[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF GASEOUS ETHYLENE OXIDE

BY WINFIELD W. HECKERT AND EDWARD MACK, JR.

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To the rapidly increasing number of homogeneous unimolecular gaseous reactions described in the recent literature, it is the purpose of the present paper to add another, namely, the decomposition of ethylene oxide. This reaction is particularly noteworthy because of the ease with which it lends itself to accurate study, and also because the course of the reaction seems to find an adequate explanation in terms of Christiansen and Kramers' hypothesis.[1]

According to this hypothesis in exothermic reactions the energy with which the freshly formed product molecules are loaded, consisting of the heat of reaction as well as the energy corresponding to the original heat of activation, may be transmitted by collision to unactivated reactant molecules, and thereby maintain a supply of activated reactant molecules, replacing those that have undergone chemical change. An obvious objection to such a mechanism is that the increasing accumulation of inert product molecules, as the reaction progresses, or the introduction of an inert gas into the system, would result in reducing the share of energy obtained by the reactant molecules from the freshly formed product, and hence would cause a much more rapid decrease in velocity than that characteristic of a unimolecular reaction.[2]

As far as the present authors are aware, no unimolecular reaction affected appreciably in this manner by inert product or foreign gas has hitherto been observed. In the case of the decomposition of diethyl ether, Hinshelwood[3] has found that helium and nitrogen have little or no effect, although the reaction products in considerable excess had a slight retarding influence.

Nature of the Reaction.—The decomposition and isomerization (to acetaldehyde) of ethylene oxide in the presence of various catalysts have been studied by Krasussky,[4] Ipatiew and Leontowitsch,[5] Nef[6] and Peytral[7] but in all of these cases the reactions have probably been heterogeneous. We have found that thermal decomposition of ethylene oxide in a pyrex

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[1] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

[2] To avoid the difficulty, Christiansen and Kramers made the somewhat forced assumption that the energy-laden product molecules could transmit their energy only to reactant molecules, and not to other molecules.

[3] Hinshelwood, *Proc. Roy. Soc. London*, **114A**, 94 (1927).

[4] Krasussky, *J. Russ. Phys.-Chem. Soc.*, **13**, 34, 76, 543 (1902).

[5] Ipatiew and Leontowitsch, *Ber.*, **36**, 2016 (1903).

[6] Nef, *Ann.*, **335**, 197 (1904).

[7] Peytral, *Bull. soc. chim.*, **39**, 206 (1926).

chamber at 380–444° is a strictly homogeneous gas reaction. This is shown by the data of Table I. The ratio of surface to volume, S/V, was varied more than six times by introducing fragments of pyrex glass tubing into the reaction chamber, without affecting the velocity of the reaction. Furthermore, the reproducibility of the velocity constants indicates clearly that the reaction is homogeneous.

Table I

Data Showing the Homogeneity of the Reaction

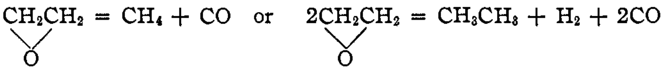
Expt.	$P_{av.}$	Temp., °C.	k_1	S/V	H_2, %
100L	72	443.5	0.0727	8.33	6.6
101L	65	443.5	.0704	8.33	...
102L	82	443.5	.0710	8.33	9.9
94–98m, 104–105m, 109–110, 112m	84.5 av.	443.5 av.	0.0720 av.	1.32 av.	7.4 av.

An attempt was made to determine whether acetaldehyde could be isolated from the partially decomposed gases, by passing ethylene oxide through a long tube heated with sulfur vapor. The boiling point of the product was taken by a micro method. The last portions of the product to boil off had a strong aldehyde odor, though hardly that of acetaldehyde. We must conclude that nearly all of the aldehyde, if it is formed at all, is immediately decomposed.

The decomposition of the ethylene oxide was carried on in an apparatus to be described shortly. The product gases were analyzed in a gas analysis apparatus according to the following scheme: dilute sulfuric acid treatment to remove excess ethylene oxide; potassium hydroxide for carbon dioxide; copper oxide at 300° to oxidize hydrogen and carbon monoxide (decrease in volume equals the volume of the hydrogen); potassium hydroxide to remove the carbon dioxide; combustion pipet. The following are some typical analyses.

