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REACTIONS IN THE SYSTEM HYDROGEN, CHLORINE, NITRIC OXIDE, AND NITROSYL CHLORIDE

PART 2.-THE THERMAL DECOMPOSITION OF NITROSYL CHLORIDE

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Experimental evidence is presented that the rate of decomposition of nitrosyl chloride is faster at 300° C than would be expected from previously published work, and that chlorine has an accelerating effect on the initial rate of decomposition. These results can be explained by the dissociation of nitrosyl chloride NOCl \rightarrow NO + Cl followed by the fast reaction Cl + NOCl \rightarrow NO + Cl₂, and this mode of decomposition will become more important than the bimolecular decomposition 2NOCl \rightarrow 2NO + Cl₂ at higher temperatures. The accelerating effect of chlorine is due to the increased rate of production of chlorine atoms.

The rate of decomposition of nitrosyl chloride has recently been investigated at temperatures between 250° and 300° C, as part of a study ¹ of the effect of nitrosyl chloride on the thermal reaction between hydrogen and chlorine. The rates observed are faster than would be predicted from the work of Tolman and Waddington ² carried out at lower temperatures. The initial rates of decomposition are also markedly increased upon the addition of chlorine, in contrast to the effect which would be expected if only the reactions (1) and (2) are operating.

$$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2 \tag{1}$$

$$2NO + Cl_2 \rightarrow 2NOCl. \tag{2}$$

EXPERIMENTAL

The decomposition was followed in the static system described in part 1 of this series,¹ by the pressure increase which is associated with the change.

It was desired to follow the initial rates of decomposition in order to eliminate the effect of the back reaction (2).

The premixed gases were admitted rapidly through a wide-bore tap into the preheated reaction vessel from the mixing vessel and Bourdon gauge. Two seconds after admission, the mixing vessel was shut off, and at 5 sec the first pressure reading was taken. Pressure readings were taken thereafter at convenient intervals, for example, every 5 sec at 300° C. The readings were extrapolated both graphically and numerically to zero time to give the initial pressure. The reproducibility of individual readings was good, and the pressure increases could be estimated to \pm 0.04 mm Hg with certainty. The results quoted are the means of several runs (usually three) and are probably accurate to \pm 0.02 mm. The pressure readings were corrected for the volume of the dead space which by careful construction of the Bourdon gauge and connecting tubing was made about 3 % of the volume of the reaction vessel at room temperature. The factors by which the pressure changes had to be multiplied were 1.063 at 300° C and 1.058 at 250° C. Some runs were followed until equilibrium was established.

The gases were prepared and purified by the methods indicated in part 1 of this series.¹ The adsorption of chlorine by the tap grease was found to be small over the longest period studied provided that the grease had been used for several runs, and the effect on the early rates was certainly negligible. The absence of any pressure change, due to heating, immediately after admitting the gases to the reaction vessel was checked using nitrogen and hydrogen.

RESULTS

The values obtained for the equilibrium constant K_E , given by $p_{Cl_2} p_{NO}^2/p_{NOCl}^2$ and calculated from the final pressure change Δp after long runs with various initial pressures of nitrosyl chloride, were in excellent agreement with those of Dixon.³ Some of the values obtained at 300° C are given in table 1, with all pressures in mm Hg. p_A is the pressure of argon used as a carrier gas (see below).

TABLE 1

<i>P</i> NOCI	4	4	6	8	8	10
P_{Cl_2}		50	70		50	50
PA	100	50	70	100	50	50
$\Delta p ~(\pm 0.02)$	1.79	1.25	1.74	3.46	2.48	3.09
K _E	136 ± 13	140 ± 5	138 ± 3	141 ± 5	140 ± 3	139 ± 2

In comparison, the value of K_E calculated from the formula given by Dixon is 138 mm at 300° C.

The rate of decomposition of the nitrosyl chloride was followed at 250° , 270° and 300° C. Some typical plots of the pressure increase early in the reaction are shown in fig. 1 for different mixtures of gases. The initial rate expected from the data of Tolman and Waddington is also shown. It will be seen that (i) the initial rate observed in the absence of added chlorine at 300° C is very nearly 5 times as large as expected; (ii) the initial rate is increased by the addition of chlorine.

