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Thesis by

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THE KINETICS OF THE THERMAL DECOMPOSITION OF TRICHLOR METHYL CHLORFORMATE

Trichlor methyl chlorformate gas is known to decompose at 300°C to give two molecules of phosgene[1] as shown by the equation

$$ClCOOCCl_3 = 2\ COCl_2 \qquad (1)$$

The liquid can be decomposed at room temperature by the addition of various metallic chlorides such as aluminum chloride[1,2] in which case, however, the reaction is

$$ClCOOCCl_3 = CO_2 + CCl_4 \qquad (2)$$

The rate of the thermal decomposition in the gas phase has been studied by us between 260 and 310°C and in the pressure range 4 to 17 mm. with the intention of providing further data on unimolecular reactions.

PREPARATION OF THE COMPOUND

The method of preparation was similar to that used by other investigators,[1,2] namely, the photochemical chlorination of methyl formate. A 100-cc. portion of methyl formate was placed in an all-glass apparatus provided with a reflux condenser cooled with ice and salt to prevent loss of the very volatile methyl formate. The flask containing the methyl formate was illuminated by a 500-watt lamp placed just above it. To avoid explosions illumination was commenced before the slow stream of "tank" chlorine was passed in. The temperature was kept at about 30°C. during the initial stages of the reaction. As the chlorination progressed the chlorine was passed in more rapidly and the temperature was gradually increased until finally it reached about 90°C. Chlorination was complete after thirty hours.

A portion of the product was distilled under reduced pressure in a small all-glass apparatus provided with a fractionating column and condenser. The middle fraction of a sample, which boiled between 50.0 and 50.1°C under 48 mm. pressure, was collected in a bulb containing calcium chloride. This supply was frozen with a carbon dioxide-ether mixture, sealed on to a high-vacuum line, pumped off and allowed to diffuse over into a second bulb immersed in carbon dioxide-ether, after which the original container was sealed off. The sample (A in Fig. 1) could be partially evaporated into the 500 cc. bulb H, frozen back into A and any non-condensed gas pumped off. Repetition of this process ensured the elimination of dissolved gas.

