phenone occurs at 74.5 mole per cent. benzophenone and at 31.9°. Evidence is presented for the existence of a metastable form of the compound with a melting point of 30.8°.

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The Kinetics of the Thermal Decomposition of Trichloromethyl Chloroformate

BY H. C. RAMSPERGER AND G. WADDINGTON

Trichloromethyl chloroformate gas is known to decompose at 300° to give two molecules of phosgene[1] as shown by the equation

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

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° 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 of 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° 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°. 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° under 48 mm. pressure, was collected in a bulb containing calcium chloride. This supply was frozen with a carbon dioxide–ether mixture, sealed onto 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 B, frozen back into A and any non-condensed gas pumped off. Repetition of this process ensured the elimination of dissolved gas.

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

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[1] Hentschel, *J. prakt. Chem.*, [2] **36,** 99, 209, 305, 468 (1887).

[2] Grignard, Rivat and Urbain, *Ann. chim.*, **9** [13], 229 (1920).

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 glycerin and this was coated with sealing wax. This joint was cooled by a copper coil carrying a stream of water. This arrangement permitted the cell to be replaced easily by another cell and made it possible to use cells of various kinds of glass. The cells had a volume of about 125 cc., and the external volume in the tubing, stopcock and click gage was about 1.5 cc. No corrections were made for this small outside volume in the calculation of rate constants.

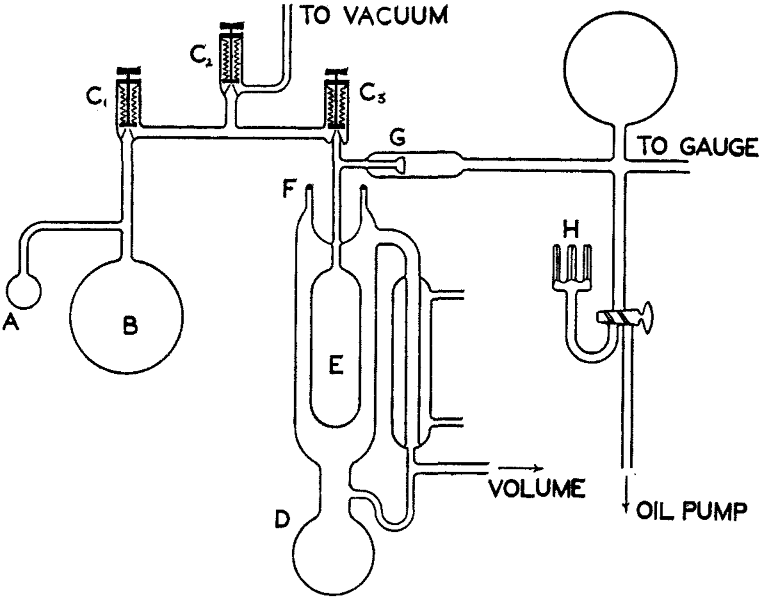

Fig. 1.—Apparatus.

Pressures were measured by means of the click gage 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 gage 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 admit-

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[3] Ramsperger, *Rev. Sci. Instruments*, **2**, 738 (1931).

[4] Smith and Taylor, THIS JOURNAL, **46**, 1343 (1924).

ting 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°. 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 hydrolyzing 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° 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.[4] Our experiments show definitely that only phosgene is formed; this would suggest that the rupture of the trichloromethyl chloroformate molecule gives two molecules of phosgene as the immediate products. Pure phosgene could not be produced from carbon monoxide and chlorine formed initially and subsequently recombining, for then the equilibrium between phosgene, 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 trichloromethyl chloroformate 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 pressure 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 trichloromethyl chloroformate.

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[5] Bodenstein and Plaut, *Z. phys. Chem.*, **110**, 399 (1924).

TABLE I

COMPLETE DATA OF THREE EXPERIMENTS

Experiment 2. $T = 290.0°C.$ $P_1 = 1.576$ 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	.664	760	1.09
2.708	.440	1164	1.10
3.152	.000		

Experiment 5. $T = 280°C.$ $P_0 = 1.503$

P, cm.	P_t	t, sec.	$k \times 10^3$ (sec.$^{-1}$)
1.503	1.503	0	
1.548	1.458	51	
1.674	1.331	206	0.588
1.857	1.148	454	.597
2.033	0.972	751	.558
2.227	.779	1132	.582
2.398	.607	1575	.561
2.589	.417	2215	.587
3.006	.000		

Experiment 9. $T = 305.0°C.$ $P_0 = 1.333$

P, cm.	P_t	t, sec.	$k \times 10^3$ (sec.$^{-1}$)
1.333	1.333	0	
1.509	1.157	50	
1.886	0.779	188	2.87
2.129	.536	320	2.83
2.273	.392	432	2.79
2.423	.242	596	2.94
2.666	.000		

When no change in the nature of the cell was made or no extra surface was added, the average rate constant was exceptionally reproducible. It was found early in the research that there was some effect of the cell wall on the rate. This is best illustrated by Fig. 2, 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 lower 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 tenfold by adding, to the cell used in Series B, Pyrex tubing which had been wiped clean and flamed, there was an increase of 15 or 20% in the rate at 290°. 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 Fig. 2, is good evidence that these runs are practically homogeneous.

