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Jerry J. Smith

(Ph.D. Thesis)

January 1965

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Contents

REACTIONS OF ACTIVE NITROGEN WITH SULFUR COMPOUNDS

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January 1965

ABSTRACT

The reactions of active nitrogen (nitrogen atoms) with several sulfur compounds have been investigated to determine the feasibility of their use in preparing sulfur-nitrogen compounds.

Reactions of N Atoms with S_2Cl_2

Active nitrogen reacts with S_2Cl_2 to form NSCl, Cl_2, SCl_2, S_8 and traces of $(SN)_x$ and S_4N_4. The rate of formation of NSCl increases linearly with increasing S_2Cl_2 flow rates at low S_2Cl_2 flow rates and becomes constant at high S_2Cl_2 flow rates. Only about 5% of the available nitrogen atoms react to form NSCl, the rest recombine to form N_2. The observed reaction is a competition between the NSCl-formation reaction and the N atom recombination reaction. The rate of formation of NSCl at high S_2Cl_2 flow rates increases linearly with increasing N atom flow rates. We conclude that the competing reactions have the same N atom and S_2Cl_2 dependences. The rate of formation of NSCl increases with increasing temperature as expected.

The third order rate constant for the recombination reaction assuming the rate law $\dfrac{d(N_2)}{dt} = k(N)^2(S_2Cl_2)$, is calculated to be 10^{15}-10^{16} ℓ^2 mole^{-2} sec^{-1}. Normal recombination reaction rate constants are about 10^9-10^{10} ℓ^2 mole^{-2} sec^{-1}. The increased rate is attributed to the

formation of a relatively stable intermediate complex (i.e. $[N \cdot S_2Cl_2]$).
The data can be explained by the reactions:

$$N + S_2Cl_2 \rightleftharpoons [N \cdot S_2Cl_2]$$

$$N + [N \cdot S_2Cl_2] \rightarrow N_2 + S_2Cl_2^*$$

$$N + N + S_2Cl_2 \rightarrow 2NSCl$$

$$S_2Cl_2^* \rightarrow S_2 + Cl_2$$

$$S_2Cl_2^* + M \rightarrow S_2Cl_2 + M^* .$$
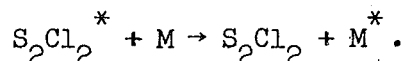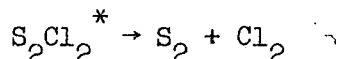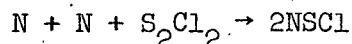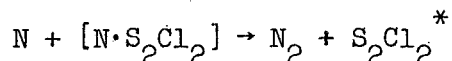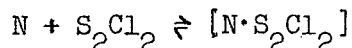
Reactions of N Atoms with Compounds Having Internal Sulfur Atoms

SCl_2, H_2S, and S_8 vapor react with N atoms to form sulfur-nitrogen compounds: SCl_2 yields NSCl and Cl_2; H_2S yields $(SN)_x$, H_2 and small amounts of NH_3 and S_7NH; and S_8 vapor yields S_4N_2, S_4N_4, and $(SN)_x$. $SOCl_2$ reacts with N atoms, but not with sulfur-nitrogen bond formation. The identified products are NOCl, SO_2, N_2O, SO_2Cl_2 and Cl_2. SO_2 is essentially inert to N atom attack.

Reactions of N Atoms with $CS_2^\dagger$ and OCS

CS_2 and OCS, compounds having external sulfur atoms, both react with N atoms to form $(SN)_x$. The other products are $(CS)_x$ and CO respectively.

A difference in the reactivities of the studied sulfur compounds is observed. Those compounds which react with sulfur-nitrogen bond formation all contain sulfur atoms having two lone pairs of electrons. This suggests that the nitrogen atom is an electrophilic reagent.

$\dagger$ R. A. Westburgy and C. A. Winkler, Can. J. Chem. <u>38</u>, 334 (1960).

I. INTRODUCTION

In the past few years, considerable interest has been shown in the reactions of active nitrogen with various compounds.[1] Studies of these reactions generally have been designed to ascertain the nature of the species which contribute to the reactivity of active nitrogen and to obtain kinetic data on active nitrogen reactions. Rarely have reactions of this type been studied from a preparative standpoint. Yet, reactions occurring in such high energy systems often lead to compounds which cannot be conveniently made by other methods.

Active nitrogen was first observed by Warburg in 1884,[2] when he discovered that nitrogen gas exhibited a characteristic yellow-orange glow after being subjected to an electrical discharge. In 1911, Strutt named the glowing gas "active nitrogen"[3] and was the first to suggest that many of its properties could be attributed to the presence of nitrogen atoms. Considerable evidence now exists which shows the reactive species in active nitrogen to be ground-state N atoms ($N(^4S)$).[4,5,6]

The spectrum of the yellow-orange afterglow (Lewis-Rayleigh afterglow) generally consists of selected bands of the nitrogen first positive system, $N_2(B^3\Pi_g - A^3\Sigma_u^+)$. The first positive bands which are most prominent are due to transitions from the twelfth, eleventh, tenth, and sixth vibrational levels of the upper, or B state. Transitions from $v = 13$ or higher have never been observed.

The currently accepted theory of the afterglow involves the recombination of N atoms along the $N_2(^5\Sigma_g^+)$ potential energy level. The $N_2(^5\Sigma_g^+)$ level, a weakly bonded state, crosses the B level at $v = 12$.[7] An inverse predissociation (preassociation) occurs at the crossing of the $^5\Sigma_g^+$ and

$B^3\Pi_g$ levels, resulting in $N_2(B^3\Pi_g)$ v = 12, 11, 10 being formed. The $N_2(B^3\Pi_g)$ then radiates to the $N_2(A^3\Sigma_u^+)$ level giving the observed afterglow.

$$N(^4S) + N(^4S) + M \rightleftharpoons N_2\ (^5\Sigma_g^+) + M$$

$$N_2\ (^5\Sigma_g^+) + M \rightarrow N_2\ (B^3\Pi_g,\ v = 12,11,10) + M$$

$$N_2\ (B^3\Pi_g,\ v = 12,11,10) \rightarrow N_2(A^3\Sigma_u^+) + h\nu\ (N_2\ \text{1st. Positive})$$
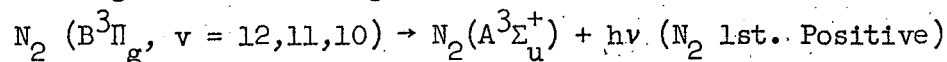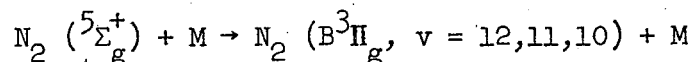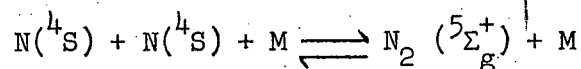
This is not the complete mechanism now proposed; but it explains the major features of the active nitrogen afterglow. (For a more complete discussion of active nitrogen, see an excellent review by Mannella[8].)

Although the chemical reactivity of active nitrogen appears to be due mainly to ground-state nitrogen atoms, recent work indicates that excited molecules, which appear most likely to be $N_2(A^3\Sigma_u^+)$, may be important in at least some active nitrogen reactions.[9] Reactions involving the excited molecules as a reactant are, however, few;[9] hence, reactions of active nitrogen are now regarded more or less as reactions involving N atoms.

Reactions of active nitrogen with sulfur-containing compounds were first reported by Strutt in 1913,[10] when he studied the reactions of N atoms with sulfur, S_2Cl_2, CS_2 and H_2S. Moldenhauer and Zimmerman[11] later studied the reaction with sulfur in more detail.

Recently, studies of the reactions of N atoms with H_2S,[12,13] CS_2,[13] and sulfur[12,14,15] have been reinvestigated, and COS[12] has been added to the list. (Results of studies of the reactions of N atoms with S_2[14] and COS[12] were reported while our work was in progress.) In most of the studies, the products were not completely characterized; most emphasis was put on the initial steps of the reaction sequences.

New and independent methods for preparing sulfur-nitrogen compounds are desirable. Until recently, the preparations of most sulfur-nitrogen compounds have required S_4N_4 as a starting material.[16] But, S_4N_4 itself is not readily available nor easily prepared.[17] (References 16 and 18 give a good review of the chemistry of sulfur-nitrogen compounds.)

The purpose of our work was to correlate the reactions of active nitrogen with sulfur compounds and to determine the feasibility of their use in preparing new sulfur-nitrogen compounds. In the course of this study we became interested in one reaction $(N + S_2Cl_2)$ in particular and investigated it in detail.

II. GENERAL EXPERIMENTAL

All the reactions in this study were carried out in a conventional flow system. The pump was a Duo-Seal Model 1402B vacuum pump. Two reaction vessels were used. They were of essentially the same design, but differed in diameter, and in the positions of the reactant inlets.

Reaction vessel (A) is shown in Fig. 1. The two reactants were introduced through the inlets designated (a) and (b). The reaction occurred immediately following the nozzle in the region (f). Non-volatile reaction products were collected on the Pyrex insert tube (e), which was removable in order to facilitate product removal and cleaning. The entire apparatus, with the exception of the tube where the dissociation (discharge zone, labeled (g)) was carried out, was constructed of ordinary Pyrex glass. The discharge tube was quartz (quartz has a much lower dielectric loss and can withstand higher temperatures than ordinary Pyrex). The insert tube was 18 mm I.D. by 33 cm long and the reaction vessel was 24 mm O.D. by 60 cm in length. The two thermometers (h) were added after several runs had been performed and were found to have no effect on the results.

Reaction vessel (B) is shown in Fig. 2. The points at which the reactants were introduced are the reverse of reaction vessel (A) (atomic nitrogen entered through the central jet). The vessel was also larger in diameter; the insert tube measured 31 mm I.D. by 30 cm in length and the reaction vessel 35 mm O.D. The discharge tube (g) was, as in (A), quartz.

The reaction vessel (either (A) or (B)) was followed by three U-tube traps, fitted with 4-mm vacuum stopcocks and ground glass joints so that they could be removed for weighing. The exit of the third trap
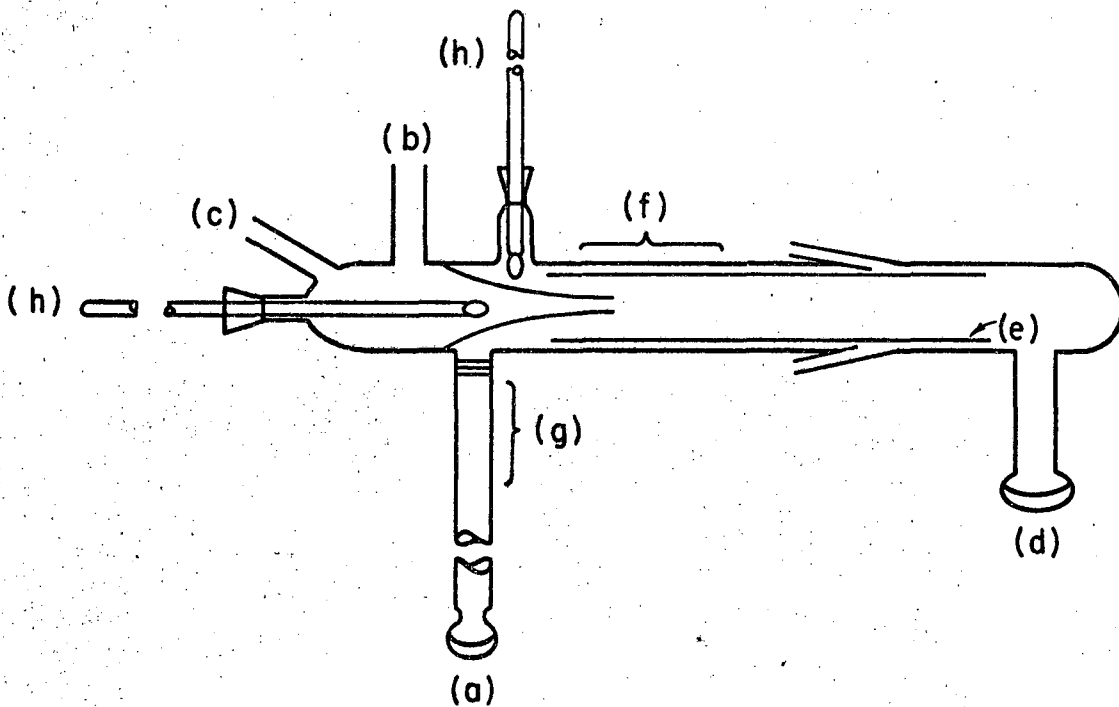
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Fig. 1. Reaction Vessel (A)

(a) Nitrogen inlet, (b) S_2Cl_2 inlet, (c) NO inlet,
(d) Exit to traps, (e) Insert tube, (f) Reaction zone,
(g) Discharge zone, (h) Thermometers.
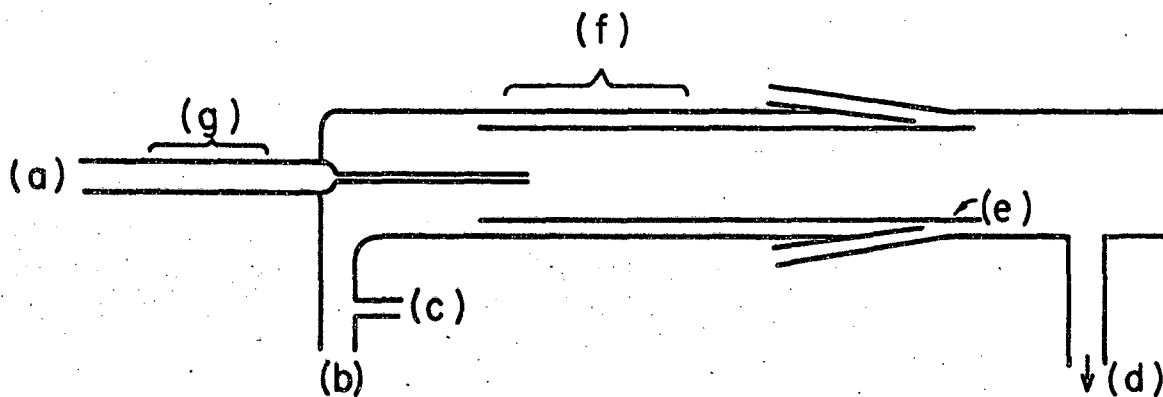
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Fig. 2. Reaction Vessel (B)

(a) Nitrogen inlet, (b) S_2Cl_2 inlet, (c) NO inlet,
(d) Exit to traps, (e) Insert tube, (f) Reaction zone,
(g) Discharge zone.

led directly to the vacuum pump. The entire system could be evacuated to 10^{-4} mm Hg.

