We wish to thank Mr. D. H. Etzler for assistance with part of the experimental work, and one of us (C. J. M. F.) is grateful to the Commonwealth Fund for a Fellowship which has made this work possible.

Summary

The decomposition of diethyl ether has been studied over the pressure range of 6 to 450 mm., and at temperatures from 473 to 562°. Gas analyses indicate that an aldehyde is always formed as an intermediate, and from the amounts of aldehydes present it is found that their rates of decomposition are greater than in the pure state. In confirmation of this the decomposition of acetaldehyde is catalyzed by small amounts of ether, which is explained by the formation of free radicals from diethyl ether, and the initiation of a chain decomposition of the aldehyde. The ether decomposition is interpreted in terms of the three simultaneous processes of molecular rearrangement, free radical formation and chain decomposition, and the importance of these processes in the decomposition of analogous substances is discussed.

BERKELEY, CALIF. RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Production of Free Radicals from Ethylene Oxide and the Catalysis of Other Reactions by Them

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The investigations of F. O. Rice and his co-workers have shown that free radicals are produced from a number of organic substances when they are passed through a hot tube. In the majority of cases the energy of activation for the production of the free radicals is considerably higher than that for the thermal decomposition of the substance, but for ethylene oxide the two energies of activation are similar.[1] Therefore, the fraction of free radicals present in the thermal decomposition of ethylene oxide should be relatively higher than in other compounds. In confirmation of this, we have found that small amounts are very effective in promoting the chain decomposition of other compounds,[2] and can be used to initiate chain reactions from 400 to 450°, just as azomethane has been used around 300°.[3] The catalysis of acetaldehyde by ethylene oxide is of special interest, firstly, as it is formed from ethylene oxide by isomerization and so any investigations on the decomposition of ethylene oxide must necessarily consider the chain decomposition of acetaldehyde, and secondly, because the kinetics are simplified by the fact that only one type of radical, the methyl radical, need be considered.

The kinetics of the decomposition of ethylene oxide were first studied by Heckert and Mack[4] and their results have recently been interpreted in terms of the free radical theory.[5] Thompson and Meissner[6] have shown that the decomposition is not a simple unimolecular reaction and that the variation of the rate with the initial pressure indicates a number of simultaneous reactions.

Experimental Procedure.—The reactions were followed in a manner similar to those described with diethyl ether.[7] The organic materials were purified by distillation, except for ethylene which was purified by fractionation after condensation at liquid air temperatures. Nitric oxide was formed *in situ* in the reaction vessel from ethyl nitrite, which under the experimental conditions decomposes instantaneously.[8]

$$2C_2H_5ONO \longrightarrow 2NO + CH_3CHO + C_2H_5OH$$

The Decomposition of Ethylene Oxide.—The pressure increase at completion is equal to the initial pressure, and the reaction is strictly homogeneous.[4] Aldehydes are formed as intermediate products of the decomposition and in order to obtain sufficiently large amounts with which to carry out tests, moderately large pressures were used and the gases removed at an early stage of the reaction. Acetaldehyde was detected by Rimini's test. formaldehyde by the resorcinol test, while a solution had a definite odor of acrolein; the ratios of unsaturated aldehydes and of formaldehyde to acetaldehyde were small. For an initial pressure of 380 mm., the total aldehyde

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[1] F. O. Rice and Johnson, THIS JOURNAL, **56**, 214 (1934).

[2] Fletcher, *ibid.*, **58**, 534 (1936).

[3] Allen and Sickman, *ibid.*, **56**, 2031 (1934).

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

[5] Sickman, *J. Chem. Phys.*, **4**, 297 (1936).

[6] Thompson and Meissner, *Nature*, **137**, 870 (1936).

[7] Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).

[8] Steacie and Shaw, *J. Chem. Phys.*, **2**, 243 (1934).

pressure was 8.8 ± 1.0 mm. after 8% pressure increase, and 3.8 ± 1.0 mm. after 25% pressure increase.

