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The Unimolecular Decomposition of Gaseous Chloropicrin

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The decomposition of gaseous chloropicrin has been investigated in the temperature range 138 to 170° C at pressures from 6 to 20 cm. The reaction is homogeneous and unimolecular, the rate constants being expressed by the equation

 $k = 4.90 \times 10^{15} e^{-37670/RT}$ sec.⁻¹.

The products of the reaction are phosgene, nitrosyl chloride, nitric oxide, and chlorine, as represented stoichiometrically by the equation

 $CCl_3NO_2 = COCl_2 + NOCl$ $\downarrow \uparrow$ $NO + \frac{1}{2}Cl_2.$

There is, however, evidence to show that at least part of the nitric oxide and chlorine are formed otherwise than by the decomposition of nitrosyl chloride.

INTRODUCTION

D EACTIONS of simple inorganic molecules **K** have the advantage that they are often more clear-cut and free from secondary changes than are organic reactions. From this point of view completely substituted organic molecules are also advantageous. Recent work in this laboratory on the decomposition of the alkyl nitrites has furnished considerable information on the effect of chemical constitution on the reaction rate. Unfortunately, however, the effect of substituents cannot be investigated since practically all substituted aliphatic nitrites are impossible to prepare. A search has therefore been made for a suitable simple molecule in which it should be possible to vary the substituents. Chloropicrin has been chosen, since it should be feasible to replace successively the chlorine atoms by other halogens.

The decomposition of chloropicrin has been previously investigated in a purely qualitative way by Gardner and Fox,¹ who found that it decomposes slowly at its boiling point into phosgene and nitrosyl chloride. A brief investigation of the kinetics of the process has also been made by Radulescu and Zamfirescu.² They heated weighed amounts of chloropicrin in sealed ampules in an oil bath, and after the lapse of different intervals of time removed the tubes and analyzed for undecomposed chloropicrin by titration with permanganate. No analysis of the products of the reaction was made. Also, no statement is made of the pressure existing in the sealed tubes, or whether the reaction was investigated in the liquid or in the vapor phase. They found the reaction to be first order, but made no test of its homogeneity. Their velocity constants were very reproducible, typical values given by them being

> $k_{131,1} = 0.11 \times 10^{-3} \text{ sec.}^{-1},$ $k_{141,2} = 0.32 \times 10^{-3} \text{ sec.}^{-1},$ $k_{151,1} = 0.97 \times 10^{-3} \text{ sec.}^{-1},$ $k_{161,2} = 3.27 \times 10^{-3} \text{ sec.}^{-1}.$

From these results we may estimate the activation energy to be about 40,000 cal.



^{*} Holder of a Studentship from the National Research Council of Canada. ¹ Gardner and Fox, J. Chem. Soc. (London) **115**, 1188

^{(1919).} ² Padulacou and Zamfrascu Bull Soc Chim Romania

² Radulescu and Zamfirescu, Bull. Soc. Chim. Romania 17, 87 (1935).

EXPERIMENTAL

The reaction was followed by observing the rate of pressure change in an all-glass system of constant volume. A diagram of the apparatus is given in Fig. 1. The entire reaction system was constructed of Pyrex glass. The reaction vessel Bhad a capacity of about 1 liter, and was immersed in an electrically heated oil bath. The temperature was controlled manually to within $\pm 0.15^{\circ}$ C, and was measured by standard mercury thermometers. The reaction vessel was connected to the magnetic hammer H and to the glass manometer G, which was of the spoon type. The tip of the glass manometer was illuminated with blue light (Corning blue green filter no. 430) and viewed through a telescope with an adjustable cross hair in the eyepiece. A number of gauges of different sensitivity were employed at various times, but in no case was the sensitivity less than 0.5 mm. The outside jacket of the glass manometer was connected to the mercury manometer Mand to an air-pressure regulating system, the glass gauge being used as a null instrument and balanced by air pressure in the jacket. All the tubing in the reaction system, including the jacket of the glass gauge and the magnetic hammer, was wound with Nichrome wire and heated electrically to 110°C during a run.

Prior to an experiment the desired amount of chloropicrin, sealed in a glass tube with a fine drawn-out tip, was placed in position under the magnetic hammer through the open end of the tube A, which was then sealed off. The oil bath was brought to the required temperature and the apparatus evacuated, all the tubing outside the bath being heated electrically to 110°C during the evacuation with the exception of that immediately surrounding the tube of chloropicrin. Finally this part of the tubing was also heated for a short time, and the reaction system was then isolated by sealing off the connecting tubing at P. The tip of the tube containing the chloropicrin was then broken off with the magnetic hammer, and the variation of pressure with time was followed by means of the glass manometer.

