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# The Reaction of Nitrogen(II) Oxide with Various Primary and Secondary Amines

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It was earlier reported that nitric oxide behaves as a Lewis acid toward diethylamine resulting in the formation of  $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$ . In order to establish this as a general reaction type the reaction has been extended to a whole series of primary and secondary amines. The preparation of the adducts, their structure and physical properties are discussed.

## Introduction

It has been reported<sup>2</sup> that diethylamine reacts with nitric oxide at  $-78^\circ$  to produce a white solid whose formula is  $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$ . Infrared and nuclear magnetic resonance spectroscopy were employed to establish the structure. It was proposed that in this reaction nitric oxide is behaving as an electron pair acceptor. In order to establish this as a general reaction type for nitric oxide, the initial research has been extended to include a series of amines. Products are obtained of widely varying stability. For example, the methylamine product decomposes spontaneously near  $-10^\circ$ , while the di-*n*-hexylamine product is stable for long periods at room temperature. Sterically hindered amines do not form products. In this article, the method of preparing the compounds, the physical properties of the compounds and evidence concerning their structure will be presented.

## Experimental

**Purification of Materials.**—The amines used in this research are commercially available and can be purified by distillation from anhydrous barium oxide. In most cases the same product is obtained by using the crude amine as that obtained using the purified product. Matheson commercial grade nitric oxide is purified by bubbling through 10 *M* sodium hydroxide and dried by passing through columns of sodium hydroxide pellets. Similar products are obtained when the nitric oxide is used directly without purification in our high pressure experiments.

Unless otherwise indicated, the ammonium salt products can be purified by flooding out of a concentrated chloroform solution with ether.

**Instrumentation.**—Infrared spectra were obtained with a Perkin-Elmer model 21 infrared spectrometer with sodium chloride optics. The instrument was frequency calibrated using the absorptions of ammonia, carbon dioxide, water vapor and polystyrene. The appropriate corrections were applied to the reported spectra. The infrared spectra obtained on pertinent compounds are filed with the American Documentation Institute.<sup>3</sup>

Nuclear magnetic resonance spectra were obtained using a Varian high resolution spectrometer employing a 60 m.c. probe. Saturated, chloroform solutions were prepared in a nitrogen atmosphere and transferred to dry sample tubes which were flushed with nitrogen. The tubes were sealed and stored at  $-78^\circ$  until the spectra were run.

**General Preparative Techniques.**—Two general preparative methods, the atmospheric pressure and the high pressure method have been employed. The same product is ob-

tained by both techniques. In general, higher yields are obtained by the high pressure reaction. If the product is unstable it is often more convenient to use the atmospheric pressure process.

In the high pressure method a 200 cc. autoclave is used as the reaction vessel. Nitric oxide is added to a large 2000 cc. high pressure autoclave which serves as a nitric oxide reservoir and makes it possible to fill the reaction vessel without opening it directly to the nitric oxide tank. The large autoclave is connected to the nitric oxide tank through a valve and to the reaction vessel through a check valve, a high pressure needle valve and a blowout valve. This assembly is to insure against a feed back of amine into the nitric oxide tank in the event of an exothermic reaction. The reaction vessel is first evacuated, filled with nitrogen and again evacuated. A mixture of equal volumes of amine and diethyl ether is drawn into the evacuated reaction vessel containing a glass liner.

The reaction vessel is cooled to  $-78^\circ$ , the nitric oxide is introduced and after a 24-hour period the autoclave is allowed to warm to room temperature. The excess nitric oxide is vented off and the product is removed. Yields vary with the amine-solvent ratio in the range of 60 to 80%. With proper stirring, near quantitative yields can probably be obtained. The yield data reported are not intended to indicate an upper limit to be expected. The reaction time variable was not investigated.

The atmospheric pressure method was described in an earlier publication.<sup>2</sup>

**Preparation of Sodium Salt Derivatives.**—In our initial report it was shown that an excess of the diethylammonium salt, dissolved in alcohol reacts with sodium ethoxide to produce the sodium salt  $\text{Na}^+\text{Et}_2\text{NN}_2\text{O}_2^-$ . The product is flooded out of solution with ether and washed with chloroform. This reaction has been carried out on many of the amine products prepared in this study providing a derivative to aid in establishing the structure of these materials. In some instances the sodium salts cannot be obtained directly by this procedure but can be obtained when slight modifications are made. These modifications will be discussed in the section on specific procedures.

