The Nitric Oxide-catalyzed Recombination of Chlorine Atoms

By T. C. CLARK and M. A. A. CLYNE

(*School of Chemical Sciences, University of East Anglia, Norwich*)

NITRIC OXIDE catalyzes the recombination of oxygen atoms[1] and hydrogen atoms[2]; at total pressures near 1 mm. Hg, the mechanism in both cases can be represented by the two steps

$$X + NO + M \xrightarrow{\text{slow}} XNO + M \qquad (1)$$

$$XNO + X \xrightarrow{\text{fast}} X_2 + NO \qquad (2)$$

We have found that a similar mechanism applies when nitric oxide is allowed to react with atomic chlorine at 0·7—2·0 mm. Hg total pressure and over the temperature range 270—620°K.

Chlorine atoms were generated by passing a mixture of redistilled chlorine and argon or helium through a 2450 Mc./sec. microwave electric discharge. Flows of chlorine atoms in oxygen or nitrogen carrier gases were generated by addition of an excess of chlorine to a stream of oxygen atoms[3] produced either by a discharge through O_2 or by addition of the stoicheiometric amount of NO to a stream of nitrogen atoms,

$$N + NO \rightarrow N_2 + O$$

$$2O + Cl_2 \rightarrow 2Cl + O_2$$

The red and infrared chlorine afterglow emission spectrum [$Cl_2(^3\Pi_{ou+} \rightarrow {}^1\Sigma_g^+)$] observed in the discharge products is due to the radiative combination of two Cl atoms,[4,5]

$$Cl(^2P) + Cl(^2P)\ (+M) \rightarrow Cl_2(^3\Pi_{ou+})\ (+\ M),$$

$$Cl_2(^3\Pi_{ou+}) \rightarrow Cl_2(^1\Sigma_g^+) + h\nu.$$

The intensity of emission, *I*, is proportional to $[Cl]^2$ at a given total pressure,[4,5] so that $\sqrt{I}$ can be used as a measure of the relative concentration of Cl. The relative integrated intensities of the chlorine afterglow emission spectrum were measured in this work with an R.C.A. 931—A photomultiplier cell and a Wratten filter No. 23A, so that emission in the wavelength range 6000—7000 Å could be detected. Absolute concentrations of Cl atoms were measured by titration with NOCl to critical extinction of the chlorine afterglow[5]; the reaction $Cl + NOCl \rightarrow Cl_2 + NO$ is known to be very rapid.[6] At 2 mm. Hg total pressure, typical partial pressures of ground state ($^2P_{3/2}$) chlorine atoms in the gas leaving the discharge were 2×10^{-3} — 5×10^{-2} mm. Hg.

TABLE

Values for the rate constants of the reactions of Cl, O, *and* H *with* NO *at* 293°K *using various third bodies* M.

Atomic species	Cl	$10^{-16}\,k_1$ (cm.^{6} mole^{-2} sec.$^{-1}$) O	H
M = He	3·5 ± 0·5	1·8[8] 1·8 ± 0·3[9]	0·66 ± 0·10[10]
Ar	2·9 ± 0·4	2·1[8] 2·7 ± 0·3[9]	0·87 ± 0·15[10]
O_2	3·9 ± 0·5	2·1[8] 2·7 ± 0·3[9]	—
N_2	3·5 ± 0·5	3·3[8] 3·1 ± 0·4[9]	—
Cl_2	3·4 ± 0·5	—	—
SF_6	3·5 ± 0·5	5·6[8]	—

In kinetic experiments on the NO + Cl reaction, atomic chlorine in various carrier gases passed from the discharge at 0·7—2 mm. Hg total pressure through a 31 mm. internal-diameter Pyrex tube with four equally-spaced inlet jets along its length for the admission of nitric oxide. Downstream from the four jets was an observation port with the photomultiplier cell, where the relative concentrations of Cl were measured. By addition of the same concentrations of nitric oxide at each of the inlets in turn and measurement of the concentrations of chlorine atoms remaining at the photomultiplier cell, the kinetics of reaction were found. A discussion of the kinetic analysis has been published previously.[7]

