THERMAL DECOMPOSITION OF NITROSYL CHLORIDE CATALYZED BY NITROGEN DIOXIDE

By P. G. Ashmore and M. G. Burnett
Dept. of Physical Chemistry, Lensfield Road, Cambridge

Received 5*th January*, 1961

The thermal decomposition of nitrosyl chloride catalyzed by nitrogen dioxide has been studied at 300°C and the rate of reaction in the presence of nitric oxide is consistent with the following mechanism:

$$\mathrm{NOCl+NOCl}\xrightarrow{1}\mathrm{2NO+Cl_2}$$

$$\mathrm{NOCl+M}\xrightarrow{3}\mathrm{NO+Cl+M}$$

$$\mathrm{NOCl+Cl}\xrightarrow{6}\mathrm{NO+Cl_2}$$

$$\mathrm{NOCl+NO_2}\xrightarrow{12}\mathrm{NO_2Cl+NO}$$

$$\mathrm{NO+NO_2Cl}\xrightarrow{13}\mathrm{NO_2+NOCl}$$

$$\mathrm{NO_2Cl+M}\xrightarrow{14}\mathrm{NO_2+Cl+M}$$

$$\mathrm{NO_2Cl+NOCl}\xrightarrow{15}\mathrm{NO_2+NO+Cl_2}.$$

Values for certain combinations of the rate constants have been found and absolute values for $k_{14.\mathrm{M}}$ at 300°C have been estimated for $\mathrm{M = NO_2}$ and $\mathrm{M = N_2}$. Fresh estimates have also been made for $k_{3,\mathrm{M}}$ at 300°C for M = NOCl, NO and N_2 and these are consistent with previous determinations.

It has been found that the addition of nitrogen dioxide leads to a very fast, but rapidly inhibited, decomposition of nitrosyl chloride during which the nitrogen-dioxide concentration remains unchanged. Ashmore and Spencer [1] found that nitrosyl chloride decomposed homogeneously at temperatures above 250°C through a radical path ((3) to (6)) involving chlorine atoms, in parallel with the bimolecular decomposition (1). They also suggested a heterogeneous radical path, but no definite evidence could be found for this in the quartz vessel used for the catalyzed decomposition. They proposed the following mechanism:

$$\mathrm{NOCl+NOCl}\underset{2}{\overset{1}{\rightleftharpoons}}\mathrm{2\,NO+Cl_2}$$

$$\mathrm{NOCl+M}\underset{4}{\overset{3}{\rightleftharpoons}}\mathrm{NO+Cl+M}$$

$$\mathrm{NO+Cl_2}\underset{6}{\overset{5}{\rightleftharpoons}}\mathrm{NOCl+Cl}$$

In the absence of nitrogen dioxide, the addition of nitric oxide to nitrosyl chloride slightly increases its initial rate of decomposition due to nitric oxide acting as M in reaction (3) (column 2, table 1). In contrast, added nitric oxide drastically reduces the catalyzed rate, as can be seen from column 3 of table 1. It therefore appears that the inhibition observed in the course of a run is due to nitric oxide formed during a run. Calculations showed that the catalysis by nitrogen dioxide cannot be due to reaction 3 with $M = NO_2$, unless nitrogen dioxide is many times more effective than nitrosyl chloride or nitric oxide, and there seems no reason for this. Calculations also showed that the inhibition of the catalyzed reaction by nitric oxide cannot be accounted for by reactions 2, 4 or 5.

TABLE 1.—RATE OF DECOMPOSITION (dp_{NOCl}/dt IN mm sec^{-1}) OF 10 mm OF NITROSYL CHLORIDE AT 300°C

NO added (mm)	rate without NO_2 present	rate with 5 mm NO_2 added
0	·028	>·6
10	·030	·079
20	·033	·073
30	·035	·072

This catalysis by nitrogen dioxide and inhibition of the catalyzed reaction by nitric oxide can be explained in terms of the formation of nitryl chloride by reaction 12 and its removal by reaction 13. Nitryl chloride can increase the rate of decomposition of nitrosyl chloride by acting as a fresh source of chlorine atoms (reaction 14) or by the bimolecular reaction 15. In either case, the overall effect is the decomposition of nitrosyl chloride without altering the concentration of nitrogen dioxide:

$$NO_2 + NOCl \xrightarrow{12} NO_2Cl + NO$$

$$NO_2Cl + NO \xrightarrow{13} NOCl + NO_2$$

$$NO_2Cl + M \xrightarrow{14} NO_2 + Cl + M$$

$$NO_2Cl + NOCl \xrightarrow{15} NO_2 + NO + Cl_2.$$

The relative rates of reactions 13 and 14 at 300°C can be estimated from the results of kinetic studies at lower temperatures. Freiling, Johnston and Ogg[2] found that $k_{13} = 0{\cdot}83 \times 10^{12} \exp -(6900/RT)$ between 1 and 71°C, and hence at 300°C $k_{13} = 1{\cdot}9 \times 10^9$ moles^{-1} cm^3 sec^{-1}. Cordes and Johnstone[3] found that $k_{14,NO_2Cl} = 5{\cdot}8 \times 10^{16} \exp -(27{,}000/RT)$ between 180 and 248°C, and hence at 300°C, $k_{14,NO_2Cl} = 1{\cdot}7 \times 10^6$ moles^{-1} cm^3 sec^{-1}. Evidently $k_{13}/k_{14} \sim 10^3$ at 300°C so that nitric oxide would be expected to cut out path 14 very effectively; as shown later, $k_{15} \leqslant k_{14}$ at 300°C, so that the bimolecular reaction 15 would also be eliminated.

