±25% for such low dielectric loss. If the value of the dielectric loss for each of the three substances measured is substituted in the Debye equation as used by Jackson and Powles[13] and given in equation (4), a moment value 0.04 D is calculated for benzene, n-heptane and cyclohexane.

$$\mu = \left[\frac{27\,\epsilon''\,kT(1 + (2\pi f\tau)^2)}{8(\epsilon' + 2)^2 Nc\pi^2 f\tau}\right]^{1/2} \qquad (4)$$

where μ is the dipole moment, ϵ'' is the dielectric loss, ϵ' is the dielectric constant, T is the absolute temperature, k is the Boltzmann constant, f is the frequency in cycles per second, τ is the relaxation time in seconds, N is Avogadro's number, and c is the density divided by the molecular weight. In the calculation of the dipole moment by this method the value of τ, the relaxation time, has been assumed to be approximately 5×10^{-12} seconds in view of the values of τ found for bromobenzene, cyclohexyl bromide and n-heptyl bromide at 25° in the 1.27 cm. measurements.[11] These moment calculations seem to indicate that moment values between 0 and 0.1×10^{-18} may be differentiated by the use of microwave absorption methods. However, these small moment values indicated by the losses are not to be interpreted as evidencing permanent asymmetry of the molecules.

Summary

The dielectric constants of n-heptane, benzene, cyclohexane, carbon tetrachloride and carbon disulfide have been measured at 577 m., 10 cm. and 1.277 cm., while additional values at 3.22 cm. have been obtained for n-heptane and benzene. The measurements at 10 cm., 3.22 cm. and 1.277 cm. are absolute determinations. The values are independent of frequency since the losses measured at 1.277 cm. for three of the non-polar liquids are so low as to be negligible in their effect on the dielectric constant. The absolute dielectric constant values are linear functions of the temperature within the accuracy of the measurements.

The dielectric loss values at 1.277 cm. have been used to calculate extremely low moment values for n-heptane, benzene and cyclohexane, possibly, the result of inductive effects. The calculations indicate that microwave absorption results may be used to differentiate between moment values of 0 and 0.1×10^{-18}.

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(13) Jackson and Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

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

Photochemical Studies. XLII. Ethylene Oxide[1]

BY ROBERT GOMER*[2] AND W. ALBERT NOYES, JR.

The only previous work on the photochemistry of ethylene oxide seems to be that of Phibbs, Darwent and Steacie[3] who investigated its mercury sensitized reactions. Trost, Darwent and Steacie[4] have studied the reactions of hydrogen atoms with ethylene oxide. The thermal reactions of this molecule have been studied extensively.[5]

The ultraviolet absorption spectrum of ethylene oxide has been photographed and interpreted recently.[6] The longest wave discontinuous absorption is found at 1713 Å. This band broadens as the pressure is increased and gives an apparent continuum to about 2120 Å.

The first experiments (carried out with a hydrogen discharge as a light source) served to show that the principal products of the direct photochemical decomposition of ethylene oxide are hydrogen, carbon monoxide, methane and ethane. Since hydrogen gas probably could not be formed unless H atoms are produced in the primary process, the work of Phibbs, Darwent and Steacie is of importance in interpreting the results of the present research. The production of methane and of ethane indicates, presumably, that CH_3 radicals are intermediates. The reactions of CH_3 radicals (formed by photochemical decomposition of mercury dimethyl) with ethylene oxide were also studied. A recent investigation[7] has served to clarify certain steps in the photochemical decomposition of mercury dimethyl.

Experimental

The ethylene oxide was specially purified by the Dow Chemical Company.[8] It was purified further by bulb-to-bulb distillation and outgassed in a high vacuum after cooling to −120°. It was free from aldehydes as shown by the method of Stotz.[9]

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* Harvard University Postdoctoral Fellow 1949–.

(1) This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

(2) E. I. du Pont de Nemours and Company Fellow, 1948–1949.

(3) M. K. Phibbs, B. de B. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 39 (1948).

(4) W. R. Trost, B. de B. Darwent and E. W. R. Steacie, *ibid.*, **16**, 357 (1948).

(5) For a summary see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, pp. 139, 308, 368 and 395.

(6) Ta-kong Liu and A. B. F. Duncan, *J. Chem. Phys.*, **17**, 241 (1949).

(7) R. Gomer and W. A. Noyes, THIS JOURNAL, **71**, 3390 (1949).

(8) The authors wish to express their appreciation to Dr. D. R. Stull of the Dow Chemical Company who prepared the ethylene oxide for Dr. W. D. Walters of this Department.

(9) E. H. Stotz, *J. Biol. Chem.*, **148**, 585 (1943). This method has been the subject of further study by W. F. Erbelding and W. D. Walters of this Laboratory.

The first experiments were made with a Hanovia hydrogen discharge tube as a light source without filters and without collimation. The radiation absorbed by the ethylene oxide must have been mainly at wave lengths below 2000 Å. This point was verified with a Schmidt–Ott vacuum fluorite spectrograph. Mercury vapor was interposed between the light source and the reaction vessel to reduce danger of a mercury sensitized reaction.

A rough estimate of quantum yields was made with a hydrogen bromide actinometer. One molecule of hydrogen was assumed to be formed per quantum absorbed.[10] This figure is valid if bromine is removed by mercury. Since the incident radiation was not monochromatic, exact corrections could not be made for absorption and reflection by the windows. The reaction is not a long chain reaction under any of the experimental conditions investigated.

The technique used for mixtures of ethylene oxide and mercury dimethyl is similar to that already described.[7]

The main products (hydrogen, carbon monoxide, methane and ethane) were usually determined by methods described in earlier articles from this Laboratory.[7] Some analyses were performed with a Blacet–Leighton apparatus.[11] Other products, particularly formaldehyde and acetaldehyde and possibly other aldehydes were found. The methods of analysis for these will be described briefly.