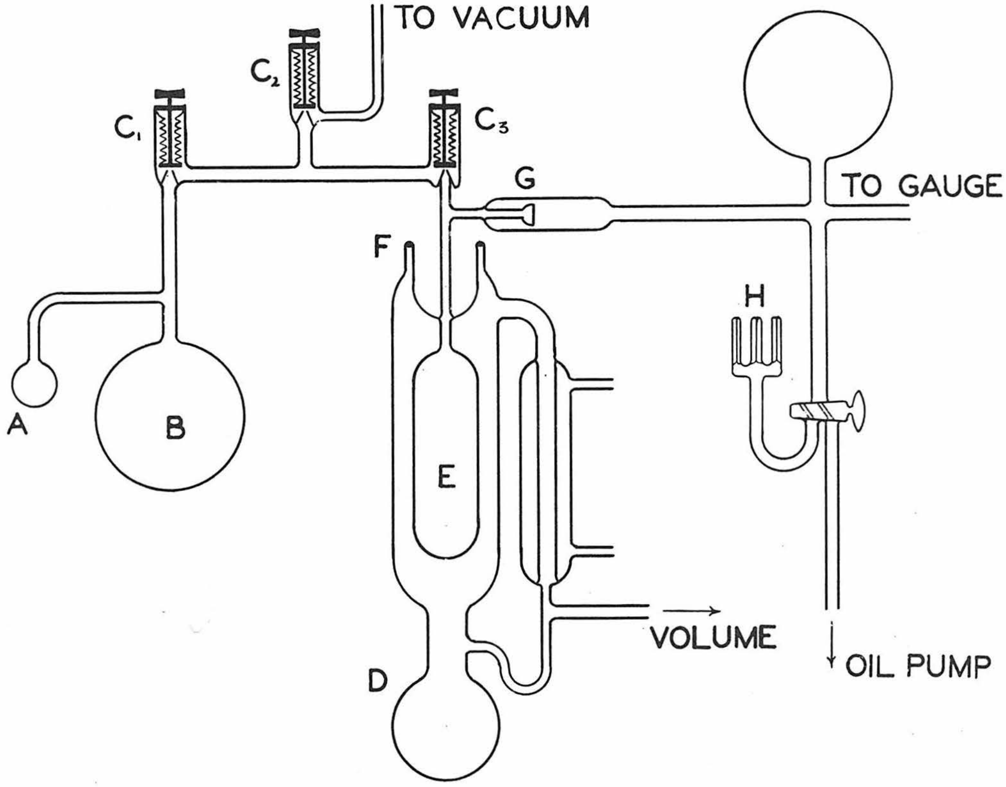

FIGURE 1

APPARATUS AND EXPERIMENTAL METHOD

A diagram of the apparatus is shown in Fig. 1. C_1, C_2 and C_3 are stopcocks specially designed to handle corrosive gases; these have been described in detail elsewhere.[3] D is a mercury boiler, and E the reaction cell, which was heated to the desired temperature by boiling the mercury under a constant pressure, maintained by having a twenty-liter bottle connected with the system and adjusting by hand the small pressure changes due to changes in the room temperature. The cell was sealed to the boiler at F with a cement of litharge and glycerine and this was cooled by a copper coil carrying a stream of water. This arrangement permitted the cell to be easily replaced by another cell and made it possible to use cells of various kinds of glass. The cells used had a volume of about 125 cc., and the external volume in the tubing, stopcock and click gauge was about 1.5 cc. No corrections were made for this small outside volume in the calculation of rate constants.

Pressures were measured by means of the click gauge G,[4] which was operated by admitting air through the controlled leak H until the click was heard. The pressure in the click system was then measured by means of a McLeod gauge designed so as to measure accurately pressures of from 1 to 5 cm. In filling the cell the opening and closing of the stopcock C_3 required only a few seconds. Time measurements were started on closing C_3. Pressure measurements were then made at time intervals chosen so that the pressure increments were approximately equal, and were continued until the reaction was about 80% complete. The final pressures were obtained by allowing the reaction to go to completion; in the runs at lower temperatures time was saved by completing the reaction at a higher temperature and using the gas laws to calculate the final pressure at the lower temperature, it having been shown that the gas laws were obeyed by the reaction products.

CHEMICAL NATURE OF THE REACTION

According to both equations (1) and (2) the final pressure should be exactly twice the initial pressure. This was verified by admitting the compound to the cell and measuring its pressure at a low temperature where decomposition was negligibly slow. The temperature was then raised and the reaction carried to completion. The gas laws had been shown to be obeyed by the compound at lower temperatures. In this manner the final-to-initial pressure ratio was found in three experiments to be 1.99, 2.00 and 1.986. To distinguish between reactions (1) and (2) the reaction products, at about 3 cm. pressure, were frozen out in a side-tube with a carbon dioxide-acetone mixture at -79 to -80°C. The pressures from three experiments were 5.4, 5.6 and 5.0 mm., agreeing quite well with the vapor pressure of phosgene at this temperature which is about 6 mm., and indicating that there could be no appreciable amount of carbon dioxide, carbon monoxide or chlorine formed. Freezing out with liquid air gave zero pressure in one case and about 0.05 mm. in another experiment, indicating the absence of non-condensable gases such as carbon monoxide. A direct analysis of the reaction product by hydrolysing with excess standard sodium hydroxide and back-titrating with standard hydrochloric acid using methyl orange indicator gave 98% of the amount of acid required if the product were pure phosgene. Incomplete hydrolysis may account for the slight discrepancy. The evidence is thus quite strong that phosgene is the only product formed.

From the known free energy of formation of phosgene from carbon monoxide and chlorine[5] it is found at 290°C and a partial pressure of 1 cm. of phosgene, that phosgene would be about 30% dissociated at equilibrium. It is also known that the rate of decomposition of phosgene at the above temperature is negligible.[5] Our experiments show definitely that only phosgene is formed; this would suggest that the rupture of the trichlor methyl chlorformate molecule gives two molecules of phosgene as the immediate products. Pure phosgene could not be produced from other radicals formed initially and subsequently recombining for then the equilibrium between phosgene and carbon monoxide and chlorine would be produced.

EXPERIMENTAL RESULTS

First order rate constants were calculated by the interval method using the equation

$$k_1 = \frac{2.303}{t_2 - t_1} \log_{10} \frac{P_{t_1}}{P_{t_2}}$$

where P_{t_1} and P_{t_2} are the partial pressures of trichlor methyl chlorformate at times t_1 and t_2 in seconds. Approximately equal amounts of reaction occurred during these time intervals. We have averaged these interval constants to obtain a rate constant for the run. No more refined statistical procedure used in obtaining an average constant would have made any material difference because of the exceptionally good first order rate constants obtained during the course of each run.

Since it was not possible to obtain a perssure reading until at least one half minute after the beginning of a run it was more accurate to calculate the partial pressure from the final pressure, using a factor of exactly two for the final-initial pressure ratio, this being justified by the experiments previously referred to.

Table I gives the complete data for three runs. The first column of figures refers to total observed pressures while the second column gives the partial pressures of trichlor methyl chlorformate.

