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Liquid Ammonia Solution. I. Absorption Spectrophotometry

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The spectra of *o*- and *p*-nitroaniline; 2,4-, 3,5-, and 2,6-dinitroaniline; and *o*-, *m*-, and *p*-nitroacetanilide have been determined in pure liquid ammonia and in liquid ammonia solutions containing excess acid or base. The nature of the equilibria established and the species present in liquid ammonia solutions of these potential indicator acids are discussed with respect to spectral and potentiometric titration data. The relative degree of ionization of these compounds is suggested to be 2,4-dinitroaniline > *o*-nitroacetanilide $\simeq$ *p*-nitroacetanilide > *m*-nitroacetanilide; the latter and the remaining nitroanilines studied ionize only in the presence of a strong base. Equipment which permits the determination of absorption spectra of liquid ammonia solutions as a function of dilution is described.

Introduction

The use of liquid ammonia as a reaction medium has been studied extensively since the pioneer work of Franklin and Kraus[1]; however, the quantitative aspects of the equilibria which can be established in this solvent and the nature of the species involved have been neglected until recently. Kraus[2] and his associates have shown that electrolytes are not completely dissociated in liquid ammonia even though these compounds may be completely ionized. Thus, the dissolution of either HCl or NaCl in liquid ammonia produces solutions which exhibit conductivity curves that are typical of weak electrolytes in water. If the analytical concentration of an ionic solute is 10^{-3} M or less the predominating species in liquid ammonia solutions are the free ions and simple ion pairs; at higher concentrations more complex ion aggregates are important.[2] Ion association would be expected to occur also in liquid ammonia solutions containing incompletely ionized solutes; thus, the species present in dilute solutions of the weakly ionized acid HX are related by eq. 1 and 2, where NH_4^+,X^- represents an ion pair. The

$$HX + NH_3 \overset{K_1}{\rightleftharpoons} NH_4^+,X^- \qquad (1)$$

$$NH_4^+,X^- \overset{K_2}{\rightleftharpoons} NH_4^+ + X^- \qquad (2)$$

equilibrium defined by eq. 2 arises because of the physical properties of the system and is described by Bjerrum's equations[3]; it might be expected that K_2 would be relatively constant for a wide variety of systems since, for a given solvent and temperature, Bjerrum's theory indicates that the dissociation constant is a function of the separation of the ions comprising the ion pair. On the other hand, the magnitude of K_1 for a series of acids more nearly reflects the chemical nature of the acid with respect to that of the solvent.

Previous investigations of the species and equilibria present in liquid ammonia solutions have employed colorometric,[4] conductometric,[5] potentiometric,[6] and kinetic methods.[7] We now present the results of a spectrophotometric study on liquid ammonia solutions of a number of substances which could act as potential indicator acids, a qualitative description of the equilibria which exist in these solutions, and a method for quantitative spectrophotometry of liquid ammonia solutions.

Experimental

Portable Absorption Cell.—Preliminary spectra of liquid ammonia solutions were obtained with a vacuum-jacketed cell (Figure 1) constructed to fit into the cell compartment of a Cary Model 14 recording spectrophotometer. The absorption cell was suspended from the inner wall of the vacuum jacket into a cavity bearing two optical windows. The upper inlet of the cell was attached to a 250-ml. dilution bulb and the lower inlet was connected to a graduated tube which was used either to estimate the volume of solution or as an inlet for gaseous ammonia. The dilution bulb was closed with a standard taper stopper provided with an exhaust to the vacuum system and two weighing pistols through which solid acid (NH_4ClO_4) or base (t-C_4H_9OK, CH_3OK, or KNH_2) could be introduced. The cells employed were constructed with either Pyrex or fused silica optical windows. A spectrophotometric determination of the length of the light path was made using the known absorbance at 277, 350, and 404.7 mμ of standard K_2CrO_4 solutions. The lower portion of the vacuum-jacketed assembly was encased with polyurethane foam in a metal box which fit snugly into the cell compartment of the Cary spectrophotometer; a metal box which excluded stray light covered the entire assembly. Solutions were prepared by either introducing a weighed quantity of solute directly into the dilution bulb or using the winch assembly (Figure 2). The dilution bulb and the gaseous ammonia inlet were surrounded by a 2-propanol–Dry Ice slush bath, and ammonia was condensed into the system. Temperature equilibrium was attained, after the required amount of ammonia had been condensed, by gentle agitation with a stream of dry helium. The cell was then mounted in the spectrophotometer and the spectrum recorded.

