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.

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[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).

surface thermopile had been calibrated by means of a standard lamp.

Results and Discussion

The net reaction between formic acid and chlorine may be represented by the equations

$$HCOOH + Cl_2 = 2HCl + CO_2 \quad (1)$$
$$(HCOOH)_2 + 2Cl_2 = 4HCl + 2CO_2 \quad (2)$$

Both of these equations and the equilibrium between the two types of molecules must be taken into consideration in order to calculate the composition of the mixture after any observed pressure change. These reactions are strictly photochemical at the temperatures used, and blank tests showed that formic acid is not affected by light of the wave lengths involved in these experiments.

That hydrogen chloride and carbon dioxide are the only products formed in appreciable amounts is shown by the fact that under no conditions were any gases obtained which could not be condensed by liquid air. In addition, the equilibrium constants $K = (HCOOH)^2/((HCOOH)_2)$ calculated on the assumption that the products are as shown above compare favorably with those reported by Ramsperger and Porter.[3] These constants were computed from the over-all pressure change in experiments carried to completion in the presence of excess chlorine.

TABLE I

RATE CONSTANTS FOR DIFFERENT PRESSURES OF CHLORINE AND FORMIC ACID

A. 500-Watt Lamp Light Source

% Formic acid reacted	Residual cm.		Slope	Temp., °C.	K used	$k_{I}(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
	Formic acid	Cl_2					
0.43	7,4	76.4	0.200	21	1.5	0.86	0.31
.48	5.2	16.0	.105	23	1.6	1.19	.50
.41	3.4	102.0	.128	22	1.55	0.78	.37
.39	2,5	8.8	.029	24	1.7	.72	.40
.44	3.7	20.1	.085	21	1.5	1.11	.51
[.29	7,8	7.0	.029	22	1.55	0.40	.14]
					Average	.93	.42

B. Hg Arc Light Source; $K = 2.1$; temp. 27°

% Formic acid reacted	Residual cm.		Slope	$k_{I}(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
	Formic acid	Cl_2			
0.32	7.1	13.4	0.036	0.33	0.138 (1)
.29	5.3	25.6	.029	.24	107
.22	15.8	11.0	.057	.36	.108 (2)
.22	10.5	23.3	.050	.27	.097
.29	9.0	12.1	.038	.32	.122
.24	7.2	23.4	.042	.29	.120 (3)
[.21	15.3	8.4	.032	.23	.073]
			Average	.30	.115

A comparison of the amounts of chlorine which have reacted at various stages of the reaction as determined from the change in light absorption and from the over-all pressure change is given in Table II. The fourth column gives the difference between the actually observed deflection of the thermopile galvanometer and that which would have been observed if an amount of chlorine had reacted corresponding to the observed pressure change. The first example shows no discrepancies other than might be expected due to experimental errors; the second shows a definite difference which starts at zero and increases regularly as the reaction progresses; the third shows a discrepancy which increases to a maximum and then disappears as the reaction goes to completion. Whenever such a difference appears it is always such that the residual chlorine pressure as calculated from the pressure change is greater than that found by the absorption measurements. This behavior could be expected if the first reaction forms an intermediate substance such as chloroformic acid which then decomposes to give the final products, carbon dioxide and hydrogen chloride. If the conditions are such that the rate of decomposition of this intermediate is sufficiently slow compared to the rate of formation, an appreciable amount of it will be built up during the course of the reaction. By analogy to the behavior of formyl chloride in the reaction between formaldehyde and chlorine, we expect the decomposition of chloroformic acid to be catalyzed by chlorine in the light and by the walls of the reaction vessel. If such conditions prevail, we should expect the greatest discrepancy in the presence of excess formic acid as is actually the case. The variability of the behavior with excess chlorine as shown by experiments 1 and 3 in Table II may be attributed to variations in the rate of the heterogeneous reaction similar to that found with formyl chloride.

Another fact which supports the hypothesis of an unstable intermediate was obtained by heating the reaction vessel after a reaction had been run with relatively low chlorine. Under these conditions, an additional pressure change of approximately one centimeter was observed. Blank experiments showed that this change could not be ascribed to the excess formic acid.