Ray and Ogg[4] have previously reported that at 25°C nitrogen dioxide catalyzed the reaction $2\,NOCl + O_2 \rightarrow 2\,NO_2Cl$ and their reaction scheme included a very rapidly established equilibrium between reactions 12 and 13.

EXPERIMENTAL

METHOD

The gases nitrosyl chloride, nitrogen dioxide, and nitric oxide were prepared and purified by conventional methods. The nitrogen was taken from a white-spot cylinder and was passed through a trap cooled in liquid nitrogen. A cylindrical quartz reaction vessel was used, 3·5 cm in diam. and 20 cm long, in an electric furnace held at 300±0·2°C.

The concentration of nitrogen dioxide was determined with a logarithmic photometer, using a light source with a band of wavelengths from 4450 to 5000 Å. In this region, direct calibration with nitrogen dioxide, nitrosyl chloride, and chlorine showed that the signals produced by equal pressures of the gases were in the ratios 133 : 9·7 : 1, and that for each gas the signal was directly proportional to its concentration over the range of pressures used in the kinetic experiments. In experiments with nitrogen dioxide present, the absorption of light by chlorine can be ignored, but corrections must be applied for absorption by any nitrosyl chloride present. The amount of nitrosyl chloride present was determined from the initial amount and the pressure change, measured on a Bourdon gauge. The pressure and photometer readings showed that the nitrogen dioxide concentration remained the same during the catalyzed runs.

In the absence of nitrogen dioxide, the decomposition of the nitrosyl chloride (with or without inert gases present) was followed by the pressure change and also by the photometer (making a correction for the chlorine formed). No significant differences could be found between the values of the velocity constants of the decomposition determined by both methods. This provides an important check that the use of the photometer does not introduce photochemical decomposition of the nitrosyl chloride, and also justifies the method used to follow the catalyzed runs.

The rates measured in this study were all within the limiting rates of response of the instruments concerned. Both Bourdon and photometer readings were recorded using a telegraph key operating an event marker on a chronograph. When Bourdon and photometer were used simultaneously, the photometer signal was recorded as a trace on Record pen recorder. Generally for the first 15-20 % of reaction, during which at least 10 observations were obtained, the change of the empirical first- or second-order rate constant, calculated from the pressure-time curve, is small and regular. This permits extrapolation of the empirical constant to zero time with an accuracy of about 5 % of the total.

REACTION SCHEME AND REACTION RATE

It appeared from preliminary experiments based on the arguments presented in the introduction that reactions 12, 13, 14 and 15, together with part of the reaction scheme proposed by Ashmore and Spencer,[1] would explain the catalytic effect of nitrogen dioxide on the decomposition of nitrosyl chloride. The heterogeneous part of the reaction scheme was omitted because tests on nitrosyl chloride alone showed the heterogeneous steps to be unimportant in the quartz vessel at 300°C. The " combination " reactions in the full scheme were not included in the scheme for the catalyzed decomposition because only the first 15-20 % of the decomposition was followed. In addition, calculation showed that reactions 2, 4 and 5 could be omitted even in the presence of added nitric oxide. A reaction similar to 6 of chlorine atoms with nitryl chloride was omitted because of the low concentrations of both species. The reaction scheme therefore reduces to the following:

$$\mathrm{NOCl+NOCl\xrightarrow{1}2\,NO+Cl_2}$$

$$\mathrm{NOCl+M\xrightarrow{3}NO+Cl+M}$$

$$\mathrm{NOCl+Cl\xrightarrow{6}NO+Cl_2}$$

$$\mathrm{NOCl+NO_2\xrightarrow{12}NO_2Cl+NO}$$

$$\mathrm{NO_2Cl+NO\xrightarrow{13}NOCl+NO_2}$$

$$\mathrm{NO_2Cl+M\xrightarrow{14}NO_2+Cl+M}$$

$$\mathrm{NO_2Cl+NOCl\xrightarrow{15}NO_2+Cl_2+NO}$$

The values of k_{13} and k_{14} at 300° have already been evaluated ($1\cdot9\times10^9$ and $1\cdot7\times10^6$ moles^{-1} cm^3 sec^{-1} respectively). The ratio k_{12}/k_{13} can be estimated, using the thermodynamic data given by Ray and Ogg[4] for nitryl chloride. This ratio is the equilibrium constant of the reaction $\mathrm{NO_2+NOCl\rightleftharpoons NO_2Cl+NO}$ and for this reaction the thermodynamic data lead to $\Delta H^\circ = 4060$ cal and $\Delta S^\circ = -4\cdot13$ cal/mole deg. Hence at 300°C, $k_{12}/k_{13} = 3\cdot5\times10^{-3}$, and $k_{12} = 6\cdot6\times10^6$ moles^{-1} cm^3 sec^{-1}. From the reaction scheme, the maximum concentration of $\mathrm{NO_2Cl}$ is

