992. *Kinetics of the Thermal Decomposition of Acetals. Part IV.[1] Sensitized Reactions.*

By M. J. MOLERA, L. ARÉVALO, and J. ORZA.

The influence of several sensitizers on the thermal decomposition of methylal and dimethyl acetal has been studied. Quantitative analyses of the products have been made by infrared spectrometry. If very small amounts of nitric oxide are added to a methylal–ethylene oxide mixture, the rate of the sensitized reaction is greatly reduced, the inhibition being transitory. Biacetyl seems to be efficient in sensitizing a reaction in a nitric oxide-inhibited methylal decomposition at 520°. Di-t-butyl peroxide has been tested over a wide temperature range (168·5—527°) but seems unsuitable as a sensitizer.

THE normal decomposition of several acetals has been previously studied and decomposition of methylal thoroughly discussed.[2,3] Also the actions of several inhibitors commonly used in pyrolyses have been compared.[1] The present paper deals with the effect of sensitizers on the decomposition of acetals.

EXPERIMENTAL

The experimental technique was described in Part I.[2]

In order to introduce vapour mixtures at accurately measured partial pressures, mixtures of the required composition were prepared in globes held at constant temperature. The partition factors between the globes and the reaction vessel were previously determined for the chosen reaction temperature in order to minimize errors in the measurement of pressure at zero reaction time.

Ethylene oxide was prepared by reaction of ethylene chlorhydrin and potassium hydroxide mixed with dry sand. The product was collected at liquid-air temperature and purified by fractional distillation. Biacetyl was a purum grade Fluka chemical. Di-t-butyl peroxide was a purum grade Noury v. der Lande chemical.

[1] Part III, Molera, Centeno, Arévalo, and Orza, *J.*, 1963, 5009.
[2] Molera, Centeno, and Orza, *J.*, 1963, 2236.
[3] Molera, Fernandez-Biarge, Centeno, and Arevalo, *J.*, 1963, 2311.

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RESULTS

Sensitization, by Ethylene Oxide, of the Decomposition of Methylal.—Pressure–time curves. The sensitizing action of ethylene oxide on the normal decomposition of methylal has been measured at 421°, 478°, and 520° and at various starting pressures. The results

TABLE 1.

Rates of pressure change for methylal, ethylene oxide, and mixtures thereof at 421°.

$CH_2(OMe)_2$ (mm.) ...	0	0	0	75	75	75	75	75	75	75	75	75
$(CH_2)_2O$ (mm.)	75·5	100	188	0	10	21	28·5	50	75·5	99·5	150·5	190
$(dp/dt)_0$ (mm./min.)	1	1·3	2·7	0	3·2	4·3	4·9	8·2	9·7	10·8	13	14·5

at 421°, represented in Table 1 and Fig. 1, show that methylal decomposes at a higher rate as the initial pressure of added ethylene oxide increases. For comparative purposes the pressure increase–time curves corresponding to the decomposition of ethylene oxide alone have been also plotted in the same Figure (curves X, XI, and XII).
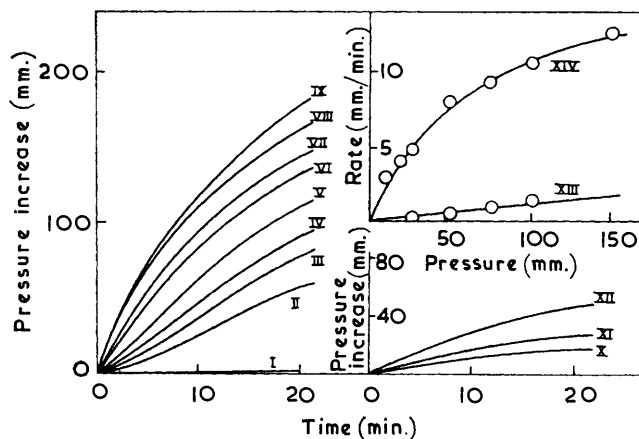

FIG. 1. 421°. (i) Initial methylal pressure 75 mm.; ethylene oxide pressure (I) 0, (II) 10, (III) 21, (IV) 28·5; (V) 50, (VI) 75·5, (VII) 99·5, (VIII) 150·5, (IX) 190 mm. (ii) Initial methylal pressure 0 mm.; ethylene oxide pressure (X) 75·5, (XI) 100, (XII) 188 mm. (XIII) Ethylene oxide rates. (XIV) Rates for methylal–ethylene oxide mixtures.