TABLE I

THE DECOMPOSITION OF ETHYLENE OXIDE

Temp., °C.	p_e, mm.	$10^3/t_{1/2}$, sec.$^{-1}$	$t_{1/2}/t_{1/3}$	$\frac{10^3}{p_e}\left(\frac{dp}{dt}\right)_{\max.}$ sec.$^{-1}$
474	283	5.85	1.86	4.2
	200	5.46	1.87	4.0
	163	5.18	1.87	4.0
	99	4.77	1.86	3.5
	96	4.76	1.86	3.6
	52.5	4.10	1.83	3.2
	48.1	4.05	1.85	3.3
	28.1	3.64	1.83	2.5
457	56.4	1.78	1.86	1.36
	46.9	1.67	1.85	1.34
441	145	0.93	1.89	0.73
	54.8	.790	1.92	.60
	52.0	.794	1.85	.63
428	53.3	.386	1.86	.28
414	52.1	.178	1.85	.13

The rate, as measured by the reciprocal of the half-time, $1/t_{1/2}$, is seen from Table I to decrease with the initial pressure, p_e; Heckert and Mack's results indicate that the rate is more nearly first order above 300 mm. The results of Table I have been used (Fig. 1) to calculate the energy of activation for initial pressures of 50 mm., and give the value 53,300 ± 800 cal., while at different temperatures

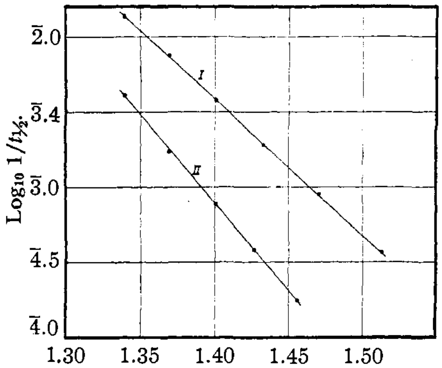
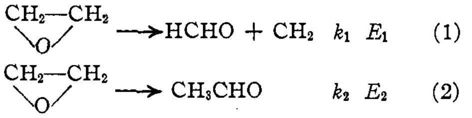


Fig. 1.—I, Acetaldehyde and ethylene oxide; II, ethylene oxide.

$$1/t_{1/2} = 1.8 \times 10^{13} \times e^{-53,300/RT} \text{ sec}^{-1}$$

The pressure–time curves show an induction period at the beginning of the reaction similar to that in other decompositions (*e. g.*, ethers, methyl alcohol) in which aldehydes are formed as intermediates. With ethylene oxide, however, its duration is proportionately less in agreement with the small fraction of aldehydes formed.

The kinetics may be interpreted on the assumptions that ethylene oxide partly decomposes to formaldehyde, and partly isomerizes to acetaldehyde: small amounts of acrolein may be produced as a side reaction by the decomposition of dioxane formed by a polymerization reaction.



$$\text{CH}_2\text{—CH}_2\text{(O)} \longrightarrow \text{HCHO} + \text{CH}_2 \quad k_1 \quad E_1 \qquad (1)$$

$$\text{CH}_2\text{—CH}_2\text{(O)} \longrightarrow \text{CH}_3\text{CHO} \quad k_2 \quad E_2 \qquad (2)$$

No methylene radicals have been detected,[9] so that they probably react extremely rapidly to form methyl radicals, which in turn lead to a chain decomposition of the aldehydes.

$$\text{CH}_2 + \text{C}_2\text{H}_4\text{O} \longrightarrow 2\text{CH}_3 + \text{CO} \quad k_3 \quad E_3 \qquad (3)$$

$$\text{CH}_3 + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3 + \text{CH}_4 + \text{CO} \quad k_4 \quad E_4 \qquad (4)$$

Methyl radicals may be removed by direct recombination either alone or in the presence of a third body.

$$2\text{CH}_3 \longrightarrow \text{C}_2\text{H}_6 \quad k_5 \quad E_5 \qquad (5)$$

$$2\text{CH}_3 + \text{M} \longrightarrow \text{C}_2\text{H}_6 + \text{M} \quad k_6 \quad E_6 \qquad (6)$$

