[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions

BY F. O. RICE AND K. F. HERZFELD

One of us has recently proposed[1] a free radical mechanism for the pyrogenic decomposition of aliphatic organic compounds from which one can predict quantitatively the products formed on heating a wide variety of organic compounds.[2]

In order to substantiate this theory fully, it will be necessary to account also for the experimental fact that the decomposition of such substances as ethane, acetone, and dimethyl ether follows the equation of a unimolecular reaction, whereas the decomposition of acetaldehyde follows an equation[3] of an order between 1 and 2; we want to show here that these experimental results are consequences of the theory.

(A) Decomposition of Ethane.—We will first write the chemical equations of the chain reactions, as postulated by the theory.

The velocity constant for the n-th reaction from left to right will be called k_n, from right to left, k'_n. Furthermore, the estimated heats of activation will be given since it is necessary to estimate the relative values of the k's.

If one writes the equilibrium conditions for (3) and (4) and multiplies the corresponding equations, one finds

$$\left(\frac{x_6 x_7}{x_1}\right)_{\text{equi}} = \frac{k_3 k_4}{k_3' k_4'} = K \qquad (3')$$

where K is the equilibrium constant. The equilibrium has been measured by Pease,[4] who finds as heat of reaction 31.4 k. cal. Therefore (3′) gives

$$E_3 + E_4 - E_3' - E_4' = 31.4 \qquad (4')$$

Similarly it follows from (6) that

$$E_\alpha + E_\beta - E_{1-\alpha} - E_{\alpha'} = 31 \qquad (6')$$

Finally $E_4' - E_4 = 103 - Q$, if 103 is the heat of dissociation of hydrogen and Q is the strength of the C–H bond in ethane (about 95); therefore

$$8 \leqq E_4' - E_4 \leqq 12 \qquad (4'')$$

Furthermore, with $E_1 = 80$ and a strength of the C–C bond of 72–76, E_1' must be between 4 and 8. We will confine our attention to the first stages of the reaction, so that all the back reactions may be neglected.[5] The proposed mechanism consists in the steps (1), (2), (3), (4) and (6).

A. REACTIONS IN THE DECOMPOSITION OF ETHANE

No.	Chemical equation	Velocity constant	Heat of activation E	E'
1	$C_2H_6 \rightleftarrows 2CH_3$	k_1, k_1'	80	8
2	$CH_3 + C_2H_6 \rightleftarrows CH_4 + CH_3CH_2$	k_2, k_2'	20	20
3	$CH_3CH_2 \rightleftarrows C_2H_4 + H$	k_3, k_3'	49	10
4	$H + C_2H_6 \rightleftarrows H_2 + CH_3CH_2$	k_4, k_4'	17	25
5	$H + H \rightleftarrows H_2$	$^1/_2k_5, {}^1/_2k_5'$	Triple collision	100
6α	$H + CH_3CH_2 \rightleftarrows C_2H_4 + H_2$	$k_6\alpha, k_6'\alpha'$	Small	60
β	$H + CH_3CH_2 \rightleftarrows C_2H_6$	$k_6(1-\alpha), k_6'\beta$	Small	90
7	$H + CH_3 \rightleftarrows CH_4$	k_7, k_7'	Small	90
8	$CH_3 + CH_3CH_2 \rightleftarrows C_3H_8$	k_8, k_8'	8	80
9	$2CH_3CH_2 \rightleftarrows C_4H_{10}$	k_9, k_9'	8	80

The concentrations are denoted as follows

C_2H_6	CH_3	CH_3CH_2	H	CH_4
x_1	x_2	x_3	x_4	x_5
C_2H_4	H_2	C_3H_8	C_4H_{10}	
x_6	x_7	x_8	x_9	

We therefore derive first the kinetic consequences of these steps alone and later show that (5), (7), (8), (9) can be neglected with a proper choice of rate constants.

The concentrations of the intermediate radicals can be arrived at by assuming their amount constant in the steady state (after an immeasurably short period).

(1) Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

(2) On the basis of this mechanism we would expect the experimental result that two organic compounds when mixed do not decompose independently of each other; see Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929); Steacie, *ibid.*, **54**, 1695 (1932); *J. Phys. Chem.*, **36**, 1562 (1932); Kassel, THIS JOURNAL, **54**, 3641 (1932); Steacie, *J. Chem. Phys.*, **1**, 313 (1933).

