418. *Kinetics of the Thermal Decomposition of Acetals. Part I.*

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The kinetics of the thermal decomposition of ethylal, dimethyl acetal, and diethyl acetal have been studied over the range 389—530° in a static system, periodic quantitative analyses of the products being made by infrared spectrometry. The observed pressure increase may be accepted as a reasonable measure of the acetal decomposed. The reaction orders and the activation energies have been determined. Ethylal decomposes mainly by a chain mechanism, but rearrangement processes are probably more important with dimethyl and diethyl acetal. Inhibition by nitric oxide is transitory, which suggests incomplete suppression of chains in the presence of that inhibitor.

We have studied the kinetics of thermal decomposition of three acetals. It was hoped that data for such similar compounds might throw light on the mechanism of their decomposition. Moreover, acetals are interesting because some of them can be used to make fuel mixtures[1] and because, when added in small amounts to the usual motor fuels, they increase their octane number.[2] The study of their thermal decomposition might assist a better understanding of their action in fuels.

Experimental

The reactions were studied in a high-vacuum apparatus by the static method. The silica reaction vessel was kept in a furnace whose temperature was controlled within ±0·5° by an electronic controller and a platinum resistance thermometer. The reactions were followed by studying the change of pressure with time and by quantitative analyses with a Perkin-Elmer infrared spectrometer model 112. The samples were fractionated before analysis, at the temperature of solid carbon dioxide or liquid air. As a check, all the analyses were repeated by direct sampling.

Preliminary calibration was made with all the identified compounds in a pure state. The spectrum of each compound was determined at several partial pressures, and optical densities at convenient wavelengths were plotted against partial pressures.

Most of the errors in the quantitative measurement of absorption with gases to which Beer's law cannot be applied (because of the presence of other gases) were eliminated by adding to the sample a gas that is transparent in the infrared region, until a constant pressure was reached inside the cell. In order to avoid the difficulty of reproducing each time the same background line we frequently used the base-line method.[3]

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[1] Medici, Szenkiserletï Közlemenyek, 1937, **3**, 116. *Chem. Abs.*, 1937, **31**, 5129; Doldi *Chimica e Industria*, 1937, **19**, 369; Serruys, *J. Soc. Ing. automobile*, 1941, **14**, 153.

[2] Raichle, Hirschberger, and Wolf, *Chem. Abs.*, 1954, **48**, 2358 ^{b}; G.P. 822,031/1951; Roberti *et al.*, *Ricerca Sci.*, 1939, **10**, 28.

[3] White, *Analyt. Chem.*, 1947, **19**, 293.

Ethylal, dimethyl acetal, methyl formate, and methyl acetate were pure chemicals supplied by British Drug Houses Ltd. Diethyl acetal, acetaldehyde, and ethyl vinyl ether were pure chemicals supplied by Fluka A.G. Methyl vinyl ether was supplied by Matheson Co. Inc. and purified by distillation from a bulb at 4° through a column at 1—2·5°; the middle portion was collected for use; its infrared spectrum did not show an appreciable amount of impurity.

Methane was prepared [4] by the action of water on methylmagnesium bromide in ether and was washed with water and aqueous potassium hydroxide. Ethylene [5] was obtained by catalytic dehydration of ethyl alcohol at 400—500° over previously dehydrated alumina. Methane and ethylene were condensed in traps cooled with liquid air, then fractionated, only the middle fractions being collected. Their purity was tested by infrared spectroscopy. Carbon monoxide was obtained by the action of concentrated sulphuric acid on pure formic acid; [5] the evolved gas was proved to be free from carbon dioxide by passage through aqueous potassium hydroxide; it was also free from other impurities that absorb in the infrared region.

Influence of the Vessel upon the Reactions.—Experiments made in two vessels of the same size and shape, one empty and the other filled with silica powder (which varies by about 500-fold the surface : volume ratio), showed that the surface of the reaction vessel has no influence on the decomposition of ethylal, reproducible results being easily obtained.

