965. *Kinetics of the Thermal Decomposition of Acetals. Part III.*[1] *The Inhibited Reactions of Methylal and Acetaldehyde Dimethyl Acetal.*

By M. J. Molera, J. Centeno, L. Arévalo, and J. Orza.

The influence of nitric oxide, propene, ethylene, toluene, and cyclohexene on the thermal decomposition of methylal and acetaldehyde dimethyl acetal in a static system has been studied. The reactions have been followed by observing the change of pressure with time and by infrared spectroscopy.

Hydrogen cyanide, nitrous oxide, and probably a nitrile are produced from the nitric oxide, which is consumed during the transitory inhibition. The results obtained are discussed and it is shown that the normal methylal chain is several hundred steps long.

A different behaviour is observed with unsaturated inhibitors. The pressure increase–time curves of the methylal decomposition are lowered by ethylene or propene below the limit reached with nitric oxide. Inhibition is not transitory. The amount of hydrogen in the products is preferentially diminished with any of either inhibitor. Ethylene or some of its products remaining adsorbed on the surface of the reaction vessel seem to have a specific influence on the decomposition of acetaldehyde dimethyl acetal.

Part I [2] of this series dealt with the thermal decomposition of ethylal and of acetaldehyde dimethyl and diethyl acetal. In Part II [1] the methylal chain decomposition was discussed by applying the steady-state approximation to the proposed mechanism.

In both Parts a few experiments which showed the inhibitory action of nitric oxide and propene on the reaction were reported. A more thorough study of the inhibited reaction of methylal and acetaldehyde dimethyl acetal has now been undertaken. The aim was to compare the action of several inhibitors that are commonly used in pyrolyses.

EXPERIMENTAL

The experimental technique has been previously described.[2]

Hydrogen cyanide was prepared for calibration by Gatterman's method. A mixture of sulphuric acid and water was dropped on finely divided potassium ferrocyanide, and the

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[1] Part II, Molera, Fernández-Biarge, Centeno, and Arévalo, *J.*, **1963**, 2311.

[2] Part I, Molera, Centeno, and Orza, *J.*, **1963**, 2234.

evolved gas was dried by passage through calcium chloride. It was purified by fractional distillation. Propene was obtained by dropping " AnalaR " isopropyl alcohol on phosphorus pentoxide. The evolved gas passed through an ice-cooled trap to condense the undecomposed alcohol and water; propene was condensed in a second trap at liquid-air temperature. Although, according to some authors,[3] there is no need to purify the propene obtained in this way, it was fractionated and only the middle fraction was collected. Nitric oxide was obtained in a Toepler tube by reaction of mercury with nitric and sulphuric acid. The tube was vigorously shaken at a pressure above 1 atm. till no more nitric oxide was evolved.

Inhibition by Nitric Oxide.—Pressure increase–time curves. (*a*) Methylal. The inhibitory action of nitric oxide on the normal decomposition of methylal has been tested at different temperatures and starting pressures. Fig. 1 shows the curves obtained at 520°.

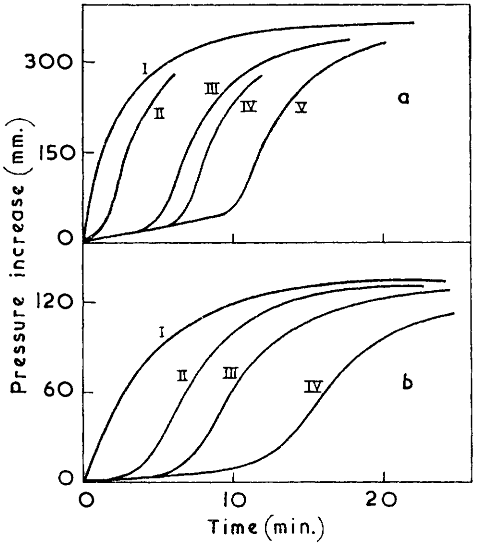

FIG. 1. (a) Methylal, 205 mm.; nitric oxide, (I) 0, (II) 1, (III) 4, (IV) 6, and (V) 10 mm. (b) Methylal, 75 mm.; nitric oxide, (I) 0, (II) 1, (III) 2, and (IV) 4 mm. All at 520°.

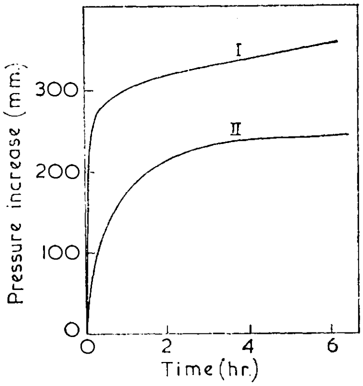

FIG. 2. Methylal, 150 mm.; nitric oxide, (I) 0 and (II) 150 mm.; at 520°.

