pound, 2,6- and 3,5-dinitroaniline, and *o*-, *p*-, and *m*-nitroaniline do not ionize in liquid ammonia but can do so in the presence of a strong base.

Acknowledgment.—We gratefully acknowledge the support of the National Science Foundation in the form of a grant (NSF G-15734).

Contribution from the Department of Chemistry of the
University of California and the Inorganic Materials Research Division
of the Lawrence Radiation Laboratory, Berkeley, California 94720

The Reactions of Atomic Nitrogen with S_2Cl_2 and Other Sulfur Compounds

By JERRY J. SMITH[1] and WILLIAM L. JOLLY

Received February 1, 1965

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 latter reactions, assuming that both reactions are first order in S_2Cl_2.

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 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 Figure 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-Aromic, 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. The flow rate f_N was usually determined before each reaction by titration[3] with nitric oxide (which entered at inlet c). The sulfur compound was introduced as a vapor or gas through a greaseless needle valve (Fisher and Porter Co., Hatboro, Pa.); 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. Nonvolatile 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 condensed in a −45° trap followed by a −196° trap. The −45° fraction was then distilled into a storage bulb equipped with a Delmar–Urry greaseless 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.—The species NSCl was identified by the infrared spectrum[4] of its vapor; S_2Cl_2, SCl_2, and Cl_2 were separated by fractional condensation in traps at −63, −112,

---

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

[2] G. G. Mannella, *Chem. Rev.*, **63**, 1 (1963).

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

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

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 nonvolatile 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° *in vacuo*. In the presence of liquid S_2Cl_2, NSCl reacts to form the yellow-brown nonvolatile compound, $S_3N_2Cl_2$.[5]

$$2NSCl + S_2Cl_2 \longrightarrow SCl_2 + S_3N_2Cl_2 \qquad (1)$$

When the latter compound is heated *in vacuo*, 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 1 hr. 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 eq. 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]

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 from one another on a silica gel column.[8] Ammonium bisulfide was 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 $(NS)_x$, H_2, NH_3, S_7NH, and sulfur. These same products, except for S_7NH, were observed by Westbury and Winkler.[10] A run in which the flow 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 $(NS)_x$ 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 μmoles/sec., S_4N_2 was produced at the rate of 0.22 μmole/sec.

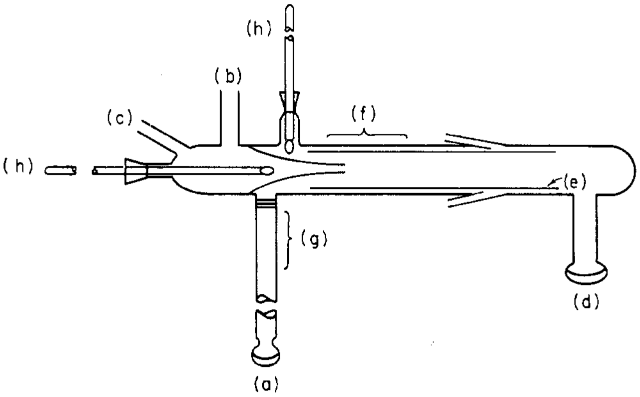

Figure 1.—Apparatus for the reaction of atomic nitrogen with sulfur compounds: (a) nitrogen inlet; (b) sulfur compound vapor inlet; (c) NO inlet; (d) exit to traps; (e) insert tube; (f) reaction zone; (g) discharge zone; (h) thermometers.

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.

TABLE I

DATA FOR TWO RUNS OF N + S_2Cl_2 AT ROOM TEMPERATURE[a]

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	0.20	0.255
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
$^1/_2$(total S recovered)	0.65	0.99

[a] f_N and $f_{S_2Cl_2}$ refer to flow rates in μmoles/sec.; other quantities are given as mmoles.

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 the principal net reaction

$$N + SCl_2 \longrightarrow NSCl + {}^1/_2Cl_2 \qquad (2)$$

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

---

(5) K. D. Maguire, J. J. Smith, and W. L. Jolly, *Chem. Ind.* (London), 1589 (1963); W. L. Jolly, K. D. Maguire, and D. Rabinovich, *Inorg. Chem.*, **2**, 1304 (1963).

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

(7) F. Feigl, "Spot Tests in Inorganic Analysis," 5th Ed., Elsevier Publishing Co., New York, N. Y., 1958, p. 374.

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

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

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

(11) G. Liuti, S. Dondes, and P. Harteck, Paper No. 103, presented before the Division of Physical Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

(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 American Chemical Society, New York, N. Y., Sept. 1963.

