Slow Gas-Phase Oxidation of Ethylal with C-14 as a Tracer

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The slow gas-phase oxidation of ethylal was investigated at low temperatures (160-190°C) by the static method. The main products were carbon oxides, water, acetaldehyde, acetic acid, ethanol and ethyl formate with some methanol, formaldehyde, formic acid, n-butane, ethylene and peroxides. Three different ethylal samples labelled with C-14 in each one of its three different positions, respectively, have been synthesized; their oxidation has been studied and the reaction products analysed by radiochromatography. A mechanism is suggested where the branching intermediates are hydroperoxides derived from ethylal.

The low temperature gas-phase oxidation of several cyclic and linear acetals, some of them labelled with C-14, has been the subject of previous work in these laboratories. This paper is concerned with the study of the slow oxidation of ethylal and of ethylal labelled with C-14 in each one of its three different positions.

EXPERIMENTAL

METHOD

The oxidation reaction was carried out under static conditions in a Pyrex vessel as previously described.[1] The reaction was followed by the change of pressure with time and by quantitative analysis of reaction products by g.l.c. Total peroxide content was determined by a spectrophotometric method.[2] Hydrogen peroxide and organic peroxides were separately detected by t.l.c.[1, 3]

PRODUCTS

C-14 labelled *para*formaldehyde and ethanol were from The Radiochemical Centre, Amersham. All chemicals used for identification or calibration purposes were either synthesized by standard methods or were of commercial origin. They were checked by g.l.c. and purified when necessary.

SYNTHESES

Ethylal was prepared by reaction of *para*formaldehyde with ethanol in the presence of phosphoric acid and calcium chloride:

$$HCHO + 2C_2H_5OH \rightarrow CH_2(OC_2H_5)_2 + H_2O.$$

Unlabelled ethylal was prepared using a 30 % excess of ethanol. Radioactive ethylal was synthesized in a 50 cm^3 round-bottomed flask using 2.5 g of *para*formaldehyde, 1.5 g of calcium chloride, 9.7 g of ethanol and 0.4 cm^3 of phosphoric acid, added in the stated order. If the radioactive compound was *para*formaldehyde, a 30 % excess ethanol was used to increase the yield. If ethanol was the radioactive substance, it was introduced first in the exact amount. An ethylal+ethanol mixture distilled at ~75°C. It was purified by refluxing over extruded sodium with stirring followed by trap to trap distillation under vacuum. The cycle was repeated three times producing an ethylal with a purity >99.5 %.

DEGRADATION

Hydrolysis of ethylal was carried out as follows; a few drops of a 10 % aqueous solution of sulphuric acid were added to 0.5 cm^3 of the labelled ethylal. About 1 mm^3 of the mixture was injected into the radiochromatographic counting system through a heated device to avoid direct contact of the acid with the injection block of the gas chromatograph. Five injections were made for each compound. Table 1 summarizes other details of the syntheses and results of the degradation experiments.

TABLE 1.—DATA ON THE SYNTHESIS OF LABELLED ETHYLAL

	compound synthesized		
	^{14}C-diethoxymethane	^{14}C-ethoxy-β-ethoxymethane	^{14}C-ethoxy-α-ethoxymethane
active component	*para*formaldehyde-^{14}C	ethanol-1-^{14}C	^{14}C-ethan-2-ol
activity/mCi	0.5	0.25	0.25
yield referred to *para*formaldehyde	59.6	45.2	44.2
chemical purity/%	99.9	99.9	99.9
specific activity/% /counts min^{-1} μmol^{-1}	7586	4709	4304
degradation products: relative activity referred to ethylal/%			
formaldehyde	100±2.9	0	0
ethanol	0	50.8±1.2	49.7±2.4

OXIDATION OF RADIOACTIVE ETHYLAL

The experimental set-up used in the oxidation of ethylal was slightly modified for use with the labelled compounds.[4] The radioactive counting system and conditions have already been described.[5]

RESULTS

ACTIVATION ENERGY

When the pressure increase is plotted against time, sigmoid curves are obtained. Pressure rise may be taken as a measure of the extent of the reaction as long as it is correlated with consumption of at least one of the reactants. Fig. 1 shows the proportionality of pressure increase with oxygen consumption (measured by g.l.c.) for the first stages of reaction, corresponding to a fuel : oxygen composition of 1 : 2* over the temperature range 160-177°C. The linearity holds until some time after the maximum reaction rate. Consequently, the maximum rate of pressure increase may be taken as a measure of the maximum reaction rate. The activation energy was evaluated by means of an Arrhenius plot between 172 and 190°C and found to be 172±14 kJ mol^{-1}.

