

429. *Kinetics of the Thermal Decomposition of Acetals.*  
*Part II.<sup>1</sup> The Methylal Chain.*

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The kinetics of the thermal decomposition of methylal has been studied over the range 472—520° and 50—450 mm. in a static system, by studying the change of pressure and by infrared analyses. The system of steady-state equations is too complex to have a straightforward solution but by means of them the experimental order is explained, several stoichiometric relations among the products become amenable to experimental test, and ratios of elementary rate constants and changes of some radical concentrations have been calculated.

PART I of this series<sup>1</sup> dealt with the thermal decomposition of ethylal, dimethyl acetal, and diethyl acetal in a static system. The present paper extends the investigation to the simplest acetal, namely, methylal. With it a more thorough study of the decomposition mechanism has been undertaken by applying the steady-state approximation.

EXPERIMENTAL AND RESULTS

The experimental technique was as described in Part I. Methylal was a purum grade "Fluka A.G." chemical.

*Influence of the Surface.*—Experiments were made in two vessels of the same size and shape, one empty and the other filled with silica powder, which varies the surface : volume ratio ~500-fold.

Plots of pressure increase against time for the first experiments in the filled vessel showed a shift towards greater values of  $\Delta p$ , compared with those obtained with the empty vessel. However, after several runs the shift decreased and finally the curves were superimposable. It seems that the thermal decomposition of methylal can be affected by the surface of the reaction vessel, but that this influence is probably relevant to a non-seasoned surface. These results suggest that in a seasoned vessel measurements refer to the true homogeneous decomposition. Other results (below) were obtained in seasoned vessels.

TABLE I.

Rates of decomposition of methylal.

520°	$p_0$	76	114	148	200	251	255	296	329	338	
	Rate	28	52	71	109	144	148	194	192	212	
510°	$p_0$	65	83	140	209	262	327	368			
	Rate	18	40	45	83	104	139	152			
500°	$p_0$	47	99	117	166	210	250	321	357	443	
	Rate	9	17	24	41	51	71	97	105	152	
492°	$p_0$	99	116	119	170	196	252	261	330	352	446
	Rate	11	17	17.5	28	33.5	48	52	69	76	106
483°	$p_0$	72	126	175	211	247	261	302	373	436	
	Rate	5.5	12.5	20	26	30	35	41	52.5	64	
472°	$p_0$	112	165	207	248	293	325	359	432		
	Rate	6.5	11	16	20	22	28.5	31.5	41.5		

Pressures are in terms of mm. of Hg. Rates are recorded as mm. of Hg/min.

*Change of Pressure.*—Methylal was studied in the range 472—520° and 50—450 mm. (Fig. 1). Short induction periods were observed at the lower temperatures.

The kinetic constants have been determined from plots of pressure increase against time because it was found that for at least the first 70% of the reaction, the amount of methylal used is proportional to  $\Delta p$  (Fig. 2). It was also shown that plots of the amounts of the products (carbon monoxide, methane, and hydrogen) against  $\Delta p$  all yield straight lines that pass through the origin, and so the pressure increase becomes a measure of the rate of consumption of methylal.

The variation of the rate of the reaction with initial methylal pressure ( $p_0$ ) is recorded for

<sup>1</sup> Part I, Molera, Centeno, and Orza, *J.*, 1963, 2234.

various temperatures in Table 1. Plots of the rate of the reaction against  $p_0$  are curves for initial pressures up to about 150 mm. At the higher pressures it might be expected that the reaction should follow a first-order law, but experiments at still higher pressures might prove that the plot is actually a curve over the whole range.

An activation energy of 45 kcal./mole has been calculated by the method of least squares from the Arrhenius equation by using the values in Table 1.

*Analysis of Products.*—The analytical work was done (a) on two different fractions from one sample and (b) also by analysis of a second sample that had been similarly pyrolysed but not fractionated.

