decomposition reaction (S9). The difference may be due solely to the fact that the allylperoxy radicals were formed at lower temperatures in the presence of a higher total concentration of radicals. The difference may also be associated with the reactivities of the peroxy radicals themselves. Although the conclusions were not certain, the allyl iodide exchange data indicated that allyl and allylperoxy radicals and iodine atoms all reacted with each other with comparable rate constants of the order of 10^{10} l./mole sec. The reactions of benzyl radicals and iodine atoms follow the same pattern. We have no information about the rate constants for reactions (S10) and (S11) of benzylperoxy radicals, but the data do suggest that reaction (S12) is slow for a radical–radical reaction. Here again, the incipient double bond in an allylperoxy radical permits radical reactions of a type not available to benzylperoxy. Examples might be

$$I\cdot + CH_2CHCH_2OO\cdot \longrightarrow ICH_2CH{=}CH_2 + O_2$$

$$2CH_2CHCH_2OO\cdot \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + 2O_2$$

or

$$CH_2{=}CHCH_2OOCH_2CH{=}CH_2 + O_2$$

The evidence for these radical–radical displacement reactions is still very tenuous.

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

The Radical-sensitized Decomposition of Formaldehyde[1]

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The decomposition of formaldehyde has been sensitized by the addition of small percentages of ethylene oxide at 384–437°; the main products are hydrogen and carbon monoxide. The kinetics of the decomposition of formaldehyde sensitized by ethylene oxide have been investigated. Packing the vessel decreases the rate, and addition of an inert gas increases the rate. The mechanism of the decomposition is discussed. Mercury dimethyl at 381° and biacetyl at 477–489° also sensitize the decomposition.

The thermal decomposition of pure formaldehyde has been studied by Fletcher[3] in the region 510–607° at 30–400 mm. Fletcher observed that the principal primary reaction yields hydrogen and carbon monoxide and has an order of about two. A reaction which produces methanol and carbon monoxide was suggested also, but no direct evidence for the presence of methanol was given. The photolysis of formaldehyde has been studied by a number of investigators and it has been established that at temperatures above 160° and with light of 3130 Å. a chain reaction takes place with the formation of hydrogen and carbon monoxide as the chief products.[4]

Formaldehyde is formed as an intermediate in the thermal decomposition of dimethyl ether,[5] as well as other decompositions, which involve free radical processes. However, several investigators[6] have reached different conclusions regarding the possibility that free radicals promote a chain decomposition of the intermediate formaldehyde. The reaction of methyl radicals with formaldehyde at 310° has been studied by Kodama and Takezaki[7] who used the thermal decomposition of azomethane as a source of free radicals. The present work has been concerned mainly with the effect of radicals upon the decomposition of formaldehyde at 380–490° which is a temperature region not far below that used for the various thermal decompositions yielding formaldehyde as an intermediate.

Experimental

The formaldehyde, the ethylene oxide and the reaction system were the same as those reported earlier.[8] Nitrogen (99.99%) was purchased from the Linde Air Products Co. Carbon monoxide from the Matheson Co. was purified by passage through a trap at −78° or −196° (at reduced pressure). Hydrogen (Ohio, 99.5%) was passed through a Baker Deoxo purifier to remove oxygen. Carbon dioxide (Ohio, 99%) was repeatedly condensed at −196° and evacuated to 10^{-4} mm. to remove non-condensable gases.

Surface effects were studied in a bulb packed with small Pyrex tubes which provided a surface to volume ratio 35 times as great as the unpacked vessel. All parts of the vacuum system in contact with formaldehyde were heated electrically to about 90° to prevent its polymerization. Before introduction into the reaction vessel a mixture of formaldehyde and sensitizer was allowed to stand in a spherical bulb at 90° for at least 30 minutes to ensure complete mixing.

Mass spectrometric analyses[9] showed that the non-condensable gases formed in the sensitized decomposition consisted principally of hydrogen and carbon monoxide along with traces of methane. Consequently the gas mixture was analyzed by oxidizing the hydrogen and carbon monoxide over hot copper oxide and absorbing the carbon dioxide on moist potassium hydroxide pellets. The methane was determined by difference. Analyses of known mixtures agreed (±0.5%) with the compositions of the mixtures as prepared.

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[1] For two thirds of the period of this study financial support was received from the Office of Naval Research.

[2] E. I. du Pont de Nemours and Company Fellow, 1950–1951.