In a typical experiment a solution of the potential indicator was prepared in liquid ammonia and its spectrum recorded; spectra were then recorded after the addition of solid base and after the addition of sufficient solid acid to make the solution acidic. Figure 3 shows the results of a typical experiment on 2,4-dinitroaniline, and Table I summarizes the major absorption bands which appear in the spectra of a series of nitroanilines. The spectra of solutions containing potassium amide could not be obtained below about 350 mμ because of an intense absorption band characteristic of the amide ion.[8]

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(1) E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **23**, 285 (1900), and references therein.

(2) V. F. Hnizda and C. A. Kraus, *J. Am. Chem. Soc.*, **71**, 1565 (1949), and references therein.

(3) N. Bjerrum, *Kgl. Danske Selskab.*, **7**, No. 9 (1926).

(4) A. H. Corwin and J. D. Reinheimer, *J. Am. Chem. Soc.*, **73**, 1184 (1951).

(5) C. A. Kraus and W. C. Bray, *ibid.*, **35**, 1315 (1913).

(6) G. W. Watt, D. M. Sowards, and W. R. McBride, *ibid.*, **77**, 5835 (1955).

(7) A. I. Shatenshtein, *ibid.*, **59**, 432 (1937).

TABLE I

ABSORPTION MAXIMA, EXTINCTION COEFFICIENTS, AND COLORS OF POTENTIAL INDICATOR ACIDS IN LIQUID AMMONIA AT −78°

	Acidic (molecular) form			Basic (ionized) form			Neutral solution	
Compound	λ_{max}	Log ϵ	Color	λ_{max}	Log ϵ	Color	λ_{max}	Color
o-Nitroacetanilide	325	3.11	Colorless	436	3.08	Yellow	325, 436	Pale yellow
m-Nitroacetanilide	340	3.77	Colorless	425	3.54	Yellow	340	Colorless
p-Nitroacetanilide	335	4.15	Colorless	451	4.46	Yellow-green	335, 451	Pale yellow
2,4-Dinitroacetanilide	...	...	...	436	4.4	Orange	436	Orange
o-Nitroaniline	425	3.58	Yellow	490	3.76	Orange-red	425	Yellow
p-Nitroaniline	402	4.23	Yellow-green	466	4.43	Yellow	402	Yellow-green
2,4-Dinitroaniline	354, 540	4.0, 3.74	Pink	354, 540	3.4, 5.14	Yellow	386, 540	Purple
3,5-Dinitroaniline	423	3.8	Yellow	487	3.3	Purple	423	Yellow
2,6-Dinitroaniline	449	4.99	Yellow	373	4.18	Colorless	449	Yellow

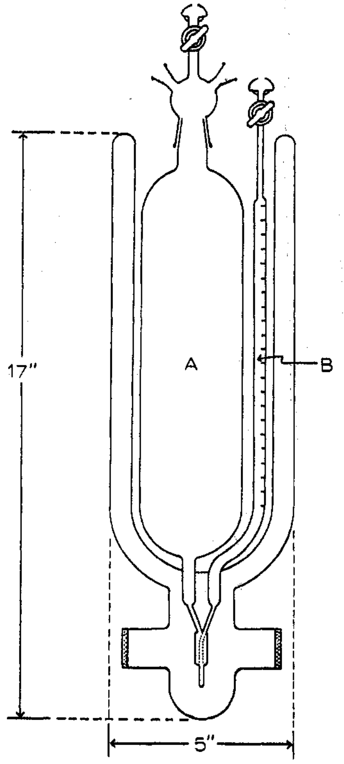

Figure 1.—Portable optical absorption cell.

Quantitative Absorption Measurements.—The permanently mounted absorption cell was used to study the applicability of Beer's law to potential indicator acid systems. A solution of the potential indicator acid of known concentration in pure liquid ammonia, in acid solution (NH_4ClO_4), or in basic solution (KNH_2, t-C_4H_9OK, or CH_3OK), could be successively diluted with either pure liquid ammonia or with acidic or basic liquid ammonia solutions. Thus, the absorption of a solution at a given wave length could be determined as a function of the concentration of potential indicator acid in pure ammonia or in solutions with a constant concentration of acid or base. The results of typical experiments appear in Figures 3 and 4.