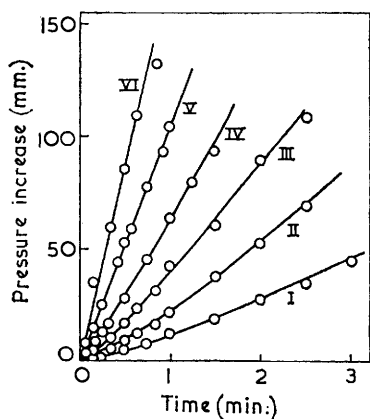


FIG. 1. Decomposition of methylal at (I) 472°, (II) 483°, (III) 492°, (IV) 500°, (V) 510°, and (VI) 520°. Initial pressures were 250 mm.

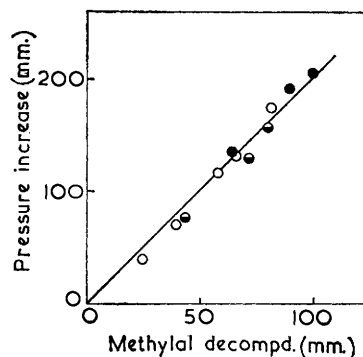


FIG. 2. Plot of pressure increase against decomposition at (●) 520°, (⊙) 492°, and (○) 459°.

The calculated values of the amounts of methylal obtained from the amounts of the products are a little higher than those obtained by direct analysis of methylal, probably owing to absorption in the tap grease.

The following compounds have been identified by infrared spectrometry in the reaction mixture: carbon monoxide, carbon dioxide, methane, methyl alcohol, methyl formate, and undecomposed methylal. Hydrogen was determined by difference and by material balances.

TABLE 2.  
Product analyses (methylal,  $p_0$  150 mm.) (pressures in mm. of Hg).

Reaction Temp. time (min.)	CH <sub>4</sub>	H·CO <sub>2</sub> Me	MeOH	CO	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>2</sub> (OMe) <sub>2</sub>	Σp	Press. in vessel
459°	8	24.5	15	—	19	14	—	121	193
	15	44	22	—	33	28	—	95	223.5
	30	72	32	7	55	40	—	75.5	281.5
	45	81.5	37	7.5	62	59	—	64	311
492	4	43.5	23	5	29	44	—	94	238.5
	6	59	33.5	5.5	78	38	—	81	295
	8	61	33	5	72	71	—	62	304
	10	97	32	5	77.5	50	—	62	323
	12	82	43.5	6	85	75.5	—	56	348
	12	75.5	38	3.5	81	102	—	53	353
	15	83	39.5	4	104	92	3	50	375.5
	20	98	39.5	7	104	104	3	40	395.5
	180	111	25	9	140	158	7.5	25	475.5
	520	2	66.5	30	7.5	59.5	51.5	—	70
4	106	36	7	93	52	3	49.5	346.5	
6	104	37	7.5	100	60.5	9	39.5	357.5	
8	113	35.5	7	107	91.5	8	31	393	
10	124	36	19	104	111	12	26	432	
12	122	34	10.5	114	117	12	29	438.5	
18	120	31	10	115	114	18	26	434	

Quantitative analyses have been made for reactions at different temperatures (459°, 492°, and 520°) and after different times. The results are recorded in Table 2.

*Influence of Inhibitors.*—Small amounts of nitric oxide (<1%) inhibit the thermal decomposition of methylal. This may be considered as full inhibition because greater amounts do not decrease the rate further. Here also, as with the other acetals previously studied, inhibition is transitory.

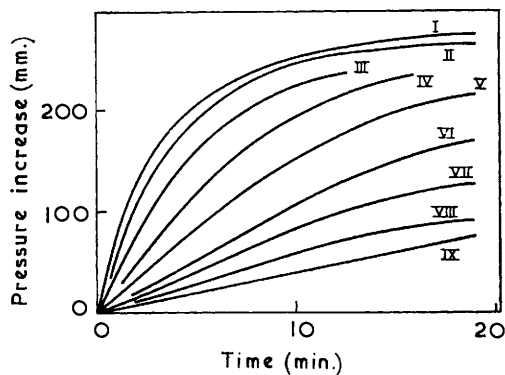
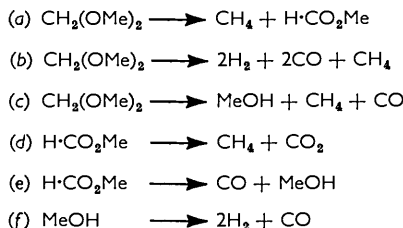


FIG. 3. Inhibition of decomposition of methylal ( $p_0$  150 mm.) at 520° by the following propene pressures: (I) 0, (II) 2, (III) 4, (IV) 12, (V) 20, (VI) 30, (VII) 46, (VIII) 100, and (IX) 151 mm.