 TABLE 2.—PRESSURE INCREASES EARLY IN THE DECOMPOSITION OF 6 mm of NITROSYL

 CHLORIDE AT 300° C.
 ALL PRESSURES IN mm Hg

time (sec)	NOCI alone	NOCI + 50 mm Cl ₂	NOC1 +50 mm Cl ₂ +50 mm H ₂	NOCi +50 mm Ci ₂ +100 mm H ₂	NOCl +70 mm Cl ₂	NOC1 +70 mm Cl ₂ +70 mm H ₂	NOC1 +50 mm Cl ₂ +50 mm H ₂ +200 mm N ₂
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	0.09	0.20	0.19	0.18	0.25	0.26	0.19
10	0.18	0.37	0.36	0.32	0.45	0.47	0.36
20	0.34	0.64	0.64	0.56	0.74	0.75	0.66
30	0.48	0.82	0.85	0.74	0.95	0.97	0.91

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The addition to the nitrosyl chloride of hydrogen as well as chlorine does not produce much additional effect. When considerable excess of hydrogen is added, the rate of decomposition decreases slightly. This is shown in table 2 by comparing column 3 with columns 4 and 5, and column 6 with column 7. The effect of adding 200 mm of nitrogen to the mixture of 6 mm of nitrosyl chloride, 50 mm of chlorine, and 50 mm of hydrogen was negligible (columns 4 and 8). The use of argon in place of chlorine gave the same rates as with nitrosyl chloride alone, and in later experiments argon was run in with the nitrosyl chloride to act as a carrier gas.

If reactions (1) and (2) were the only reactions occurring, it would be expected that the initial rate of decomposition would be unaltered by the addition of chlorine; later in the reaction, the rate would be lower because of the effect of chlorine on the back reaction (2). This does happen at 250° C, but at higher temperatures the effect of chlorine on the back reaction is more than counterbalanced by some other reaction. This is shown in fig. 2*a*, *b*, *c*. At 250° C the decomposition curve in the presence of 70 mm Cl₂ and 70 mm H₂ gradually falls below the curve for 50 mm Cl₂ and 50 mm H₂; at 270° C, however, the position is reversed, and at 300° C the curves are clearly differentiated.



FIG. 1.—The pressure increase in the initial stages of decomposition of 6 mm of nitrosyl chloride at 300° C, with and without chlorine. The bottom curve shows the pressure increase expected from Waddington and Tolman's data. All pressures in mm Hg.

The increase of the initial rate in the presence of higher pressures of chlorine and hydrogen is not due in any way to the formation of hydrogen chloride; the figures of table 2 demonstrate this, and separate experiments ¹ have established that there is an induction period for the formation of hydrogen chloride from chlorine and hydrogen in the presence of nitrosyl chloride. During the induction period extremely little hydrogen chloride is formed. The end of the induction period is shown by the arrows in fig. 2a, b, c.

DISCUSSION

A simple explanation can be given of the enhanced rates of decomposition at higher temperatures and of the effect of adding chlorine. It is that at these temperatures the dissociation of the Cl-N < bond sets in

NOCl
$$\xrightarrow{\kappa_2}$$
 NO + Cl, (3)

followed by the fast reaction ⁴

$$Cl + NOCl \xrightarrow{\kappa_6} NO + Cl_2.$$
 (4)

(The rate constants are numbered in conformity with part 1 of this series of papers.)

Let it be assumed that (3), which is the rate-determining step in this new decomposition path, is a unimolecular decomposition with an activation energy equal to the Cl-N < bond dissociation energy of 38 kcal mole⁻¹. The frequency



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factor ⁶ probably lies between 10^{12} and 10^{13} sec⁻¹. Taking the lower of these figures to test whether the proposed path can account for the observed results, the value of k_2 at 300° C is 4×10^{-3} sec⁻¹; and the initial rate of decomposition of 6 mm of nitrosyl chloride would be $2k_2[\text{NOCI}] = 0.05$ mm sec⁻¹. Concentrations are here expressed as mm Hg at 300° C for convenience. This rate may be compared with a rate (-d[NOCI]/dt) calculated from the formula given by Tolman and Waddington for the bimolecular decomposition (1) of 0.0066 mm sec⁻¹, and with the experimentally measured rate of 0.034 mm sec⁻¹.