High purity dry nitrogen from a cylinder passsed through a purification train consisting first of a $Mg(ClO_4)_2$ and "Drierite" drying tube, followed by a tube containing activated copper (prepared by reducing CuO with hydrogen) at 400°C and finally a trap packed with glass beads and cooled to -78°C. The gas then passed through a flow meter and a needle valve into the discharge tube. The entire system from the cylinder to the needle valve was maintained under a positive pressure of approximately 3 lbs/sq in. to insure that any leaks were to the outside. The molecular nitrogen flow was always held constant at $0.98X10^{-4}$ moles/sec. (The pressure of the system was 3-mm Hg.)

The nitrogen was dissociated into atoms with a microwave discharge. Two different sources were used. One was a 100 watt diathermy unit (Baird Atomic, Inc., Cambridge, Mass.) producing 2450 Mc microwaves, the other a Raytheon QK-60 magnetron coupled to an 8 cm cavity. Satisfactory results (about 1% dissociation) were obtained with either. The microwave is not the most efficient way of dissociating nitrogen, but is much simpler and cleaner than condensed or pulsed discharges.

The nitrogen atom flow rate was determined by titration with nitric oxide.[19] The three traps were cooled with liquid nitrogen, the molecular nitrogen flow adjusted and the discharge established. The nitric oxide was introduced, from a constant volume source, into the nitrogen stream until the nitrogen atom flow rate was matched. The rate of NO addition was then measured by measuring the change in pressure of the reservoir system.

The "end point" (i.e. the point at which the NO flow rate equals the nitrogen atom flow rate) is easily observable visually. The end point reaction

is:

$$N + NO \rightarrow N_2 + O \qquad (II-1)$$

No light emission accompanies this reaction. If however less NO is added

than required, the reaction of the excess nitrogen atoms with the oxygen

atoms produced in reaction (II-1) occurs:

$$N + O \rightarrow NO^* \qquad (II-2)$$

$$NO^* \rightarrow NO + h\nu \qquad (II-3)$$

The light emitted is the blue air afterglow and when mixed with the nitrogen

Lewis-Rayleigh afterglow appears violet. When greater than the required

amount of NO is added, the reaction emits a green-white light according to

the reactions:

$$N + O \rightarrow NO_2^* \qquad (II-4)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (II-5)$$
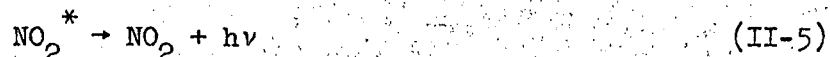
The end point is then the point at which no light emission occurs. Re-

cently, doubt has been raised as to the validity of the NO titration for

determining nitrogen atom flow rates, and the HCN production from ethylene

suggested as an alternative (See Appendix, Sec. E).

When possible, products were first identified by infrared spectro-

scopy. Spectra of volatile products were recorded using a 5 cm gas cell,

2.5 cm in diameter fitted with NaCl or KBr windows. Solid products,

which collected in the insert tube were treated in two ways. First, follow-

ing a run, the insert tube was removed and the solids washed with carbon di-

sulfide. Infrared spectra of the CS_2 solutions were recorded. The bulk

of the solids, however, failed to dissolve so a second method was used.

KBr pellets were made and placed in the insert tube immediately prior to

running the reaction. The solids then formed on the pellets as well as

the glass of the insert tube. After the run, the pellets were removed

and the spectra recorded.

III. THE REACTION OF ACTIVE NITROGEN WITH DISULFUR DICHLORIDE

R. J. Strutt[10] investigated the reaction of active nitrogen with disulfur dichloride (S_2Cl_2) in 1913. He reported, "Vapour of chloride of sulphur fed into active nitrogen, yields a bright yellow deposit, which consists, at all events in part, of ordinary sulphide of nitrogen". Nothing further was reported about the reaction other than that a blue luminosity accompanied it.

Since S_2Cl_2 is one of the more common and important sulfur compounds, we felt it worthwhile to investigate its reaction with nitrogen atoms further.

A. Experimental

Eastman Kodak S_2Cl_2 (practical) was distilled under high vacuum (10^{-3} mm Hg) into a -45°C cold trap followed by a trap at -196°C. The -45°C fraction was then redistilled into a storage bulb fitted with a 4-mm Delmar-Urry greaseless stopcock, (Delmar Scientific Laboratories, Inc., Maywood, Illinois). The infrared spectrum showed the common impurities (SCl_2, $SOCl_2$, and SO_2Cl_2) to be absent.

S_2Cl_2 was introduced into the reaction vessel through a needle valve (Fischer and Porter Co., Hatboro, Pennsylvania). (S_2Cl_2 has a vapor pressure of about 10 mm at room temperature (25°C) and can be fed into the nitrogen stream without heating). The flow was adjusted to the desired rate and left unchanged until the reaction was terminated. The flow rate was determined by weighing the storage bulb before and after the reaction.

Reaction vessel (A) was used for most of the study. However, reaction vessel (B) was used briefly in the study of surface effects

(see Sec. D). In all runs, the three cold traps were cooled with liquid nitrogen. The quantities of products were measured by weighing. All other experimental details were discussed in Article II (General Experimental).

B. Products

When the S_2Cl_2 vapor was fed into the active nitrogen stream, a blue flame[20] was produced; solids deposited on the insert tube immediately following the flame, and yellow and red substances were collected in the series of liquid nitrogen cold traps. The solids which formed in the insert tube ranged in color from yellow to black and appeared as a thin film over the inside of the tube.

A portion of the material collected in the cold traps could be removed from the traps by warming to room temperature; however, a yellow-brown crystalline solid always remained. This solid turned dark upon exposure to moisture. With heating under vacuum, the material turned to a dark solid and finally to a yellow powder. This behavior is identical to that of $S_3N_2Cl_2$ under similar circumstances.[21]

When the volatile material was transferred, immediately after warming to room temperature, to an infrared cell and the spectrum recorded, absorption bands attributable to NSCl,[22] SCl_2, and S_2Cl_2 were observed. Some chlorine was also identified by its reaction with KI, and its physical properties.

Infrared spectra of the solid in the insert tube showed tetrasulfur tetranitride (S_4N_4), along with some polymeric sulfur nitride $(NS)_x$, to be

present. The bulk of the solid appeared, however, to be sulfur.[+]

When the volatile products of the reaction were allowed to stand in
the traps at room temperature for one hour or more, or if they were al-
ternately condensed and warmed several times, the amount of $S_3N_2Cl_2$ was
observed to increase. The infrared spectrum of the remaining vapor no
longer showed the NSCl absorption, indicating that the NSCl could be
quantitatively converted to $S_3N_2Cl_2$. The conversion reaction takes place
only in the presence of S_2Cl_2,[23,24] otherwise, the NSCl will trimerize to
$(NSCl)_3$.[25]

The conversion reaction is probably

$$2NSCl + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2 \qquad \text{(III-1)}$$
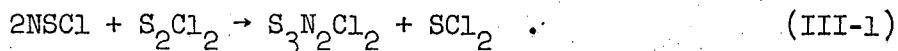
When an excess of S_2Cl_2 is present, all the NSCl can be removed as
$S_3N_2Cl_2$. This offers a convenient method for measuring the NSCl yield
since the $S_3N_2Cl_2$ is the only non-volatile material formed in the traps.
Thus, at the completion of a run, the three traps were allowed to warm
to room temperature and stand for at least one hour until all the NSCl
had been converted to $S_3N_2Cl_2$. The volatile products were then removed
and the traps weighed. The NSCl yield was calculated on the basis of
reaction (III-1).

[+] Attempts were made to dissolve the solid in nitric acid. Most of the
solid failed to dissolve, and the residue had the appearance of sulfur.
Addition of silver nitrate to the solution gave no precipitate. Heating
of the solid in KOH solution gave very little ammonia indicating the
nitrogen content was low. Allowing the solid to sit in the air for ex-
tended periods (several days) caused no appreciable change in weight.

C. S_2Cl_2 Dependence of the NSCl Rate of Formation

Since NSCl is the principal nitrogen-containing product in the reaction, and since the amount produced can easily be determined, a study of the mechanism leading to its formation was undertaken.

The dependence of the rate of formation of NSCl on the S_2Cl_2 flow rate was determined by running the reaction at several S_2Cl_2 flow rates while keeping the total nitrogen and atomic nitrogen flow rates constant. (The pressure of the system was essentially that of the undissociated nitrogen. The flow rates of nitrogen atoms and S_2Cl_2 were less than 1% of the molecular nitrogen flow rate. Thus, varying the nitrogen atom flow rate and/or the S_2Cl_2 flow rate had essentially no effect other than changing their relative amounts. This allowed the effect of either on the NSCl rate of formation to be studied independently of the other.) The results are shown in Table I.[†] ($f_{S_2Cl_2}$ and f_N are the flow rates of S_2Cl_2 and N atoms respectively; F_{NSCl} is the rate of formation of NSCl.) A plot of the rate of formation of NSCl versus the flow rate of S_2Cl_2 is shown in Fig. 3.

At low S_2Cl_2 flow rates, the rate of formation of NSCl increases linearly with the S_2Cl_2 flow rate. When however, the rate of formation of NSCl reaches approximately one twenty-fifth (1/25) of the nitrogen atom flow rate, a leveling-off occurs. Increasing the S_2Cl_2 flow rate above this point leads to no further increase in the rate of formation of NSCL. Since the leveling occurs at such a low percentage of the available nitrogen atoms, the reaction forming NSCl is apparently not the primary nitrogen atom removal reaction.

[†] It will be noticed that a slightly different "plateau" value was obtained when inserts were changed. We have no definite explanation for this. However we feel that it is probably due to a change in the flow characteristics of the system.

TABLE I. S_2Cl_2 Dependence of the NSCl
Rate of Formation

$f_N = 0.9$ μmole sec^{-1}	
$f_{S_2Cl_2}$ (μmole sec^{-1})	F_{NSCl} (μmole sec^{-1})
0.017	0.014
0.026	0.023
0.035	0.030
0.036	0.028
0.038	0.037
0.038	0.032
0.053	0.032
0.121	0.031
0.127	0.039
0.142	0.036
0.169	0.036
0.593	0.034
0.738	0.035
0.836	0.033
0.159*	0.045*
0.177*	0.044*
0.19 *	0.046*
0.388*	0.044*
1.59 *	0.043*

* Data obtained with smaller diameter insert tube
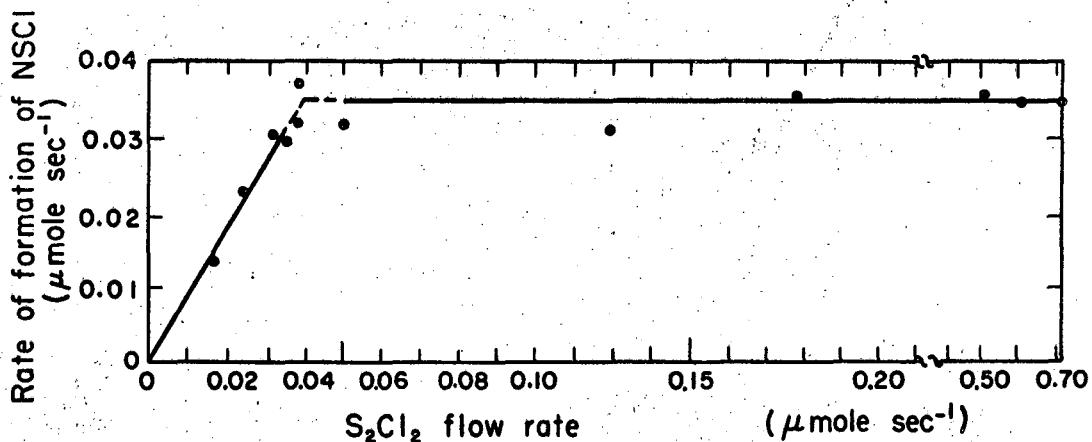
Fig. 3. A plot of the rate of formation of NSCl vs
the S_2Cl_2 flow rate.

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The yellow nitrogen afterglow, which in the absence of foreign sub-
stances indicates the presence of nitrogen atoms, decreases as the flow rate
of S_2Cl_2 increases and is completely replaced by a short blue flame at
the point where the leveling of the rate of formation of NSCl occurs. At
this point, all the nitrogen atoms are reacting. Since no other nitrogen-
containing product is formed in significant amounts, the principal reaction
leading to nitrogen atom destruction must be the nitrogen atom recombination
reaction.

