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

The Thermal Decomposition of Ethylene Oxide[1,2]

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The thermal decomposition of ethylene oxide has been studied in the temperature range from 350 to 440° and at pressures from 180 to 440 mm. The rate of disappearance of ethylene oxide has been determined by analyzing for the unreacted ethylene oxide. In agreement with previous investigations the experiments indicate that the reaction is approximately first order. By the addition of propylene the rate at 400° can be reduced to 46% of its normal value. The reaction in the presence of propylene is first order. The activation energies for the reactions with and without added propylene are 57.4 and 52.7 kcal., respectively. The rate of disappearance of ethylene oxide in the presence of decomposing mercury dimethyl is faster than the rate for pure ethylene oxide.

Introduction

The homogeneous thermal decomposition of ethylene oxide in the temperature range 380–500° has been studied by a number of investigators.[3–7] From the measurements of the rate of pressure increase for experiments at different initial pressures, the reaction appears to be approximately first order at initial pressures above 250 mm.[3,4,5] During a single experiment a small induction period is observed in the rate of pressure increase.[3] Recently it has been found that the rates of decomposition and the activation energy determined by infrared analyses *in situ* and those determined by pressure measurements are in good agreement provided the rates obtained from the latter are based on the actual ratio of the final to the initial pressure.[7]

That free radicals are present during the thermal decomposition of ethylene oxide has been indicated by various studies.[3,4,8,9,10] The mechanism of the thermal decomposition suggested by Fletcher and Rollefson[4b,11] is

$$(CH_2)_2O \longrightarrow HCHO + CH_2 \qquad (1)$$
$$(CH_2)_2O \longrightarrow CH_3CHO \qquad (2)$$
$$CH_2 + C_2H_4O \longrightarrow 2CH_3 + CO \qquad (3)$$
$$CH_3 + CH_3CHO \longrightarrow CH_3 + CH_4 + CO \qquad (4)$$
$$2CH_3 \longrightarrow C_2H_6 \qquad (5)$$
$$2CH_3 + M \longrightarrow C_2H_6 + M \qquad (6)$$

In this mechanism no reaction of methyl radicals with ethylene oxide has been postulated. Since reaction (1) has been assumed from the analysis of products to account for the decomposition of 14% of the ethylene oxide,[4b] according to this mechanism not more than 14% of the ethylene oxide would disappear by a reaction of radicals with ethylene oxide (3). To ascertain the fraction of ethylene oxide disappearing by radical reactions was one of the purposes of the present study.

The inhibiting effects of propylene[12] and nitric oxide[4,5c,10] upon the decomposition have been studied previously by means of pressure measurements. In the case of nitric oxide it has been assumed that it is the induced chain decomposition of acetaldehyde which is subject to inhibition and not the main reaction by which ethylene oxide disappears.[4b,10] The isomerization to form acetaldehyde which has been regarded as the most important reaction would not produce a change in pressure.

In order to obtain more information about the effect of propylene and, also, the influence of methyl radicals upon the rate of disappearance of ethylene oxide, the present investigation, in which the unreacted ethylene oxide could be determined by analysis, was undertaken. This thermal study was also of interest in connection with the photochemical investigation of this molecule.[13]

Experimental

Materials.—The specially purified ethylene oxide, kindly supplied by Dr. D. R. Stull of the Dow Chemical Company for this investigation, was found to contain about 0.004% acetaldehyde, 0.0006% formaldehyde, and no detectable amount of peroxides. Moreover, two runs with ethylene oxide from the Matheson Company gave results in agreement with those found for the Dow material. The propylene employed in most of the experiments was obtained from the Ohio Chemical and Manufacturing Company and had a stated purity of 99.5%. Similar results were observed also with a sample of propylene from the Matheson Company (after degassing) and with another sample prepared from *n*-propyl alcohol.

The mercury dimethyl was prepared in this Laboratory by Dr. R. Gomer according to the method of Gilman and Brown.[14] The vapor pressure of the compound agreed with the values given by Linnett and Thompson.[15] In addition, this sample was shown to be effective in promoting the chain decomposition of dimethyl ether at 398°.

Dry nitrogen with a stated purity of 99.99% was purchased from the Linde Air Products Corporation.

Apparatus and Method.—The cylindrical Pyrex reaction vessel (500 ml.) was mounted with the long axis vertical and surrounded by three concentric aluminum tubes, each having a wall thickness of 6 mm., to maintain longitudinal temperature uniformity. Aluminum plugs were placed at both ends of the reaction bulb. The other details concerning the furnace and the method of temperature regulation are similar to the apparatus already described.[16] Temperature meas-

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[1] This work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I with the University of Rochester. Abstracted from a Ph.D. thesis submitted by K. H. Mueller.

