1040. *The Thermal Decomposition of Acetaldehyde: the Formation of Ethane and Acetone.*

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By analysis of the products of pyrolysis at 523° of acetaldehyde at an initial pressure of 250 mm. and of acetaldehyde (250 mm.) plus carbon dioxide (200 mm.) it has been found that $\cdot CH_3 + \cdot COCH_3 \longrightarrow CH_3COCH_3$ and to a lesser extent $2CH_3\cdot + X \longrightarrow C_2H_6 + X$ are the principal chain-ending steps. The added carbon dioxide increases the rates of both chain-initiating and chain-ending steps in such a way that the initial overall rate of decomposition of acetaldehyde is unchanged. As predicted from the suggested mechanism, the addition of ethane to acetaldehyde at 523° decreases the initial rate of decomposition and increases the overall order of the reaction.

In a previous Paper [1] it was shown from analysis of the hydrogen formed that the chain-initiating step in the decomposition of acetaldehyde is a second-order split of CH_3CHO into $\cdot CH_3 + \cdot CHO$ for pressures of 100—300 mm. of acetaldehyde at 502—536°. The usually accepted chain-terminating step is the combination of $\cdot CH_3$ radicals and this was assumed to be of third-order under the above conditions to lead to the observed overall order of reaction of 3/2. It has been shown [2] that a chain reaction initiated by a second-order step has an overall order of 3/2 when the chain-terminating step is either a $\beta\mu$ or a $\beta\beta(M)$ reaction (β = a radical which does not decompose, μ = a radical which decomposes). Hence in the acetaldehyde decomposition several alternative chain-terminating steps are theoretically possible and an investigation of the various possibilities is now described.

The results show that at 523° and 250 mm. pressure of acetaldehyde the principal chain-ending step is $\cdot CH_3 + \cdot COCH_3 \longrightarrow CH_3COCH_3$. Of the alternative reactions only $\cdot CH_3 + \cdot CH_3 + M \longrightarrow C_2H_6 + M$ occurs to a measurable extent. This latter reaction is of importance when accounting for overall rates of decomposition in the presence of added gases.

EXPERIMENTAL

This was as described previously [1] with the following additions:

Materials.—Carbon dioxide was obtained by allowing the solid " Drikold " to evaporate. The gas was dried (P_2O_5), condensed in a trap cooled in liquid nitrogen, and after fractionation between −130 and −196° was stored in a sampling bulb. Ethane from a cylinder was condensed in a trap cooled in liquid nitrogen and after pumping was fractionated between −130 and −196°; a middle fraction was stored in a sampling bulb.

Operation.—In runs where acetaldehyde was decomposed in the presence of carbon dioxide and of ethane the required amounts of the latter were introduced into the reaction vessel and the pressure noted before admission of the acetaldehyde.

Acetone determinations were made by transferring all the condensable products to the gas-sampling vessel and subsequently passing them through a 2-m. column of tetraethylene glycol dimethyl ether.

Ethane, ethylene, and carbon dioxide were separated from the remainder of the condensable products by fractionation between traps at −130 and −196° and the mixtures were analysed by passage through a 70-cm. charcoal column. For ethane estimations in the presence of large amounts of carbon dioxide a 1-m. column of molecular sieve 5A was used. Hydrogen was employed as carrier gas in all cases.

Pressure–time measurements were made by using a constant-volume manometer,[3] in conjunction with two cathetometers one fixed and focused on the constant head and the other movable and focused on the moving limb of the manometer.
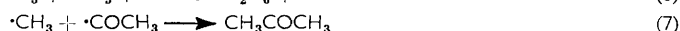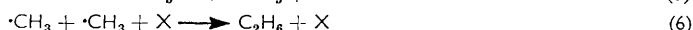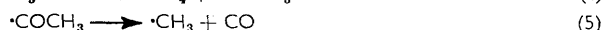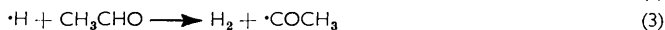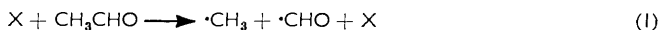
[1] Trenwith, *J.*, 1963, 4426.
[2] Bril, Goldfinger, Letort, Mattys, and Niclause, *Bull. Soc. chim. belges*, 1950, **59**, 263.
[3] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