The pressure–time curves (*cf.* Fig. 1) are essentially the same whether excess chlorine or excess formic acid were present. Under no conditions

TABLE II

CHARACTERISTIC EXPERIMENTS SHOWING THE EFFECT OF THE FORMATION OF CHLOROFORMIC ACID

Time, sec.	% Formic acid reacted	Cm. Cl_2 absorption	ΔP	$D_{abs.} - D_{\Delta P}$	$k_I(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
1. Initial Pressure, 10.5 cm. Formic Acid, 19.5 cm. Cl_2						
30	0.12	17.6	17.4	−0.2	0.43	0.16
60	.22	15.8	15.4	− .4	.41	.16
105	.32	13.5	13.4	0	.33	.14
155	.41	11.6	12.0	.4	.29	.12
220	.49	10.2	10.5	.4	.27	.12
330	.59	8.7	8.7	0	.25	.12
720	.74	6.2	6.1	− .2		
2. Initial Pressure, 20.3 cm. Formic Acid, 19.3 cm. Cl_2						
8	0.03	18.0	18.3	0.1	0.43	0.12
23	.07	16.4	16.8	.4	.43	.12
38	.10	15.0	15.5	.3	.43	.12
93	.22	10.0	11.0	1.9	.36	.11
154	.29	7.1	8.1	2.0	.26	.08
335	.37	4.3	5.5	3.2	.12	.04
1200	.50	1.5	2.8	3.3	..	..
3. Initial Pressure, 9.4 cm. Formic Acid, 27.3 cm. Cl_2						
30	0.16	23.9	24.6	0.4	0.39	0.16
60	.24	22.5	23.4	.6	.29	.12
90	.35	20.6	21.6	.9	.29	.12
120	.40	19.8	20.7	.7	.27	.12
180	.50	18.5	19.2	.6	.23	.11
300	.65	16.3	16.8	.6	.19	.095
600	.82	14.1	14.3	.3	.16	.091
3600	.94	12.6	12.6	0		

do they show an initial "foot" which could be attributed to the time required to build up the intermediate (*cf.* the reaction between formaldehyde and chlorine[2]). This is in accord with the data in Table II which show that the concentration of the intermediate does not attain its maximum value until a considerable amount of reaction has occurred.

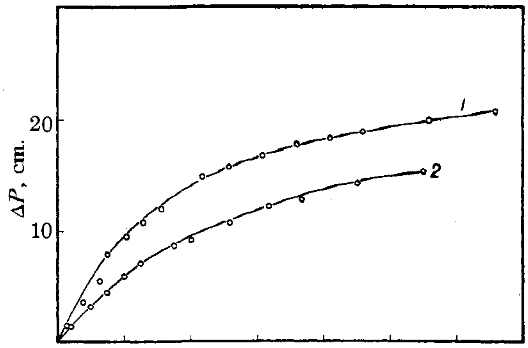

Fig. 1.—Pressure change–time curves: (1) initial pressure, 20.3 cm. formic acid, 19.3 cm. Cl_2; (2) initial pressure, 10.5 cm. formic acid, 19.5 cm. Cl_2.

The rate law for the reaction was deduced from an analysis of the data represented by curves of the type shown in Fig. 1, and separate tests in which the light intensity was varied by the use of calibrated screens. The constants tabulated in Tables I and II are calculated from the equations

$$\frac{-d(Cl_2)}{dt} = k_1(I_{abs.})^{1/2}\,(HCOOH) = k_I(I_0)^{1/2}\,(Cl_2)^{1/2}\,(HCOOH) \quad (1)$$

$$\frac{-d(Cl_2)}{dt} = k_{II}(I_{abs.})^{1/2}\,[H(COOH) + (HCOOH)_2] = k_{II}(I_0)^{1/2}\,(Cl_2)^{1/2}\,[(HCOOH) + (HCOOH)_2] \quad (2)$$

The exponent of $(I_{abs.})$ was found to change from one-half to one as the chlorine pressure or the light intensity was lowered. This effect manifests itself in the data shown in the tables as a falling off in the values of k_I and k_{II}. The results in brackets in Table I and those in Table II illustrate this behavior. The decrease in the constants can be attributed partly to the formation of chloroformic acid which makes the actual chlorine less than that calculated from the pressure change and the initial pressure. In experiments in which relatively large amounts of the intermediate appear, this effect is especially noticeable. It is obvious, however, that the influence of the change of the exponent of $I_{abs.}$ is much greater. With light intensities such as were used in these experiments, the square root law held for chlorine pressures of 10–15 cm. of sulfuric acid or greater.

A comparison of values of k_I and k_{II} listed in Tables I and II shows a slight preference for the law involving k_{II}. The most strenuous tests are those experiments with excess chlorine in which a large fraction of the formic acid was used up (1 and 3, Table II). In these both constants show a decrease as the run progresses but k_I shows a drop of roughly 45% over the same range that k_{II} drops only 25%.

These constants are calculated by plotting the residual chlorine pressure against time, drawing tangents to the curves at the desired points and using the slopes of these tangents in the rate laws (1) and (2). They represent constants derived from differential rates rather than averages over the range indicated. It is concluded from the data which have been acquired that the single and double molecules react with approximately the same speed.