TABLE I

Complete Data of Three Experiments

Experiment 2. $T = 290.0°C$ $P_o = 1.576$ cm.

P, cm.	P_t	t, sec	$k \times 10^3 (sec^{-1})$
1.576	1.576	0	
1.712	1.436	63	
1.888	1.260	181	1.11
2.087	1.061	334	1.12
2.279	0.869	513	1.11
2.484	0.664	760	1.09
2.708	0.440	1164	1.10
3.152	0.000		

TABLE I (cont)

Experiment 5. $T = 280.0°C$ $P_o = 1.503$

P, cm.	P_t	t, sec	$k \times 10^4 (sec^{-1})$
1.503	1.503	0	
1.548	1.458	51	
			5.88
1.674	1.331	206	
			5.97
1.857	1.148	454	
			5.58
2.033	0.972	751	
			5.82
2.227	0.779	1132	
			5.61
2.398	0.607	1575	
			5.87
2.589	0.417	2215	
3.006	0.000		

Experiment 9. $T = 305.0°C$ $P_o = 1.333$

P, cm.	P_t	t, sec	$k \times 10^3 (sec^{-1})$
1.333	1.333	0	
1.509	1.157	50	
			2.87
1.886	0.779	188	
			2.83
2.129	0.536	320	
			2.79
2.273	0.392	432	
			2.94
2.423	0.242	596	
2.666	0.000		

When no change in the nature of the cell was made or no extra surface was added the average rate constant was exceptionally reproduceable. It was found early in the research that there was some effect of the cell wall on the rate. This is best illustrated by Figure II, in which log k is plotted against 1/T for two series of runs. Series A was made in a pyrex cell containing pyrex tubing; the cell and contents having been treated with a chromic acid cleaning solution, while Series B was carried out in an empty pyrex cell which had merely been wiped free of dust and flamed very thoroughly.

The curvature exhibited by the plot of Series A runs indicates that in these runs there were two simultaneous reactions differing in energy of activation, while the straight line of Series B shows that the reaction was homogeneous or very nearly so. All Series B runs, particularly those at low temperatures have lower rates than those of Series A. The results of Series A are typical of reactions in which, in addition to a homogeneous reaction, there is present a heterogeneous reaction of lower energy of activation. In Series B the heterogeneous reaction has been practically eliminated. When, however, the surface to volume ratio was increased ten-fold by adding, to the cell used in Series B, pyrex tubing which had been wiped clean and flamed, there was an increase of of 15 or 20% in the rate at 290°C. If we assume that the original surface had the same catalytic activity as the added surface then the wall reaction in Series B runs would amount to only about 2%. This fact together with the straight line obtained in Figure 2 is good evidence that these runs are practically homogeneous.