We were not able to study the influence of changing the vessel on the decomposition of diethyl acetal. Even when this acetal is repeatedly pyrolysed only in the empty vessel, it is very difficult to get reproducible results. A peculiar feature of the irreproducibility is that usually the reaction rate oscillates between a " lower " and a " higher " value, the latter being almost three times the former. We found that the reaction is inhibited by the products from previous runs that have remained adsorbed on the surface. That the " lower " rate values belong to an inhibited reaction was proved by the action of nitric oxide which reduces the rates to the same values. The " higher " rates correspond to the uninhibited reaction.

The products from decomposition of dimethyl acetal seem to have a similar influence upon the reaction.

General Form of the Δp–Time Curves.—During the thermal decomposition of any of the three acetals, the total pressure inside the reaction vessel increased, though short induction periods were observed at the lower temperature studied with ethylal.

Where no induction period was observed, the initial portion of the Δp–time curve is a straight line passing through the origin, and there is the normal decrease in rate as the reaction comes to an end. Estimation of the initial rate presents no difficulty and the measurements made in this way seem to have a simple meaning because, at zero reaction time, only the primary fission of the acetal takes place. On the curves which show an induction period, the rate is taken for comparative purposes as the maximum slope. The plot of the amount of ethylal consumed against pressure (Fig. 1) is a straight line, and the pressure increase may be accepted as a reasonable measure of the ethylal transformed.

Dimethyl acetal and diethyl acetal were not analysed at temperatures where the reaction is slow enough to find out whether a similar plot for the first part of the reaction is a straight line or not. By analogy, it seems safe to assume that the pressure increase is again a measure of the amount of acetal consumed.

Order of the Reactions.—The kinetic results are recorded in Table 1.

The order at zero reaction time, calculated for ethylal from the plots of log rate against log P_0, where P_0 is the initial pressure, is between one and two, increasing towards two as the temperature decreases (Fig. 2).

It is not possible to see which order the Δp–time curves follow, because the induction periods interfere with the calculation. But at one of the higher temperatures studied (526°), where no induction periods are observed, the plot of log $(p_\infty - p)$ against time may be considered as a straight line up to 50% reaction change.

For dimethyl and diethyl acetal (Table 1), the plots of rate against P_0 may be considered as straight lines and consequently the order at zero reaction time is one. The usual plots of log $(p_\infty - p)$ against time for typical experiments with both acetals showed a first-order law up to 50% reaction for dimethyl acetal and 70% for diethyl acetal (Fig. 3).

Activation Energies.—Activation energies were calculated by the method of least squares

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[4] Baume and Perrot, *Compt. rend.*, 1909, **148**, 39.

[5] Klemenc, " Die Behandlung und Reindarstellung von Gasen," 1948; J. B. Senderens, *Compt. rend.*, 1930, **190**, 1167.

from the Arrhenius equation by using the values in Table 1. Only for the decomposition of ethylal does it vary with initial pressure:

	Ethylal				Me_2 acetal	Et_2 acetal
Initial pressure (mm.)	100	150	200	250	100—300	80
Activation energies (kcal./mole) ...	51·4	46·8	43·2	40·3	54·3	26·1

Analyses of Products.—Ethylal. Analyses have been made at 488° and 526° and different reaction times. The results are recorded in Table 2. That acetaldehyde and methyl formate were formed was not apparent from the first spectra taken but evidence was found by carefully studying the region around 1750 cm.$^{-1}$. Carbon dioxide was absorbed in concentrated carbon dioxide-free aqueous potassium hydroxide and precipitated as barium carbonate. It was determined quantitatively by means of the 721 cm.$^{-1}$ band.

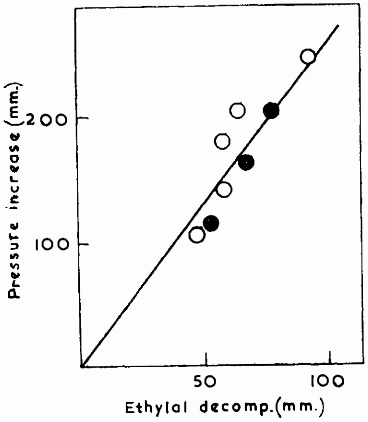

FIG. 1. Plot of the amount of ethylal decomposed against the increase in pressure at (○) 488° and (●) 526°.