$$k_{12}[\mathrm{NOCl}][\mathrm{NO_2}]/(k_{13}[\mathrm{NO}]+\Sigma k_{14,\mathrm{M}}[\mathrm{M}]+k_{15}[\mathrm{NOCl}]).$$

As the concentrations used are each about 1×10^{-7} mole cm^{-1} and as $k_{15}\leqslant k_{14}\leqslant k_{13}$, it follows that in most of the catalyzed reactions

$$[NO_2Cl]_{max}=k_{12}[NOCl][NO_2]/k_{13}[NO]\sim3{\cdot}5\times10^{-10}\text{ moles cm}^{-3}.$$

The rate at which NO_2Cl is formed by reaction 12 is $\sim6\times10^{-8}$ mole cm^{-3} sec^{-1}. Therefore, (i) the maximum concentration of NO_2Cl is a very small fraction of the concentration of the main reactants, (ii) this maximum value is reached in a small fraction of a second, compared with several seconds for the half-life of the catalyzed reaction. Hence, it is justifiable to treat the nitryl chloride as reaching a steady stationary state. It is clearly justifiable to do so for Cl atoms. The reaction scheme then leads to a rate expression

$$\frac{d(1/[NOCl])}{dt}=k_1+\frac{2\Sigma k_{3,M}[M]}{[NOCl]}+\frac{2\Sigma k_{14,M}[M]k_{12}[NO_2]}{k_{13}[NO][NOCl]}+\frac{2k_{12}k_{15}}{k_{13}}\frac{[NO_2]}{[NO]}.$$

In all cases, parallel studies of the rate of decomposition of nitrosyl chloride under similar conditions to the catalyzed runs were performed without added nitrogen dioxide. The second-order velocity constants k_0 in the absence of nitrogen dioxide are given by

$$k_0=k_1+\frac{2\Sigma k_{3,M}[M]}{[NOCl]}. \tag{1}$$

In the presence of nitrogen dioxide, let k_e be the experimentally determined velocity constant, and let $k=k_e-k_0$. Then,

$$k=k_e-k_0=\alpha\frac{[NO_2]}{[NO]}+\beta\frac{[NO_2]}{[NOCl]}+\gamma\frac{[NO_2]^2}{[NO][NOCl]} \tag{2}$$

where

$$\alpha=\frac{2k_{12}k_{15}}{k_{13}}+\frac{2k_{12}k_{14,NOCl}}{k_{13}}, \tag{3}$$

$$\beta=2k_{3,NO_2}+\frac{2k_{12}k_{14,NO}}{k_{13}}, \tag{4}$$

$$\gamma=\frac{2k_{12}k_{14,NO_2}}{k_{13}}. \tag{5}$$

Before describing the tests of eqn. (2), it is necessary to indicate the reasons for rejecting any reaction scheme based on the NO_3 radical as intermediate.

(*a*) $NO_2+NO_2\rightarrow NO+NO_3$
(*b*) $NO_3+NOCl\rightarrow 2NO_2+Cl$
(*c*) $NO_3+NOCl\rightarrow NO_2Cl+NO_2$
(*d*) $NO_3+NOCl\rightarrow NO_2+NO+OCl$.

This might be formed [5] by decomposition of NO_2 in reaction (*a*), and react with NOCl in any of reactions (*b*), (*c*) or (*d*) to increase the rate of its decomposition. The inhibition by NO might then be due to the reverse of reaction (*a*). However, the maximum additional rate would be twice the rate of reaction (*a*) as no chain reaction is involved in the nitrosyl chloride decomposition. Experimental determinations [5, 6] of k_a show that the additional rate at 300° would be less than $6\times10^2[NO_2]^2\sim6\times10^2\,[NOCl]^2$, whereas the observed additional rate is never less than $2\times10^4\,[NOCl]^2$ under these conditions (rates in mole cm^{-3} sec^{-1}). Hence these schemes fail to explain the observed rates.

TESTS OF THE RATE EXPRESSION

The main tests consisted of three sets of experiments, each set being designed to test the dependence of k on one of the components NO, NOCl, and NO_2. Each determination of k involves separate determination of k_0 (the second-order velocity constant in the absence of NO_2) and k_e (the second-order velocity constant in the presence of the selected amount of NO_2). In addition, the effect of nitrogen on the catalyzed reaction was shown to be in agreement with the expression (see eqn. (10), (11)) for k. The determination of k_0 for pure NOCl revealed changes in the second-order constant at high concentrations, and this was investigated in more detail later in § II.