At the higher sensitizer pressures studied, the rate of pressure change increases slowly, in all probability largely owing to the decomposition of the large amounts of ethylene oxide that are present rather than to an increase in the rate of decomposition of methylal.

Analyses. In the ethylene oxide-sensitized decomposition of methylal most of the products appear to be qualitatively the same as those obtained by normal decomposition. Only keten has been detected as a new product.

To check which of the products were due to decomposition of ethylene oxide, as well as to determine the relative amounts formed under the present experimental conditions, the experiments shown in Table 2 were undertaken. Analytical samples were taken by direct partition between the reaction vessel and the infrared analysis cell. Absorption due to keten overlaps that due to carbon monoxide; moreover, the amount of the former is much greater than of the latter when compared on the basis of equal partial pressures of both compounds, and, consequently, only the amounts of keten in the samples could be safely calculated. The error introduced by neglecting the presence of carbon monoxide amounts to only a few units % in the optical-density measurements. Material balances show that the differences under the diff. heading are mixtures of CO ~75%, H_2 ~12·5%, and C_2H_6 ~12·5%, in agreement with the results obtained by previous investigators.[4]

[4] Steacie, " Atomic and Free Radicals Reactions," Rheinhold Publ. Corp., New York, 1954.

TABLE 2.

Products of decomposition of ethylene oxide alone, formed in 20 minutes at 421°
(pressures in mm.).

Initial $(CH_2)_2O$	$(CH_2)_2O$ in product	CH_4	Keten	Me·CHO	Diff.	Total pressure in vessel
31·5	20·8	7	0·8	0·3	12·5	39
40	26·5	6·5	4·3	—	14·5	49·5
75	46·8	14·7	6·7	0·8	22·5	92·5

The products obtained in 20 min. by sensitized decomposition of 75 mm. (initial) of methylal with the addition of various amounts of ethylene oxide at 421° were analysed after fractionation of the samples at liquid-air temperature (Table 3).

Some differences were observed between the total pressure as measured on the manometer and the sum of the products analytically evaluated for the fraction condensed at liquid-air temperature. We therefore ran several control experiments in which only methylal was pyrolyzed at 421°. The results obtained, together with those obtained with only ethylene oxide in Table 2, show the differences to be due to loss of methylal, which is probably absorbed in the tap grease. Material balances between reactants and product confirm this conclusion and in the results below these differences have been systematically added to the amounts of methylal found by infrared spectroscopy.

The sensitized decomposition of methylal at 421° has been also studied for different

TABLE 3.

Ethylene oxide-sensitized decomposition of methylal : initial methylal pressure 75 mm.,
temperature 421° (pressures in mm.).

$(CH_2)_2O$ initial	Time (min.)	Total press. (sample)	$(CH_2)_2O$ in product	$CH_2(OMe)_2$	CH_4	CO	$H·CO_2Me$	MeOH	Keten	Diff. (vol.)
3·5	20	117	4·5	60	20	17·5	9	1	—	10·5
6·3	20	127·5	6·5	51	24	23·5	10	1	—	10
9·8	20	139·5	9·5	47	28	24·5	11	1·5	—	18
21·5	20	173·5	15	40	33	33	13·5	—	—	29·5
29·8	20	193	20	32	42·5	39·5	13	1	1·5	34·5
40·5	20	216·5	28·5	40	46	43·5	17·5	1	3·5	43·5
75	4	183	67	67	19	17	9	—	4·3	—
75	6	200	42	36·5	26·5	24	12·5	—	4·5	17
75	6	200	76	48	31·5	25	14	0·8	5·4	5
75	10	233·5	68	29·5	42	41·5	18	—	5	26
75	10	233	63	40	42	32	17·5	—	5	33·5
75	14	257	58·5	20	48	37·5	18·5	—	4·2	65
75	18	273	53	25·5	49	42	19·5	1·8	3·6	77
75	30	305·5	50	—	69·5	54	19	0·8	4·3	99
75	45	325	43	—	85·5	90	16	1·7	3·6	80
75	63	348·5	39	—	99	96·5	12·5	0·3	—	96

