[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Ethylene Oxide[1,2]

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Analyses have been made to determine the concentrations of acetaldehyde, formaldehyde and ketene present during the homogeneous thermal decomposition of ethylene oxide in the neighborhood of 400°. Addition of propylene increases the pressure of acetaldehyde and decreases the pressure of ketene during the early stages of the decomposition. When mercury dimethyl is added to ethylene oxide to the extent of about 10%, the ketene pressure after 10 to 20 minutes of reaction at 400° is raised considerably and the acetaldehyde pressure is lowered. Under all conditions studied the formaldehyde pressure was found to be small.

In a previous publication[3] it has been reported that the rate of disappearance of ethylene oxide at 400°, as determined by chemical analysis, can be decreased to about half of its normal value by the addition of propylene. This result indicated that a portion of the thermal reaction of ethylene oxide involves free radical processes which are inhibited by propylene. Moreover, the rate of disappearance of ethylene oxide in the presence of decomposing mercury dimethyl was found to be faster than the rate for pure ethylene oxide.[3]

Various intermediate products which contain oxygen have been observed in the thermal decomposition of ethylene oxide in the region 380–500°. Acetaldehyde has been postulated[4] and later identified as an intermediate product.[5–8] Formaldehyde[5] has been found to be present in small amounts, and acrolein[5] also has been reported as a product. Ketene (but not formaldehyde) has been identified in the decomposition at 410–470° by means of infrared measurements[8] and has been found mass-spectrometrically in the decomposition under high-temperature, low-pressure conditions.[9]

The purpose of the present study was to ascertain the effect of propylene and the influence of methyl radicals upon the formation of the oxygenated intermediate products present during the pyrolysis of ethylene oxide.

Experimental

The materials and apparatus used in this work were the same as those described in the earlier publication.[3] The acetaldehyde in the products was determined usually by the *p*-hydroxybiphenyl colorimetric method[10]; the concentration of acetaldehyde was calculated from a measurement of the absorbance of the colored solution at 570 mμ (maximum absorption) as determined with a Model DU Beckman spectrophotometer. With only small amounts of formaldehyde present any absorption at 570 mμ due to formaldehyde was ordinarily negligible, but small corrections were made whenever necessary.[11] The presence of ethylene oxide, propylene or acetic acid (which would be formed from ketene) was found to have no effect upon the determination of acetaldehyde under the experimental conditions employed.

The *p*-hydroxybiphenyl colorimetric method also provided an indication that propionaldehyde is not present at 400° in amounts comparable to those of acetaldehyde. For this purpose the ratio of the absorbance of the solution at 460 mμ to that of 570 mμ was employed. The products from two experiments carried out at 400° for 44 minutes with about 415 mm. of ethylene oxide in the presence and absence of 114 mm. of propylene gave ratios (A_{460}/A_{570}) in the range 0.05–0.09, in agreement with the values obtained for acetaldehyde. The ratio for the color produced from propionaldehyde is approximately 0.4.[12]

Formaldehyde was determined qualitatively and quantitatively in the products by the use of the modified Schryver colorimetric method described by Matsukawa.[13] The development of a red color in this test has been reported by Matsukawa as a relatively specific test for formaldehyde. The shape of the absorption curve and the position of the maximum (at $\sim$520 mμ) of the colored substance formed by the products from ethylene oxide after ten minutes at 438° corresponded to those from pure formaldehyde. For the determination of the concentration of formaldehyde the absorbence of the red solution at 525 mμ was used. When the color reaction takes place in the presence of a large excess of acetaldehyde and ethylene oxide, the absorbence of the resulting solution is slightly lower than that from formaldehyde alone and to compensate for this effect corrections were applied. The determination of formaldehyde was not affected by the presence of propylene.