For purposes of analysis the reaction vessel in the oil bath was replaced by a cylindrical vessel heated by a removable electric furnace. The cylindrical vessel carried a narrowed portion at its base for the condensation of reaction products, and a small tip in which they could be sealed off.

Chloropicrin was obtained from the Eastman Kodak Co. It was fractionated before use, and was then sealed off in vacuum in small tubes.

THE COURSE OF THE REACTION

As pointed out above, Gardner and Fox found that chloropicrin decomposes at its boiling point into phosgene and nitrosyl chloride. In the temperature range of the present investigation, 138° to 170°C, NOCl decomposes slowly into nitric oxide and chlorine. We would therefore expect that the final products of the reaction would be phosgene and an equilibrium mixture of NOCl, NO, and Cl₂. This equilibrium has been investigated by Dixon.3 The total pressure increases at completion obtained in the present investigation are in excellent agreement with values calculated from Dixon's results. Thus, for example, at 160°C and initial pressures of 9 and 12 cm of chloropicrin, the assumption of equilibrium amounts of NOCl, NO, and Cl₂ leads to predicted pressure increases at completion of 111 and 110 percent. Experimental values at the end of 15 hours reaction time were 111 and 112 percent, respectively.

In order to check the reaction products, however, they were examined by an analytical method which has been previously described.⁴ This method depends on the action of the gases on mercury, phosgene being unaffected, NOCl replaced by an equimolecular amount of NO, and chlorine entirely removed. The amount of NOCl is thus equal to the NO formed, and the amount of chlorine to the decrease in pressure. The method is capable of considerable accuracy in the absence of NO₂. NO₂ reacts with mercury yielding half its molecular amount of NO. Consequently when NO_2 is present the decrease in pressure on reaction with mercury indicates the amounts of NO₂ and chlorine only within the limits consistent with this decrease. Moreover, the amount of NO formed will also be indefinite as a measure of the NOCl present to the extent of the amount of NO_2 .

Two analyses of the products of the reaction at completion gave the results shown in Table I. ^aDixon, "Bodenstein Festband," Zeits. f. physik.

Chemie, 479 (1931). ⁴ Steacie and Smith, Can. J. Research, in press.

 TABLE I. Products of the reaction at completion.
 Reaction time—approximately 3 hours.

Tempera- ture, °C	Initial	Products, moles/mole of CCl2NO2				
	PRESSURE, cm	COCl ₂	NOCI	Cl2	NO	
160 170	12.3 8.1	0.91 0.91	0.83 0.81	0.08 0.12	0.19 0.27	

These results are calculated on the assumption that NO_2 is absent at this stage of the reaction, as will be shown later. The fraction recorded as phosgene exhibited the vapor pressure of this substance when condensed. It will be seen that the amount of phosgene is lower than that required by the mechanism given above. However, the amount of NO is somewhat high, and considering the difficulty of condensation it is possible that some of the NO recorded is really uncondensed phosgene. If we assume that 0.04 cm and 0.08 cm of the recorded NO are really phosgene, respectively, the products balance in a quite satisfactory manner, as shown by Table II. It should be pointed out that the extent of dissociation of NOCl reported in the tables is not necessarily the actual amount existing at the temperature of the reaction, since NO and chlorine combine at an appreciable rate even at room temperature.

The condensed products at liquid-air temperature showed a slight green coloration, indicating the presence of some NO₂, which would combine with NO to form blue N₂O₃, which in the presence of NOCl yields a green coloration. A consideration of the pressure change accompanying the chloropicrin decomposition shows that there cannot have been much nitrogen dioxide present. This was confirmed by adding small amounts of NO and NO₂ to NOCl and observing the color at liquid air temperature. One percent of NO_2 , combined as N_2O_3 , gave a definite green color to the mixture. NO2 is therefore not an important product of the reaction. It appears to result from purely secondary changes, since the longer the time allowed for an experiment to go to completion the more NO_2 appeared to be formed. During the early stages of the decomposition no evidence of the presence of NO2 was found. Moreover, a number of runs were carried on for 15 hours, and partial recombination of the NO

TABLE II. Products of the reaction (corrected).

Tempera- ture, °C	INITIAL Pressure, cm	Products, moles/mole of CCl ₃ NO ₂				
		COCl ₂	NOCI	Cl ₂	NO	
160 170	12.3 8.1	0.95 0.99	0.83 0.81	0.08 0.12	0.15 0.19	

and chlorine was accelerated by several condensations and evaporations. These indicated only a small pressure drop on reaction with mercury, as shown by the data of Table III. Considering that recombination is not complete, so that some chlorine is certainly present, the amount of NO_2 formed during 15 hours cannot be great.