[3] C. J. M. Fletcher, *Proc. Roy. Soc.* (*London*), **A146**, 357 (1934). Other results have been reported by R. Klein, M. D. Sheer and L. J. Schoen, Abstracts, A.C.S. Meeting, Cincinnati, Ohio, Mar. 29–Apr. 7, 1955, p. 27Q.

[4] (a) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951); (b) E. C. A. Horner, D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **50**, 1201 (1954).

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[9] Performed by Dr. F. L. Mohler and the staff of the National Bureau of Standards.

The methanol in the presence of a large excess of formaldehyde was determined (within ~ 10%) by a modification of procedures described earlier.[10] The presence of methanol in the sensitized decomposition was demonstrated also by (a) mass spectrometric identification and (b) a test described by King and Bell.[11] Quantitative mass spectrometric analyses[9] for methanol in the products from two sensitized experiments agreed (within 5%) with the results of the chemical analysis for methanol in the products from similar experiments.

Glyoxal, which was tested for by a modification of the method of Tommila,[12] was not present in sufficient quantity to be detected in the products from the sensitized decomposition of formaldehyde in the unpacked bulb at 415°.

Unreacted formaldehyde was determined by a modification of the sodium sulfite procedure described by Walker.[13] The analytical method was checked using pure formaldehyde and mixtures of nitrogen and formaldehyde. It was found that with an empirical correction of +3% an accuracy of about ±2% could be obtained.

Results

Pure Formaldehyde.—Prior to the investigation of the sensitized decomposition, experiments with pure formaldehyde were carried out. At temperatures of 415° or lower the pressure rise indicated that the rate of decomposition of pure formaldehyde to form hydrogen and carbon monoxide is very small. With a formaldehyde pressure of 115 mm. the initial rate of pressure rise was about 0.2% per min. at 475° and 1.6% per min. at 512°. The analyses of the reaction products, however, gave evidence that a slow reaction which produces methanol takes place at temperatures near 415°. Preliminary experiments in the unpacked vessel and others in the packed vessel showed that for 131 mm. of formaldehyde after 40 min. at 415° the amount of non-condensable gas formed (5.7 ± 0.1 mm.) is approximately equal to the methanol produced (5.5 ± 0.7 mm.). The analyses for the small amounts of formaldehyde disappearing which represent the differences in two large quantities (initial amount − unreacted material) are not of great reliability, but the values found (7–8 mm.) are about one and a half times the amount of either product. The data indicate the probable occurrence of the reaction

$$2H_2CO \longrightarrow CH_3OH + CO$$

In the packed vessel not more than a slight increase in the rate of this reaction occurred with a 35-fold increase in the surface to volume ratio.

Other experiments which were performed at 415° gave the following results. The addition of 50–60 mm. hydrogen to 60–70 mm. formaldehyde did not have any significant effect upon the amount of methanol formed during 40 minutes. For experiments with formaldehyde alone, rate constants for methanol formation were calculated on the basis of the integrated second-order equation assuming that the amount of formaldehyde disappearing is equal to twice the quantity of methanol formed. With initial pressures from 110 to 240 mm. the value remained approximately constant ($k \cong 0.4$ l./mole min.) indicating that the reaction is nearly second order. Since the percentage of reaction in the experiments was small, the order of the reaction was also determined from a plot of the logarithm of the average rate of methanol formation against the logarithm of the average pressure of formaldehyde during a reaction. The order calculated by this method was 1.7.

On the basis of four experiments covering the temperature range 393–458° the activation energy of the reaction appears to be about 31 kcal./mole and the frequency factor is approximately $0.9 \times 10^8 T^{1/2}$, liters/mole min.

Products of the Sensitized Decomposition.—A radical-sensitized decomposition was found to occur, as might have been expected from the data of Fletcher and Rollefson.[6a] Addition of about 1% ethylene oxide is sufficient to cause the decomposition of almost all of the formaldehyde in a mixture of the two gases. In order to establish the stoichiometry of the sensitized decomposition, analyses were made for the major reaction products and the unreacted formaldehyde (see Table I). For each experimental condition investigated, analyses for non-condensables, methanol and formaldehyde were not made on the same reaction mixture from a single experiment, but on three reaction mixtures from three different experiments, as nearly identical as possible. Small corrections were applied in order to make the experimental conditions comparable. The pressure of CO formed (column 7) is approximately equal to the sum of the pressures of H_2, CH_4 and CH_3OH (columns 4, 5 and 6). The sum of the pressures of CH_3OH and CO (columns 6 and 7) is nearly equal to the pressure of H_2CO which has disappeared (column 8). The pressure increase (column 3) is essentially the same as the