**Diethylamine.**—Since our initial report on this reaction,<sup>2</sup> we have been able to increase our yield from the reported 11 to 63% by treating an ether solution of the amine (4 ether to 1 amine mole ratio) with nitric oxide at high pressure. With agitation or stirring of the reaction mixture nearly quantitative yields may result.

The product can be prepared in the pure amine indicating that ether functions only as a solvent for the reaction. Diisopropyl ether and pentane solvents produce the same product without any appreciable difference in yield. The yield is very much dependent on the temperature, only a very slight amount of product is obtained when the reaction is carried out at room temperature.

**Di-*n*-propylamine.**—This product is conveniently prepared by the high pressure technique. The product undergoes a characteristic reaction with hydrochloric acid to evolve nitric oxide. It melts with decomposition at  $96-97^\circ$  in a sealed melting point tube and decomposes in a few days at room temperature. The n.m.r. spectrum of this product is similar to that of di-*n*-propylammonium chloride. Elemental analyses are in good agreement with theoretical.

Calcd. for  $[\text{CH}_3(\text{CH}_2)_2]_2\text{NH}_2^+[\text{CH}_3(\text{CH}_2)_2]\text{NN}_2\text{O}_2^-$ : C, 54.91; H, 11.54; N, 21.35. Found: C, 54.61; H, 11.39; N, 21.39.

The sodium salt of this compound cannot be prepared by the reaction with sodium ethoxide unless the reaction is carried out at low temperatures ( $0^\circ$ ) and under nitrogen. The product precipitates from solution upon evaporation of the

(1) Abstracted in part from the Ph.D. thesis of B. R. Karstetter, University of Illinois, 1960.

(2) Russell S. Drago and F. E. Paulik, *J. Am. Chem. Soc.*, **82**, 96 (1960). Pertinent references to other nitric oxide reactions are contained in this article.

(3) Material supplementary to this article has been deposited as Document number 6461 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting \$1.25 for photoprints or \$1.25 for 35 mm. microfilm in advance payment by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

solvent under vacuum. The infrared spectra of the sodium salt contains many of the same absorptions as the ammonium salt but the intense  $\bar{\nu}$ -H<sub>2</sub> stretching frequency is absent.

*Anal.* Calcd. for Na<sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>]: C, 39.33; H, 7.72; N, 22.94. Found: C, 37.93; H, 7.10; N, 21.36.

**Diisopropylamine.**—The reaction between diisopropylamine and nitric oxide was carried out under atmospheric and high pressure conditions. In both instances the desired product, R<sub>2</sub>NH<sub>2</sub><sup>+</sup>R<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>, was not obtained. Instead, a small amount of white solid (2% yield based on amine) precipitated. The product melts at 138–139° and has an elemental analysis in good agreement with diisopropylammonium nitrite.

*Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>NO<sub>2</sub><sup>-</sup>: C, 48.61; H, 10.90; N, 18.90. Found: C, 48.55; H, 10.72; N, 18.71.

The reported<sup>4</sup> melting point for the nitrite is 136–137°.

**Di-*n*-butylamine.**—This product is prepared in 80% yield by the high pressure technique. It is considerably more stable than the di-*n*-propylamine product and can be stored at room temperature in the presence of air for several days before noticeable decomposition occurs. The product is insoluble in water and melts in a sealed tube at 101°. The infrared and nuclear magnetic resonance spectra support its formulation as [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>.

The n.m.r. spectra shows the characteristic  $\bar{\nu}$ NH<sub>2</sub> peak, a peak for the methylene bonded to nitrogen (N-CH<sub>2</sub>-) and a complex absorption due to CH<sub>3</sub> and the other CH<sub>2</sub> groups. The alkylammonium chloride spectra is similar.

*Anal.* Calcd. for [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 60.32; H, 12.05; N, 17.58. Found: C, 60.36; H, 11.81; N, 17.24.

**Di-*sec*-butylamine.**—This reaction when carried out at high pressure yields a very small amount of material identified as the alkylammonium nitrite.

Calcd. for C<sub>8</sub>H<sub>18</sub>NH<sub>2</sub><sup>+</sup>NO<sub>2</sub><sup>-</sup>: C, 54.50; H, 11.46; N, 15.89. Found: C, 54.50; H, 11.48; N, 15.51.