In some of the experiments the determination of the total aldehyde content of the reaction mixture was made by the use of a modification of the Ripper bisulfite method.[14]

Ketene was detected in the products by its infrared absorption at 4.6–4.7 μ and by its reaction with water to form acetic acid. The titration of the acetic acid with a standard base solution was used for the quantitative determination of ketene. Precautions were taken to avoid errors which might result from the presence of carbon dioxide. The carbon monoxide in the fraction of products volatile at −196° was determined by the use of Cosorbent reagent from the Burrell Corporation.

Results and Discussion

The results of analyses to determine the quantities of formaldehyde and acetaldehyde present during the decomposition of ethylene oxide at 400° are shown in Table I.

The data in Table I which show the presence of a small amount of formaldehyde confirm the detection of formaldehyde reported earlier by Fletcher and Rollefson[5] and are not in disagreement with the conclusions of Simard and his co-workers[8] who stated that the presence of formaldehyde to the order of 1% of the sample composition could not be excluded on the basis of their infrared

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[1] This work was supported by the Office of Naval Research.

[2] Abstracted from a Ph.D. thesis submitted by K. H. Mueller.

[3] K. H. Mueller and W. D. Walters, THIS JOURNAL, **73**, 1458 (1951).

[4] W. W. Heckert and E. Mack, Jr., *ibid.*, **51**, 2706 (1929).

[5] (a) C. J. M. Fletcher, *ibid.*, **58**, 534 (1936); (b) C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936).

[6] R. V. Seddon and M. W. Travers, *Proc. Roy. Soc.* (*London*), **156A**, 234 (1936).

[7] H. W. Thompson and M. Meissner, *Trans. Faraday Soc.*, **34**, 1222 (1938).

[8] G. L. Simard, J. Steger, T. Mariner, D. J. Salley and V. Z. Williams, *J. Chem. Phys.*, **16**, 836 (1948).

[9] F. P. Lossing, K. U. Ingold and A. W. Tickner, *Disc. Faraday Soc.*, No. 14, 34 (1953).

[10] E. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).

[11] The initial studies of the applicability of colorimetric methods to the analysis of acetaldehyde and formaldehyde in the present reaction mixtures were made by W. F. Erbelding and H. N. Cripps in this Laboratory.

[12] R. Gomer, private communication.

[13] D. Matsukawa, *J. Biochem.* (*Japan*), **30**, 385 (1939).

[14] M. Ripper, *Monatsh.*, **21**, 1079 (1900).

TABLE I

ALDEHYDES PRESENT DURING THE DECOMPOSITION OF ETHYLENE OXIDE

Temp., °C.	$P^\circ_{(CH_2)_2O}$ mm.	$P^\circ_{C_3H_6}$ mm.	$P^\circ_{Hg(CH_3)_2}$ mm.	$\frac{P_{H_2CO}}{P^\circ_{(CH_2)_2O}}$ %	$\frac{P_{CH_3CHO}}{P^\circ_{(CH_2)_2O}}$ %
Reaction time, 10.1 min.					
401	266	0	0	0.04	1.02
401	226	0	0	.04	1.04
400	211	92	0	.01	1.75
400	224	92	0	.01	1.64
401	277	0	24	.01	0.85
Reaction time, 20.1 min.					
401	261	0	0	0.04	1.31
400	223	87	0	.01	2.92
400	279	0	25	.02	1.12
398	237	0	0	..	1.49[a]
398	231	87	0	..	2.96[a]

[a] Total aldehydes determined by the bisulfite–iodine titration. On the basis of the ethylene oxide analyses reported earlier[3] the percentages of ethylene oxide disappearing after 10.1 minutes for the experiments above should be approximately: (a) 8% for the pure compound, (b) 4% with added propylene, and (c) 15% with added mercury dimethyl. After 20.1 minutes the percentages are: (a) 14%, (b) 7% and (c) 23%.