Results and Discussion

Minor products of pyrolysis of acetaldehyde at 523° and 250 mm. pressure are shown in Fig. 1. The curves indicate that hydrogen, acetone, ethane, and ethylene are primary products whilst carbon dioxide is a secondary one. Small peaks were observed on the chromatograms of the condensable products using the tetraethylene glycol dimethyl ether column which corresponded in retention time with propionaldehyde and ethanol but insufficient of either was present to allow of a mass spectrometric analysis. Water could not be detected among the products.

The initial rates of formation of hydrogen, acetone, and ethane are 0·00278, 0·00260, and 0·00024 ml./min., respectively, so that initially $d([CH_3COCH_3] + [C_2H_6])dt \simeq d[H_2]/dt$ and this relationship was found to hold during the first six minutes of the decomposition. From this it was concluded that both acetone and ethane are chain-ending products formed by reactions (6) and (7) and that these are the only significant chain-terminating steps. The overall mechanism can be written:

$$X + CH_3CHO \longrightarrow \cdot CH_3 + \cdot CHO + X \qquad (1)$$
$$\cdot CHO \xrightarrow{\text{Walls}} CO + \cdot H \qquad (2)$$
$$\cdot H + CH_3CHO \longrightarrow H_2 + \cdot COCH_3 \qquad (3)$$
$$\cdot CH_3 + CH_3CHO \longrightarrow CH_4 + \cdot COCH_3 \qquad (4)$$
$$\cdot COCH_3 \longrightarrow \cdot CH_3 + CO \qquad (5)$$
$$\cdot CH_3 + \cdot CH_3 + X \longrightarrow C_2H_6 + X \qquad (6)$$
$$\cdot CH_3 + \cdot COCH_3 \longrightarrow CH_3COCH_3 \qquad (7)$$

The carbon dioxide formed can be accounted for by the secondary reaction of carbon monoxide $2CO \longrightarrow CO_2 + C$ which is known to occur at 550°.[4] The source of the small quantities of ethylene is obscure. The reaction

$$\cdot CH_3 + CH_3CHO \longrightarrow CH_4 + \cdot CH_2CHO \qquad (8)$$
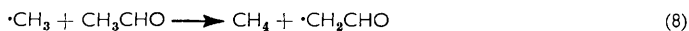
has been postulated as an alternative to (4) [5] and the aldehyde radical produced would be expected to decompose yielding a methylene biradical and hence, eventually, ethylene. A process of this kind would, however, involve several steps and would hardly lead to the production of ethylene as a primary product.

For convenience the overall mechanism has been considered in two parts: mechanism 1, involving only (6) as the chain-ending step and mechanism 2 involving only (7). Initially only acetaldehyde is present and under these conditions the rate equations are

$$-d[CH_3CHO]/dt = k_4(k_1/k_6)^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \quad \text{for mechanism 1 and}$$
$$-d[CH_3CHO]/dt = (k_1k_4k_5/k_7)^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \text{ for mechanism 2.}$$

Inserting the appropriate activation energies and A factors given in Table 1 the theoretical rate constants are $k = 10^{14 \cdot 3} \exp(-42800/RT)$ (ml./mole)$^{\frac{1}{2}}$ sec.$^{-1}$ and $k = 10^{14 \cdot 9} \exp(-47000/RT)$ (ml./mole)$^{\frac{1}{2}}$ sec.$^{-1}$ for mechanisms 1 and 2, respectively. Both agree satisfactorily with the experimental expression $k = 10^{12 \cdot 4} \exp(-46000/RT)$ (ml./mole)$^{\frac{1}{2}}$ sec.$^{-1}$.[6]

