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The Thermal Decomposition of Nitrosyl Chloride

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The thermodynamics and kinetics of the reaction

$$2NO + Cl_2 \rightleftharpoons 2NOCl$$

have been studied by a number of investigators. The work of Trautz and Wachenheim[1] and the recent determinations by Dixon[2] have established the conditions for equilibrium over the temperature range from 170 to 465° with some precision. The kinetics of the reaction involved in the formation of nitrosyl chloride from nitric oxide and chlorine have also been the subject of extensive experiments by Kiss[3] and by Trautz.[4] The results show the reaction to be homogeneous and of the third order over a wide range of pressure and temperature. However, the fact that the technique used was not well adapted for the manipulation of corrosive gases and that the reverse reaction was not taken into account even at the highest temperatures, would suggest that the absolute value of the rate constants obtained may be somewhat in error.

The only work on the rate of the reverse reaction, namely, the decomposition of nitrosyl chloride, is that of Taylor and Denslow.[5] Using a flow method at 1020°K., where the decomposition is very fast, they were able to establish the order of magnitude of the rate but the experimental difficulties were such that no precise information on the kinetics of the reaction was obtainable. It is true that the rate of decomposition of nitrosyl chloride may be calculated from the rate of the reverse reaction and the equilibrium constant, but the accuracy of this procedure is limited by the data on the reverse reaction.

Hence, in view of the general dearth of satisfactory data on homogeneous bimolecular reactions, an experimental determination of the characteristics of the nitrosyl chloride decomposition was undertaken.

Preparation of the Compound

Nitrosyl chloride was prepared by two independent methods.

(a) The method of Scott and Johnson,[6] known to give a satisfactory product, was employed without, however, introducing all the minor refinements which they used for atomic weight work. By passing dry hydrogen chloride into nitrosyl sulfuric acid, obtained from sulfur dioxide and fuming nitric acid, nitrosyl chloride is produced. This procedure, followed by subsequent low-temperature distillation to eliminate hydrogen chloride, in an all-glass apparatus, gave a product of satisfactory purity. The reproduction of Dixon's values for the equilibrium between nitrosyl chloride, nitric oxide and chlorine was evidence that only traces of impurity could be present.

(b) It is known[7] that nitrogen dioxide and potassium chloride react according to the expression

$$KCl + 2NO_2 \longrightarrow KNO_3 + NOCl$$

Under appropriate conditions nitrosyl chloride of 97% purity may be obtained directly by this method, which can then be purified by distillation. In making use of this reaction nitrogen dioxide from a tank was passed through a 60-cm. column of potassium chloride, containing 2.4% water, at such a rate that the reaction zone never reached the top. The resulting nitrosyl chloride was condensed in a trap with a carbon dioxide–ether mixture, then distilled at −50° to free from non-volatile impurities, and finally distilled several times with intermittent pumping off of volatile impurities through a greaseless valve.[8]

Experimental Procedure

The course of the reaction was determined by following the pressure increase at constant volume. The supply of nitrosyl chloride, contained in a small flask closed by a greaseless valve was connected to the 200-cc. Pyrex reaction cell through another valve of the same type. The temperature of the hydrogenated cotton-seed oil-bath, in which the cell was heated, was controlled by a mercury regulator of conventional type to within 0.2°. The bath liquid mentioned may be used up to 250° without excessive smoking and odor if the system is moderately well closed. The thermometer used was calibrated against a thermometer which had been tested by the Bureau of Standards. Pressures were followed by means of a click gage, the manufacture and use of which have been described elsewhere.[9] Below 2.5 cm. a rough McLeod gage was used in conjunction with the click gage in place of the mercury manometer used at higher pressures. The unheated portion of the reaction system, consisting of short leads of small glass tubing to the greaseless valve and click gage, had a total volume of 1.5 cc. Neglect of this small volume in the calculation of rate constants caused no appreciable error although it had to be considered in the calculation of equilibrium constants.

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(1) Trautz and Wachenheim, *Z. anorg. allgem. Chem.*, **97**, 241(1916).

(2) Dixon, *Z. physik. Chem.*, Bodenstein Band, 679 (1931).

(3) Kiss, "Dissertation," Budapest, 1913; *Rec. trav. chim.*, **42**, 112, 665 (1923); **43**, 68 (1924).

(4) Trautz, *Z. anorg. Chem.*, **86**, 285 (1914); Trautz and Wachenheim, *ibid.*, **97**, 241 (1916); Trautz and Henglein, *ibid.*, **110**, 237 (1920).

(5) Taylor and Denslow, *J. Phys. Chem.*, **31**, 374 (1927).

(6) Scott and Johnson, *ibid.*, **33**, 1975 (1929).

(7) Whittaker, Lundstrom and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

(8) Ramsperger, *Rev. Sci. Inst.*, **2**, 738 (1931).