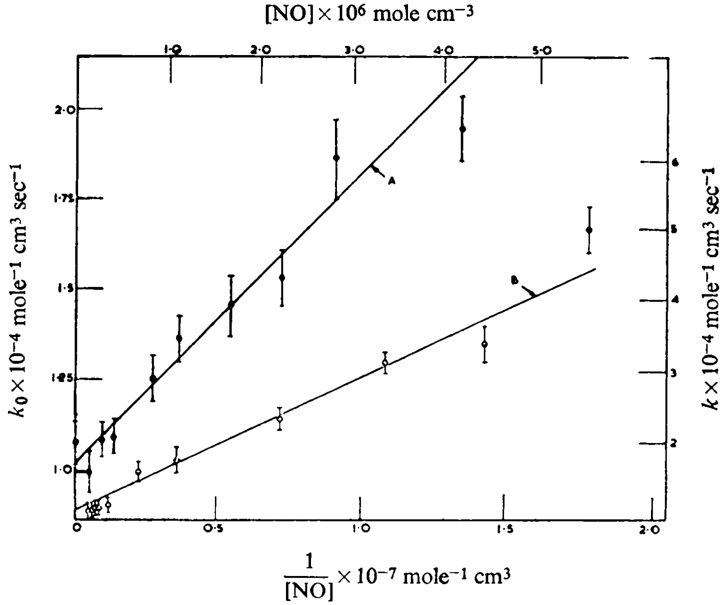

FIG. 1.—Line A, plot of k_0 against [NO]; line B, plot of k against 1/[NO].

I. VARIATION WITH [NO]

With [NOCl] = $2{\cdot}80 \times 10^{-7}$ mole cm^{-3}, and $[NO_2] = \frac{1}{2}$[NOCl] in the catalyzed runs, it follows that

$$k_0 = k_1 + 2k_{3,\mathrm{NOCl}} + 2k_{3,\mathrm{NO}}\frac{[\mathrm{NO}]}{[\mathrm{NOCl}]} \tag{6}$$

$$k = \frac{1}{[\mathrm{NO}]}\left\{\alpha[\mathrm{NO_2}] + \frac{\gamma[\mathrm{NO_2}]^2}{[\mathrm{NOCl}]}\right\} + \frac{\beta[\mathrm{NO_2}]}{[\mathrm{NOCl}]} \equiv \frac{A_1}{[\mathrm{NO}]} + B_1. \tag{7}$$

Fig. 1 (line A) shows that k_0 varies linearly with [NO]. From the slope, the value of $k_{3,\mathrm{NO}}$ can be found. Fig. 1 (line B) shows that k varies linearly with $[\mathrm{NO}]^{-1}$ and from the slope a value for $\left(\alpha + \frac{\gamma}{2}\right) \times 1{\cdot}4 \times 10^{-7}$ can be determined (table 2).

II. VARIATION WITH [NOCl]

With [NO] = $8{\cdot}40 \times 10^{-7}$ mole cm^{-3}, and $[NO_2]$ = (1/6) [NO] in the catalyzed runs, the expression for k_0 is the same as in 1, but for k,

$$k = \frac{1}{[\mathrm{NOCl}]}\left\{\beta\mathrm{NO_2} + \frac{\gamma[\mathrm{NO_2}]^2}{[\mathrm{NO}]}\right\} + \frac{\alpha[\mathrm{NO_2}]}{[\mathrm{NO}]} \equiv \frac{A_2}{[\mathrm{NOCl}]} + B_2. \tag{8}$$

As k_0 is the same as in 1, the plot of k_0 against $[NOCl]^{-1}$ should be a straight line with the same intercept as the line in fig. 1*a* and with slope $2k_{3,NO}[NO]$. Fig. 2 (line A) shows the experimental points with line A drawn to satisfy the above conditions, using the value of $k_{3,NO}$ derived in § I. The points are a reasonable fit to the line for low pressures of NOCl, but the velocity constant is unexpectedly small at pressures above 10 mm.