TABLE I

ANALYSES OF THE REACTION MIXTURES IN THE ETHYLENE OXIDE-SENSITIZED DECOMPOSITION OF FORMALDEHYDE

P_0^F,[a] mm.	P_0^E,[a] mm.	ΔP, mm.	Pressures of the products, mm. H_2	CH_4	CH_3OH	CO	ΔH_2CO, mm.
Temp. 415.5 ± 0.5°; reaction time 20.2 min.							
60	1.9	17	18	0.1[b]	1	20	20
124	2.1	34	35	.6	3	39	44
184	2.0	44	45	.6	8	54	59
244	1.9	55	56	.2	10	68	80
118	4.0	47	48	.5	4	53	56
Temp. 416°; reaction time 40.2 min.							
115	1.9	56	56	.4	6	65	69
178	2.4	88	89	1	11	100	110
114	4.3	83	82	2	7	90	100
112p	4.4	3p			8p		8p[c]
Temp. 394°; reaction time 40.2 min.							
121	2.0	20	20	0.3	2	24	24
Temp. 435.5°; reaction time, 35.2 min.							
118p	4.7	15p					26p
Temp. 437°; reaction time, 20.2 min.							
122	2.0	81	80	1	5	89	91

[a] P_0^F and P_0^E mean the initial pressures of formaldehyde and ethylene oxide, respectively. [b] Pressures of methane given to one significant figure; pressures of other products to the nearest mm. [c] p denotes packed reaction vessel with 35 times the surface to volume ratio.

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(13) J. F. Walker, "Formaldehyde," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1953, p. 382.

sum of the pressures of H_2 and CH_4 (columns 4 and 5). Since the methane (from the ethylene oxide) is quite small, the pressure increase seems to be a satisfactory measure of the amount of hydrogen formed during the reaction.

From these data it seems that the formaldehyde which disappears and the products which are formed can be accounted for by two main reactions

$$H_2CO \longrightarrow H_2 + CO \qquad (1')$$

$$2H_2CO \longrightarrow CH_3OH + CO \qquad (2')$$

along with the decomposition of a small amount of sensitizer which yields chiefly methane and carbon monoxide. Since reaction (1′) is negligible in the absence of sensitizer and reaction (2′) does not result in any pressure change, the rate of pressure rise can be taken as a measure of the rate of the sensitized decomposition into hydrogen and carbon monoxide. The results of experiments in the packed bulb show that increasing the surface markedly decreases the rate of reaction (1′) and that no important surface reactions take place resulting in the loss of formaldehyde. The inhibiting effect of increased surface confirms the chain character of reaction (1′).

In an attempt to compare the rates of methanol formation with and without sensitizer the amounts of methanol formed were used to calculate second-order rate constants. In this computation the variation of the formaldehyde concentration due to hydrogen and carbon monoxide formation was also taken into account. The values of k_{2nd} at 415° seemed to be about 50% larger in the presence of 2 mm. of ethylene oxide than in the case of pure formaldehyde, those in the presence of more ethylene oxide being even slightly higher. Although some of this increase may be due to the formation of an alcohol other than methanol, the mass spectrometric results showed that in the sensitized decomposition 85–89% of the condensable products (vapor pressure less than 1 mm. at −78°) was methanol. The results of Fletcher and Rollefson[6a] indicate that very little of the methanol formed will be decomposed by the ethylene oxide present. Methanol analyses for two experiments in the packed vessel showed that increasing the surface has not increased the rate of methanol formation in the sensitized reaction and may have reduced the rate slightly.

Kinetics of the Sensitized Decomposition.—In view of the analytical results, pressure measurements were considered to be a satisfactory means of studying the kinetics of the sensitized decomposition. It was found that the initial portions of the pressure–time curves are very nearly linear, even to approximately 30% pressure increase. This behavior will be considered later. In experiments continued until the rate of pressure increase was essentially zero, the ratio of the final to the initial pressure was about 1.9, the difference between this figure and 2.0 being attributable to the methanol formation which results in no pressure change.