As has been mentioned, the second experimental arrangement used, permitted a determination of the quantum yield. Some of the values obtained are listed in Table III. It is to be noted that even at the relatively low pressures employed in these experiments, the maximum quantum yields are around two thousand. This value is comparable with the chain length of the hydrogen–chlorine reaction under similar conditions.

TABLE III

QUANTUM YIELDS OF CHLORINE–FORMIC ACID REACTION AT 3650 Å. AND 27°

Initial cm. formic acid	Initial cm. Cl_2	Cm. Cl_2 reacted	Time, sec.	Yield
6.41	22.7	3.0	49	2145
		6.6	172	1413
9.4	27.3	6.7	90	2106
		7.5	120	1794
13.5	30.3	5.6	82	1981
		11.7	230	1595
6.4	15.3	5.8	140	1712
10.5	19.5	7.9	155	2230
		9.3	220	1659

The light sensitized reaction between methyl formate and chlorine has been reported[6] as forming methyl chloroformate followed by substitution in the methyl groups in the presence of excess chlorine. Therefore, a quantitative study of this reaction was undertaken in the possibility of observing the stages in the chlorination of the formate radical in a case the intermediate of which had been isolated. A typical chlorine–time curve is shown in Fig. 2. From this curve it is apparent that no discrete steps in the chlorination can be detected. Substitution is occurring in the methyl group simultaneously with substitution in the formate radical. The absence of any pressure change indicated that there was no decomposition of the chlorine derivatives.[7] The quantum yields for the chlorine–methyl formate experiments are of the same order of magnitude as those of the formic acid reaction.

The facts which have been presented show that the photochemical reaction between chlorine and formic acid is a chain reaction which proceeds at least partially through chloroformic acid; the final products are carbon dioxide and hydrogen chloride. The following set of reactions will account for all of the observed facts including the rate laws

$$Cl_2 + h\nu = Cl + Cl^* \qquad (1)$$
$$Cl + HCOOH = COOH + HCl \qquad (2)$$
$$COOH = CO_2 + H \qquad (3a)$$
$$COOH + Cl_2 = ClCOOH + Cl \qquad (3b)$$
$$H + Cl_2 = HCl + Cl \qquad (4a)$$
$$ClCOOH = CO_2 + HCl \qquad (4b)$$
$$Cl + Cl + (M) = Cl_2 \qquad (5)$$

Step (5) becomes $Cl + (M) = {}^1/_2Cl_2$ when $I_{\text{abs.}}$ replaces $I_{\text{abs.}}{}^{1/2}$. For the double molecules (2) and (3) are replaced by

$$(HCOOH)_2 + Cl = (HCOOH)(COOH) + HCl \qquad (2')$$
$$(HCOOH)(COOH) = (HCOOH) + CO_2 + H \qquad (3'a)$$
$$(HCOOH)(COOH) + Cl_2 = HCOOH + ClCOOH + Cl \qquad (3'b)$$

The failure to obtain higher concentrations of chloroformic acid may be attributed to 3a and 3′a since they supply a path to the final products which does not involve this intermediate. The competition between 3a and 3b and 3′a and 3′b requires that larger amounts of chloroformic acid should be obtained with high chlorine concentrations unless there is a chlorine catalyzed decomposition as well. Apparently such a situation exists as is shown by experiments made in the presence of excess chlorine.

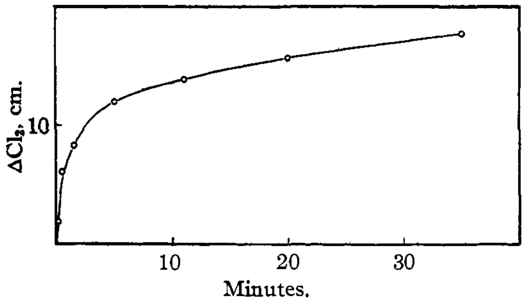

Fig. 2.—Chlorine reacted–time curve for initial pressures: 15.3 cm. $HCOOCH_3$, 58.5 cm. Cl_2.

The theoretical rate law calculated from the mechanism by the usual procedure is

$$\frac{-d(Cl_2)}{dt} = \frac{\sqrt{2}k_2}{\sqrt{k_5}}(I_{\text{abs.}})^{1/2}(HCOOH) \text{ or}$$
$$(\sqrt{2}k_2'/\sqrt{k_5})(I_{\text{abs.}})^{1/2}((HCOOH)_2)$$

Since reactions 3, 3′ and 4 do not affect the final form of the rate law, they may be replaced by any others which will allow for the formation of some chloroformic acid and give carbon dioxide and hydrogen chloride as the final products.

Summary

An investigation of the photochemical reaction between chlorine and formic acid has shown (1) there is no marked difference in the reactivity of the single and double molecules, (2) the reaction proceeds through a chain mechanism involving

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(6) Kling, Florentin, Lassieur and Schmutz, *Compt. rend.*, **169**, 1046 (1919).

