotte and Noyes[13] deduced a value of 10^9 sec.$^{-1}$, and similar free-radical decompositions have been found to have A-factors of this order of magnitude[14]), the experimental figure of 10^5 sec.$^{-1}$ is so low as to contraindicate a homogeneous mechanism. This result, together with the conflicting observations on the order of the reaction, leads to the conclusion that the decomposition of the formyl radical is, under the experimental conditions employed, a heterogeneous process. The observation that, with the packed vessel, the five-fold increase in surface area leads to a shift of the $[H_2]$–time curve to the left, and a comparable decrease in the induction period, further supports this conclusion.

The wall-reactions $\cdot CHO \longrightarrow H\cdot + CO$ (2*a*) and $2H\cdot \longrightarrow H_2$ have been suggested as the most likely means of formation of hydrogen in the low-temperature photolysis of acetaldehyde,[10] and (2*a*) is now preferred to (2) in the thermal decomposition mechanism, but at the higher temperatures the hydrogen would probably be desorbed and react according to scheme (3).

The activation energies of reactions (1*a*), (4), and (6*a*) being taken as 73·8, 7·5,[15] and zero kcal. mole^{-1}, respectively, an overall activation energy of 44·4 kcal. mole^{-1} is found for the decomposition of acetaldehyde, in good agreement with the experimental value of 46 kcal. mole^{-1}.[16]

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[10] Dorman and Buchanan, *Austral. J. Chem.*, 1956, **9**, 34.
[11] Reed, *Trans. Faraday Soc.*, 1956, **52**, 1195.
[12] Calvert, *J. Phys. Chem.*, 1957, **61**, 1206.
[13] Marcotte and Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 783.
[14] Trotman-Dickenson, *J. Chem. Phys.*, 1951, **19**, 261.
[15] Brinton and Volman, *J. Chem. Phys.*, 1952, **20**, 1053.
[16] Letort, *J. Chim. phys.*, 1937, **34**, 265, 355, 428.