For the purpose of summarizing the results the rate of the sensitized decomposition into hydrogen and carbon monoxide can be expressed by an equation of the form

$$(dP/dt) = d(H_2)/dt = k(C_2H_4O)^{n_1}(H_2CO)^{n_2}(M)^{n_3}$$

where the term $(M)^{n_3}$ allows for the effect of total pressure upon the reaction. The order with respect to each reactant was determined from a plot of the logarithm of the initial rate *vs.* the logarithm of the initial concentration of that reactant (other variables constant).

The data for log $(dP/dt)_0$ *vs.* log (P_0^F) from experiments without added inert gas at 415 and 435° are shown in curves A and B in Fig. 1 and the data for log $(dP/dt)_0$ *vs.* log (P_0^E) are shown in curves A and B in Fig. 2. Most of the points for curve A in Figs. 1 and 2 represent averages of several experiments. From the slopes of these lines the order of the reaction with respect to ethylene oxide was found to be 0.6 and that with respect to formaldehyde to be 0.8 both at 415 and 435°. If formaldehyde is acting as a reactant and as an "inert gas" in these experiments, the value of 0.8 represents $n_2 + n_3$. The results which were obtained at 435° in the packed reaction vessel are shown as curve C in Fig. 1 and Fig. 2.[14] From these data the order of the reaction was found to be approximately 0.9 with respect to each reactant. While these results are not as precise as those obtained in the unpacked vessel, they indicate that increasing the surface has produced a significant increase in the order with respect to ethylene oxide.

Added Gases.—The effect of various gases upon the rate in the unpacked vessel can be obtained from an inspection of the data in Table II. Experiments 199 and 207, in which no sensitizer was added, gave evidence that the observed results are not due to some direct effect which the inert gas or an impurity has upon formaldehyde itself. Experiment 171 which shows the influence of the products upon the rate offers an explanation of the fact that the rate of pressure increase during an experiment decreases only slowly as the decomposition proceeds.

TABLE II

EFFECT OF INERT GASES UPON THE RATE OF THE ETHYLENE OXIDE-SENSITIZED DECOMPOSITION OF FORMALDEHYDE

Temp. 415.5°; $P_0^{H_2CO}$ = 120 mm.; $P_0^{C_2H_4O}$ = 2.00 mm.

Expt. no.	Added gas	Press., mm. added gas	$(dP/dt)_0$, mm./min.
(5)[a]	..	0	1.62
(3)	CO	59	1.79
(2)	N_2	62	1.82
(3)	H_2	61	2.02
171	Products	65	2.02
(3)	H_2CO	60	2.28[b]
(2)	N_2	119	1.96
198	N_2	468	2.74
210	CO_2	480	4.07
199[c]	N_2	562	~0.03[c]
207[c]	CO_2	480	~ .04[c]
(4)[c]	..	0	~ .02[c]

[a] Number in parentheses denotes the number of experiments which have been averaged. [b] Rate for a total pressure of 180 mm. formaldehyde instead of 120 mm. [c] No ethylene oxide added.

Additional experiments were performed to study

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(14) It is to be noted that the differences in the slopes of the lines in Fig. 1 or 2 show that changes in the experimental conditions can alter the values of n_1 and n_3 and may affect the mechanism to some extent.