Of the figures given in Table 1 all have been determined experimentally or can be reasonably assumed except the frequency factor for reaction (6) which has been estimated as follows. In the thermal decomposition of acetaldehyde alone it is assumed that initially ethane and acetone are formed only by reactions (6) and (7) so their initial rates of formation are related by the equation:

$$d[CH_3COCH_3]/d[C_2H_6] = k_7[\cdot CH_3][\cdot COCH_3]/k_6[\cdot CH_3]^2[CH_3CHO].$$

[4] Brandner and Urey, *J. Chem. Phys.*, 1945, **13**, 351.
[5] Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 47.
[6] Letort, *J. Chim. Phys.*, 1937, **34**, 265, 355, 428.

TABLE 1.

Kinetic parameters for elementary reactions.

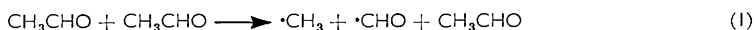| Reaction	Frequency factor (sec.$^{-1}$, or ml. mole^{-1} sec.$^{-1}$, or ml.^{2} mole^{-2} sec.$^{-1}$)	Activation energy (kcal.)	k at 523° (sec.$^{-1}$, or ml. mole^{-1} sec.$^{-1}$, or ml.^{2} mole^{-2} sec.$^{-1}$)	Ref.
1	$10^{18.8}$	70·5	$10^{-0.6}$	1 *
3	10^{13} †	6·0	$10^{11.4}$	7
4	10^{12}	7·5	$10^{9.9}$	8
5	10^{12}	16	$10^{7.6}$	9
6	$10^{14.3}$	0 †	$10^{14.3}$	see text
7	10^{13} †	0 †	10^{13}	

* The figures quoted here were derived from the values of k_{1a} reported previously,[1] but neglecting the low-temperature figure, which owing to the relatively long induction period was considered unreliable.   † Assumed values.

From the steady state concentrations of [·COCH$_3$] and [·CH$_3$], we have for both mechanisms 1 and 2 [·COCH$_3$]/[·CH$_3$] = (k_4/k_5) [CH$_3$CHO], hence

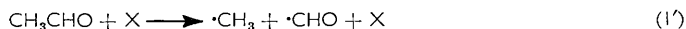$$d[CH_3COCH_3]/d[C_2H_6] = k_7k_4/k_5k_6.$$

By using the experimental slopes and the values quoted for k_4, k_5, and k_7, k_6 was found to be $10^{14.3}$ ml.^{2}mole^{-2} sec.$^{-1}$.   This value was taken to be the frequency factor for reaction (6) since the activation energy must be very small.
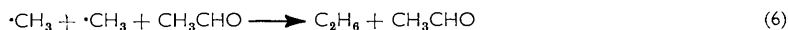
For the decomposition of acetaldehyde in the presence of inert gases equations (1) and (6) must include both X = acetaldehyde and also X = inert gas.   Thus (1) becomes

$$CH_3CHO + CH_3CHO \longrightarrow ·CH_3 + ·CHO + CH_3CHO \tag{1}$$

and

$$CH_3CHO + X \longrightarrow ·CH_3 + ·CHO + X \tag{1'}$$

and (6) becomes

$$·CH_3 + ·CH_3 + CH_3CHO \longrightarrow C_2H_6 + CH_3CHO \tag{6}$$

and

$$·CH_3 + ·CH_3 + X \longrightarrow C_2H_6 + X \tag{6'}$$

The theoretical rate equations for mechanisms 1 and 2 are now

$$-d[CH_3CHO]/dt = k_4 \left[\frac{2k_1[CH_3CHO]^2 + 2k_1'[CH_3CHO][X]}{k_6[CH_3CHO] + k_6'[X]} \right]^{\frac{1}{2}} [CH_3CHO]$$

and

$$-d[CH_3CHO]/dt = \left[\frac{k_1k_4k_5}{k_7}[CH_3CHO] + \frac{k_1'k_4k_5}{k_7}[X] \right]^{\frac{1}{2}} CH_3CHO]$$

respectively.   The ratios of the initial rates of decomposition in the presence of and in the absence of an added gas (R_x/R_a) are

$$\frac{R_x}{R_a} = \left[\frac{1 + (k_1'[X])/(k_1[CH_3CHO])}{1 + (k_6'[X])/(k_6[CH_3CHO])} \right]^{\frac{1}{2}} \text{ for mechanism 1}$$

and

$$\frac{R_x}{R_a} = [1 + (k_1'[X])/(k_1[CH_3CHO])]^{\frac{1}{2}} \text{ for mechanism 2.}$$