(9) Smith and Taylor, THIS JOURNAL, **46**, 1393 (1924).

Individual runs were conducted as follows. Previous to the experiment the cell was evacuated for some time with a mercury diffusion pump. The supply of nitrosyl chloride (maintained at the temperature of solid carbon dioxide when not in use) was allowed to warm up to a temperature where its vapor pressure was somewhat greater than the pressure desired. The click gage was adjusted so that it would click when the predetermined pressure had been reached in the cell. The valves closing the supply bulb and reaction cell were opened until the click was heard and then rapidly closed. This operation took only a few seconds. Pressure measurements were commenced immediately and were continued at convenient intervals throughout the course of the run. Initial pressures were obtained by plotting pressure against time and extrapolating to zero time. The error involved in the extrapolation, save in the case of the fastest runs, was small on account of the slight curvature of the plot and short time interval over which the extrapolation had to be made. Many runs were allowed to proceed until the final equilibrium was reached, thus obtaining a check on the purity of the compound with the help of Dixon's figures. In order to test the homogeneity of the reaction several runs were made in which the surface-to-volume ratio had been increased about ten-fold by packing with short lengths of Pyrex tubing.

Experimental Results

The thermal decomposition of nitrosyl chloride presumably proceeds according to the reversible reaction

$$2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$$

the rate of decomposition following the expression

$$-\frac{d(\text{NOCl})}{dt} = k_2(\text{NOCl})^2 - k_3(\text{NO})^2(\text{Cl}_2)$$

This expression is difficult to integrate but was used in differential form, without appreciable error, by substituting the change in concentration corresponding to successive time intervals. Remembering that $k_2 = k_3K$, where K is the equilibrium constant for the reaction, the second order constant is then given by the relation

$$k_2 = \frac{\Delta(\text{NO})2K}{\Delta t[2K(\text{NOCl})^2_{\text{av.}} - (\text{NO})^3_{\text{av.}}]}$$

where the indicated averages were taken as the arithmetical means of the concentrations at the beginning and end of the time interval Δt. The values of K used at different temperatures were calculated from Dixon's[2] equation which covers the temperature range from 170 to 465°. Rate measurements were made down to 150°; hence a small and perfectly safe extrapolation was necessary to obtain the equilibrium constant at the lowest temperatures.

A summary of all experiments is given in Table I The first column gives the number of the experiment, and the second column the temperature of the bath in degrees centigrade. The third column gives the initial pressure of the nitrosyl chloride in centimeters of mercury obtained with the help of extrapolation back to zero time, except in runs 2 and 26, where it was necessary to calculate the initial pressure from the final pressure and equilibrium, owing to an unusually long delay in obtaining the first pressure reading. The fourth column gives the specific reaction rate k_2 in cc. mole^{-1} sec.$^{-1}$ for the bimolecular decomposition calculated as indicated above, and the last column gives the specific reaction rate k_3 in cc. mole^{-2} sec.$^{-1}$ for the trimolecular reverse process calculated from the relation

$$k_3 = k_2/K$$

TABLE I

Expt.	T, °C.	p_0, cm.	k_2 cc. mole^{-1} sec.$^{-1}$	k_3 cc. mole^{-2} sec.$^{-1}$
18	150.1	17.35	3.52	1.93×10^8
19	150.1	22.33	3.88	2.13
16	170.0	10.60	12.55	2.78
17	170.0	12.74	13.25	2.94
14	179.8	10.32	24.1	3.36
15	179.8	11.53	23.3	3.25
12	189.9	9.40	42.6	3.88
13	189.9	6.71	43.4	3.95
10	200.0	9.87	77.90	4.72
11	200.0	9.89	74.65	4.52
1	209.8	8.82	118	4.95
2	209.8	20.82	123	5.16
9	209.8	8.37	126.5	5.32
20	209.8	9.75	125.5	5.27
21	209.8	8.21	123	5.17
22	209.8	3.34	121	5.08
28	209.8	7.57	124	5.21
3	219.6	6.24	217	6.31
4	219.6	4.12	229	6.65
27	219.6	4.47	224	6.52
7	229.9	6.60	385	8.04
8	229.9	4.68	354.5	7.38
23	240.4	1.57	582	8.41
24	240.4	2.26	549	7.95
25	250.7	1.34	996	10.3
26	250.7	1.85	1100	11.4

Experiments 1 to 20 were made with nitrosyl chloride prepared from potassium chloride and nitrogen dioxide while in runs 21 to 28 a sample prepared from nitrosyl sulfuric acid was used. It is seen that the method of preparation of the compound has substantially no effect on the rate of the reaction. Runs 27 and 28 as well as several unlisted preliminary experiments were made in a cell packed with short lengths of Pyrex tubing which served to increase ten-fold the ratio of surface area to volume. The results show plainly that the decomposition is homogeneous, as has been shown by previous investigators to be the case for the reverse reaction.