The method of Matsukawa,[12] for the determination of formaldehyde, was found to be quantitative. Mueller[13] and Cripps and Walters[12] found that acetaldehyde in fifty-fold excess did not interfere (error less than 15%) and Mueller[13] observed that a 20,000-fold excess of ethylene oxide did not introduce an error greater than 15% in the determination of formaldehyde by this method.

Beer's law was found to be obeyed by the colored compound formed in the Matsukawa method.[12] The optical density at 525 mμ is 0.369 c, where c is the concentration of formaldehyde in the original solution in grams $\times 10^{-6}$/ml. The optical density is defined by $D = \log_{10} I_0/I$, where I_0 is the incident intensity and I the transmitted intensity.

Acetaldehyde was determined by the method of Stotz,[9] using a 10% copper sulfate solution. This methods is based on the formation of colored compounds with *p*-hydroxybiphenyl by all lower aldehydes in concentrated sulfuric acid solution. Erbelding and Walters[9] found that the colored compound formed with acetaldehyde obeys Beer's law at 570 and at 610 mμ, but that the compound formed with formaldehyde does not do so at either wave length. Smooth curves were found, however, when optical density was plotted against[9] concentration in the case of formaldehyde. Erbelding and Walters[9] found that formaldehyde and acetaldehyde gave approximately additive optical densities at both wave lengths if the formaldehyde concentration did not exceed 4×10^{-6} g./ml.

If formaldehyde is determined by Matsukawa's method and the appropriate optical density is subtracted from that of the mixture, acetaldehyde can be determined with satisfactory accuracy.

It was found in the present work that the wave length of maximum absorption changes smoothly from 570 to 610 mμ as acetaldehyde/formaldehyde changes from infinity to zero, and that it is approximately independent of the two concentrations as long as they are below 5×10^{-6} g./ml. Plots of the optical density at maximum absorption against acetaldehyde concentration (at several wave lengths) together with the ratio, give absolute concentrations by interpolation. The greatest accuracy is obtained in the middle of the range where the ratio is approximately unity.

Analyses for formaldehyde will be inaccurate if determined from the ratio, but acetaldehyde as a function of total optical density at peak wave length is not very dependent on the ratio, so that analyses for acetaldehyde will be reasonably good. The two methods provide independent checks on the analyses.

Propionaldehyde was found to give a peak absorption at 575 mμ and Beer's law is obeyed at all wave lengths. Mixtures of acetaldehyde and propionaldehyde show only very small deviations from additivity for their optical densities. Table I shows the wave lengths of maximum absorption and the optical densities for the three aldehydes mentioned.

TABLE I

DATA CONCERNING COMPOUNDS FORMED FROM *p*-HYDROXY BIPHENYL AND VARIOUS ALDEHYDES

Aldehyde	Wave lengths of maximum absorption	Optical density ($\log_{10} I_0/I$)	Limits of detection $\times 10^6$ g./ml.
HCHO	445 mμ	......	
	610	$0.796 \log_{10} (c + 1.949) 0.588$	0.5
CH_3CHO	430	0.0225 c	
	570	.143 c	0.1
CH_3CH_2CHO	440	.0126 c	
	575	.0379 c	5

The methods just described can be used for either mixtures of formaldehyde and acetaldehyde or of acetaldehyde and propionaldehyde. Solutions maintain color for several hours, although some fading was noticed in the case of propionaldehyde. Mixtures of formaldehyde and propionaldehyde were not investigated. Ternary mixtures cannot be resolved. Probably the limit of error is

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[10] E. Warburg, *Sitzb. preuss. Akad. Wiss. Physik.-math. Klasse*, 314 (1916).

[11] Certain modifications in the techniques for the Blacet-Leighton method have been described by R. Gomer in an article to appear in *Anal. Chem.* shortly. This article contains references to earlier work.

[12] D. Matsukawa, *J. Biochem. (Tokyo)*, **30**, 386 (1939). This method has been improved by H. Cripps and W. D. Walters of this Laboratory.

[13] K. Mueller, Ph.D. Thesis, Department of Chemistry, University of Rochester, 1949. This work was performed under the supervision of Professor W. D. Walters.

10–20% for a single aldehyde, but for mixtures it is much greater unless concentrations are low. It should not exceed 50–100% in any case encountered in this work. The determination of formaldehyde by the method of Matsukawa[12] should be accurate within 10–15%.

Preliminary Results

Table II shows preliminary data obtained with ethylene oxide by the use of the hydrogen discharge as a light source. The analyses for formaldehyde are not reliable since they were obtained by the *p*-hydroxybiphenyl method only. These results served mainly to identify the principal products and to indicate the desirability of studying the reactions of CH_3 radicals with ethylene oxide.

TABLE II

RATES OF FORMATION OF VARIOUS PRODUCTS DURING IRRADIATION OF ETHYLENE OXIDE

Light source, Hanovia hydrogen discharge; absorbed wave length, <2000 A.; dimensions of cell, 20.0 × 2.4 cm.; temp., 27°; rates in mm. pressure × 10^3/hr. (measured at 27°; in a volume of 590 cc. Multiplication by 9.7 × 10^{-14} gives moles/cc./sec. in the reaction vessel.

Run	Press. $(CH_2)_2O$, mm.	R_{CO}	R_{CH_4}	R_{H_2}	$R_{C_2H_6}$	R_{CH_3CHO}	R_{HCHO}
13	28	85	13.5	35.3	Present	3.1	(4.5)
15	64	111	18.6	41.6	Present	4.5	(6.6)
16	100	120	22	44.3	Present	7.5	(11.1)
17	148	122	23.7	47.3	Present	(6.2)	(9.1)
18	288	135	24.4	54.1	Present	?	?