Figure 3 represents a "titration" of the nitrogen atoms with the
S_2Cl_2. The nitrogen atoms are being removed by two reactions; one
forms NSCl, the other forms N_2. At low S_2Cl_2 flow rates, nitrogen atoms
are in excess, hence the NSCl formation rate increases linearly with the
S_2Cl_2 flow rate. The leveling of the NSCl rate of formation occurs when
the S_2Cl_2 is in excess. (Excess S_2Cl_2 is recovered at S_2Cl_2 flow rates
greater than 0.04 µmole sec^{-1}.)

A check of the reaction at the low S_2Cl_2 flow rates revealed that
the solid that formed in the traps was $(NSCl)_3$ and not $S_3N_2Cl_2$. (All of
the NSCl could be converted to the trimer by letting the traps stand.)
$(NSCl)_3$ is canary yellow, as opposed to the yellow-brown of $S_3N_2Cl_2$.
Furthermore, when the yellow solid was heated, the bulk of it vaporized
to NSCl (identified by its infrared spectrum) which could be reconverted
to the yellow solid again by merely condensing. Addition of S_2Cl_2 to the
yellow solid caused the color to change and led to a weight increase
(a sample which weighed .0050 gm. was found to weigh .0060 gm after
treatment with S_2Cl_2) as expected from the reaction[22]

$$2/3 \ (NSCl)_3 + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2$$
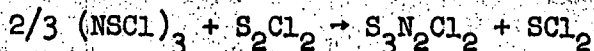
The NSCl rate of formation in the S_2Cl_2-dependent region was calculated on the basis of:

$$3NSCl \rightarrow (NSCl)_3$$
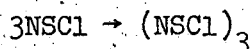
The fact that the NSCl formation rate becomes independent of the S_2Cl_2 flow rate at the higher flow rates indicates that the two reactions (NSCl formation and recombination) have the same S_2Cl_2 dependence. Otherwise, the NSCl formation rate would be expected to go either up or down at higher S_2Cl_2 flow rates, depending on which reaction had the higher order in S_2Cl_2. Both reactions are apparently first order in S_2Cl_2, since all of the known nitrogen atom recombinations are first order in the inert molecule.[28]

The amount of S_2Cl_2 required to extinguish the nitrogen afterglow is very small compared to the amount of undissociated molecular nitrogen present. (Typical flow rates were 10^{-4} moles sec^{-1} N_2; and 10^{-7} moles sec^{-1} S_2Cl_2.) The S_2Cl_2 must be a considerably more efficient third body for the nitrogen atom recombination reaction than molecular nitrogen.

A lower limit for the value of the rate constant $k_{S_2Cl_2}$ for the reaction

$$N + N + S_2Cl_2 \rightarrow N_2 + S_2Cl_2 \quad\quad\quad (III-2)$$
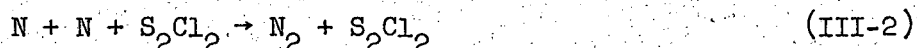
can be calculated, assuming that the reaction rate is second order in (N); and the calculated constant can be compared with the rate constant $k_{N_2} = 5.7 \times 10^9 \ell^2$ $mole^{-2}$ sec^{-1} for the corresponding reaction in which N_2 instead of S_2Cl_2 serves as the third body.[28] The rate constant for reaction (III-2) is easily derived. The rate of formation of N_2 will be

$$\frac{d(N_2)}{dt} = k_{S_2Cl_2} (N)^2 (S_2Cl_2)$$

If we let N_o be the initial concentration of nitrogen atoms and χ be the concentration of N_2 formed at any time t, minus the initial concentration of N_2, the differential rate equation becomes

$$\frac{d\chi}{dt} = k_{S_2Cl_2}((N_o) - 2\chi)^2 \cdot (S_2Cl_2).$$

(The concentration of S_2Cl_2 is presumed to remain constant because the S_2Cl_2 destroying reaction is slow compared to the recombination reaction. A look at Fig. 3 will show that the S_2Cl_2 concentration does change by about 30%, but this will have little effect on the magnitude of the rate constant). The rate equation, after integrating and applying the initial conditions, $\chi = 0$, at t = 0, is

$$k_{S_2Cl_2} = \frac{\chi}{(N_o)((N_o)-2\chi)(S_2Cl_2)t} \quad .$$

The time t in the above expression can be approximately determined. As mentioned previously, the reaction of N atoms with S_2Cl_2 is accompanied by a blue flame. If we assume that complete mixing occurs, and that the blue flame marks the recombination reaction zone, the time of the reaction will be the time required for the gas to flow the length of the flame. The observed flame length was 2 cm when the flow rates of N_2, N and S_2Cl_2 were 10^{-4} moles sec^{-1}, 10^{-6} moles sec^{-1}, and 10^{-7} moles sec^{-1} respectively. The velocity of the gas flowing through the reaction vessel is essentially that of the molecular nitrogen. The diameter of the reaction vessel was 2 cm, the pressure 3 mm Hg, and the temperature 298°K. The volume of N_2 per sec. flowing in the system is therefore,

$$10^{-4} \frac{moles}{sec} \times \frac{760mm}{3mm} \times \frac{298°K}{273°K} \times \frac{22.4 \, \ell \, (STP)}{mole} = .62 \frac{\ell}{sec} .$$

The velocity v of the gas is then

$$v = \frac{.62 \, \ell}{sec} \times \frac{10^3 cc}{\ell} \times \frac{1}{3.14 cm^2} = 2.0 \times 10^2 \frac{cm}{sec} .$$

And the time t required for the gas to travel 2 cm is

$$t = \frac{2 \; cm}{2.0 \times 10^2 \; \frac{cm}{sec}} = 10^{-2} \; sec.$$

Before numerically calculating $k_{S_2Cl_2}$ it is necessary to calculate the N atom and S_2Cl_2 initial concentrations. This can be done knowing that .62 $\ell \, sec^{-1}$ of gas flow through the system. The initial concentration of N and S_2Cl_2 will be

$$(N_o) = \frac{10^{-6} \; moles/sec}{.62 \; \ell \; /sec} = 1.6 \times 10^{-6} \frac{moles}{\ell} \; ;$$

$$(S_2Cl_2) = 1.6 \times 10^{-7} \frac{moles}{\ell} .$$

The only remaining unknown is χ. We can assume that the reaction is complete when 90% of the N atoms have recombined, that is when $\chi = .45(N_o)^{\dagger}$. $k_{S_2Cl_2}$ is then equal to
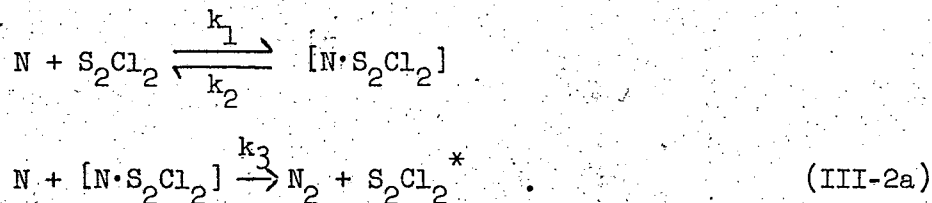

$\dagger$ A plot of the rate of recombination $(\frac{d\chi}{dt})$ vs. t for the reaction shows immediately that the assumption is valid. At the point where $\chi = .45(N_o)$, the rate has dropped to 10^{-2} times its original value and decreases very slowly from then on.

$$\frac{.45}{(1.6\times10^{-7}\frac{mole}{\ell})(1.6\times10^{-7}\frac{mole}{\ell})(10^{-2}\ sec)}\ ;\ k_{S_2Cl_2} = 1.7\times10^{15}\ \frac{\ell^2}{mole^2 sec}\ .$$

(The value of $k_{S_2Cl_2}$ is probably a lower limit since the observed time is an upper limit, and the S_2Cl_2 concentration decreases slightly during the reaction). If one calculates the rate constant $k_{S_2Cl_2}$ when $\chi = .49(N_o)$ (the reaction is 98% complete), the value is $9.6\times10^{15}\ \ell^2\ mole^{-2}\ sec^{-1}$ or approximately $10^{16}\ \ell^2\ mole^{-2}\ sec^{-1}$.

A rate constant of 10^{15}-$10^{16}\ \ell^2\ mole^{-2}\ sec^{-1}$ for a normal trimolecular recombination reaction is not possible. Kinetic theory predicts[42] tri-molecular rate constants of 10^9-$10^{10}\ \ell^2\ mole^{-2}\ sec^{-1}$, well below the 10^{15}-$10^{16}\ \ell^2\ mole^{-2}\ sec^{-1}$ observed for reaction (III-2). (The rate constant for the recombination reaction with N_2 as the third body can be considered a typical trimolecular rate constant. It has the value $5.7\times10^9\ \ell^2\ mole^{-2}\ sec^{-1}$).[28] In order to explain the increased rate of reaction (III-2), it is necessary to propose the formation of an inter-mediate complex such as $[N\cdot S_2Cl_2]$. The mechanism for reaction (III-2) can be formulated as

$$N + S_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [N\cdot S_2Cl_2]$$

$$N + [N\cdot S_2Cl_2] \overset{k_3}{\rightarrow} N_2 + S_2Cl_2^* \qquad\qquad (III\text{-}2a)$$

The rate of formation of N_2 will now be[‡]

---

[*] Excited S_2Cl_2 molecule

[‡] The steady state assumption has been applied to the complex $[N\cdot S_2Cl_2]$.

$$\frac{d(N_2)}{dt} = \frac{k_1 k_3 (N)^2 (S_2 Cl_2)}{k_2 + k_3 (N)}$$

(we have neglected the product forming reactions). There are two limiting cases for the rate of N_2 formation, $k_2 \gg k_3 (N)$ or $k_2 \ll k_3 (N)$. When $k_2 \gg k_3 (N)$, the reaction is second order in (N), and the rate constant has the value $\frac{k_1 k_3}{k_2}$. If however, $k_2 \ll k_3 (N)$, the reaction (III-2a) becomes first order in nitrogen, the rate law becomes $\frac{d(N_2)}{dt} = k_1 (N)(S_2 Cl_2)$, and the rate constant is k_1, a bimolecular rate constant in ℓ mole^{-1} sec^{-1}.

The question that now arises is whether the reaction is second order in nitrogen atoms like normal recombination reactions, or is it first order? The nitrogen atom dependence cannot be determined from the data. However, there are two reasons why the reaction is probably second order in (N).

First, if we consider the reaction to be first order in nitrogen with a rate law of

$$\frac{d(N_2)}{dt} = k(N)(S_2 Cl_2),$$

the rate constant k is equal to k_1, which is the rate constant for the following reaction,

$$N + S_2 Cl_2 \xrightarrow{k_1} [N \cdot S_2 Cl_2] .$$
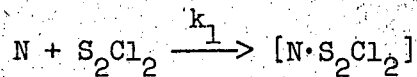
The value of k_1 necessary to give the observed rate can be calculated from the integrated rate expression, which, using the same notation and conditions as earlier (e.g. $\chi = (N_2)_t - (N_2)_o$), is

$$k_1 = \frac{\ln(N_o) - \ln((N_o) - 2\chi)}{(S_2 Cl_2)t}$$

or numerically, k_1 equals ($\chi = .45(N_o)$, $t = 10^{-2}$ sec.)

$$k_1 = 1.4 \times 10^9 \, \ell \, \text{mole}^{-1} \, \text{sec}^{-1}$$

(when $\chi = .49(N_o)$), $k_1 = 2.4 \times 10^9 \, \ell \, \text{mole}^{-1} \, \text{sec}^{-1}$).

However, k_1 could be approximately $10^{11} \, \ell \, \text{mole}^{-1} \, \text{sec}^{-1}$, since rate constants for reactions such as radical recombinations (e.g. $CH_3 + CH_3 \rightarrow C_2H_6$) or radical-molecule reactions of $10^{11} \, \ell \, \text{mole}^{-1} \, \text{sec}^{-1}$ have been observed.[29] The observed rate is thus approximately 100 times slower than might be expected were the reaction first order in (N).

Secondly, we can calculate reasonable values for k_2 and $k_3(N)$ for reaction (III-2a) which suggest the reaction to be second order in (N). Assuming that the recombination reaction in which N_2 serves as a third body also proceeds by a two step mechanism such as (III-2a), the rate expression for N_2 formation will be

$$\frac{d(N_2)}{dt} = \frac{k_1 k_3 (N)^2 (N_2)}{k_2 + k_3(N)} \ .$$

Since the reaction is observed[28] to be second order in (N), $k_2 \gg k_3(N)$ and the observed rate constant $k_{N_2} = \frac{k_1 k_3}{k_2} = 5.7 \times 10^9 \, \ell^2 \, \text{mole}^{-2} \, \text{sec}^{-1}$. By assuming $k_1 \sim k_3 = 10^{11} \, \ell \, \text{mole}^{-1} \, \text{sec}^{-1}$ (reasonable rate constants for this type of bimolecular reaction, see above), a value for k_2 can be calculated

$$k_2 = \frac{10^{22}}{6 \times 10^9} \, \text{sec}^{-1} \cong 10^{12} \, \text{sec}^{-1} \ .$$

If k_1 and k_3 remain unchanged in going from N_2 as the third body to S_2Cl_2, the 10^5-10^6 increase in $k_{S_2Cl_2}$ over k_{N_2} can be attributed to a 10^5-10^6 decrease in k_2 which makes $k_2 \sim 10^6$-$10^7 \, \text{sec}^{-1}$ for reaction (III-2a).

With the concentration of N atoms = 10^{-6} mole ℓ^{-1}, $k_3(N)$ equals $10^{11}(10^{-6})$ = 10^5 sec^{-1}, and k_2 = 10-100$k_3(N)$. Therefore, the reaction could still be second order in (N).

D. Effect of Surface on the Reaction

The same NSCl versus S_2Cl_2 behavior would be expected if the reaction were surface-controlled, with only the S_2Cl_2 absorbed on the surface subject to attack. In order to check this possibility reaction vessel (B) was assembled.