Thus with mechanism 2 there is an increase in the rate of decomposition in the presence of an added gas whilst for mechanism 1 there is either an increase or a decrease, depending on whether k_1'/k_1 is greater or less than k_6'/k_6.

The influence of carbon dioxide on overall rates of decomposition of acetaldehyde has been examined.   Pressure-time curves for acetaldehyde alone at 50 and 250 mm. pressure and in the presence of carbon dioxide at 250 mm. pressure are shown in Fig. 2.   These indicate that although the fall off in rate of decomposition of acetaldehyde is more rapid in the presence of carbon dioxide, the initial rates are unchanged.   The analytical results

[7] Trost, Darwent, and Steacie, *J. Chem. Phys.*, 1948, **16**, 353.
[8] Dorman and Buchanan, *Austral. J. Chem.*, 1956, **9**, 25.
[9] Marcotte and Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 783.

for the decomposition of acetaldehyde (250 mm.) plus carbon dioxide (200 mm.) are shown in Fig. 3, the appropriate curves from Fig. 1 being included for comparison. Whilst acetone yields are unchanged, the rates of formation of hydrogen and of ethane are seen to increase as would be expected. According to the overall mechanism suggested, addition of
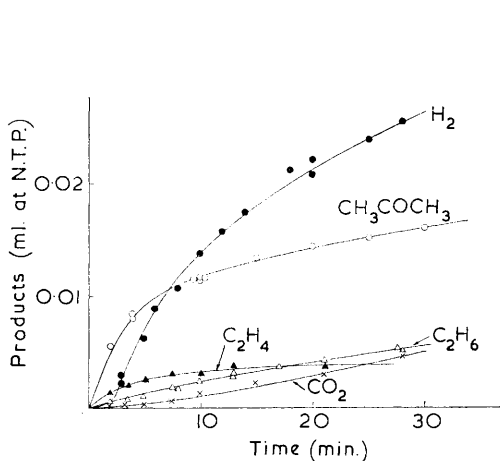

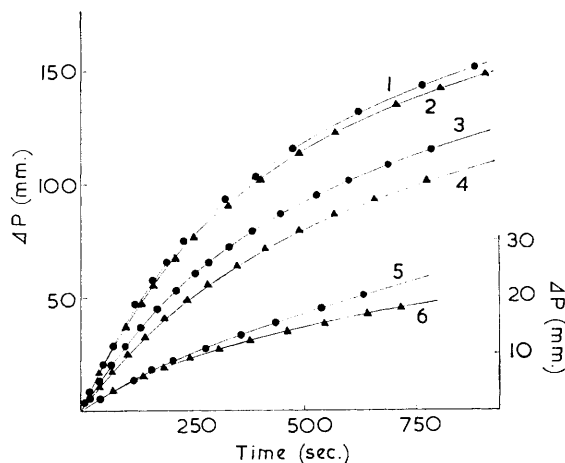FIG. 1.   Products of pyrolysis at 523° of 250 mm. acetaldehyde.