(A) **Cell and Dilution Equipment.**—The apparatus in which quantitative spectrophotometric absorption measurements were made is shown in Figure 5. A 11.01 ± 0.01 mm. optical cell with fused silica windows was suspended from the bottom of the inner wall of a vacuum-jacketed vessel using graded seals. Silica windows (A) were attached to the outer walls of the vessel with picein wax, and the entire system was evacuated continuously at B with an oil diffusion pump backed by a mechanical pump. With the contents of the vessel at −75° no condensation was ob-

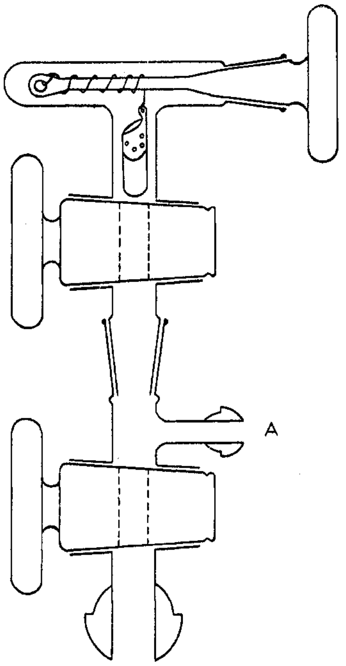

Figure 2.—Sample winch.

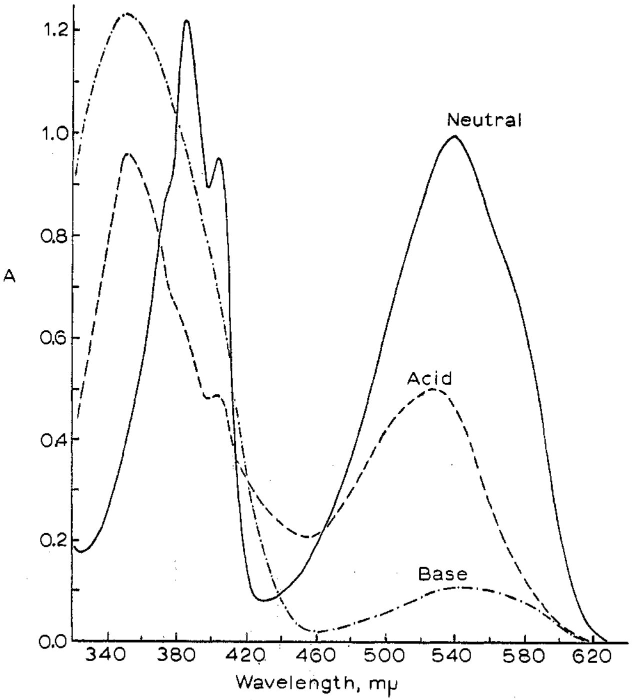

Figure 3.—Absorption spectra of 2,4-dinitroaniline in liquid ammonia at −78°.

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(8) (a) R. E. Cuthrell, Ph.D. Dissertation, The University of Texas, 1964; (b) H. J. Eding, Ph.D. Dissertation, Stanford University, 1952; (c) R. A. Ogg, Jr., *J. Chem. Phys.*, **14**, 399 (1946).