Since the reaction is accompanied by a blue flame, the reaction zone can be easily observed. In reaction vessel (A), the blue flame does in fact touch the walls. In reaction vessel (B), the nitrogen atoms are introduced through the center jet and the S_2Cl_2 along the outside. At high S_2Cl_2 flow rates, no nitrogen atoms would be expected to reach the walls of the reaction tube. Thus, any NSCl which would form would have to be due to gas phase reaction. In actuality, even relatively low S_2Cl_2 flow rates caused the flame to shorten and be confined to a small volume right at the end of the nitrogen jet.

The results obtained with reaction vessel (B), are shown in Table II. (f_N and $f_{S_2Cl_2}$ are the flow rates of N atoms and S_2Cl_2 respectively; F_{NSCl} is the rate of formation of NSCl.). The data presented in Table II cannot be correlated directly with the data in Table I, since the two reaction vessels (A) and (B) were of different design and no attempt was made to duplicate the conditions (i.e. gas velocity, amount of reactant per cross sectional area). However, it can be readily seen that appreciable NSCl yields are obtained from a gas phase reaction. This indicates that the reaction is not surface controlled.

TABLE II. Data from Reaction Vessel (B)

f_N(μ moles sec^{-1})	$f_{S_2Cl_2}$(μ moles sec^{-1})	F_{NSCl}(μ mole sec^{-1})
1.5	10.0	~ 0.09
1.53	0.304	0.099
0.76	0.167	0.048

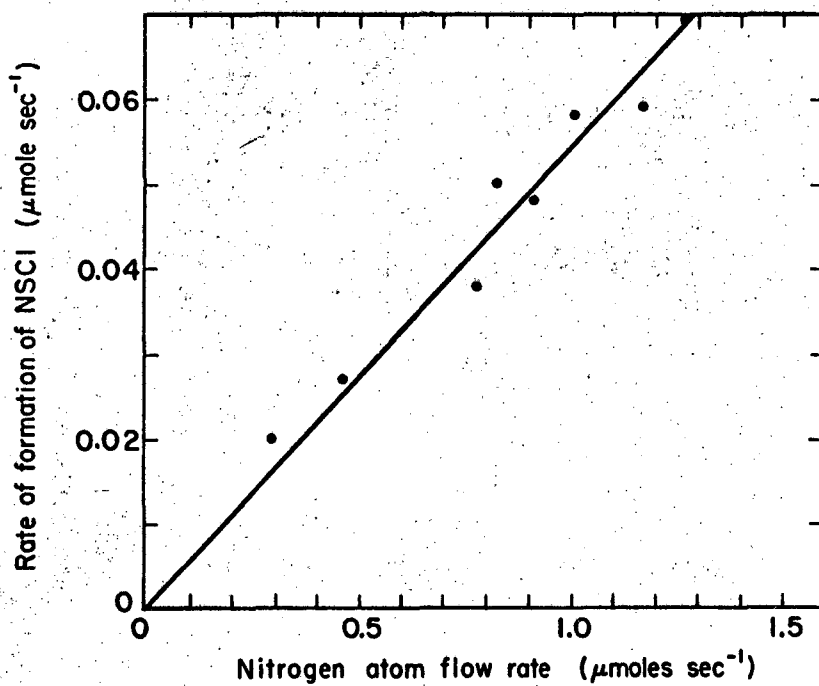### E. The Nitrogen Atom Dependence of the Reaction

The effect of the nitrogen atom flow rate on the rate of formation of NSCl was determined by measuring the rate of formation of NSCl at several N atom flow rates. The flow rates of S_2Cl_2 used were large enough to be in the "plateau" region (S_2Cl_2-independent region; see Fig. 3), and can be considered constant. The molecular nitrogen flow was also held constant. The nitrogen atom concentration was varied by varying the power output of the microwave source. The results are shown in Table III. A plot of the NSCl rate of formation versus the nitrogen atom flow rate is shown in Fig. 4. The rate of formation of NSCl is observed to increase linearly with an increase in the atomic nitrogen flow rate. This indicates that the rates of the NSCl formation reaction and the recombination reaction have the same dependence on the flow rate of N.

F. Mechanism Discussion

It must be noted that the data relating the rate of formation of NSCl to the S_2Cl_2 flow rate (Sec. C) and the atomic nitrogen flow rate (above) may not be conclusive evidence for the true kinetic dependence on these two reagents.

The kinetics will depend on the nature of the flow in the reaction

Fig. 4. A plot of the rate of formation of NSCl
vs the nitrogen atom flow rate.

TABLE III. Nitrogen Atom Dependence of the NSCl Rate of Formation

| f_N (μ moles sec^{-1})	$f_{S_2Cl_2}$ (μ moles sec^{-1})	F_{NSCl} (μ mole sec^{-1})
0.30	0.13	0.020
0.47	0.11	0.027
0.78	0.16	0.038
0.82	0.18	0.050
0.91	0.19	0.048
1.02	0.11	0.060
1.17	0.26	0.059
1.27	1.20	0.069

vessel. Reactions carried out in flow systems of the type used here (no preliminary mixing) may be diffusion reactions, when the reaction is fast compared to the rate of mixing, homogeneous reactions, when the reaction is slow compared to the rate of mixing, or intermediate when the reaction and the mixing have comparable rates.

The reaction was clearly not a pure diffusion reaction because the operating pressure was 3.0-mm Hg (simple diffusion reactions only occur at low pressures (0.001-0.01 mm Hg)).[29] Furthermore, for reaction vessel (A), the flame, if it were a simple diffusion flame, would be spherical in shape and centered on the S_2Cl_2 inlet nozzle (diffusion should occur equally in all directions.) The observed flame was by no means spherical, but was elongated and pointed downstream. Thus, treating the reaction as a simple diffusion reaction would be meaningless.

Since no rigorous treatment can be applied to a combination diffusion-homogeneous reaction, we have used a homogeneous reaction

treatment for the mechanistic interpretation. For the reaction to be homogeneous, complete mixing of the reactants should take place before reaction. The flow rates of the reactants would then be proportional to concentrations, since the molecular nitrogen flow rate remained constant (changing the flow rate of either the atomic nitrogen or the S_2Cl_2 would be equivalent to changing its concentration). In addition, we have applied the steady-state assumption to the intermediate complexes (i.e. $[N \cdot S_2Cl_2]$). The application of this type of kinetic treatment for active nitrogen reactions is not without precedence. Forst, et.al.[27] applied a similar treatment to the reactions of active nitrogen with methyl chloride and with methyl cyanide.

Several mechanisms can be proposed which will explain the data. These mechanisms can be divided into three general categories, designated here as Case A, Case B, and Case C. In all three Cases, the recombination reaction will be reaction (III-2a). In Case A, the competing reactions have a common intermediate complex $[N \cdot S_2Cl_2]$. The NSCl formation reaction is then either a unimolecular decomposition of the $[N \cdot S_2Cl_2]$ complex formed in the recombination reaction,

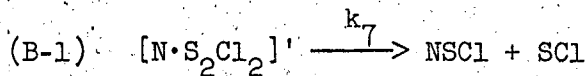$$(A-1) \quad [N \cdot S_2Cl_2] \xrightarrow{k_4} NSCl + SCl \; ,$$
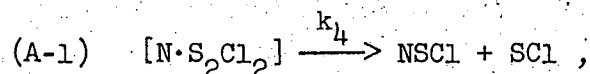
or an attack of a second nitrogen atom on the complex to form either one or two NSCl's,

$$(A-2) \quad N + [N \cdot S_2Cl_2] \xrightarrow{k_4} 2NSCl$$

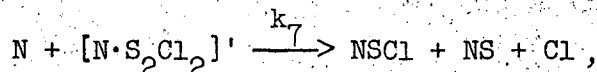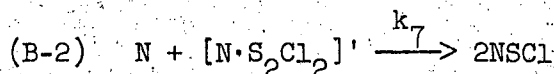$$N + [N \cdot S_2Cl_2] \xrightarrow{k_4} NSCl + NS + Cl.$$
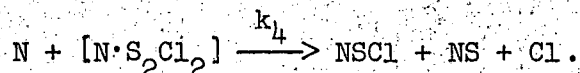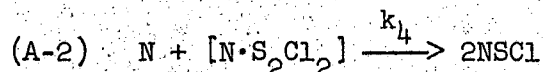
(The products NS + Cl were chosen over NCl + S because the former

are more stable.) Product formation reactions, sharing a common inter-
mediate with the nitrogen atom recombination reaction, have been proposed
on several previous occasions[13,26,27] to explain active nitrogen reactions.

Case B assumes that both reactions (recombination and product forma-
tion) proceed via complex formation, but with each having a different
complex (separate complexes). The NSCl formation reactions will then be

$$N + S_2Cl_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} [N \cdot S_2Cl_2]'$$

$$\text{(B-1)} \quad [N \cdot S_2Cl_2]' \xrightarrow{k_7} NSCl + SCl$$

or

$$\text{(B-2)} \quad N + [N \cdot S_2Cl_2]' \xrightarrow{k_7} 2NSCl$$

$$N + [N \cdot S_2Cl_2]' \xrightarrow{k_7} NSCl + NS + Cl,$$
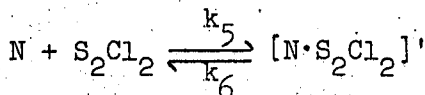
where $[N \cdot S_2Cl_2]'$ is some complex other than the one formed in reaction
(III-2a). Mechanisms, as in Case B, have not yet been proposed in ex-
plaining active nitrogen reactions, but we see no reason why they are
not equally as probable as Case A.

Case C is the simple case in which the NSCl formation reaction is
assumed to proceed without complex formation. This corresponds to Case
B when the lifetime of the complex $[N \cdot S_2Cl_2]'$ is very small. The NSCl
formation reactions are

$$\text{(C-1)} \quad N + S_2Cl_2 \xrightarrow{k_8} NSCl + SCl$$

$$\text{(C-2)} \quad N + N + S_2Cl_2 \xrightarrow{k_9} 2NSCl$$

$$N + N + S_2Cl_2 \xrightarrow{k_9} NSCl + NS + Cl .$$
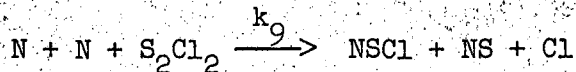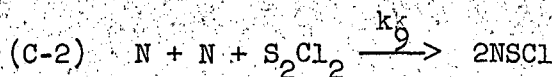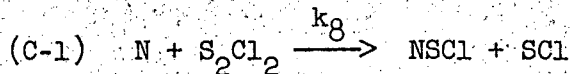
Some of the above mechanistic possibilities can be eliminated because they fail to predict the observed nitrogen atom dependence. For Cases B and C, the rate of formation of N_2 for the recombination reaction

$$N + S_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [N \cdot S_2Cl_2]$$

$$N + [N \cdot S_2Cl_2] \xrightarrow{k_3} N_2 + S_2Cl_2^* \qquad \text{(III-2a)}$$
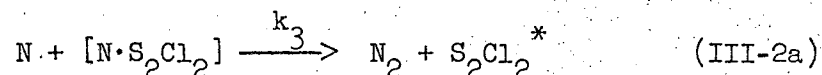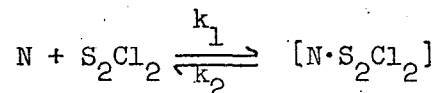
is (assuming a steady state in the complex)

$$\frac{d(N_2)}{dt} = \frac{k_1 k_3 (N)^2 (S_2Cl_2)}{k_2 + k_3(N)} \quad .$$

The rate of N_2 formation has two possible nitrogen atom dependences, depending on whether k_2 is greater or less than $k_3(N)$. Therefore, the nitrogen atom dependence predicted by each of the mechanisms in Cases B and C will also depend on the magnitudes of k_2 and $k_3(N)$. For Case B, reactions (B-2), the nitrogen atom dependence predicted will also depend on k_6 and $k_7(N)$ since

$$\frac{d(NSCl)}{dt} = \frac{k_5 k_7 (N)^2 (S_2Cl_2)}{k_6 + k_7(N)}$$

Case A is somewhat unique since the NSCl formation reaction also requires the intermediate complex from mechanism (III-2a). The rate of formation of N_2 for Case A reaction (A-1), will be

$$\frac{d(N_2)}{dt} = \frac{k_1 k_3 (N)^2 (S_2Cl_2)}{k_2 + k_4 + k_3(N)}$$

---

* Excited S_2Cl_2 molecule

and for (A-2)

$$\frac{d(N_2)}{dt} = \frac{k_1 k_3 (N)^2 (S_2 Cl_2)}{k_2 + k_4 (N) + k_3 (N)} .$$

Table IV is a tabulation of the mechanisms and indicates which ones can be eliminated on the basis of the observed nitrogen atom dependence. It also shows what conditions (as regards rate constants) the remaining mechanisms require. (The calculations made in preparing Table IV are given in Appendix Sec. F.)

Several mechanisms are consistent with the observed nitrogen dependence. It is impossible, on the basis of the observed data to determine exactly which of the mechanisms is most probable. It is, however, possible to draw some conclusions. If the mechanism is Case A, that is, a common inter-mediate is shared by the competing reactions, the NSCl formation reaction is (A-2) regardless of the relative magnitudes of k_2 and $k_3(N)$. Further-more, if the recombination reaction is second order in nitrogen atoms $(k_2 \gg k_3(N))$, the NSCl formation reaction must also be second order in (N). Only for $k_2 \ll k_3(N)$, when the recombination reaction becomes first order in (N), can the NSCl formation reaction be first order in (N), and then only for Case B or C.