[2] For detailed tables supplementary to this article, order Document 3027 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.80 for photocopies (6 × 8 inches) readable without optical aid.

[3] W. W. Heckert and E. Mack, Jr., THIS JOURNAL, **51**, 2706 (1929).

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

[5] (a) H. W. Thompson and M. Meissner, *Nature*, **137**, 870 (1936); (b) *Trans. Faraday Soc.*, **32**, 1451 (1936); (c) *ibid.*, **34**, 1222 (1938).

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

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

[8] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 160.

[9] L. S. Echols, Jr., and R. N. Pease, THIS JOURNAL, **58**, 1317 (1936).

[10] E. W. R. Steacie and H. O. Folkins, *Can. J. Research*, **B17**, 105 (1939).

[11] See also D. V. Sickman, *J. Chem. Phys.*, **4**, 297 (1936).

[12] F. O. Rice and O. L. Polly, *ibid.*, **6**, 273 (1938).

[13] R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **72**, 101 (1950).

[14] H. Gilman and R. E. Brown, *ibid.*, **52**, 3314 (1930).

[15] J. W. Linnett and H. W. Thompson, *Trans. Faraday Soc.*, **32**, 681 (1936).

[16] D. W. Vanas and W. D. Walters, THIS JOURNAL, **70**, 4035 (1948).

urements were made with chromel–alumel thermocouples which were compared at frequent intervals with a platinum platinum–13% rhodium thermocouple which had been calibrated at the melting point of zinc (419.5°) in an apparatus of the type recommended by the National Bureau of Standards.[17] It is believed that the absolute values of the temperatures do not have an uncertainty amounting to more than 0.5°. A reaction vessel packed with thin-walled Pyrex tubes provided an 18-fold increase in surface to volume ratio compared to the unpacked bulb.

The ethylene oxide supply bulb was designed so that it could be weighed on an analytical balance before and after a sample of ethylene oxide had been taken. In the calculation of the results a correction was applied for the small amount of the ethylene oxide remaining outside the heated zone of the reaction vessel. When the decomposition of ethylene oxide in the presence of propylene was studied, the propylene was usually introduced into the reaction vessel just prior to the introduction of ethylene oxide, but in some experiments mixtures of propylene and ethylene oxide were prepared in a mixing bulb and allowed to mix before introduction into the reaction bulb. No differences in the results were observed. The latter procedure was always followed when mercury dimethyl was used. In the experiments with mercury dimethyl, two mercury-sealed, graphite-lubricated stopcocks[18] and a Warrick–Fugassi valve[19] were used in the portion of the apparatus in contact with the mercury dimethyl vapor.

Analysis for Ethylene Oxide.—The amount of ethylene oxide remaining undecomposed after a definite time of reaction was determined by a modified Lubatti method.[20] With known samples of pure ethylene oxide it was found that an empirical correction factor not exceeding 1.1% was needed to obtain an accuracy of ±0.3% in the analysis for ethylene oxide. Known mixtures containing ethylene oxide, acetaldehyde, formaldehyde and acetic acid were prepared; acetic acid would be formed from the ketene in the products. These samples could be analyzed quantitatively for ethylene oxide. Moreover, propylene did not interfere with the method of analysis.

The removal of the undecomposed ethylene oxide for analysis was accomplished by expansion of the reaction charge through a series of spirals kept at −196° into three evacuated bulbs. More than 90% of the contents of the reaction bulb could be removed quickly; the amount not removed was measured and corrected for. This procedure for the recovery of ethylene oxide from mixtures containing non-condensable gases was checked by the use of a known mixture of ethylene oxide and nitrogen. The recovery was found to be complete within the experimental error of ±0.3%. The presence of propylene or acetaldehyde did not affect the recovery.

Results and Discussion

Pure Ethylene Oxide.—The rate of reaction of ethylene oxide at 400° was determined by analyzing for the ethylene oxide remaining unreacted after a definite time interval in the reaction vessel. The results of experiments at various initial pressures and different reaction times are summarized in Table I and Fig. 1. For comparison purposes values of the rate constants corrected to 400° are given in the table. The experimental data show that the fraction of ethylene oxide reacting in a given time is practically independent of the initial pressure in the range studied, 200–400 mm. On the basis of the analytical measurements the reaction may be regarded as approximately first order in agreement with the conclusion reached by means of pressure measurements. At the larger percentages of reaction (45–60%) the first order constants appear to be somewhat smaller than those obtained for smaller amounts of reaction. Curve 1 in Fig. 1 shows graphically the percentages of ethylene oxide which have disappeared at various times of reaction at 400°. For this graph the experimental results were corrected to 400° and averaged for each time of reaction.