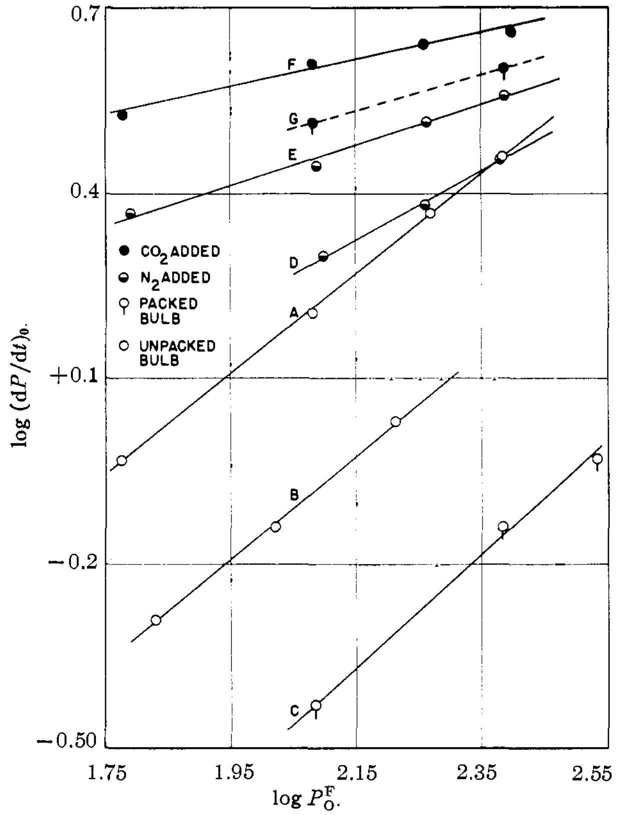

Fig. 1.—Change in the initial rate of pressure rise (mm./min.) with the initial pressure of formaldehyde, P^{F}_{0}, mm.: A, 415.5°, P^{E}_{0} (initial pressure of ethylene oxide) = 2.0 mm.; B, 435.5°, P^{E}_{0} = 4.1 mm., curve shifted downwards 0.9 unit; C, packed bulb, 435°, P^{E}_{0} = 2.1 mm.; D, 415.5°, P^{E}_{0} = 2.0 mm., total pressure ~240 mm., N_2 added; E, 415.5°, P^{E}_{0} = 2.0 mm., total pressure ~615 mm., N_2 added; F, 415.5°, P^{E}_{0} = 2.0 mm., total pressure ~600 mm., CO_2 added; G, packed bulb, 435°, P^{E}_{0} = 2.1 mm. total pressure ~550 mm., CO_2 added, curve shifted upwards 0.5 unit.

the influence of inert gases upon the kinetics of the decomposition. The results of these measurements in the unpacked reaction vessel are presented as curves D, E and F in Fig. 1 and curves D and E in Fig. 2; the results of measurements in the packed vessel are shown as curve G in Fig. 1 and curve F in Fig. 2. The values of the order with respect to each reactant at constant total pressure are given in Table III. The values of the order in the absence of added inert gas are presented for comparison. Both in the packed and unpacked reaction vessels the addition of an inert gas to maintain a constant total pressure reduces the order with respect to formaldehyde while leaving the order with respect to ethylene oxide almost unchanged. Carbon dioxide has a greater effect than nitrogen.

TABLE III

SENSITIZED DECOMPOSITION OF FORMALDEHYDE

Added gas	Total pressure, mm.	Order with respect to $(CH_2)_2O$		Apparent order with respect to H_2CO	
		Unpacked	Packed	Unpacked	Packed
None		0.6[3]	0.9	0.8[2]	0.9
N_2	~240			.5[5]	
N_2	~600	.5[6]		.3	
CO_2	~600	.5	.9	.2	.3

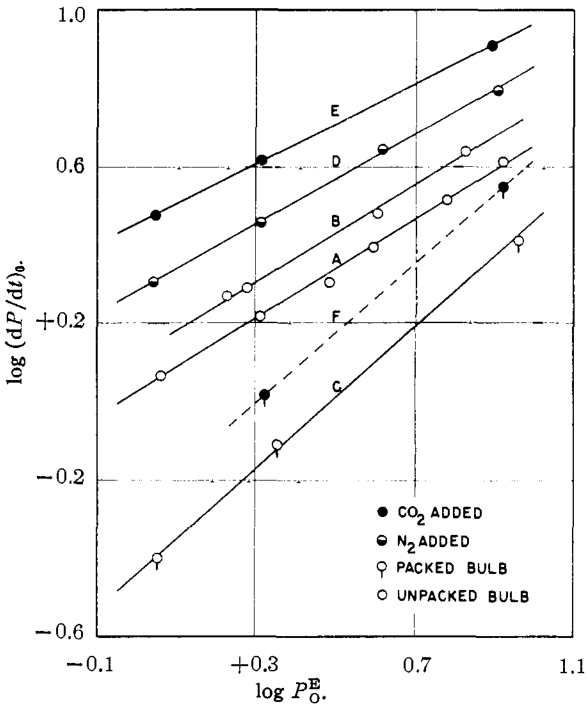

Fig. 2.—Effect of the change in the initial pressure of ethylene oxide, P^{E}_{0} upon the initial rate of pressure rise (mm./min.): A, 415.5°, P^{F}_{0} = 120 mm.; B, 435.5°, P^{F}_{0} = 110 mm., curve shifted downwards 0.3 unit; C, packed bulb, 435°, P^{F}_{0} = 240 mm.; D, 415.5°, P^{F}_{0} = 120 mm., total pressure ~600 mm., N_2 added; E, 415.5°, P^{F}_{0} = 120 mm., total pressure ~600 mm., CO_2 added; F, packed vessel, 435°, P^{F}_{0} = 120 mm., total pressure ~550 mm., CO_2 added