Results with Mixtures of Mercury Dimethyl and Ethylene Oxide

Tables III, IV, V and VI present the rates of formation of products formed during irradiation of mixtures of mercury dimethyl and ethylene oxide by light absorbed only by mercury dimethyl. The main variables studied were the following: (a) concentrations of reactants, (b) temperature, (c) intensity. The light intensity was not measured quantitatively but was varied over a wide range by the use of two different light sources and by the use of neutral density filters.[7] The effect of an added foreign gas which would reduce the rate of diffusion to the walls was investigated in one series of experiments.

TABLE III

RATES OF FORMATION OF PRODUCTS IN THE PHOTOLYSIS OF MERCURY DIMETHYL IN THE PRESENCE OF ETHYLENE OXIDE: EFFECT OF TEMPERATURE AT CONSTANT CONCENTRATION AND LIGHT INTENSITY

Cell 20 cm. in length, 2.4 cm. in diameter; light source, S-353 arc; ethylene oxide pressure 100 mm. (in cell at 300°K.); mercury dimethyl pressure 20.0 mm. (in cell at 300°K.); rates of formation given in microns/hour at 300°K. and in a volume of 590 cc. Barred quantities refer to runs in the absence of ethylene oxide. Rates must be multipled by 9.70 × 10^{-14} to convert to moles/cc./second.

Run	Temp., °C.	R_{CO}	R_{CH_4}	$R_{C_2H_6}$	$\bar{R}_{CH_4}$	$\bar{R}_{C_2H_6}$	R_{CH_4}/R_{CO}
B-9	150	3.40	12.0	71	4.6	77	3.5
B-1	174	9.60	24.5	88	10.0	97	2.6
B-5	175	7.30	26.2	85	10.4	95	3.6
B-4	200	14.2	48	87	19.5	101	3.4
B-3	220	25.7	82	80	34	102	3.2
B-7	220	22.4	88	87	35	104	3.9
B-8	220	19.0	79	81	30	94	4.1
B-2	248	57.1	182	(88)[a]	72	(129)[a]	3.2
B-6	250	54.7	181	102	71	(121)[a]	3.3

[a] Total C_2 hydrocarbons, ethylene not determined.

TABLE IV

RATES OF FORMATION OF PRODUCTS IN THE PHOTOLYSIS OF MERCURY DIMETHYL IN THE PRESENCE OF ETHYLENE OXIDE: EFFECT OF CHANGES IN LIGHT INTENSITY AT 175° AND CONSTANT PRESSURE

Cell 20 cm. in length, 2.4 cm. in diameter; light sources, S-353 and A-H6 arcs; ethylene oxide pressure 100 mm., mercury dimethyl pressure 5.0 mm. (in cell at 300°K.); temperature 175°; rates of formation given in microns/hour at 300°K. in a volume of 590 cc. Barred quantities refer to runs in the absence of ethylene oxide. Rates must be multiplied by 9.70 × 10^{-14} to convert to moles/cc./second. $R_{C_2H_6}$ is a rough measure of intensity.

Run	R_{CO}	R_{CH_4}	$R_{C_2H_6}$	$\bar{R}_{CH_4}$	$\bar{R}_{C_2H_6}$	R_{CH_4}/R_{CO}	$R_{C_2H_6}/R_{CH_4}$
E-6	70	160	1780	...	...	2.3	11.1
E-8	50	117	950	...	...	2.4	8.1
E-7	34	87	610	...	...	2.5	7.0
E-5	31	80	550	14	630	2.6	6.8
E-1	6.6	21	51	3.2	56	3.1	2.5
E-2	4.7	12	19	1.8	23	2.6	1.6
E-3	1.7	5.1	3.3	0.74	4.8	3.0	0.65
E-4	1.2	3.2	1.3	0.54	2.2	2.7	0.41

TABLE V

RATES OF FORMATION OF PRODUCTS IN THE PHOTOLYSIS OF MERCURY DIMETHYL IN THE PRESENCE OF ETHYLENE OXIDE: EFFECT OF CARBON DIOXIDE AND VARIATIONS IN ETHYLENE OXIDE PRESSURE AT 175° AND CONSTANT LIGHT INTENSITY

Cell 20 cm. in length, 2.4 cm. in diameter; light source, S-353 arc; mercury dimethyl pressure, 20.0 mm. (in cell at 300°K.); temperature, 175°. Rates of formation given in microns/hour at 300°K. and in a volume of 590 cc. Barred quantities refer to rates in the absence of ethylene oxide. Rates must be multiplied by 9,70 × 10^{-14} to convert to moles/cc./second.

Run	Ethylene oxide pressure	R_{CO}	R_{CH_4}	$R_{C_2H_6}$	$\bar{R}_{CH_4}$	$\bar{R}_{C_2H_6}$	R_{CH_4}/R_{CO}
D-1[a]	49	3.9	18.9	90	10.6	103	4.9
C-1	50	4.4	18.3	93	10.1	98	4.2
D-2[a]	153	9.0	36.2	75	10.8	100	4.0
C-2	200	9.7	38.7	79	10.3	99	4.0

[a] Carbon dioxide added to bring total pressure to 220 mm. (at 300°K.).

The Mechanism in Mixtures of Mercury Dimethyl and Ethylene Oxide

A mechanism for the photochemical decomposition of mercury dimethyl has been presented recently.[7] This mechanism is in general agreement with data found in this Laboratory as well as elsewhere. The primary process has not been elucidated, although CH_3 radicals must be formed.