The products of the reaction are thus essentially COCl₂, NOCl, NO, and Cl₂. There is, however, some evidence that all the NO and Cl₂ do not result from a simple secondary decomposition of NOCl. From the rate constants of the NOCl decomposition throughout the temperature range of our investigation⁵ calculations show that when 50 percent of the chloropicrin has been decomposed less than 1 percent of the NOCl formed will have dissociated into NO and Cl₂. Actual experiments were made by cooling the reaction vessel as quickly as possible after 25 or 50 percent of the chloropicrin had decomposed, and measuring the residual pressure at -103° C (at which temperature NO is all in the vapor phase, while the other products have a negligible vapor pressure). These measurements are only approximate, since the residual pressures are small, but they should give the order of magnitude of the partial pressure of NO. The results are given in Table IV.

Although these measurements are very rough, they indicate unequivocally that more NO is present than can be accounted for by the known rate of decomposition of NOCI. Furthermore, the

TABLE III. Products of reaction after recombination.

	Products, in Arbitrary Units			
TEMPERATURE, C	COC12	NOCI	Cl2	
160 160 160	10.8 11.7 10.5	10.5 11.2 10.6	0.4 0.35 0.2	
160	9.45	8.85	1.1	

⁵ Waddington and Tolman, J. Am. Chem. Soc. 52, 689 (1930).

Tempera- ture, °C	INITIAL CHLOROPICRIN PRESSURE, CM	Approximate Percent De- composition of Chloropicrin	P _{NO} , cm	Percent Decom- position of NOCI
160	15.5	48	0.8	15
	15.2	21	0.3	14
140	14.0	48	0.55	11
	19.0	26.5	0.15	5

TABLE IV. Decomposition of NOCl during the intermediate

stages of the reaction.

TABLE V. Data for typical experiments. TEMPERATURE 145.2°C 161.7°C 170.2°C INITIAL PRESSURE 10.8 cm 11.5 cm 11.3 cm % REAC % % Time, Min. REAC $k \times 10^4$ sec.⁻¹ Time. Min. REAC- $k \times 10^4$, TION sec.⁻¹ TIME MIN. $k \times 10^5$ sec.-1 TION TION 10 2 5.29.3 7.9 4.54.52 9.0 20 4 10.4 4 7.9 4.6 18.27.830 12.3 6 14.3 4.3 6 27.48.2 35.4 40 17.3 7.9 10 23.5 4.5 8 8.4 50 20.415 33.0 4.5 10 42.07.78.3 60 20 24.041.0 4.4 12 49.0 8.5 70 26.8 7.7 25 49.5 4.6 14 54.5 8.5 90 30 56.0 4.059.0 33.28.3 7.5 16 110 40 38.47.365.0 4.4 18 64.5 8.6 130 7.7 50 74.0 20 69.0 45.0 4.5 8.6 150 50.07.760 81.0 4.6

form of the pressure-time curves, and the agreement of the unimolecular constants throughout a run indicate that the reaction cannot be a rapid decomposition into phosgene and NOCl, followed by a slow decomposition of NOCl. The rate of recombination of NO and Cl₂ to NOCl is also slow, so that it cannot be assumed that we have

$$CCl_3NO_2 = COCl_2 + NO + \frac{1}{2}Cl_2$$

followed by recombination of NO and Cl_2 . The only alternatives seem to be, therefore, (a) NOCl and NO+ Cl_2 are produced independently,



followed by a later slow establishment of the equilibrium. (b) Some sort of "hot molecule" mechanism, such as

$$CCl_{3}NO_{2} = COCl_{2} + NOCl^{*},$$
$$NOCl^{*} + M = NOCl + M,$$
$$NOCl^{*} = NO + Cl,$$
$$2Cl = Cl_{2}.$$

(c) Some complex mechanism involving atoms or radicals which leads ultimately to the formation of NOCl, NO, and Cl₂.

In any case, secondary changes do not seem to be of any importance in the early stages of the reaction, and it appears to be justifiable to use the pressure change as a measure of the progress of the reaction.

THE RATE OF REACTION

Data for typical experiments are given in Table V. In calculating the percentage reaction from the pressure change, the effect of a 10 to 15 percent decomposition of NOCl is practically cancelled by the correction for 5 percent dead space, so that the percentage pressure increase is a direct measure of the percentage reaction. (Actually completion corresponds to a few percent more than 100 pressure increase, but this is almost entirely due to the very slow secondary decomposition of NOCl.) It will be seen from

TABLE VI. Summarized rate data.