The results, together with those obtained previously,[1] at 150 mm. methylal pressure show that nitric oxide has only a transitory action on this reaction. When small amounts ($<0{\cdot}5\%$) of nitric oxide are present, the reaction rate is decreased to a very low value. However, after a time which depends upon the proportion of inhibitor added, the Δp–time curve rises steeply.

It was desirable to make experiments at greater nitric oxide concentrations in order to find out whether permanent inhibition could be obtained, but the results were not exactly comparable with those given above because the initial rate was somewhat increased, owing perhaps to a different process produced by nitric oxide and superimposed on the inhibited reaction. However, by several experiments it was shown that, during the decomposition of methylal at 150 mm. initial pressure together with 150 mm. of nitric oxide, the pressure increased smoothly and no abrupt change was observed as with small quantities of nitric oxide. After reaction for 6 hr. the pressure increase was less than that of the normal methylal decomposition (Fig. 2).

(*b*) Acetaldehyde dimethyl acetal. During the study [2] of the normal decomposition of this acetal there was some difficulty in obtaining reproducible results, a difficulty that is enhanced when an inhibitor is added. It seemed that the lack of reproducibility was due to the inhibitor, ethylene or nitric oxide (or some of the products formed from them), remaining adsorbed on the surface of the reaction vessel and markedly decreasing the reaction rate. Ethylene is a

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[3] Batuecas, *J. Chim. phys.*, 1934, **31**, 165; Burrel and Robertson, *J. Amer. Chem. Soc.*, 1915, **37**, 2188.

product in the normal decomposition, which explains why some difficulty was also met with in experiments without an added inhibitor. The rates of the normal and the inhibited reaction seem to be decreased similarly owing to the influence of the adsorbed layer.

It is difficult to obtain a " clean " surface when studying the inhibited reaction, so all the experiments were made in a reproducible state of covered surface that was found to be established spontaneously after the previous use of inhibitors. When necessary, the vessel was seasoned by cleaning it repeatedly with air or oxygen followed by thorough pumping.

Experiments were carried out at several temperatures and at different starting pressures of both acetal and nitric oxide, which show that here also the inhibition is transitory.

TABLE 1.

Products (in mm.) of decomposition of methylal (150 mm.) in presence of nitric oxide (5 mm.) at 520°.

Time (min.)	Total press.*	CO	CH_4	$CH_2(OMe)_2$	$H{\cdot}CO_2Me$	CO_2	H_2	MeOH
5·5	168	8	15	118	6·5	—	9	11
10·5	183	17·5	24	119	11	2	1	8·5
11·25	201	22	32	118	18	—	4·5	6·5
12·0	239	36·5	56	82·5	22·5	—	33	8·5
14·0	308	57	63	63	35	14·5	65	9·5
15·75	346	74	85	39·5	33	20	88·5	6
20·0	384·5	100	103	23	30	20	100	8·5
28·0	416	106·5	107·5	28·5	37·5	17	108·5	10

* Sampling.

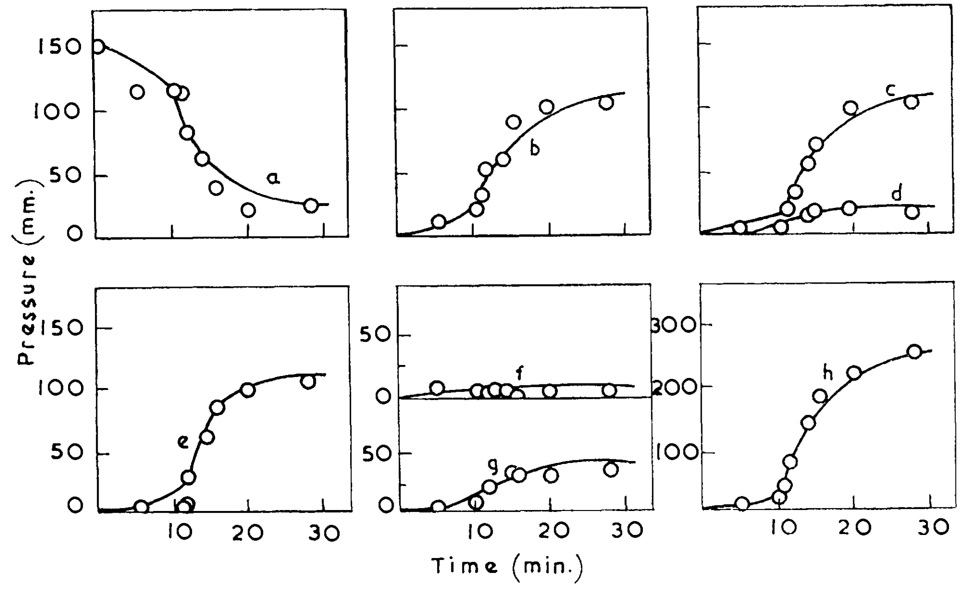

FIG. 3. Products from methylal (150 mm.) and nitric oxide (5 mm.) at 520°: (a) $CH_2(OMe)_2$; (b) CH_4; (c) CO; (d) CO_2; (e) H_2; (f) MeOH; (g) $H{\cdot}CO_2Me$; (h) Δp.

