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THE REACTIONS OF ATOMIC NITROGEN WITH S_2Cl_2

AND OTHER SULFUR COMPOUNDS

Jerry J. Smith and William L. Jolly

February 1965

The Reactions of Atomic Nitrogen with S_2Cl_2
and Other Sulfur Compounds

by Jerry J. Smith[1] and William L. Jolly

ABSTRACT

Atomic nitrogen reacts as an electrophilic reagent toward sulfur
compounds. Divalent sulfur compounds (H_2S, CS_2, OCS, S_8, S_2Cl_2, SCl_2)
yield sulfur-nitrogen compounds. Sulfur compounds containing sulfur
atoms with a positive formal charge (SO_2, $SOCl_2$) yield no sulfur-
nitrogen compounds. The rate law for the reaction of atomic nitrogen
with S_2Cl_2 to form NSCl is similar to that for the S_2Cl_2-catalyzed
nitrogen recombination reaction. Mechanisms are proposed for the
reactions, assuming that both reactions are second order in atomic
nitrogen and first order in S_2Cl_2.

(1) Taken from the Ph.D. thesis of J. J. Smith, University of California,
1965. (Lawrence Radiation Laboratory Report UCRL-11763)

Introduction

We have studied the reactions of active nitrogen with various sulfur compounds in the hope of finding useful synthetic methods for sulfur-nitrogen compounds. Although interesting sulfur-nitrogen compounds generally formed, the yields were disappointingly low in most cases. One exception was the reaction with S_2Cl_2 vapor, in which good yields of NSCl were formed. In order to find the optimum conditions for the synthesis and to learn something about the mechanism of this reaction, we have carried out a relatively detailed study of the reaction kinetics.

A considerable body of evidence indicates that the principal, if not the only, chemically reactive species in active nitrogen is atomic nitrogen in its ground state.[2] We have not found it necessary in the

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(2) G. G. Mannella, Chem. Revs., 63, 1 (1963).

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interpretation of our data to consider any other elemental nitrogen species. Thus hereafter we refer to the reactions of active nitrogen as those of atomic nitrogen.

Experimental

Apparatus. - The glass reaction vessel used in most of the studies is pictured in Fig. 1. High-purity nitrogen gas passed, successively, through a magnesium perchlorate drying tube, a tube containing activated copper at 400°, a trap at -78°, a flow-meter, a needle valve, and the quartz tube (g) into the reaction vessel. The flow rate of molecular

nitrogen (f_{N_2}) was always held constant at 98 μmoles/sec., and the

pressure in the reaction vessel was approximately 3 mm. A microwave

discharge was established in tube (g) either by means of a 100-watt,

2450 Mc diathermy unit (Baird-Atomic, Inc., Cambridge, Mass.) or a

Raytheon QK-60 magnetron coupled to a cylindrical cavity. The atomic

nitrogen flow rate (f_N) could be varied by varying the power of the

microwave source. f_N was usually determined before each reaction by

titration[3] with nitric oxide (which entered at inlet (c)). The sulfur

(3) G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys., 27, 1141 (1957).

compound was introduced as a vapor or gas through a greaseless needle

valve (Fisher and Porter Co., Hatboro, Penna.); the vapor or gas entered

at inlet (b). The flow-rate for compounds which are liquid at room

temperature was determined by weighing a storage bulb before and after

the runs; the flow-rate for gaseous compounds was determined by pressure-

volume measurements. Reaction occurred immediately beyond the nozzle

in the region (f). Non-volatile reaction products collected on the

insert tube (e) (18 mm. i. d. and 33 cm. long), which could be removed

to facilitate characterization of the products and cleaning. The exit

(d) was connected to a series of three liquid nitrogen-cooled U-traps,

each fitted with a pair of stopcocks and ground joints so that it could

be removed for weighing. The exit of the third trap led directly to the

vacuum pump.

The reaction of atomic nitrogen with elementary sulfur was carried

out using a special apparatus consisting of a discharge tube joined to

a vertical tube that served as a reflux column for the sulfur. The

atomic nitrogen passed through the refluxing sulfur to a series of

liquid nitrogen traps.