FIG. 2.   Pressure–time curves at 523°; right hand ordinate applies to curves 5 and 6 only. Curve 1, 250 mm. acetaldehyde; 2, 250 mm. acetaldehyde + 200 mm. carbon dioxide; 3, 200 mm. acetaldehyde; 4, 200 mm. acetaldehyde + 200 mm. ethane; 5, 50 mm. acetaldehyde; and 6, 50 mm. acetaldehyde + 250 mm. carbon dioxide.

carbon dioxide should not change the rate of acetone formation. This observation therefore confirms that the acetyl-radical decomposition (reaction 5) is in its first order region; a higher order would lead to an increase in acetone formation as reaction (7) would then require the presence of a third body in order to lead to an overall order of 3/2. In the
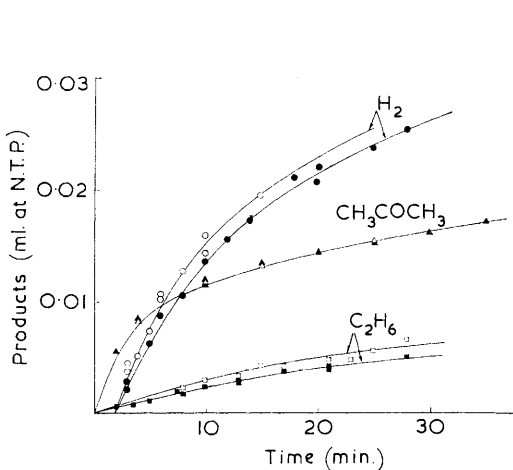

FIG. 3.   Products of pyrolysis at 523° of 250 mm. acetaldehyde (filled points) and of 250 mm. acetaldehyde + 200 mm. carbon dioxide (open points).
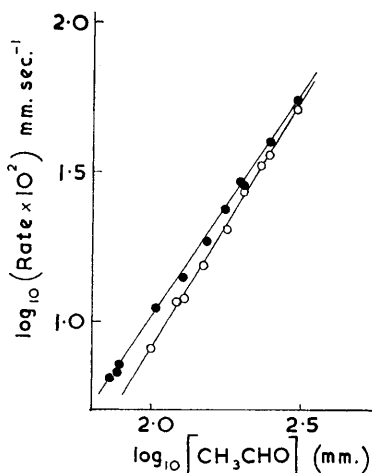
FIG. 4.   Plots of $\log_{10}$rate against $\log_{10}$ pressure (mm.) at 523°. Filled points, acetaldehyde alone; open points, acetaldehyde with 108 mm. ethane.

presence of carbon dioxide the initial rate of formation of hydrogen is given by $d[H_2]/dt = k_1[CH_3CHO]^2 + k_1'[CH_3CHO][CO_2]$ whilst for acetaldehyde alone $d[H_2]/dt = k_1[CH_3CHO]^2$. Thus k_1'/k_1 can be estimated from the initial slopes of the $[H_2]$–time curves and similarly k_6'/k_6, can be determined from the $[C_2H_6]$-time graphs. At 523° these ratios were found to be $k_1'/k_1 = 0.12$ and $k_6'/k_6 = 0.28$. (Since k_1'/k_1 in particular, depends on a small difference between two large quantities the limits of error in the figure quoted will be appreciable, probably of the order of $\pm 60\%$). Substituting these values into the equations for R_x/R_a we have, when $[CH_3CHO] = [CO_2]$, $R_x/R_a = 0.935$ and 1.058 for mechanisms 1 and 2, respectively, so it is not unreasonable to find that carbon dioxide has a negligible effect on the initial overall rate of decomposition.
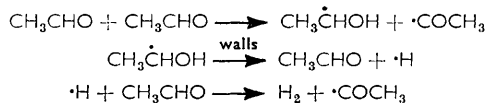
For the decomposition of acetaldehyde in the presence of ethane, the ratio k_6'/k_6 would be expected to be much greater than 0.28 whilst k_1'/k_1 could have a value similar to that found for carbon dioxide. A measurable decrease in the overall rate of decomposition would therefore be expected and, at sufficiently high concentrations of ethane, there should be an increase in the overall order of the reaction. A complicating factor would be the dissociation of ethane itself which would tend to increase the rate of acetaldehyde decomposition. From the rate constants of the initial steps in the acetaldehyde and ethane decompositions [1,10] the relative rates of production of methyl radicals are 10 : 1, respectively, at 523° so the acceleration due to ethane decomposition would be expected to be small.