(3) Kassel [*J. Phys. Chem.*, **34**, 1166 (1930); "Annual Survey of American Chemistry," 1932, p. 31] has mentioned these problems but was unable to solve them.

(4) Pease and Durgan, THIS JOURNAL, **52**, 1262 (1930).

(5) Of course in equilibrium the rate of each reaction is equal to that of its own back reaction (principle of detailed balancing).

$$dx_2/dt = k_1x_1 - k_2x_1x_2 = 0 \quad (10)$$
$$dx_3/dt = k_2x_1x_2 - k_3x_3 + k_4x_1x_4 - k_6x_3x_4 = 0 \quad (11)$$
$$dx_4/dt = k_3x_3 - k_4x_1x_4 - k_6x_3x_4 = 0 \quad (12)$$

From these equations[6]

$$x_2 = k_1/k_2, \text{ and} \quad (13)$$
$$x_3 = x_1\sqrt{k_1k_4/2k_6k_3} \quad (14)$$
$$x_4 = \sqrt{k_1k_3/2k_4k_6} \quad (15)^7$$

The number of hydrogen atoms, x_4, is then independent of x_1, the amount of ethane (at moderate pressures). The reason for this is that the production of H through (3) as well as its destruction through (6) are both proportional to x_1.

We have taken into account the fact that the rates of formation of ethylene and methane are k_3x_3 and k_1x_1, respectively;[2,10] since the methane yield is small, we must have

$$k_3x_3 \gg k_1x_1 \text{ or } \sqrt{k_1k_3k_4/2k_6} > k_1 \quad (16)$$

Furthermore, in order to exclude the chain-destroying reactions (5), (7), (8) and (9) we have assumed that

$$\frac{1}{2}k_5x_4^2 < k_6x_3x_4 \quad \text{or} \quad \frac{k_5}{2k_6}\frac{k_3}{k_4} < x_1 \quad (17)$$
$$\frac{1}{2}k_9x_3^2 < k_6x_3x_4 \quad \text{or} \quad \frac{k_9}{2k_6}\frac{k_4}{k_3}x_1 < 1 \quad (18)$$
$$k_7x_2x_4 < k_6x_3x_4 \quad \text{or} \quad \frac{k_7k_1}{k_2} < \sqrt{\frac{k_1k_4k_6}{2k_3}} \quad (19)$$
$$k_8x_2x_3 < k_6x_3x_4 \quad \text{or} \quad \frac{k_8k_1}{k_2} < \sqrt{\frac{k_1k_3k_6}{2k_4}}\,x_1 \quad (20)$$

Before discussing these equations, we will write the over-all equation for the decomposition of ethane

From (13), (14) and (15)

$$\frac{dx_1}{dt} = -x_1\left[\frac{3}{2}k_1\left(1 - \frac{k_3(1-\alpha)}{3k_4}\right) + \sqrt{\frac{k_1k_3k_4}{2k_6}}\right] \quad (21)$$

Of this, $-{}^1/_2k_1x_1$ is the primary reaction, and

$$2 + \alpha + 2\sqrt{\frac{k_3k_4}{2k_1k_6}} \sim 2e^{\frac{E_1 - E_3 - E_4}{2RT}}$$

is the length of the chain.

Marek and McClure[8] have measured the heat of activation and have found that

$$^1/_2(E_1 + E_3 + E_4 - E_6) = 73 \text{ k. cal., or}$$
$$E_3 + E_4 = 66 \quad (22)$$

In the discussion of reactions (16)–(20), we remark that Marek's measurements[8] extend over temperatures from 873–973° abs. and x_1 from $^1/_3$ to $^1/_8$; we measure x in volume concentrations relative to normal pressure and temperature. If we assume that the accuracy of the first order is assured within 10%, the inequality sign in (17) and (18) means that the left side is not larger than one-fifth of the right (see footnote 7, quadratic equation).