Products. (*a*) Methylal. In order to make the qualitative analysis of products from nitric oxide as complete as possible, 150 mm. of methylal were pyrolysed with 150 mm. of nitric oxide at 520° for 6 hr. and the resulting mixture was fractionated and analysed by infrared spectrophotometry. Besides the usual products from the methylal itself, a quantity of hydrogen cyanide that roughly corresponded to 15% of the initial nitric oxide was obtained.

Spectra of samples obtained under different experimental conditions were also measured and a small band overlapping with the carbon dioxide absorption was observed. In order to collect a greater amount of this compound, six mixtures of 75 mm. of methylal and 30 mm. of nitric oxide were allowed to react for 10 min. at 560° and the whole of the products were fractionated at several temperatures between solid carbon dioxide and room temperature. The unknown compound vaporised after most of methylal, methyl formate, and hydrogen cyanide and simultaneously with the first amounts of methyl alcohol.

Detailed study of the corresponding spectrum (lithium fluoride prism) showed that the stronger band had a central minimum and two maxima at 2279 and 2258 cm.$^{-1}$. Other weak bands were also recorded. They seemed to belong to a nitrile but, though spectra of several pure compounds have been made and carefully measured, we have been unable to identify it.

Small quantities of nitrous oxide were also detected.

Quantitative analyses of products have been made at two different temperatures. Table 1 and Fig. 3 give the results obtained at 520°. The products were analysed in the usual way after fractionation of the sample at solid carbon dioxide temperature. Only the sum of the hydrogen and carbon dioxide is obtained, by difference between the total pressure of the volatile fraction and the partial pressures of the other compounds. The actual pressures of hydrogen and carbon dioxide have been calculated from the values of the sum of both together with the material balances.

It was not possible to analyse quantitatively the very small amounts of products from nitric oxide.

The products formed from methylal seem to be the same in the uninhibited and in the inhibited reaction, though it is not known whether the quantitative composition of the mixture is the same because the partial pressures involved are too small to be accurately measured.

(*b*) Acetaldehyde dimethyl acetal. Analyses are recorded for two temperatures in Table 2, and those at 460° are plotted in Fig. 4. Most of the product curves show the abrupt change from the inhibited to the uninhibited reaction. Methyl vinyl ether seems to be used up after being formed, because a smooth rise followed by a decrease is observed in the pressure–time curve. The figures " Diff." in Table 2 correspond to a mixture of " nitrile," nitrous and nitric oxide (when not completely consumed), and probably hydrogen. Some nitrogen or water may also have been produced in small amounts. Although we have not identified the " nitrile " it is presumably the compound obtained in the decomposition of methylal.

TABLE 2.

Products (mm.) of decomposition of acetaldehyde dimethyl acetal (150 mm.) in presence of nitric oxide [(A) 10 mm., (B) 20 mm.] at (A) 460° and (B) 489°.

Expt. no.	Time (min.)	Total press.*	CO	CH_4	C_2H_4	HCN	MeOH	Me vinyl ether	MeOAc	CO_2	Diff.	Nitrile †
						(A) *At* 460°.						
1	10·5	183	24·5	17	—	0·3	12·5	9	10	—	8	—
2	18·5	205	37	28	1	0·7	15·5	12	14·5	0·5	14·5	0·020
3	30·5	239	45	43	1·5	1	25	11	20·5	1·5	23	0·025
4	37·4	294	80·5	65·5	2·5	1·2	20·5	8·5	26	1·5	35	—
5	42·2	332	82·5	81	3	1·2	27	7	29	1	49	0·027
6	54·5	363	115	89·5	3	1·5	34·5	6	29·5	0·5	53	0·046
7	17·5	204·5	21	32	—	—	8	8	10	—	47·5	—
8	29·0	238	30	35	1	—	12	10	15	5	50	—
9	35·0	279	44	53	1·5	—	14	15	22	4	61·5	—
10	48·5	352·5	117	103	3·5	—	26	5	31	—	13	—
						(B) *At* 489°.						
11	5·0	221	25·5	35	—	—	9	8·5	17	1	12	—
12	8·0	246·5	37	53	1·5	1·5	11·5	8·5	20·5	1·5	10·5	0·024
13	10·0	274	39	46	2·5	2·5	20	12·5	22·5	—	55	—
14	11·0	276·5	50·5	66·5	2·5	—	13·5	6·5	21·5	1·5	29·5	0·043
15	14·0	294	52	60	2·5	2·5	21·5	12	26·5	1	26·5	0·085
16	14·0	313	60	66	3	3·5	26·5	14	28·5	—	39·5	—

* Sampling. † Supposed nitrile, estimated spectrophotometrically.