The pressure–time curves shown in Fig. 2 for 200 mm. of acetaldehyde alone and with 200 mm. of ethane indicate that an overall inhibition of acetaldehyde decomposition by ethane does occur. The logarithmic plots of initial rate against acetaldehyde pressure with and without a fixed pressure of ethane are shown in Fig. 4. From the slopes of the straight lines the overall order of the decomposition reaction was found to increase from 1.50 for acetaldehyde alone to 1.65 for acetaldehyde plus a fixed pressure of 108 mm. ethane.

The decrease in initial rate of decomposition of acetaldehyde in the presence of ethane may be linked with the more marked fall off in rate of decomposition with time in the presence of carbon dioxide. With this added gas, formation of ethane has been found to be more rapid and hence, after a given reaction time, higher concentrations of ethane will be present than with acetaldehyde alone.

Conclusions as to the order of the methyl-radical recombination under our experimental conditions are conflicting. Laidler and Wojciechowski,[10] by extension of the low-temperature results of Dodd and Steacie,[11] favour a third-order reaction, whilst Quinn,[12] from estimations of the methane produced in the decomposition of ethane, has concluded that the reaction $C_2H_6 \longrightarrow 2CH_3\cdot$ is in its first-order region so that the methyl-radical recombination is of second order. Both the observed increase in the rate of formation of ethane in the presence of carbon dioxide reported here and the overall order of the acetaldehyde decomposition coupled with the second order chain-initiating step provide strong support for a pressure-dependent methyl-radical recombination at 500—530° and acetaldehyde pressures of 100—300 mm.

Added in Proof.—In a Paper on the thermal decomposition of acetaldehyde [13] alternative mechanisms have been suggested for the formation of hydrogen and acetone. Eusuf and Laidler suggest that hydrogen results, in part, from the reactions:

$$CH_3CHO + CH_3CHO \longrightarrow CH_3\dot{C}HOH + \cdot COCH_3$$
$$CH_3\dot{C}HOH \xrightarrow{\text{walls}} CH_3CHO + \cdot H$$
$$\cdot H + CH_3CHO \longrightarrow H_2 + \cdot COCH_3$$

[10] Laidler and Wojciechowski, *Proc. Roy. Soc.*, 1961, *A*, **260**, 91.
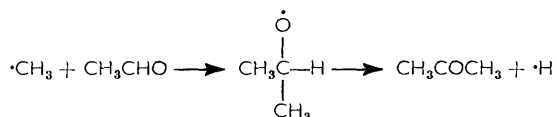[11] Dodd and Steacie, *Proc. Roy. Soc.*, 1951, *A*, **223**, 283.
[12] Quinn, *Proc. Roy. Soc.*, 1963, *A*, **275**, 190.
[13] Eusuf and Laidler, *Canad. J. Chem.*, 1964, **42**, 1851.

since the wall reaction is more likely to have an activation energy of $26 \cdot 3$ kcal. mole^{-1} than our reaction (2). Although, from this aspect, the above mechanism is more satisfactory, it does not explain the increase in hydrogen yields in the presence of added carbon dioxide so that our mechanism must be assumed to contribute, in part, to the overall reaction.

For the formation of acetone, the reactions

$$\cdot CH_3 + CH_3CHO \longrightarrow CH_3\overset{\overset{\textstyle \cdot O}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-H \longrightarrow CH_3COCH_3 + \cdot H$$

have been suggested. Two arguments against this process are: (1) the graphs of hydrogen and of acetone formed against reaction time should be very similar since the reaction $\cdot H + CH_3CHO \longrightarrow H_2 + \cdot COCH_3$ must be fast at the experimental temperature, so that the observed induction periods in the hydrogen–time curves cannot be accounted for; (2) the process leads to a theoretical expression in which the rate of formation of hydrogen is dependent on $[CH_3CHO]^{\frac{3}{2}}$, which does not agree with the second order dependence found experimentally. Thus although the scheme we have suggested for acetone formation is not entirely without ambiguity we feel that it is preferable in that it accounts more satisfactorily for the experimental observation.