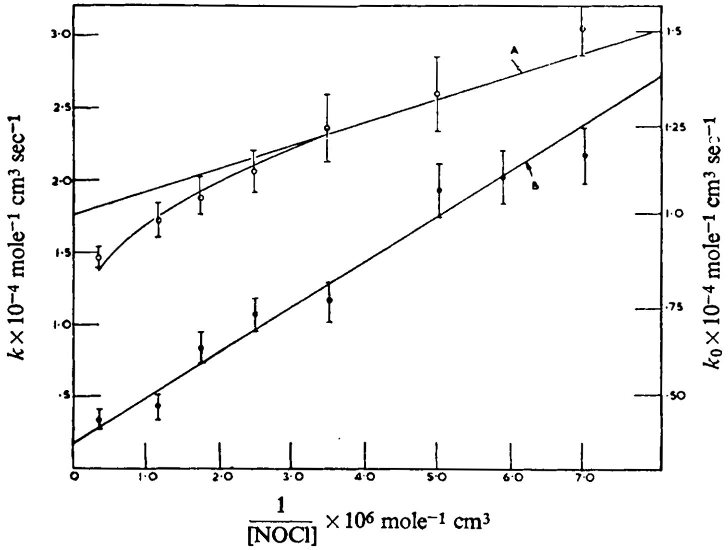

FIG. 2.—Line A, expected linear plot of k_0 against $1/[NOCl]$. Points ○ are expt. k_0; curve is corrected plot. Line B, plot of k against $1/[NOCl]$.

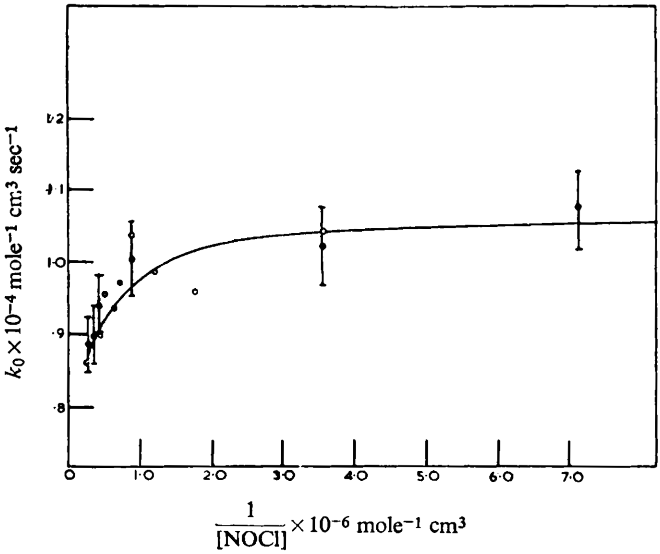

FIG. 2*b*.—Effect of high values of [NOCl] on k_0.
● photometer results; ○ Bourdon results.

Fig. 2*b* shows a series of experiments in which k_0 is plotted against $[NOCl]^{-1}$ in the absence of nitric oxide. It suggests that the deviation of the velocity constant seen in fig. 2 (line A) is not due to variation of the term $k_{3,\mathrm{NO}}$. If the limiting value at low concentrations of NOCl is accepted as the true bimolecular constant $k_1+2k_{3,\mathrm{NOCl}}$, corrections for the higher pressures may be calculated from the results of fig. 2*b* and applied to the line A in fig. 2. The result of allowing for such deviations is shown by the curved line in fig. 2, which agrees well with the experimental points. The deviation shown by fig. 2*b* is referred to in the discussion.

Fig. 2 (line B) also shows the plot of k against $[\mathrm{NOCl}]^{-1}$ and it is linear as predicted by the expression for k. From the slope, a value for $\left(\beta+\frac{\gamma}{6}\right)\times 1{\cdot}4\times 10^{-7}$ can be determined (table 2).

III. Variation with [NO$_2$]

With $[\mathrm{NO}] = [\mathrm{NOCl}] = 1{\cdot}40\times 10^{-7}$ mole cm^{-3}. The value of k_0 for this mixture was determined accurately and used to determine k. The variation of k with $[\mathrm{NO_2}]$ was tested by plotting $k/[\mathrm{NO_2}]$ against $[\mathrm{NO_2}]$:

$$\frac{k}{[\mathrm{NO_2}]} = [\mathrm{NO_2}]\left\{\frac{\gamma}{[\mathrm{NO}][\mathrm{NOCl}]}\right\}+\frac{\alpha}{[\mathrm{NO}]}+\frac{\beta}{[\mathrm{NOCl}]} \equiv A_3[\mathrm{NO_2}]+B_3. \tag{9}$$

Fig. 3 shows that the results obey this equation.

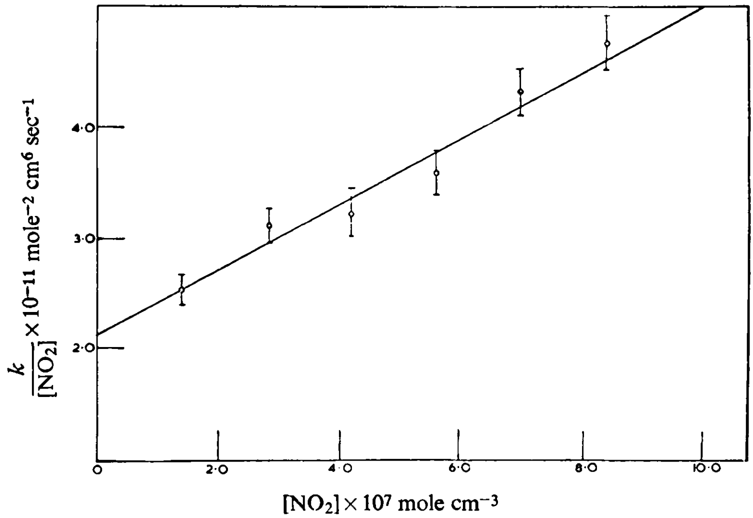

FIG. 3.—Effect of NO$_2$ on k.