The reaction is inhibited also by propene but it is necessary to add nearly 150 mm. of propene to obtain the same reduction in the initial rate as with only 0.5 mm. of nitric oxide; however, the inhibition is not transitory with propene (Fig. 3).

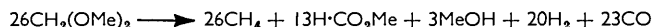
#### DISCUSSION

*Stoichiometry.*—The following partial equations (written only from the point of view of stoichiometry) seem to explain formation of all the products:



Of these, the first two are the most important, and the last three probably occur only at the higher temperatures, where secondary decomposition of the products commences. The form of the curves at 520° suggests that methyl formate decomposes.

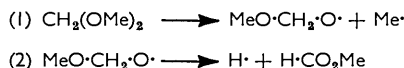
At 459°, secondary decomposition, if present, must be unimportant and so the stoichiometry of the reaction may be established at this temperature:



which again implies that reactions (a) and (b) account for most of the products.

*The Chain Sequence.*—The kinetic constants, analyses of products, and action of inhibitors may be explained by a chain mechanism as follows:

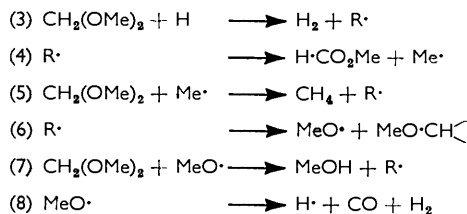
(a) *Initiation.*



The initial splitting could be also into a methoxyl radical and the remaining radical, but this would not greatly affect the whole chain process.

(b) *Propagation.* It seems obvious that in propagation attack is on one hydrogen atom of the  $\text{CH}_2$  group of methylal. In the following, R denotes the radical  $(\text{MeO})_2\text{CH}\cdot$

We then propose the steps:



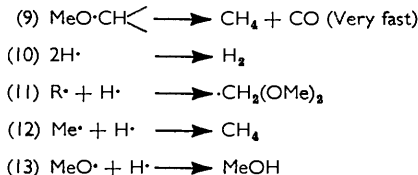
Acetaldehyde has not been detected among the products over the range studied; consequently, the rearrangement  $\text{CH}_2(\text{OMe})_2 \longrightarrow \text{MeOH} + \text{Me}\cdot\text{CHO}$  seems to be excluded, and this is the reason why methoxyl radicals should be present in order to account for the methyl alcohol formed.

The small quantity of carbon dioxide formed could be explained partially by the reaction:



though it is more likely to arise from the secondary decomposition of methyl formate that occurs at the higher temperatures studied.

(c) *Termination.*



The reaction  $2\text{Me}\cdot \longrightarrow \text{C}_2\text{H}_6$  has not been considered because ethane is not produced. Reactions of a radical with a different one have also not been considered, as no other products have been detected in the mixtures.

*Steady-state Equations.*—The steady-state approximation requires that

$$k_3\text{MH} - (k_4 + k_6)\text{R} + k_5\text{MA} + k_7\text{MB} - k_{11}\text{RH} = 0; \quad (\text{i})$$

$$k_1\text{M} + k_4\text{R} - k_5\text{MA} - k_{12}\text{HA} = 0; \quad (\text{ii})$$

$$k_1\text{M} - k_3\text{MH} + k_8\text{B} - k_{10}\text{H}^2 - k_{11}\text{RH} - k_{12}\text{HA} - k_{13}\text{HB} = 0; \quad (\text{iii})$$

$$k_6\text{R} - \text{B}(k_7\text{M} + k_8 + k_{13}\text{H}) = 0, \quad (\text{iv})$$

where M, H, A, B, and R denote the concentrations of methylal, hydrogen atoms, and methyl, methoxyl, and R radicals, respectively.