measurements. The formaldehyde analyses are of interest in connection with the consideration of the reaction

$$(CH_2)_2O \longrightarrow CH_2 + CH_2O \qquad (1)$$

which has been suggested as the main initial reaction producing free radicals.[5b] Since it appears that a considerable fraction of the molecules of ethylene oxide decompose to form radicals,[3,5b,9] the small amount of formaldehyde present during the decomposition indicates that reaction 1 is not the major radical producing reaction. In the experiments in which propylene was added to decrease free radical chain reactions the concentration of formaldehyde was very low. This result gives evidence that a large quantity of formaldehyde is not originally formed by reaction 1 and then lost by a radical sensitized decomposition.[15]

Although the present data do not exclude the possibility that significant quantities of methylene radicals are formed by a reaction not producing formaldehyde, methylene radicals have not been detected in mass spectrometric experiments.[9] As the primary process responsible for the production of most of the free radicals in the decomposition of ethylene oxide the following reaction[9,16] appears to be the most likely

$$(CH_2)_2O \longrightarrow (\text{Intermediate}) \longrightarrow CH_3 + HCO \quad (2)$$

Most of the HCO radicals probably decompose into H and CO, but it is possible that formaldehyde may eventually be formed as a result of the reaction of some of the formyl radicals.

The data in Table I give evidence that the addition of propylene causes an increase in the concentration of acetaldehyde during the initial stages of the decomposition at 400°. Increases in the acetaldehyde pressure when propylene is present have also been observed in similar experiments at 444° and in experiments with about 400 mm. of ethylene oxide at 400°. Moreover, that the pressure of aldehydes after 20 minutes of reaction at 400° is raised by a factor of at least 2–2.2 by the addition of propylene was also confirmed semi-quantitatively by a polarographic method of analysis. A possible explanation for the increase in acetaldehyde is that propylene suppresses the reactions responsible for the decomposition of acetaldehyde more than it decreases the reactions by which acetaldehyde is formed. It does not appear likely that the increase is due mainly to a reaction in which propylene causes an additional amount of ethylene oxide to form acetaldehyde, particularly in view of the inhibitory effect of propylene upon the rate of disappearance of ethylene oxide.[3] The explanation suggested above would be in accord with the previously postulated mechanisms[5b,17] in which the intermediate acetaldehyde is formed by an isomerization

$$(CH_2)_2O \longrightarrow CH_3CHO \qquad (3)$$

and decomposed by a radical induced reaction

$$CH_3CHO + R \longrightarrow RH + CH_3CO \longrightarrow RH + CH_3 + CO \quad (4)$$

In this connection an analysis was made for carbon monoxide formed in the decomposition of ethylene oxide (250–300 mm.) in the presence and absence of 84 mm. of propylene at 400°. It was found that the amount of carbon monoxide formed in 20 minutes in the presence of propylene was only 7% of that formed in the normal reaction. This result indicates that carbon monoxide is produced mainly by processes involving free radicals.

The decrease in the concentration of acetaldehyde with added mercury dimethyl (Table I) is presumably due to the enhancement of the sensitized decomposition of acetaldehyde by the free radicals formed from the mercury dimethyl. In other experiments at lower temperatures (330–350°) the addition of about 10% mercury dimethyl to ethyl-

TABLE II

EFFECT OF ADDED SUBSTANCES UPON THE AMOUNT OF KETENE PRESENT

Temp., °C.	$P^\circ_{(CH_2)_2O}$ mm.	$P^\circ_{C_3H_6}$ mm.	$P^\circ_{Hg(CH_3)_2}$ mm.	React. time, min.	$P^{A.S.}_{CH_2CO}/P^{Norm.}_{CH_2CO}$
400	204	0	22	10.1	~4
399	220	88	0	10.1	0.2
399	191	87	22	10.1	1.8
400	224[a]	0	17	20.1	1.82[a]
399	212[a]	88	0	20.1	0.29[a]
399	202	87	0	44.4	0.54
399	219	87	0	90.1	0.98

[a] Average of two experiments. $P^{A.S.}_{CH_2CO}$ and $P^{Norm.}_{CH_2CO}$ represent the pressures of ketene in the presence and absence of an added substance, respectively; column six gives the ratio. In this comparison differences in the initial pressure have been corrected on the basis that the ketene pressure is approximately proportional to the ethylene oxide pressure.