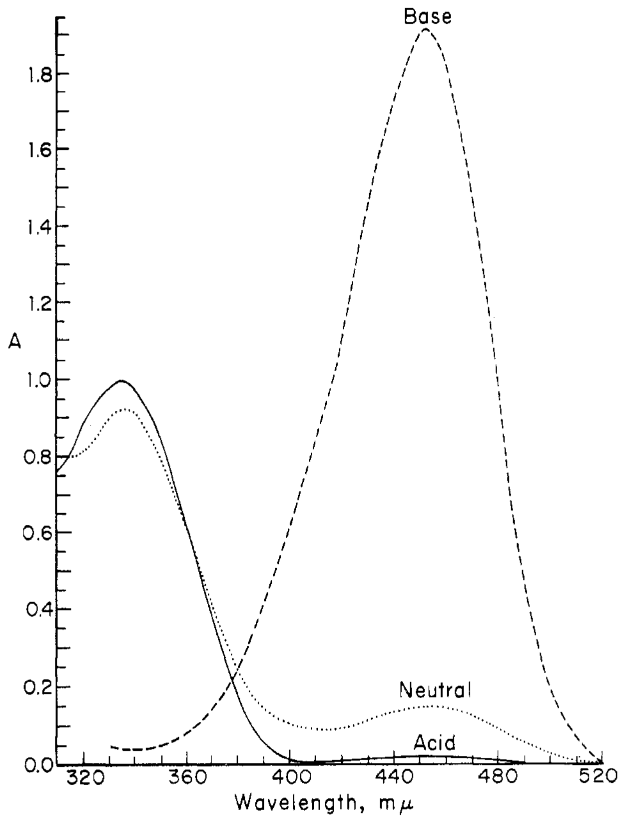

Figure 4.—Absorption spectra of *p*-nitroacetanilide in liquid ammonia at −78°.

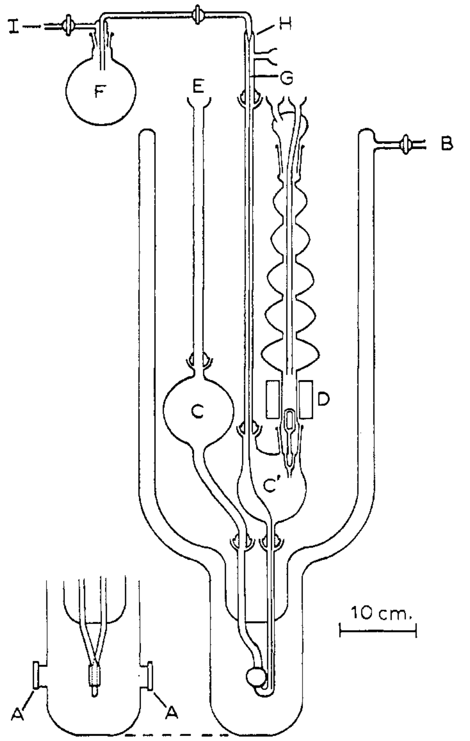

Figure 5.—Optical absorption cell and dilution equipment.

served on the outer quartz windows. Two 500-ml. dilution bulbs (C and C′) were attached through ball and socket joints to the absorption cell; these bulbs contained the greater portion of the solution under investigation and acted as surge chambers during mixing. One of the dilution bulbs (C′) carried a solenoid-operated greaseless valve; earlier versions of the apparatus incorporated a metal bellows valve which was difficult to operate under these conditions but otherwise gave good service. The dilution buret consisted of five progressively smaller bulbs separated by 0.5-in. pieces of tubing, each with a fiducial mark. The volumes of the bulbs in the dilution buret, calibrated with water, permitted approximately equivalent progressive dilutions of the original solution. Each dilution bulb carried a 1-cm. diameter tube which could be used as a sample inlet as well as an outlet for gaseous ammonia or helium. The dilution flasks were attached to two vacuum lines either of which could be used as an exhaust or as a source of anhydrous ammonia or helium. The sample, contained in a glass boat, was introduced into the dilution bulb through two 10-mm. hollow-bore stopcocks using the winch arrangement shown in Figure 2. The tubing between the stopcocks could be evacuated and filled with dry helium through A, Figure 2. Rotation of the male portion of the standard-taper joint unwound a nylon thread to which the sample boat was attached. The apparatus illustrated in Figure 5 was mounted permanently on the optical axis of a Zeiss PMQ spectrophotometer. Since the latter is a single-beam instrument and it was impractical to move the cell and its associated equipment in and out of the beam, the beam was diverted in a reproducible manner around the absorption cell using front surface mirrors. Air was the working reference, but all the data are corrected for the absorptivity of pure anhydrous ammonia as determined in the same apparatus. The spectrophotometer and all associated equipment was enclosed by an opaque curtain when optical measurements were made.