Two independent expressions for R/M may be thence derived:

$$\frac{\text{R}}{\text{M}} = \frac{\text{H}}{2k_6k_8} \left( 2k_3 + k_{10} \frac{\text{H}}{\text{M}} \right) (k_7\text{M} + k_{13}\text{H} + k_8) \quad (\text{v})$$

$$\text{and} \quad \frac{\text{R}}{\text{M}} \left( \frac{k_4k_{12}}{k_5\text{M} + k_{12}\text{H}} + \frac{k_6k_{13}}{k_7\text{M} + k_{13}\text{H} + k_8} + k_{11} \right) = \frac{k_1k_5\text{M}}{\text{H}(k_5\text{M} + k_{12}\text{H})} - \frac{k_{10}}{2} \cdot \frac{\text{H}}{\text{M}} \quad (\text{vi})$$

Substitution of the R/M value from (v) into (vi) gives the general expression that relates H and M; this is a fifth-order equation which cannot be solved for H. However, as will be shown, some chain steps offer a minor contribution to the mechanism and may be neglected, thus simplifying the treatment.

The rate of consumption of methylal may be expressed by

$$-d\text{M}/dt = k_1\text{M} + k_3\text{MH} + k_5\text{MA} + k_7\text{MB} - k_{11}\text{RH}, \quad (\text{vii})$$

and subtraction of (i) from (vii) gives the simpler expression

$$-\frac{1}{M} \cdot \frac{dM}{dt} = k_1 + (k_4 + k_6) \frac{R}{M} \quad (\text{viii})$$

If methylal were consumed according to a first-order law,  $R/M$  should be a constant in (viii). Consideration of equations (v) and (vi) shows that this condition would probably be fulfilled if  $H$ ,  $H/M$ , and  $M$  were constant. But, as the value of  $M$  changes greatly in the course of the reaction, it is not possible to accept that  $H$  and  $H/M$  remain simultaneously constant. Consequently, a first-order law would probably require that steps (7), (10), and (12) were negligible.

The experimental behaviour is considered to be almost that required by a first-order law, but close examination shows some deviations. This raises the suspicion that among steps (7), (10), and (12) there is one or more which participate in the proposed mechanism.

Let us consider the building-up rates of the products if steps (10) and (12) are ignored:

$$d[\text{CH}_4]/dt = -dM/dt = k_1M + (k_4 + k_6)R; \quad (\text{ix})$$

$$d[\text{CO}]/dt = k_6R\{1 + k_8/(k_7M + k_8 + k_{13}H)\}; \quad (\text{x})$$

$$d[\text{H}\cdot\text{CO}_2\text{Me}]/dt = k_1M + k_4R; \quad (\text{xi})$$

$$d[\text{H}_2]/dt = k_3MH + k_6k_8R/(k_7M + k_8 + k_{13}H); \quad (\text{xii})$$

$$d[\text{MeOH}]/dt = k_6R(k_{13}H + k_7M)/(k_7M + k_8 + k_{13}H). \quad (\text{xiii})$$

If step (7) were also neglected (*i.e.*,  $k_7 = 0$ ), the following would be obtained from the preceding equations together with (vi):

$$\frac{k_{11}}{k_3k_6} = \frac{4k_1 - 2V_{\text{MeOH}}}{(V_{\text{CO}} + V_{\text{MeOH}})(V_{\text{CO}} - V_{\text{MeOH}})}, \quad (\text{xiv})$$

where  $V$  denotes the corresponding rates divided by  $M$ .

The condition

$$2k_1M > d[\text{MeOH}]/dt \quad (\text{xv})$$

is immediately derivable from (xiv) but is unacceptable if long chains are assumed because  $k_1M$  is the chain-initiation rate. This result implies that the derivation of (xiv) fails because it does not account for the methyl alcohol found experimentally; in other words, step (7) cannot be neglected in the proposed mechanism. Only  $k_{10}$  and  $k_{12}$  may be equated to zero, which is a reasonable conclusion if the need of a third body in the corresponding steps is taken into account.