ANALYTICAL RESULTS

Analytical experiments were carried out at 177°C on 1 : 2 ethylal + oxygen mixtures at a total initial pressure of 180 Torr. Results in fig. 2 are expressed in Torr in the reaction vessel. Under the peroxides heading, the total amount of the O_2^{2-} group determined by spectrophotometry is also given in Torr. Small amounts of trioxan

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* Fuel : oxygen ratios are expressed throughout on a volume basis.

were detected by combined g.l.c. and m.s. Ethylal pressures were determined by the difference between the total pressure in the reaction vessel and that corresponding to reaction products and oxygen. Small amounts of ethyl carbonate were also detected.

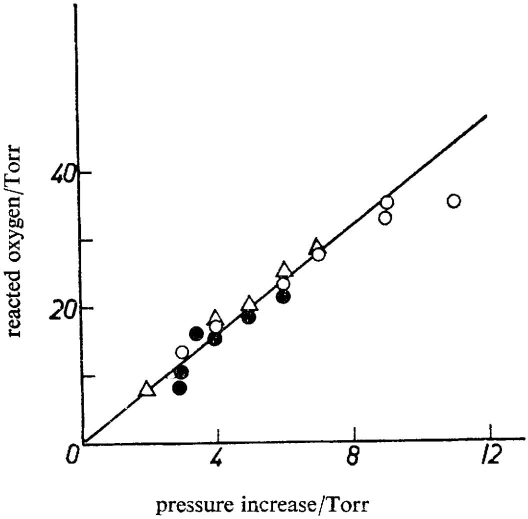


FIG. 1.—Oxidation of 1 : 2 ethylal+oxygen mixtures, initial pressure 180 Torr. ○, 177 ; △, 170 ; ●, 160°C.

Peroxides formed at 177°C were separated by t.l.c. Two spots (R_F = 0.22 and 0.76, respectively) were detected. The R_F of the first spot was the same as that of hydrogen peroxide. The second spot is probably due to a hydroperoxide or a mixture of hydroperoxides derived from ethylal. Separation of isomeric hydro-

TABLE 2.—OXIDATION PRODUCTS OF LABELLED ETHYLAL

oxidation products	pressure /Torr	^{14}C-diethoxy-methane activity/%	^{14}C-ethoxy-β-ethoxymethane activity/%	^{14}C-ethoxy-α-ethoxymethane activity %/
ethyl formate	2.6	100±3	53±5	47±3
methanol	0.8	23±1	44±2	0
ethanol	3.1	0	50±4	49±1
acetaldehyde	7.0	0	45±5	47±4
carbon monoxide	2.0	7±1	13±1	31±2
carbon dioxide	5.8	63±3	3±1	12±2
formaldehyde	0.6	32±4	10±1	27±4
acetic acid	3.7	5±1	57±4	52±4
formic acid	0.9	0	50±2	0
ethylene	0.09	0	47±3	52±8
n-butane	0.24	0	60±4	51±4
ethyl carbonate	0.01	99±2	99±4	99±3
ethylal		100±1.1	100±3.5	100±1.0

Activities are relative to that of ethylal peroxides derived from the ethylal molecule is not expected under the experimental conditions used.[3]

Samples were taken from oxidation experiments interrupted at different reaction times over the first 6 min of reaction. They were kept in a dry ice bath and simultaneous thin-layer chromatograms were subsequently run. An increase and a later decrease in the intensity of the spot at $R_F = 0.76$ was observed. The maximum intensity corresponds to a reaction time of 3 min. The hydrogen peroxide spot had a lower intensity than the spot at $R_F = 0.76$ at reaction times <3 min, but their intensities were similar thereafter.