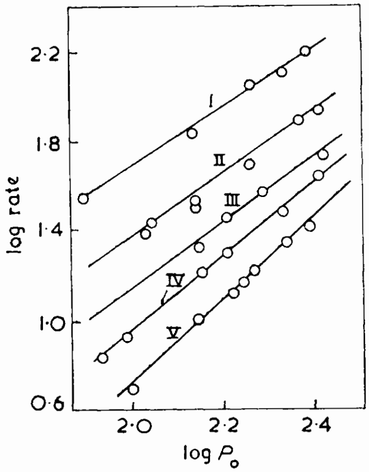

FIG. 2. Kinetic results for decomposition of ethylal at (I) 530·3° (n = 1·3), (II) 511·5° (n = 1·4), (III) 498° (n = 1·5), (IV) 488·5° (n = 1·7), and (V) 478·5° (n = 1·9) (n = reaction order).

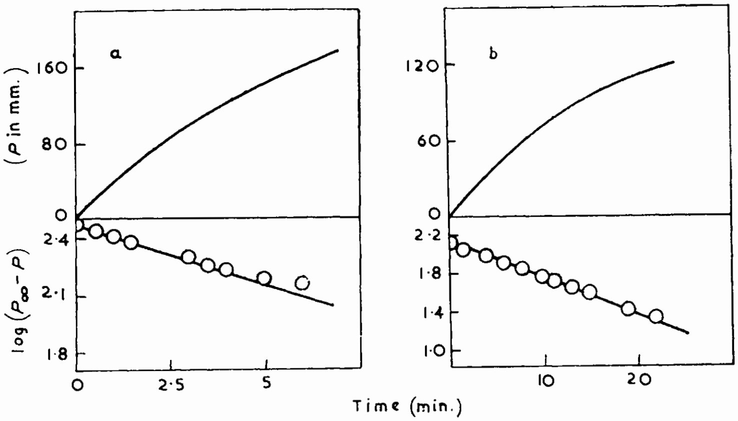

FIG. 3. Rate of pressure increase for (a) dimethyl acetal at P_0 150 mm. and 460° and (b) diethyl acetal at P_0 80 mm. and 411°.

The presence of hydrogen was proved by fractionation of the mixture at liquid-air temperature, followed by quantitative analysis of the uncondensed portion at different temperatures

TABLE 1.

Variation of rate of decomposition with pressure.

P_0 in mm. Rates in mm./min.