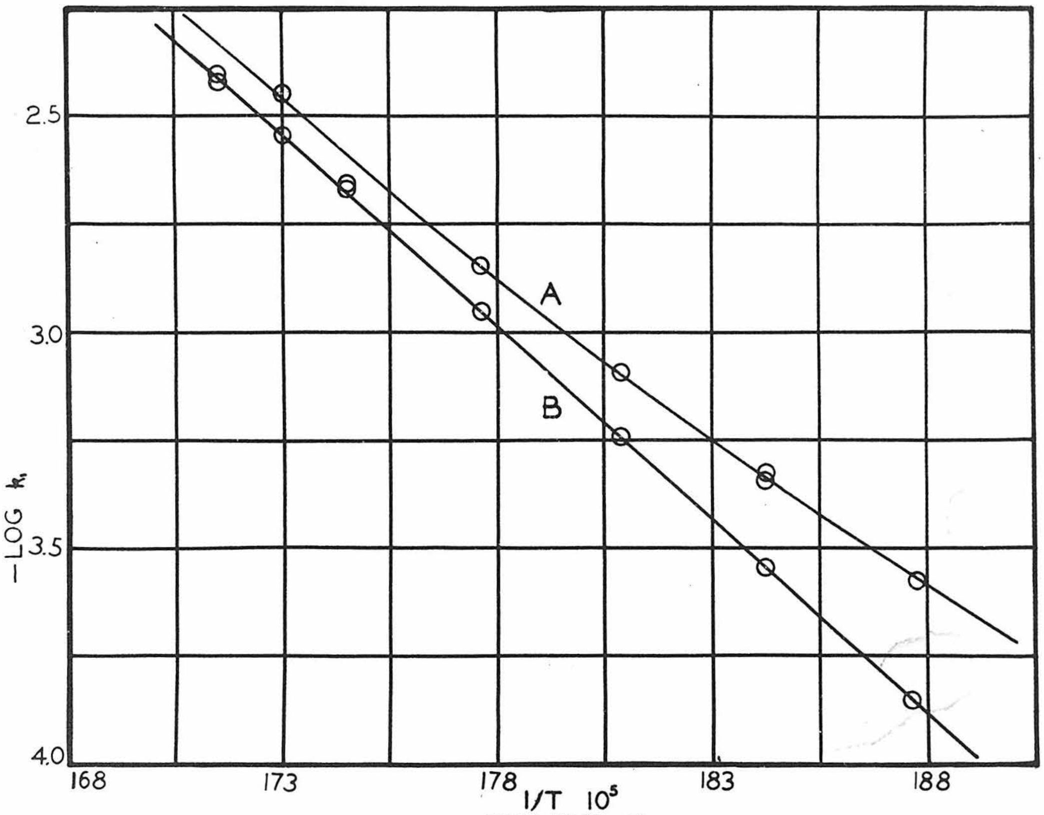

FIGURE 2

Many further unsuccessful attempts, using cells packed with tubing, were made to obtain surfaces free from catalytic activity. More careful flaming of the tubing sometimes gave results similar to those just described, but in other cases the rates were faster. Various chemical treatments such as thorough washing with cleaning solution, hot nitric acid or sodium hydroxide solution again gave results similar to Series A. Treating the cell with hot concentrated hydrochloric acid often gave results which were identical with those of Series B, but with added tubing similarly treated the rates were again 15 to 20% faster. Soft glass or quartz cells gave rates which were 10 to 20% faster than Series B runs. The use of different samples of trichlormethyl chlorformate never altered the rate which had been characteristic of the cell used.

From the slope of the straight line of Figure 2 the energy of activation is found to be 41,500 cal. per mole. The equation for the rate constant is $k_{,} = 1.4 \times 10^{13} \times e^{-41,500/RT}$.

Table II gives a summary of series B runs.

TABLE II

Expt.	Temp. °C	Initial Pressure	Av. k x 10^3	Number of constants
11	260.0	1.640	0.143	6
4	270.0	1.293	0.289	7
5	280.0	1.503	0.579	6
2	290.0	1.576	1.11	5
6	290.0	0.445	1.08	5
3	290.0	1.609	1.11	5
7	300.0	1.187	2.20	4
8	300.0	1.267	2.15	4
13	300.0	1.513	2.22	4
14	300.0	1.337	2.16	5
1	305.0	1.398	2.84	3
9	305.0	1.333	2.86	4
10	310.0	1.564	3.78	3
12	310.0	1.472	3.98	3
		- - - - - - - - - - -		
21	270.0	1.468	0.286	6
17	280.0	1.677	0.593	7
19	290.0	1.594	1.12	5
22	290.0	1.330	1.11	6
18	305.0	1.568	2.98	4
20	305.0	1.413	2.88	4

The average of the average deviations of the rate constants for all runs is only 2.18%. Runs 18 to 22 were made with a new portion of the compound and reproduced the earlier experiments almost perfectly.

The first order constant is evidently independent of the initial pressure over the pressure range investigated. It would have been desirable to obtain data at lower pressures in order to test rather severely the theory of unimolecular reactions, but the catalytic effect of the walls at lower pressures would very probably be greater and would therefore be a serious disturbing factor.

We may calculate a lower limit to the number of oscillators required to fit the theory. An examination of specific heat data at high temperatures of highly chlorinated organic molecules such as CCl_4 shows that these have unusually high specific heats. This would indicate that the oscillators of such molecules are of sufficiently low frequency that we will be justified in considering them as classical oscillators. We then find that with 14 oscillators and a diameter of 8×10^{-8} cm. the rate constant at 4 mm. pressure will be about 4% below the high pressure rate.[6] Since the maximum number of oscillators which this molecule could contain is 18, we have here a reaction whose rate at the lowest pressures approaches fairly close to the maximum permitted by theory.

SUMMARY

The thermal decomposition of trichlor methyl chlorformate has been studied over a temperature range of 260 to 310°C and a pressure range from 4 to 17 mm. The reaction has been found to be first order and homogeneous save for a slight trace of wall catalysis. The rate constant is given by the expression

$$k = 1.4 \times 10^{13} e^{-41,500/RT}$$

The maintenance of the high pressure rate over the pressure range studied is accounted for if the molecule is assumed to have a diameter of 8×10^{-8} cm. and to have 14 classical oscillators.

The sole product of the decomposition is phosgene; the equilibrium between phosgene, carbon monoxide and chlorine not being established.