TABLE VI

ALDEHYDE PRODUCTION IN THE PHOTOCHEMICAL DECOMPOSITION OF MERCURY DIMETHYL IN THE PRESENCE OF ETHYLENE OXIDE

Cell 20 cm. in length, 2.4 cm. in diameter; light source, S-353 arc; ethylene oxide pressure 100.0 mm. (in cell at 300°K.); temperature, 175°. Rates of formation of products given in microns/hour at 300°K. in a volume of 590 cc. Rates must be multiplied by 9.70×10^{-14} to convert to moles/cc./second. Acetaldehyde dark rate: 2.74 microns/hour. Barred quantities refer to runs in the absence of ethylene oxide. R''_{CH_4} represents rate of CH_4 formation due to ethylene oxide.

Run	Mercury dimethyl pressure (at 300°K.), mm.	R_{CO}	R_{CH_4}	$R_{C_2H_6}$	$\bar{R}_{CH_4}$	$\bar{R}_{C_2H_6}$	$R''_{CH_4} - R_{CO}$
B-11	20	7.4	26.3	72	10.5	89	8.4
B-12	13.5	14.5	50.1	250	14.4	280	21.2

	Excess aldehyde by *p*-hydroxybiphenyl method			
	As acetaldehyde		As propionaldehyde	
Run	at 440 mμ	at 575 mμ	at 440 mμ	at 575 mμ
B-11	0.5	2.2	6.4	6.4
B-12	1.06	4.1	13.1	11.7

The number of CH_3 radicals produced per quantum absorbed may be temperature dependent. The following treatment of the data would not be affected by such a variation.

The addition of ethylene oxide to mercury dimethyl (see Table III) lowers somewhat the amount of ethane produced and causes a substantial increase in the rate of formation of methane. Carbon monoxide and certain aldehydes (see Table VI) are also produced when ethylene oxide is present. These effects were not observed at room temperature. It appears certain, therefore, that CH_3 radicals react with ethylene oxide, at least at temperatures above 150°.

The following facts are found by inspection of the data in Tables III–VI: (a) methane formation rises sharply in the presence of ethylene oxide; (b) the increase in methane formation is always greater than the amount of carbon monoxide produced; (c) ethane formation decreases in the presence of ethylene oxide. The larger the increase in methane formation the greater the decrease in ethane formation. On the other hand, the larger the rate of formation of carbon monoxide the less the decrease in rate of ethane formation.

It is concluded from these facts that CH_3 radicals react with ethylene oxide to give methane, but that the resulting radical (presumably with the empirical formula C_2H_3O) does not always dissociate into CH_3 and carbon monoxide but a certain fraction of the time enters into a compound which still contains oxygen. This compound (or compounds) might be either an oxide or an aldehyde. Evidence for, but not proof of, the formation of propionaldehyde is given in Table VI.

The mechanism given below is advanced to explain the facts presented above. The initial formation of CH_3 radicals upon absorption of radiation by mercury dimethyl is assumed.

$$CH_3 + CH_3 = C_2H_6;\ R'_{C_2H_6} = k_1(CH_3)^2 \quad (1)$$

$$CH_3 + Hg(CH_3)_2 = C_2H_6 + CH_3 + Hg;\quad R''_{C_2H_6} = k_2(CH_3)(D) \quad (2)$$

where (D) is the concentration of mercury dimethyl. This reaction almost certainly does not proceed in a single step[7] and hence is probably not a simple inversion reaction. Reaction (2) is, however, rate determining but the details of the mechanism of ethane formation by this process need not concern us at present.

$$CH_3 + Hg(CH_3)_2 = CH_4 + CH_2HgCH_3;\quad R'_{CH_4} = k_3(CH_3)(D) \quad (3)$$

$$CH_2HgCH_3 + CH_3 = C_2H_5HgCH_3;\quad -R_X = k_4(CH_3)(X) \quad (4)$$

where X refers to the CH_2HgCH_3 radical. $C_2H_5HgCH_3$ has not been identified, but the rate of (4) does not affect the conclusions to be drawn.

$$CH_3 + (CH_2)_2O = CH_4 + C_2H_3O;\quad R''_{CH_4} = k_5(CH_3)(E) \quad (5)$$

where (E) is the concentration of ethylene oxide.

$$C_2H_3O = CH_3 + CO;\ R_{CO} = k_6(C_2H_3O) \quad (6)$$

$$CH_3 + C_2H_3O = CH_3C_2H_3O;\ R_Y = k_7(CH_3)(C_2H_3O) \quad (7)$$

where R_Y is the rate of formation of an oxide or aldehyde of the empirical formula shown but whose nature cannot be specified with certainty. (Subscripts of rate constants throughout this article correspond with the numbers of the equations to which they refer.)

It is seen in Tables III–VI that except at low light intensities the rates of ethane formation in the presence and in the absence of ethylene oxide do not differ by more than 20%. Since $(1.2)^{1/2}$ differs from 1.2 by less than 10%, the ratio of CH_3 radical concentration in the presence of ethylene oxide to that in the absence of ethylene oxide will not be in error by more than 10% whether it is calculated from the rate of (1) alone or from the sum of the rates of (1) and (2). Since most of the ethane must be formed by (1), we may write to a good first approximation

$$(CH_3)/(\overline{CH_3}) = (R_{C_2H_6}/\bar{R}_{C_2H_6})^{1/2} \quad (8)$$

where the barred quantities throughout this article will refer to experiments with no ethylene oxide present and the unbarred quantities to experiments at the same mercury dimethyl concentration with ethylene oxide present.