reaction times, the initial partial pressures of methylal and ethylene oxide being 75 mm. (Table 3).

The influence of nitric oxide. If very small amounts of nitric oxide are added to the methylal–ethylene oxide mixtures, the decomposition rate is greatly reduced, showing that nitric oxide is an inhibitor of the reaction. The inhibition seems to be transitory, the inhibition time depending on the initial partial pressure of nitric oxide (Fig. 2).

The question next arises whether the inhibitory effect of nitric oxide is due to its reaction with radicals formed from ethylene oxide or from sensitized methylal. Some curves corresponding to the action of nitric oxide on the decomposition of ethylene oxide have been obtained (Fig. 3), the higher temperature (478°) being chosen because this reaction is almost unnoticeable at 421°; these show that the great rate reduction in the sensitized decomposition of methylal at 421° in the presence of nitric oxide cannot be

explained in terms of a reaction between the inhibitor and the ethylene oxide or of any of its decomposition products. The possibility still remains that nitric oxide has reacted with the radicals produced in the ethylene oxide decomposition and that, therefore, no methylal chain reaction occurred.

Fletcher and Rollefson [5] and Steacie and Folkins [6] have, however, already studied the inhibitory effect of nitric oxide on the decomposition of ethylene oxide, following this reaction by the pressure increases. From their results, the induced chain decomposition of the acetaldehyde formed by isomerization of ethylene oxide was considered to be the actual subject of nitric oxide inhibition instead of the main reaction which is responsible for the disappearance of ethylene oxide.

Consequently, a more satisfactory explanation of our experimental results seems to be that here, too, the methylal chain reaction is itself inhibited by nitric oxide after the
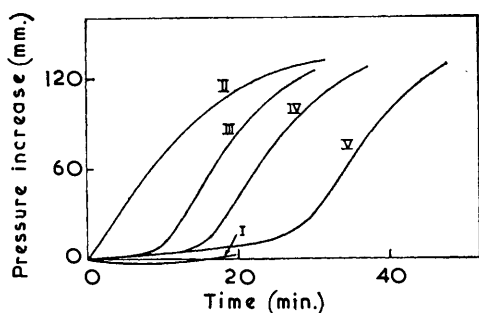

FIG. 2. 421°. Methylal 75 mm. Ethyl-
ene oxide (I) 0, (II—V) 75 mm. Nitric
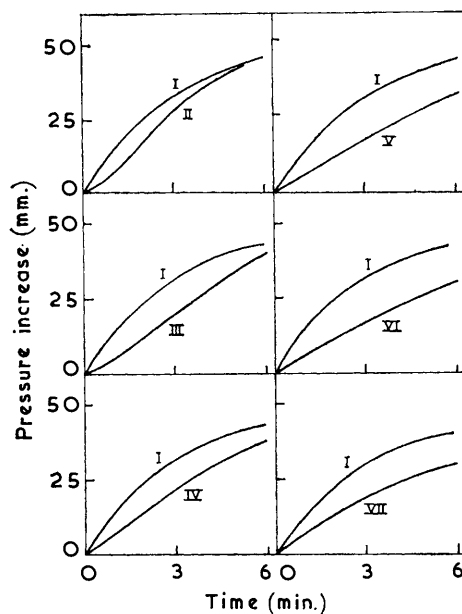oxide (I) 0, (II) 0, (III) 1, (IV) 2·5, (V)
4 mm.