The products from acetaldehyde dimethyl acetal seem to be the same in the inhibited and the uninhibited reactions at the two temperatures studied.

Inhibition by Propene.—Pressure increase–time curves. Increasing amounts of propene,

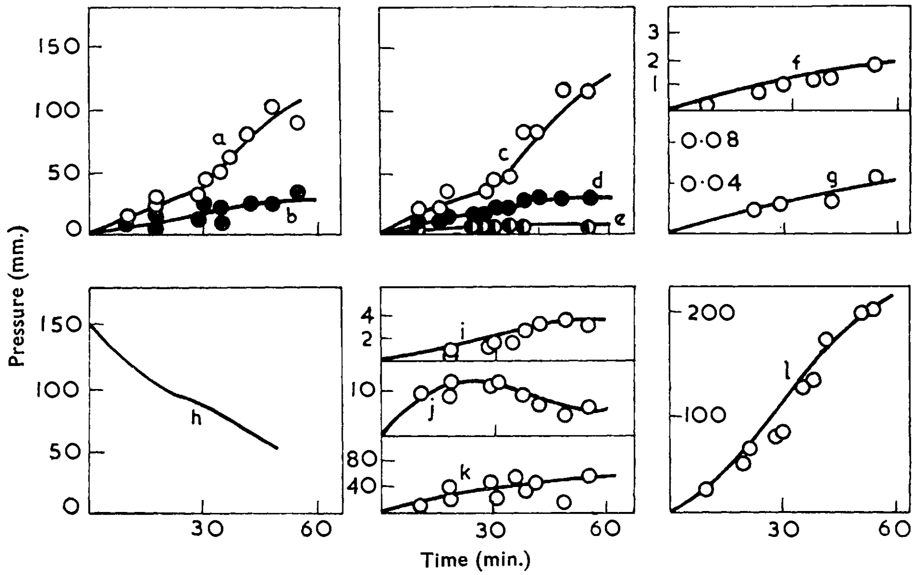

FIG. 4. Products from acetaldehyde dimethyl acetal (150 mm.) and nitric oxide (10 mm.) at 460°: (a) CH_4; (b) MeOH; (c) CO; (d) MeOAc; (e) CO_2; (f) HCN; (g) "nitrile" (scale records optical density); (h) $Me{\cdot}CH(OMe)_2$; (i) C_2H_4; (j) $MeO{\cdot}CH{:}CH_2$; (k) diff.; (l) Δp.

added to methylal in the range studied, cause a shift towards lower pressure increases in the Δp–time curves (Fig. 5) and for comparatively high propene : methylal ratios there is an initial decrease in pressure which perhaps denotes polymerisation followed by decomposition.

The pyrolysis of acetaldehyde dimethyl acetal is also inhibited by propene, the Δp–time curves becoming initially negative with large amounts of propene. The inhibition for both

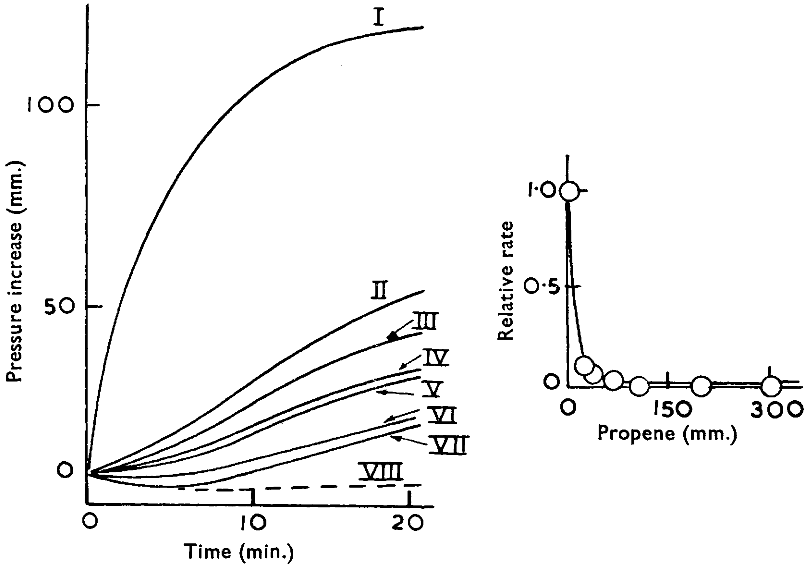

FIG. 5. Methylal, 75 mm.; propene, (I) 0, (II) 25, (III) 29·5, (IV) 65·5, (V) 105, (VI) 201, and (VII) 297 mm. Curve (VII), methylal 0, propene 296 mm. All at 520°.

acetals seems to be permanent but no lower limit may be determined in the Δp–time curves because they become more negative the greater the partial pressure of propene.