Since different added gases do not have the same efficiencies (see Table II), some of the observed increase in rate when the total pressure is maintained constant and the pressure of formaldehyde is raised may be the result of a change in the composition of the "inert gas mixture." Therefore, a portion of the 0.2 (or 0.3) order with respect to formaldehyde in the presence of added carbon dioxide may be due to the increased effectiveness of the mixture as an inert gas when the percentage of formaldehyde is increased. From the trend in Table III it appears that if a higher pressure of carbon dioxide were used or a more efficient inert gas were found, the order with respect to formaldehyde might be lowered. The change in formaldehyde order from 0.8 to 0.2 in the unpacked vessel and from 0.9 to 0.3 in the packed vessel probably occurs because the role of formaldehyde as an inert gas has been taken over by the added gas. However, it is also possible that the kinetics of the decomposition in the unpacked vessel have been altered in the presence of added gas by a change in the principal chain-terminating reaction.

The effect of the variation in the total pressure was studied. In a series of experiments at 415° in the unpacked vessel (120 mm. H_2CO, 2 mm. $(CH_2)_2O$) the total pressure was varied from 183 to 596 mm. by the addition of nitrogen. A plot of log(dP/dt)$_0$ *vs.* log (total pressure) was not exactly linear, the order with respect to total pressure increasing from less than 0.3 to about 0.4. Likewise the data from three preliminary experiments at 435° in which carbon dioxide was used to increase the total pressure from 120 to 560 mm. in the packed vessel indicated that the order increases from about 0.5 to 0.8. This lack of linearity of the log–log plot is probably due to the alteration of the composition of the mixture as the total pressure is increased. The rates obtained in four experiments at 415° with formaldehyde at pressures from 61 to 244 mm. and 2.0 mm. ethylene oxide were compared with the rates of four similar experiments in which carbon dioxide had been added to increase the total pressure to about 600 mm. in each case. The increase in rate gave an order of about 0.6 with respect to the total pressure.

The inert gas data can be treated also in a manner similar to that used by Horner, Style and Summers[4b] for the photolysis of formaldehyde. If the rate for a constant formaldehyde and constant ethylene oxide pressure has the following dependence on the pressure of added gas M′

$$R = (\mathrm{d}P/\mathrm{d}t)_0 = a + b(\mathrm{M}')$$

then the increase in rate caused by the inert gas obeys the relationships

$$\Delta R = b(\mathrm{M}') \text{ or } \Delta R/(\mathrm{M}') = b$$

The results for added gas pressures of 120 mm. or more are shown in Table IV; the data from experiments with only 60 mm. added gas are not accurate enough to be used for this comparison since the small increase in rate is obtained as the difference in two larger quantities.

The results indicate that the increase in rate is approximately proportional to the pressure of the added gas and that nitrogen is about one-half as effective as carbon dioxide.

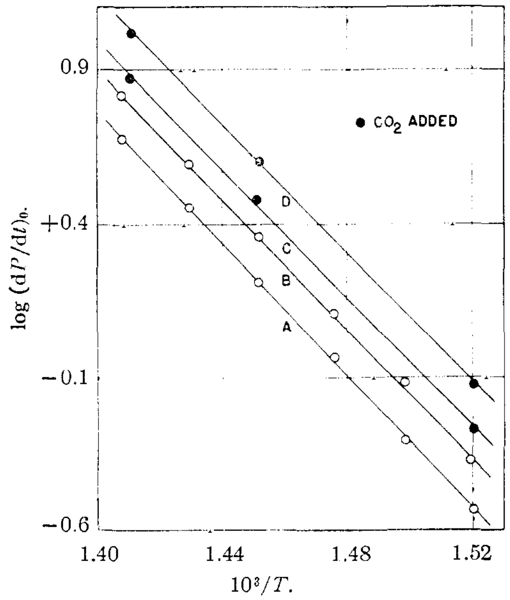

Fig. 3.—Change in the initial rate of the sensitized decomposition with temperature: A, P_0^F = 120 mm., P_0^E = 2.0 mm.; B, P_0^F = 180 mm., P_0^E = 2.0 mm.; C, P_0^F = 120 mm., P_0^E = 1.0 mm., total pressure ~600 mm.. CO_2 added; D, P_0^F = 120 mm., P_0^E = 2.0 mm., total pressure ~600 mm.. CO_2 added.