Reagents. - Eastman Kodak S_2Cl_2 (Practical) was fractionally con-

densed in a -45° trap followed by a -196° trap. The -45° fraction was

then distilled into a storage bulb equipped with a Delmar-Urry grease-

less stopcock (Delmar Scientific Laboratories, Inc., Maywood, Ill.).

The infrared spectrum showed the absence of impurities such as SCl_2,

$SOCl_2$ and SO_2Cl_2.

Spectroscopic grade (99.999+%) sulfur (American Refining and

Smelting) was used for the studies of the reaction of atomic nitrogen

with sulfur. Sulfur dichloride was prepared by the treatment of S_2Cl_2

with an excess of chlorine, followed by fractional condensation in a

series of traps at -63°, -112°, and -196°. The SCl_2 collected in the

-112° trap. A commercial sample of $SOCl_2$ was purified by distillation

through a -45° trap into a -78° trap. Sulfur dioxide, hydrogen sulfide,

and carbonyl sulfide were obtained from the Matheson Scientific Co.

The SO_2 was used without purification, the H_2S was distilled through a

-130° trap into a -196° trap, and the OCS was fractionally condensed in

a -130° trap followed by a -196° trap. Reagent grade carbon disulfide

was used.

Product Characterization. - NSCl was identified by the infrared

spectrum[4] of its vapor; S_2Cl_2, SCl_2, and Cl_2 were separated by fractional

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(4) O. Glemser and H. Richert, Z. anorg. allgem. Chem., 307, 313 (1961).

condensation in traps at -63°, -112° and -196°, and were identified by their vapor pressures, their chemical reactivities, and their colors. In the absence of S_2Cl_2, NSCl slowly forms the bright yellow non-volatile trimer, $S_3N_3Cl_3$. This reaction proceeds readily when the NSCl is in the liquid state at room temperature or lower. The reaction is reversed by heating to about 90° <u>in vacuo</u>. In the presence of liquid S_2Cl_2, NSCl reacts to form the yellow-brown non-volatile compound, $S_3N_2Cl_2$:[5]

(5) K. D. Maguire, J. J. Smith and W. L. Jolly, <u>Chem. Ind.</u>, 1589
     (1963); W. L. Jolly, K. D. Maguire and D. Rabinovich, <u>Inorg. Chem.</u>,
     <u>2</u>, 1304 (1963).

$$2NSCl + S_2Cl_2 \rightarrow SCl_2 + S_3N_2Cl_2 \tag{1}$$
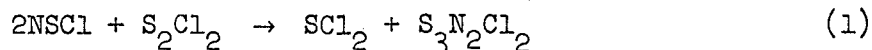
When the latter compound is heated <u>in vacuo</u>, it first darkens and then is converted to yellow S_4N_3Cl.[5] Yields of NSCl were measured by allowing the material to stand in tared traps containing excess S_2Cl_2 for at least one hour at room temperature. After pumping out the remaining volatile material, the $S_3N_2Cl_2$ was weighed, and the corresponding amount of NSCl calculated on the basis of equation 1.

Volatile products that formed in the reactions of atomic nitrogen with other sulfur compounds were separated, when possible, by fractional condensation, and were identified by their infrared spectra. In the case of S_4N_2 (which formed in the $N + S_8$ reaction), identification was based on its dark red color, its low volatility at room temperature,

its iodine-like odor, and its spontaneous decomposition to solids at room temperature.[6]

(6) M. Becke-Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen", Akademie Verlag, Berlin, 1957.

Solid materials which collected in the insert tube and, in some cases, in the traps were generally identified by their infrared spectra. Polymeric sulfur nitride, $(SN)_x$, was identified by its dark blue color and its conversion to S_4N_4 by hot solvents. Sulfur was identified by the blackening of mercury by a solution of the material in carbon disulfide.[7] Sulfur, S_4N_4 and S_7NH were chromatographically separated

(7) F. Feigl, "Spot Tests in Inorganic Analysis", 5th ed., Elsenier Publ. Co., New York, 1958, p. 374.

from one another on a silica gel column.[8] Ammonium bisulfide was

(8) M. Villena-Blanco and W. Jolly, J. Chromatog., 16, 214 (1964).

separated into NH_3 and H_2S by fractional condensation in traps at $-130°$ (NH_3) and $-196°(H_2S)$.