Analyses. Quantitative analyses of the products of decomposition of methylal are recorded in Table 3. Most of the products are the same as are obtained from the normal decomposition of methylal, but ethylene is a new product which seems to be formed in small amounts owing to disappearance of some propene during the reaction. Also no difference that could be ascribed to hydrogen was observed in the volatile fractions, either at liquid-air or at solid carbon dioxide temperatures. The small methylal losses are probably due to absorption in the tap grease.

TABLE 3.

Products (mm.) of decomposition of methylal (75 mm.) inhibited by propene (10 min.) at 520°.

C_3H_6 (initial)	CO	CH_4	C_2H_4	C_3H_6 (prod.)	$CH_2(OMe)_2$	$H{\cdot}CO_2Me$	MeOH	H_2	Total press.*
0	55	55	0	0	18	20	4	43	195
26	14	21·5	4·5	22	46	6·5	3	—	123·5
48	17	19	4	37	45·5	6·5	1·5	—	146·5
72	15	16	4·5	65	52	4·5	5·5	—	163
102	15	16·5	4·5	93·5	62	5	—	—	187
147·5	6·5	12	6	136	53·5	3·5	2	—	230
197·5	14·5	15	8·5	187	56	3·5	4	—	280

* Sampling.

The partial pressure of each product is considerably decreased by the action of propene. The curves seem to reach a lower limit of decrease when methylal and propene are in equimolecular amounts, but the Δp–time curve does not reflect this fact because it may be further decreased by larger additions of the inhibitor.

Inhibition by Ethylene.—Pressure increase–time curves. If ethylene is added to methylal, the pressure changes are less. Experiments at different temperatures and with various pressures of methylal and ethylene show the size of this effect to depend on the partial pressure of ethylene. If this is large enough, the curves become slightly negative, as in the case of propene. No lower limit has been found in the Δp–time curves and it is likely that the decrease in pressure would appear greatly magnified if the reaction were studied at ethylene pressures above 1 atm. On the other hand, inhibition by ethylene seems to be independent of the initial methylal pressure (Fig. 6).

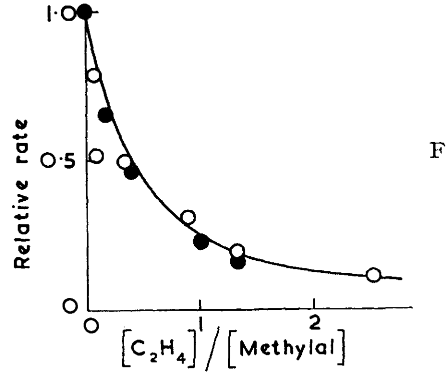

FIG. 6. Relative rates of disappearance of methylal. Methylal, (●) 150, (○) 75 mm.; at 520°.

The action of ethylene on the decomposition of acetaldehyde dimethyl acetal seems at first sight to be similar. However, this is illusory. A remarkable effect is due to ethylene (or of some product formed from ethylene) remaining adsorbed on the surface of the reaction vessel. The rate of pressure increase is considerably decreased by this adsorbed layer (curves I and II, Fig. 7), the reduction being as great as is obtained with further addition of ~100 mm. of ethylene. No such influence has been observed in the decomposition of methylal.

Analyses. (*a*) Methylal. Analyses are recorded in Table 4. In experiments 1—5 fractionation was at solid carbon dioxide temperature. Differences were found between the total pressure and the sum of the analysed products in the non-condensed fraction but could not be ascribed to hydrogen (as in the uninhibited decomposition of methylal [1]) because the material balances did not fit. This points to the likely presence of a hydrocarbon. In further experiments (6—11) fractionation was at liquid-air and at solid carbon dioxide temperatures. The small differences in the first fraction (gaseous at liquid-air temperatures) may be ascribed to hydrogen. There are also differences in the middle fraction (gaseous at solid carbon dioxide temperature) which are probably due to ethane formed by reaction of ethylene with methylal. There were none of the strong characteristic bands of the ethane spectrum and it is possible that amounts such as those involved would not be detected in the reaction mixture owing to overlapping of the bands. Moreover, if the differences are supposed to correspond to ethane, the material balances fit rather well. Small differences in the third fraction are mostly due to formation of some carbon dioxide.