As mentioned previously (Sec. C) it is possible for k_2 to be greater than $k_3(N)$ and still have the observed rate of recombination. (Whether or not k_2 is in fact greater than $k_3(N)$ cannot be determined without actually measuring the nitrogen atom dependence of the recombination.) Assuming this to be the case, the NSCl formation reaction is second order in (N). Since there is no way to distinguish among reactions (A-2),((B-2), $k_6 \gg k_7(N)$), and (C-2), the NSCl formation reaction can only be

TABLE IV. Mechanisms for the Reaction of Active Nitrogen with S_2Cl_2

Mechanism	Product Formation Reaction	$\dfrac{d(NSCl)}{dt}$	$\dfrac{d(N_2)}{dt}$	$\dfrac{d(NSCl)}{d(N_2)}$	Recombination Reaction $k_2 \gg k_3(N)$	$k_2 \ll k_3(N)$
Case A Common Intermediate	(A-1)	$\dfrac{k_4 k_1 (N)(S_2Cl_2)}{k_2+k_4+k_3(N)}$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_4+k_3(N)}$	$\dfrac{k_4}{k_3(N)}$	Inconsistent†	Inconsistent†
	(A-2)	$\dfrac{2k_4 k_1 (N)^2 (S_2Cl_2)}{k_2+k_4(N)+k_3(N)}$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_4(N)+k_3(N)}$	$\dfrac{2k_4}{k_3}$	Consistent	Consistent
Case B Separate Intermediates	(B-1)	$\dfrac{k_7 k_5 (N)(S_2Cl_2)}{k_6+k_7}$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_3(N)}$	$\dfrac{k_5 k_7 (k_2+k_3(N))}{k_1 k_3 (N)(k_6+k_7)}$	Inconsistent	Consistent
	(B-2) $k_6 \gg k_7 N$	$\dfrac{2k_7 k_5 (N)^2 (S_2Cl_2)}{k_6}$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_3(N)}$	$\dfrac{2k_7 k_5 (k_2+k_3(N))}{k_6 k_3 k_1}$	Consistent	Inconsistent
	(B-2) $k_6 \ll k_7 N$	$2k_5(N)(S_2Cl_2)$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_3(N)}$	$\dfrac{2k_5 (k_2+k_3(N))}{k_3 k_1 (N)}$	Inconsistent	Consistent
Case C No Intermediate	(C-1)	$k_8(N)(S_2Cl_2)$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_3(N)}$	$\dfrac{k_8 (k_2+k_3(N))}{k_1 k_3 (N)}$	Inconsistent	Consistent
	(C-2)	$2k_9(N)^2(S_2Cl_2)$	$\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2+k_3(N)}$	$\dfrac{2k_9 (k_2+k_3(N))}{k_1 k_3}$	Consistent	Inconsistent

† Indicates whether the mechanism's predicted nitrogen atom dependence is consistent or inconsistent with experiment when the indicated relative values of k_2 and $k_3(N)$ are assumed.

represented by one of the general reactions

$$2N + S_2Cl_2 \rightarrow 2NSCl \qquad (III-6)$$

$$2N + S_2Cl_2 \rightarrow NSCl + NS + Cl \cdot \qquad (III-7)$$

G.   The Reaction at Elevated Temperatures

The NSCl rate of formation would be expected to increase at higher temperatures.   The nitrogen atom recombination reaction surely has a very low activation energy whereas the NSCl formation reaction would have an appreciable activation energy since bond breakage must occur.

Reaction vessel (A) was modified by adding the two thermometers (h). The decision to use thermometers for measuring the temperature instead of thermocouples was due primarily to ease of modification of the reaction vessel.

The two reactants were preheated with ordinary heating tapes wrapped around the tubing leading to the reaction vessel. It was found necessary to insulate the reaction vessel in order to prevent the reactants from again reaching ambient temperatures due to collisions with the cooler walls.

The reaction vessel was heated to the proper temperature by allowing the heated nitrogen to pass for several minutes before starting the reaction. The reaction was then carried out as usual except at the higher temperature. The results are shown in Table V. (The symbols f_N and $f_{S_2Cl_2}$ refer to the flow rates of nitrogen atoms and S_2Cl_2 respectively, F_{NSCl} is the rate of formation of NSCl.) The expected results are obtained.

It would have been interesting to have gone to increasingly higher

TABLE VI. Mass Balance for the Reaction of Active Nitrogen with S_2Cl_2

	Run #1	Run #2
f_N (μmoles/sec)	0.9	1.02
$f_{S_2Cl_2}$ (μmoles/sec)	0.068	0.11
S_2Cl_2 used (moles X 10^4)	6.9	9.3
$S_3N_2Cl_2$ (moles X 10^4)	2.0	2.6
SCl_2 (moles X 10^4) observed	1.9	2.1
from Reaction (III-1) expected	2.1	2.5
Cl_2 obs. (moles X 10^4)	1.7	3.2
S_2Cl_2 unreacted (moles X 10^4)	0.5	0.6
Solids obs. (gms)	0.013	0.028
S_2Cl_2 accounted for[a] (moles X 10^4)	6.2	8.9
Sulfurs added (moles X 10^4)	13.8	18.6
Sulfurs recovered (moles X 10^4)[b]	13.0[c]	19.8[c]
	11.6[d]	16.8[d]

[a] S_2Cl_2 accounted for is the sum total of the S_2Cl_2 unreacted plus that required in the following reactions:

$$2N + S_2Cl_2 \rightarrow 2NSCl \qquad (III-6)$$

$$2NSCl + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2 \qquad (III-1)$$

$$S_2Cl_2 \rightarrow S_2Cl_2 \qquad (III-10)$$
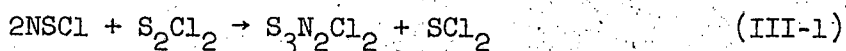
(The substitution of reaction (III-7) for reaction (III-6) leads to exactly the same results).

[b] Recovered as $S_3N_2Cl_2$, SCl_2, unreacted S_2Cl_2, and solids (sulfur or $(NS)_x$).

[c] Assuming the solid in the insert to be sulfur.

[d] Assuming the solid in the insert to be $(NS)_x$.

the run. The "unreacted S_2Cl_2" is that which is recovered unchanged in the traps. The remaining S_2Cl_2 has then reacted to form either NSCl, or other products (i.e., SCl_2, $S_3N_2Cl_2$, S_8 and Cl_2). It is important that either all the S_2Cl_2 be accounted for, or that a sulfur balance be obtained. The Table gives both an S_2Cl_2 balance and a sulfur atom balance.

Run #2 gives a very good sulfur balance. In Run #1 the "sulfur recovered" is lower than "sulfur added", but the difference is within the limits of experimental error (10%). Run #2 is also consistent with the fact that a portion of the solid in the insert is S_4N_4.

The amount of SCl_2 observed in the products corresponds to that expected from reaction (III-1) alone. Apparently, SCl_2 is only a secondary product and not formed in the initial reaction of nitrogen atoms and S_2Cl_2.

It is not possible to determine anything further about the mechanism from these data. Two reactions were proposed ((III-6), (III-7)) for the NSCl formation reaction. They differ in the amount of NSCl that can be obtained from one S_2Cl_2 molecule. The data in Table VI will not allow us to distinguish between the reactions.

NS is a principal product of (III-7) and not (III-6). However, little NS (as $(NS)_x$, S_4N_4) is actually observed in the products. This is partial evidence against reaction (III-7). NS apparently reacts with nitrogen atoms[14] to form nitrogen and sulfur:

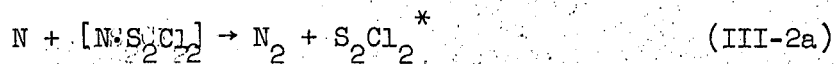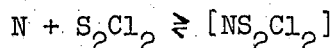$$N + NS \longrightarrow N_2 + S. \qquad\qquad (III-8)$$

Some of the NS might be destroyed before appearing as products if reaction (III-8) were fast compared to reaction (III-2a). But, in the reactions of active nitrogen with H_2S, COS, or CS_2 (see Article IV), essentially the

same conditions exist as far as the recombination reaction is concerned, and $(NS)_x$ is found in appreciable yields in spite of reaction (III-8).

Reaction (III-7) is not necessary to explain the presence of the small amounts of S_4N_4 and $(NS)_x$. A small amount of NS can easily be formed by reaction (III-11).

The reaction of active nitrogen with S_2Cl_2 may be represented by the mechanism:

$$N + S_2Cl_2 \rightleftharpoons [NS_2Cl_2]$$

$$N + [N \cdot S_2Cl_2] \rightarrow N_2 + S_2Cl_2^* \qquad \text{(III-2a)}$$

$$2N + S_2Cl_2 \rightarrow 2NSCl . \qquad \text{(III-6)}$$

The electronically excited $S_2Cl_2^*$ produced in reaction (III-2a) probably undergoes two reactions

$$S_2Cl_2^* + M \rightarrow S_2Cl_2 + M^* \qquad \text{(III-9)}$$

$$S_2Cl_2^* \rightarrow S_2^* + Cl_2 . \qquad \text{(III-10)}$$

Reaction (III-10) is quite probable since the amount of energy available from the recombination (225 kcal) is more than sufficient to decompose the S_2Cl_2 molecule. This is probably another principal S_2Cl_2 destroying reaction.

Small amounts of NS are possible from the reaction of nitrogen atoms with the S_2^{14} formed in reaction (III-10),

$$N + S_2 \rightarrow NS + S . \qquad \text{(III-11)}$$

IV. REACTIONS OF ACTIVE NITROGEN WITH COMPOUNDS
HAVING INTERNAL SULFUR ATOMS

A. Sulfur

The reaction of N atoms with sulfur has been investigated on several occasions. Strutt[10] sublimed sulfur into a stream of active nitrogen and obtained a yellow product, suggested to be S_4N_4, and a blue compound, suggested to be $(NS)_x$. He reported that a blue flame accompanied the reaction. Moldenhauer and Zimmerman[11] passed an electrical discharge through a heated tube containing nitrogen and sulfur. They separated three products from the excess sulfur, S_4N_4, S_5N_2 (later shown to be S_4N_2)[41] and $(NS_2)_x$ (probably $(NS)_x$).[16] Liuti, et.al.,[12] recently reported that solid sulfur failed to react with N atoms. Reaction to form "NS polymers" (detected by mass spectrometry), was observed however, when the sulfur was heated. A rather complete mechanistic study of the reaction of N atoms with S_2 was recently completed by Bett and Winkler[14] in which they also observed S_4N_4, $(NS)_x$ and S_4N_2 as the ultimate products.

We have focussed our attention on the reaction of N atoms with S_8 sulfur molecules, by working at lower temperatures ($< 250°C$).

Initial experiments were performed in a crude apparatus not previously described in this work. The apparatus consisted of a straight quartz discharge tube which had been sealed at right angles to a vertical tube of similar diameter (~ 15 mm O.D.); the latter served as a reflux column for the sulfur. The N atoms passed through the refluxing sulfur to a series of liquid nitrogen traps.

Spectroscopic grade (99.999+%) sulfur (American Refining and Smelting) was used for this study. The reaction was accompanied by a blue

flame. After operating for several minutes, the solids which collected in the reaction tube varied in color from orange-brown near the reaction zone to blue in the tube above it. The volatile materials which formed in the trap were brown to orange in color. Upon warming the traps, the orange material melted to a dark red liquid. This liquid behaved much like oil (beaded on the glass, etc.) and decomposed to solids on standing at room temperature. It was found to have a very strong iodine-like odor. These characteristics are the same as those of S_4N_2.[16] The red material was also found to decompose to sulfur and a non-condensable gas upon heating to a temperature greater than 100°C. The material was apparently S_4N_2. The S_4N_2 was found to be the only volatile product formed in the reaction. The vapor pressure of S_4N_2 is, however, quite low, and it cannot be distilled easily on a vacuum line at room temperature. In fact, on occasions, S_4N_2 condensed in the walls of the reaction vessel before reaching the traps. The reaction was found to be non-reproducible as far as the yield of S_4N_2 was concerned. Reactions apparently performed under the same conditions gave different results. Sometimes only traces of S_4N_2 were observed (visually); other times rather large amounts were observed. (In one excellent run, the rate of formation of S_4N_2 was determined by weighing and found to be 0.22 μmoles sec^{-1}. The flow rate of N atoms was not measured, but can be presumed to be about 1-2 μmoles sec^{-1}. Sulfur was in excess). Difficulty was experienced in determining the S_4N_2 yield because S_4N_2 decomposes readily at room temperature, and several minutes were required to transfer it to a vessel to be weighed.

S_4N_4 was also found to be present. It was identified by dissolving a portion of the solids in CS_2 and examining the infrared spectrum of the solution. $(NS)_x$ was observed (its blue color was easily recognized

in this system).

Several runs were performed in reaction vessel (B), in which a chunk of sulfur had been placed immediately in front of the N atom inlet nozzle. The sulfur was heated with a heating tape to the point where sufficient sulfur vapor existed to create a sharply defined blue reaction flame. Essentially the same results were observed as before, except that S_4N_4 was discovered in the traps along with the S_4N_2. This S_4N_4 probably came from the decomposition of the S_4N_2 to sulfur and S_4N_4 (some sulfur was also detected by its reaction with mercury in CS_2 solutions;[31] S_4N_4 gives a negative test). In runs of 51 and 60 min. rates of formation of S_4N_2 of 0.02 and 0.04 μmole sec^{-1} respectively were observed (the actual yields were probably a little higher since some of the S_4N_2 probably decomposed). The N atom flow rate was approximately 1.5 μmoles sec^{-1}. The S_4N_4 was never accurately determined, but it was never large enough for the reaction to be considered as a preparative method. Were it not for the difficulty in separating the S_4N_2 from the reaction products (the time required to transfer it coupled with its instability), the reaction might be a preparative method for this product.