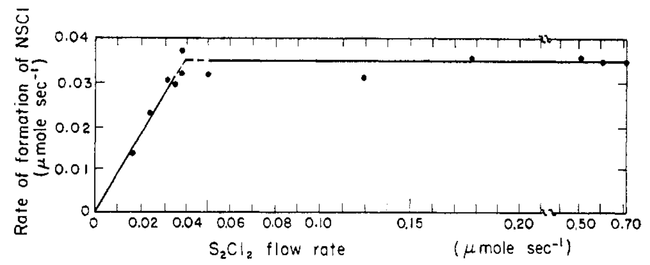

Figure 2.—The rate of formation of NSCl as a function of the S_2Cl_2 flow rate; flow rate of atomic nitrogen = 0.9 μmole/sec.

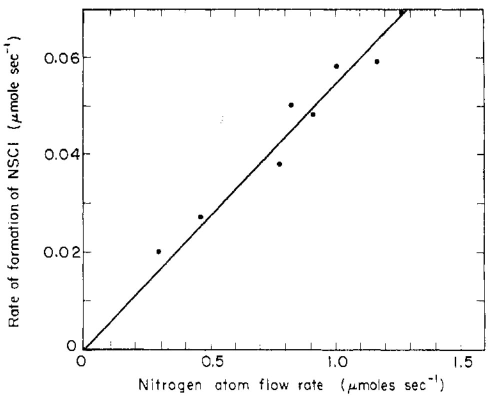

Figure 3.—The rate of formation of NSCl as a function of the nitrogen atom flow rate; flow rate of $S_2Cl_2 > 0.1$ μmole/sec.

rates of 0.075, 0.075, and 1.28 μmoles/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 Figure 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 $f_N = 1.5$ μmoles/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 Figure 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.	$f_{S_2Cl_2}$[a]	F_{NSCl}[b]
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

[a] Flow rate of S_2Cl_2 in μmoles/sec. [b] Rate of formation of NSCl in μmoles/sec.

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. 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 nitrogen closely parallels that of the "soft" atoms O, Cl, Br, and I, which have been observed to react most readily with polarizable nucleophiles.[16]

Liuti, *et al.*,[11] observed that SO_3 is inert toward

---

(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.

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

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 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, 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 almost always been found to be second order in the recombining species.[19] However, although we believe it is reasonable to assume that both reactions are second order in atomic nitrogen, this assumption is not required by the mechanisms which we shall propose.

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

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

$$N + N \cdot S_2Cl_2 \xrightarrow{k_3} N_2 + S_2Cl_2^* \qquad (4)$$

The rate of formation of N_2 is

$$\frac{d(N_2)}{dt} = \frac{k_1k_3(N)^2(S_2Cl_2)}{k_2 + k_3(N)}$$

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

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

$$N + S_2Cl_2 \rightleftarrows N \cdot S_2Cl_2 \qquad (3)$$

$$N + N \cdot S_2Cl_2 \longrightarrow 2NSCl \qquad (5)$$

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.

$$S_2Cl_2^* \longrightarrow S_2 + Cl_2 \qquad (6)$$

As an alternative mechanism, we may assume that the nitrogen recombination reaction is sometimes accompanied by cleavage of the S_2Cl_2 molecule and that the SCl fragments can react with atomic nitrogen to form NSCl or can react with themselves to form S_2 and Cl_2.

$$N + S_2Cl_2 \rightleftarrows N \cdot S_2Cl_2 \qquad (3)$$

$$N + N \cdot S_2Cl_2 \longrightarrow N_2 + 2SCl \qquad (7)$$

$$N + SCl \longrightarrow NSCl \qquad (8)$$

$$2SCl \longrightarrow S_2 + Cl_2 \qquad (9)$$

The present data do not permit us to choose between these mechanisms.

If we assume that the slow step in both the recom-

---

[17] W. Forst, H. G. V. Evans, and C. A. Winkler, *J. Phys. Chem.*, **61**, 320 (1957).

[18] J. T. Herron, J. L. Franklin, P. Brandt, and V. H. Dibeler, *J. Chem. Phys.*, **30**, 879 (1959).

[19] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd Ed., John Wiley and Sons, New York, N. Y., 1961, pp. 108, 109.

[20] Reference 19, p. 75.

bination and NSCl-producing reactions is the reaction of atomic nitrogen with $N \cdot S_2Cl_2$, then we predict 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.

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Preparation and Properties of Bis(trifluoromethylsulfuryl) Peroxide and Trifluoromethyl Trifluoromethanesulfonate

BY RONALD E. NOFTLE AND GEORGE H. CADY

Received March 4, 1965

Electrolysis of trifluoromethanesulfonic acid at −23° yields the unstable compound bis(trifluoromethylsulfuryl) peroxide, which decomposes explosively to perfluoroethane, sulfur trioxide, and the ester, trifluoromethyl trifluoromethanesulfonate.