Consequently, in the following treatment the chain sequence proposed will be considered with only the exception of steps (10) and (12).

*The Order at Zero Reaction Time.*—If the theory is to be acceptable, expressions should be derivable for the experimental order.

By solving for  $M$  in the general equation that results from (v) and (vi), we obtain

$$M = \frac{k_1k_6k_8}{k_3k_7k_{11}} \cdot \frac{1}{H_2} - \frac{k_{13}}{k_7} \cdot H - \frac{k_6k_{13} + k_8k_{11}}{k_7k_{11}}, \quad (\text{xvi})$$

which is still much too complicated for direct solution.

According to equation (xvi), the value of  $H$  should increase as  $M$  diminishes and the presence of the term  $k_7M$  lowers the hydrogen-atom concentration in the reaction mixture.

If an almost zero reaction time were considered, where the steady-state approximation might already apply, then  $M \approx M_0$  and the hydrogen-atom concentration would attain its lower value  $H_0$ .

From equations (vi), (ix), and (xvi) the following is derived at  $t = 0$ :

$$\begin{aligned} -(\frac{dM}{dt})_0 &= M_0\{k_1 + P[\sqrt{1+x} - 1/\sqrt{1+x}]\} \\ &= k_1M_0 + M_0Px/\sqrt{1+x}, \end{aligned} \quad (\text{xvii})$$

where

$$x = \frac{k_7k_{11}}{k_8k_{13}} \cdot M_0 + \frac{k_{11}(k_8 + k_{13}H_0)}{k_8k_{13}} \quad (\text{xviii})$$

and

$$P = \frac{k_4 + k_6}{k_{11}} \sqrt{\frac{k_1k_3k_{13}}{k_8}} \quad (\text{xix})$$

The  $k_1M_0$  term may be neglected in (xvii) if, as has been supposed, steady-state conditions hold. Though not exact, this is a fair assumption provided a comparatively high temperature is chosen where no induction period is found in the  $\Delta p$ -time curves. So, from inspection of equation (xvii), a reaction order not far from 1.5 would be expected. This conclusion has been checked experimentally in the 472–520° range in Fig. 4 where the series of parallel straight lines corresponds to a 1.3 order.

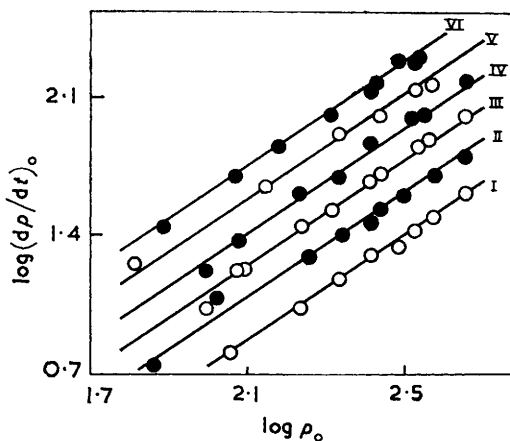


FIG. 4. Plots showing a 1.3 order at (I) 422°, (II) 483°, (III) 492°, (IV) 500°, (V) 510°, and (VI) 520°.

Moreover, it can be shown that the experimental results are in accordance with the theoretical implications of eqn. (xvii), by fitting the parameters involved.

As will be seen below, there are reasons to believe that  $k_{13}H_0$  is rather small with respect to  $k_8$ . Consequently,  $x$  might be considered as a linear function of  $M_0$ :

$$x = aM_0 + b. \quad (\text{xx})$$

Plotting the experimental values of  $-\frac{1}{M_0} \left( \frac{dM}{dt} \right)_0$  at 492° against  $M_0$  enables values of  $a$ ,  $b$ , and  $P$  to be found that lead to superimposition of the experimental function on the theoretical equation (xvii). Table 3 shows the values used in the calculation. The following values then lead (Fig. 5) to a satisfactory fit:

$$a = k_7k_{11}/k_8k_{13} \approx 0.002 \text{ min.}^{-1}; \quad b/a = (k_8 + k_{13}H_0)k_7 = 168 \text{ mm.}$$

$$P = 0.15 \text{ min.}^{-1}.$$

TABLE 3.  
Values at 492°.