Sickman[5] has assumed that methyl radicals recombine only at ternary collisions; the experimental results on the induced decomposition of acetaldehyde indicate, however, that a direct bimolecular association also occurs. Let the pressure of ethylene oxide be x_1, of methylene radicals be x_2, of acetaldehyde be x_3, of methyl radicals be x_4, and let the total pressure, including that of inert gases, be P; then, when steady concentrations of methylene and methyl radicals are established, if reaction 1 is first order

$$x_4 = \sqrt{\frac{2k_3x_1x_2}{k_5 + k_6P}} = \sqrt{\frac{2k_1x_1}{k_5 + k_6P}} \qquad (1)$$

It is justifiable to assume that $k_2 > k_1$, as the ratio of formaldehyde to acetaldehyde is small, and the amount of hydrogen, which would be formed from the decomposition of formaldehyde, is only 7% of the reaction products. Furthermore, as the amounts of aldehyde built up are in general agreement with the assumption that there is no direct formation of carbon monoxide and methane from ethylene oxide (see later), it is apparent that the pressure increase is mainly due to reaction 4. The observed rate of pressure increase, (dp/dt), is thus given by

$$\left(\frac{dp}{dt}\right) \sim k_4x_4x_3 \sim k_4x_3\sqrt{\frac{2k_1x_1}{k_5 + k_6P}} \qquad (2)$$

This rate increases (during which time there is an induction period) until the acetaldehyde pressure

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[9] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Maryland, 1935 ,p. 161.

is a maximum, x_3'. As this occurs at a very early stage, one may put $x_1 = p_e$, and at this time, $t_{\text{max.}}$

$$k_2 p_e = k_4 x_4 x_3' \qquad (3)$$

so that

$$x_3' = \frac{k_2 p_e}{k_4} \sqrt{\frac{k_5 + k_6 P}{2k_1 p_1}} \qquad (4)$$

and

$$(\mathrm{d}p/\mathrm{d}t)_{\text{max.}} \sim k_2 p_e \qquad (5)$$

The maximum rate is actually (see Table I) proportional to rather more than the first power of the ethylene oxide pressure, and so inert gases may slightly increase $(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$ if they help to maintain the Maxwell–Boltzmann distribution of activated molecules. Hydrogen, which is usually far more effective in this way than other gases, has been found to increase the rate of reaction. On the other hand, it follows from equation 4 that inert gases which contribute to the term P, or substances such as nitric oxide which remove free radicals,[10] should increase the maximum amounts of aldehydes and, therefore, of $t_{\text{max.}}$ and of $t_{1/2}/t_{1/3}$. The effect of inert gases found by Heckert and Mack,[4] and the results with small amounts of nitric oxide, p_{NO}, given in Table II are in agreement with these deductions. The fact, however, that $(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$ is not changed by small amounts of nitric oxide, indicates that not the isomerization of ethylene oxide, but only the subsequent decomposition of acetaldehyde is a chain reaction.

TABLE II

THE EFFECT OF NITRIC OXIDE ON THE DECOMPOSITION OF ETHYLENE OXIDE

Temp. 441°C.

p_e, mm.	p_{NO}, mm.	$t_{\text{max.}}$, sec.	$(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$, mm./sec.	$t_{1/2}/t_{1/3}$	$t_{1/2}$, sec.
180	..	60	0.14	1.87	960
182	3	240	.15	1.74	980
177	6	330	.14	1.69	1030

The Catalysis of Organic Reactions by Ethylene Oxide.—As ethylene oxide produces relatively to most other organic compounds a copious supply of free radicals, it is extremely suitable for the study of the extent to which chain reactions involving free radicals may occur. It is possible to invent a chain mechanism for the decomposition of nearly every organic molecule but without knowledge of the kinetics of the separate steps it is often impossible to predict whether such mechanisms will take place. Our experiments contrast the ease with which acetaldehyde and diethyl ether may be made to undergo chain decompositions, compared to the difficulty with which acetone and methyl alcohol decompose in the presence of free radicals. The induced decomposition of acetaldehyde has been used to test for chain-breakers as well as to illustrate the efficiency of inert gases in promoting the recombination of methyl radicals at ternary collisions.