TABLE I

RATE OF DISAPPEARANCE OF ETHYLENE OXIDE AT 400°[21]

Temp., °C.	$P^0_{C_2H_4O}$, mm.	$P^0_{C_3H_6}$, mm.	Reacn. time, min.	Reacn. (anal.), %	$k \times 10^2$ min.$^{-1}$ (cor. to 400°)
400.0	279	0	10.1	8.4	0.87
401.0	427	115	20.1	7.2	.35
400.5	439	0	20.1	13.9	.72
400.7	414	247	44.4	13.9	.32
399.3	201	122	44.4	12.9	.33
400.8	415	0	44.4	28.6	.72
399.6	303	0	44.4	27.4	.74
400.7	203	0	44.4	26.8	.67
400.4	386	215	90.1	25.5	.32
400.4	418	0	90.1	44.6	.64
399.9	202	0	90.1	44.4	.66
399.9	388	297	160	41.5	.34
401.0	411	0	160	62.4	.57

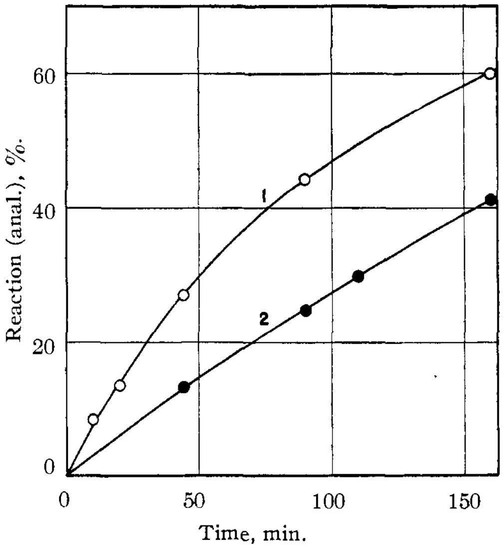

Fig. 1.—Decomposition of ethylene oxide at 400° with and without added propylene: ○, pure; ●, propylene added, ($P_{C_3H_6}/P^{\circ}_{C_2H_4O} > 0.5$).

Since an induction period is observed in the pressure–time curve, the determination of the amount of ethylene oxide reacting during the early portion of the decomposition was of interest. Although the accuracy of the results is lower for short reaction times and for small percentages of reaction, the results give evidence that there is no induction period in the disappearance of ethylene oxide.

Addition of Propylene.—The results from experiments at 400° with added propylene are given also in Table I. Inspection of the data shows that the addition of propylene can reduce the rate of disappearance of ethylene oxide to approximately one-half its normal rate. A plot of the amount

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(17) W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

(18) L. S. Echols, Jr., *Ind. Eng. Chem., Anal. Ed.*, **10**, 527 (1938).

(19) E. L. Warrick and P. Fugassi, *ibid.*, **15**, 13 (1943).

(20) O. F. Lubatti, *J. Soc. Chem. Ind.*, **54**, 424T (1935); method of the Dow Chemical Company, ML046.26.

(21) On account of space limitations only selected representative runs are given in Tables I–III. For other data see ref. 2.

of reaction *vs.* time is shown as Curve 2 in Fig. 1. The effect of an increase in the amount of propylene upon the amount of reaction (after 44 min. at 400°) is shown by Curve 1 in Fig. 2. From this plot it appears that the maximum inhibition has been reached when the ratio of propylene to ethylene oxide has been increased to about 0.5. Also, for a given propylene–ethylene oxide ratio the percentage of reaction does not seem to depend on the pressure of ethylene oxide.

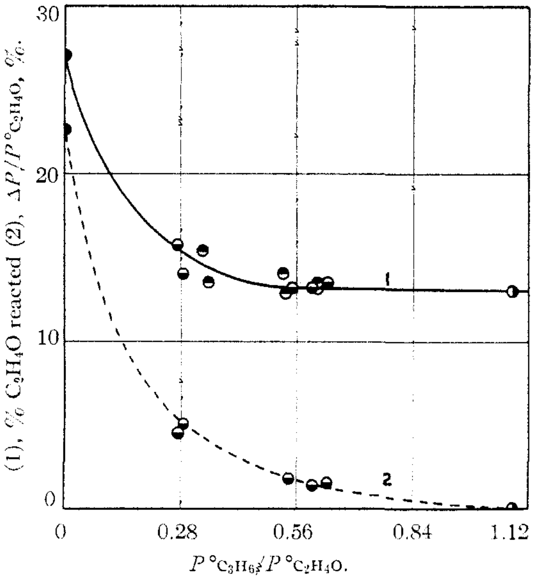

Fig. 2.—Effect of propylene upon the amount of ethylene oxide disappearing during 44.4 min. at 400° and upon the pressure increase: curve 1, % C_2H_4O disappearing; curve 2, $\Delta P/P°_{C_2H_4O}$ in %; ◒, $P°_{C_2H_4O} > 380$ mm. ◓, $P°_{C_2H_4O} <$ 260 mm.; ◑, $P°_{C_2H_4O} = 331$ mm.