IV. Variation with [N$_2$]

With $[\mathrm{NO}] = 3[\mathrm{NOCl}] = 8{\cdot}40\times 10^{-7}$ mole cm^{-3} and $[\mathrm{NO_2}] = \frac{1}{2}[\mathrm{NOCl}]$ in the catalyzed runs, the expressions for k_0 and k are

$$k_0 = k_1+2k_{3,\mathrm{NOCl}}+2k_{3,\mathrm{NO}}\frac{[\mathrm{NO}]}{[\mathrm{NOCl}]}+2k_{3,\mathrm{N_2}}\frac{[\mathrm{N_2}]}{[\mathrm{NOCl}]}, \tag{10}$$

$$k = \frac{\alpha[\mathrm{NO_2}]}{[\mathrm{NO}]}+\frac{\beta[\mathrm{NO_2}]}{[\mathrm{NOCl}]}+\frac{\gamma[\mathrm{NO_2}]^2}{[\mathrm{NO}][\mathrm{NOCl}]}+\frac{2k_{12}k_{14,\mathrm{N_2}}[\mathrm{N_2}][\mathrm{NO_2}]}{k_{13}[\mathrm{NO}][\mathrm{NOCl}]}$$
$$\equiv A_4[\mathrm{N_2}]+B_4. \tag{11}$$

The plots of k_0 against $[\mathrm{N_2}]$ (fig. 4, line B) are linear, as predicted, and the value of $k_{3,\mathrm{N_2}}$ obtained from the slope of the line agrees well with the value obtained in a similar set of experiments without NO present. The plot of fig. 4 (line A) shows that k also varies linearly with $[N_2]$ and from the slope of the line $k_{12}k_{14,N_2}/k_{13}$) can be found.

There is some evidence to suggest that at higher concentrations of nitrogen, the slope of line A in fig. 4 decreases, but further work is necessary to decide this point.

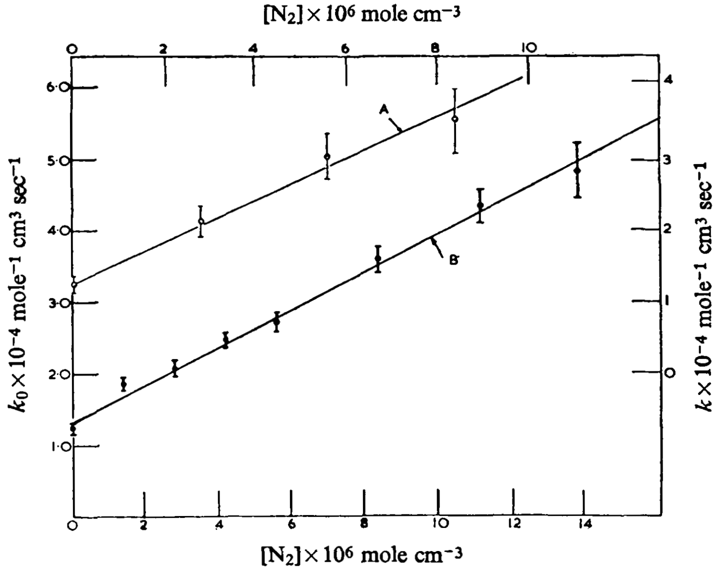

FIG. 4.—Line A, plot of k against $[N_2]$ (upper scale); line B, plot of k_0 against $[N_2]$ (lower scale).

The experimental values of the slopes and intercepts of the plots of k in fig. 1, 2, 3 and 4 are collected in tables 2 and 3, together with the theoretical expressions for the slopes and intercepts. From the slopes, α, β and γ can be evaluated, and hence the calculated intercepts. There is good agreement between the calculated and the experimental intercepts.

TABLE 2.—SLOPES OF PLOTS

fig.	theor. expression	expt. value	units
1	$\left(\alpha+\frac{\gamma}{2}\right)1{\cdot}40\times10^{-7}$	$(1{\cdot}87\pm{\cdot}33)\times10^{-3}$	sec^{-1}
2	$\left(\beta+\frac{\gamma}{6}\right)1{\cdot}40\times10^{-7}$	$(3{\cdot}12\pm{\cdot}60)\times10^{-3}$	sec^{-1}
3	$\dfrac{\gamma}{1{\cdot}96\times10^{-4}}$	$(2{\cdot}95\pm{\cdot}38)\times10^{17}$	mole^{-3} cm^9 sec^{-1}
4	$\dfrac{k_{12}}{k_{13}}\dfrac{k_{14,N_2}}{1{\cdot}84\times10^{-7}}$	$(2{\cdot}87\pm{\cdot}74)\times10^{9}$	mole^{-2} cm^6 sec^{-1}