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THE INTERPRETATION OF THE THERMAL DECOMPOSITION OF NITROUS OXIDE

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Unimolecular reactions have heretofore been decompositions or rearrangements of large molecules and it has in general been necessary to assign a considerable number of degrees of freedom to give a theoretical interpretation of the rate. It is, therefore, of considerable interest that the relatively simple molecule, nitrous oxide, has now been shown quite definitely to decompose unimolecularly.[1,2]

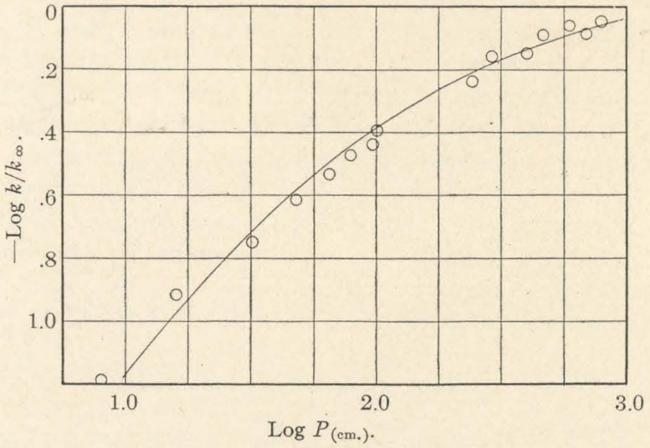

FIGURE 1

As usual the rate is first order at high pressures, but the rate constant falls off at lower pressures. The investigators have shown that the rate as a function of the pressure follows an equation which is the same as that required by Theory I of Rice and Ramsperger. It remains to determine the number of degrees of freedom (squared terms) and molecular diameter required quantitatively to fit the data; a matter of some importance because the unusually simple character of the molecule would not permit the use of more than two or three oscillators and some questionable rotational energy.

We have applied Theories I and II of Rice and Ramsperger[3] and Theory III of Kassel[4] and find that but two squared terms (one classical oscillator) are required to fit the data at 665°C. For this case Theory III is identical with Theory I and Theory II is also practically identical. Figure 1 shows the usual plot of log k/k_∞ against log P based on Theories II and III.

The curve is theoretical, while the points are experimental. The molecular diameter chosen was 3.05×10^{-8} cm., the critical energy $E = 53{,}000$ cal. p. mol. and $k_\infty = 1.78 \times 10^{-3}$. The molecular diameter chosen is close to the kinetic theory value (3.32×10^{-8} cm.). The interpretation on the basis of Theory III requires that 53,000 calories be the critical energy for the breaking of the bond between a nitrogen atom and an oxygen atom. By using the latest value of the heat of dissociation of the oxygen molecule (118,000 calories) and the heat of formation of the nitrous oxide molecule (17,000 calories) we find a minimum value for the breaking of this bond, namely, $118{,}000/2 - 17{,}000 = 42{,}000$ calories. It is, of course, required only that the experimental value be as great or greater than this figure.

The experimental basis for the interpretation of unimolecular reactions is now better than for bimolecular or trimolecular reactions, a situation quite the contrary to that existing six years ago. Sufficient data for a test of theories is available in at least four cases including such very different molecules as nitrous oxide, which requires but two squared terms and methyl isopropyl di-imide with thirty-three squared terms. The following table gives a list of recognized unimolecular reactions, giving the pressure and temperature ranges that have been studied, the constants in the equation for the rate constant $k_\infty = Ae^{-Q/RT}$ and the number of classical squared terms required by Theory II or III to fit the data. In the case of nitrogen pentoxide Kassel's quantum treatment is necessary to give even a partially satisfactory agreement. In this case a vibrational specific heat of at least 20 cal. p. mol. and a diameter of 17×10^{-8} cm. is required.[5]

DATA FOR UNIMOLECULAR REACTIONS

SUBSTANCE REACTING	P, CM.	T, °C	A	Q CAL. P. MOL	N
C_2H_5CHO[6]	2.0 to 40.0	450 to 600	$>1.38 \times 10^{12}$	54,000	11
$C_2H_5—O—C_2H_5$[7]	2.5 to 50.0	426 to 588	$>3.09 \times 10^{11}$	53,000	> 6
$CH_3—O—CH_3$[8]	3.0 to 90.0	422 to 552	1.52×10^{13}	58,500	11
$CH_3—N{=}N—CH_3$[9]	0.026 to 70.79	278 to 327	1.07×10^{16}	51,200	25
$CH_3—N{=}N—C_3H_7$[10]	0.0058 to 13.12	250 to 332	2.80×10^{15}	47,480	33
$C_3H_7—N{=}N—C_3H_7$[11]	0.025 to 4.60	250 to 290	5.6×10^{13}	40,900	>40
$CH_3—N{=}N—NHCH_3$[12]	0.019 to 8.0	200 to 230	4.05×10^{11}	33,800	14
d-pinene[13]	17.0 to 116.0	184 to 237	5.40×10^{14}	43,700	>20
Ethylene oxide[14]	2.4 to 90.5	378 to 445	9.9 to 10^{12}	52,000	>14
N_2O_5[15,16,17]	0.00042 to 70.0	0 to 65	4.5×10^{13}	24,700	30[5]
N_2O[1,2]	8.1 to 800	560 to 667	4.0×10^{9}	53,000	2