B. Sulfur Dichloride

Since NSCl was found as a product of the reaction of N atoms with S_2Cl_2, it was only natural to expect that it would also result from the reaction of N atoms with SCl_2 by a reaction such as:

$$N + SCl_2 \rightarrow NSCl + Cl .$$
(IV-1)

The reaction was studied in reaction vessel (A). SCl_2 was prepared by the reaction of S_2Cl_2 with chlorine on a vacuum line. Fifty millimeters of purified S_2Cl_2 (see Sec. III-A) was distilled into a bulb of about 200 ml

capacity. Chlorine, which had been purified by passing through a trap at -112°C and condensed at -160°C, was introduced into the bulb to a pressure of about one atmosphere. The bulb was allowed to stand at room temperature for several hours. (The chlorine addition was repeated three times.) The resultant mixture (S_2Cl_2, SCl_2 and Cl_2) was fractionally condensed in a series of traps (-63.5°C, -112°C, and -196°C). The SCl_2 was collected at -112°C. It was then redistilled into a storage bulb. The bulb was weighed before and after each run.

The reaction, as in the case of S_2Cl_2, was accompanied by a blue flame. The intensity (visually) appeared less than that for the S_2Cl_2 reaction. Very little solid formed in the insert tube. The volatile products were yellow-orange in color. The infrared spectrum of the volatile products indicated the presence of NSCl and SCl_2. Chlorine, identified by its reaction with KI, and its physical properties (color, approximate melting point) was also observed to be present.

Yield determinations were made in three runs. The products were separated by fractional condensation through cold traps of -63.5°C, -112°C, and -196°C. The bulk of the NSCl was removed by the -63.5°C trap. A slight amount carried over to the -112°C trap where the SCl_2 was collected. The chlorine was trapped at -196°C. The yields were determined by weighing each product separately. The data are shown in Table VII.

A look at the chlorine yield shows immediately that an excess of chlorine was obtained. This indicates that some of the material added to the nitrogen atom stream was chlorine instead of SCl_2. This is not surprising in view of the fact that SCl_2 disproportionates to S_2Cl_2 and Cl_2
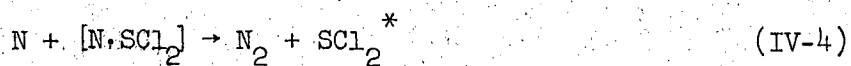
TABLE VII. Data for the Reaction of N Atoms with SCl_2

Run #	1	2	3
f_N (μmoles sec^{-1})	0.89	1.03	1.03
$f_{SCl_2}^{\dagger}$ (μmoles sec^{-1})	0.17	0.16	2.32
$SCl_2^{\dagger}$ added (moles X 10^4)	10.5	9.7	67.0
F_{NSCl} (μmole sec^{-1})	0.037	0.045	0.23
SCl_2 recovered (moles X 10^4)	2.33	1.94	30.0
S observed (moles X 10^4)	<0.3	<0.3	—
Cl_2 observed (moles X 10^4)	8.45	8.05	42.0

† a portion of the material added was Cl_2 instead of SCl_2

Cl_2

$$2SCl_2 \rightarrow S_2Cl_2 + Cl_2 \ . \tag{IV-2}$$

The reaction of active nitrogen with SCl_2 may proceed by a mechanism such as:

$$N + SCl_2 \rightleftharpoons [N \cdot SCl_2] \tag{IV-3}$$

$$N + [N \cdot SCl_2] \rightarrow N_2 + SCl_2^* \tag{IV-4}$$

$$N + SCl_2 \rightarrow NSCl + Cl \tag{IV-5}$$

$$SCl_2^* + M \rightarrow SCl_2 + M^* \ . \tag{IV-6}$$

With the excess Cl_2 around, one would not expect much sulfur or NS as products. This does not rule out reactions such as:

$$N + SCl_2 \rightarrow NS + Cl_2 \tag{IV-7}$$

$$SCl_2^* \rightarrow S + Cl_2 \ . \tag{IV-8}$$

Higher yields of NSCl can apparently be obtained from SCl_2 than from S_2Cl_2 at room temperature.

C. Thionyl Chloride

We have briefly studied the reaction of active nitrogen with thionyl chloride ($SOCl_2$).

Crude $SOCl_2$[†] was purified by distillation (in vacuo) through a $-45°C$ trap into a trap at $-78°C$. The $-78°C$ fraction was then redistilled into a tared storage bulb.

The reaction was accompanied by a blue flame, whose intensity appeared to be considerably less than, for example, that of the S_2Cl_2 reaction. (The flame is possibly due in part to S_2, since S_2 is observed when $SOCl_2$ is passed through a microwave discharge.[30] The S_2 would probably arise from the decomposition of the $SOCl_2$ after serving as the third body for the nitrogen atom recombination).

The products of the reaction were found to be unreacted $SOCl_2$, NOCl, N_2O, SO_2Cl_2, Cl_2 and small amounts of sulfur. The chlorine was identified by its physical properties, and its reaction with KI. The NOCl, $SOCl_2$, SO_2Cl_2, and N_2O were identified by infrared spectroscopy. In addition to the identified products, a very small amount of an unidentified red material was observed. This red solid formed in the traps as a thin film on the glass. It was insoluble in all the common organic solvents, but dissolved with decomposition in 95% ethanol. The yield of the solid was typically never more than one or two milligrams in a 90 min. run.

[†]The $SOCl_2$ used in this study came from the Chemistry Department of the University of California, Berkeley, and bore no manufacturer's label.

Evidently, little or no reaction occurs between the N atoms and the sulfur of the $SOCl_2$, even if the unidentified material contains a nitrogen-sulfur bond.

The reaction may involve an initial attack of the N atoms on the oxygen of the $SOCl_2$ to form NO. The NOCl, SO_2 and N_2O would then result from the reaction of NO with $SOCl_2$.[†]

D. Sulfur Dioxide

Liuti, et.al., recently reported[12] that when SO_2 is fed into a stream of active nitrogen, the nitrogen afterglow is extinguished and no other emitting species is formed. They indicated, however, that reaction may have taken place but failed to elaborate. We therefore included SO_2 in the series of sulfur compounds studied here.

Reaction vessel (B) was used as the reaction vessel. Addition of the SO_2 caused the nitrogen Lewis-Rayleigh afterglow to decrease, but a relatively large amount of SO_2 was required to completely extinguish it. No flame was observed, and no significant decomposition of the SO_2 occurred. A run of 61 min. at a nitrogen atom flow rate of 1.67 µmoles sec^{-1} and an SO_2 flow rate of 1.2 µmoles sec^{-1} gave no measurable products other than the unreacted SO_2. (A slight trace of white solids formed in the insert tube, but the amount was not even measurable.)

In one experiment, the amount of SO_2 required to extinguish the nitrogen afterglow was determined. An SO_2 flow rate of 120±10 µmoles sec^{-1}

[†] In a controlled experiment, unmeasured quantities of NO and $SOCl_2$ were mixed in a trap and allowed to stand at room temperature for approximately one hour. An infrared spectrum of the mixture showed NOCl, SO_2, N_2O and unreacted NO and $SOCl_2$ to be present.

was needed to extinguish the afterglow of a nitrogen stream whose nitrogen atom flow rate was 0.95 µmole sec^{-1}. (This can be roughly compared to S_2Cl_2 for example, which under the same conditions, requires only 0.04 µmole sec^{-1} to recombine all the nitrogen atoms. SO_2 must be approximately 10^3 times less efficient as a third body for the nitrogen atom recombination.) For all practical purposes, SO_2 is inert to nitrogen atom attack.

E. Hydrogen Sulfide

The reaction of N atoms with H_2S had been studied previously on two separate occasions. Strutt[10] in his early work on the reactivity of active nitrogen reported that the reaction gave a yellow deposit which he concluded was S_4N_4. He proposed the initial reaction to be:

$$N + H_2S \rightarrow NS + H_2 ; \qquad\qquad\qquad (IV-9)$$

more recently, Westburgy and Winkler[13] made a rather extensive study of the reaction and proposed a more detailed mechanism. They also reported that a large fraction of the solid which deposited was probably polymeric $(NS)_x$, the remainder being mostly sulfur. Small quantities of ammonia were obtained.

We have investigated the reaction to characterize further the products and to determine if the reaction can be used as a preparation for any specific sulfur-nitrogen compound.

Matheson's hydrogen sulfide was purified by distillation through a -130°C trap into a -196°C trap. The H_2S was then transferred to the reservoir system. The flow rate was determined by measuring the pressure change in the constant volume reservoir.

Reaction vessel (A) was used for the study; the traps were cooled

to -196°C. The reaction was accompanied by the usual blue flame.[20] The solid, which deposited on the insert tube, was nearly black in color. Yellow and white volatile substances were obtained. When the traps were warmed to room temperature, a yellow solid formed which gradually disappeared. The solid was found to decompose on slight warming to give NH_3 and H_2S and was apparently NH_4HS. A small amount of solid always remained in the traps and was identified as sulfur (the solid was insoluble in water, but dissolved in CS_2. When a drop of mercury was added to the CS_2 solution, the mercury surface became coated with a layer of black solid).[31] The infrared spectrum of a KBr pellet which had been placed in the insert tube prior to the run showed bands corresponding to S_7NH.[32] The heptasulfur imide (S_7NH) had not been previously reported as a product of the reaction.

The S_7NH could be separated from the remainder of the solid products (($NS)_x$, S_x) by chromatography.[33] The insert tube was placed in an air condenser which was mounted on a 250 ml flask containing approximately 50 ml carbon tetrachloride which had previously been dried over "drierite". The CCl_4 was then refluxed over the insert tube for 3 hours. At the end of the refluxing, the CCl_4 was light yellow in color. A small amount of sulfur remained in the insert tube. The CCl_4 solution was allowed to cool and then was poured onto a 1.6 by 20 cm cylindrical silica gel column which had previously been washed carefully with dry CCl_4. The products were eluted with CCl_4. Three distinct bands were observed. The first consisted of sulfur[†] followed closely by the S_7NH. The third was yellow in color and

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[†] The material was presumed to be sulfur. It was yellow in color and preceded the S_7NH off the column. The amount however, was very small, not more than 1 or 2 mg.

was identified by infrared spectroscopy as S_4N_4. A portion of the material remained on the column and was dark brown in color. It could be removed with acetone and was found to be S_4N_4 (identified by its infrared spectrum). The amount of each product was determined by weighing.

The ammonia was separated from the unreacted H_2S by fractional condensation. The NH_3 could be trapped at -130°C and the H_2S at -196°C. Infrared spectra of each fraction showed the absence of the other products (i.e. no NH_3 was observed in the -196°C fraction). Some H_2S may have been present in the -130°C fraction because H_2S has a low extinction coefficient and small amounts could not be detected. Any retained in the -130°C trap would come from NH_4HS formation. The yield of ammonia was determined by weighing. The results are shown in Table VIII.

S_7NH accounts for approximately 30% (by weight) of the solid produced. S_x (possibly S_8) accounts for about 34% and the $(NS)_x$ the remaining 36%. The S_7NH probably results from the reaction of the imine radical (NH) with sulfur fragments (i.e. S and S_2)(nitrogen and hydrogen atoms, both of which are present, react to form the NH^{34} which either is hydrogenated further tor form NH_3 or reacts with the sulfur to form S_7NH). Since no S_4N_4 is observed initially in the solid in the insert tube, that which is separated by chromatography must come from the $(NS)_x$.

TABLE VIII. Data for the Reaction of

N Atoms with $H_2S^\dagger$

Run #	f_N	F_{H_2S}	F_{NH_3}	F_{S_7NH}	$F_{NS}^\ddagger$
1	1.01	2.74	0.39	~ 0.01	——
2	1.00	1.08	0.11	0.012	0.081

$\dagger$ All units are μmoles sec^{-1}; f = flow rate; F = rate of formation.

$\ddagger$ Assuming conversion of NS to S_4N_4 via

$$4(NS)_x \rightarrow X\ S_4N_4$$
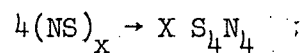
V. REACTIONS OF ACTIVE NITROGEN WITH COMPOUNDS

HAVING AN EXTERNAL SULFUR ATOM

A. Carbon Disulfide

Strutt[10] reported in 1913 that carbon disulfide (CS_2) reacted with active nitrogen to form two polymers. One was a blue solid which he concluded was $(NS)_x$; the other corresponded to $(CS)_x$ which had been observed earlier by Dewar and Jones.[35] Westburgy and Winkler[13] later studied the reaction more carefully. They found the products to be $(NS)_x$, $(CS)_x$, and sulfur and proposed a detailed mechanism for the reaction.

We have only briefly looked at the reaction and have observed essentially the same results obtained by Westburgy and Winkler.[13] Since the only nitrogen containing product was $(NS)_x$, yield determinations were not performed.

B. Carbonyl Sulfide

The reaction of active nitrogen with carbonyl sulfide (OCS) was reported by Liuti, et. al.,[12] to give NS and CO presumably via:

$$N + OCS \longrightarrow NS + CO . \qquad (V-1)$$
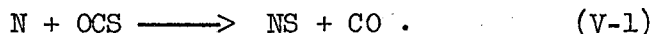
The products NS and CO were detected by mass spectrometry. We further investigated the reaction in order to determine if other sulfur-nitrogen compounds were formed. Matheson's carbonyl sulfide was distilled (in vacuo) into a trap at -130°C. It was then redistilled into the reaction vessel reservoir system.