Initial Pressure, cm	t ₂₅ , sec.	t ₅₀ , sec.	INITIAL PRESSURE, cm	<i>t</i> 25, sec.	t ₅₀ , sec.	
	Т	`emperatu	re 1 7 0.2°C			
20.7	300	710	7.2	310	744	
16.75	310	710	7.1	321	760	
11.3	324	750	4.3	310	744	
9.1	335	792				
	Т	emperatu	re 161.7°C			
18.4	600	1510	11.5	645	1584	
17.3	618	1518	11.2	612	1650	
16.5	690	1584	9.2	660	1560	
16.1	642	1530	7.8	690	1548	
13.1	600	1590	7.5	672	1698	
11.8	678	1602	6.6	690	1680	
	T_{i}	emperatu	re 153.5°C			
18.0	1440	3600	10.5	1560	3900	
17.7	1452	3540	9.2	1560	3510	
13.0	1524	3600	8.75	1548	3900	
12.5	1518	3900				
	T_{i}	emperatus	re 145.2°C			
18.2	3660	9300	11.0	3840	9300	
16.8	3720	9360	10.8	3900	9000	
Temperature 138.0°C						
19.6	7980		12.3	8040		
16.0	8100	·		0010		
Temperature 170.2°C—Packed Bulb						
16.0	337	780	6.65	300	740	
9.6	320	680		200	. 10	
Temperature 161.7°C—Packed Bulb						
20.7	610	1800	8.35	655	1680	
11.0	633	1780	0.00		1000	

Table V that satisfactory unimolecular constants are obtained.

Summarized data for all runs are given in Table VI. The packed bulb had a surface-volume ratio 15 times that of the empty vessel, so that it is evident that the surface has no appreciable effect on the rate of reaction.

The results may perhaps indicate a slight falling-off in rate at low pressures. The effect, however, is too small to establish with certainty. The rate of reaction at low pressures is at present under investigation. Since the high pressure rate appears to have been practically attained in the experiments given in Table VI, the temperature coefficient of the reaction has been calculated merely from the average values of t_{25} and t_{50} , without attempting an extrapolation to infinite pressure rates. These average values are given in Table VII. It will be seen that the average ratio of t_{50} to t_{25} over the whole temperature range is 2.42, as compared with the theoretical value of 2.41 for a unimolecular reaction.

In Fig. 2 the logarithms of t_{25} and t_{50} are plotted against 1/T. From the slopes of the lines we obtain 37,450 and 37,900 cal., respectively, for the activation energy. Whence, taking the mean of these, and making a rough extrapolation to infinite pressure of the results at 153.5,° we obtain

 $k = 4.90 \times 10^{15} e^{-37670/RT}$ sec.⁻¹.

This is a rather high value for the nonexponential factor.

The above value of the activation energy is in fairly good agreement with that calculated from Radulescu and Zamfirescu's results, *viz.* approximately 40,000 cal. Our velocity constants are, however, higher than theirs by a factor of about 2. They make no definite statement of the

Temperature, °C	<i>t</i> ₂₅ , sec.	<i>t</i> ₅₀ , sec.	t 50/t 25	
170.2 161.7 153.5 145.2	315 650 1525 3780	744 1587 3701 9315	2.36 2.44 2.43 2.46	
138.0	8040	mean = 2.42		

TABLE VII. Mean values of rate data.



conditions of pressure, etc. during their experiments. It appears probable, however, that their runs were really made with the chloropicrin almost entirely in the liquid phase. (They merely state that the chloropicrin was heated in an oil bath "en ampoules scellées a la lampe.") This would appear to be the cause of the difference in the rates.

It was hoped at the outset that it would be possible to compare the decomposition of chloropicrin with that of the analogous nonhalogenated compound, nitromethane. The decomposition of this substance has been investigated by Taylor and Vesselovsky,⁶ but the mechanism of the decomposition appears to be entirely different from that of chloropicrin, and no comparison of activation energies, etc. is possible. The difference in behavior is perhaps due to the higher strength of the C-H bond relative to that of C-Cl. In the case of nitromethane C-H splits are thus forbidden, and only the NO₂ group can participate in the primary step. With chloropicrin, however, C-Cl bonds presumably break as well.

⁶ H. A. Taylor and Vesselovsky, J. Phys. Chem. 39, 1095 (1935).