We assume that all unimolecular reactions have rate constants $10^{14}\,e^{-E/RT}$ sec.$^{-1}$, while for all bimolecular reactions the constant is $10^9\,e^{-E/RT}$, with the following exceptions: the reunion of 2H needs a triple collision and has therefore a rate of about $k_5x_4^2 = 10^6x_4^2$; to satisfy both (17) and (18), it is necessary that $k_9/k_6 = 10^{-3}$. (23)

If $E_9 = 8$ k. cal., there must be an additional steric or probability factor of 10^{-1} in k_9. If the strength of the C–C bond were 76 instead of 72, E_9 would equal 4 and a factor of 10^{-2} would be necessary. As there is no reason to single out reaction (9), we will assume this factor $^1/_{10}$ and $E = 8$ k. cal. for all reactions involving the reunion of radicals.

Then (16) is fulfilled automatically, since from (22), equations (17) and (18) are equivalent to $k_9/1.6k_6 = k_3/k_4 = 50$ or $32 \geqq E_3 - E_4 \geqq 28$. (24) The values chosen in Table I comply with this inequality; they are selected in view of equation (27′) of the back reaction and condition (4″). (19) and (20) are fulfilled with a wide margin.

The final equation for the decomposition of ethane is then

$$\frac{dx_1}{dt} = -kx_1;\ \log k = \frac{1}{2}\log\frac{k_1k_3k_4}{2k_6} = 13.7 - \frac{73{,}000}{2.3RT} \quad (22')$$

compared with Marek and McClure's empirical value

$$\log k = 15.12 - \frac{73{,}200}{2.3RT} \quad (22'')$$

The length of the chain is

$$2e^{(80-17-49)/2RT} \sim 100$$

which is in reasonably good agreement with the fact that 2% of methane has been found among the decomposition products (rate of formation $k_2x_1x_2 = k_1x_1$). The chain length is rather sensitive to changes in $E_3 + E_4$.

(A′) The Formation of Ethane from Hydrogen and Ethylene.—This reaction has been investigated by Pease.[9] The mechanism follows without any new assumption directly from our previous investigation.

(6) At low pressures (10) would take the form $k_1x_1 - k_1'x_2^2 = 0$. At high pressures $k_1'x_2^2:k_2x_2 = k_1'k_1:k_2^2$ or $10^5 - (E_1 + E_1' - 2E_2)/2.3\,RT$ which is small compared with 1 if $E_2 < 32$.

(7) The exact equation is

$$\frac{k_1k_4}{2k_3k_6}\left(1 - k_8 - \frac{k_1}{k_2}\right) = x_4^2\left\{1 + \frac{k_5}{2k_6}\frac{k_3 - k_8\,k_1/k_2}{k_4}\frac{1}{x_1} - \frac{k_9}{2k_6}\frac{k_4}{k_3 - k_8\,k_1/k_2}\,x_1\right\} + \left(\frac{k_8}{k_9} + \frac{k_7}{k_6}\frac{k_3 - k_8\,k_1/k_2}{k_4}\frac{1}{x_1}\right)\frac{k_1}{k_2}x_4$$

(8) Marek and W. B. McClure, *Ind. Eng. Chem.*, **23**, 878 (1931).

(9) R. N. Pease, THIS JOURNAL, **54**, 1876 (1932).

The mechanism involves ($6\alpha'$) as production of the chain-carriers H and CH_3CH_2, and then the chain (3') and (4').

As equations for the condition of constancy of the carriers we have for H:

$$k_6'\alpha'x_6x_7 - k_6x_3x_4 + k_3x_3 - k_3'x_4x_6 + k_4'x_3x_7 - k_5x_4^2 = 0 \quad (23)$$

and for CH_3CH_2:

$$k_6'\alpha'x_6x_7 - k_6x_3x_4 - k_3x_3 + k_3'x_4x_6 - k_4'x_3x_7 = 0 \quad (24)$$

The main reaction, disappearance of ethylene, is given by

$$-\frac{dx_6}{dt} = k_6'\alpha'x_6x_4 + k_3'x_4x_6 - k_3x_3 - k_6\alpha x_3x_4 \quad (25)$$

In (23) $k_5'x_4^2$ can be neglected in comparison with $k_3'x_4x_6$, as is shown by inserting (26). (23) and (24) lead to

$$x_3^2 = x_6^2\frac{k_3'k_6'\alpha'x_7}{k_4'x_7 + k_3}, \text{ or} \quad (26)$$

$$-\frac{dx_6}{dt} = k_6(1-\alpha)x_3x_4 + k_4'x_3x_7 = k_6'(1-\alpha)x_6x_7 + x_6x_7\sqrt{\frac{k_3'k_6'\alpha'k_4'^2x_7}{k_4'x_7 + k_3}} \quad (27)$$