The product melts at 108° and has an infrared spectrum expected for the alkylammonium nitrite.

**Di-*n*-amylamine.**—This product can be prepared by the high pressure technique. It is very stable; samples have been stored at room temperature in air for long periods without noticeable decomposition. The product melts with decomposition at 101–103°. Elemental analysis infrared and nuclear magnetic resonance spectra are in agreement with the formulation of this material as [CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>.

*Anal.* Calcd. for [CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 64.12; H, 12.40; N, 14.96. Found: C, 63.82; H, 12.16; N, 15.03.

**Di-*n*-hexylamine.**—The di-*n*-hexylamine product was prepared in 62% yield by the high pressure technique. The purified compound is insoluble in water, stable without noticeable decomposition for at least three months and melts at 100–102°. The infrared and nuclear magnetic resonance spectra have ammonium ion absorptions similar to the alkylammonium chloride. Elemental analysis support the formula [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>.

*Anal.* Calcd. for [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>]<sub>2</sub>NH<sub>2</sub><sup>+</sup>[CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>]<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 66.91; H, 12.66; N, 13.01. Found: C, 67.13; H, 12.64; N, 12.93.

**Piperidine.**—The piperidine-nitric oxide compound was prepared in 70% yield by the high pressure technique. The product is very soluble in chloroform and somewhat soluble in ether. It is best purified by washing the crude material with ether but can be flooded from a chloroform solution with heptane. Its stability is similar to that of the diethylamine product. It melts with decomposition at 69–71°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub><sup>+</sup>C<sub>5</sub>H<sub>10</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 52.14; H, 9.65; N, 24.33. Found: C, 52.01; H, 9.52; N, 23.85.

The sodium salt can best be prepared by a technique described later in which the intermediate ammonium salt is not isolated. The sodium salt is hygroscopic and poor elemental analyses were obtained on the samples prepared. The infrared spectra indicates conclusively that this is the sodium salt, Na<sup>+</sup>C<sub>5</sub>H<sub>10</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>, and that the product contains

water. All absorptions attributed to the ammonium ion have disappeared, but the general appearance of the rest of the spectra is similar to the ammonium salt.

**Methylamine.**—The methylamine product was prepared by the atmospheric pressure method. After nitric oxide was passed through the solution for a few hours the solution became deep orange in color and a large amount of solid precipitated. After 22 hr. the system was allowed to warm and the color disappeared. Upon filtration and further warming to near room temperature the white solid instantly decomposed into a cloud of white fumes. No further work was done because of the instability of the product.

***n*-Propylamine.**—The *n*-propylamine product is best prepared by the atmospheric pressure method. It is slightly more stable than the methylamine product but too unstable to obtain the infrared spectrum at room temperature or elemental analysis. In order to establish this material as *n*-C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub><sup>+</sup>*n*-C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup> the sodium salt was prepared. This is accomplished by carrying out the reaction between sodium ethoxide and the ammonium salt without isolating the ammonium salt. At the end of the reaction the system is thoroughly flushed with nitrogen and a solution of sodium ethoxide in ethanol is added to the cold reaction mixture. Excess ethoxide is avoided to simplify purification. The mixture is stirred for 2 hr. under a nitrogen atmosphere, allowed to warm to room temperature and immediately filtered. The product is fairly stable and is purified by washing with small portions of chloroform, ethanol and ether. Elemental analysis and the infrared spectrum on the sodium salt indicate that the *n*-propylamine reaction is similar to the secondary amine reactions.

*Anal.* Calcd. for Na<sup>+</sup>CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NHNN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 25.53; H, 5.73; N, 29.78. Found: C, 24.99; H, 5.46; N, 29.33.

**Isopropylamine.**—The isopropylamine product was obtained in 33% yield by the high pressure method. It is much more stable than the product obtained with *n*-propylamine. A sample was kept for two days, at room temperature in a vacuum desiccator over anhydrous calcium chloride. The product was purified by washing with ether. It is insoluble in chloroform and many other appropriate solvents. It is soluble in alcohol but very difficult to recover from this solvent. The product melts with decomposition at 71°.

*Anal.* Calcd. for (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub><sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CHNN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 40.42; H, 10.18; N, 31.45. Found: C, 40.29; H, 10.10; N, 31.00.