Temp.										
					Ethylal					
478·5°	P_0	102	143	170	182·5	189	223·5	252	255	
	Rate	5	10	13·5	15	17	23	26·5	26·5	
488·5°	P_0	87	98	145	164	219	260			
	Rate	7	8·5	17	20	31	44			
498°	P_0	93·5	145	167	197	237	271			
	Rate	15	21	29	38	49	55			
511·5°	P_0	109	112	142	142	237	262			
	Rate	25	28·5	33·5	35	80	90			
530·3°	P_0	80	138	185	220	247				
	Rate	37	70	116	128	164				
					Dimethyl acetal					
420°	P_0	52	75·5	142	216	244	309	326		
	Rate	3·2	4	6·2	9·5	10	13·8	14		
430°	P_0	58	101	146	211	263·5	348·5			
	Rate	4	6	9·5	15	18	24			
436·5°	P_0	57	63	102	159	200·5	247	261	266	300
	Rate	7·5	7·5	11·5	17	22	25	24	30	30·5
447·5°	P_0	32	61	97	156	183	228	271		
	Rate	5·3	9·6	25	31·5	34	49	59		
457°	P_0	79	118	134	173	212	238	282	298	
	Rate	27	28	40	53	67	70	78	88	
465°	P_0	59	106	114	138	176	224	243	269	311
	Rate	20	48	60	52	91	110	104	124	150
					Diethyl acetal					
389°	P_0	20	31	41·5	51	62	68	82	85	
	Rate	3·2	3·8	5·7	5·2	7·2	7	7·4	10	
395°	P_0	28·5	37	40	52·5	53	59	74	84	
	Rate	6·5	7	8·5	8	7·5	11	13	15	
402°	P_0	34	42	47	54·5	63·5	69	77	81	94
	Rate	7	9	10	8·5	12	14	11·5	13·5	12·5
410·5°	P_0	22·5	30·5	41·5	42·5	57·5	61·5	72·5	80	87·5
	Rate	6	9·5	12·5	9	13·5	14	13·5	18	17·5
420°	P_0	28·5	36	53	61	61·5	70·5	76	78	82
	Rate	7·3	10·7	13	14·5	15	20	17·5	24	21·5
431°	P_0	24·5	40·5	47	60·5	70	81			
	Rate	11·7	17	18	24	26	30			
442°	P_0	37·5	50	63	72	80	92·5			
	Rate	20·5	29	36	41·5	46	51			
453°	P_0	43	52	64	64	75	82	95		
	Rate	32	41·5	51	49	53	59	71		

TABLE 2.

Products (amounts in mm.) formed from ethylal at P_0 150 mm.

Time (min.)	Ethylal	MeOH	C_2H_4	Me formate	Me·CHO	CO	CH_4	CO_2	H_2	Diff.*
					At 488°.					
10	103	6	25·5	1·5	9	26	17·5	8	24	—
15	91	8·5	29	4	8	44	24·5	6	38·5	—
20	91	9	32	2	7	45	35·5	18	73	—
30	85	12	31	3	5·5	66	43·5	16	83	—
					At 526°.					
2	96·5	3·5	31	4	10·5	40	17	5·5	46	20
4	82	5	30·5	1·5	12	31	27	20·5	98	19·5
6	71	4·5	36·5	0·5	12·5	58·5	49·5	19	101·5	29
10	56	4	35·5	9	1·5	67·5	55	21·5	126	34
18 †		8	33	8·5	2	81	54·5	22	148	
45 †		9	26		7		70	27		

* Probably water.

† These results are incomplete because they refer to analyses made only by direct sampling.

and starting pressures; a difference between the total pressure (as measured on the manometer) and the sum of the partial pressures of the analysed compounds proves that hydrogen has been produced.

The following infrared bands were also used for analysis: methane 1304; methanol 1032 and 1054; methyl formate 1761·5; ethylal 1393·5 and 859·2; acetaldehyde 1761·5; ethylene 949 cm.$^{-1}$.

In the analyses of the condensed fraction from ethylal, some small differences in pressure in the cell between analyses and manometer readings were found at the higher temperature studied (526°; Fig. 5). These are presumed to be due to water though no direct qualitative analysis of water was made.

Dimethyl acetal. Analyses of products formed at 460° are recorded in Table 3. Dimethyl acetal was determined by a band at 882 and methyl acetate by one at 1764 cm.$^{-1}$, with correction for the absorption due to the acetal. Under the heading " Diff. (uncond.) " the figures refer mostly to hydrogen but there may have been also small quantities of ethane which could not be detected by infrared spectrometry if its partial pressure were low enough.

TABLE 3.

Products (amounts in mm.) formed from dimethyl acetal at 460° and P_0 150 mm.

Time (min.)	CO	CH_4	C_2H_4	Me_2 acetal	MeOH	MeOAc	Me vinyl ether	Σp	Total press. (sampling)	Diff.
2	41	27	2	78	16	16·5	11·5	192	218	26
4	53·5	44·5	2·5	64	23	22	32·5	242	273	31
8	78	100	4	45	37·5	29·5	37·5	331·5	331·5	0
12	99	88·5	4·5	30	39·5	25·5	36	323	368·5	45·5
20	141	128	5·5	35·5	47	27	23	407	419·5	12·5

Diethyl acetal. Table 4 records results for diethyl acetal decomposing at 411° and 80 mm.