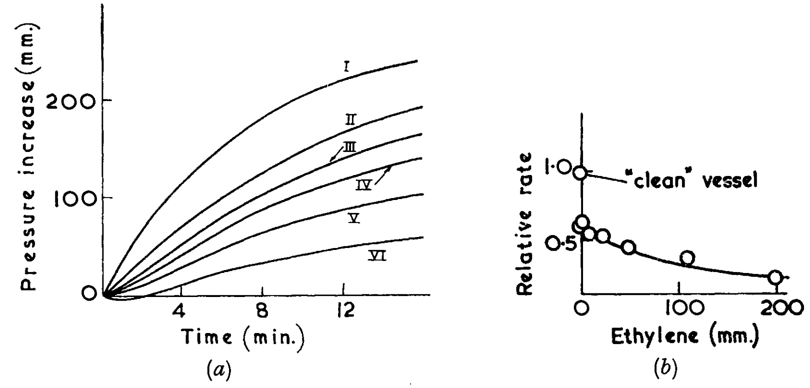

FIG. 7. Acetaldehyde dimethyl acetal, 150 mm.; ethylene, (I) 0, (II) 0, (III) 24, (IV) 50, (V) 110, and (VI) 200 mm.; at 460°.

TABLE 4.

Products (mm.) formed in decomposition of methylal (75 mm.) inhibited by ethylene at 520° (10 min.).

Expt. no	Initial C_2H_4	CO	CH_4	C_2H_4	$CH_2(OMe)_2$	$H{\cdot}CO_2Me$	MeOH	H_2	Diff.*	CO_2	Total press.†
1	26		47	15	24	16	—	39		1·5	182
2	70		32	46·5	38	12	2·5	38		8	192·5
3	101		26	69	44	10·5	1·5	33·5		5	213
4	152·5		20	115	45	9	—	27		1·5	248·5
5	201		19	152	48·5	8·5	—	43·5		—	290·5
6	37·5	40	37·5	23	31·5	18·5	1	8	15	7	178·5
7	38·5	40	41	19	28	18·5	—	6·5	14	4	185
8	83·5	28·5	26	53	35	15	2·5	—	24	2·5	197·5
9	84·5	31·5	31	52	37	14	—	—	28	12	197·5
10	114	23	22	74	35·5	13·5	2·5	1·5	27·5	4	214·5
11	114·5	16	24·5	72	41	13·5	—	3·5	37·5	9·5	218

* See text. † Sampling.

(*b*) Acetaldehyde dimethyl acetal. In the ethylene inhibited reaction of this acetal most of the products appear to be qualitatively the same as those from the normal decomposition.

Quantitative analyses, recorded in Table 5, show that the amounts of ethylene found by analysis are considerably smaller than the initially introduced partial pressures. They also diminish with longer reaction but no products from the reaction of ethylene itself have been detected. This can be explained if a polymer is formed that disappears from the gaseous phase owing to its low partial pressure at room temperature, or if some ethane is formed, its bands being overlapped by the absorption due to the other compounds present in the mixture.

In fact, material losses were observed but some of the acetal was proved to be absorbed in the tap grease, so the amounts of the possible polymer cannot be determined. On the other hand, if some ethane is formed these amounts would be included with hydrogen in Table 5 under the " Diff." heading.

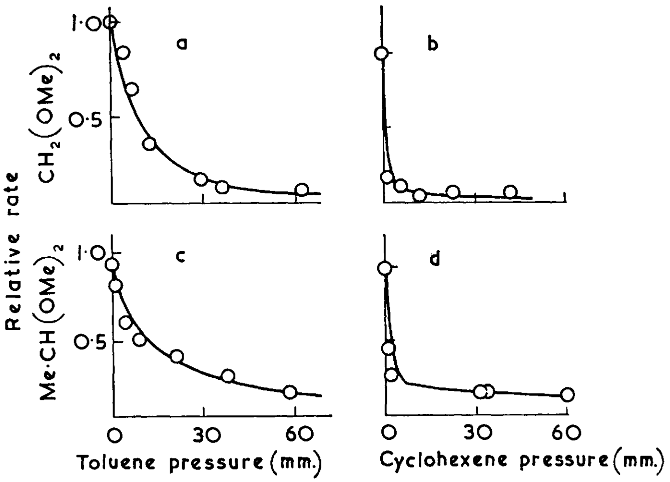

FIG. 8. (a, b) Methylal (75 mm.) at 520°. (c, d) Acetaldehyde dimethyl acetal (75 mm.) at 489°.

Here again the remarkable influence of the surface of the vessel on the reaction should be emphasised. The adsorbed layer of ethylene (or of a product formed from ethylene) does not seem to lower the appearance rates of all the products to the same extent. Methyl alcohol and carbon monoxide are decreased by such an amount as almost to explain the total decrease in the pressure curves.

TABLE 5.

Products (mm.) of decomposition of acetaldehyde dimethyl acetal (150 mm.) inhibited by ethylene at 460°.