In Table II are given the complete data for two experiments. The magnitude of deviation from the mean value of the rate constants for these two runs is of the same order as for all other runs.

TABLE II

Expt. 12. Temp., 189.9°; K, cc. mole^{-1}, 1.09×10^{-7}

Time	p, cm.	$(NO)_{av.}$ cc. mole^{-1}	$(NOCl)_{av.}$ cc. mole^{-1}	k_2 cc. mole^{-1} sec.$^{-1}$
0	9.40			
62	9.45			
469	9.70	1.20×10^{-7}	31.36×10^{-7}	43.2
913	9.95	2.93	29.63	45.0
1552	10.24	4.80	27.76	43.7
2340	10.48	6.64	25.92	39.0

Expt. 3. Temp., 219.6°; K, cc. mole^{-1}, 3.45×10^{-7}

Time	p, cm.	$(NO)_{av.}$ cc. mole^{-1}	$(NOCl)_{av.}$ cc. mole^{-1}	k_2 cc. mole^{-1} sec.$^{-1}$
0	6.24			
73	6.35			
237	6.56	1.39×10^{-7}	18.93×10^{-6}	233
451	6.77	2.77	17.55	218
712	6.99	4.16	16.16	209
1087	7.22	5.63	14.69	209

In Fig. 1 the values of $\log_{10} k_2 - {}^1/_2 \log_{10} T$ have been plotted against $1/T$. From the slope of this line the value of E in the equation

$$k_2 = A T^{1/2} e^{-E/RT}$$

is obtained. A fairly satisfactory expression for the rate constant over the temperature range studied is given by

$$k_2 = 4.3 \times 10^{11} T^{1/2} e^{-24,000/RT} \text{ cc. mole}^{-1} \text{sec.}^{-1}$$

where the energy of activation E is in calories.

It is interesting to compare this with the rate predicted by the relationship

$$k_2 = 2Ze^{-E/RT}$$

where Z is the total number of collisions conveniently expressed in moles colliding per cc. per second, E is the activation energy as obtained above and the factor 2 arises from the fact that 2 molecules decompose at each successful collision. Z in moles colliding per cc. per second is given by the expression[10]

$$Z = 10^{28.2922} \sigma^2 (T/M)^{1/2}$$

Taking the molecular diameter σ as 3×10^{-8} cm., the value of k_2 obtained in this way is found to be ten times as large as the experimental value. If the simple collision theory of bimolecular reactions is a good approximation to the truth, then from the direction of the deviation between theory and experiment the conclusion could be drawn that only about 1 collision in 10 between activated molecules leads to reaction. Other well-known bimolecular reactions, namely, the decompositions of hydrogen iodide[11] and of nitrogen dioxide,[12] the hydrogenation of ethylene,[13] and the dimerization of ethylene,[14] isoprene[15] and 1,3-butadiene[16] all give evidence of the same phenomenon with the factor decreasing in the order mentioned from approximately 1 to 1 to about 1 to 10,000. The explanation usually given is that an orientation as well as an energy requirement must be satisfied before reaction can occur.

When plotted on a large scale the curve of log $k_2 - {}^1/_2$ log T vs. $1/T$ exhibits a small curvature in the direction of increasing activation energy at higher temperatures, an effect which is reasonably well established in the case of the decomposition of hydrogen iodide. The accuracy of the present data, however, does not warrant a precise statement as to the reality or magnitude of this possible effect, which Kassel[17] has shown to be theoretically plausible.

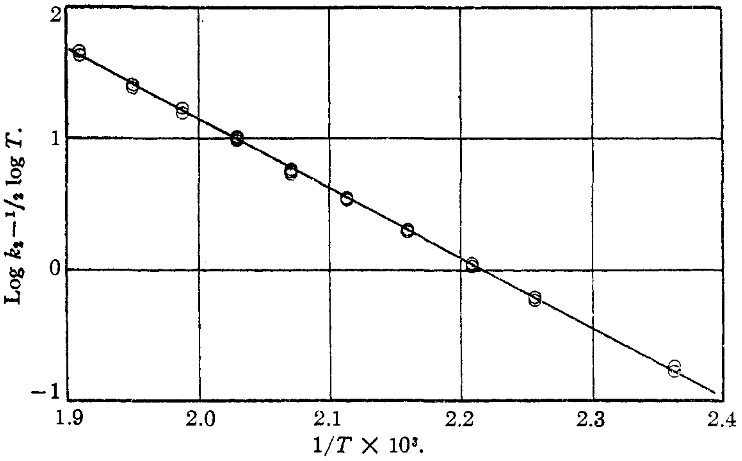

Fig. 1.