TABLE 4.

Products (amounts in mm.) formed from diethyl acetal at 411° and P_0 80 mm.

Time (min.)	Et_2 acetal	EtOH	Et vinyl ether	Me·CHO	C_2H_4	CO	CH_4	Total press. (sampling)	Diff. (uncond.)	Diff. (cond.)
4	14	39·5	18·5	12·5	13·5	8	1·5	121·5	—	10·5
6	7	51·5	13·5	14·5	16·5	10·5	2	128	—	9·5
8	17	34	16·5	19·5	21	17	4·5	146	—	12·5
10	8	55	11	21	26	18·5	6	159	—	4·3
15	10	48·5	8·5	22·5	29	12·5	8	158·5	7	7·5
20	11·5	38	7	27	36·5	34	14·5	205	8	20
30	12	31	4	29·5	43·5	33	16	209	8	34·5

The two last columns refer to differences between total pressures and partial pressures due to various components found in the fractions that were respectively uncondensed and condensed in solid carbon dioxide. It is doubtful whether the differences in the volatile fraction can be ascribed to hydrogen or are accumulated errors. The differences in the condensed fraction, on the other hand, are large enough to indicate that water is probably present.

The following infrared bands were used for analysis: ethyl vinyl ether 1610 and 813·6; ethanol 1248·5, after correction for ethyl vinyl ether, diethyl acetal, and methane; diethyl acetal 1150·3 cm.$^{-1}$, after correction for ethyl vinyl ether and acetaldehyde.

Effect of Nitric Oxide.—Nitric oxide has an inhibitory action in the pyrolyses of the acetals. Small percentages (about 1%) inhibit the reaction markedly; this may be considered as " full " inhibition because greater amounts do not further decrease the rate (Figs. 4—6).

A characteristic feature of the inhibition for ethylal and dimethyl acetal is that it is only transitory. After some time, which increases with the quantity of added nitric oxide, the rate increases quickly and the pressure increase at the end of the reaction seems to be the same for both the " normal " and the inhibited reaction at low initial nitric oxide pressures. The amount of inhibition may be expressed in terms of the ratio of the initial rate for the pure acetal, r_0, to the slowest initial rate in the presence of inhibitor, r_{inh} (maximum inhibition).

	Pressure (mm.)	Temp.	r_0/r_{inh}
Ethylal	150	526°	6·7
Dimethyl acetal	150	460	1·8
Diethyl acetal	80	411	2·3

The Δp–time inhibited curve for diethyl acetal (Fig. 6) does not show any evidence of transitory inhibition, perhaps because decomposition of this acetal is less inhibited; consequently, the transition from the inhibited to the normal curve is not so abrupt and only a continuously smooth curve is observed.

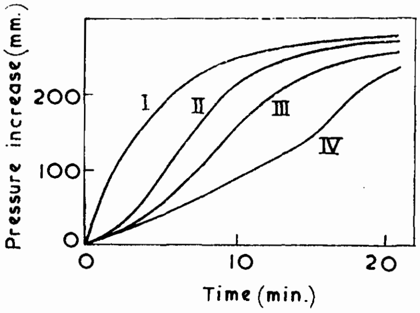

FIG. 4.

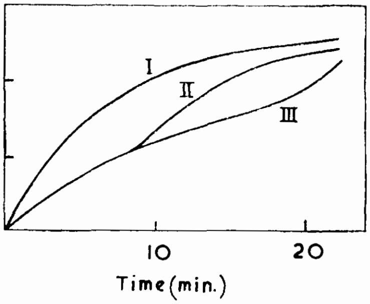

FIG. 5.

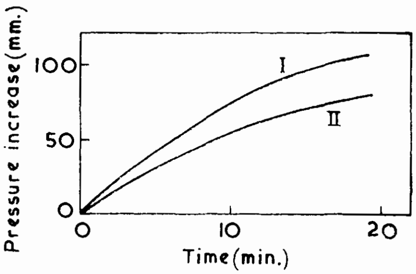

FIG. 6.