Results

The reaction of sulfur compounds with atomic nitrogen was always

accompanied by a blue flame, due principally to emission from excited

S_2 molecules.[9] Hydrogen sulfide reacted with atomic nitrogen to form

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(9) J. J. Smith and B. Meyer, J. Mol. Spectr., 14, 160(1964).

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$(NS)_x$, H_2, NH_3, S_7NH, and sulfur. These same products, except for

S_7NH, were observed by Westburgy and Winkler.[10] A run in which the flow-

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(10) R. A. Westburgy and C. A. Winkler, Can. J. Chem., 38, 334 (1960).

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rates of atomic nitrogen and H_2S were each about 1.0 µmole/sec. produced

NH_3 at 0.11 µmole/sec., S_7NH at 0.012 µmole/sec., $(NS)_x$ (calcd. as NS)

at 0.081 µmole/sec., and S_x (calcd. as S_8) at 0.01 µmole/sec. Brief

studies of the reactions of carbon disulfide and carbonyl sulfide with

atomic nitrogen indicated, in agreement with previous studies,[10,11] that

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(11) G. Liuti, S. Dondes and P. Harteck, Paper no. 103, presented before

the Division of Physical Chemistry at the 145th National A.C.S.

Meeting, New York, N. Y., September, 1963.

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$(NS)_x$ is the only nitrogen-containing product of these reactions. The

reaction of atomic nitrogen with elementary sulfur yielded S_4N_2, S_4N_4,

and $(NS)_x$.[12] In one run with an atomic nitrogen flow-rate of 1-2

(12) This result is consistent with the findings of Moldenhauer and Zimmerman[13] and Bett and Winkler.[14]

(13) W. Moldenhauer and A. Zimmerman, Chem. Ber., 62, 2390 (1929).

(14) J. A. S. Bett and C. A. Winkler, Paper no. 104, presented before the Division of Physical Chemistry at the 145th National Meeting of the A. C. S., New York, September, 1963.

μmoles/sec., S_4N_2 was produced at the rate of 0.22 μmol/sec.

The principal product of the reaction of S_2Cl_2 with atomic nitrogen was NSCl, which was generally quantitatively converted to $S_3N_2Cl_2$ according to reaction 1. Sulfur, along with traces of S_4N_4 and $(NS)_x$, formed in the insert tube; SCl_2 and Cl_2 collected in the cold traps with the NSCl. Quantitative yield data for two runs are presented in Table I. It will be noted that, in each run, the total sulfur recovered (in the form of S_2Cl_2, SCl_2, NSCl, and S_x) agrees with that introduced (in the form of S_2Cl_2) with an error of only 6%. Thus we have confidence in our methods of analysis and in the fact that no significant amounts of sulfur compounds were lost in the runs. More detailed data on this reaction are presented in the following sections.

In the reaction of SCl_2 with atomic nitrogen, NSCl and Cl_2 were the only products observed. It was found that large amounts of chlorine, due to disproportionation of the SCl_2, were introduced along with the SCl_2. However, quantitative yield data for several runs indicated

Table I.

Data for Two Runs of $N + S_2Cl_2$

(Flow rates in μmoles/sec. and quantities in mmoles)

f_N	0.9	1.02
$f_{S_2Cl_2}$	0.068	0.11
S_2Cl_2 introduced	0.69	0.93
S_2Cl_2 recovered	0.05	0.06
$S_3N_2Cl_2$ formed	.20	.255
NSCl equiv. to $S_3N_2Cl_2$ formed	(0.40)	(0.51)
SCl_2 formed	0.19	0.21
Cl_2 formed	0.17	0.32
Sulfur (as S) formed	0.41	0.88
$\frac{1}{2}$(total S recovered)	0.65	0.99

the following principal net reaction:

$$N + SCl_2 \rightarrow NSCl + \tfrac{1}{2}Cl_2 \tag{2}$$

In three runs with atomic nitrogen flow rates around 1.0 μmoles/sec., NSCl was formed at the rates 0.037, 0.045 and 0.23 μmole/sec., corresponding to SCl_2 flow rates of 0.075, 0.075 and 1.28 μmole/sec., respectively.