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THE THERMAL CHLORINATION OF CHLOROFORM

It is well known that mixtures of chlorine and methane react readily at about 400°C.[1] If chlorine is in excess, the reaction may be explosive, in which case carbon and hydrogen chloride will be the main products. However, if methane is in excess the reaction goes smoothly in step-wise fashion, giving methyl chloride, methylene dichloride, chloroform and finally carbon tetrachloride. A study of this slow chlorination of methane has been made recently.[2] Owing to the complicated nature of the system, the above reaction is not particularly suitable for quantitative study. It would seem that a st udy of the last step of the reaction, namely, the thermal chlorination of chloroform would be better adapted to reaction rate work and would give further information on chain reactions to which class, preliminary experiments showed this reaction to belong.

This same reaction has recently been studied photochemically in carbon tetrachloride solution.[3] A rate expression has been determined and a mechanism has been suggested which agrees qualitatively with the experimental results and which is energetically reasonable. The possibility of comparing the photochemical and thermal rates added interest to the investigation.

EXPERIMENTAL METHOD

A static method of following the reaction was employed. Reference to Figure 1 will make clear the experimental procedure.

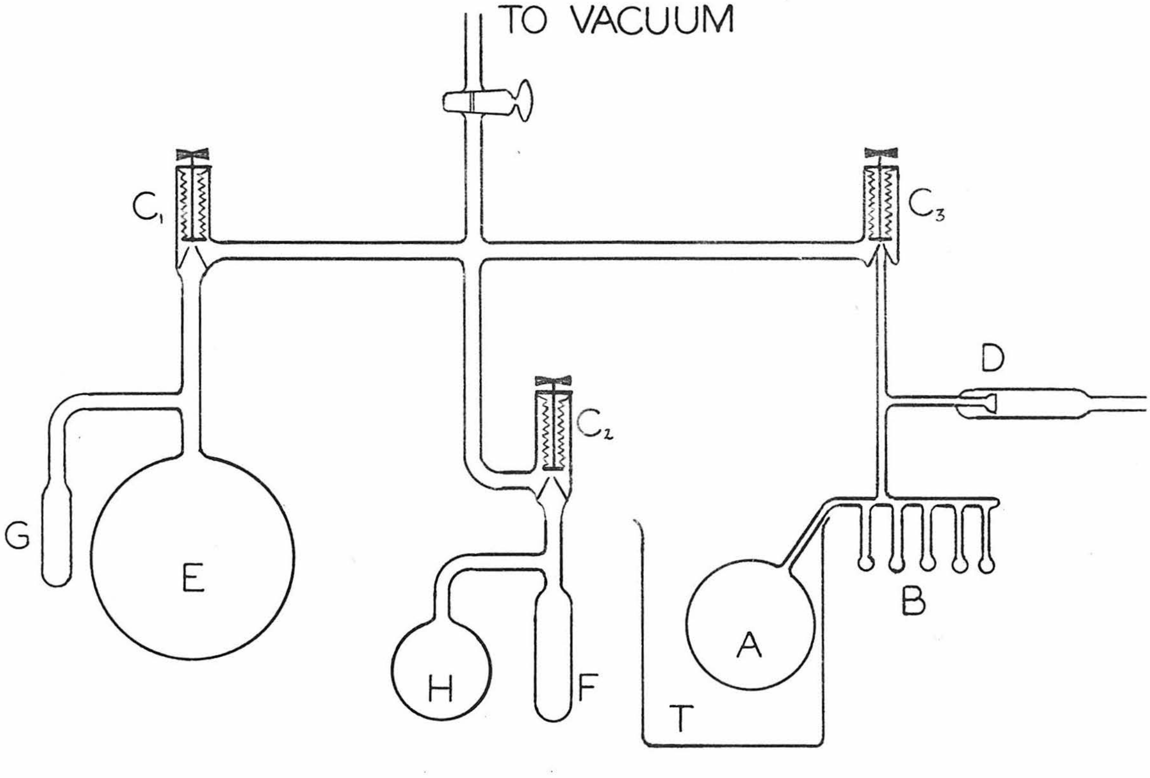

Figure 1

The thermostat T contained, besides the reaction cell A, a stirrer, thermo-regulator and thermometer. The bath liquid, "hydrogenated cotton-seed oil" proved to be very satisfactory. Temperature was maintained constant to within 0.1°C.