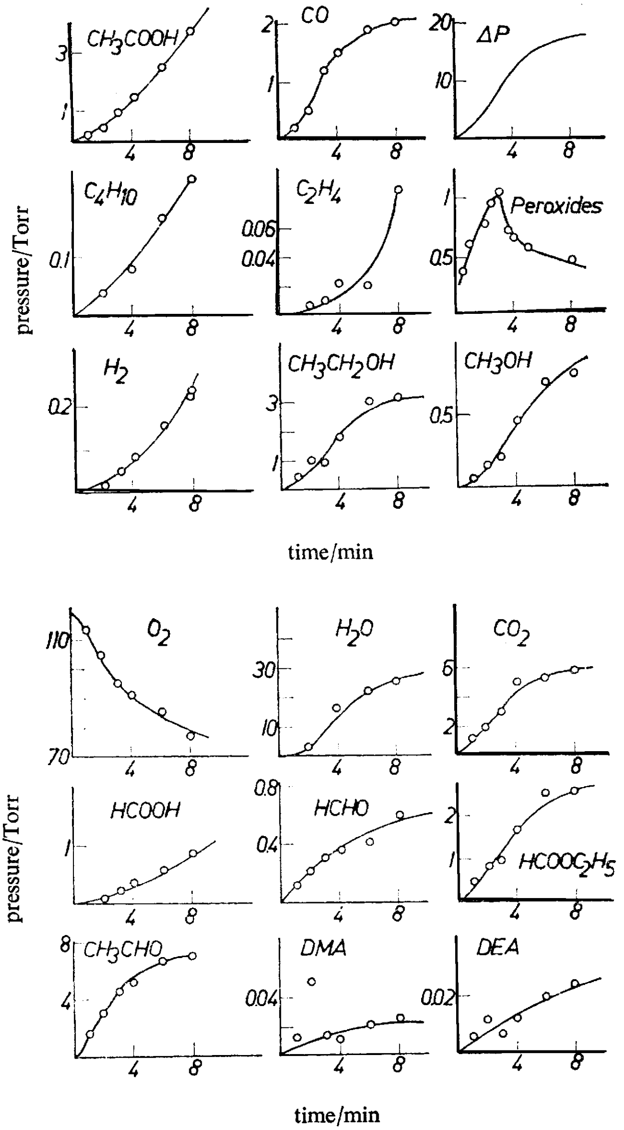


FIG. 2.—Oxidation products in 1 : 2 ethylal+oxygen mixtures at 177°C, initial pressure 180 Torr

RADIOCHROMATOGRAPHIC ANALYSES

Oxidation experiments for ^{14}C-diethoxymethane, ^{14}C-ethoxy-β-ethoxymethane and ^{14}C-ethoxy-α-ethoxymethane were made under the conditions already mentioned for reaction times of 10 min. Results in table 2 are mean values of 3 to 6 experiments for each reaction product. Activities are expressed as a percentage of those corresponding to the parent ethylal molecule. Pressures of products are expressed in Torr in the reaction vessel.

DISCUSSION

The pressure increase against time curves obtained in ethylal oxidation are sigmoid in shape at low temperatures. Autocatalysis suggests that the oxidation is a chain reaction with degenerate branching. The active intermediate is presumed to be a hydroperoxide (or a mixture of isomeric hydroperoxides) derived from ethylal. Hydroperoxides were found to be responsible for degenerate branching in the slow oxidation of other acetals.[4] In ethylal oxidation at 177°C, the maximum concentration of total peroxides, the maximum intensity of the spot of the organic peroxides at $R_F = 0.76$ by t.l.c. and the maximum reaction rate were located at a reaction time of 3 min (fig. 2).

Chains are probably initiated by H-atom abstraction from ethylal. The three possibilities are:

$$CH_2(OC_2H_5)_2 + O_2 \rightarrow HO_2^{\bullet} + \overset{\bullet}{C}H(OC_2H_5)_2 \tag{1}$$

$$\rightarrow HO_2^{\bullet} + CH_3\overset{\bullet}{C}HOCH_2OC_2H_5 \tag{2}$$

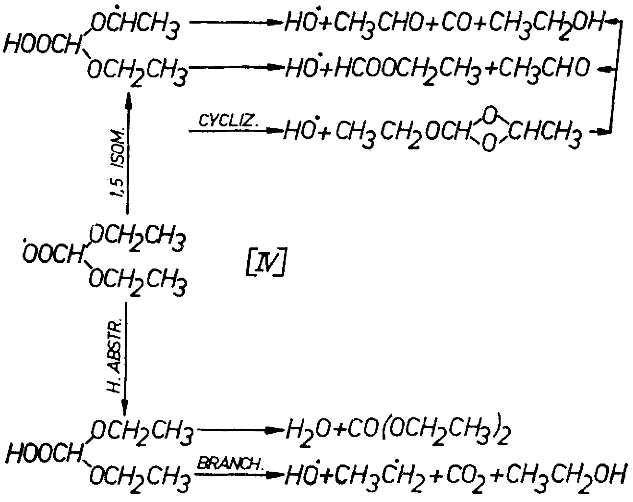
$$\rightarrow HO_2^{\bullet} + \overset{\bullet}{C}H_2CH_2OCH_2OC_2H_5. \tag{3}$$

Radicals formed in reactions (1), (2) and (3) will be mentioned hereafter as radicals I, II and III, respectively.