It is evident by reference to reactions (3) and (5) that

$$R_{CH_4}/\bar{R}_{CH_4} = (1 + k_5(E)/k_3(D)(R_{C_2H_6}/\bar{R}_{C_2H_6})^{1/2} \quad (9)$$

Equation (9) permits evaluation of k_5/k_3 since it contains only measured quantities. Table VII shows k_5/k_3 obtained over a wide range of experimental conditions. The ratio is remarkably constant and is even independent of temperature. Thus the grand average of k_5/k_3 at 175° is 0.33, whereas the average of the three values at 220° is 0.35. In fact 0.35 was obtained both at 150

TABLE VII

EFFECT OF TEMPERATURE, REACTANT PRESSURES AND LIGHT INTENSITY ON THE RATIO k_5/k_3 AND THE MATERIAL BALANCE OF THE PHOTOLYSIS OF MERCURY DIMETHYL IN THE PRESENCE OF ETHYLENE OXIDE

Reactant pressures in mm. in cell at 300°K. Product rates given in microns/hour at 300°K. in a volume of 590 cc. Barred quantities refer to runs in the absence of ethylene oxide. Rates must be multiplied by 9.70×10^{-14} to convert to moles/cc./second. Light intensity kept constant in all runs marked B, C, D (S-353 arc). Light intensity varied about 1000-fold in runs marked E (S-353 and A-H6 arcs).

Run	Temp., °C.	Pressure Ethylene oxide	Pressure Mercury dimethyl	$R_{C_2H_6}/\bar{R}_{C_2H_6}$	$\sqrt{R_{C_2H_6}/\bar{R}_{C_2H_6}}$	k_5/k_3	$R_{C_2H_6}+R_{CH_4}-R_{CO}$	$\bar{R}_{C_2H_6}+\bar{R}_{CH_4}$
B-9	150	100	20	0.92	0.96	0.348	79.6	81.8
B-1	174	100	20	.90	.95	.316	103	107
B-5	175	100	20	.90	.95	.328	104	106
B-4	200	100	20	.86	.93	.324	120	120
B-3	220	100	20	.79	.89	.342	136	136
B-7	220	100	20	.83	.91	.347	153	140
B-8	220	100	20	.86	.93	.357	141	124
B-2	248	100	20	(.68)	(.83)	.410	(213)	(201)
B-6	250	100	20	(.84)	(.92)	.352	(227)	(192)
C-1	175	50	20	.94	.97	.346	107	109
D-1[a]	175	49	20	.87	.93	.373	105	113
B-5	175	100	20	.90	.95	.328	104	106
D-2[a]	175	153	20	.75	.87	.373	102	111
C-2	175	200	20	.79	.89	.322	108	110
E-5	175	100	5	.87	.93	.263	598	644
E-1	175	100	5	.92	.96	.283	65.3	58.9
E-2	175	100	5	.84	.92	.322	26.3	24.2
E-3	175	100	5	.69	.83	.367	6.74	6.58
E-4	175	100	5	.61	.78	.328	3.36	2.70
Average value						.343		

[a] Carbon dioxide added to bring total pressure to 220 mm. (in cell at 300°K.).

and at 250°. The energies of activation for methane formation by reactions (3) and (5) must, therefore, be identical within experimental error. It has already been shown[7] that $E_3 = 9000 + {}^1/_2 E_1$ and hence we may write

$$E_5 = 9000 + {}^1/_2 E_1 \qquad (10)$$

It is probably safe to assume that two CH_3 radicals are produced per quantum absorbed at the temperatures in Table VII. Hence the number of CH_3 radicals produced per unit volume per unit time is $2I_a + R_{CO}$, where I_a is the number of quanta absorbed per cc. per second and R_{CO} is the number of molecules of carbon monoxide produced per cc. per second. The material balance for CH_3 radicals gives

$$2I_a + R_{CO} = 2R'_{C_2H_6} + R'_{CH_4} + R''_{CH_4} + R_Y - R_X \qquad (11)$$

But $R''_{CH_4} = R_{CO} + R_Y$ and $R'_{CH_4} = -R_X$. If z is the fraction of ethane formed by reaction (2)

$$I_a + z\,R_{C_2H_6} = R_{C_2H_6} + R_{CH_4} - R_{CO} \qquad (12)$$

In the absence of $(CH_2)_2O$ the similar expression is

$$I_a + \bar{z}\,\bar{R}_{C_2H_6} = \bar{R}_{C_2H_6} + \bar{R}_{CH_4} \qquad (13)$$

Since z and $\bar{z}$ should be approximately equal and in any case should be small except at low light intensity, it follows that

$$R_{C_2H_6} + R_{CH_4} - R_{CO} \cong \bar{R}_{C_2H_6} + \bar{R}_{CH_4} \qquad (14)$$

The data in Table VII show (14) to be obeyed approximately at all temperatures and light intensities studied over a fourfold variation in ethylene oxide pressure.

The mechanism as given in equations (1)–(7) must be incomplete, however, because it leads to the following relationship which is not obeyed (Table IV)

$$R_{CH_4}/R_{CO} = k_3(D)/k_5(E) + k_7R_{CH_4}/k_5k_6(E) + 1 \qquad (15)$$

It may be assumed that the radical C_2H_3O will decompose according to (6) (some such step is necessary to explain the formation of carbon monoxide) and also isomerize, possibly according to the equation

$$C_2H_3O = CH_2CHO;\ \text{rate} = k_{16}(C_2H_3O) \qquad (16)$$

Reaction (16) could be followed by (7) with resultant production of propionaldehyde. The inclusion of (16) leads to the expression

$$R_{CH_4}/R_{CO} = (k_6 + k_{16})(1 + k_3(D)/k_5(E))/k_6 \qquad (17)$$

While Equation (17) fits the data (see Fig. 1), it must be emphasized that it is impossible to prove that the complete mechanism offers a unique solution to the problem. Propionaldehyde is almost certainly one of the products and hence there is some support for the proposed mechanism. Another mechanism based on polymer formation also gives the right form of equation. Attempts to find evidence for polymer formation failed.