(7) A small white deposit appeared on the walls of the reaction vessel when water vapor was admitted after the reaction of chlorine with either formic acid or methyl formate had started. No effect was observed with moisture and the initial reactants. Amounts of this white substance sufficient for analysis could not be obtained, and its formation affected the reaction chiefly through a diminution in rate.

the formation of appreciable quantities of an intermediate, probably chloroformic acid. If excess chlorine is present or if the reaction vessel is heated to destroy any residual intermediate, the products are solely carbon dioxide and hydrogen chloride. A mechanism which will account for the observations has been presented.

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

The Heat Capacity and Entropy of Potassium Permanganate from 15 to 300° Absolute. The Entropy and Free Energy of Permanganate Ion

BY OLIVER L. I. BROWN, WENDELL V. SMITH AND WENDELL M. LATIMER

As part of a general program for the evaluation of the entropies of the common inorganic ions, the entropy of potassium permanganate has been determined.

Material.—Kahlbaum "For analysis with guarantee" grade potassium permanganate was used in the first series of heat capacity runs. These measurements demonstrated that the sample contained water. The material was removed from the calorimeter, ground in a mortar, and dried over sulfuric acid in a darkened desiccator. The sample was then analyzed by titration with sodium oxalate solution. Within experimental error (±0.1%) the sample was 100% potassium permanganate.

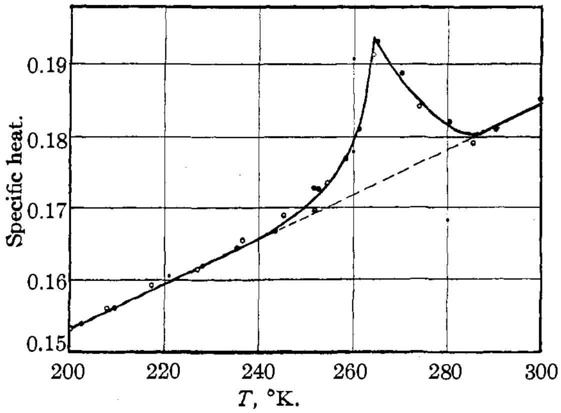

Fig. 1.—Specific heat of wet sample of potassium permanganate.

TABLE I

SPECIFIC HEAT OF SERIES I (WET SAMPLE)

Run	T, °K.	C_p, cal./gram/deg.	ΔT
1	202.67	0.1539	6.426
2	209.69	.1561	6.176
3	221.15	.1605	6.898
4	228.15	.1619	6.678
5	235.37	.1643	7.542
6	243.53	.1667	8.417
7	251.76	.1696	8.060
8	251.69	.1727	7.538
9	258.37	.1768	7.236
10	265.00	.1931	7.573
11	252.58	.1726	9.776
12	261.24	.1809	9.162
13	270.26	.1887	9.460
14	280.40	.1819	9.640
15	290.41	.1808	10.520
16	300.04	.1851	11.149
17	200.34	.1532	7.234
18	208.12	.1560	9.132
19	217.34	.1592	10.281
20	227.06	.1614	9.836
21	236.47	.1654	9.320
22	245.35	.1689	8.898
23	254.39	.1732	9.586
24	264.14	.1912	9.720
25	274.10	.1840	10.885
26	285.55	.1789	11.895

Heat Capacity Measurements.—The heat capacities were determined by the experimental method used by Latimer and Greensfelder.[1] One calorie was assumed equal to 4.1833 int. joules. The molecular weight of potassium permanganate was taken as 158.03. Measurements on Series I were made on a sample of 133.034 g. (weight *in vacuo*). An anomaly was found in the heat capacities, which appeared to be due to the presence of considerable water included in the sample. On removing the sample from the calorimeter the crystals were found to decrepitate upon heating, confirming the presence of water. The specific heats of the sample in the neighborhood of the melting point of water are presented in Table I and plotted as a function of temperature in Fig. 1. The half filled circles represent runs 1–7 (Oct. 14, 1933), the filled circles runs 8–16 (March 28–29, 1934), the open circles runs 17–26 (April 4, 1934). The area between the dotted curve and the solid curve corresponds to 0.28 cal., and after subtracting 0.02 cal. for the heat absorbed by the solution of potassium permanganate in the liquid water formed, corresponds to the melting of 0.0033 g. of water in each gram of sample. Although the eutectic of ice and potassium permanganate occurs at about 272.5°K., the maximum of the observed "hump" occurs at 265°K. and the abnormal specific heats persist even down to about 245°K. In view of the large amount of water present it was decided to dry the sample as described above, and repeat the entire series of measurements, even though it appeared reasonable that the heat capacity of dry potas-

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[1] Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).