(1) **The Decomposition of Acetaldehyde.**—Mixtures were made up in which the ratio of the pressure of ethylene oxide, p_e, to acetaldehyde, p_a, was small, and the rates of pressure increase were measured at a number of different initial pressures, p_0. The rate of the uncatalyzed acetaldehyde decomposition was always negligible in comparison with that of the catalyzed reaction. The relative rates of reaction have been compared from the half-times, *i. e.*, the times for a pressure increase of 50%, as the "end-points" are double the total initial pressure, p_0. Figure 2 shows the variation of $1/t_{1/2}$ with p_0 at 441°, and it is seen from Table III that $1/t_{1/2}$ is proportional to the square root of the ethylene oxide pressure, but for a constant ethylene oxide pressure decreases slightly with p_0. It has been shown previously that some recombination of free radicals occurs at ternary collisions, and the present results indicate that ethylene oxide or acetaldehyde can act as the third body. Substituting in equation 2, the initial rate, $(\mathrm{d}p/\mathrm{d}t)'$, of the induced reaction is given by

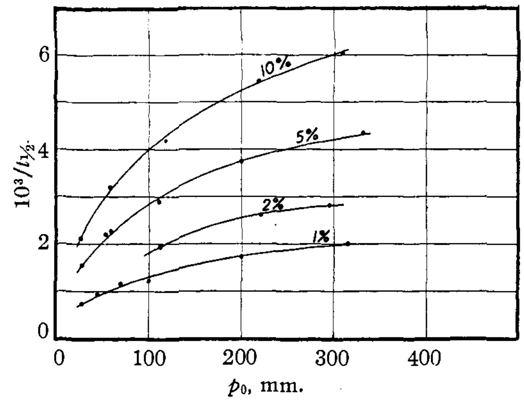

Fig. 2.—Rates of reaction of acetaldehyde with various percentages of ethylene oxide. Temp. 441°C.

$$\left(\frac{\mathrm{d}p}{\mathrm{d}t}\right)' = k_4 \sqrt{p_e} \times p_a \times \sqrt{\frac{2k_1}{k_5 + k_6 p_0}} \qquad (6)$$

Approximate values of the constants may be obtained by a comparison with the experimental

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(10) Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936).

results, on the assumption that the correction due to the decomposition of the ethylene oxide is small. The mean values of $1/(t_{1/2}\sqrt{p_e})$ may be expressed in the form

$$\frac{1}{t_{1/2}\sqrt{p_e}} = \frac{1.39 \times 10^{-3}}{(1 + 1.93 \times 10^{-3}p_0)^{1/2}} \qquad (7)$$

from which the calculated results of Table III have been derived. As the initial rate is found by experiment to equal approximately 0.77 $p_a/t_{1/2}$, it follows that

$k_4\sqrt{2k_1}/\sqrt{k_5} = 1.07 \times 10^{-3}$, and $k_6/k_5 = 1.93 \times 10^{-3}$

Table III

Values of $10^3/t_{1/2}\sqrt{p_e}$ for Different Mixtures of Acetaldehyde and Ethylene Oxide at Different Initial Pressures, Temp. 441°

p_e/p_0	p_0 = 300 mm.	200 mm.	100 mm.	50 mm.
0.10	1.09	1.18	1.23	1.32
.05	1.09	1.19	1.25	1.33
.02	1.15	1.22	1.24	..
.01	1.13	1.21	1.26	1.31
Mean	1.115	1.20	1.245	1.32
Calculated	1.11	1.18	1.27	1.33

Table IV

The Retardation of the Chain Decomposition of Acetaldehyde by Various Substances

Gas	Temp., °C.	p_e/p_0	p_0, mm.	p_g, mm.	$t_{1/2}$, sec.	$t_{1/2}'/t_{1/2}$
Helium	441	0.10	120	222	264	0.90
		.10	55.3	115	342	.90
		.05	119	240	385	.87
		.05	121	120	351	.95
		.05	53.5	121	502	.90
		.01	69.0	153	995	.90
Nitric		.05	208	2.3	804	.32
oxide		.05	199	5.0	1548	.17
		.05	148	18	8100	.036
Ethylene		.05	102	102	1160	.31
Diethyl ether	465	.05	196.5	10	111.5	1.00
Acetone		.05	114.7	19.8	150	0.99
		.05	67.2	88.8	236.5	.81
Methyl		.05	33.2	10.0	364	.72
alcohol		.048	97.8	100.5	327	.45
		.048	94.7	100.8	325	.45