Curve 2 in Fig. 2 shows that the percentage pressure increase ($\Delta P/P^0_{C_2H_4O}$ in %) continues to diminish with increasing amounts of added propylene and is not a satisfactory measure of the percentage of ethylene oxide reacting. In the experiments with initial pressures of ethylene oxide of 200–260 mm. the observed pressure increases (which are not shown in Fig. 2) seem to lie slightly above Curve 2.

The experimental data indicate that for the maximally inhibited experiments the first order constant does not change when the initial ethylene oxide pressure is reduced from 400 to 200 mm. Moreover, for experiments with $P^0_{C_3H_6}/P^0_{C_2H_4O} >$ 0.5 the first order constant remains essentially unchanged over the range of reaction studied (from 13 to 42% reaction). Since these results give evidence that the reaction not inhibited by propylene is first order, rate constants which have been calculated by means of the first order rate equation have been used for the comparison of experiments with and without added propylene. The rate of the maximally inhibited reaction is about 46% of the rate of pure ethylene oxide in the region of 12 to 30% reaction.

Activation Energy.—Experiments were performed also at temperatures above and below 400°. For the determination of the over-all activation energy of the reaction of ethylene oxide alone, the rate was measured in experiments with about 200 mm. of ethylene oxide carried to approximately 25% reaction. The plot of log *k* *vs.* $1/T$ is given in Fig. 3. For the activation energy in the presence of propylene similar experiments were carried out in the presence of about 150 mm. of propylene. The activation energies for the reactions with and without added propylene were found to be 57.4 and 52.7 kcal., respectively. The latter value is in good agreement with the previous values obtained by pressure measurements, namely, 52[3] and 53 kcal.[5] for the higher pressure range. The rate constant for the reaction of pure ethylene oxide can be expressed as

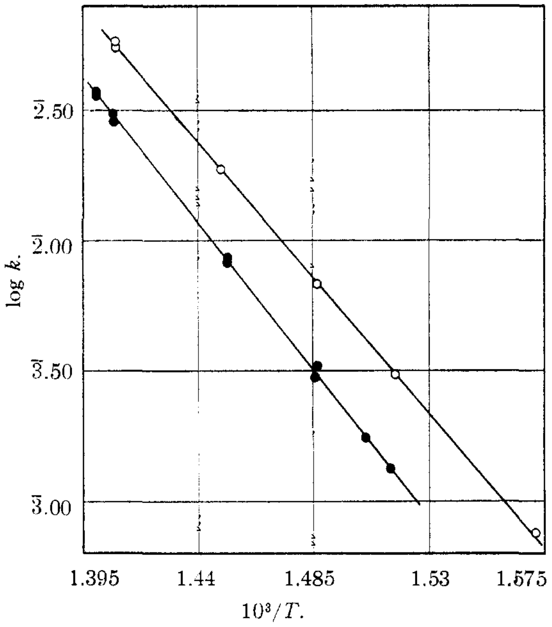

Fig. 3.—Change in rate with temperature: ○, pure ethylene oxide; ●, ethylene oxide in the presence of propylene.

$$k = 9.0 \times 10^{14} e^{-52,700/RT} \text{ min.}^{-1}$$

and for the reaction in the presence of propylene

$$k = 1.32 \times 10^{16} e^{-57,400/RT} \text{ min.}^{-1}$$

In units of sec.$^{-1}$ the frequency factors would be 1.5×10^{13} and 2.2×10^{14}, respectively.