When the OCS was fed into the nitrogen stream the blue flame replaced the nitrogen afterglow, and the blue to black $(NS)_x$ began forming on the walls of the insert tube. The only volatile products observed were unreacted OCS and a tract of CO (most of the CO would be

expected to pass through the three liquid nitrogen traps). The CO which was formed was inert to further nitrogen atom attack (no carbon-nitrogen compounds (i.e. $(CN)_2$) were observed, and the CN emission in the flame must have been either absent or extremely weak, since the flame had the usual blue color).

Several attempts were made to catalyze the dimerization of the NS produced in this reaction to S_2N_2. The only reported preparation of S_2N_2 involves the pyrolysis of S_4N_4 at 300°C.[16] Hence, an independent method of preparation would be desirable. $(NS)_x$ is also found as a product of the S_4N_4 pyrolysis. Goehring also reported[16] that the presence of silver or glass wool improved the yields of S_2N_2. Therefore, we attempted to prepare S_2N_2 from the reaction of N atoms on OCS using silver or glass wool in the reaction zone. However, no material resembling S_2N_2 was ever obtained. The silver wool was observed to turn black presumably with the formation of Ag_2S. The usual dark deposit of $(NS)_x$ was obtained.

The reaction of N atoms with OCS probably parallels the N atom - CS_2 reaction, because the two molecules (OCS, CS_2) are similar. Both were found to catalyze the N atom recombination reaction, indicating that a nitrogen atom-reactant complex is probably formed.[13] (The initial step in the N atom - CS_2 reaction is proposed to be complex formation).[13] The reactions can be represented by the mechanism:

$$N + M \rightleftharpoons [N:M]$$

$$N + [N:M] \longrightarrow N_2 + M^*$$

$$[N:M] \longrightarrow NS + (M - S)$$
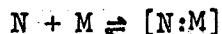
Where $M = CS_2$ or COS. (This is merely a generalization of the mechanism proposed for the N atom - CS_2 reaction).[13] The M^* (excited CS_2 or OCS)

may lead to some secondary products such as sulfur,

$$CS_2^* \longrightarrow CS + S$$
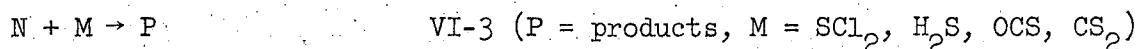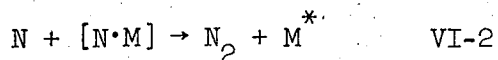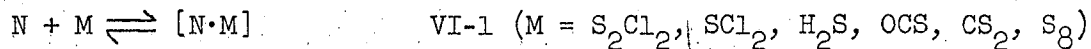
$$OCS^* \longrightarrow CO + S \ .$$
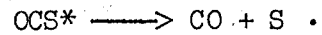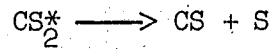
In both reactions, NS is the only sulfur nitride formed (the NS polymerizes immediately upon reaching the walls of the reaction vessel and is observed as $(NS)_x$). Since the sulfurs in both molecules are external, it is not unusual to find NS as a principal product. Other sulfur containing molecules with external sulfur atoms might also be expected to react similarly with N atoms.
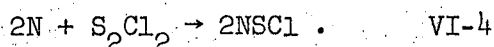
VI. GENERAL CONCLUSIONS

All of the observed reactions of active nitrogen with sulfur compounds are accompanied by a blue flame. (SO_2 is an exception, but no reaction occurs). This blue flame is probably due to S_2 or NS or both. The flames for the reactions ($N + S_2Cl_2$) and ($N + H_2S$) have been studied spectroscopically[20] and found to be due to NS ($B^2\Pi - X^2\Pi$) and S_2 ($^3\Sigma_u^- - ^3\Sigma_g^-$).

It is interesting to note the different reactivities of the sulfur compounds studies. SO_2 is essentially inert to N atom attack. Little or no reaction occurs between the N atom and the sulfur in $SOCl_2$. On the other hand, S_2Cl_2, SCl_2, H_2S, CS_2, S_8, S_2, and OCS are all observed to react with sulfur-nitrogen bond formation. Those compounds which react all contain sulfur atoms having two lone pairs of electrons. This suggests that the nitrogen atom is an electrophilic reagent. The presence of the lone pairs of electrons would aid the formation of the N atom - sulfur compound complex,[26] which apparently occurs in all the reactions (the rate at which the recombination reaction occurs requires the formation of an intermediate, see section III-C). The electrons in the N atom p-orbitals would overlap the electrons in the orbitals of the sulfur. The case of $SOCl_2$ is somewhat different, complex formation occurs, but N atom attack probably takes place at the oxygen. SO_2 apparently does not form a complex with the N atoms. The recombination reaction is catalyzed only slightly by the SO_2. The recombination is probably trimolecular with the SO_2 slightly more efficient than N_2 or the inert gases[28] because of its larger size and greater number of degrees of freedom.

A general mechanism can be formulated for N atom sulfur compound reactions (let M represent the sulfur compound).

$$N + M \rightleftharpoons [N \cdot M] \qquad VI\text{-}1 \quad (M = S_2Cl_2, SCl_2, H_2S, OCS, CS_2, S_8)$$

$$N + [N \cdot M] \rightarrow N_2 + M^* \qquad VI\text{-}2$$

$$N + M \rightarrow P \qquad VI\text{-}3 \quad (P = \text{products}, M = SCl_2, H_2S, OCS, CS_2)$$

or:

$$2N + S_2Cl_2 \rightarrow 2NSCl . \qquad VI\text{-}4$$

The excited M^* either decomposes to give by-products such as sulfur, or undergoes collisional de-excitation.

The reaction involving S_2Cl_2 is interesting in that it apparently involves 2 N atoms in the product forming step. This is possibly due to the molecules being somewhat symmetric with two identical sites for N atom attack.

None of the reactions studied appear to be useful as preparative methods. The yields are generally too small for the difficulties involved, and all the products observed have been prepared by other methods.

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APPENDICES

A. Plasma Jet Studies

Within the last few years, there has developed a strong interest in plasma jet chemistry. Three possible applications for plasma jet chemistry are the decomposition of compounds to form the elements, the formation of free radicals for use in subsequent reactions, and probably the most interesting, the formation of thermodynamically unstable compounds. For synthetic purposes, the plasma may serve as a heat source alone (e.g. when argon is the plasma gas) or as a reactant (as when nitrogen is used). Indeed, nitrogen plasmas have been used to prepare several endothermic nitrogen-containing compounds.[36]

Normally a plasma torch consists of a chamber containing a water-cooled tungsten cathode at one end and a water-cooled copper anode at the other. The copper anode also serves as an exit nozzle. The plasma gas enters the chamber near the cathode and flows rapidly between the electrodes and out the nozzle. When an arc is established between the electrodes, a flame-like discharge or "plasma jet" is formed. The plasma thus formed is essentially in the absence of an external electrical field.[37]

The production of compounds with the plasma jet depends on the temperature achieved and the quenching velocity of the compounds formed at these temperatures. Only thermodynamically unstable compounds can be prepared at the high plasma temperatures, since the chemical equilibrium must be favorable to product formation. This of course, does not mean that stable products cannot be formed. They may, but only as the temperature decreases. Furthermore, the desired equilibrium must then be frozen by rapid quenching.

Since reasonably efficient yields of cyanogen have been reported[36,39] from the reaction of carbon with a nitrogen plasma, we thought that sulfur might also react with a nitrogen plasma. Preliminary studies were therefore made to determine if large scale production of sulfur nitrides could be accomplished.

A Thermal Dynamics plasma torch capable of developing 40 KW of power was used. A Thermal Dyanmics powder feed unit was used for introducing the sulfur into the plasma. Nitrogen served as both the carrier and plasma gas.

Two quenching methods, gas and liquid, were used in the investigation. The gas quench system consisted of a steel cylindrical chamber eight inches in diameter and four feet long which was attached to the plasma torch. A water jacket allowed the entire metal surface to be cooled. A stainless steel insert (cold finger) extended coaxially through the chamber to the tip of the jet.

The liquid quench system consisted of a reservoir containing carbon tetrachloride, and a six inch supplementary nozzle which was fitted to the torch so that the flame could be introduced directly into the liquid. The carbon tetrachloride was evaporated after each run and the residue examined.
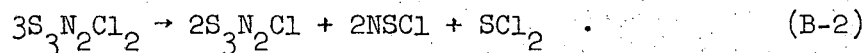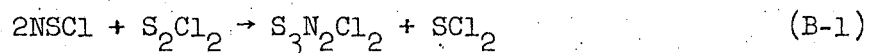
Runs were of 1-15 minutes duration. No sulfur nitrides were ever observed in either case. The solids which were removed from the insert in the air quench system were found to be sulfur. The residue left from the liquid quench runs was found to contain carbon tetrachloride pyrolysis products, principally hexachlorobenzene. Small amounts of disulfur dichloride were also observed.

It must be noted that this investigation was by no means exhaustive. The lack of evidence for sulfur nitride formation does not mean that future attempts would be fruitless.

B. The Gas Phase Reaction of NSCl with S_2Cl_2

An attempt was made to study the gas phase reaction of NSCl with S_2Cl_2 by heating a mixture of the vapors at about 85°C. It was thought that S_3N_2Cl might result from the reaction sequence:

$$2NSCl + S_2Cl_2 \rightarrow S_3N_2Cl_2 + SCl_2 \qquad\qquad (B-1)$$

$$3S_3N_2Cl_2 \rightarrow 2S_3N_2Cl + 2NSCl + SCl_2 . \qquad\qquad (B-2)$$

$S_3N_2Cl_2$ is known to decompose by reaction (B-2) at this temperature[21] and evidence already exists[23] for reaction (B-1) which takes place rapidly in the liquid state.

The reaction was tried several times in sealed tubes at temperatures varying from 65-100°C. NSCl was made by heating $(NSCl)_3$ in a high vaccum at 110°.[25] The tubes were examined after about one hour and in no case was solid formation observed. However, when the vapors were allowed to condense, solid formation occurred immediately on the vessel walls. The solid was identified as $S_3N_2Cl_2$. Infrared spectra of the volatile phase after heating always showed residual NSCl indicating that it was in excess. Thus, the gas phase reaction of NSCl and S_2Cl_2 is apparently slow.

C. The Gas Phase Reaction of NSCl With Water

The gas phase reaction of NSCl with a deficiency of water was investigated.

The NSCl was made by heating $(NSCl)_3$ to 110° in a vacuum.[25] Two experimental procedures were used. In one, the water was added to the NSCl and in the other NSCl was added to the water. The reaction appeared the same with either procedure. Immediately upon mixing, a white solid formed on the walls of the reaction vessel....

In order to identify the products, the reaction was carried out in an infrared gas cell. The spectra of the products showed them to be NH_4Cl and SO_2. Excess NSCl was also observed.

In one quantitative run, 16.7 μmoles of water was found to give 8.6 μmoles of SO_2 for a ratio of $2H_2O$ per SO_2 (amounts of H_2O and SO_2 were determined volumetrically on the vacuum line). The reaction is apparently

$$NSCl + 2H_2O \rightarrow NH_4Cl + SO_2 .$$
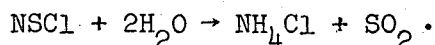
It might be noted that no evidence was found for the formation of HNSO as in the case of NSF.[22]

D.   The Reaction of Chlorine With $S_3N_2Cl_2$

It was discovered by accident that when chlorine is introduced into a vessel containing $S_3N_2Cl_2$ that $(NSCl)_3$ and NSCl are formed. The reaction was then carried out in a flow system to determine if NSCl was the primary product.

Chlorine at atmospheric pressure was passed over the solid $S_3N_2Cl_2$ and through a trap at $-78°C$. The $S_3N_2Cl_2$ became moist with a red liquid which was identified as SCl_2. The trap was removed from the system and evacuated while cooled with liquid nitrogen. It was then allowed to warm slowly and most of the chlorine was removed. A portion of the remaining material was transferred to the infrared cell and the spectrum recorded. A large amount of NSCl was observed. Furthermore, large amounts of yellow solid (presumably $(NSCl)_3$) formed in the cell and in the trap indicating that more NSCl was present than actually seen in the infrared spectrum. No effort was made to determine the exact quantity. $(NSCl)_3$ also remained in the tube where the chlorination took place. It was probably formed as a result of NSCl polymerization in the SCl_2 solution. Jolly and Maguire[21] report that quantitative conversion of $S_3N_2Cl_2$ to $(NSCl)_3$ can be obtained if care is taken to prevent the NSCl from escaping.
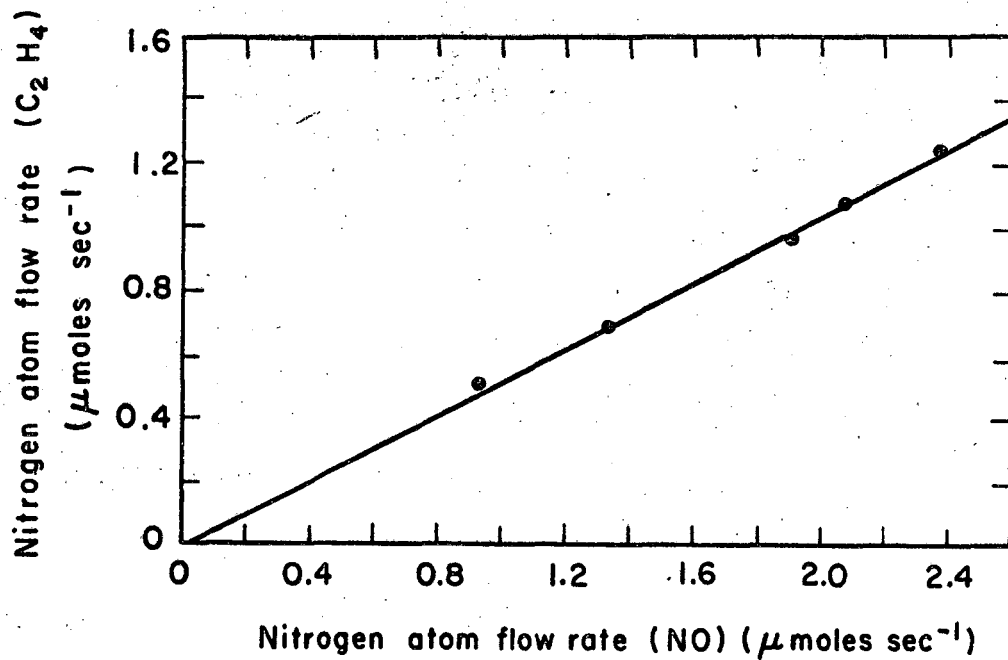
E. Determination of the Ratio $f_N(NO)/f_N(C_2H_4)$

As mentioned previously, the HCN production from the reaction of active nitrogen with ethylene, $2N + C_2H_4 \rightarrow 2HCN + H_2$, has been suggested as a more accurate means of measuring atomic nitrogen flow rates than the nitric oxide reaction.[38] Since a controversy exists, a comparison of the two methods was made on reaction vessel (A) so that the data could be interpreted in terms of either method.