Pease's investigations show the reaction to be unimolecular within the range of 773–825°K. and down to $x_7 \sim 1/_6$. Again taking 10% as the limit of accuracy, this means that

$$k_3/k_4' \times 6 \leq 1/5, \text{ or} \quad (27')$$
$$E_3 - E_4' \geqq 24$$

which is fulfilled by the values of the heats of activation which we have selected.

We find therefore for the resultant reaction

$$\sqrt{\frac{k_3'k_6'\alpha'}{k_6}}\,k_4' \times x_6x_7 \quad (28)$$

with a resultant heat of activation

$$\frac{1}{2}(E_3' + E_4' + E\alpha') = \frac{1}{2}(35 + 60) = 47.5 \text{ k. cal.} \quad (28')$$

which value is in good agreement with the experimental value of Pease, 43.5.

If this is the predominant mechanism rather than the direct reaction, then the agreement of the velocities as measured by Marek (forward reaction) and by Pease (back reaction) with the equilibrium is somewhat fortuitous.

The sum of the apparent heats of activation of the forward and back reactions according to our calculations is

$$\frac{1}{2}(E_1 + E_3 + E_4 - E_3' - E_4' - E\alpha')$$

or according to (4')

$$\frac{1}{2}(E_1 - E\alpha' + Q)$$

or according to (6')

$$Q + \frac{1}{2}(E_1 + E_{1-\alpha} - E_\alpha - E_\beta)$$

and this is Q only if $E_1 - E_\beta' - E_\alpha + E_{1-\alpha} = 0$.

(B) Decomposition of Acetone.—Again numbering the equations and substances as in the case of ethane, we have

	Reaction
(1)	$CH_3COCH_3 \rightleftarrows CH_3 + CH_3CO$
(2)	$CH_3CO \rightleftarrows CH_3 + CO$
(3)	$CH_3 + CH_3COCH_3 \rightleftarrows CH_4 + CH_3COCH_2$
(4)	$CH_3COCH_2 \rightleftarrows CH_2 = CO + CH_3$
(5)	$CH_3 + CH_3 \rightleftarrows C_2H_6$
(6)	$CH_3 + CH_3COCH_2 \rightleftarrows CH_3COC_2H_5$
(7)	$2CH_3COCH_2 \rightleftarrows (CH_3COCH_2)_2$

	Reaction constant	Heat of activation	
(1)	k_1, k_1'	$E_1 = 70$	
(2)	k_2, k_2'	$E_2 = 10$	
(3)	k_3, k_3'	$E_3 = 15$	
(4)	k_4, k_4'	$E_4 = 48$	
(5)	k_5, k_5'	$E_5 = 8$	
(6)	k_6, k_6'	$E_6 = 8$	
(7)	k_7, k_7'	$E_7 = 8$	$E_7' = 45$

As before, we number substances, denoting concentrations as follows:

CH_3OCH_3		CH_3	CH_3CO	CH_3COCH_2
x_1		x_2	x_3	x_4
CH_2CO	CO	CH_4	C_2H_6	$CH_3COCH_2CH_3$
x_5	x_6	x_7	x_8	x_9

Proceeding in a manner similar to A we arrive at the following equations for the intermediate products as condition for the steady state

$$\frac{dx_2}{dt} = k_1x_1 + k_2x_3 - k_3x_1x_2 + k_4x_4 - k_6x_2x_4 = 0 \quad (8)$$

$$\frac{dx_3}{dt} = k_1x_1 - k_2x_3 = 0 \quad (9)$$

$$\frac{dx_4}{dt} = k_3x_2x_1 - k_4x_4 - k_6x_2x_4 = 0 \quad (10)$$

which lead to the following results

$$x_3 = (k_1/k_2)x_1 \quad (9')$$
$$x_2 = \sqrt{k_1k_4/k_6k_3} \quad (11)$$
$$x_4 = x_1\sqrt{k_1k_3/k_6k_4} \quad (12)$$

The concentration of CH_3COCH_2, the main carrier of the chain, is proportional to x_1 (concentration of CH_3COCH_3) because it is produced by a collision of methyl radicals with acetone (the concentration of methyl is constant, since it is produced by the dissociation of acetone and disappears by collision with CH_3COCH_2, which has a concentration proportional to that of acetone).