The sodium salt was prepared by reacting the isopropylammonium salt slurred in ethanol with slightly less than the stoichiometric amount of NaOEt. After stirring for five minutes the product was precipitated by adding ether. The sodium salt was thoroughly washed with ethanol and ether. It is quite stable at room temperature although some decomposition was detected after five days. The sodium salt explodes in an open melting-point tube at 122°.

*Anal.* Calcd. for Na<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub>NN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 25.53; H, 5.73; N, 29.78. Found: C, 25.51; H, 5.80; N, 29.58.

***n*-Butylamine.**—This salt is more stable than that of *n*-propylamine but decomposes in a cloud of white fumes after four or five minutes at room temperature. The atmospheric pressure method is best suited for ease of preparation.

*Anal.* Calcd. for CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub><sup>+</sup>CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHNN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 46.56; H, 10.67; N, 27.16. Found: C, 45.31; H, 10.30; N, 28.23.

The sodium salt is prepared without isolating the ammonium salt. It is purified by washing with alcohol and ether. Fairly extensive decomposition of the sodium salt was noted within 24 hr. at room temperature. The product explodes in an open melting-point tube at 98°.

*Anal.* Calcd. for Na<sup>+</sup>CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHNN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 30.95; H, 6.51; N, 27.09. Found: C, 30.58; H, 7.03; N, 27.59.

**Isobutylamine.**—The stability of this ammonium salt is comparable to the product obtained with *n*-butylamine and is most conveniently prepared by the atmospheric pressure method. The sodium salt is made without isolating the intermediate ammonium salt. The product is filtered under nitrogen and washed with chloroform, alcohol and ether. It explodes in an open melting-point tube at 118°.

*Anal.* Calcd. for Na<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>NHNN<sub>2</sub>O<sub>2</sub><sup>-</sup>: C, 30.95; H, 6.51; N, 27.09. Found: C, 30.88; H, 6.54; N, 26.68.

(4) J. K. Wolfe and K. L. Temple, *J. Am. Chem. Soc.*, **70**, 1414 (1948).

*sec*-Butylamine.—No product was obtained by either the high pressure or atmospheric pressure method outlined above.

*tert*-Butylamine.—No product was obtained by either the high pressure or atmospheric pressure method. A very small amount of *tert*-butylammonium nitrite was obtained. It melts with decomposition at 126–127°.

Calcd. for  $(\text{CH}_3)_3\text{CNH}_3^+\text{NO}_2^-$ : C, 39.97; H, 10.08; N, 23.32. Found: C, 39.47; H, 9.77; N, 22.83.

*n*-Amylamine.—This product has a stability comparable to that of methylamine and is best prepared by the atmospheric pressure method. When filtered cold, the product disappears in a cloud of white smoke below room temperature. The instability prevented our characterization of the product, but it is assumed to be similar to the other amine products.

Cyclohexylamine.—The cyclohexylamine product is one of the more stable primary amine products being comparable in stability to that of isopropylamine. Elemental analysis and infrared spectra were obtained. The product melts with decomposition at 71–72°. It is purified by washing with ether and drying in a vacuum desiccator.

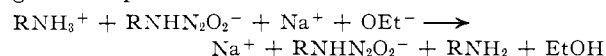
Anal. Calcd. for  $\text{C}_6\text{H}_{11}\text{NH}_3^+\text{C}_6\text{H}_{11}\text{NHN}_2\text{O}_2^-$ : C, 55.77; H, 10.16; N, 21.69. Found: C, 55.91; H, 10.07; N, 20.96.

Aniline.—The reaction between aniline and nitric oxide is very exothermic. In the one instance in our experience, a violent explosion occurred. The heat generated melted the high pressure tubing used in our system.

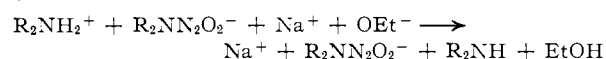
### Discussion

The reaction between diethylamine and nitric oxide was reported earlier. This reaction has now been extended to include a whole series of amines, demonstrating that the behavior of nitric oxide as a Lewis acid is a general reaction type. The products obtained for this new series of amines have been established as ammonium salts of the general formula  $\text{R}_2\text{NH}_2^+\text{R}_2\text{NN}_2\text{O}_2^-$  or  $\text{RNH}_3^+\text{RNHN}_2\text{O}_2^-$  for secondary and primary amines, respectively. Elemental analysis, infrared spectra, nuclear magnetic resonance spectra and the preparation of sodium salt derivatives support the above formulation.