$-\frac{1}{M_0} \left( \frac{dM}{dt} \right)_0$ (min. <sup>-1</sup> )...	0.0583	0.0655	0.0783	0.0867	0.0950	0.1016	0.1071
$M_0$ (mm.) .....	60	100	150	200	250	300	350

The Reaction Order.—From expressions (v) and (ix) the following may be derived:

$$-d \ln M = A_0 dt + A_1 M dt, \quad (\text{xxi})$$

where

$$A_0 = k_1 + (k_4 + k_6) k_3 H (k_{13} H + k_8) / k_6 k_8 \quad (\text{xxii})$$

and

$$A_1 = (k_4 + k_6) k_7 k_3 H / k_6 k_8. \quad (\text{xxiii})$$

The experimental results seemed explicable if a first-order law held to >50% conversion, but this is not the only explanation. Equation (xxi) does not contradict these results provided  $A_0 + A_1 M$  remains almost constant throughout the reaction. In that case, a plot of  $\ln M$  against time would yield an approximately straight line and the apparent order would be unity. However, if longer reaction times are considered, some discrepancies from order one are to be expected from equation (xxi). In fact, in the plot

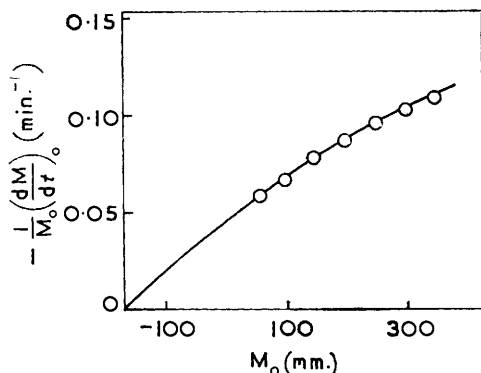


FIG. 5. Coincidence of experimental points and calculation.

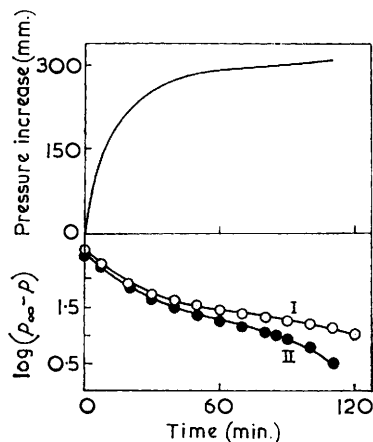


FIG. 6. Plots for decomposition of methylal ( $p_0$  150 mm.) at  $497^\circ$ : (I)  $p_\infty$  300 mm.; (II)  $p_\infty$  310 mm.

of  $\log(p_\infty - p)$  against  $t$  (which is equivalent to the plot of  $\ln M$  against time) a straight line is no longer obtained (Fig. 6). This result is in agreement with equation (xxi) according to which an upward curvature at the shorter times is to be expected. Unfortunately there is no fixed criterion for the choice of  $p_\infty$ , so the exact position of the straight line is ignored and the parameters of equation (xxi) cannot be calculated.

It should be emphasised that it is the presence of the  $k_7 M$  term and, in consequence, the influence of step (7) on the mechanism which are greater than casual inspection indicates and are decisive for the curvature. If very long times are considered, the curves are seen to be sigmoid, the downward curvature being produced by secondary decomposition of the products or, more probably, by the influence of the  $p_\infty$  selected.

*Stoichiometric Relations.*—Several relations among the formation rates of the products may be derived from equations (ix)—(xiii). The rates may be replaced by concentrations because the curves so obtained are similar in shape and could be superimposed on the rate curves by changing the scales (provided high temperatures are avoided where secondary decompositions intervene).