The reaction vessel was assembled as in all other cases. The discharge was established and the system allowed to equilibrate for several minutes. The three traps were cooled with liquid nitrogen. The atomic nitrogen flow rate was then determined by the nitric oxide titration method. Without interrupting the discharge, the traps were warmed in order to remove the nitric oxide reaction products. They were cooled again and a continuous excess of ethylene was added to the atomic nitrogen stream for about fifteen minutes (the time necessary to get an easily measurable amount of HCN).

Upon termination of the reaction, the HCN was distilled into a bulb containing dilute aqueous KOH. The bulb was removed and shaken well. The amount of HCN produced was then determined by titration with standard silver nitrate. The active nitrogen flow rate was determined on the basis of the reaction:

$$2N + C_2H_4 \rightarrow 2HCN + H_2 \ .$$
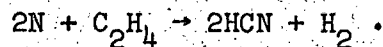
The results are shown in Table A-I. Figure A-1 shows the plot of atomic nitrogen flow rate (as calculated from the NO titration) versus the atomic nitrogen flow rate (as calculated from the ethylene reaction).

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Fig. A-1. A plot of the nitrogen atom flow rate as determined
by the ethylene reaction vs the nitrogen atom flow rate
as determined by nitric oxide titration.

The ratio $f_N(NO)/f_N(C_2H_4)$ is approximately 2; that is, the NO titration shows the atomic nitrogen flow rate to be twice as great as does the ethylene reaction. It is interesting to note that the ratio remains fairly constant over a wide range of total nitrogen flow rates and pressure as well as atomic nitrogen flow rates.

Even if the NO titration is in error, it is not invalid. Often in work of this type, a factor of 2 is unimportant, particularly when qualitative results are sought. Furthermore, in the entire series of experiments reported here, the conclusions are the same when the atomic nitrogen flow rate as determined by either method is used. The NO titration remains the simpler and easier method for determining atomic nitrogen flow rates.

TABLE A-I. A comparison of the flow rate of atomic nitrogen as determined by nitric oxide titration with that determined by HCN formation from ethylene.

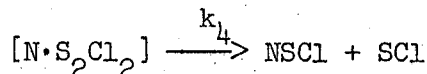| $f_{N_2}(\frac{moles}{sec} \times 10^4)$	P(mm Hg)	$f_N(NO)(\frac{\mu moles}{sec})$	$f_N(C_2H_4)(\frac{\mu moles}{sec})$	$\frac{f_N(NO)}{f_N(C_2H_4)}$
0.76	2.9	0.930	0.508	1.82
1.14	4.0	1.33	0.687	1.94
1.79	4.5	1.91	0.971	1.97
2.48	5.0	2.38	1.24	1.92
3.03	6.1	2.08	1.08	1.92

F.   Calculations of the N Atom Dependences for the N + S_2Cl_2
Reaction Mechanisms

It is not necessary to calculate exactly how the yield of NSCl will

vary as a function of nitrogen atom concentration before eliminating some

of the mechanisms of Sec. III-E. A mechanism, in order to be consistent

with the experimental results must predict the ratio of the rate of forma-

tion of NSCl to the rate of formation of N_2 to be nitrogen independent.

That is, the rate of formation of NSCl, $\frac{d(NSCl)}{dt}$, and the rate of formation

of N_2, $\frac{d(N_2)}{dt}$, must have the same dependence on nitrogen atom concentration.
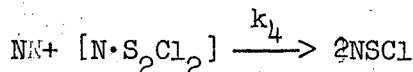
Case A. The recombination reaction and the product (NSCl) formation

reaction have a common intermediate. Two general mechanisms were proposed,

the recombination reaction:

$$N + S_2Cl_2 \underset{k_2}{\overset{k}{\rightleftharpoons}} [N \cdot S_2Cl_2]$$

$$N + [N \cdot S_2Cl_2] \xrightarrow{k_3} N_2 + S_2Cl_2^*,$$
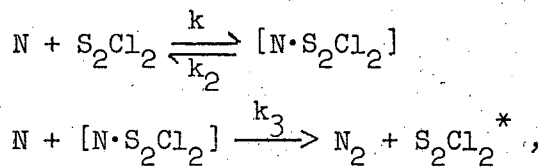
plus the NSCl formation reaction (A-1);

$$[N \cdot S_2Cl_2] \xrightarrow{k_4} NSCl + SCl$$

or the recombination reaction plus reaction (A-2):

$$N + [N \cdot S_2Cl_2] \xrightarrow{k_4} 2NSCl$$

(we have used the reaction in which 2NSCl's are formed instead of

NSCl + NS + Cl, the rate of formation of NSCl will differ by a factor of

2 because of the amount of NSCl produced, but as far as predicting the N

atom dependence, they will be the same).

Considering first, reaction (A-1) as the NSCl forming reaction,

$$\frac{d(NSCl)}{dt} = k_4([N \cdot S_2Cl_2]) \text{ and } \frac{d(N_2)}{dt} = k_3(N)([N \cdot S_2Cl_2])$$

$$[N \cdot S_2Cl_2] = \frac{k_1(N)(S_2Cl_2)}{k_2 + k_4 + k_3(N)}$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{k_4}{k_3(N)}$$

The relative rate will change with nitrogen atom concentration, and the mechanism can be ruled out.

When (A-2) is the product reaction,

$$\frac{d(NSCl)}{dt} = 2k_4(N)([N \cdot S_2Cl_2]) \text{ and } \frac{d(N_2)}{dt} = k_3(N)([N \cdot S_2Cl_2])$$

$$[N \cdot S_2Cl_2] = \frac{k_1(N)(S_2Cl_2)}{k_2 + k_4(N) + k_3(N)}$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{2k_4}{k_3} \quad ,$$

a nitrogen atom independence is predicted and the mechanism is a possibility.
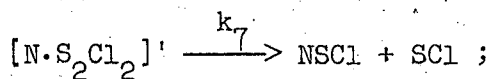
Case B. The recombination reaction and the product formation reaction have different intermediates. The recombination reaction remains the same as in Case A, and $\frac{d(N_2)}{dt}$ becomes:

$$\frac{d(N_2)}{dt} = \frac{k_3 k_1(N)^2(S_2Cl_2)}{k_2 + k_3(N)} \quad .$$

The product formation reaction is either

$$(B-1) \qquad N + S_2Cl_2 \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [N \cdot S_2Cl_2]'$$

$$[N \cdot S_2Cl_2]' \xrightarrow{k_7} NSCl + SCl \; ;$$
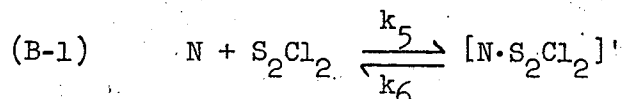
$[N \cdot S_2Cl_2]'$ = a complex different from $[N \cdot S_2Cl_2]$ in the recombination reaction. Or,

$$(B-2) \quad N + [N \cdot S_2Cl_2]' \xrightarrow{k_7} 2NSCl \text{ (or NSCl + NS + Cl)} .$$
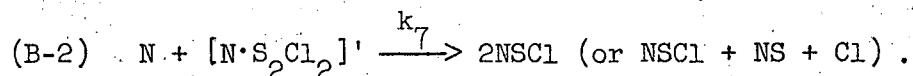
Consider (B-1) first:

$$\frac{d(NSCl)}{dt} = k_7 C'$$

$$C' = [N \cdot S_2Cl_2]' = \frac{k_5(N)(S_2Cl_2)}{k_6 + k_7}$$

$$\frac{d(NSCl)}{dt} = \frac{k_7 k_5(N)(S_2Cl_2)}{k_6 + k_7}$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{\dfrac{k_7 k_5(N)(S_2Cl_2)}{k_6 + k_7}}{\dfrac{k_3 k_1 (N)^2 (S_2Cl_2)}{k_2 + k_3(N)}}$$

Two possibilities exist,

$$\text{(a)} \quad k_2 \gg k_3(N)$$

$$\text{(b)} \quad k_2 \ll k_3(N) .$$

(a) $\quad \dfrac{d(NSCl)}{d(N_2)} = \dfrac{k_2 k_5 k_7}{k_1 k_3 (N)(k_6 + k_7)} \qquad$ Nitrogen dependent

(b) $\quad \dfrac{d(NSCl)}{d(N_2)} = \dfrac{k_5 k_7}{k_1 (k_6 + k_7)} \qquad$ Nitrogen independent

(a) can be eliminated.

(B-2)

$$\frac{d(NSCl)}{dt} = \frac{2k_7 k_5 (N)^2 (S_2 Cl_2)}{k_6 + k_7 (N)}$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{\dfrac{2k_7 k_5 (N)^2 (S_2 Cl_2)}{k_6 + k_7 (N)}}{\dfrac{k_3 k_1 (N)^2 (S_2 Cl_2)}{k_2 + k_3 (N)}} \; .$$

There are four possibilities

$$\text{(c)} \quad k_6 \gg k_7 (N), \quad k_2 \gg k_3 (N)$$

$$\text{(d)} \quad k_6 \gg k_7 (N), \quad k_2 \ll k_3 (N)$$

$$\text{(e)} \quad k_6 \ll k_7 (N), \quad k_2 \ll k_3 (N)$$

$$\text{(f)} \quad k_6 \ll k_7 (N), \quad k_2 \gg k_3 (N) \; .$$

(c) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{2k_2 k_5 k_7}{k_1 k_3 k_6}$ Nitrogen independent

(d) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{2k_5 k_7 (N)}{k_1 k_6}$ Nitrogen dependent

(e) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{2k_5}{k_1}$ Nitrogen independent

(f) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{2k_2 k_5}{k_1 k_3 (N)}$ Nitrogen dependent
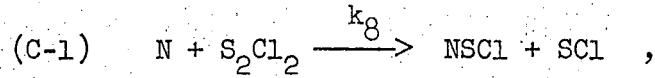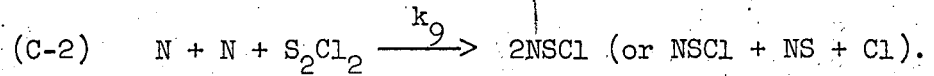
(d) and (f) can be eliminated.

Case C.

The product formation reaction involves no complex formation. The recombination reaction is the same as in Case A with

$$\frac{d(N_2)}{dt} = \frac{k_3 k_1 (N)^2 (S_2 Cl_2)}{k_2 + k_3 (N)}$$

The product formation reaction will be either

$$\text{(C-1)} \qquad N + S_2Cl_2 \xrightarrow{\ k_8\ } NSCl + SCl \quad,$$

or

$$\text{(C-2)} \qquad N + N + S_2Cl_2 \xrightarrow{\ k_9\ } 2NSCl \ (\text{or } NSCl + NS + Cl).$$

<u>(C-1)</u>

$$\frac{d(NSCl)}{dt} = k_8(N)(S_2Cl_2)$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{k_8(N)(S_2Cl_2)}{\dfrac{k_1 k_3(N)^2(S_2Cl_2)}{k_2 + k_3(N)}} \quad.$$

The two possibilities are:

$$\text{(g)} \quad k_2 \gg k_3(N)$$

$$\text{(h)} \quad k_2 \ll k_3(N) \quad.$$

For (g) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{k_2 k_8}{k_1 k_3(N)}$ \qquad\qquad Nitrogen dependent

(h) $\dfrac{d(NSCl)}{d(N_2)} = \dfrac{k_8}{k_1}$ \qquad\qquad Nitrogen independent

(g) can be eliminated.

<u>(C-2)</u>

$$\frac{d(NSCl)}{dt} = 2k_9(N)^2(S_2Cl_2)$$

$$\frac{d(NSCl)}{d(N_2)} = \frac{2k_9(N)^2(S_2Cl_2)}{\dfrac{k_1 k_3(N)^2(S_2Cl_2)}{k_2 + k_3(N)}} \quad.$$

The possibilities are

$$\text{(i)} \quad k_2 \gg k_3(N)$$

$$\text{(j)} \quad k_2 \ll k_3(N) \quad .$$

For (i)

$$\frac{d(NSCl)}{d(N_2)} = \frac{2k_2k_9}{k_1k_3} \qquad\qquad \text{Nitrogen independent}$$

$$\text{(j)} \qquad \frac{d(NSCl)}{d(N_2)} = \frac{2k_9(N)}{k_1} \qquad\qquad \text{Nitrogen dependent}$$

(j) can be eliminated.

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