Addition of Nitrogen.—In their investigation of the decomposition of ethylene oxide by pressure measurements Heckert and Mack[3] observed that the rate for a 2.3 : 1 mixture of nitrogen and ethylene oxide is about 9% smaller than the normal rate. Similar results were obtained with several other inert gases. In the present study it was of interest to determine by analysis the amount of ethylene oxide disappearing in the presence of nitrogen and to compare the results with those obtained with ethylene oxide alone and in the presence of propylene. The experimental data are given in Table II. It is seen that the addition of nitrogen reduces the rate to about 93% of its normal value whereas propylene decreases it to 46%. The effects of an inert gas upon thermal reactions may be interpreted in several ways and this subject has

TABLE II

EFFECT OF ADDED NITROGEN AND OF SURFACE UPON THE RATE OF DISAPPEARANCE OF ETHYLENE OXIDE

Temp., °C.	$P^0_{C_2H_4O}$, mm.	Added subst.	$P^0_{A.S.}$, mm.	Time, min.	Reacn. (anal.), %	$k \times 10^2$ min.$^{-1}$
399.6	201	N_2	155	51.1	27.9	0.64
399.5	250	..	0	44.4	26.3	.69
399.4[p]	265[a]	..	0	44.4	30.8[a]	.83[p]
400.2	256[a]	C_3H_6	86	44.4	14.6[a]	.36
399.6[p]	250	C_3H_6	83	44.4	19.0	.48[p]

[a] Average of two runs. [p] Indicates packed bulb with 18-fold increase in surface to volume ratio.

been discussed recently.[22] Moreover, if radical recombination in the decomposition of ethylene oxide occurs in part as a three-body collision,[4b] nitrogen may facilitate the disappearance of radicals or atoms by acting as a third body.

Homogeneity.—The results obtained manometrically in earlier studies have indicated that the decomposition of ethylene oxide in the usual reaction vessels proceeds almost entirely as a homogeneous reaction. In the present work the homogeneity of the reaction both in the absence and presence of propylene was investigated by analyzing for the undecomposed ethylene oxide. In Table II a comparison is made of the rates in the packed and unpacked reaction bulbs. From the results obtained with an 18-fold increase in surface to volume ratio it seems that with or without added propylene not more than 3% of the reaction in the unpacked vessel takes place on the surface.

Effect of Mercury Dimethyl.—The influence of methyl radicals upon the disappearance of ethylene oxide was studied by adding mercury dimethyl which decomposes thermally to produce methyl radicals. The data which are presented in Table III show that a greater amount of ethylene oxide reacts when mercury dimethyl is present. From the analyses, as well as the pressure measurements, it was observed that the effect is particularly noticeable during the initial stages of the reaction when the added mercury dimethyl is decomposing. Exact data concerning the rate of production of methyl radicals from mercury dimethyl under the present experimental conditions are not available. Cunningham and Taylor[23] have observed that the thermal decomposition of mercury dimethyl is complex and that the rate is accelerated in the presence of hydrogen. From our experiments at 400° in the presence of ethylene oxide it appears that 90% or more of the mercury dimethyl has decomposed during the first 20 minutes. Thus, the results in Table III indicate that methyl radicals can react with ethylene oxide molecules, but the average chain length of the sensitized reaction is not large. These conclusions are in agreement with the findings of Gomer and Noyes in their study of the reaction of methyl radicals (produced photochemically from mercury dimethyl) with ethylene oxide in the temperature range 150–250°.[13]

TABLE III

EFFECT OF MERCURY DIMETHYL UPON THE DISAPPEARANCE OF ETHYLENE OXIDE

In all experiments with added mercury dimethyl, $P_{C_2H_4O}$ is the pressure measured in the mixing bulb; at 400° the initial pressure in the reaction vessel should be approximately the same value. P_{MD} represents the pressure of mercury dimethyl in the mixing bulb.

Temp., °C.	Reacn. time, min.	$P_{C_2H_4O}$, mm.	$P_{MD}/P_{C_2H_4O}$, %	React. (anal.), %
400.0	10.1	250–300[a]	0	8.4
400.3	10.1	255	10.4	16.8
400.0	20.1	270–450[a]	0	13.5
400.3	20.1	245	10.2	24.9
350.2	120	229	0	4.3
350.1	120	217	7.6	13.5

[a] Average of a number of runs.

Discussion.—The present study has given evidence that propylene, in addition to any effect upon the subsequent reactions of intermediate products, also reduces the rate of disappearance of ethylene oxide itself. The experiments with mercury dimethyl and with propylene may be explained by assuming that a reaction of the type

$$R + C_2H_4O \longrightarrow RH + C_2H_3O \text{ (where } CH_3 \text{ may serve as R)}$$

can occur and that this type of reaction accounts for a large fraction of the ethylene oxide which reacts in the normal decomposition. The propylene inhibition, as in other studies[12,24] may be attributed mainly to a reaction of propylene with radicals. A consideration of the fate of the C_2H_3O radical, as well as other phases of the mechanism, will not be undertaken at the present time, but will be included in a subsequent publication in which analyses for the intermediate products will be presented.

ROCHESTER, N. Y. RECEIVED SEPTEMBER 28, 1950

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