The following inequalities have been assumed

$$k_6x_2x_4 \ll k_4x_4 \text{ or } k_1k_6/k_4k_3 \ll 1 \quad (13)$$
$$k_5x_2^2 \ll k_1x_1 \text{ or } k_5k_4/k_6k_3 \ll x_1 \quad (14)$$

Equation (13) leads to

$$E_3 + E_4 - 78 \ll 0 \qquad (13')$$

and is easily fulfilled. (14) means that

$$10^5\, e^{(E_6 - E_5 + E_3 - E_4)/RT} \ll x_1 \qquad (14')$$

Within the range of the experiments (T = 800 to 900° Abs., $x_1 \geqq {}^1/_{24}$) and with the accuracy we have assumed before, $E_4 - E_3 \geqq 26$.

We can neglect reaction (9), since after a few seconds a steady state of equality between reactions (9) and (9') is reached.[10]

One finds then for the decomposition of the acetone[11]

$$dx_1/dt = k_1x_1 - k_3x_2x_1 \qquad (15)$$

or leaving out unimportant terms

$$dx_1/dt = -kx_1, \text{ with } k = \sqrt{k_1k_3k_4/k_6} \qquad (15')$$
$$\log k = 14.5 - (62{,}500/2.3RT) \qquad (15'')$$

while Hinshelwood and Hutchinson[12] give 15 − (68,500/2.3RT).

The chain length is given by

$$\sqrt{\frac{k_3k_4}{k_1k_6}} \sim 3\, e^{15/2RT} \sim 300$$

Thus the formula for the chain length is, except for a factor 2, the same as that for ethane, the numerical difference being due to the difference in the heats of activation.

(C) Decomposition of Dimethyl Ether.—This reaction has been investigated by Hinshelwood.[13] The mechanism according to the theory of free radicals is given below. For an intermediate stage two ways of reaction are possible, namely, (2), or (3) + (4). It will be seen later that the results of the calculations are the same for both alternatives.

DECOMPOSITION OF DIMETHYL ETHER

No.	Chemical equation	Reaction constant	E	E'
(1)	$CH_3OCH_3 \rightleftarrows CH_3 + CH_3O$	k_1, k_1'	80	
(2)	$CH_3O + CH_3OCH_3 \rightleftarrows CH_3OH + CH_2OCH_3$, or	k_2, k_2'	15–25	
(3)	$CH_3O \rightleftarrows HCHO + H$, and	k_3, k_3'	20–45	
(4)	$H + CH_3OCH_3 \rightleftarrows H_2 + CH_2OCH_3$	k_4, k_4'	10–15	
(5) } chain	$CH_3 + CH_3OCH_3 \rightleftarrows CH_4 + CH_2OCH_3$	k_5, k_5'	15	
(6) }	$CH_2OCH_3 \rightleftarrows CH_3 + HCHO$	k_6, k_6'	38	
(7)	$2CH_3 \rightleftarrows C_2H_6$	k_7, k_7'	8	80
(8)	$CH_3 + CH_2OCH_3 \rightleftarrows C_2H_5OCH_3$	k_8, k_8'	8	
(9)	$2CH_2OCH_3 \rightleftarrows (CH_3OCH_2)_2$	k_9	8	45
(10)	$2CH_3O \rightleftarrows (CH_3O)_2$ unstable		8	45
(11)	$CH_3O + CH_2OCH_3 \rightleftarrows CH_3OCH_2OCH_3$	k_{11}		
(12)	$H + CH_3 \rightleftarrows CH_4$	k_{12}		
(13)	$H + CH_3O \rightleftarrows CH_3OH$	k_{13}		
(14)	$H + CH_2OCH_3 \rightleftarrows CH_3OCH_3$	k_{14}		

We again give indices to the different substances

CH_3OCH_3	CH_3	CH_3O	H	CH_2OCH_3	CH_4
1	2	3	4	5	6
HCO	H_2	C_2H_6	CH_3OH	$CH_3CH_2OCH_3$	
7	8	9	10	11	

and use x with the corresponding subscript to denote concentration.