B is a group of small bulbs each having an easily broken tip, and which could be sealed off easily one at a time, by means of a hand-torch. D is a click gauge[4] which is operated by a slow air leak and McLeod gauge (see page 3, part I). C_1, C_2, C_3,[5] are special stopcocks with which it is possible to manipulate chlorine or other corrosive gases without contamination of the gas with stopcock grease or other lubricant. E is a three-liter flask for the chlorine supply and F is the chloroform supply.

Runs were made as follows. The system was thoroughly evacuated by means of a diffusion pump. The click gauge was "set" so that it would click as soon as the desired pressure was obtained in the cell. Either chloroform or chlorine was admitted to the cell until the click was heard. C_3 was closed, the pressure was read accurately, the connecting tubing pumped down (through a soda-lime tube in the case of chlorine), the click set again and the second gas admitted, time measurements being started as the second click was heard. After the total pressure had been read accurately the partial pressure of the second gas admitted was found by simple subtraction. Experiment showed that there was no pressure change during a given run. To terminate a run a small Dewar flask of liquid air was placed about one of the bulbs B. Both reactants and products froze over into B almost completely within five seconds. The bulb was then sealed off and broken under the surface of a potassium iodide solution. The liberated iodine was titrated with thiosulphate; potassium iodate was then added, which liberated iodine in amount equivalent to the hydrochloric acid present.

PREPARATION OF THE COMPOUNDS

A small bulb G of tank chlorine was frozen with liquid air and sealed on to the three-liter flask E, which was then pumped out thoroughly. The chlorine was vaporized and refrozen, then pumped again. Repeating this process removed all non-condensable gases. Water vapor was removed by condensing the chlorine in a tube containing P_2O_5 (not shown in diagram).

The chloroform used was U.S.P. grade which had been successively washed with concentrated sulfuric acid, distilled water, dilute potassium hydroxide solution, and finally distilled water until free from alkali. It was then distilled, dried, redistilled and nitrogen was bubbled through it to remove as much dissolved oxygen as possible. Finally, a small bulb of chloroform, F in Fig. 1, was sealed on to the high vacuum line, frozen with liquid air and pumped off. It was then boiled gently and distilled over into the volume H, frozen back into F, and pumped again. This process was repeated several times.

EXPERIMENTAL RESULTS

Preliminary experiments showed that the reaction took place at a measurable rate at 220° to 230°C. Analyses of the reaction products for chlorine and hydrochloric acid always agreed, within 0.5% or better, with the chlorine initially present, indicating that the reaction, as would be expected, follows the equation

$$CHCl_3 + Cl_2 = CCl_4 + HCl$$

Early in the research experiments were made to determine the effect of increased surface upon the rate. These are shown in Table I.

TABLE I

Experiments at 220°C with unpacked Pyrex cell

Experiment	Vol. cell cc.	P_0Cl_2 cm	P_0CHCl_3 cm	Time of run min.	$\%Cl_2$ reacted
7	115	6.15	5.81	24	57
8	520	5.75	5.53	26	55
Experiments with cell packed with Pyrex tubing					
6	185	4.88	4.91	24	3.6
9	185	5.03	5.82	28	9.3

Runs 6 and 9 show that the packed cell has slowed up the reaction considerably. This behavior is characteristic of chain reactions, the chain being terminated by collision with the wall. In the presence of this inhibitory effect, any positive heterogeneous catalysis will fail to be observed. Runs 7 and 8 indicate that a five-fold change in volume of the reaction cell had little in any influence on the rate. No great accuracy is claimed for the foregoing experiments.

All subsequent runs were made in a cell having a volume of 528 cc. Using a fairly large volume it was hoped that surface effects would be reduced to a minimum. To what extent this has been realized is not known.

Table II gives a summary of a number of runs in which the same supply of chlorine and chloroform was used throughout. This was necessary in order to obtain comparable results since slight differences in the method of preparation of the chlorine and chloroform cause considerable deviation in the absolute rate of the reaction.