FIGS. 4—6. Inhibition by nitric oxide of the decomposition of (Fig. 4) ethylal at 526° and P_0 150 mm., (Fig. 5) dimethyl acetal at 460° and P_0 150 mm., and (Fig. 6) diethyl acetal at 411° and 80 mm.

Amounts (mm.) of nitric oxide are: Fig. 4, I 0, II 1, III 3, and IV 7·5; Fig. 5, I 0, II 5, III 17; Fig. 6, I 0, II 5.

The inhibitory action of propene on the pyrolysis of acetals has also been tested; propene seems to be less efficient than nitric oxide. It is necessary to add nearly 150 mm. of propene to get the same reduction in the initial rate as with only a few mm. of nitric oxide, but, when achieved, the inhibition is not transitory.

DISCUSSION

The behaviour of ethylal is different from that of the other acetals. The preceding results, especially the variation of order with temperature, suggest a composite mechanism. Nevertheless, some results could also be explained in terms of a chain reaction if it is assumed that chain ending (a process of lower activation energy) is dominant at high pressures, and chain initiating at low pressures. The variation of the frequency factor at 483·5° is also in favour of this hypothesis.

The pressure-increase–time curves for dimethyl and diethyl acetal, together with an order unity for the first half of the reaction and a lower degree of inhibition with nitric oxide, seem to indicate that the chain mechanism is of less importance than for ethylal. This is especially so for diethyl acetal, where the very low frequency factor ($4 \cdot 8 \times 10^5$ sec.$^{-1}$) almost excludes chain processes. However, the action of nitric oxide indicates that the reaction is partially inhibited, so chain processes cannot be quite disregarded.

Material balances in the decomposition of ethylal are not quantitative. The losses are significant at the higher temperature and appear to increase with time of reaction (Table 5). Small amounts of ethylal are probably absorbed in the tap grease, which could explain the loss of oxygen. But large losses, up to 30%, of carbon cannot be due to experimental error and must be ascribed to condensation products. The forms of the product–time curves corresponding to acetaldehyde, methyl alcohol, and ethylene are suggestive of secondary reactions. Among these, ethylene is the most likely to give condensation products owing to sensitized polymerization by the radicals present.[6] In fact, a dark residue was found after a number of runs in a packed reaction vessel.

TABLE 5.

Percentage of atoms not accounted for in products from ethylal at 526°.

Reaction time (min.)	2	4	6	10
C	15	22	22	30·5
H	14	15	15	21·5
O	6	8	4·5	6·5

It is a little difficult to establish the stoicheiometry of the reaction, as the products themselves react at the two temperatures where analyses were made, but several modes of decomposition may explain the whole reaction from the stoicheiometric point of view:

$$\begin{array}{ll}
(1) & CH_2(OC_2H_5)_2 \longrightarrow CO_2 + 2C_2H_4 + 2H_2 \\
(2) & CH_2(OC_2H_5)_2 \longrightarrow CO_2 + 2CH_4 + C_2H_4 \\
(3) & CH_2(OC_2H_5)_2 \longrightarrow CH_3{\cdot}CHO + CH_3{\cdot}OH + C_2H_4 \\
(4) & CH_2(OC_2H_5)_2 \longrightarrow CH_4 + 2CH_3{\cdot}CHO \\
(5) & CH_2(OC_2H_5)_2 \longrightarrow H{\cdot}CO_2CH_3 + C_2H_4 + CH_4
\end{array}$$

Secondary reactions:

$$\begin{array}{ll}
(6) & CH_3{\cdot}CHO \longrightarrow CH_4 + CO \\
(7) & H{\cdot}CO_2CH_3 \longrightarrow CH_3{\cdot}OH + CO \\
(8) & H{\cdot}CO_2CH_3 \longrightarrow CH_4 + CO_2 \\
(9) & CH_3{\cdot}OH \longrightarrow CO + 2H_2 \\
(10) & C_2H_4 \longrightarrow \text{Condensed product}
\end{array}$$