Another expression derivable from the mechanism is

$$R_{C_2H_6}/R_{CH_4} = k_1R_{CH_4}/(k_3(D) + k_5(E))^2 + k_2(D)/(k_3(D) + k_5(E)) \qquad (18)$$

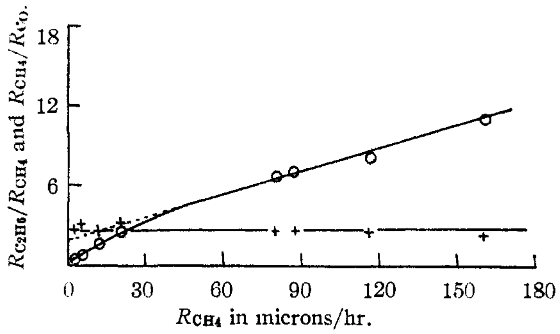

Fig. 1.—$R_{C_2H_6}/R_{CH_4}$ *vs.* R_{CH_4} (circles) and R_{CH_4}/R_{CO} *vs.* R_{CH_4} (crosses) in mixtures of ethylene oxide (100 mm.) and mercury dimethyl (5 mm.) at 175° and variable intensity (see Table IV).

Figure 1 shows that $R_{C_2H_6}/R_{CH_4}$ *vs.* R_{CH_4} gives a straight line at constant temperature, constant (E) and (D), and variable light intensity. The deviations at low light intensities can be explained as in the previous work[7] by splitting reaction (2) into two steps: (a) $CH_3 + Hg(CH_3)_2 \rightleftarrows$ complex; (b) complex $+ CH_3 = C_2H_6 + 2 CH_3 + Hg$. The slope of the straight line can be calculated from k_1/k_3^2 obtained in the previous article[7] and the value of k_5/k_3 found above. The calculated slope is 0.045 hour/micron and the found value is 0.054 hour/micron.

The quantity R''_{CH_4} may be seen by inspection to be given by

$$R''_{CH_4} = R_{CH_4} - \bar{\bar{R}}_{CH_4} (R_{C_2H_6}/\bar{R}_{C_2H_6})^{1/2} \qquad (19)$$

R_{CO}/R''_{CH_4} will be the fraction of C_2H_3O radicals which decompose to $CH_3 + CO$. The data in Table VIII show this fraction to be very independent of temperature and of light intensity. Mueller and Walters[13] have studied recently the reaction of CH_3 radicals (produced thermally from mercury dimethyl) with ethylene oxide and find no evidence for a long-chain reaction even at 400°. The stability of C_2H_3O may result from resonance in the form CH_2CHO.[14]

The mechanism herein presented for the reactions of CH_3 radicals with ethylene oxide agrees with the facts. It should be noted again that the two reactions for methane formation by hydrogen abstraction (reactions (3) and (5)) have the same activation energy whereas the "effective cross section" for the reaction with mercury dimethyl is about six times that for ethylene oxide. This matter will be discussed in a later communication from this Laboratory.

Results on the Direct Photochemical Decomposition of Ethylene Oxide

The three principal variables investigated in connection with the direct photochemical decomposition of ethylene oxide were light intensity, pressure and temperature. The latter was particularly important since it was shown in the preceding sections that CH_3 radicals react very slowly with ethylene oxide at room temperature.

TABLE VIII

EFFECT OF PRESSURE, TEMPERATURE AND LIGHT INTENSITY ON THE FATE OF THE C_2H_3O RADICAL

Reactant pressures refer to the cell at 300°K. Intensity kept constant in runs B (S-353 arc). R''_{CH_4} refers to rate of methane formation due to ethylene oxide, as found from equation (19).

Run	Temp., °C.	Pressure, mm. Ethylene oxide	Pressure, mm. Mercury dimethyl	R_{CO}/R''_{CH_4}
B-9	150	100	20	0.45
B-1	174	100	20	.64
B-5	175	100	20	.45
B-4	200	100	20	.48
B-3	220	100	20	.50
B-7	220	100	20	.40
B-8	220	100	20	.39
B-2	248	100	20	.47
B-6	250	100	20	.48

Tables IX and X show data obtained with variable light intensity at room temperature as well as at several temperatures.

Mechanism of the Photochemical Decomposition of Ethylene Oxide

The presence of large amounts of hydrogen among the products of the direct photochemical decomposition of ethylene oxide indicates that probably H atoms are produced in the primary process. If one H atom is produced per quantum absorbed, the remainder of the molecule will have the empirical formula C_2H_3O and in this respect should be similar to the radical produced when CH_3 reacts with ethylene oxide to form methane. However, the latter radical is reasonably stable even at 250°, whereas the rate of production of carbon monoxide is too great to ascribe a similar stability to the radical produced in the primary process.

Some of the relationships in Table XI would be obtained if hydrogen atoms, carbon monoxide and CH_3 were all produced in the primary process, but in that event methane would be produced by the reaction $CH_3 + H = CH_4$, since hydrogen abstraction by CH_3 is too slow at room temperature to account for the observed quantities of methane.

The ratio ethane/methane decreases as the intensity increases. This is in direct contrast with cases in which ethane is formed by radical combination and methane by hydrogen abstraction.[15] Any proposed mechanism must account for this fact.

Many different mechanisms were proposed and tested. The one finally adopted is not a unique solution to the problem but in all respects is more logical than any other. The mechanism fits all of the data within experimental error.