FIG. 3. 478°. Ethylene oxide 75 mm.
Nitric oxide (I) 0, (II) 2, (III) 5, (IV)
11, (V) 18·5, (VI) 55, (VII) 200 mm.

decomposition has been sensitized by ethylene oxide. The remarkable similarity in the shapes of the Δp–time curves corresponding to the nitric oxide-inhibited normal decomposition of methylal [3] and of those plotted in Fig. 2 strongly supports this assumption.

Sensitization, by Ethylene Oxide, of the Decomposition of Dimethyl Acetal.—Pressure–time curves. The sensitizing action of ethylene oxide on the thermal decomposition of dimethyl acetal has been studied at 399°. Curves showing the influence of varying amounts of ethylene oxide on a fixed amount of dimethyl acetal and of varying amounts of dimethyl acetal at a fixed amount of ethylene oxide are shown in Figs. 4a and b. Here curves IX and X show that the pressure increase due to the decomposition of each compound alone is relatively very small, even at the higher partial pressures considered in these experiments.

Analyses. Quantitative analyses have been made, for different reaction times, of the products formed at 399° in the decomposition of 75 mm. (initial) of dimethyl acetal

[5] Fletcher and Rollefson, *J. Amer. Chem. Soc.*, 1936, **58**, 2135.
[6] Steacie and Folkins, *Canad. J. Res.*, 1939, **17**, B, 105.

and 40 mm. (initial) of ethylene oxide. Analyses showing the influence of different amounts of ethylene oxide for a fixed reaction time (20 min.) on the decomposition of 75 mm. (initial) of dimethyl acetal are recorded in Table 4.

TABLE 4.

Ethylene oxide-sensitized decomposition of dimethyl acetal at 399°: initial dimethyl acetal pressure 75 mm. (pressures in mm.).

$(CH_2)_2O$ initial	Time (min.)	$(CH_2)_2O$ in product	$Me \cdot CH(OMe)_2$	CO	CH_4	MeOAc	Keten	MeOH	Me vinyl ether	Δp
40	11	29·5	60·5	15·5	22	8·5	—	—	—	20
40	15	32	56	15	26	11·5	0·8	1·5	—	27
40	20	33·5	46·5	22·5	31	12	0·8	1·5	—	34
40	30	35·5	30·5	26	47·5	15·5	0·8	2	—	42
40	40	25·5	42·5	37·5	52	16·5	1·2	2·5	—	60·5
10·3	20	12	49·5	12	22·5	9·5	—	1·2	—	21
20	20	19·5	51·5	14	26	10·5	—	—	—	27·5
31	20	24·5	54·5	13	28·5	10	—	—	1·5	30

It seems that the products are qualitatively the same as in the normal decomposition of dimethyl acetal. A small amount of keten formed in the decomposition of ethylene oxide was found. Other products, such as hydrogen, ethane, and acetaldehyde, which are

FIG. 4. 399°. (I—IV, X) Dimethyl acetal 75 mm. and ethylene oxide 10, 20, 40, 60, and 0 mm., respectively. (V—VIII) Ethylene oxide 40 mm. and dimethyl acetal 11·5, 21, 40, and 61 mm., respectively. (IX) Ethylene oxide 75 mm.
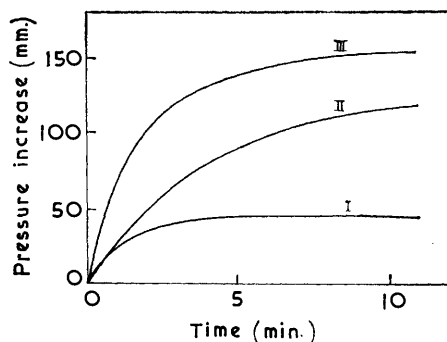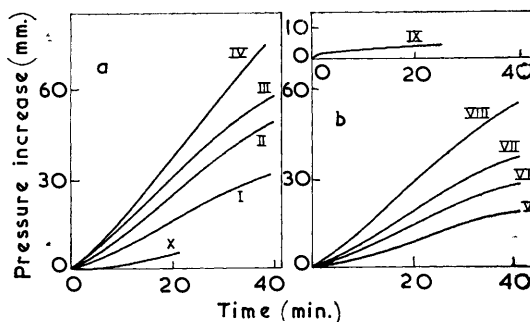