Thionyl chloride reacted with atomic nitrogen to give NOCl, N_2O, SO_2Cl_2, Cl_2, small amounts of sulfur, and a trace of an unidentified red solid. No sulfur-nitrogen compound was identified among the products. In agreement with Liuti et al,[11] SO_2 was found to be inert toward atomic nitrogen. An SO_2 flow rate of 120 μmoles/sec. was required to extinguish the afterglow in a 0.95 μmole/sec. stream of atomic nitrogen.

Effect of S_2Cl_2 Flow Rate on NSCl Production. - The dependence of the rate of formation of NSCl (F_{NSCl}) on the S_2Cl_2 flow rate ($f_{S_2Cl_2}$) was determined while keeping the molecular and atomic nitrogen flow rates constant. The flow rates of nitrogen atoms and S_2Cl_2 were each less than 1% of the molecular nitrogen flow rate. A plot of F_{NSCl} against $f_{S_2Cl_2}$ is shown in Fig. 2. At low S_2Cl_2 flow rates, F_{NSCl} increases linearly with $f_{S_2Cl_2}$. However when F_{NSCl} reaches the value $f_N/25$, a leveling-off occurs. With very low S_2Cl_2 flow rates, the yellow nitrogen afterglow (indicative of excess nitrogen atoms) was observed. The afterglow decreased in intensity as the S_2Cl_2 flow rate increased, and was completely replaced by a blue flame when the plateau region was reached. The apparent flame length was 2 cm. when f_{N_2}, f_N and $f_{S_2Cl_2}$ were approximately 100, 1 and 0.1 μmoles/sec., respectively. The sides of the

flame touched the walls of the glass insert tube. In order to check the possibility of the reaction being surface-controlled, several runs were made using a reaction vessel of larger diameter, with the atomic nitrogen entering through the central nozzle and the S_2Cl_2 entering through the main tube. With this apparatus, the flame did not touch the glass walls, and yet very appreciable yields of NSCl were obtained. For example, $F_{NSCl} = 0.10$ μmole/sec. when $f_N = 1.5$ μmole/sec. and $f_{S_2Cl_2} = 0.30$ μmole/sec.

Effect of Atomic Nitrogen Flow Rate on NSCl Production. - The dependence of F_{NSCl} on f_N was determined while keeping f_{N_2} constant and while using S_2Cl_2 flow rates large enough ($f_{S_2Cl_2} > 0.1$ μmole/sec.) to ensure operation in the plateau region. A plot of F_{NSCl} against f_N is shown in Fig. 3. Within experimental error, a linear dependence of F_{NSCl} on f_N is observed.

Effect of Temperature on NSCl Production. - The inlet tubes for the atomic nitrogen and the S_2Cl_2 were wrapped with heating tape, and part of the main reaction tube was insulated with asbestos. Several runs (for which $f_N = 0.9$ μmole/sec.) were carried out at various temperatures; the data are presented in Table II. Considerable decomposition of the S_2Cl_2 vapor (evidenced by sulfur deposition) occurred above 180°. Therefore, the two runs carried out at 320° may not be significant because of the probable introduction of SCl_2 along with the S_2Cl_2. It is clear, however, that the fraction of the atomic nitrogen converted to NSCl increased with increasing temperature.

Table II.

Data for the N + S_2Cl_2 Reaction
at Elevated Temperatures

Temp. °C	$f_{S_2Cl_2}$ (μmole/sec.)	F_{NSCl} (μmole/sec.)
30	0.19	0.037
100	0.37	0.073
120	0.33	0.077
320	0.24	0.088
320	1.29	0.135

Discussion

Reactivity of Sulfur Compounds. - Of the eight sulfur compounds
whose reactivity with atomic nitrogen we studied, only thionyl chloride
and sulfur dioxide did not react to give a sulfur-nitrogen compound.
We believe that in the reactions which yielded sulfur-nitrogen compounds,
the nitrogen atoms attacked the sulfur atoms in the sulfur compounds;
presumably no such attack occurred in the cases of $SOCl_2$[15] and SO_2.