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(15) That propylene probably does not react with or destroy formaldehyde to an appreciable extent under the conditions above has been shown by Dr. J. E. Longfield in this Laboratory.

(16) A similar reaction has been suggested for the photochemical decomposition by R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **72**, 101 (1950).

(17) D. V. Sickman, *J. Chem. Phys.*, **4**, 297 (1936).

ene oxide appears to result in a slight increase in the amount of acetaldehyde (or higher aldehyde) present after reaction times of 30–65 minutes. Thus it seems that under certain conditions a portion of the aldehyde may be formed as a result of reactions initiated by methyl radicals.

The results in Table II show that the addition of methyl radicals (from the mercury dimethyl) increases the amount of ketene considerably above the value normally found in the thermal decomposition of ethylene oxide. Moreover, the addition of propylene lowers markedly the quantity of ketene present during the initial stages of the reaction. These observations point to the conclusion that the formation of ketene is chiefly the result of reactions in which radicals participate. One can assume that methyl radicals react as

$$CH_3 + (CH_2)_2O \longrightarrow CH_4 + C_2H_3O \qquad (5)$$

At least two reactions may be postulated by which the C_2H_3O radical[18] may produce ketene

$$C_2H_3O \longrightarrow CH_2CO + H \qquad (6a)$$

$$\xrightarrow{+R} CH_2CO + RH \qquad (6b)$$

In view of the data in Table II the molecular reaction

$$(CH_2)_2O \longrightarrow CH_2CO + H_2 \qquad (7)$$

which Lossing, Ingold and Tickner[9] suggested for secondary consideration in addition to 6a does not appear to be an important method of producing ketene under the conditions used in the present study.

The increase in ketene pressure with added mercury dimethyl shown by the results in Table II has been observed also in a qualitative manner by means of infrared absorption measurements of the reaction products. Moreover, when the products from the reaction of a mixture of acetaldehyde and mercury dimethyl (10%) at 398° were examined by the infrared method, no ketene was detected, indicating that the increase in ketene does not arise from the radical sensitized decomposition of acetaldehyde.

With respect to the ketene data at the longer times in Table II it should be pointed out that in the presence of propylene the ketene pressure rises slowly as the reaction time is increased whereas the concentration of ketene in the decomposition of pure ethylene oxide has already passed through its maximum before 90 minutes of reaction time.

In the present work several analyses for carbon monoxide were made during the initial stages of the decomposition of 250–300 mm. of pure ethylene oxide at 400°. The percentages of carbon monoxide in the gases volatile at −196° averaged 47 and 50% after 10 and 20 minutes of reaction, respectively. These values are slightly lower than that calculated on the basis of the non-condensable gases in Heckert and Mack's analyses[4] (53% CO, 8% H_2, 39% CH_4) which presumably represent the composition in the later stages of the reaction. A single analysis[19] of the reaction mixture for the hydrogen present after ten minutes at 400° indicated that hydrogen constitutes 16.7% of the gases volatile at −196°. This preliminary result giving evidence that the hydrogen content is greater during the early portion of the reaction is in agreement with the observation of Simard and his co-workers[8] that the percentage of hydrogen decreases during the decomposition.

Although the present findings have given information concerning the nature of some of the reactions which are occurring in the thermal decomposition of ethylene oxide, it does not appear desirable to present a consideration of the entire mechanism until additional data are available, particularly information about the reactions which ketene undergoes and the reactions by which the radicals are destroyed.

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[18] This radical can undergo reactions other than the formation of ketene. For a consideration of some of the reactions, see ref. 16; A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); and W. R. Trost, B. deB. Darwent and E. W. R. Steacie, *ibid.*, **16**, 353 (1948).

[19] Analyzed by Dr. R. Gomer in this Laboratory.