During the course of this investigation it was observed that water adsorbed on the walls of the apparatus was sufficient to interfere with the investigation of liquid ammonia solutions of moisture-sensitive compounds even after the individual pieces were dried in a vacuum oven and the assembled equipment was evacuated with an oil diffusion pump overnight. The simple expedient of rinsing the walls of the apparatus with liquid ammonia reduced the interference by adsorbed water to less than the experimental error of the measurement. Thus, the dilution vessels were provided with a means for removing liquid ammonia solutions while the thermostat was in operation (Figure 5). A 1-l. round-bottom evacuable flask (F) was connected to a polyethylene tube (G) by means of a heat seal at H; the polyethylene tube extended to a point below the absorption cell. In practice the waste ammonia flask was cooled with Dry Ice and evacuated, and liquid ammonia was removed from the optical cell by manipulating the connecting stopcock; all but about 1 ml. of liquid ammonia could be removed by this procedure. Several successive experiments could be conducted without dismantling the equipment since the solutions from the previous experiment and the solvent used to rinse the apparatus could be collected in flask F and allowed to evaporate through I into a hood.

(B) **Thermostat.**—The large vacuum-jacketed vessel containing the dilution equipment was filled with ethanol, which served as a heat-transfer medium; liquid nitrogen was used as the refrigerant. Using air pressure, liquid nitrogen was forced from a 25-l. storage vessel through a coil of copper tubing immersed in the bath liquid. The spent nitrogen gas was vented into the atmosphere through a drying tube; the bath was agitated by an immersed centrifugal pump during the course of the experiment. When the temperature of the bath liquid fell below the desired value, a thermistor controller actuated a solenoid valve releasing the air pressure on the liquid nitrogen container and stopping the flow of refrigerant. An increase in bath temperature closed the solenoid valve, initiating the flow of refrigerant. In the course of normal operations, the solenoid valve was actuated four to six times per minute, and the bath temperature was maintained to ±0.1° of the desired value over a 6–10 hr. period.

The temperature of the solution in the absorption cell was monitored by a polyethylene-encased thermistor which extended parallel to G; the leads were brought through a wax seal.

(C) **Gas-Handling System.**—The vacuum and gas-handling system consisted of two parallel, horizontal manifolds with connections to the dilution bulbs and buret, a helium purification train, a source of dry ammonia, and pressure regulators. The latter consisted of mercury manometer bubblers with leveling bulbs, one-way shut-off valves, and water-filled carboys to absorb vented ammonia. Either manifold could be evacuated or filled with dry gas or used as an exhaust line independent of the other.

(D) **Method of Mixing Solutions.**—Dry helium was obtained by passing commercial helium over activated alumina and activated charcoal maintained at −196° and then through a glass frit immersed in a solution of sodium metal in liquid ammonia. The dry gas was used to force the solution from one dilution bulb to the other through the absorption cell. About 13 l. of dry nitrogen was required to mix the liquid ammonia solutions during one experiment, but for water-sensitive compounds this volume of gas could not be effectively dried in a short time with the equipment described. In this case, a Toepler pump was used to circulate a small volume of carefully purified helium through the apparatus which in turn forced the liquid ammonia solution back and forth through the absorption cell.

Titration Apparatus.—The apparatus was adapted from the design of Watt and Sowards.[9] A platinum differential electrode system employing a portion of the solution to be titrated as the reference electrode and a platinum wire immersed in the titrated solution as the indicating electrode was used to follow the course of the titration. Potential measurements were made with a Leeds and Northrup Model 7664 pH indicator.

Chemicals.—All potential indicator acids studied were of the highest quality available commercially and were purified to a constant melting point by vacuum sublimation or recrystallization from appropriate solvents followed by rigorous drying. Commercial synthetic ammonia was stored in 10-l. steel cylinders containing sodium metal and was distilled a second time from sodium prior to use. Potassium amide was prepared by allowing redistilled reagent grade potassium to react with anhydrous liquid ammonia. Sodium methoxide and potassium *t*-butoxide were obtained from the reaction of the metals with the appropriate anhydrous alcohols followed by removal of the excess alcohol *in vacuo*. Air-sensitive compounds were weighed and transferred to the sample winch (Figure 2) in a helium-filled drybox, the atmosphere of which was equilibrated with sodium–potassium alloy.