TABLE 3.—INTERCEPTS OF PLOTS

fig.	theor. expression	expt. value	calc. value	units
1	$\frac{1}{2}\beta$	$(1{\cdot}11\pm{\cdot}11)\times10^{4}$	$1{\cdot}07\times10^{4}$	mole^{-1} cm^3 sec^{-1}
2	$\frac{1}{6}\alpha$	$(1{\cdot}68\pm{\cdot}84)\times10^{3}$	$1{\cdot}75\times10^{3}$	mole^{-1} cm^3 sec^{-1}
3	$\dfrac{\alpha+\beta}{1{\cdot}40\times10^{-7}}$	$(2{\cdot}13\pm{\cdot}25)\times10^{11}$	$2{\cdot}27\times10^{11}$	mole^{-2} cm^3 sec^{-1}
4	$\frac{1}{6}\alpha+\frac{1}{2}\beta+\frac{1}{12}\gamma$	$(1{\cdot}25\pm{\cdot}18)\times10^{4}$	$1{\cdot}25\times10^{4}$	mole^{-1} cm^3 sec^{-1}

From the expressions for α, β and γ, and for the slope of the line in fig. 4, using the value of k_{12}/k_{13} evaluated earlier in this paper, the following values have been calculated for 300°C:

$$\begin{aligned} k_{14,\mathrm{NO_2}} &= (8{\cdot}3 \pm 1{\cdot}1) \times 10^5, \text{ and} \\ k_{14,\mathrm{N_2}} &= (6{\cdot}9 \pm 1{\cdot}8) \times 10^5 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \\ k_{3,\mathrm{NOCl}} &= 2750 \pm 270,\ k_{3,\mathrm{NO}} = 400 \pm 60;\ \text{and} \\ k_{3,\mathrm{N_2}} &= 360 \pm 40 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \\ 2k_{3,\mathrm{NO_2}} + 2k_{12}k_{14,\,\mathrm{NO}}/k_{13} &= (2{\cdot}13 \pm {\cdot}43) \times 10^4 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}, \\ k_{15} + k_{14,\mathrm{NOCl}} &= (1{\cdot}5 \pm {\cdot}4) \times 10^6 \text{ moles}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \end{aligned}$$

DISCUSSION

The tests which have been described give quantitative support to the reaction scheme proposed for the catalyzed decomposition. The values of some velocity constants derived in the tests are also in agreement with estimates made from the results of other investigators and this provides further support for the scheme.

Thus previous studies of the decomposition of nitryl chloride by itself and in the presence of other gases allow estimates of $k_{14,\mathrm{NO_2}}$ and $k_{14,\mathrm{N_2}}$ at 300°C for comparison with the experimental values reported here, if it is assumed that (*a*) the expression found by Cordes and Johnston [3] for $k_{14,\mathrm{NO_2Cl}}$ between 180 and 248°C can be extrapolated to 300°C, and (*b*) the ratios $k_{14,\mathrm{M}}/k_{14,\mathrm{NO_2Cl}}$ found by Johnston and Volpe [8] at 203° hold at 300°C. Calculations based on these assumptions give

$$\begin{aligned} k_{14,\mathrm{NO_2}} &= 2{\cdot}2 \times 10^6 \text{ (expt. } 0{\cdot}8 \times 10^6) \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}, \\ k_{14,\mathrm{N_2}} &= 0{\cdot}5 \times 10^6 \text{ (expt. } 0{\cdot}7 \times 10^6) \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \end{aligned}$$

The agreement is good for N_2, but poor for NO_2. The conditions under which the investigations of Johnston and Volpe [8] and Cordes and Johnston [3] were carried out involved lower pressures of added gases and much higher pressures of nitryl chloride. These differences, together with the temperature extrapolation involved in calculating $k_{14,\mathrm{NO_2Cl}}$ at 300°C may be the cause of the disagreement.

Although simple functions of $k_{3,\mathrm{NO_2}}$, $k_{4,\mathrm{NO}}$, $k_{14,\mathrm{NOCl}}$ and k_{15} have been evaluated in the summary of results, it is not possible to determine the constants separately. The relationships do, however, define the maximum values the constants can have, and these turn out to be reasonable:

$$\begin{aligned} k_{3,\mathrm{NO_2}} &\leqslant 10^4 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}, \\ k_{14,\mathrm{NO}} &\leqslant 3 \times 10^6 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}, \\ k_{15} &\leqslant 1{\cdot}5 \times 10^6 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}, \\ k_{14,\mathrm{NOCl}} &\leqslant 1{\cdot}5 \times 10^6 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \end{aligned}$$

It is unlikely that k_{15} is as high as its maximum value determined in this way, for the velocity constant of the comparable reaction 1 is very much lower at 300° (about 35×10^3 mole^{-1} cm^3 sec^{-1}); however, if the activation energy of 15 were less than that of 1 by about 6·5 kcal, which is just possible, the difference could be accounted for.

