Reactions of Oxygen Atoms with Hydrogen Cyanide, Cyanogen Chloride and Cyanogen Bromide

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The reactions of oxygen atoms with hydrogen cyanide, with cyanogen chloride and with cyanogen bromide, have been studied in a discharge flow system at temperatures between 450 and 650°K. The mechanisms are

 $\begin{array}{l} O+XCN = NCO+X\\ O+NCO = NO+CO\\ \end{array}$ The following Arrhenius expressions were obtained for the initial steps. $O+HCN, \ k=5\cdot2\times10^{12} \exp{(-8,100\pm1,200/RT)} \operatorname{cm^{3} mole^{-1} sec^{-1}},\\ O+CICN, \ k=1\cdot5\times10^{12} \exp{(-6,900\pm700/RT)} \operatorname{cm^{3} mole^{-1} sec^{-1}},\\ O+BrCN, \ k=1\cdot4\times10^{13} \exp{(-9,700\pm1,200/RT)} \operatorname{cm^{3} mole^{-1} sec^{-1}}. \end{array}$

Harteck and Kopsch¹ reported slight reaction of oxygen atoms with hydrogen cyanide and with cyanogen, and observed CN emission from the latter reaction. The only kinetic studies of the reaction of oxygen atoms with cyanogen derivatives have involved C_2N_2 itself.^{2, 3}

The reactions of atomic oxygen with HCN, ClCN and BrCN are of interest, since the abstraction of a terminal atom by O is never less than 20 kcal/mole endothermic. The reactions which are observed in discharge flow systems must therefore proceed by a different mechanism; this is shown to be a substitution, yielding NCO which is rapidly converted by O to NO and CO.

EXPERIMENTAL

Fig. 1 shows the discharge flow system. Nitrogen atoms were generated by an 18 Mc/sec 200 W radio-frequency discharge in a quartz section about 50 cm upstream from the flow tube. The long flow-time between discharge and reaction zone eliminated any metastable atoms or excited molecules.

The 27.5 mm int. diam. Pyrex flow tube had 7 jets for the admission of gases. Nitric oxide was introduced through J.1 and J.6. Cyanogen derivatives were added in turn through J.2 to J.5 which were spaced 20.1 cm apart and through J.7 to maintain the same total pressure at the photomultiplier cell when the initial concentration of oxygen atoms was found. The central portion of the flow tube was heated in a furnace to temperatures between 450 and 650° K; this was monitored by thermocouples at 5 points along its length. The heated portion of the flow tube was wrapped in copper gauze and the maximum temperature deviation along the flow tube was 3°K. The furnace extended 15 cm upstream from J.2 to ensure the gases reached its temperature before this point. The flow tube was cooled with an air jet just beyond the furnace exit.

The pressure at both ends of the flow tube was measured on either a McLeod gauge or silicone oil manometer. Most experiments were carried out around 2 mm Hg when the viscous pressure drop was negligible; at lower pressures allowance

was made for this effect. Under the experimental conditions used, errors arising from radial and axial diffusion gradients were also negligible.

The flow rates of gases entering the reaction system were measured on calibrated capillary flowmeters and the total pressure was controlled by a large stopcock at the downstream end of the flow tube. In some experiments the flow tube was poisoned with phosphoric acid. When Ogryzlo's procedure ⁴ was followed closely, the air afterglow intensity was not as steady as in the absence of the coating. A steady emission intensity was only achieved when the treatment with hot potassium hydroxide, which precedes the acid washing, was omitted.



FIG. 1.—The discharge flow system. D, quartz discharge tube with external electrodes; W, double Wood's horn light trap; M, outlet to pressure measuring devices; R, furnace; F, photomultiplier housing; Q, quartz window; P, to pump and regulating stopcock.

Light intensity measurements were made using an R.C.A. 931A photomultiplier mounted in a movable light-proof housing positioned 10 cm downstream from J.6. A Wratten no. 61 filter was used for quantitative measurements of the air afterglow intensity. Emission spectra were recorded on Ilford H.P.3 or Kodak I.R. E.R. plates using a Hilger f/4 spectrograph with interchangeable glass and quartz optics.