Expt. no.	Initial C_2H_4	Time (min.)	Total press.*	CH_4	CO	C_2H_4	MeOAc	MeOH	Me vinyl ether	Diff.
1 †	0	18	398	128	130	6	31	50	10	30
2	0	18	351·5	124·5	91	3	35·5	18·5	9·5	28
3	20	18	354·5	137·5	90·5	12	36	8	10	24·5
4	35	18	330	99·5	72	24·5	30·5	7·5	4	24·5
5	50	18	335	95·5	74	30·5	27·5	9	5	32·5
6	60	18	337·5	87·5	70·5	46·5	25·5	8	4·5	21·5
7	100	18	360	79·5	71	71·5	30·5	7	11	13
8	150	18	394	62	73	104·5	30·5	7	7·5	3·5
9	150	10	355	43	38·5	108·5	22·5	1·5	10	26·5
10	150	30	443	93·5	80	64	27·5	15	10	91·5

* Sampling. † In a " clean " vessel.

Inhibition by Other Compounds.—Toluene and cyclohexene seem also to act as inhibitors (Fig. 8)

Relative Efficiences of Inhibition.—The inhibitors used in this research seem to be effective in the decreasing order: nitric oxide, cyclohexene, toluene, propene, ethylene.

DISCUSSION

The experimental results on nitric oxide inhibition of the thermal decomposition of organic compounds raise the question whether nitric oxide is completely used up during inhibition. Stubbs and Hinshelwood [4] claim that only a small amount of the nitric oxide disappears in the decomposition of paraffins. Their evidence was obtained from experiments where the inhibited reaction of n-heptane was allowed to proceed until the rate reached a maximum. Further additions of nitric oxide made at this point seemed to have practically no effect on the rate. However, the most straightforward explanation of the transitory inhibition of the acetals (or of any other compound) seems to be that the inhibitor is entirely consumed. In order to check it, the reaction of a mixture of **150** mm. of methylal and 5 mm. of nitric oxide was allowed to proceed until the Δp–time curve rose steeply, and further amounts of nitric oxide were added at different stages of the reaction. The Δp–time curves suddenly flattened whenever the addition was made (broken curves, Fig. 9) showing without any ambiguity that the inhibitory action of nitric oxide depends upon its being present. This is taken as evidence that nitric oxide is exhaustively consumed during the inhibition of methylal decomposition.

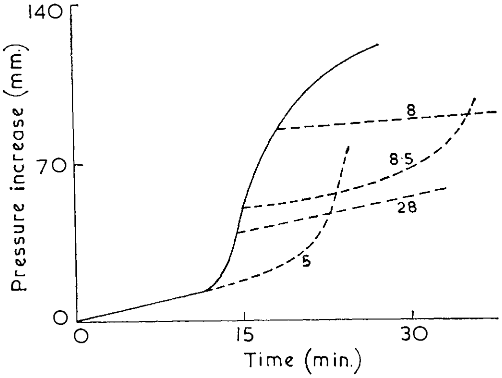

FIG. 9. The solid line denotes reaction of methylal, 150 mm., and nitric oxide, 4 mm., at 520°. The broken lines denote effect of further additions of nitric oxide (mm. as stated on the curves). All at 520°.

It should be emphasised that there is a reason which might explain a different behaviour of nitric oxide when inhibiting the decomposition of n-heptane and that of methylal. In the normal decomposition of n-heptane, appreciable quantities of olefins are formed which are themselves inhibitors and consequently the so-called normal reaction is in fact partially inhibited. On the contrary, no unsaturated compounds are produced from methylal; its normal reaction is really uninhibited and so nitric oxide is not in competition with another inhibitor whose concentration increases as the reaction proceeds. From this point of view, methylal constitutes a unique example among the four acetals studied in this research because ethylene and other unsaturated compounds are produced in the normal decomposition of the others.

We have also plotted the initial concentration of nitric oxide against the inhibition times (solid line, Fig. 10). A straight line is obtained only if it is accepted as a criterion to measure the inhibition time at the points where the nitric oxide concentration starts to be insufficient to maintain complete inhibition. No other criterion seems adequate because the curve would show an induction period several minutes long (broken lines, Fig. 10) for the building up of radicals, which is probably fictitious because no such induction periods are observed in the Δp–time curves. The proportionality between the initial concentration of nitric oxide and the inhibition time shows that the rate of consumption of the inhibitor does not depend on its concentration and that it is probably controlled by the rate of appearance of the radicals.

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[4] Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458.

In the inhibited methylal reaction, nitric oxide is being consumed as the residual reaction proceeds, until its concentration decreases below the limit of complete inhibition. Chains then develop, methylal starting to decompose in its uninhibited way and the Δp–time curves rising to a maximum slope that shows the normal decrease as the reaction comes to an end.

Consequently, the maximum slope belongs to the uninhibited reaction rate of the amounts [M] of methylal whose decomposition has been suppressed owing to inhibition.