The term k_6P of equation 1 is composite when more than one type of molecule is present, but the value of k_6/k_5 just obtained will refer predominantly to acetaldehyde. The rate of reaction has been found to be retarded by helium (Table IV), and the increase in $t_{1/2}$ by approximately 10% with a 2–1 helium ratio, indicates that for helium k_6/k_5 is 1.4×10^{-3}. It follows from equation 7 that for the pressures used, the number of free radicals which combine at ternary collisions is rather smaller than the number which combine directly either on the surface or in the gas phase. Experiments carried out at 446° in a reaction vessel packed with tubes showed the rate to be slower by about 30%, although the surface–volume ratio was increased by a factor of eleven: it is evident, therefore, that at this temperature the recombination of free radicals is mainly a homogeneous reaction. At temperatures around 300°, Allen and Sickman[3] have found that the induced decomposition of acetaldehyde is retarded by over 50%. This decrease in the retardation by the surface at higher temperatures agrees with the investigations of Paneth, Hofeditz and Wunsch[11] who have found that the heterogeneous recombination of free radicals decreases with the temperature. At temperatures and pressures sufficiently low for heterogeneous recombination to predominate, inert gases, by impeding the diffusion of radicals to the walls will, therefore, increase and not decrease the rate of reaction.

The energy of activation of the induced reaction was determined for a mixture containing 5% of ethylene oxide at initial pressures of approximately 200 mm. (Fig. 1). The half-times satisfy the equation

$$1/t_{1/2} = 2.1 \times 10^{10} \times e^{-41,500/RT} \text{ sec.}^{-1}$$

The energy of activation (41,500 ± 500 cal.) can be lower than that for ethylene oxide as the rate has been found to depend upon the square root of the ethylene oxide concentration.

Now that the rate of the induced acetaldehyde decomposition is known, it is possible to compare the amounts of acetaldehyde actually formed from ethylene oxide with those calculated on the assumption that practically all of the ethylene oxide isomerizes to acetaldehyde. From equations 1, 3, 5 and 6, the initial rate of the induced reaction, and the maximum rate of the ethylene oxide decomposition with the same ethylene oxide pressure are related by the expression

$$\left(\frac{dp}{dt}\right)' \Big/ \left(\frac{dp}{dt}\right)_{\text{max.}} \sim p_a/x_3'$$

Comparing these rates at 441° for p_e = 30 mm., $x_3' \sim 3$ mm. However, from equation 4, it follows that x_3' is roughly proportional to $\sqrt{p_e}$, so that for p_e = 380 mm., $x_3' \sim 11$ mm. The aldehydes determined experimentally at an early stage of the reaction were 8.8 mm. for this initial pressure.

The chain length of the acetaldehyde induced reaction may be expressed in terms of the fraction,

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[11] Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 372 (1935).

z, of methyl radicals produced from ethylene oxide. At 441° with a mixture containing 20 mm. of ethylene oxide and 180 mm. of acetaldehyde $(dp/dt)' = 1.34$ mm./sec. At the same temperature extrapolation of the results with ethylene oxide alone gives for $p_e = 20$ mm. a maximum rate of 0.012 mm./sec. Therefore, the chain length is approximately $100/z$. Assuming that the hydrogen and ethane that are present in the reaction products from ethylene oxide are formed solely by way of reaction 1, the observed products (CO, 50%; CH_4, 36%; H_2, 7%; C_2H_6, 7%) would indicate that 14% of the ethylene oxide decomposes to methylene and formaldehyde. The fraction decomposing in this way may, of course, vary with the initial pressure, but if it is not very different at lower pressures, z will be approximately 0.3 as two methyl radicals are formed by reaction 3 from each methylene radical.