The value of $k_{3,\mathrm{NOCl}}$ obtained in this work seems very reasonable. This value, $2{\cdot}75 \times 10^3$ mole^{-1} cm^3 sec^{-1}, agrees well with Ashmore and Spencer's value [1] of $3{\cdot}2 \times 10^3$. The value of $k_{3,\mathrm{NOCl}}$ quoted is actually the limiting value as $[\mathrm{NOCl}] \rightarrow 0$ mentioned in § II of the results. It is thought that the relatively small variation of $k_{3,\mathrm{NOCl}}$ with [NOCl] may be due to the transition from second-order to first-order kinetics of reactions such as 3 at high pressure. Plotting $1/k_{3,\mathrm{NOCl}}$ against [NOCl] on fig. 5 shows that

$$k_{3,\mathrm{NOCl}} = A/(1 + B[\mathrm{NOCl}]), \tag{12}$$

as would be expected if the simple Hinshelwood-Lindemann treatment of unimolecular reactions is applied to reaction 3. A similar small change with pressure, obeying relation 12, has been observed in other work performed at 411°C, but in both cases a quantitative approach in terms of unimolecular reaction theory suggests that the pressures at which this change occurs are anomalously low for a triatomic molecule.[7]

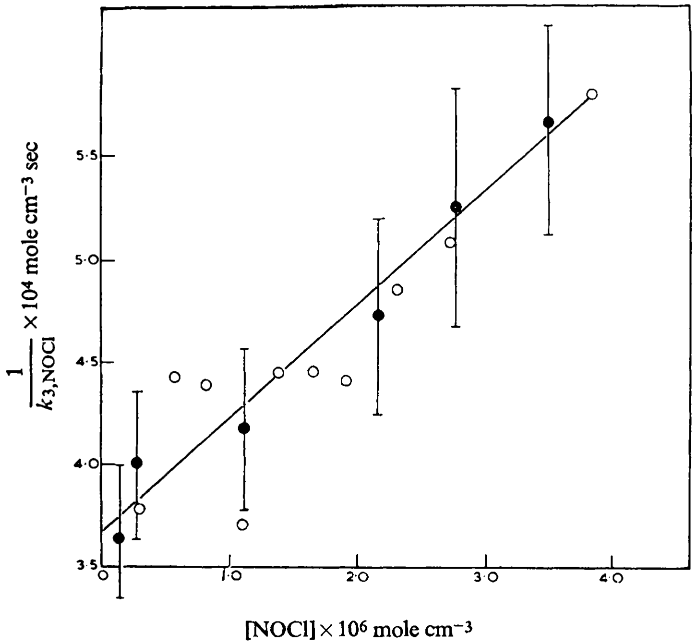

FIG. 5.—Effect of [NOCl] on $k_{3,\text{NOCl}}$. ● photometer results; ○ Bourdon results.

The rates at low concentrations of nitrosyl chloride show no definite indication of a first-order decomposition similar to that attributed by Ashmore and Spencer to heterogeneous reactions. Whereas Ashmore and Spencer found that k_0 was a linear function of 1/[NOCl] over the range 1×10^6 to 4×10^6 mole^{-1} cm^3, with slope $5{\cdot}2 \times 10^{-4}$ sec^{-1}, the points within this range in fig. 2*b* could be fitted to lines with slopes between 0 and 1×10^{-4} sec^{-1}. Thus there might be some small heterogeneous contribution to the decomposition in this vessel at low pressures. The constants $k_{3,\text{NO}}$ and k_{3,N_2} have about the values expected for the molecules concerned as third bodies, and their ratio (1.1) is not very different from the ratio of the constants for the reverse reactions which Ashmore and Spencer determined[1] as 1·4 ± 0·3.

The authors would like to express their gratitude to the Royal Society for a grant to defray part of the cost of the photometer.

[1] Ashmore and Spencer, *Trans. Faraday Soc.*, 1959, **55**, 1868.
[2] Freiling, Johnston and Ogg, *J. Chem. Physics*, 1952, **20**, 327.
[3] Cordes and Johnston, *J. Amer. Chem. Soc.*, 1954, **76**, 4264.
[4] Ray and Ogg, *J. Chem. Physics*, 1959, **31**, 168.
[5] Ashmore and Levitt, *Research* (*corr.*), 1954, **7**, 335.
[6] Burnett, unpublished work.
[7] Trotman-Dickenson, *Gas Kinetics* (Butterworths Sci. Publ., London, 1955).
[8] Johnston and Volpe, *J. Amer. Chem. Soc.*, 1956, **78**, 3903.
[9] Schumacher and Sprenger, *Z. Elektrochem.*, 1929, **35**, 653; *Z. physik. Chem. B*, 1931, **12**, 115.