Turning now to the third order reverse reaction, Fig. 2 gives a plot of values of $\log_{10} k_3 - {}^1/_2 \log_{10} T$ against $1/T$. The plot presents not

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[10] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co., Inc., New York.

[11] Bodenstein, *Z. physik. Chem.*, **13**, 56 (1895); **22**, 1 (1897); **29**, 295 (1898).

[12] Bodenstein and Ramstetter, *ibid.*, **100**, 107 (1922).

[13] Pease, THIS JOURNAL, **54**, 1876 (1932).

[14] Pease, *ibid.*, **52**, 1158 (1930); **53**, 613 (1931).

[15] Vaughan, *ibid.*, **55**, 4109 (1933).

[16] Vaughan, *ibid.*, **54**, 3863 (1932).

[17] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., New York.

only our own calculated values for the specific rate k_3 as given in the last column of Table I, but also the directly measured values of k_3 obtained by Kiss and by Trautz in so far as they fall within the temperature range which we have investigated. The satisfactory internal coherence of our own data and the reasonable agreement of the directly measured data therewith will be noted.

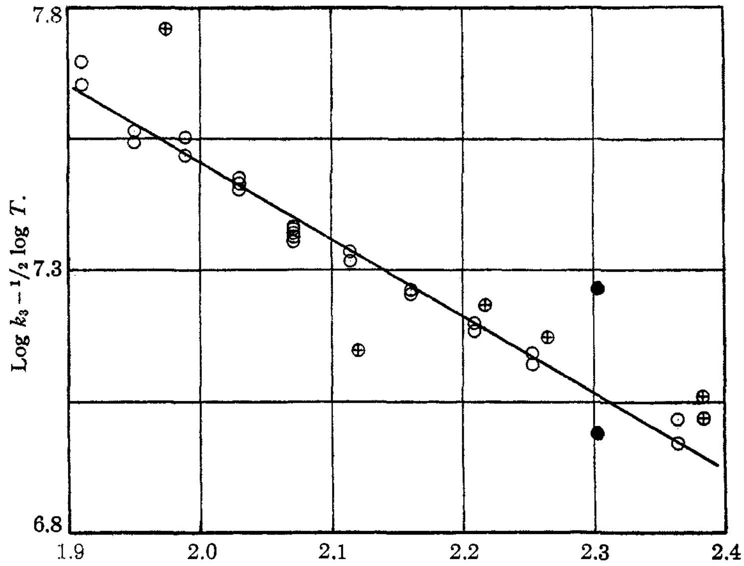

Fig. 2.—●, Trautz; ⊗, Trautz and Wachenheim; O, Waddington and Tolman.

If the data on the third order reaction are represented by an expression of the form

$$k_3 = AT^{1/2}e^{-E/RT}$$

the energy of activation E definitely appears in this case to increase with temperature, an effect which is even more marked when the larger temperature range directly investigated by Kiss and by Trautz is considered.[17] Over our own temperature range the results can be roughly represented by the expression

$$k_3 = 3.15 \times 10^{10}T^{1/2}e^{-6860/RT}\text{ cc. mole}^{-2}\text{ sec.}^{-1}$$

where the energy of activation is again given in calories.

It is interesting to compare this with the rate predicted by the relationship

$$k_3 = 2Ze^{-E/RT}$$

where Z is the total number of triple collisions from which reaction could arise. Assuming that such collisions occur when the surfaces of two NO molecules are simultaneously within some small distance δ of the surface of a Cl_2 molecule we can obtain for Z the approximate expression[10]

$$Z = (N_1)^2(N_2)(4\pi\ \sigma_{12}^2)^2\ \delta \left(\frac{RT(M_1 + M_2)}{2\pi M_1M_2}\right)^{1/2}$$

where N_1 and N_2 are the number of molecules of NO and Cl_2, respectively, which would be present in unit volume when the gases are themselves taken at unit concentration, σ_{12} is their mean diameter, and M_1 and M_2 the corresponding molecular weights. The theoretical expression thus obtained for k_3, using $\sigma_{12} = 3 \times 10^{-8}$ cm., agrees with the experimental one provided we assign to δ the very small value 4×10^{-13} cm. This figure, which we would have to regard as the maximum separation between the surfaces of our idealized spherical molecules when reaction takes place, is small enough to justify the provisional assignment of triple collisions as the actual mechanism by which the reaction does occur.

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Summary

The homogeneous thermal decomposition of nitrosyl chloride has been studied over the temperature range 150.1 to 250.7°. The reaction may be interpreted satisfactorily as a bimolecular decomposition accompanied by a trimolecular reverse reaction. The specific rate constant as a function of temperature for the decomposition reaction is given by the expression

$$k_2 = 4.3 \times 10^{11}T^{1/2}e^{-24{,}000/RT}\text{ cc. mole}^{-1}\text{ sec.}^{-1}$$

with the energy of activation in calories.

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