Nitrogen (B.O.C. White Spot) was passed at slightly below atmospheric pressure over copper turnings at 1000°K followed by two traps at 77°K and a U-tube filled with phosphorus pentoxide. It then passed through another trap at 77°K and low pressure. After this purification the gas was hardly dissociated and small quantities of air, freed from water vapour and carbon dioxide, were added to the nitrogen flow just before the discharge to increase dissociation. The amount of O_2 added in this way was always less than 0.01 % of the total flow.

Nitric oxide (Matheson) was purified by passing over sodalime at 195° K and phosphorus pentoxide. The solid was pumped at 77° K for 5 min and distilled until white.

Hydrogen cyanide was dried with phosphorus pentoxide and distilled twice before use.

Crystalline cyanogen bromide (Eastman Kodak or Koch-Light) was distilled several times after drying with phosphorus pentoxide. Both samples gave the same experimental results.

Cyanogen chloride (I.C.I.) was purified in a similar way.

The purity of the three cyanogen derivatives was checked by measurement of their vapour pressures at two temperatures and by their infra-red spectra. No evidence of their polymerization was found at any stage.

RESULTS AND DISCUSSION

Ground state $({}^{3}P)$ oxygen atoms were produced by adding a slight excess of nitric oxide to active nitrogen at J.1 using the rapid reaction,

$$N + NO = N_2 + O. \tag{1}$$

REACTION OF OXYGEN ATOMS WITH CYANIDES

The no. 61 filter-photomultiplier combination was calibrated for measurement of absolute oxygen atom concentrations by recording the air afterglow intensity I past the endpoint of reaction (1). Since

$$I = I_0[O][NO], (i)$$

plots of I against the flow rate of added nitric oxide were linear their slopes giving $I_0[O]_0$ and the intercepts on the abscissa giving $[O]_0$.

EMISSION SPECTRA

The three compounds were added in turn through J.2. Weak CN violet emission $(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ was observed in each reaction. This emission was about 1000 times weaker than in the $O+C_2N_2$ reaction where ground-state CN is a primary product and has a steady-state partial pressure of the order of 10^{-6} mm.³ There was evidence that CN emission in the present system was associated with the small quantities of oxygen added to catalyze the nitrogen dissociation and it was therefore concluded that CN is not an intermediate in the reactions studied here. The intensity of CN emission was never sufficient to affect measurements of the air afterglow.

A careful search was made for emission up to 8500 Å using I.R. E.R. plates. No emission from either the chlorine afterglow or the bromine afterglow (which have their maximum intensities at 7500 and 8500 Å respectively) was detected in exposures of up to 10 h.

STOICHIOMETRY OF NITRIC OXIDE PRODUCTION

An approximately ten-fold excess of reactant was added in turn through J.2-J.5 and J.7; small flows of nitric oxide were introduced simultaneously through J.6. The resulting air afterglow emission intensity at a position 10 cm downstream was



FIG. 2.—Determination of O atoms removed and of NO produced in the O+ClCN reaction. Total pressure 1.96 mm Hg; temp. 625° K; [ClCN] = 3.04×10^{-10} mole cm⁻³; [O]₀ = 0.44×10^{-10} mole cm⁻³.

plotted against added nitric oxide as in fig. 2. According to relation (i), the slopes of the lines in fig. 2 are proportional to the oxygen atom concentration at the photomultiplier and the increased negative intercepts on the abscissa give the amount of nitric oxide produced in the reaction.² The experiment in which reactant was added at J.7 maintained the correct pressure conditions at the photomultiplier needed to

obtain an accurate value for the initial line, which gives the excess of nitric oxide added at J.1 above that needed to titrate all the nitrogen atoms.

For all three reactions the stoichiometry was 2.0 ± 0.4 oxygen atoms removed for each nitric oxide molecule formed. Representative results at various pressures and temperatures are given in table 1, these correspond to maximum NO production using the longest reaction times.