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(15) The products which formed in the case of $SOCl_2$ can be explained in
      terms of attack at the oxygen atom to form NO. NO and $SOCl_2$ were
      observed to react to form NOCl, SO_2, and N_2O.

It is significant that the sulfur atoms in the latter compounds differ
from those in the other sulfur compounds in that they have only one lone
pair of electrons and consequently have positive formal charges. It
appears that atomic nitrogen reacts as an electrophilic reagent which
favors attack at polarizable donor atoms. This behavior of atomic nitro-
gen closely parallels that of the "soft" atoms O, Cl, Br and I, which
have been observed to react most readily with polarizable nucleophiles.[16]

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(16) R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).

Liuti et al[11] observed that SO_3 is inert toward atomic nitrogen;
this result is consistent with the idea that atomic nitrogen is unreactive
toward sulfur atoms with positive formal charges. However, these same
investigators reported that atomic nitrogen reacts with S_2O to form

only S_2 and NO. The only rationalization we can offer for the latter

result is that the alternative products, NS and SO, are thermodynamically

unstable with respect to the observed products.

Mechanism of the N + S_2Cl_2 Reaction. - The interpretation of the

kinetic data depends on the nature of the flow in the reaction vessel.

We shall assume, as others[17] have, that instantaneous mixing occurred

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(17) W. Forst, H. G. V. Evans and C. A. Winkler, J. Phys. Chem., 61,

320 (1957).

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at the nozzle and that the reaction mixture flowed uniformly down the

tube. We assume that the concentration of a reactant at any point was

proportional to the flow rate of that reactant at the nozzle. The

assumption of instantaneous mixing is not completely valid; some

diffusional mixing undoubtedly took place downstream of the nozzle.

However, even if the reaction flame had been completely diffusion-

controlled, it seems probable that the reactant concentrations in the

zones of fastest reaction would have been approximately proportional to

the flow rates of the reactants at the nozzle.

Atomic nitrogen which is fed into a stream of S_2Cl_2 vapor reacts in

only two ways: it undergoes recombination to form N_2, using molecular

S_2Cl_2 as a third body, and it reacts with S_2Cl_2 to form NSCl. Figure 2

corresponds to a "titration" curve for these reactions. In the sloping

portion of the curve, atomic nitrogen was in excess; in the plateau

region, S_2Cl_2 was in excess. Both reagents were essentially completely

consumed at the equivalence point (the onset of the plateau). From the

height of the plateau, it is clear that the rate of disappearance of

N atoms by recombination is about 25 times that by the NSCl-producing

reaction. The fact that the ratio of the rates of the reactions

under conditions of excess S_2Cl_2 is independent of the S_2Cl_2 flow rate

indicates that both reaction rates have the same dependence on S_2Cl_2

concentration. Third-body-catalyzed nitrogen recombination reactions

have always been found to be first order in the third body;[18] therefore,

(18) J. T. Herron, J. L. Franklin, P. Brandt and V. H. Dibeler,

J. Chem. Phys., 30, 879 (1958).

we assume that both reactions are first order in S_2Cl_2. The fact that

F_{NSCl} is proportional to f_N indicates that the rates of the recombination

reaction and the NSCl-producing reaction have the same dependence on

atomic nitrogen concentration. Recombination reactions have always been

found to be second order in the recombining species;[19] therefore, we

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", 2nd ed.,

Wiley and Sons, New York, 1961, pp. 108-109.

assume that both reactions are second order in atomic nitrogen.