From equation (ix) the following relation is immediately obtainable:

$$[\text{CH}_4] = M_0 - M. \quad (\text{xxiv})$$

From (ix)—(xi) and (xiii) we obtain

$$[\text{CO}] + [\text{MeOH}] + 2[\text{H}\cdot\text{CO}_2\text{Me}] = 2[\text{CH}_4], \quad (\text{xxv})$$

and from (ix)—(xiii) and (v)

$$[\text{CO}] = [\text{MeOH}] + [\text{H}_2]. \quad (\text{xxvi})$$

The results from relations (xxiv—xxvi) are reported in Tables 4 and 5. Calculations have not been made for higher temperatures because of secondary decomposition of methyl formate and, perhaps, of methyl alcohol.

TABLE 4.

Results (pressures in mm.) of calculations [ $p_0$  for  $\text{CH}_2(\text{OMe})_2$ , = 150 mm.].

Temp.	459°					495°				
	8	16	24	32	40	4	8	12	16	20
Time (min.)	120	100	85	75	70	105	73	55	44	40
[ $\text{C}_3\text{H}_8\text{O}_2$ ]	27	48	62	72	78	43	71	86	94	100
[ $\text{CH}_4$ ]	147	148	147	147	148	148	144	141	138	140
[ $\text{C}_3\text{H}_8\text{O}_2$ ] + [ $\text{CH}_4$ ]										

TABLE 5.

Results (pressures in mm.) of calculations [ $p_0$  for  $\text{CH}_2(\text{OMe})_2$  = 150 mm.].

Temp.	459°			492°		
	4	16	32	4	8	12
Time (min.)	11	35	56	43	70	88
[CO]	2	4	6.5	5	6	7
[MeOH]	7	23.5	68	20	33	39
[H·CO <sub>2</sub> Me]	27	86	130.5	88	142	173
[CO] + [MeOH] + 2[H·CO <sub>2</sub> Me]	28	92	142	86	142	172
2[CH <sub>4</sub> ]	10	33	55.5	43	71	87
[MeOH] + [H <sub>2</sub> ]						

*Ratios among the Rate Constants.*—From expressions (ix) and (xi) the following may be derived, where  $k_1$  is very small and may be neglected:

$$\frac{k_8}{k_4} = \frac{V_{\text{CH}_4} - k_1}{V_{\text{H}\cdot\text{CO}_2\text{Me}} - k_1} - 1 \approx \frac{V_{\text{CH}_4}}{V_{\text{H}\cdot\text{CO}_2\text{Me}}} - 1. \quad (\text{xxvii})$$

(The  $V$ 's, as previously, denote the corresponding rates divided by M.)

Equations (ix—xiii) and use of the R/M values from equation (v) lead to

$$\frac{k_7}{k_8} + \frac{k_{13}}{k_8 k_3} \cdot \frac{V_{\text{H}_2}}{2M} = \frac{2V_{\text{MeOH}}}{MV_{\text{H}_2}}. \quad (\text{xxviii})$$

If equations (vi), (ix—xiii), and (xxviii) are used, we obtain

$$\frac{k_7}{k_8} + \frac{2k_1}{MV_{\text{H}_2}} - \frac{k_{11}}{2k_3 k_8 M} (V_{\text{CO}} + V_{\text{MeOH}}) = \frac{2V_{\text{MeOH}}}{MV_{\text{H}_2}}. \quad (\text{xxix})$$

Relations (xxvii—xxix) constitute a set of independent equations and, although others may be obtained, they are derivable from them.

By using the experimental values of the appearance rates of the products from Table 6 it is possible to calculate the ratios among the rate constants in the preceding equations.

TABLE 6.

Rates (mm./min.) of formation of products from methylal ( $p_0$  150 mm.).

Temp.	Time (min.)	d[H <sub>2</sub> ]/dt	d[CO]/dt	d[CH <sub>4</sub> ]/dt	d[H·CO <sub>2</sub> Me]/dt	d[MeOH]/dt	M (mm.)
459°	4	2	2.5	3.45	1.6	0.32	135
	16	1.45	1.7	2.17	1.05	0.2	105
	32	0.88	0.95	1	0.5	0.08	71
492	4	8.2	8	8.3	4.3	1.1	105
	8	5.9	5.3	5.5	2	0.55	73
	12	4.1	3.5	3	1	0.3	55

The ratio  $k_8 : k_4$  obtained in this way from equation (xxvii) is about unity at 459°. The results at 492° are a little doubtful because some methyl formate is probably decomposed, but the ratio is still of the same order of magnitude.