It has recently been found that small quantities of nitric oxide can retard certain reactions, due to the elimination of any chain reactions by the removal of free radicals by the nitric oxide.[10] Table IV, which gives the ratio of the half-time, $t_{1/2}'$, in the absence of nitric oxide to the half-time, $t_{1/2}$, in the presence of nitric oxide, shows that the chain decomposition of acetaldehyde is retarded markedly. Organic substances such as acetone and methyl alcohol, when present in large quantities, can also act as chain-breakers (Table IV); this indicates that they can compete effectively with acetaldehyde for methyl radicals, but that the re-formation of a methyl radical is less frequent, either on account of the relative stability of the radicals CH_3O and CH_2COCH_3, or due to their relative ease of recombination with other radicals, *e. g.*

$$CH_3 + CH_3OH \longrightarrow \dot{C}H_4 + CH_3O$$
$$CH_3O \longrightarrow HCHO + H$$
$$CH_3O + CH_3 \longrightarrow CH_3OCH_3$$

Ethylene also retards the rate of pressure increase but its influence is complicated by the decrease in pressure which must occur from its polymerization.

(2) **Diethyl Ether.**—With a mixture containing 5% of ethylene oxide the initial rate at 441° for an ether pressure of 180 mm. is increased by a factor of twenty and the reaction goes 82% toward completion. If the chain length of the ethylene oxide catalyzed reaction is not very different from that of the chains in the normal ether decomposition, it is apparent that the proportion of free radicals produced directly from ether is only about one four-hundredth of the proportion from ethylene oxide: considerably less than one ether molecule in a thousand, therefore, forms a free radical. Extrapolation of the ether decomposition inhibited by nitric oxide[10] indicates that some 15% of the ether decomposes by a non-chain reaction, so that it follows that in the uncatalyzed reaction there is an appreciable decomposition which takes place neither to free radicals nor by a chain reaction, but rather by a direct molecular rearrangement.[7] Further, the chains must be few and long rather than numerous and short.

(3) **Ethylene.**—The rate of polymerization of 176 mm. of ethylene is twenty times greater in the presence of 3.7 mm. of ethylene oxide at 441°.

(4) **Acrolein.**—The rate of decomposition at 470° is increased by a factor of four with 10% of ethylene oxide.

(5) **Methyl Alcohol.**—Some interaction between free radicals and methyl alcohol occurs which (a) decreases the rate of pressure increase as compared to that for the pure ethylene oxide, and (b) leads to the decomposition of some fraction of the methyl alcohol. Thus at 465° for $p_e = 98$ mm., $t_{1/2} = 173$ sec. In the presence of 105 mm. of methyl alcohol, $t_{1/2} = 211$ sec., but the final end-point indicates that 24.5% of the methyl alcohol has decomposed. The uncatalyzed reaction is inappreciable at this temperature.[12]

We wish to thank Dr. O. K. Rice for many helpful discussions, and one of us (C. J. M. F.) is grateful to the Commonwealth Fund for a Fellowship, which has made this work possible.

Summary

The main reaction of ethylene oxide when heated to temperatures around 450° is an isomerization to acetaldehyde. Free radicals are also formed at the same time and decompose the acetaldehyde by a chain mechanism though they do not affect the isomerization process. Though the fraction of free radicals formed from ethylene oxide is comparatively small, it is relatively much higher than for most other organic compounds, and small amounts effectively catalyze the decomposition of other substances. The induced decomposition of acetaldehyde has been studied in detail, and the rate varies with the square root of the ethylene oxide concentration and with rather less than the first power of the acetaldehyde concentration; it is retarded slightly by helium,

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[12] Fletcher, *Proc. Roy. Soc.* (London), **A147**, 119 (1934).

moderately by acetone and methyl alcohol and considerably by nitric oxide. The energy of activation of this induced reaction is 41,500 ± 500 cal., and the kinetics have been explained by a chain decomposition initiated by free radicals, which disappear partly at ternary collisions and mainly in the gas phase.