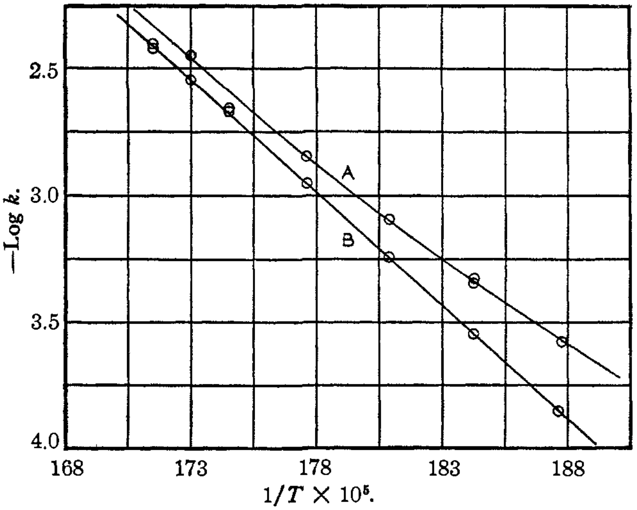

Fig. 2.—Curve A, cell packed with Pyrex tubing; Curve B, cell empty.

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 trichloromethyl chloroformate never altered the rate which had been characteristic of the cell used.

From the slope of the straight line of Fig. 2 the energy of activation is found to be 41,500 cal. per mole. The equation for the rate constant is $k_1 = 1.4 \times 10^{13} \times e^{-41,500/RT}$.

Table II gives a summary of Series B runs.

TABLE II

Expt.	Temp., °C.	Initial pressure	Av. $k \times 10^3$	Number of constants	Expt.	Temp., °C.	Initial pressure	Av. $k \times 10^3$	Number of constants
11	260	1.640	0.143	6	9	305	1.333	2.86	4
4	270	1.293	.289	7	10	310	1.564	3.78	3
5	280	1.503	.579	6	12	310	1.472	3.98	3
2	290	1.576	1.11	5					
6	290	0.445	1.08	5	21	270	1.468	0.286	6
3	290	1.609	1.11	5	17	280	1.677	0.593	7
7	300	1.187	2.20	4	19	290	1.594	1.12	5
8	300	1.267	2.15	4	22	290	1.330	1.11	6
13	300	1.513	2.22	4	18	305	1.568	2.98	4
14	300	1.337	2.16	5	20	305	1.413	2.88	4
1	305	1.398	2.84	3					

The average of the average deviations of the rate constants for all runs is only 2.18%. Runs 17 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 agree with theory. An examination of specific heat data at high temperatures of highly chlorinated organic molecules such as carbon tetrachloride 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. Doing so, making use of the formulation of the calculation given by Kassel,[6] we then find that with the reasonable assumptions of fourteen oscillators and a diameter of 8×10^{-8} cm., the rate constant at 4 mm. pressure would be about 4% below the high pressure rate. 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 trichloromethyl chloroformate has been studied over a temperature range of 260 to 310° 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

$$k_1 = 1.4 \times 10^{13} e^{-14,500/RT}$$

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[6] Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1931, p. 103, eq. 24.

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

The possible equilibrium between phosgene, carbon monoxide and chlorine was not found to occur as a result of the reaction, the sole product of the decomposition being phosgene.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Effect of Gaseous Impurities on the Radiochemical Combination of Carbon Monoxide and Oxygen

BY CHARLES ROSENBLUM

Part of the recent work on the carbon monoxide oxidation under the influence of radon[1] involved a study of the effect of certain gaseous impurities possibly occurring in traces in the reactants as a result of the methods employed for their preparation. These foreign substances were water vapor, formic acid vapor and gaseous nitrogen.

The formic acid was prepared by reduced pressure distillation[2] in the presence of phosphorus pentoxide, and saturation of a $2CO:1O_2$ mixture was effected at 21.3°. Another sample of the reaction mixture was saturated with water vapor at 21.5°. A measured volume of tank nitrogen, purified by passing through a train containing, besides a liquid air trap, tubes of fused potassium hydroxide, sublimed phosphorus pentoxide and yellow phosphorus, was added to a third quantity of reactants. The gas mixtures so prepared were confined with radon in small spherical vessels[3] and the progress of the reaction followed manometrically.

Table I shows the reaction in gases wet with water vapor. Here $e^{-\lambda t}$ is the fraction of radon left after time t, E_0 is the initial amount of radon in curies, $P_{2CO + 1O_2}$ is the partial pressure of dry reactants, D is the diameter of the reaction vessel, and $(k\mu/\lambda)''_{\text{corr.}}$ is the velocity constant corrected for the catalytic efficiency of carbon dioxide and for the effect of recoil atoms.[1]

From the inverse square of diameter law[4] the velocity constant in a sphere of this size should be about 31,[1] which may be considered in agreement for experiments of this kind. It then appears that water vapor has little effect on the radiochemical carbon monoxide oxidation. That water vapor has a negligible effect is in accord with its radiochemically inert nature.[5]

[1] Lind and Rosenblum, *Proc. Nat. Acad. Sciences*, **18**, 374 (1932).

[2] Jones, *J. Soc. Chem. Ind.*, **38**, 362T (1919).

[3] Lind and Bardwell, THIS JOURNAL, **47**, 2675 (1925).

[4] Lind, *ibid.*, **41**, 531 (1919).

[5] Duane and Scheuer, *Le Radium*, **10**, 33 (1913).