The analytical results obtained from dimethyl acetal suggest that its decomposition could be explained, as far as the stoicheiometry is concerned, by the processes:

$$\begin{array}{l}
CH_3{\cdot}CH(OCH_3)_2 \longrightarrow CH_3{\cdot}OH + C_2H_3{\cdot}OCH_3 \\
CH_3{\cdot}CH(OCH_3)_2 \longrightarrow CH_3{\cdot}CO_2CH_3 + CH_4
\end{array}$$

The carbon monoxide and more methane are probably formed by secondary decomposition of the products.

Diethyl acetal yields ethyl alcohol among the products which decompose after being formed. In a number of studies,[7] it has been shown that thermal decomposition of ethyl alcohol involves both dehydration to ethylene and dehydrogenation to acetaldehyde. The latter reaction is followed by decomposition of acetaldehyde to methane and carbon

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[6] Wang and Winkler, *Canad. J. Res.*, 1943, **21**, *B*, 97.

[7] Peytral, *Bull. Soc. chim. France*, 1920, **27**, 34.

monoxide. No free-radical mechanism has been proposed for the ordinary decomposition. but experiments with ethyl alcohol containing biacetyl show that a promoted chain decomposition can occur.[8]

Small pressure losses occurred during sampling. Material balances show that the losses amount to about 33% for carbon, 35% for hydrogen, and 23% for oxygen, calculated on the starting diethyl acetal. This seems to indicate that a polymerization product is formed during the reaction; it may originate in the ethyl vinyl ether that disappears after being formed.

According to the above suggestions, a tentative set of stoicheiometric reactions for the decomposition of diethyl acetal, may be:

$$\begin{array}{lrcl}
(1) & CH_3{\cdot}CH(OC_2H_5)_2 & \longrightarrow & C_2H_3{\cdot}OC_2H_5 + C_2H_5{\cdot}OH \\
(2) & C_2H_3{\cdot}OC_2H_5 & \longrightarrow & CH_3{\cdot}CHO + C_2H_4 \\
(3) & C_2H_5{\cdot}OH & \longrightarrow & CH_3{\cdot}CHO + H_2 \\
(4) & C_2H_5{\cdot}OH & \longrightarrow & C_2H_4 + H_2O \\
5) & CH_3{\cdot}CHO & \longrightarrow & CH_4 + CO \\
(6) & C_2H_3{\cdot}OC_2H_5 & \longrightarrow & \text{Condensed product}
\end{array}$$

These equations do not explain why the amount of carbon monoxide is greater than the amount of methane. Probably the reason is that the decomposition of ethyl vinyl ether is less simple than we have assumed; indeed, Wang and Winkler[6] found that the thermal decomposition of this ether always produces more carbon monoxide than methane.

We must also consider the action of nitric oxide. Whether maximum inhibition corresponds to complete suppression of chains or not has been the subject of much controversy. The efficiencies of propene and nitric oxide as inhibitors in the thermal decomposition of hydrocarbons[9] have been compared. The similarity of these results has been given great weight, as seeming to indicate complete suppression of chains. This conclusion, however, should be accepted with reserve for acetals until more analytical results are available. The transitory effect of nitric oxide on their decomposition and the permanent inhibitory action of propene show the importance of the nature of the inhibitor. It is very unlikely that in this case the fully inhibited reaction corresponds to complete suppression of chains, when the experimental results appear to show a fictitious induction period produced by the presence of nitric oxide, during which the latter is probably consumed until the reaction proceeds again freely along the same path as the uninhibited reaction.

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[8] Rice and Walters, *J. Amer. Chem. Soc.*, 1941, **63**, 1701.

[9] Smith and Hinshelwood, *Proc. Roy. Soc.*, 1942, *A*, **180**, 237; Stubbs and Hinshelwood, *ibid.*, 1950, *A*, **200**, 458.