Discussion

The nature of the species present in liquid ammonia solutions of nitroanilines and nitroacetanilides, which are potential indicator acids in this solvent, was studied by considering the variation of the absorption spectra of these substances which occurred upon the incremental addition of excess strong acid or base; the applicability of Beer's law to neutral, acidic, and basic solutions; and potentiometric titration data. The number of protons which could be removed from an indicator acid was obtained from titration data, and the relative magnitude of ionization was estimated from spectral data.

The spectral data (Table I) suggest that *o*- and *p*-nitroaniline and *o*-, *p*-, and *m*-nitroacetanilide can act as acids in liquid ammonia (eq. 3). Beer's law studies

$$O_2NC_6H_4NHR + NH_2^- \rightleftharpoons O_2NC_6H_4NR^- + NH_3 \tag{3}$$
$$R = H, COCH_3$$

indicate that *o*- and *p*-nitroacetanilide undergo spontaneous ionization in the pure solvent whereas the other three compounds lose protons only in the presence of amide ions. These data and the fact that liquid ammonia solutions of dinitrobenzenes and certain mononitrobenzenes show only one maximum in the visible region, the position and intensity of which are time-independent in contrast to liquid ammonia solutions of trinitro aromatic compounds,[10] suggest that complex compounds are not formed with the solvent. According to expectation, *o*- and *p*-nitroacetanilide were found to be stronger acids than the corresponding nitroanilines and *m*-nitroacetanilide was observed to be a weaker acid than either *o*- or *p*-nitroacetanilide.

Spectral data for 2,4-, 3,5-, and 2,6-dinitroaniline; Beer's law studies on neutral, acidic, and basic solutions of these substances; and potentiometric data are consistent with the formation of complexes with the solvent (eq. 4) and with amide ion (eq. 5) (*cf.* the recent

$$(O_2N)_2C_6H_3NH_2 + NH_3 \longrightarrow \text{complex I} \tag{4}$$

$$\text{complex I} + NH_2^- \rightleftharpoons \text{complex II}^- \tag{5}$$

$$\text{complex I} + NH_2^- \rightleftharpoons (\text{complex I})^- + NH_3 \tag{6}$$

observation for N,N-disubstituted polynitroanilines[10]) and that they may behave as acids (eq. 6). The complexes formed with the solvent or with amide ion are probably of the Meisenheimer type.[10]

Color changes similar to those observed in liquid ammonia were obtained for 2,4-dinitroaniline in various solvents (benzene, acetone, dimethylformamide, dimethyl sulfoxide) using different strong bases, but the color of the neutral solutions in each case was yellow; the incremental addition of base caused the solutions to turn purple first and then yellow. The suggestion that 2,4-dinitroaniline can exist in an ionized form in liquid ammonia is supported by the isolation of the purple monopotassium salt of this substance.[11] A possible alternate explanation for the formation of a complex ion in strongly basic solution is the formation of a dipotassium salt, but these alternatives cannot be distinguished on the basis of data available at this time.

Spectral data (Table I) indicate that 3,5-dinitroaniline is a weaker acid than 2,4-dinitroaniline and that a molecular complex is formed between ammonia and the molecular form of 3,5-dinitroaniline (eq. 4).[10] The absence of a measurable ionization of this compound is probably due to the unfavorable positioning of the strongly electron-withdrawing nitro groups on the aromatic nucleus with respect to the amine function. 2,6-Dinitroaniline does not lose protons in the presence of a strong base but rather it forms a molecular complex (eq. 5). Infrared studies on aqueous solutions of nitroanilines indicate that intermolecular hydrogen bonding does not occur unless the nitro groups are in the 2- and 6- positions of the aromatic nucleus,[12] and a similar effect in liquid ammonia solutions would explain the apparent lack of ionization in this solvent.

The results reported here suggest that the relative degree of ionization of the substances investigated is 2,4-dinitroaniline > *o*-nitroacetanilide > *p*-nitroacetanilide > *m*-nitroacetanilide; the latter com-

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(9) G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 454 (1955).

(10) R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 161 (1962).

(11) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103**, 508 (1913).

(12) L. K. Dyall and A. N. Hambly, *Australian J. Chem.*, **11**, 513 (1958).

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.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Reactions of Atomic Nitrogen with S_2Cl_2 and Other Sulfur Compounds

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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,

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[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).