	Expt. 85K	Expt. 93M	Expt. 87K
H_2, %	6.2	7.8	7.9
C_2H_6, %	6.6	7.7	7.0
CH_4, %	37.5	35.1	35.3
CO, %	49.6	49.0	49.9

Analyses were also made for hydrogen with palladium black. These checked with the above. Ammoniacal cuprous chloride was used to determine the carbon monoxide in some cases. The ethane was not identified, and all higher hydrocarbons were calculated as ethane. The percentage of hydrogen varied somewhat, but an average of ten experiments gave 7.4. No factor, surface, temperature, pressure, etc., could be found which determined the percentage of hydrogen. It would appear, therefore, that the reaction occurs in two ways with perhaps acetaldehyde as an intermediate compound.

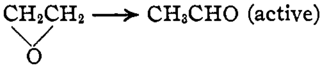


$$\underset{\diagdown O \diagup}{CH_2CH_2} = CH_4 + CO \quad \text{or} \quad 2\underset{\diagdown O \diagup}{CH_2CH_2} = CH_3CH_3 + H_2 + 2CO$$

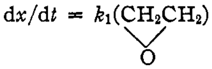
In any case, at the completion of the reaction, the pressure is just doubled.

	Expt. 107M	Expt. 108M
Initial pressure, cm.	30.92	23.21
Final pressure, cm.	61.86	46.42

There is considerable evidence that the decomposition of ethylene oxide is not as simple as it is represented above. There is a perceptible induction period. This lasts for a period of about one and one-half minutes at 444°, and for nearly fifteen minutes at 400°. During this time the velocity increases. The induction period is followed by a period when the unimolecular law holds quite accurately. At still later stages the velocity falls off due to the accumulation of reaction products, methane and carbon monoxide. Other inert gases are shown to have a similar retarding effect. The fact that ethylene oxide isomerizes so readily to give off 23,300 cal.[8] per mole, together with the facts above, leads us to postulate the following mechanism.

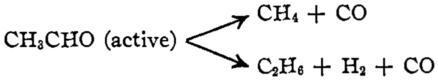


$$\underset{\diagdown O \diagup}{CH_2CH_2} \longrightarrow CH_3CHO \text{ (active)} \qquad (1)$$



$$dx/dt = k_1(\underset{\diagdown O \diagup}{CH_2CH_2})$$

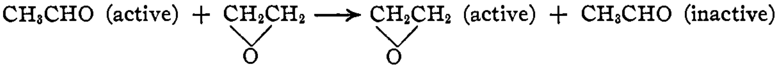
E = 52,000 cal.
Q = 23,300 cal.
75,300 cal.



$$CH_3CHO \text{ (active)} \begin{cases} \nearrow CH_4 + CO \\ \searrow C_2H_6 + H_2 + CO \end{cases} \qquad (2)$$

$dx/dt = k_2$ (CH$_3$CHO) (active)
E and Q very small

$$CH_3CHO\text{(active)} + X \longrightarrow CH_3CHO \text{ (inactive)} + X \text{ (energy-laden)} \qquad (3)$$



$$CH_3CHO \text{ (active)} + \underset{\diagdown O \diagup}{CH_2CH_2} \longrightarrow \underset{\diagdown O \diagup}{CH_2CH_2} \text{ (active)} + CH_3CHO \text{ (inactive)}$$

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO \qquad (4)$$

Hinshelwood and Hutcheson[9] have shown that acetaldehyde decomposes bimolecularly in the neighborhood of 444°. The energy of activation was found to be 45,500 cal. for two moles. Acetaldehyde molecules, if formed by the above mechanism, would have about 75,000 cal. per mole, or more than three times the amount necessary for activation. They would probably decompose unimolecularly under these conditions, and collisions with inert molecules would tend to cause them to lose some of their large load of energy. According to the theory of Rice and Ramsperger, or that of

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[8] Estimated from the heats of combustion given by Berthelot: for ethylene oxide, 6870 cal./g., *Ann. chim. phys.*, [5] **27**, 374 (1882); for acetaldehyde, 6338 cal./g., *Compt. rend.*, **129**, 920 (1899).

[9] Hinshelwood and Hutcheson, *Proc. Roy. Soc. London*, **118A**, 380 (1926).

Kassel, the loss of this energy would lower their rate of decomposition until finally the reaction would be of the second order. Collision with ethylene oxide molecules would perhaps result in the activation of the latter. This would not reduce the rate.