Since the central CH_2 group in ethylal is between two ether oxygen atoms, the CH bond dissociation energies will decrease in the order $H—CH_2CH_2OCH_2OC_2H_5 >$ $H—CH(CH_3)OCH_2OC_2H_5 > H—CH(OC_2H_5)_2$, and thus only reaction (1) is likely to be important as far as chain initiation is concerned. The presence of radical I in the reaction mixture seems to be proved by the fact that diethyl acetal (which could be formed by combination with methyl radicals) was found among the products.

However, the radicals I, II and III, may be equally important in chain propagation. They may be formed by H-atom abstraction by the HO· radical present in the combustion system. This reaction has a very low activation energy and is almost unselective with respect to the type of C—H bond. It is likely to be responsible for the large amount of water (~50 % of products) formed during the process. This reaction will be followed by oxygen molecule addition to form radicals $(C_2H_5)_2CHOO\cdot$ (radical IV), $C_2H_5OCH_2OCH(OO\cdot)CH_3$ (radical V) and $C_2H_5OCH_2OCH_2CH_2OO\cdot$ (radical VI). Approximate calculations show that the addition reactions are exothermic, the peroxidic radicals being formed with excess energy. Reaction schemes for the three peroxy radicals are shown below. This mechanism is supported, at least qualitatively, by the results with labelled ethylal presented in table 2.

Part of the ethylal skeleton (CH_3CH_2OCH) seems to be preserved in ethyl formate formed in reactions (5), (10), (14) and (16). The ethyl groups of the ethylal molecule are the main source of ethanol [reactions (4), (8), (9), (15) and (17)], acetaldehyde [reactions (4), (5), (9), (10), (12), (14), (16) and (17)] and ethylene [reaction (15)].



$HOOCH(O\dot{C}HCH_3)(OCH_2CH_3) \rightarrow H\dot{O} + CH_3CHO + CO + CH_3CH_2OH$ (4)

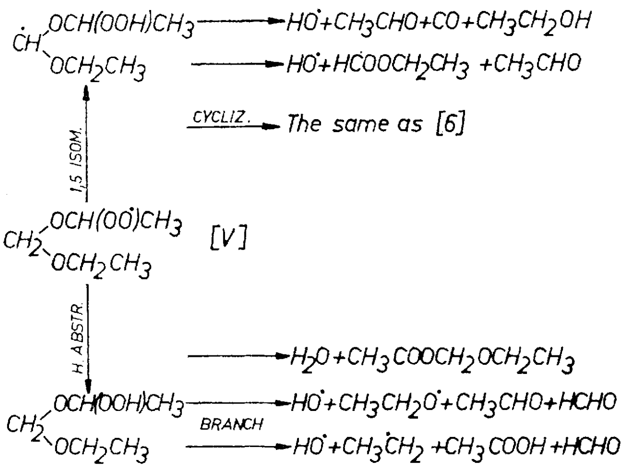
$\rightarrow H\dot{O} + HCOOCH_2CH_3 + CH_3CHO$ (5)

$\xrightarrow{CYCLIZ.} H\dot{O} + CH_3CH_2OCH\langle O, O\rangle CHCH_3$ (6)

$[IV]\ \dot{O}OCH(OCH_2CH_3)_2$

$HOOCH(OCH_2CH_3)(OCH_2CH_3) \rightarrow H_2O + CO(OCH_2CH_3)_2$ (7)

$\xrightarrow{BRANCH.} H\dot{O} + CH_3\dot{C}H_2 + CO_2 + CH_3CH_2OH$ (8)



$\dot{C}H(OCH(OOH)CH_3)(OCH_2CH_3) \rightarrow H\dot{O} + CH_3CHO + CO + CH_3CH_2OH$ (9)

$\rightarrow H\dot{O} + HCOOCH_2CH_3 + CH_3CHO$ (10)

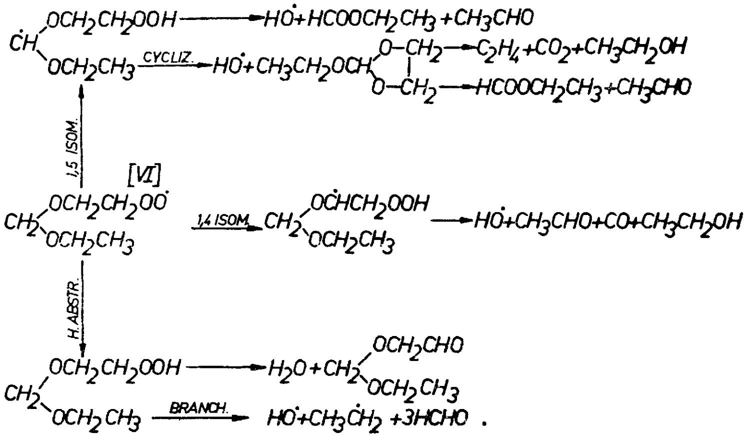
$\xrightarrow{CYCLIZ.}$ The same as [6]