TABLE IV

DECOMPOSITION OF FORMALDEHYDE SENSITIZED BY ETHYLENE OXIDE IN THE PRESENCE OF ADDED GAS

Temp. 415.5°; P_0^E = 2.0 mm.

P_0^F, mm.	Added gas	(M′), mm.	ΔR, mm./min.	100 × $\Delta R/(\mathrm{M}')$
62	N_2	548	1.37	0.25
123	N_2	468	1.12	.24
183	N_2	407	0.92	.23
243	N_2	374	.72	.19
123	N_2	179	.45	.25
125	N_2	120	.34	.28
60	CO_2	532	2.43	.46
120	CO_2	480	2.47	.51
181	CO_2	419	2.08	.50
249	CO_2	332	1.58	.48
120	H_2CO	122	1.28	1.05

Activation Energy.—The influence of temperature upon the rate of the sensitized decomposition was investigated over the region 384–437°. The results for experiments in the unpacked vessel are summarized in Fig. 3. The slopes of the log $(\mathrm{d}P/\mathrm{d}t)_0$ *vs.* $1/T$ plots were found to be so nearly identical that the apparent activation energy obtained from any of the lines would fall within the range 48 ± 1.5 kcal./mole. A consequence of this finding is that either the mechanism of the reaction is the same with and without added inert gas or if this is not the case, only mechanisms of approximately equal activation energy can be considered as possible. It is to be noted that if the rate of change in the formaldehyde concentration had been obtained for constant concentrations at different temperatures (instead of constant pressures) the calculated activation energy of a sensitized decomposition of 3/2 order would not be more than 0.7 kcal./mole higher than the value above.

Discussion

The following equations will account for the formation of the main products of the sensitized decomposition[15]

$$(\mathrm{CH_2})_2\mathrm{O} \longrightarrow \mathrm{CH_3} + \mathrm{HCO} \qquad (1)$$

$$\mathrm{CH_3} + \mathrm{H_2CO} \longrightarrow \mathrm{CH_4} + \mathrm{HCO} \qquad (2)$$

$$\mathrm{HCO} \longrightarrow \mathrm{H} + \mathrm{CO} \qquad (3)$$

$$\mathrm{H} + \mathrm{H_2CO} \longrightarrow \mathrm{H_2} + \mathrm{HCO} \qquad (4)$$

As in the photolysis at elevated temperatures[4] reactions 3 and 4 should constitute the chain carrying reactions.

The accelerating effect of an inert gas has been found in this work and also in the photolysis where the following explanations have been advanced: (a) the inert gas molecule participates in reaction 3

$$\mathrm{HCO} + \mathrm{M} \longrightarrow \mathrm{H} + \mathrm{CO} + \mathrm{M} \qquad (3a)$$

where M is either a foreign gas or formaldehyde[4b]; (b) the inert gas hinders the diffusion of HCO radicals to the walls[4a]

$$\mathrm{HCO} + (\text{wall}) \longrightarrow \text{Products} + (\text{wall}) \qquad (5)$$

The expression proposed[4a] for the rate of chain termination in the photolysis was $k_5(\mathrm{HCO})(\text{wall})/(\mathrm{M})^n$ where n lies between 0 and 1. In addition, an

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[15] In this scheme the radical reactions which might lead to methanol have not been included since this product is formed in small amount compared to the quantities of hydrogen and carbon monoxide in the unpacked bulb.

added gas might act as a third body or might affect the activity of the surface for chain termination.

In Table V the order of the sensitized decomposition in terms of the ethylene oxide pressure (E), the formaldehyde pressure (F), and the total pressure (M) is given for various reaction schemes. A predicted pressure dependence of (E)(M) will be obtained if one uses the preceding scheme with reaction (3a) plus a chain-ending process at the wall which depends upon (HCO) but not upon the total gas pressure. A similar dependence will be obtained for case Ib. Although the condition and amount of the surface would be expected to affect the rate of a process occurring at the surface, for the sake of brevity no term of the type (wall) has been included in the expressions in Table V. The predicted dependence for cases Ia and Ib will be in reasonable agreement with the observed dependence $(E)^{0.9}(F)^{0.9}$ in the packed bulb if it is assumed that the role of formaldehyde is chiefly that of an inert gas.