TABLE 1.

reaction	pressure (mm Hg)	temp (°K)	reaction time (sec)	flow rate of NO produced (μ mole sec ⁻¹)	flow rate of O removed (μ mole sec ⁻¹)	stoichiometry [0] removed [NO] produced
O+HCN	1.61	469	0.139	0.018	0.028	1.6
	1.95	521	0.170	0.016	0.036	2.3
	1.98	519	0.176	0.024	0.023	2.2
	1.99	571	0.157	0.036	0.068	1.9
	2.04	574	0.138	0.030	0.065	2.2
	2.25	547	0.177	0.026	0.055	2.1
	4·01	471	0.348	0.012	0.023	1.9
O+ClCN	1.40	612	0.106	0.015	0.028	1.9
	1.96	625	0.132	0.022	0.048	2.1
	1.98	530	0.157	0.013	0.024	1.9
	2.01	582	0.157	0.021	0.041	2.0
	2.06	525	0.167	0.016	0.032	2.0
	2.70	570	0.216	0.025	0.051	2.0
	3.09	524	0.268	0.020	0.042	2.1
O+BrCN	1.20	610	0.088	0.010	0.023	2.3
	1.75	552	0.132	0.016	0.032	2.0
	1.98	627	0.159	0.018	0.037	2.1
	2.00	634	0.158	0.016	0.031	2.0
	2.01	588	0.128	0.016	0.031	2.0
	2.62	546	0.216	0.024	0.048	2.0
	3.45	591	0.246	0.017	0.038	2.2

KINETICS OF OXYGEN ATOM REMOVAL

The kinetics of oxygen atom removal were studied with excess reactant (normally $[XCN] = 7-10[O]_0$). Under these conditions, $\log_{10}[O]$ at the observation point varied linearly with t and with [XCN]; typical results are shown in fig. (3). The method used to analyze the kinetics automatically allows for parallel first-order processes removing oxygen atoms, such as wall recombination and the reaction O+NO+M.⁵ As the activation energies for all three reactions are below 10 kcal/ mole the highly endothermic step

$$O + XCN = XC + NO$$
 (2)

can be eliminated. The observed kinetics and nitric oxide production are explained either by

$$O + XCN = NCO + X \tag{3}$$

followed by
$$O + NCO = NO + CO$$
, (4)

or

$$O + XCN = CO + NX \tag{5}$$

followed by O + NX = NO + X. (6)

REACTION OF OXYGEN ATOMS WITH CYANIDES

For both mechanisms, the rate constant of oxygen atom removal is twice that of the initial step. Experiments were conducted at pressures between 1.0 and 5.0 mm Hg, and no evidence could be found of a pressure dependence in the rate constant although the small decays gave limited accuracy at total pressures below 1.5 mm.



FIG. 3.—First-order decay plots for O+XCN reactions. (a), at constant reactant concentration; (b) at constant reaction time.

ACTIVATION ENERGIES

The activation energies were determined at 2.0 ± 0.1 mm total pressure. All the rate constants (15-18 for each substance) are given in the Arrhenius plots of fig. 4. Least-squares analyses of these data yield the following rate expressions for the

initial step taking the overall stoichiometry to be two oxygen atoms removed per initial step.

 $k_{\text{HCN}} = 5.2 \times 10^{12} \exp(-8,100 \pm 1,200/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$ (454°K to 574°K) $k_{\text{ClCN}} = 1.5 \times 10^{12} \exp(-6,900 \pm 700/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$ (518°K to 635°K)

 $k_{\rm BrCN} = 1.4 \times 10^{13} \exp(-9,700 \pm 1,200/RT) \,{\rm cm^3 \ mole^{-1} \ sec^{-1}}.$ (550°K to 638°K)



FIG. 4.—Arrhenius plots for the O+XCN reactions at 2.0 ± 0.1 mm Hg total pressure.