FIG. 5. 520°. (I) Biacetyl 30 mm. (II) Methylal 75 mm. (III) Biacetyl 30 mm. and methylal 75 mm.

usually formed in the normal decomposition of ethylene oxide, have not been detected owing to the amounts of the latter compound used up during the reaction.

Biacetyl-Sensitization of the Decomposition of Methylal.—*Pressure–time curves.* Experiments were made at 390°, 424°, 486°, and 520°. As an example, the results obtained at 520° are plotted in Fig. 5, showing that methylal and biacetyl decompose at similar rates and that the influence of biacetyl on the decomposition of methylal, if any, is unimportant.

Klute and Walters [7] reported that nitric oxide does not inhibit the decomposition of biacetyl. Consequently, the possibility of studying whether biacetyl is a sensitizer of the nitric oxide-inhibited decomposition of acetal was considered. The results are plotted in Figs. 6—9.

Fig. 6 shows that if a fixed amount of biacetyl (15 mm.) is added at 520° to the decomposing mixture corresponding to the pyrolysis of methylal (75 mm.) inhibited by
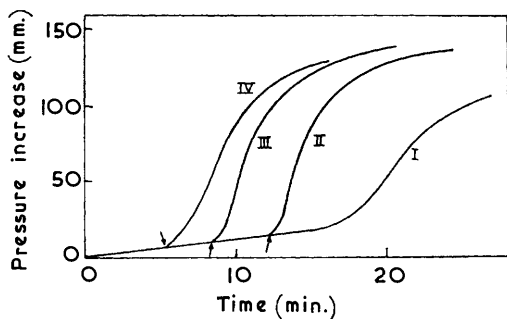
FIG. 6. 520°. (I) Initial pressures: methylal 75 mm., nitric oxide 5 mm. (II—IV) Effect of further addition of biacetyl 15 mm. at the times shown by the arrows.
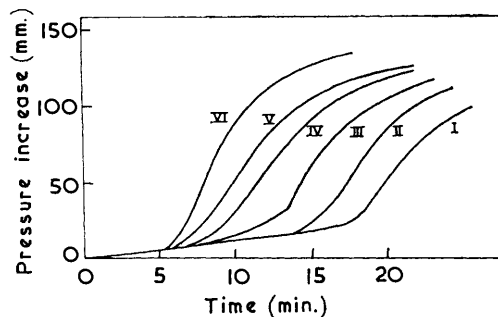
FIG. 7. 520°. Initial pressures: methylal 75 mm., nitric oxide 5 mm., biacetyl (I) 0, (II) 5, (III) 6·5, (IV) 8, (V) 10, (VI) 15 mm. added after 5½ min.
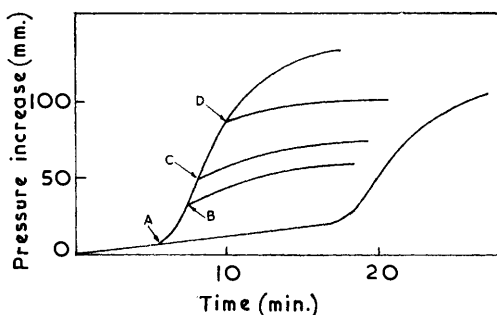
FIG. 8. 520°. Effect of nitric oxide on the biacetyl-sensitised reaction. Initial pressures, methylal 75 mm., nitric oxide 5 mm., with a further addition of biacetyl 15 mm. after 5½ min. Additions: (A) biacetyl 15 mm., (B) NO 18 mm., (C) NO 15·5 mm., (D) NO 18 mm.
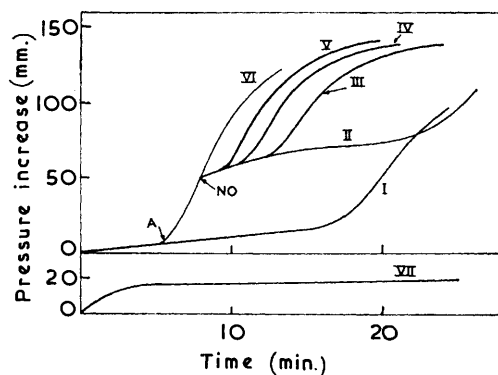
FIG. 9. 520°. Initial pressures: methylal 75 mm., nitric oxide 5 mm. (I) Without further addition. (II—VI) with a further addition (A) of biacetyl 15 mm. and (B) 14·5, 11·5, 10, 10, and 0 mm., respectively, of further nitric oxide. (VII) Decomposition of biacetyl 15 mm.