TABLE II

Runs made at 230°C in 528 cc. Pyrex flask

Expt.	P_oCl_2 cm	P_oCHCl_3 cm	Heating time min.	k_2	$k_{3/2}$	%Cl_2 reacted
18	3.12	10.71	25.15	34	2.1	16.0
19	2.92	10.21	25.22	33	2.0	15.0
21	4.58	10.57	25.25	33	1.7	15.1
20	6.27	11.26	25.27	39	1.7	17.6
22	7.11	10.58	25.27	45	1.7	19.7
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28	10.00	4.72	25.13	68		27.0
29	10.66	2.95	25.47	69		33.0
30	9.87	1.62	25.13	74		31.0

Experiments 18 to 22 were made in the attempt to determine the effect of chlorine on the rate. As can be seen the initial pressure of chloroform was approximately the same in each experiment while the chlorine pressure was varied from 2.92 to 7.11 cm. The column headed k_2 gives the rate constants for the reaction calculated by means of the equation

$$-\frac{dCl_2}{dt} = k_2(Cl_2)(CHCl_3)$$

concentrations being expressed in mols per cc. and time in seconds. The next column gives constants (in arbitrary units) calculated from the equation

$$-\frac{dCl_2}{dt} = k\ (Cl_2)^{3/2}\ (CHCl_3)$$

the rate being assumed proportional to the three halves power of the chlorine concentration. An average value of the chloroform concentration was taken, this being constant assumed in the integration which is not a bad assumption since the chloroform concentration is always considerably greater than the chlorine and the reaction was always stopped when only about 20% complete. It would seem that the rate depends on the chlorine concentration almost linearly. The fact that the amount of chlorine which reacts varies only from 15 to 19.7% for a 2.5-fold change in chlorine concentration lends support to the view. The reaction is sensitive to traces of impurities and to the condition of the cell wall either of which facts may contribute to the drift in the rate constants.

Experiments 28 to 30 indicate fairly clearly a first order dependance of the rate on the chloroform concentration. The constants "k_2" are calculated from the rate expression

$$-\frac{d\,CHCl_3}{d\,t} = k(CHCl_3)(Cl_2)$$

As can be seen the rate constants do not drift badly and the fraction of chlorine reacted is about the same in each experiment. Comparing runs 21 and 28 it might be noted that changing the chlorine to chloroform ratio from approximately 1:2 to 2:1 doubles the chlorine conversion; this would be true of a second order reaction.

It may be mentioned that on several occasions when small amounts of air inadvertently got into the reaction cell the rate of the reaction was slowed down considerably. This would seem to be another case of chlorine atom chain being broken by oxygen. Whenever sufficient air was present to inhibit the reaction noticeably the freezing down of the reaction products in the seal-off bulbs was very slow and incomplete, hence rapid condensation of the reaction products was a guarantee of the absence of undesirable non-condensable gases.

Further experiments are being carried out to determine more precisely the effect of chlorine and chloroform on the rate and also the effect of hydrogen chloride which probably enters into the reaction mechanism.

DISCUSSION OF THE RESULTS

The foregoing investigation is neither complete nor free from uncertainties. However, certain facts have been gleaned from the experiments. Firstly, in the absence of any considerable concentration of the reaction products, the rate is in qualitative accord with the rate expression

$$-\frac{dCl_2}{dt} = k_2(Cl_2)(CHCl_3)$$

Secondly it is a chain reaction, the chain, in part at least, being broken by collision with the cell wall.

As far as they go these results agree with the mechanism proposed by Schwab and Heyde,[3] namely,

(1) $Cl_2 = Cl$

(2) $Cl + CHCl_3 = CCl_3 + HCl$

(3) $CCl_3 + Cl_2 = CCl_4 + Cl$

(4) $CCl_3 + HCl = CHCl_3 + Cl$

(5) $Cl = \frac{1}{2}Cl_2$

In the thermal case this gives a rate expression

$$-\frac{dCl_2}{dt} = \frac{k_3k_2\frac{k_1}{k_5}(Cl)^2(CHCl_3)}{k_5(Cl_2) + k_4(HCl)}$$

which reduces to

$$-\frac{dCl_2}{dt} = \frac{k_2k_1}{k_5}(Cl_2)(CHCl_3)$$

when the hydrogen chloride concentration is small. It is not suggested that this mechanism is correct, in particular, more careful experiments varying the size and shape of the reaction vessel will have to be made in order to get an insight into the nature of the chain terminating process.

SUMMARY

(1) The chlorination of chloroform has been shown to proceed smoothly at 230°C, the products being carbon tetrachloride and hydrogen chloride.

(2) The reaction is of the chain type, the chains being terminated by the cell wall.

(3) The rate of the reaction shows a first order dependence on both the chlorine and chloroform concentrations.

(4) The reaction is inhibited by traces of oxygen.

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