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[14] See F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins University Press, Baltimore, Md., 1935. This was suggested in connection with acetaldehyde decomposition.

[15] See L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16** 557 (1948).

TABLE IX

RATES OF FORMATION OF PRODUCTS IN THE PHOTOLYSIS OF ETHYLENE OXIDE—VARIATION OF LIGHT INTENSITY

Reaction cell 20.0 cm. in length, 2.4 cm. in diameter; light source, Hanovia H_2 discharge tube; ethylene oxide pressures refer to cell at 300°K. Product rates of formation given in microns/hour at 300°K. in a volume of 590 cc. Rates must be multiplied by 9.7×10^{-14} to convert to moles/cc./sec.

Run	Pressure, mm.	Temp., °C.	R_{CO}	R_{CH_4}	R_{H_2}	$R_{C_2H_6}$	R_{CH_3CHO}	R_{CH_2O}
O-1	100	27	2.2	0.31	0.99	1.22	0.3	0.1
O-10[a]	100	27	9.5	1.55	3.3	2.51	?	?
O-2	100	27	16.3	2.68	6.5	6.8	0.8	0.9
O-3	100	27	50	9.2	19.9	19.5	2.0	2.6
O-4	100	27	58	14.0	23.6	27.0	4.1	3.8
20	100	27	100	17.5	37.0	39.0	9.0	(6.0)
O-12[b]	10	27	3.19	0.22	1.55	1.5	?	?
O-11[a]	10	27	3.27	0.21	1.52	1.5	?	?
O-6	10	27	12.6	1.66	7.04	5.4	2.8	1.6
O-7	10	27	27.0	3.39	13.5	10.7	(6.2)	(1.8)

[a] 10-cm. quartz cell, containing mercury vapor, interposed between reaction vessel and lamp. [b] Same cell interposed, mercury frozen down.

TABLE X

VARIATION OF TEMPERATURE

Run	Pressure, mm.	Temp., °C.	R_{CO}	R_{CH_4}	R_{H_2}	$R_{C_2H_6}$	R_{CH_3CHO}	R_{CH_2O}
26	55	27	32.3	6.1	12.3	Present	2.5[a]	(3.7)
25	40	(175)	81	22	42	Present[b]	(6.1)[a]	?
O-3	100	27	50	9.2	20	20	2.0[a]	2.6
T-1	100	175	78	13.6	40	24[b]	5.0[a]	7.0
T-2	100	220	95	28	57	25[b]	8.9[a]	11
T-3	100	250	118	49	66	24[b]	?	?

[a] Acetaldehyde and/or higher aldehydes. [b] Total C_2 hydrocarbon, ethylene not determined.

TABLE XI

VARIOUS RELATIONS BETWEEN THE PRODUCTS OF THE PHOTOLYSIS OF ETHYLENE OXIDE

Run	Pressure, mm.	Temp., °C.	CO/H_2	CO/CH_4	$\frac{CO}{CH_4 + 2C_2H_6}$	$\frac{CO}{CH_4 + 2H_2}$	$\frac{CH_4}{C_2H_6}$	$\frac{C_2H_6}{H_2}$
O-1	100	27	2.19	7.06	0.792	0.912	0.253	1.23
O-10	100	27	7.85	6.10	1.43	1.15	.620	0.755
O-2	100	27	2.49	6.08	1.00	1.03	.394	1.04
O-3	100	27	2.51	5.45	1.04	1.02	.470	0.979
O-4	100	27	2.87	4.84	0.997	1.11	.519	1.14
20	100	27	2.70	5.71	1.05	1.09	.472	1.06
O-11	10	27	2.16	15.3	1.02	1.00	.143	0.987
O-6	10	27	1.79	7.59	1.01	0.805	.307	.770
O-7	10	27	2.00	8.00	1.09	.890	.317	.795
T-1	100	175	1.94	5.70	1.27	.835	.574	.591
T-2	100	220	1,65	3.40	1.22	.664	1.11	.436
T-3	100	250	1.79	2.43	1.24	.654	2.07	.357

The primary step is assumed to be

$$(CH_2)_2O + h\nu = CH_3 + HCO$$

The HCO radical has been suggested in many connections by other authors. Its heat of dissociation to H + CO is nearly zero and hence its thermodynamic stability would be nearly independent of temperature. It seems to be formed from hydrogen atoms and carbon monoxide at temperatures up to 200° and probably higher.[16] Its detailed reactions are not known but several are probable. The principal reactions which concern us in this discussion are

$$HCO = H + CO; \; R'_{CO} = k_{21}(HCO) \qquad (21)$$

(The reverse of this reaction can probably be neglected both because the H atom concentration was low and because carbon monoxide was never allowed to accumulate to an appreciable extent in the system.)

$$CH_3 + HCO = CH_4 + CO; \quad R''_{CH_4} = k_{22}(CH_3)(HCO) \qquad (22)$$

$$CH_3 + H\ (+ M) = CH_4\ (+ M); \quad R'_{CH_4} = k_{23}(CH_3)(H)(M) \qquad (23)$$

$$CH_3 + CH_3 = C_2H_6; \; R_{C_2H_6} = k_1(CH_3)^2 \qquad (1)$$

$$H + H\ (+ M) = H_2\ (+ M); \; R_{H_2} = k_{24}(H)^2(M) \qquad (24)$$

$$CH_3 + HCO = CH_3CHO; \quad R_{CH_3CHO} = k_{25}(CH_3)(HCO) \qquad (25)$$

$$H + HCO = HCHO; \; R_{HCHO} = k_{26}(H)(HCO) \qquad (26)$$

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[16] See W. Frankenberger, *Z. Elektrochem.*, **36**, 757 (1930), who found HCHO and $(HCO)_2$ to be formed up to 200°.