nitric oxide (5 mm.) after different reaction times, the pressure increase–time curves suddenly change to greater pressure increases.

The results obtained when increasing amounts of biacetyl are added after fixed reaction time (5½ min.) to the decomposing mixture of methylal (75 mm.) and nitric oxide (5 mm.) are plotted in Fig. 7. A similar effect is obtained if a fixed amount of nitric oxide (5 mm.) or increasing amounts of biacetyl are added at zero reaction time.

Figs. 6 and 7 indicate that biacetyl may sensitise the inhibited decomposition of methylal. Figs. 8 and 9 show that the sensitised reaction may again be suddenly

[7] Klute and Walters, *J. Amer. Chem. Soc.*, 1945, **67**, 550.

inhibited if nitric oxide is added. Moreover, the inhibition time increases with the pressure of nitric oxide added when the other conditions remain unchanged.

The above results may be explained in one of the two following ways: either biacetyl can start a methylal chain reaction that is not inhibited by nitric oxide; or biacetyl reacts with nitric oxide, the assumed sensitization being only a suppression of inhibition owing to the consumption of nitric oxide by the biacetyl added. The latter possibility seems to be excluded by the results, already mentioned,[7] of previous investigators. However, some experiments made by us in order to check the possible effect of nitric oxide on biacetyl seem to show that there is a reaction between them, a decrease in the Δp–time curves corresponding to 75 mm. initial methylal pressure ($\sim$12%) being observed at high nitric oxide : biacetyl ratios. Similar results have been obtained at higher methylal pressures (150 mm.).

Analyses. Some analyses have been made in studying the possible reaction of nitric oxide with biacetyl. Qualitative analyses of the products formed from 75 mm. of biacetyl and 50 mm. of nitric oxide in 14 min. at 520° show an appreciable amount of hydrogen cyanide ($\sim$10 mm.). Moreover, we have detected several bands around 2300 cm.$^{-1}$ and carefully measured their frequencies which correspond to one (or more than one) product

TABLE 5.

Nitric oxide-inhibited decomposition of biacetyl at 520° initial biacetyl pressure
30 mm.; initial nitric oxide pressure 10 mm. (pressures in mm.).

Time (min.)	Ac$_2$	CH$_4$	Keten	C$_2$H$_4$	HCN	Nitrile	Diff. (CO)	Total press. in vessel
2	25	16	$\sim$28	1·8	1·6	0·445		73
4	8	17·5	$\sim$24	2	2·3	0·478	29·5	82
9	5	20·5	$\sim$17	2·1	2·9	0·445	38·5	82

whose identity has not as yet been established. Quantitative analyses of the products obtained from 30 mm. of biacetyl and 10 mm. of nitric oxide after several reaction times are shown in Table 5. The optical densities which correspond to the unknown product are under the heading nitrile because most nitriles absorb at $\sim$2300 cm.$^{-1}$ and the possibility that one product is a nitrile cannot be ruled out.