ROLE OF SURFACE

Although the rate constants are within a factor of 10 of each other where the measurements overlap and lie in the order $k_{\text{HCN}} > k_{\text{CICN}} > k_{\text{BrCN}}$, differences in the observed activation energies give an equally wide spread of pre-exponential factors but with $A_{\text{BrCN}} > A_{\text{HCN}} > A_{\text{CICN}}$. This unexpected observation prompted a careful examination of potential experimental errors. One possibility is that the heterogeneous recombination of halogen atoms formed in reactions (3) or (6), if rapid, could induce a catalytic chain recombination of oxygen atoms:

$$O + X_2 = OX + X \tag{7}$$

$$O + OX = O_2 + X \tag{8}$$

$$\overset{\text{wall}}{2X \to X_2}.$$
 (9)

REACTION OF OXYGEN ATOMS WITH CYANIDES

The observed stoichiometry of nitric oxide formation is evidence against this process, which would increase oxygen atom consumption without yielding nitric oxide. Notwithstanding, the O+ClCN reaction was re-examined in a tube whose walls had been poisoned with phosphoric acid to reduce halogen atom recombination.⁴ In these experiments, which were carried out at 2.0 ± 0.1 mm pressure, the first-order decay plots for atomic oxygen were slightly curved. Their initial slopes were in excellent agreement with values found in the uncoated tube, but the average slopes gave rate constants about 15 % lower. As the poisoning used was not very effective in reducing oxygen atom recombination, we concluded that the lower apparent rate constants were due to poisoning of the surface to oxygen-atom recombination by cyanogen chloride or one of its decomposition products. A similar effect has been noticed with cyanogen.³ There is therefore no evidence that reactions (7), (8)and (9) are significant in our system.

MECHANISM OF REACTION

The following exothermicities:

$$\Delta H_3 = -23(X = H), -47(X = Cl), -60(X = Br) \text{ kcal/mole},$$

 $\Delta H_5 = -36(X = H), -46(X = Cl), -57(X = Br) \text{ kcal/mole},$

can be calculated using the JANAF tables ⁶; $\Delta H_f(BrCN)^7 = 43 \text{ kcal/mole}$, $\Delta H_f(\text{NCO})^2 = 16 \text{ kcal/mole}$ and $\Delta H_f(\text{NBr}) = \Delta H_f(\text{NCl}) = 72 \text{ kcal/mole.}^8$ The last three values have uncertainties of $\pm 5 \text{ kcal/mole}$; for $\Delta H_f(\text{NCO})$, this affects all three values of ΔH_3 equally. For both paths, the second step is an atom transfer reaction which is 70-80 kcal/mole exothermic. This should always be very rapid as it is for O + NCO (ref. (9)) and O + NH (ref. (10)). The absence of emission by the intermediates formed in reactions (3) or (5) is therefore not surprising. Only for X = H is reaction (5) significantly more exothermic than (3), and even here the difference is probably insufficient to favour path (5) which involves rupture of a triple bond as well as of a single bond.

For the related reaction,¹¹

$$N + NO_2 = N_2O + O, \ \Delta H = -42 \text{ kcal/mole}, \qquad (10a)$$

$$=$$
 NO+NO, $=$ -79 kcal/mole, (10b)

$$= N_2 + O_2, = -122$$
 kcal mole, (10c)

the first path, which corresponds to (3) above, is the most rapid although path (c)which corresponds to (5) above is 80 kcal/mole more exothermic. We therefore conclude that reactions (3) and (4) provide the dominant path in all cases, and that the above Arrhenius expressions refer to reaction (3).

RATE EXPRESSIONS

The transition state theory predicts a pre-exponential factor of 3×10^{11} cm³ $mole^{-1} sec^{-1}$ for reaction (3) (and for reaction (5)). This cannot be construed as evidence that the A factor of the O+ClCN reaction is more accurate than the others since the closely related $O + C_2 N_2$ reaction ² ³ has an A factor of 2.5×10^{13} cm³ $mole^{-1} sec^{-1}$. Equally, the differences in pre-exponential factors give no evidence that these reactions have different transition states. It is therefore more useful to compare the actual rate constants rather than the Arrhenius parameters.

1843

P. B. DAVIES AND B. A. THRUSH

The observed rate constants for reaction (3) increase with the energy of the bond broken and therefore decrease with increasing exothermicity of the initial step. This behaviour is the reverse of that generally observed in series of abstraction reactions, and suggests that the increase in size of the substituent X in the order H, Cl, Br inhibits the formation of the transition state.

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