By means of equation (xxviii) the values of  $k_7/k_8$  and of  $k_{13}/(k_8 k_3)$  are obtainable in



principle if the experimental values at two different times from Table 6 are substituted and the resulting system is solved for the rate constant ratios.

However, in this way the experimental errors lead to uncertainty and only the orders of magnitude are real. Nevertheless, the following inequalities may be derived from equations (xxviii) and (xxix):

$$\frac{2k_1}{d[\text{H}_2]/dt} + \frac{k_7}{k_8} > \frac{2}{M} \frac{d[\text{MeOH}]/dt}{d[\text{H}_2]/dt} > \frac{k_7}{k_8}$$

and hence

$$\frac{k_7}{k_8} \sim \frac{2}{M} \cdot \frac{d[\text{MeOH}]/dt}{d[\text{H}_2]/dt}, \quad (\text{xxx})$$

which allows us to calculate the value  $k_7/k_8$ ; it is  $0.0025 \text{ mm.}^{-1}$  at  $459^\circ$ . The error incurred by neglecting the term  $\frac{2k_1}{d[\text{H}_2]/dt}$  would be in the third significant figure if  $k_1 = 1.5 \times 10^{-5} \text{ min.}^{-1}$ , and in the second if  $k_1 = 7 \times 10^{-5} \text{ min.}^{-1}$ .

Incidentally, being a different form of equation (xxviii), namely,

$$\frac{k_7 M}{k_8} + \frac{k_{13} H}{k_8} = \frac{2V_{\text{MeOH}}}{V_{\text{H}_2}}, \quad (\text{xxxii})$$

and the value obtained for  $k_7/k_8$  justifies considering  $(k_{13}H_0 + k_8)$  as almost constant, as it is done in expressions (xviii) and (xx).

*Variation of the Radical Concentrations.*—Some equations may be derived from the preceding by rearrangement and substitution which allow us to calculate changes in radical concentrations.

From expressions (ix—xii) and (v) we derive

$$k_3 H = \frac{1}{2} V_{\text{H}_2}, \quad (\text{xxxii})$$

and

$$k_6 R = (V_{\text{MeOH}} + \frac{1}{2} V_{\text{H}_2}) M, \quad (\text{xxxiii})$$

where the value of the first term in each equation may be calculated at different reaction times (Table 7).

The hydrogen-atom concentration is roughly constant throughout the reaction but increases with temperature. The differences observed in Table 7 might be explained as due to the errors involved in the measurement of the concentration of the molecular hydrogen present in the reaction mixtures.

TABLE 7.

Concentrations of radicals.

Temp.	459°			492°			
	Time (min.)	4	16	32	4	8	12
Reaction (%)	7.8	27	45	30	50	63	73
$k_3 H$ (min. <sup>-1</sup> )	0.0074	0.0069	0.0062	0.039	0.040	0.039	—
$k_6 R$ (min. <sup>-1</sup> mm.)	1.9	1.1	1	4	3.5	2	0.8

The concentration of the R radicals varies appreciably throughout an experiment and, as might be expected, is greater the higher the temperature. Table 7 shows that  $k_6 R \gg k_3 H$ , although it is not possible to specify whether  $k_6 > k_3$  or  $R > H$  or, perhaps, both.

The preceding mathematical treatment shows that the proposed chain sequence explains all the experimental facts concerning the decomposition of methylal, although it does not necessarily exclude other mechanisms. Several possibilities have intentionally

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been left out of account. One such is the equilibrium  $\text{Me}\cdot + \text{H}_2 \rightleftharpoons \text{H}\cdot + \text{CH}_4$ , which would not affect the results because certain steps in our chain sequence are equivalent to it. Another is initiation of the chain by the fission  $\text{CH}_2(\text{OMe})_2 \rightarrow \text{MeO}\cdot + \text{MeO}\cdot\text{CH}_2\cdot$  and participation of the latter radical in the propagation, the reason being that there is no need to postulate these radicals in order to explain the results.

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