It was found that an overall third-order kinetic equation was accurately followed, $d[Cl]/dt = -2k_1[NO][Cl][M]$, exactly as was observed for the reactions of NO with O[1] and with H.[2,10] No significant concentrations of any product of reaction could be detected on analysis of the reaction products condensed at −183°C. The primary step in the NO + Cl reaction is,

$$NO + Cl + M \rightarrow NOCl + M + 38 \text{ kcal. mole}^{-1},$$

while the nitrosyl chloride formed is rapidly removed in the secondary reaction

$$NOCl + Cl \rightarrow NO + Cl_2 + 20 \text{ kcal. mole}^{-1}.$$

The overall reaction is therefore exactly analogous to the reactions of nitric oxide with oxygen and hydrogen atoms, and can be considered to be a nitric oxide-catalyzed recombination of atomic chlorine. Both the oxygen and hydrogen atom reactions are chemiluminescent in the green[1] and infrared regions,[2] respectively, so that the NO + Cl reaction might be expected to yield chemiluminescent emission at wavelengths longer than 8000 Å. We have searched for such an emission with detectors extending up to 8500 Å, but so far unsuccessfully; it is intended to examine a region of the spectrum lying at longer wavelengths than 8500 Å.

The rate constants k_1 for the NO + Cl + M reaction under a variety of conditions have been measured, and the values at room temperature for various third bodies M are shown in the Table, together with previous data for the oxygen[8,9] and hydrogen[10] reactions.

The temperature coefficients of k_1 for the third bodies Ar, Cl_2, and SF_6 have been measured over the range 270—620°K, and correspond to (negative) Arrhenius activation energies of (−1·1 ± 0·1), (−0·7 ± 0·2), and (−1·2 ± 0·2) kcal. mole^{-1} respectively.

The similarity of the values for k_1 at 20°c and their dependences on the nature of M for the NO + Cl + M and NO + O + M reactions, respectively, is most striking; it should also be noted that the activation energy for the reaction $NO + O + Ar \rightarrow NO_2 + Ar$[9] is $-(1{\cdot}8 \pm 0{\cdot}4)$ kcal. mole^{-1}, similar to the value of $-(1{\cdot}1 \pm 0{\cdot}1)$ kcal. mole^{-1} found for the reaction NO + Cl + M in the present work.

We have also made some preliminary experiments on the reaction of NO_2 with atomic chlorine in an argon carrier gas. This reaction is about five times faster than the nitric oxide reaction, and appears to follow a third-order mechanism with a rate constant of about 1×10^{17} cm.^{6} mole^{-2} sec.$^{-1}$ at 293°K; nitryl chloride, initially formed, is apparently rapidly removed by reaction with excess of atomic chlorine;

$$NO_2 + Cl + Ar \xrightarrow{\text{slow}} NO_2Cl + Ar,$$

$$NO_2Cl + Cl \xrightarrow{\text{fast}} Cl_2 + NO_2.$$

Further studies are in progress. The preliminary results, however, again point to the analogy with the corresponding atomic oxygen reaction proposed in this case by Ford and Endow,[11] $O + NO_2 + M \rightarrow NO_3 + M$; the rate constant for the latter reaction has been determined as $1{\cdot}0 \times 10^{17}$ cm.^{6} mole^{-2} sec.$^{-1}$ (for $M{=}N_2$) at room temperature.[11]

(*Received, April 5th,* 1966; *Com.* 223.)

[1] F. Kaufman, *Proc. Roy. Soc.*, 1958, *A*, **247**, 123.
[2] M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305.
[3] M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, in the press.
[4] L. W. Bader and E. A. Ogryzlo, *J. Chem. Phys.*, 1964, **41**, 2926.
[5] E. Hutton and M. Wright, *Trans. Faraday Soc.*, 1965, **61**, 78.
[6] W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, 1952, **48**, 52.
[7] M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc.* 1963, *A*, **275**, 544.
[8] F. Kaufman and J. R. Kelso, Symposium on Chemiluminescence, Duke Univ., 1965, p. 65.
[9] M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc.*, 1962, *A*, **269**, 404.
[10] M. A. A. Clyne and B. A. Thrush, *Discuss. Faraday Soc.*, 1962, **33**, 139.
[11] H. W. Ford and N. Endow, *J. Chem. Phys.*, 1957, **27**, 1156.