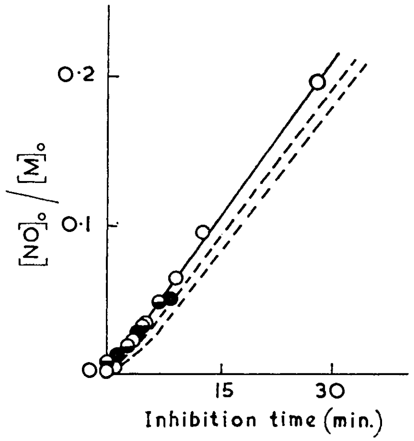

FIG. 10.

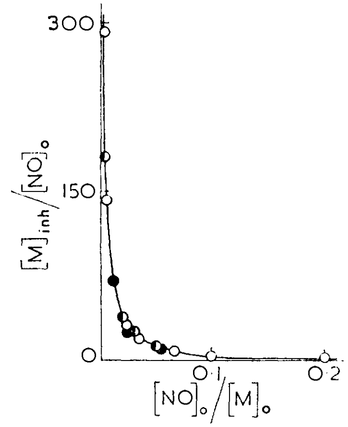

FIG. 11.

FIGS. 10 and 11. Methylal: ● 75 mm.; ○ 150 mm.; ◒ 205 mm.; at 520°.

The [M] values in Table 6 have been obtained by means of a rate–initial pressure plot of the normal decomposition. For comparative purposes among the results obtained at three different starting methylal pressures $[M]_0$, the relative initial nitric oxide concentrations $[NO]_0/[M]_0$ have been calculated.

In Fig. 11 are plotted the $[M]/[NO]_0$ ratios (*i.e.*, the number of methylal molecules that have been inhibited by one of nitric oxide) against the values of $[NO]_0/[M]_0$. All the experimental points fit the same curve; so the inhibition process is dependent on the

TABLE 6.

Ratios, etc., for reaction at 520° (M = methylal).

$[M]_0$ (mm.)	$[NO]_0/[M]_0$	Max. slope (mm./min.)	[M] (corresponding to max. slope) (mm.)	$[M]/[NO]_0$
75	0	30	75	—
	0·013	26	72	72
	0·026	22	63	31·5
	0·053	18	55	13·7
150	0	80	150	—
	0·0033	74	147	294
	0·0066	73	144	144
	0·026	64	132	33
	0·0366	57	121	22
	0·066	46	104	10·4
	0·099	47	104	6·9
	0·198	35	87	2·9
205	0	115	205	—
	0·005	100	183	183
	0·02	85	163	40·7
	0·03	92	172	28·6
	0·05	74	147	14·7

relative nitric oxide concentration rather than on the initial methylal pressure. The number of methylal molecules whose reaction has been suppressed by one of nitric oxide quickly decreases as the nitric oxide concentration increases, which may be explained by accepting again that during " complete " inhibition the rate is not controlled by the actual reaction between nitric oxide and the radicals, the slower process probably being the building up of the radicals themselves.

It is unfortunate that the transitory character of methylal inhibition makes it very difficult to measure experimentally the minimum nitric oxide concentration necessary to get complete inhibition. The corresponding value $[M]/[NO]_0$ in Fig. 11 would represent the absolute length of the methylal decomposition chain. However, according to the preceding brief discussion, " complete " inhibition is obtained at the lower concentration of nitric oxide considered in Table 6 and Fig. 11. Consequently, it may be safely inferred that the chain should be several hundred steps long and greater than about 300.

A general feature of nitric oxide inhibition of the decomposition of organic compounds seems to be that the Δp–time curves are not reduced to a zero value. Whether the remaining reaction is a chain-free molecular process, or whether it corresponds to a fixed state of incomplete suppression of chains, has been the matter of much controversy.[5]

The similarity of the results with propene and nitric oxide in previous investigations, where the same inhibition limit appears to have been reached with each inhibitor, has been given great weight as seeming to indicate complete suppression of chains. But this conclusion does not apply to the present results on the decomposition of methylal. The inhibition is transitory owing to consumption of the inhibitor only if the latter is nitric oxide; if an olefin (ethylene or propene) is used the inhibition is permanent even when the reaction is not completely inhibited owing to use of an insufficient amount of olefin. Secondly, pressure–time curves obtained with increasing amounts of olefin decrease below the inhibition limit reached with nitric oxide. Also there are significant differences in the products, as found by quantitative analyses, molecular hydrogen seeming to disappear only if the inhibitor is propene or ethylene.

It should be emphasised that the function of an inhibitor is simply to provide an alternative path for the active intermediates which propagate the chain in the uninhibited reaction. Therefore, it would be perhaps unfortunate to believe in a general mechanism of inhibition and it would probably be more adequate to consider the process of inhibition as a competitive reaction whose peculiarities would depend, as in any other process, on the nature of the reactants, *i.e.*, the inhibitor, the compound that is being decomposed, and the radicals involved.

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