The synthesis of peroxydisulfuryl difluoride, $S_2O_6F_2$, by electrolysis of fluorosulfuric acid[1] suggests that other new peroxides may be prepared by electrolysis of their corresponding strong acids. This suggestion was confirmed while this work was in progress by a report of the electrolytic preparation of dimethanesulfonyl peroxide, $(CH_3SO_3)_2$, from CH_3SO_3H.[2] When trifluoromethanesulfonic acid, CF_3SO_3H, was electrolyzed under high vacuum at about −23° in a cell similar to that described by Dudley,[1] the products obtained at the anode included bis(trifluoromethylsulfuryl) peroxide, $CF_3SO_2OOSO_2CF_3$. As a cold sample of this liquid compound was allowed to warm up, it decomposed suddenly[3] and with evolution of heat when its temperature reached about 10°. The products formed were perfluoroethane, sulfur trioxide, and the new ester, trifluoromethyl trifluoromethanesulfonate, $CF_3SO_3CF_3$. Although esters of trifluoromethanesulfonic acid containing hydrocarbon[4-6] and polyfluorohydrocarbon[7] groups have been reported, this ester appears to be the first instance of a perfluorocarbon trifluoromethanesulfonate. Trifluoromethyl trifluoromethanesulfonate is resistant to hydrolysis by water but does hydrolyze at 100° in 0.1 *N* sodium hydroxide.

The products observed from the decomposition of $(CF_3SO_3)_2$ can be explained on the basis of the following hypothetical mechanism

$$CF_3SO_3SO_3CF_3 \longrightarrow 2CF_3SO_3\cdot$$

$$CF_3SO_3\cdot \longrightarrow CF_3\cdot + SO_3$$

$$CF_3SO_3\cdot + CF_3\cdot \longrightarrow CF_3SO_3CF_3$$

$$2CF_3\cdot \longrightarrow C_2F_6$$

Experimental

Materials.—Trifluoromethanesulfonic acid was prepared by distillation from a mixture of barium trifluoromethanesulfonate[8] and concentrated sulfuric acid.[9] The product was redistilled and the fraction boiling near 56° under 15 mm. pressure was used.

Electrolysis.—The electrolysis cell employed for this work was similar in design to Dudley's cell C.[1] It was a small glass cell which could be cooled in a dewar vessel and operated under vacuum with separate collection of gaseous or volatile products from the anode and cathode. The cathode was a 1-cm. square piece of platinum foil, and the anode consisted of two 26 gauge platinum wires of 3 cm. length wound about each other. Since the conductivity of the pure trifluoromethanesulfonic acid was very low, a 0.1 *m* solution of sodium trifluoromethanesulfonate in trifluoromethanesulfonic acid was used. This was prepared by adding 0.202 g. of dry sodium chloride and 33.1 g. of trifluoromethanesulfonic acid to the cell, care being taken to exclude moisture from the system. The hydrogen chloride produced was pumped away. The cell was held at about −23° (to minimize transfer of the acid under vacuum) by a carbon tetrachloride slush bath, and the traps for collecting products were held at the boiling point of oxygen. When 36 volts was applied to the cell, a current of 0.014 amp. passed. A copper coulometer was used to measure the total charge passed.

While the cell was operating, a noncondensable gas was evolved at the cathode, and mass spectral analysis showed it to be hydrogen. No oxygen could be detected as a product at the anode. After about 10 hr. of steady operation, a blue color, also observed by Dudley, developed in the liquid occupying the cathode compartment of the cell. The liquid in the anode compartment remained colorless. In some runs the material in the anode trap was allowed to warm to room temperature while transferring the vapor to another trap at −183°. When the mixture of materials including trifluoromethanesulfonic acid approached about 10°, a sudden evolution of gas and heat was observed. The volatile products were separated by fractional codistillation[10] and each cut was analyzed by infrared spectroscopy.

The products were C_2F_6, $(CF_3)_2SO_3$, SO_3, and small amounts

---

[1] F. B. Dudley, *J. Chem. Soc.*, 3407 (1963).

[2] R. N. Haszeldine, R. B. Heslop, and J. W. Lethbridge, *ibid.*, 4901 (1964).

[3] Although the authors experienced no violent or destructive explosions due to the decomposition of $(CF_3SO_3)_2$ during the course of this work (possibly due to the fact that only small samples were prepared), larger samples might be expected to explode with considerable force, and caution should be exercised when working with this material.

[4] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

[5] T. J. Brice and P. W. Trott, U. S. Patent 2,732,398 (1956).

[6] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

[7] J. Burdon, *Tetrahedron*, 1 (1965).

[8] Gift from the Minnesota Mining and Manufacturing Co.

[9] J. M. Kidd and R. N. Haszeldine, *J. Chem. Soc.*, 4228 (1956).

[10] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).