If we consider the first two reactions above and integrate the differential equation for the successive reactions, we obtain the following equation

$$\frac{a - x}{a} = \frac{k_2}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_2 t}$$

where $a - x$ is the partial pressure of the ethylene oxide at the time t. The application of this equation is somewhat difficult. However, in the present case k_2 is large and k_1 is small. Hence, immediately following the induction period, the second term on the right drops out and we obtain the following expression for k_1

$$\frac{a - x_1}{a - x_2} = e^{-k_1 t_1}/e^{-k_1 t_2}$$

$$k_1 = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

This may then be used to calculate k_2

$$k_2 = \frac{k_1 Y_2}{Y_2 - e^{-k_1 t_2}}, \quad Y_2 = (a - x_2)/a$$

The time t_2 must be taken such that $k_1 e^{-k_2 t_2}/(k_2 - k_1)$ has become vanishingly small.

Having obtained a value for k_2, it is now possible to calculate values for k_1 over the entire interval.

$$k_1 = \frac{2.303}{t} \log \frac{A}{Y_t + Be^{-k_2 t}}$$

where

$$A = k_2(k_2 - k_1), \quad B = k_1(k_2 - k_1)$$

The values of k_1 calculated in this manner and shown in Table II and IIA are very satisfactory. Without this treatment of the decomposition as a two-stage reaction, the constant k_3, calculated directly from the pressure data by the classical unimolecular equation, is found to vary by several hundred per cent., at least at those lower temperatures where the induction period is long enough to be followed.

It is possible to consider the induction period as merely due to the building up of a number of "reaction chains" as demanded by the Christiansen-Kramers theory. On such an hypothesis the energy-laden products would activate ethylene oxide molecules by collision with them. Such a picture, as previously indicated, would agree qualitatively with the experimental data. It seems certain that an intermediate state of some nature occurs during the reaction.

Measurement of Reaction Velocity.—A number of different samples of ethylene oxide were used, all of which gave the same velocity constant. Most of the samples were prepared by distilling an Eastman Kodak product at least three times over freshly burned calcium oxide. Low-boiling fractions were retained, giving a final sample boiling from 9.95–10.00° (corrected). This is two degrees lower than the boiling point reported in the literature.

The sample was kept in the dark in Bulb B in cold water, Fig. 1. Ethylene oxide was found to decompose slowly at room temperature. A sample taken from an old iron tank was 18% unabsorbed by sulfuric acid; this unabsorbed portion analyzed 50% of carbon monoxide. To avoid any error due to such decomposition, the storage tank S was pumped out before each run.

The apparatus, shown in Fig. 1, was the conventional set-up. Constant temperature was secured by boiling sulfur in the jacket J, where the pressure was controlled by the height of the water in the tube N. The five-gallon carboy G was connected to a pump which operated at a rate sufficient to pull an occasional bubble through the tube N. The outer jacket was heated by an auxiliary electric furnace, maintained at about 300°. The sulfur was boiled with a Fischer burner. The upper end was cooled with an air blast and several turns of lead pipe supplied with cold water. The whole lower part was enclosed in an asbestos box.

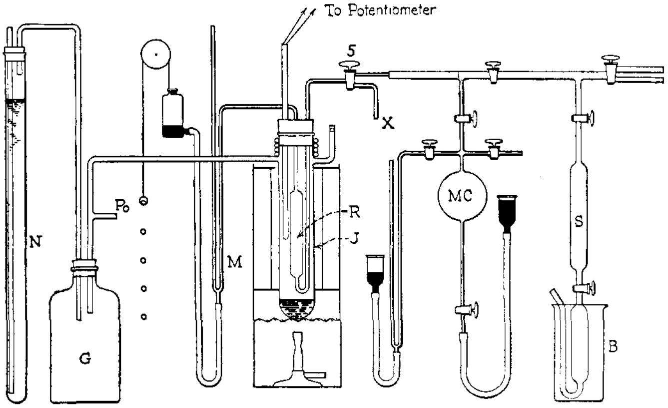

Fig. 1.

The temperature was measured with a calibrated chromel–alumel thermocouple and a potentiometer. It was possible to measure changes in temperature of 0.1°. The absolute temperatures are probably correct to within 0.5°.