The sequence of reactions (3) (rate-determining) followed by (4) (rapid) is thus quite capable of accounting for the difference between the observed rate and that calculated for (1). If this difference is attributed solely to the proposed decomposition path, and the activation energy is taken as 38 kcal mole⁻¹, then the value of the frequency factor would be $6 \times 10^{11} \text{ sec}^{-1}$. The activation energy of (3) is greater than that of (1) which is only 24 kcal mole⁻¹, and so the difference between the observed rate and that calculated from (1) will increase with rise of temperature; also, the activation energy calculated from the slope of log $k_{expt.}$ against 1/T plots will increase, as was observed by Tolman and Waddington and by Taylor and Welinsky (see fig. 1 of ref. (7)), although this increase was then attributed to other causes.

When chlorine is added, a new source of chlorine atoms is provided

$$Cl_2 \xrightarrow{\kappa_3} 2Cl$$
 (5)

$$2Cl \xrightarrow{\kappa_8} Cl_2. \tag{6}$$

The equilibrium concentrations of chlorine atoms and molecules satisfy the equations $[Cl]^2/[Cl_2] = k_3/k_8 = K_D$. K_D , the equilibrium constant of the dissociation, has been tabulated ⁸ and at 300° C has a value $2 \cdot 76 \times 10^{-14}$ mm. The equilibrium concentration of chlorine atoms in 50 mm of chlorine at 300° C is thus $1 \cdot 2 \times 10^{-6}$ mm. If this concentration of chlorine atoms were maintained when 6 mm of nitrosyl chloride was added to 50 mm of chlorine, then the initial rate of decomposition of the 6 mm of nitrosyl chloride due to (4) would be

$$k_6 \times 6 \times 1.2 \times 10^{-6} \text{ mm sec}^{-1}$$
.

The value of k_6 can be calculated from the expression given by Burns and Dainton; ⁴ at 300° C it is 1.27×10^5 mm sec⁻¹. Hence the rate of decomposition of nitrosyl chloride due to the added chlorine might be as high as

$$1.27 \times 10^5 \times 7.2 \times 10^{-6}$$
 or 0.90 mm sec⁻¹.

In fact the observed excess rate due to the added chlorine can be seen from table 2 to be about $(0.37 - 0.18)/10 \times 2$, or $0.038 \text{ mm sec}^{-1}$. Hence the proposed effect of adding chlorine is potentially capable of accounting for the increase in rate; the observed effect is less than the predicted because the concentration of the chlorine atoms is far below the normal concentration as long as 6 mm of nitrosyl chloride are present. Under these circumstances, the association reaction (6) is probably very slow compared with (4), because its rate depends on [Cl]². Consequently, inert gases such as argon and nitrogen which might operate by assisting (6) by three-body collisions, have no effect on the initial rate of decomposition (compare columns 4 and 8 of table 2).

When hydrogen is added, the reaction

$$Cl + H_2 \xrightarrow{k_4} HCl + H$$
 (7)

competes with (4) for chlorine atoms. However, the values of k_6 and k_4 are such that the reaction (7) is slow compared with reaction (4) unless large concentrations of hydrogen are added.¹ Consequently, as was observed, the initial rate of decomposition is only affected by large pressures of hydrogen and is then decreased.

The reaction $NO + Cl_2 \rightarrow NOCl + Cl$

It seems possible that the portion of the excess rate which can be attributed to reactions yielding chlorine atoms could be used to calculate the rate constants of these reactions, just as k_2 was estimated above. The measurements made so far suggest that the rate of production of chlorine atoms from molecular chlorine is proportional to the first power of the chlorine pressure. However, it would be premature to push this further until experiments have been made to check the site of this reaction; it is usually assumed (from experiments on the hydrogen + chlorine reaction) that the wall reaction is faster than the gas phase reaction at temperatures below 300° C. Further experiments are projected to test these suggested mechanisms.

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