It is possible to estimate an effective third-order rate constant

for the recombination reaction from flow data in the plateau region and

the apparent length of the reaction flame. By assuming that the apparent

tail of the flame corresponds to only 90% consumption of the N atoms,

that instantaneous mixing occurred at the nozzle, and that the S_2Cl_2

concentration was constant throughout the flame, we have estimated a rate constant of approximately 10^{15} ℓ^2 mole^{-2}sec^{-1}. (Errors caused by non-validity of the assumptions are such as to cause the estimated rate constant to be too small.). This estimated value is much greater than the value 10^9 - 10^{10} ℓ^2 mole^{-2} sec^{-1} predicted by kinetic theory for a normal termolecular reaction.[20] In order to explain the high estimated

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(20) Ref. 19, p. 75.

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rate constant, it is necessary to assume the formation of an intermediate, $N \cdot S_2Cl_2$. The mechanism for the recombination is then

$$N + S_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} N \cdot S_2Cl_2 \tag{3}$$

$$N + N \cdot S_2Cl_2 \xrightarrow{k_3} N_2 + S_2Cl_2^* \tag{4}$$
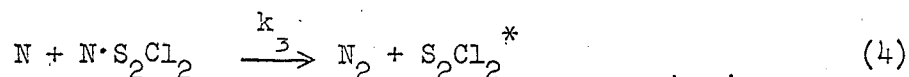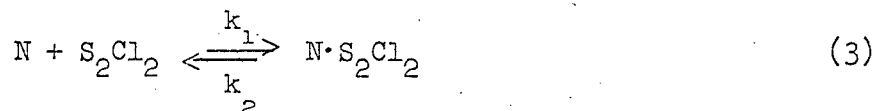
The rate of formation of N_2 is

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

It can be shown that the estimated effective third order rate constant is consistent with our assumption that the rate is second order in atomic nitrogen (i.e., $k_2 \gg k_3(N)$). If we assume $k_1 \approx k_3 = 10^{11}$ $\ell \cdot$ mole^{-1} sec^{-1} (a typical value for a bimolecular recombination reaction[20]), then $k_2 = 10^{11} \cdot 10^{11}/10^{15} = 10^7$ sec^{-1}. Typically, the initial concentration of atomic nitrogen was about 10^{-6} $\underline{M}$; hence $k_3(N) \approx 10^{11} \cdot 10^{-6} = 10^5$. Thus the condition $k_2 \gg k_3 (N)$ was probably satisfied.

The following mechanism for the formation of NSCl is consistent with the data.

$$N + S_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N \cdot S_2Cl_2 \qquad (3)$$

$$N + N \cdot S_2Cl_2 \overset{k_4}{\longrightarrow} 2NSCl \qquad (5)$$
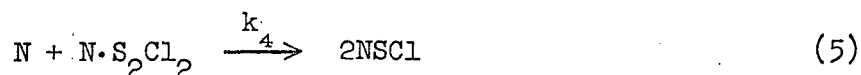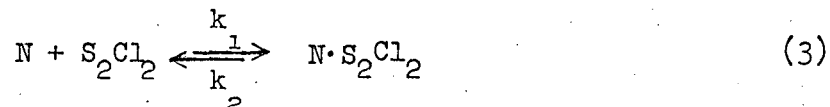
The sulfur and chlorine which are observed by-products of the reaction can be accounted for by assuming that a small fraction of the excited $S_2Cl_2^*$ molecules from the N-atom recombination decomposes as follows:

$$S_2Cl_2^* \longrightarrow S_2 + Cl_2$$
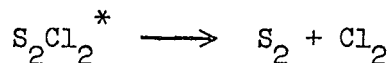
As an alternative to reaction 5, we might write

$$N + N \cdot S_2Cl_2 \longrightarrow NSCl + NS + Cl \qquad (6)$$
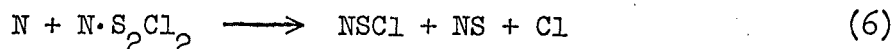
In order to account for the formation of sulfur and the lack of appreciable $(NS)_x$ formation, we would then have to assume that NS was consumed as follows:

$$N + NS \longrightarrow N_2 + S \qquad (7)$$

However, the fact that good yields of $(NS)_x$ were obtained in the reactions of atomic nitrogen with H_2S, CS_2, OCS and S_8 argues against this alternative.