Only CH_3 (2) and CH_2OCH_3 (5) are involved as intermediaries in the chain. Accordingly CH_3O (3), and H (4) in the second mechanism, are present in much smaller quantities. Therefore, we are going to neglect beforehand the reactions in which (2) or (5) disappear by collision with (3) or (4), that is, reactions (10) to (14).

We start with the consideration of the first mechanism and find for the three intermediate compounds

$$CH_3 \quad dx_2/dt = k_1x_1 - k_5x_1x_2 + k_6x_5 - k_7x_2^2 - k_8x_2x_5 = 0 \qquad (16)$$

$$CH_3O \quad dx_3/dt = k_1x_1 - k_2x_1x_3 - k_1'x_2x_3 = 0 \qquad (17)$$

(10) One easily finds $x_{10} = k_7x_4^2/k_7'\,(1 - e^{-k_7't})$; x_{10} has reached $1 - 10^{-5}$ of its final value after a time $11.5/k_7' = 10^{-13}\, e^{15/RT}$, which is only a few seconds at the utmost. At that time the excess of CH_3COCH_2 combining with itself over the reproduction of this radical through the dissociation of $(CH_3COCH_2)_2$ is $10^{-5}\, k_7x_4^2 = 10^{-5}k_7\,(k_1k_3/k_6k_4x_1^2)$. This is small compared with k_1x_1. The stationary value of $x_{10} = k_7x_4^2/k_7' = 10^{-5}\, e^{-16/RT}$.

(11) In the decomposition of both acetone and dimethyl ether there are two chain carriers, the methyl group and a heavy carrier. The chain could be terminated in three ways: by recombination of two methyl groups, by recombination of two heavy groups, or by combination of one methyl and one heavy group. The latter mechanism is necessary to give the right order of reaction. It is predominant over the recombination of two methyl groups, because with the assumed heats of activation there are more heavy radicals than methyl groups present; the recombination of the two heavy radicals is relatively insignificant because of the chemical instability of the bond which is formed, thus permitting the resulting product to be decomposed very quickly into its components. We have not assigned a large activation energy to the recombination of methyl radicals [see Heitler and Schuchowitzki, *Phys. Zeit. der Sowjetunion*, 3, (1933)], because our experimental work indicates that this is contrary to the experiments.

(12) Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **A111**, 245 (1926).

(13) Hinshelwood and Askey, *ibid.*, **A115**, 215 (1927).

CH_2OCH_3 $dx_5/dt = k_2x_1x_3 + k_5x_1x_2 - k_6x_5 - k_8x_2x_5 - k_9x_5^2 = 0$ (18)

From these equations

$$x_3 = k_1/k_2 \quad (19)$$

$$x_2 = \sqrt{k_1k_6/k_8k_5} \quad (20)^{14}$$

$$x_5 = x_1\sqrt{k_1k_5/k_8k_6} \quad (21)$$

The following reactions have been neglected

$$k_1'x_2x_3 \ll k_2x_1x_3 \quad \text{or} \quad k_1'\sqrt{k_1k_6/k_8k_5} \ll k_2x_1 \quad (22)$$

$$k_7x_2^2 \ll 2k_8x_2x_5 \quad \text{or} \quad k_7k_6/2k_8k_5 \ll x_1 \quad (23)$$

(22) is automatically fulfilled, and (23) gives

$$(10^5/2)e^{(E_5 - E_6)/RT} \leqq x_1/5 \quad (23')$$

with the same accuracy as before; or with $x_1 \sim {}^1/_6$, $E_5 - E_6 \geqq 23$.

The rate of decomposition of the ether is given by $dx_1/dt = -2k_1x_1 - k_5x_1x_2$ or

$$\log k = {}^1/_2 \log \frac{k_1k_5k_6}{k_8} = 14.5 - \frac{62{,}500}{2.3RT} \quad (24)$$

Hinshelwood gives $13.2 - (58{,}500/2.3RT)$.

Methane is formed at the rate $k_5x_2x_1$ (see dimethyl ether).

Formaldehyde, HCHO, at the same rate, since $k_6x_5 = k_5x_2x_1$.