The following reactions of the HCO radical may occur but they would not influence the conclusions to be drawn. They have all been suggested by various authors.

$$HCO + HCO = H_2 + 2CO;\ R''_{CO} = k_{27}(HCO)^2 \quad (27)$$

$$= HCHO + CO;\ R'_{HCHO} = k_{28}(HCO)^2 \quad (28)$$

$$= (HCO)_2;\ R_{(HCO)_2} = k_{29}(HCO)^2 \quad (29)$$

The hydrogen abstraction reactions (5) and (30) will have to be considered under some experimental conditions, that is, at the higher temperatures.

$$H + (CH_2)_2O = H_2 + C_2H_3O;\ R_{C_2H_3O} = k_{30}(H)(E) \quad (30)$$

The following relationships are obtained from the mechanism

$$R_{C_2H_6} = R_{HCHO} + R_{H_2} \quad (31)$$

$$R_{CO} = R_{HCHO} + 2R_{H_2} + R_{CH_4} \quad (32)$$

$$R_{CO} = R_{C_2H_6} + R_{H_2} + R_{CH_4} \quad (33)$$

Reaction (30) is neglected in arriving at equations (31) and (32). Equations (31) and (32) are obeyed within the limit of accuracy of the determination of HCHO. Equation (33) is obeyed from room temperature to 175° and it should be valid provided the C_2H_3O radical formed during hydrogen abstraction can only do one of the following: (a) dissociate into CH_3 and CO; (b) capture an H atom; (c) capture a CH_3 radical.

Since equation (33) is not obeyed at temperatures over 175°, reactions other than those listed must become important.

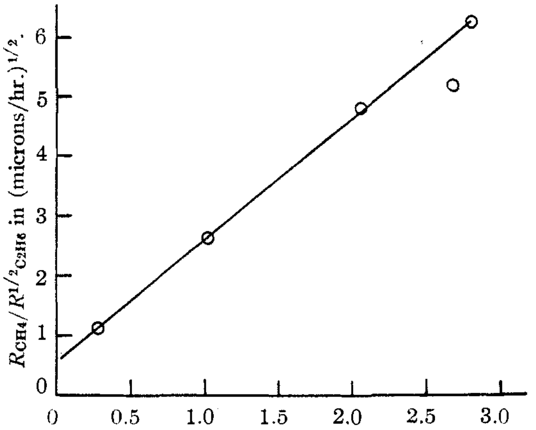

Fig. 2.—$R_{CH_4}/R^{1/2}_{C_2H_6}$ *vs.* $R^{1/2}_{C_2H_6}$ in $(CH_2)_2O$ (100 mm.) at 27° and variable intensity; light source, Hanovia H_2 discharge. Multiplication of either ordinate or abscissa by 3.12×10^{-7} gives (moles/cc./sec.)$^{1/2}$.

A detailed equation for $R_{CH_4}/R_{C_2H_6}$ is very complicated if all of the above steps are included in the derivation. It can be seen with the aid of certain approximations, however, that this ratio will increase as the intensity increases. If attention is directed to reactions (1), (21), (22), (23), (25), (27), (28) and (29) (which should account for the bulk of product formation), it can be shown that

$$R_{CH_4}/R_{C_2H_6} = a - b/R^{1/2}_{C_2H_6} \quad (34)$$

where a and b are complex constants involving several of the rate constants. Since $R^{1/2}_{C_2H_6}$ increases with increase in intensity, $R_{CH_4}/R_{C_2H_6}$ will increase with increase in intensity. If part, but not all, of the primary process gives CH_3 + H + CO, this conclusion will still be valid. Figure 2 shows a plot of $R_{CH_4}/R^{1/2}_{C_2H_6}$ *vs.* $R^{1/2}_{C_2H_6}$ which, by equation (34), should be a straight line.

The hydrogen abstraction reaction (30) leading to hydrogen formation must become important at high temperatures since the rate of formation of hydrogen is too large to be accounted for by the other equations. Since Trost, Darwent and Steacie[4] have shown that hydrogen atoms react with ethylene oxide this conclusion seems amply justified. At 30° other competing reactions of hydrogen atoms seem to predominate under the conditions of these experiments.

The mechanism as outlined accounts, therefore, for the observed facts. Each step in the mechanism is reasonable, but detailed proof of all steps is not available at the present time. It would be advisable to have precise quantum yield data when and if monochromatic light of the proper wave length becomes available.

Summary

1. The reactions of CH_3 radicals with ethylene oxide have been studied.

2. The heat of activation of the reaction $CH_3 + (CH_2)_2O = CH_4 + C_2H_3O$ is about 9000 calories more than one half of the heat of activation of the reaction $CH_3 + CH_3 = C_2H_6$.

3. The radical C_2H_3O, produced simultaneously with methane formation, decomposes partially into CH_3 + CO and partially is stable enough to combine with other atoms or radicals. The ratio of the two amounts is nearly temperature independent.

4. The principal products of the direct photochemical decomposition of ethylene oxide are methane, ethane, hydrogen and carbon monoxide. Smaller amounts of formaldehyde and of acetaldehyde are also produced.

5. The primary process of the direct reaction is probably $(CH_2)_2O + h\nu = CH_3 + HCO$ (or, perhaps, H + CO).

6. Since the ratio methane/ethane increases with increasing intensity during the direct reaction, methane must be formed by some process other than hydrogen abstraction from ethylene oxide and the reaction $CH_3 + HCO = CH_4 + CO$ is suggested.

7. The complete mechanism of the direct reaction cannot be given, but a reasonable mechanism which accounts for the data up to 175° has been presented.

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