Table 6 records analyses for different reaction times corresponding to the decomposition of 75 mm. (initial) of methylal inhibited by 5 mm. of nitric oxide with addition of biacetyl after 5½ min. The differences between the pressures measured on the manometer and the sum of the partial pressures analysed in the fraction uncondensed at liquid-air temperature should be ascribed to molecular hydrogen. Similar small differences have also been found in the medium fraction, between liquid-air and solid-carbon dioxide temperatures. They are probably due to small amounts of ethane which is not detectable by infrared spectrometry owing to its small absorbing power under the conditions of these analyses.

Experiments with Di-t-butyl Peroxide.—Experiments on the influence of di-t-butyl peroxide as a possible sensitizer of methylal decomposition have been made over the large temperature range 168·5—527°.

At first sight, the pressure increase–time plots obtained at 527° and 505° with 75 mm. (initial) methylal pressure and peroxide pressures up to 50 mm. showed a rate decrease for increasing peroxide pressures which, however, was due to the high decomposition rate of the peroxide at these temperatures. There is a very rapid increase in pressure before the total amount of the methylal and peroxide mixture has reached the reaction vessel; consequently, the apparent initial pressure inside the reaction vessel corresponds to a methylal-poor mixture owing to the considerable amount of decomposition products present. The measured rate is then lower in the presence of di-t-butyl peroxide.

Experiments were made also at 423°, 416°, 401°, and 316°, where the normal methylal decomposition is not detectable, but here too di-t-butyl peroxide decomposed too quickly.

TABLE 6.

Nitric oxide-inhibited decomposition of methylal sensitized by biacetyl, at 520°: initial methylal pressure 75 mm.; initial nitric oxide pressure 5 mm.; biacetyl 15 mm. added after $5\frac{1}{2}$ min. (pressures in mm.).

Expt.	Time (min.)	$CH_2(OMe)_2$	Ac_2	CH_4	CO	$H \cdot CO_2Me$
1	5′ 30″	66	15	6	5·5	
2	5′ 30″	66	15	5·5	2·5	
3	8′ 10″	41		19	22	12·5
4	12′ 15″	28		28·5	26	13·5
5	16′ 15″	17		48	47·5	15
6	17′ 45″	23		56	48·5	14
7	20′	22		45	48	15·5
8	19′	14·5		46	46·5	15
9	22′	23·5		39·5	39·5	14
10	20′	19		46	46	18·5
11	10′	25	8	48·5		21
12	18′	33	10·5	63		14

Expt.	MeOH	HCN	Keten	Nitrile	Diff. (vol.)	Diff. (cond.)	Total press.
1	2	0·15				2	101
2	3	0·08			7	3·4	102·5
3	1·5	0·05	1		40	2·5	143
4	3·5	0·31	0·5		67	7	184
5	1·5	0·48			81	8·5	226·5
6	1	0·40			83	3	232·5
7	3	0·32		0·12	81·5	11	230
8	2	0·30		0·09	76	18	225
9	2·5	0·50		0·19	86	10	224
10	6·5	0·63		0·16			236
11	5	0·47		0·26			197
12	6·5	0·64		0·29			242·5

In experiments 1—7, fractionation at liquid-air temperature; experiments 8 and 9, at liquid-air and solid-CO_2 temperatures; experiments 10—12, direct sampling.

At still lower temperatures (185—168·5°), where the peroxide decomposes at a measurable rate, it does not sensitize the decomposition of methylal. The methylal chain transmission rate is probably very low at these temperatures and no chain reaction would occur even if some attack of the peroxide-derived radicals on the methylal molecules were to take place.

INSTITUTO DE QUIMICA FÍSICA " ROCASOLANO,"
C.S.I.C., MADRID, SPAIN.