CH_3OH: $k_2x_3x_1 = k_1x_1$, which is equal to the primary reaction.

$CH_3CH_2OCH_3$: $k_8x_2x_5 = k_1x_1$, which is again equal to the primary reaction.

C_2H_6: $k_7x_2^2 = k_7k_1k_6/k_5k_8$, which is less than the primary reaction.

In the low pressure region this situation is reversed; the formation of ethane is then equal to the primary reaction and responsible for the breaking of the chain, while the formation of ethyl methyl ether, which terminates the chain in the high pressure region, is now proceeding at the rate $(k_8k_5/k_7k_6)2k_1x_1^2$, which is slower than that of the primary reaction.

In the low pressure range, we have for the expression $k_5x_2x_1$, which governs the disappearance of the ether and the production of methane and formaldehyde

$$k_5\sqrt{\frac{2k_1}{k_7}}x_1^{3/2} \sim 10^{12}\, e^{-(2E_5 + E_1 - E_7')/2RT}\, x_1^{3/2} \quad \text{or} \quad (25)$$

$$\ln k' = 27.6 - (51{,}000/RT) \quad (25')$$

In the high pressure range, the chain length is given by

$$\sqrt{\frac{k_6k_5}{k_8k_1}} \sim 3e^{-(E_6 + E_5 - E_1 - E_8)/2RT} \sim 200{,}000 \text{ (at 800° Abs.)} \quad (26)$$

the formula being similar to that arrived at in the studies of the decomposition of ethane and acetone.

We have now to discuss the alternative mechanism, given by (3) and (4), instead of (2). One finds instead of (19) that $x_3 = k_1/k_3$, but (20) and (21) are unchanged. Therefore this mechanism leads to approximately the same results as the other except for the fact that instead of methyl alcohol, hydrogen is formed at the rate $k_4x_1x_4$ which is smaller than k_1x_1.

Kassel and also Steacie[15] have shown that in a mixture of dimethyl ether and ethyl ether each compound decomposes faster than would correspond to its partial pressure. These authors explain this through a so-called "cross activation." However, this phenomenon follows directly from the theory of free radicals, as each of the ethers supplies the radicals which enter into the chain reactions of both.

(D) Decomposition of Acetaldehyde.—This reaction has been investigated by Hinshelwood and Hutchinson,[12] Fletcher and Hinshelwood[16] and by Kassel.[17] The latter found the initial rate to be proportional to the $^5/_3$ power of the concentration. From the ratio of the time it takes to decompose the aldehyde by $^1/_2$ to the time it takes to decompose it to $^1/_3$, Fletcher and Hinshelwood conclude that a succession of three different second order reactions occur in the pressure range from 0.2 to 1000 mm. If one plots, however, the logarithm of the initial velocity against the logarithm of the pressure as did Kassel one gets very accurately the 1.5 order reaction in the range between 1000 and 100 mm. or from 400 to 40 mm., (these two ranges are for runs at different temperatures).

It will be shown here that a rate proportional to the 1.5 power of the concentration follows directly from the theory of free radicals, as does also the composition of the products, as well as the heat of activation of the reaction.

The theory as far as it is developed here does not predict what happens in the case of such large percentage decompositions as are considered in Fletcher and Hinshelwood's calculation.

REACTION MECHANISM

No.		Chemical equation	Velocity constant	Heat of activation E	E'
(1)		$CH_3CHO \rightleftharpoons CH_3 + HCO$	k_1, k_1'	70	8
(2)		$HCO \rightleftharpoons CO + H$	k_2, k_2'		
(3)		$H + CH_3CHO \rightleftharpoons H_2 + CH_3CO$	k_3, k_3'		
(4)	chain	$CH_3CO \rightleftharpoons CH_3 + CO$	k_4, k_4'	10	
(5)	chain	$CH_3 + CH_3CHO \rightleftharpoons CH_4 + CH_3CO$	k_5, k_5'	15	
(6)		$2CH_3 \rightleftharpoons C_2H_6$	k_6, k_6'	8	
(7)		$CH_3 + CH_3CO \rightleftharpoons CH_3COCH_3$	k_7, k_7'	8	
(8)		$2CH_3CO \rightleftharpoons CH_3COCOCH_3$	k_8, k_8'	8	45

(14) The exact formula for x_2 is $x_2^2 = \dfrac{k_1k_6}{k_8k_5}\,\dfrac{1}{1 + (k_7k_6/2k_8k_5)(1/x_1)}$. In deriving it, $k_9x_5^2$ has not been considered for the same reasons as the analogous reaction in the case of acetone.