The only bond which must be even partially broken in forming the activated complex of the recombination reaction is the weak bond between the nitrogen atom and the S_2Cl_2 molecule in the $N \cdot S_2Cl_2$ intermediate. On the other hand, partial cleavage of the relatively strong S-S bond in

S_2Cl_2 occurs in forming the activated complex of the NSCl-producing reaction. Thus one predicts the activation energy for the recombination reaction to be less than that for the NSCl-producing reaction. This prediction is in accord with the fact that the yield of NSCl, based on atomic nitrogen, was found to increase with increasing temperature.
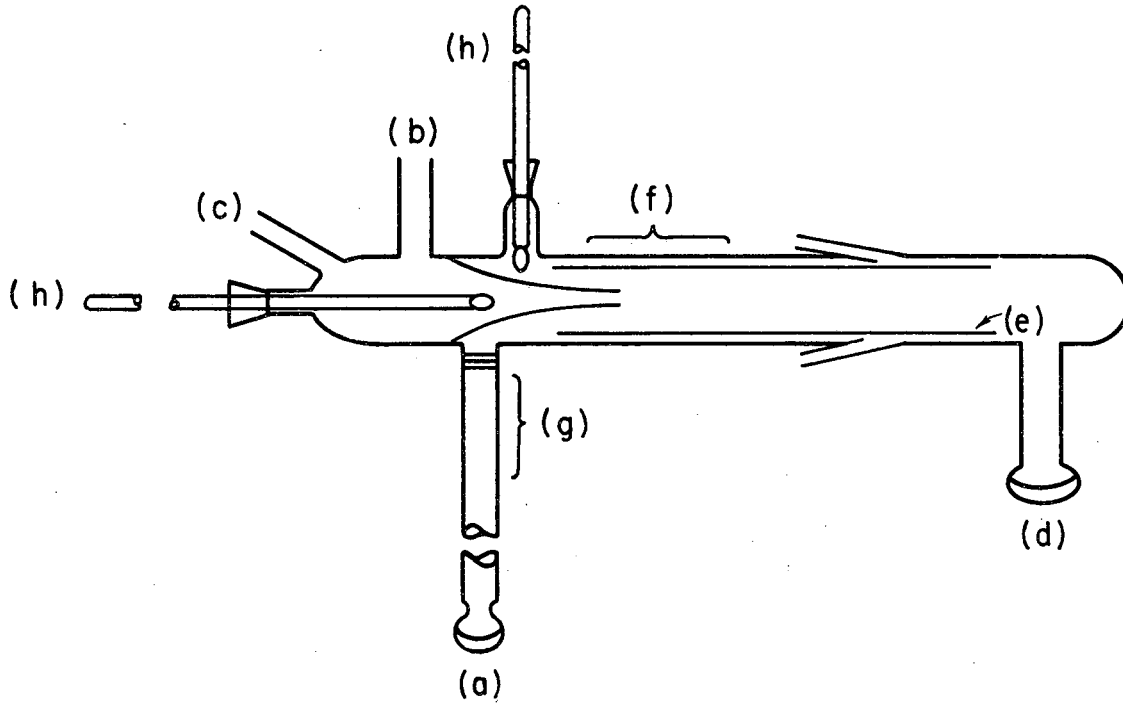
Figure Captions

Figure 1. - Apparatus for the reaction of atomic nitrogen with sulfur

compounds. (a) nitrogen inlet; (b) sulfur compound

vapor inlet; (c) NO inlet; (d) exit to traps; (e) insert

tube; (f) reaction zone; (g) discharge zone; (h) thermo-

meters.

Figure 2. - The rate of formation of NSCl as a function of the S_2Cl_2

flow rate. Flow rate of atomic nitrogen = 0.9 μmole/sec.

Figure 3. -· The rate of formation of NSCl as a function of the nitrogen

atom flow rate. Flow rate of S_2Cl_2 > 0.1 μmole/sec.

Fig. 1

MU-34899

Fig. 2

Fig. 3