The reaction chamber R was blown from pyrex tubing. It was connected to the stopcock 5 by means of 1-mm. tubing, and to the manometer M with 1.5-mm. capillary. The manometer M was made from 2-mm. capillary. The left arm was 2 meters long; the right, 1 meter long. The mercury leveling bulb was maintained at such a height that the right column could be read within 10 cm. of the top of the manometer arm. Thus the total dead space varied between 0.6 and 0.9 cc. This usually represented about 0.3% of the volume of the reaction chamber. The meter stick in the manometer was compared with a standard meter stick. The apparatus was frequently cleaned by pumping hot chromic acid through it. It was washed with distilled water, acetone and ether. A vaseline–paraffin mixture was used on all of the stopcocks. Stopcock 5 was enclosed in a metal container and surrounded with water maintained at a suitable temperature.

For experiments dealing with the effect of inert gases, a chamber, MC, was attached, in which it was possible to mix the gases thoroughly before passing them into the reaction chamber. A water jacket, not shown in the drawing, maintained a constant temperature while filling the mixing chamber.

The procedure in making a run was briefly as follows. The reaction chamber was evacuated with an oil pump and stopcock 5 was closed. The chamber S and the connecting tubes were evacuated and filled with ethylene oxide. Stopcock 5 was opened and zero time was counted (with a stop watch) when one-half of the desired amount of ethylene oxide had entered. The bulb was raised until the mercury stood within a few centimeters of the top of the right arm of the manometer. Readings on both arms were taken as desired. If it was desired to analyze the gases, they were removed at X. The temperature and barometric pressure were read at frequent intervals.

The total pressure P_1 was calculated from the manometer readings. From this the total pressure P_2, if there had been no dead space, was calculated by means of the equation

$$P_2 = P_1(1 + vT_R/VT_m)$$

where v is the dead space to the top of the mercury, V is the volume of the chamber, T_m is the temperature of the manometer and T_R that of the

TABLE II

COMPLETE DATA FOR EXPERIMENT 168m AT 378.5°

Time, minutes	V	P_{at}	Manometer readings Left	Manometer readings Right	P_1	Correction	P_2	$a - x$	k_1	k_2	k_3
0	0.015752	73.92	21.00	94.62	....	..	107.42	106.36	....	..	....
1	.....	...	128.78	95.73	106.67	0.79	107.46	106.32	....	..	....
1	.....	...	....	95.61	106.79	.79	107.58	106.20	0.00223	..	0.00076
5	.....	...	....	95.28	107.22	.80	108.02	105.76	.00242	..	.00113
10	.015752	...	....	94.62	107.88	.84	108.72	105.06	.00219	..	.00123
20	.....	...	....	93.19	109.21	.89	110.10	103.68	.00187	..	.00128
30	.....	...	....	91.26	111.14	.98	112.12	101.66	.00192	..	.00150
45	.....	...	134.66	94.18	114.10	.89	114.99	98.79	.00192	..	.00164
60	.....	...	....	91.57	116.71	1.01	117.72	96.06	.00191	0.15	.00170
75	.015746	...	....	89.06	119.22	1.06	120.28	93.50	.00189	..	.00272
90	.....	...	142.68	94.51	121.89	0.93	122.82	90.96	.00188	..	.00174
105	.....	73.92	....	92.21	125.19	1.05	125.24	88.54	.00187	..	.00175

TABLE IIA

VELOCITY CONSTANTS FOR EXPERIMENT 125m AT 414.5°

Time, minutes	P_2	$a - x$	k_1	k_2	k_3
0	116.51	115.30	...	...	...
1/2	116.76	115.05	...	...	...
1	117.18	114.63	0.0162	...	0.00506
2	118.19	113.62	.0150	...	.00732
3	119.60	112.21	.0149	...	...
4	121.00	110.81	.0146	...	...
5	122.56	109.25	.0146	...	.0108
6	124.12	107.69	.0147	...	...
7	125.72	106.09	.0147	...	...
8	127.39	104.42	.0149	...	...
9	128.74	103.02	.0147	...	...
10	130.31	101.50	.0147	...	.0128
11	131.78	100.03	.0147	...	...
12	133.23	98.58	.0147	...	...
13	134.70	97.11	.0147	0.753	...
18	141.37	90.44	.0143	...	.0135

reaction chamber. Since the pressure just doubles, the final pressure would be $2P_2$, providing all of the ethylene oxide in the manometer were to decompose. In order to estimate the partial pressure P_0 of the ethylene oxide actually in the chamber, the following equation was used

$$P_0 = 2(P_2)_0 - P_2 \frac{3v_0T_R}{2VT_m} - (P_2)t$$

At best this is an approximation. However, the error probably at no time exceeds $0.5v_0T_R/VT_m \cdot P_2$, which represents an error of 0.5% or less.