$[V]\ CH_2(OCH(O\dot{O})CH_3)(OCH_2CH_3)$

$\rightarrow H_2O + CH_3COOCH_2OCH_2CH_3$ (11)

$CH_2(OCH(OOH)CH_3)(OCH_2CH_3) \rightarrow H\dot{O} + CH_3CH_2\dot{O} + CH_3CHO + HCHO$ (12)

$\xrightarrow{BRANCH} H\dot{O} + CH_3\dot{C}H_2 + CH_3COOH + HCHO$ (13)



$\dot{C}H(OCH_2CH_2OOH)(OCH_2CH_3) \rightarrow H\dot{O} + HCOOCH_2CH_3 + CH_3CHO$ (14)

$\xrightarrow{CYCLIZ.} H\dot{O} + CH_3CH_2O\dot{C}H\langle O{-}CH_2, O{-}CH_2\rangle \rightarrow C_2H_4 + CO_2 + CH_3CH_2OH$ (15)

$\rightarrow HCOOCH_2CH_3 + CH_3CHO$ (16)

$[VI]\ CH_2(OCH_2CH_2O\dot{O})(OCH_2CH_3) \xrightarrow{1,4\ ISOM.} CH_2(O\dot{C}HCH_2OOH)(OCH_2CH_3) \rightarrow H\dot{O} + CH_3CHO + CO + CH_3CH_2OH$ (17)

$CH_2(OCH_2CH_2OOH)(OCH_2CH_3) \rightarrow H_2O + CH_2(OCH_2CHO)(OCH_2CH_3)$ (18)

$\xrightarrow{BRANCH.} H\dot{O} + CH_3\dot{C}H_2 + 3HCHO\ .$ (19)

At least 95 % of the acetic acid is also formed from the ethyl groups of ethylal [reaction (13)]. However, more complicated reactions must be responsible for the formation of formic acid, as it is only derived from the terminal carbon atoms of ethylal, probably by a double attack of oxygen. The ethylal skeleton seems to be preserved in ethyl carbonate [reaction (7)]. 90 % of the formaldehyde [reactions (12), (13) and (19)] is formed from all three carbon atoms next to the oxygen atoms of ethylal. Reactions (8), (13) and (19) show that n-butane may be produced by ethyl radical recombination. 60 % of the carbon dioxide [reactions (8) and (15)] has its origin in the central carbon atom of ethylal. It looks likely that CO is formed from the central carbon atom of ethylal in reactions (4), (9) and (17). However according to the tracer results, 60 % of the carbon monoxide is formed by the α-carbon atoms of the ethyl groups of ethylal; therefore, it might be produced by further oxidation of the products and mainly by acetaldehyde. 80 % of the methanol is formed by the terminal carbon atoms of ethylal. The scission of the O—O bond of a hydroperoxy alkyl radical often leads to formation of a heterocyclic ring and a HO• radical.[6] Accordingly, reaction (6) and (15)-(16) might be tentatively proposed. Steps (11) and (18) were proposed by analogy with step (7), although the carbonyl compounds postulated have not been identified. However, these reactions are highly exothermic and are therefore possible on energetic grounds. Chain termination is probably due to mutual interaction of RO_2 radicals to give inert products or to removal of such radicals at the surface of the reaction vessel.

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[1] M. J. Molera, J. A. García-Domínguez and A. U. Acuña, *J. Chem. Soc.* (*B*), 1971, 1916.
[2] M. J. Molera, J. A. García-Domínguez and J. M. Santiuste, *Anales de Quim*, 1974, **70**, 579 (in English).
[3] M. J. Molera, J. A. García-Domínguez and J. M. Santiuste, *Anales de Quim*, in press (in English).
[4] M. J. Molera, J. A. García-Domínguez and A. U. Acuña, *Anales de Quim*, 1974, **70**, 559 (in English).
[5] M. J. Molera, J. A. García-Domínguez, and J. M. Santiuste, *Anales de Quim*, 1977, **73**, 467 (in English).
[6] A. Fish, in *Organic Peroxides*, ed. D. Swern (John Wiley and Sons, London, 1970), vol. I, p. 141.

(PAPER 7/441)