BERKELEY, CALIF. RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemical Reaction of Chlorine with Formic Acid

BY HELEN L. WEST[1] AND G. K. ROLLEFSON

Introduction

A study of the photochemical reaction between formic acid and chlorine was undertaken because it offered the possibility of proceeding in stages involving the formation of an intermediate substance, less stable than that found in the formaldehyde chlorine reaction,[2] but stable enough to exist in appreciable concentrations in the reacting mixture. Furthermore, on account of the measurable equilibrium existing between single and double molecules of formic acid, it was possible to test the relative reactivity of the two forms. The results presented in this paper show the formation of the expected intermediate, chloroformic acid, but do not show any appreciable difference in reactivity between the single and double molecules.

Materials and Apparatus

Anhydrous formic acid was prepared from Merck 90% C. P. acid by a preliminary dehydration with copper sulfate followed by repeated distillations *in vacuo* from finely pulverized boric anhydride. Before each of three distillations the acid remained in contact with the boric anhydride for at least one day. In order to prevent any slow thermal decomposition, the purified formic acid was kept in a trap immersed in a liquid air bath. The purity of the acid was evidenced by the agreement of the vapor pressures with those reported by Ramsperger and Porter[3] and Coolidge.[4]

The melting point determined from the vapor pressure-temperature curve was 8.3 ± 0.05°.

The chlorine was prepared by heating anhydrous cupric chloride. The supply used for the second series of experiments was purified by fractional distillation and stored in a three-liter bulb. It was admitted to the reaction vessel by means of a stopcock lubricated with Shell Apiezon grease (this was found to be practically inert toward both chlorine and formic acid). The absorption coefficient of this chlorine was found to be 26 at 3650 Å. in good agreement with the values given by Gibson and Bayliss.[5]

Comparison of data obtained under similar conditions using this chlorine and also chlorine prepared directly from copper chloride showed no essential differences provided the copper chloride had been heated to the decomposition temperature numerous times. Unless this treatment were followed, an inhibitory effect upon the reaction resulted.

A sample of Eastman Kodak Co. C. P. methyl formate was vacuum distilled from phosphorus pentoxide.

In the first series of experiments a spherical Pyrex reaction vessel of 250 cc. capacity was employed. Although the temperature coefficient of the reaction is negligible, some thermostating was necessary to prevent variations in the equilibrium constant for the relation of single to double molecules of formic acid. Water at temperatures from 20–25° was allowed to run over the cell. The light source was a 500-watt tungsten lamp, placed 80 cm. from the reaction bulb. The course of the reaction was determined by the pressure change. Due to the reactivity of formic acid, the pressure had to be read indirectly by means of a click gage connected externally to a sulfuric acid manometer. All pressures are recorded in cm. of sulfuric acid.

In order to provide an independent method for the determination of the amount of chlorine which had reacted, a second series of experiments was performed in which in addition to measuring the pressure change a simultaneous measurement of the absorption of light by chlorine could be made. These experiments were carried out using a cylindrical Pyrex reaction vessel, 15 cm. long with plane windows at the ends, which was immersed in a water-bath. The bath could be thermostated accurately at any desired temperature between 20 and 30°. The light both for the absorption measurements and the photoactivation process was supplied by a quartz Hereaus mercury arc focused by a pair of quartz lenses and passed through a Corning violet ultra filter No. 586 so as to isolate the groups of lines near 3650 Å. After the light had passed through the reaction vessel, it was focused on a Moll surface thermopile connected to a sensitive galvanometer. Variations in intensity of the arc were corrected for by taking simultaneous readings on another thermopile illuminated by a beam which had not passed through the reaction vessel. Quantum yields were calculated from these data after the

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[1] Swarthmore Sigma Xi Fellow, 1934–1935.

[2] Krauskopf and Rollefson, THIS JOURNAL, **56**, 2542 (1934).

[3] (a) Ramsperger and Porter, *ibid.*, **48**, 1267 (1926); (b) Ramsperger and Porter, *ibid.*, **50**, 3036 (1928).

[4] Coolidge, *ibid.*, **50**, 2166 (1928).

[5] Gibson and Bayliss, *Phys. Rev.*, **44**, 188 (1933).