Ethylene oxide is not associated in the vapor phase.

Order of Reaction.—The decomposition of ethylene oxide is a first-order reaction without question. Table III gives values of k_1 taken over a large range of pressures.

TABLE III

VELOCITY CONSTANT k_1 AT DIFFERENT PRESSURES

Expt.	Temp., °C.	$P_{av.}$, cm.	k_1	$k_1(444)$
142m	443.1	90.5	0.0707	0.0739
145m	443.1	96.0	.0709	.0741
146m	443.5	64.7	.0716	.0735
147m	443.6	59.9	.0719	.0736
155m	444.0	28.5	.0666	.0666
162m	443.7	2.42	.0617	.0627

If the reaction were bimolecular, k_1 calculated at an interval averaging a pressure of 2.42 cm. would be enormously smaller than at 96.0 cm- These constants were calculated over the two to five-minute interval immediately following the induction period.

The induction period becomes more noticeable as the temperature is lowered. It is impossible to evaluate k_2 at 444°. At 394° values can be calculated, but the error is large.

TABLE IV

VELOCITY CONSTANT k_2 AT DIFFERENT PRESSURES (T = 394.3°)

Expt.	$P_{av.}$	k_1	k_2
169m	83.9	0.00486	0.353
170m	41.5	.00474	.472
171m	21.3	.00471	609
172m	11.8	.00464	Too large to calculate
250m	52.9	.00473	.495
251m	31.8	.00475	.654
253m	17.1	.00454	Too large to calculate

Apparently k_2 becomes larger with decrease in pressure. This is in agreement with the mechanism advanced, since the decomposition of activated acetaldehyde molecules is more likely to take place when there is a greater time between deactivating collisions.

In Fig. 2 the results of a number of experiments at approximately 444° are shown. The logarithm of the partial pressure of the ethylene oxide is plotted against time, with the logarithm scale shifted to bring all of the experiments together. The falling off of the rate with accumulation of products is clearly shown. This is not proportional to the pressure of the products, but more nearly to the ratio of their pressure to that of the ethylene oxide. After a steady state has been reached, the pressure of activated acetaldehyde molecules will be nearly proportional to the partial pressure of the undecomposed ethylene oxide. Since the first point on these graphs must be estimated, the nature of the induction period at this temperature must remain unknown.

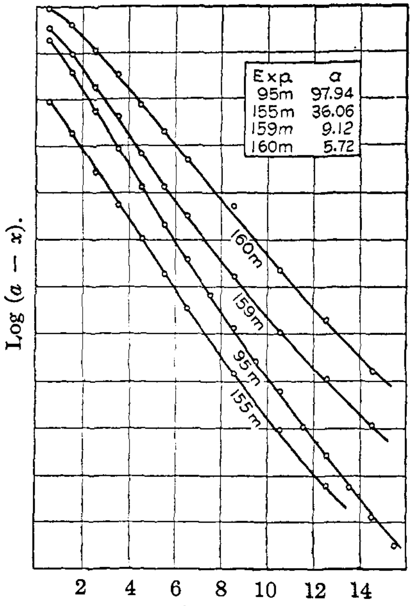

Fig. 2.

Energy of Activation.—Table V gives a summary of the data (at the higher pressures) from which the energy of activation may be calculated. Figure 3 shows a plot of $-\log k_1$ against $1/T$. The usual straight line is obtained. The energy of activation E, calculated by equating the slope of this line to $E/2.303R$, is 52,000 cal.