TABLE V

Case	Reaction	Chain-ending process Eq.	Dependence	Pressure depend. of the chain decomp.
Ia	3a	5	(HCO)	(E)(M)
Ib	3	5	$(HCO)(M)^{-1}$	(E)(M)
IIa	3a	6	$(HCO)^2$	$(E)^{1/2}(M)$
IIa′	3a	6	$(HCO)^2(M)$	$(E)^{1/2}(M)^{1/2}$
IIIa	3a	7	(H)(HCO)	$(E)^{1/2}(F)^{1/2}(M)^{1/2}$

The observation that the ethylene oxide order with and without added gas changes from a value of almost one in the packed bulb to one-half in the unpacked bulb can be interpreted in terms of a change in the chain-ending reaction from first to second order with respect to radical (or atom) concentration. Chain terminating reactions other than 5 which might be considered are (without specifying the possible participation of an inert gas or the walls)

$$HCO + HCO \longrightarrow \text{Products} \qquad (6)$$

$$H + HCO \longrightarrow \text{Products} \qquad (7)$$

Case IIa in Table VI involving reaction 3a and reaction 6 with a second-order dependence on (HCO) yields a dependence of $(E)^{1/2}(M)$ which would be close to the observed dependence $(E)^{0.6}(F)^{0.8}$ in the unpacked bulb without added gas provided that formaldehyde is acting mainly as an inert gas. That the order is slightly above 0.5 for ethylene oxide may be due to some wall termination by reaction 5. With added gas the order decreases to 0.5. The same predicted expression would be obtained with reaction 3 if a process with the dependence $(HCO)^2(M)^{-1}$ were assumed for chain ending.

The fact that hydrogen is more effective than nitrogen or carbon monoxide in raising the rate and also carbon dioxide is more effective than nitrogen seems to be somewhat more readily interpreted on the basis of the participation of the inert gas in reaction 3a than on the basis of the influence upon the rate of diffusion of the radicals to the wall.[4b]

If the inert gas effects of formaldehyde and the added gas are considered separately, *i.e.*, substitution of $HCO + H_2CO$ and $HCO + M'$ for 3a, the rate expression for IIa will appear as

$$(dP/dt)_0 \cong k'(E)^{1/2}(F) + k''(E)^{1/2}(M')$$

or for constant values of (E) and (F)

$$(dP/dt)_0 \cong a + b(M')$$

in accord with the data shown in Table IV.

Any chain termination by reaction 6 which involves a third body (Case IIa′) tends to decrease the order with respect to (M).

For case IIa (or IIa′) the predicted activation energy would be $E_{3a} + {}^1/_2(E_1 - E_6)$. If one takes $E_1 = 67 \pm 5$ kcal./mole,[16] $E_{3a} = 14$ kcal./mole,[4] and $E_6 = 0$, one obtains an activation energy of 47.5 ± 2.5 kcal./mole which agrees with the observed value.

It appears that the principal method of chain termination in the unpacked bulb is reaction 6 which probably takes place in the gas phase. Inclusion of reaction 7 as a process for the destruction of radicals would result in a dependence upon the pressure of formaldehyde as a reactant (in addition to its inert gas effect). However, case IIIa cannot be correct for the experiments in the unpacked bulb with added carbon dioxide (Table III) because the observed order with respect to formaldehyde does not exceed 0.2. Moreover, a complete substitution of 7 for 6 in the mechanism would decrease the predicted activation energy by 4–5 kcal./mole (assuming that $E_4 = 5$ kcal./mole[4a]). Since the activation energy in the unpacked vessel is approximately the same with and without added gas, reaction 7 does not appear to be the major chain-ending reaction in the absence of added gas.

Other Sensitizers.—Experiments with 110 mm. formaldehyde at 380° showed that mercury dimethyl (1.1–1.4%) can induce a chain decomposition of formaldehyde. Analyses of the products gave evidence that the decomposition is similar to that sensitized by ethylene oxide. Likewise it was observed that a rapid chain decomposition of formaldehyde occurs at 477–489° when biacetyl (0.7–5.4%) is present. However, at 230° the addition of 2.9 mm. of di-*t*-butyl peroxide to 117 mm. of formaldehyde did not induce a chain decomposition with a large mean chain length since the small amount of formaldehyde disappearing within 20 minutes was of the same order of magnitude as the peroxide added.

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(16) Based on the values for the C–O bond in $(CH_2)_2O$ from H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945). From the data of Fletcher and Rollefson[6a] together with current values of $E_{act.}$ for radical reactions, a value of $E_1 = 67$–68 can be computed for the radical producing reaction in $(CH_2)_2O$ sensitization.