(15) Kassel, THIS JOURNAL, **54**, 3641 (1932); Steacie, *J. Chem. Phys.*, **1**, 313 (1933).

(16) Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

(17) Kassel, *J. Phys. Chem.*, **34**, 1166 (1930).

We again number the concentrations:

CH_3CHO	CH_3	HCO	H	CH_3CO
x_1	x_2	x_3	x_4	x_5

The difference in reaction order of acetaldehyde and the other compounds discussed in this paper is due to the fact that the two carriers of the chain, CH_3 and CH_3CO, are present in quite different amounts (because of the particular values of the heats of activation). Therefore, the more abundant of the two, CH_3, disappears finally through recombination, according to (6), instead of through combination with CH_3CO (according to 7), as happens in the other decompositions considered in this paper.

The steady state of the two intermediate substances not occurring in the chain is given by

$$\text{for HCO } k_1x_1 - k_2x_3 = 0 \quad (9)$$
$$\text{for H } \quad k_2x_3 - k_3x_4x_1 = 0 \quad (10)$$

It follows immediately that

$$x_3 = k_1x_1/k_2 \quad (9')$$
$$x_4 = \frac{k_2x_3}{k_3x_1} = \frac{k_1}{k_3} \quad (10')$$

For the two carriers of the chain we find:

$$\text{for } CH_3 \quad k_1x_1 + k_4x_5 - k_5x_2x_1 - k_6x_2^2 - k_7x_2x_5 = 0 \quad (11)$$
$$\text{for } CH_3CO \quad k_3x_1x_4 - k_4x_5 + k_5x_2x_1 - k_7x_2x_5 = 0 \quad (12)$$

These equations lead to

$$x_2 = \sqrt{k_1/k_6}\,\sqrt{x_1} \quad (13)$$
$$x_5 = \sqrt{k_5/k_6}\,x_1{}^{3}/{}_{2} \quad (14)$$

For the final reaction, the disappearance of acetaldehyde, one gets

$$-\mathrm{d}x_1/\mathrm{d}t = 2k_1x_1 + k_3x_1x_4 + k_5x_2x_1 = 2k_1x_1 + k_5\sqrt{k_1k_6}\,x_1{}^{3}/{}_{2} \quad (15)$$

The experimental value for the heat of activation is 45.5 k. cal., the theoretical value is

$${}^1/{}_2(E_1 - E_6 + E_5) = 46$$

The constant factor is in our units (1 mole in 22,400 cc. at 0°) about 10^{12}. Kassel's value, divided by $(22,000)^{2/3}$ is 6×10^{10}.

We have assumed $k_6x_2^2 \ll k_4x_5$, $k_5/k_4 \ll k_6/k_7$, both of which are amply fulfilled. We are grateful to Dr. L. Kassel for constructive criticism in connection with this paper.

Summary

A discussion of the reaction mechanism postulated by the theory of free radicals shows that the decompositions of ethane, acetone and dimethyl ether must be of the first order, the dissociation of acetaldehyde of the 1.5th order, while the formation of ethane from ethylene and hydrogen is of the second order. The essential condition in the first order equation is that the chain shall be terminated by a reaction between the two different carriers of the chain. In acetaldehyde the 1.5 order results from the fact that the chain is terminated by the reaction of two methyl groups. This difference is due to a difference in the heats of activation. The heats of activation can be determined from the measured reaction rates with considerable certainty, and it is seen that they fit the observed orders of the reaction, whereas assigning different values to the heats of activation might be expected to lead to a different order. Although there is as yet no experimental evidence for the presence of reaction chains in these decompositions and, further, there has been no direct experimental demonstration even of the presence of free radicals below 700° and above a few mm. pressure, nevertheless it should be pointed out that the only way to avoid chain reactions as the explanation of the measured rates would be to increase the heats of activation involved to quite improbable values.

BALTIMORE, MD. RECEIVED AUGUST 3, 1933