Table V

Velocity Constant k_1 at Various Temperatures

Expt.	Temp., °C.	k_1	Expt.	Temp., °C.	k_1
199m	444.8	0.0793	120m	425.1	0.0251
142m	443.1	.0707	121m	425.2	.0265
143m	443.1	.0709	122m	424.7	.0281
144m	443.1	.0702	124m	414.4	.0154
145m	443.1	.0709	125m	414.5	.0147
134m	442.4	.0668	140m	411.6	.0131
135m	442.4	.0693	141m	411.6	.0130
136m	442.4	.0663	130m	399.1	.00622
137m	442.3	.0670	131m	397.7	.00573
138m	434.8	.0458	132m	396.8	.00542
139m	424.0	.0249	169m	394.1	.00484
			168m	378.5	.00191

The Effect of Inert Gases.—It was thought that a study of the rate of decomposition of ethylene oxide in the presence of a number of inert gases would yield some interesting information with regard to the exchange of energy during collision. Table VI gives a summary of the experimental data. Traces of oxygen interfere with the observation of the induction period and give false values for k_2.

In Table VI $P_{av.}$ is the average partial pressure of the ethylene oxide during the interval in which k_1 was calculated. The column headed P_g is the partial pressure of the inert gas. The column P_{CO} is one-half of the average pressure of the products during the interval. All of the experiments are corrected over short temperature intervals to 394.3°.

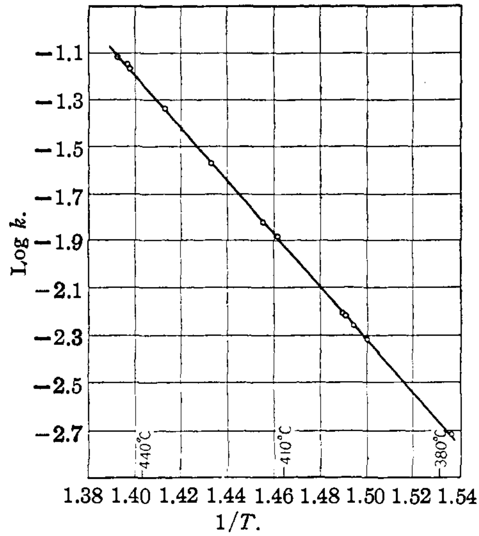

Fig. 3.

In addition to those listed in the table, ethylene, ammonia, methyl bromide, *n*-butane and *iso*pentane were tried. In the first case there was probably a polymerization of the ethylene and a combination with the ethylene oxide. Ammonia apparently reacted somewhat with the oxide while in the *mixing chamber*, and the resulting compound dissociated during the first several minutes of the experiment. This suggests that the decomposition of aminoethyl alcohol might yield another unimolecular reaction. Methyl bromide, *n*-butane and *iso*pentane were found to "crack" in the presence of ethylene oxide. The velocity of "cracking" was greater in the presence of ethylene oxide than in its absence, which suggests that these substances were obtaining energy of activation from the ethylene oxide decomposition.

The two sets of experiments on carbon dioxide indicate that within the limits of experimental error the depression of k_1 is proportional to the ratio of pressure of the inert gas to that of the ethylene oxide.

In the case of the hydrocarbons, it is at once apparent that the depression of the velocity constant is related to the complexity of the molecule. The isosteres, nitrogen and carbon monoxide, both cause the same depression. Carbon dioxide, with several more degrees of freedom and a larger collision area, though with a smaller velocity of translation, exhibits a slightly greater depression.

Argon and neon depress the rate less than any of the other gases. Their collisions are perhaps the most elastic and they have but three degrees of

TABLE VI

EFFECT OF INERT GASES (T = 394.3°)

Expt.	$P_{av.}$	P_g	P_{CO}	k_1	k_2
Blank (average)	31.8	..	4.4	0.00473	0.654
Carbon Dioxide					
175m	29.4	69.4	3.6	.00423	.345
176m	30.4	71.9	3.7	.00422	.389
177m	31.9	75.4	3.8	.00420	.340
	30.6	72.2	3.8	.00422	.358
248m	32.1	37.1	4.1	.00445	.355
249m	32.0	37.0	4.1	.00437	.449
	32.1	37.1	4.1	.00441	.402
Carbon Monoxide					
193m	30.9	72.5	4.0	.00431	.420
194m	31.9	74.8	4.1	.00429	.421
195m	30.4	71.2	3.9	.00429	.346
	31.1	72.6	4.0	.00430	.396
Nitrogen					
183m	28.3	67.9	3.8	.00432	.395
184m	30.7	70.7	3.8	.00429	.419
185m	31.1	71.3	3.7	.00430	.287
189m	31.0	72.6	4.0	.00431	.433
190m	33.3	77.5	4.2	.00427	.404
	30.8	72.0	3.9	.00430	.388
Methane					
240m	32.4	72.7	3.4	.00402	.296
241m	32.2	73.3	3.8	.00407	.369
242m	31.3	74.9	3.8	.00413	.385
243m	30.9	73.4	3.5	.00407	.319
	31.7	73.6	3.6	.00407	.342
Ethane					
222m	31.3	72.7	3.5	.00347	1.16[a]
224m	30.7	71.9	2.9	.00346	0.236
225m	31.5	73.8	3.0	.00355	.217
226m	31.5	73.6	3.0	.00344	.259
	31.2	73.0	3.1	.00348	.237
Propane					
228m	32.7	75.0	3.0	.00339	.271
229m	32.2	73.8	3.0	.00331	.257
231m	30.6	72.4	3.1	.00341	.507[a]
	31.8	73.7	3.0	.00337	.264

TABLE VI (*Concluded*)

Expt.	$p_{av.}$	p_g	p_{CO}	k_1	k_2
		*Iso*butane			
214m	30.5	71.8	3.0	.00283	.315
215m	30.0	71.0	3.1	.00286	.495
216m	32.0	74.6	2.8	.00280	.480
	30.8	72.5	3.0	.00283	.430
		Argon			
255m	31.8	71.5	4.2	.00450	.644
256m	32.4	72.8	4.2	.00447	.445
	32.1	72.1	4.2	.00449	.544
		Helium			
257m	32.2	70.1	3.9	.00415	.377
258m	32.6	70.9	3.9	.00420	.355
	32.4	70.5	3.9	.00418	.366
		Neon			
259m	31.4	72.3	4.4	.00456	.503
260m	32.0	72.7	4.1	.00441	.329
	31.7	72.5	4.3	.00449	.416

[a] Not included in average.

freedom (translational). Helium, however, depresses the rate considerably.

The Effect of Hydrogen.—While investigating the decomposition of di-ethyl ether at low pressures, Hinshelwood and his students have shown that the presence of sufficient hydrogen will restore the high pressure rate of decomposition. They attributed this to the fact that hydrogen, traveling at high velocities and making many collisions, was peculiarly fitted for maintaining the Maxwellian distribution of energy among the decomposing molecules. No other gas was found to have this effect.

TABLE VII

THE EFFECT OF HYDROGEN

Expt.	Temp., °C.	$p_{av.}$	p_{H_2}	k_1	k_2
190m	394.3	28.4	74.0	0.00700	1.02
191m	394.3	28.8	72.6	.00716	.53
192m	394.3	28.8	75.7	.00714	1.43
	394.3	28.7	74.1	.00710	
196m	444.6	24.4	76.2	.110	
197m	444.8	23.5	74.4	.111	
198m	444.9	25.6	80.9	.109	
	444.8	24.5	77.2	.110	

$E = 51{,}500$ cal.

Table VII shows a number of results of experiments with ethylene oxide in the presence of about one atmosphere of hydrogen. The rate is increased about 40% at each temperature. The heat of activation calculated on the basis of these experiments is 51,500 calories, the same as before within the limits of experimental error.

Study of the decomposition of ethylene oxide is being continued at much lower pressures to collect sufficient data for testing the validity of the Rice and Ramsperger equations.

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Summary

It has been shown that the thermal decomposition of ethylene oxide is a strictly homogeneous unimolecular reaction, exhibiting an induction period and a decrease in rate of decomposition in the presence of inert gases. The velocity of decomposition may be represented by the equation

$$\ln k_1 = 34.02 - 52{,}000/RT$$

A mechanism for the decomposition has been advanced involving a unimolecular isomerization to acetaldehyde molecules of high energy content and their subsequent unimolecular decomposition into carbon monoxide and methane. Collision of activated acetaldehyde molecules with inert gases and the consequent interference with the Christiansen-Kramers mechanism for activation, have been regarded as the cause of the damping effect of inert gases. A study of the velocity of decomposition has been made in the presence of ten inert gases. The fact that the presence of hydrogen increases the velocity of decomposition, together with a slight falling off of the velocity constant with decrease in pressure, has been cited as evidence that the reaction at ordinary pressures is in a process of change from a unimolecular reaction to a bimolecular reaction.

COLUMBUS, OHIO