Most of the ammonium salts undergo the reaction with sodium ethoxide represented by the general equations



or



Elemental analyses of the sodium salt derivative are in good agreement with theoretical. The slight variations reported are due to the difficulty of purification and hygroscopicity of these derivatives.

The infrared spectra<sup>3</sup> serve to confirm the formulation of these amine-nitric oxide products as ammonium salts. The secondary amine hydrochlorides have strong bands in the 2800–2400  $\text{cm}^{-1}$  region arising from the  $\overset{+}{\text{N}}\text{-H}$  stretch. The  $\overset{+}{\text{N}}\text{H}_2$  deformation appears in the 1600–1550  $\text{cm}^{-1}$  region. The spectra of the products in the regions outlined above indicate the presence of the substituted ammonium ion in the products. In general, the absorptions in the product are shifted to lower frequencies indicating rather extensive hydrogen bonding. In every case these absorptions have disappeared in the sodium salt, although

the general appearance of the rest of the spectrum is unchanged except for some frequency shifts due to lattice effects and the absence of hydrogen bonding.

In the primary amine hydrochlorides there are intense broad bands in the 3200–2800  $\text{cm}^{-1}$  region associated with  $\overset{+}{\text{N}}\text{H}_3$  stretching modes. There are bands of medium intensity in the 1610–1550 and 1510–1480  $\text{cm}^{-1}$  regions arising from  $\overset{+}{\text{N}}\text{H}_3$  deformations. The conversion of the primary amine-nitric oxide products to the sodium salts results in the disappearance of the broad band due to  $\overset{+}{\text{N}}\text{H}_3$  stretching modes. In this region an intense sharp absorption attributed to the  $\overset{+}{\text{N}}\text{-H}$  stretching vibration in the anion,  $\text{RNHN}_2\text{O}_2^-$ , appears. It occurs at 3253, 3186 and 3164  $\text{cm}^{-1}$  in the sodium salts of the *n*-propylamine, *n*-butylamine and isobutylamine products, respectively.

A careful examination of the infrared spectra of alkyl ammonium chlorides, the alkylamine-nitric oxide products and the sodium salts of these products indicates that the  $\overset{+}{\text{N}}\text{-O}$  and  $\overset{+}{\text{N}}\text{-N}$  stretching frequencies occur in the 1215 to 1129  $\text{cm}^{-1}$  region. The  $\overset{+}{\text{N}}\text{-O}$  absorptions in the secondary amine-nitric oxide addition compounds occur at lower frequencies than those in the primary amine compounds. The more basic secondary amines would be expected to feed more electron density into the system and increase the single bond character of the  $\overset{+}{\text{N}}\text{-O}$  bond.

The nuclear magnetic resonance spectra of the nitric oxide products of di-*n*-propylamine, di-*n*-butylamine, di-*n*-amylamine and di-*n*-hexylamine have been obtained and compared with the spectra of the corresponding amine hydrochlorides. All of the spectra were obtained on saturated chloroform solutions of the compounds. The n.m.r. spectra serve as confirmatory evidence for the structures proposed and are consistent with the spectrum of the diethylamine compound. The  $\overset{+}{\text{N}}\text{-H}$  resonance in the nitric oxide products and the amine hydrochlorides occurs at lower fields than the solvent chloroform peak. This eliminates structures which place hydrogens on the oxygen for they would occur at higher fields. The next peak observed in the spectra is at higher field strength than the chloroform peak and is due to the  $>\overset{+}{\text{N}}\text{-CH}_2\text{-}$  protons. The other  $\text{-CH}_2\text{-}$  resonances overlap the  $\text{-CH}_3$  resonance and give rise to a complex absorption at higher fields. The above evidence is all in support of our postulate that the products of the nitric oxide reaction with primary and secondary amines are best formulated as ammonium salts of the general formula  $\text{R}_2\text{NH}_2^+\text{R}_2\text{NN}_2\text{O}_2^-$  and  $\text{RNH}_3^+\text{RNHN}_2\text{O}_2^-$ .

Several of the amines studied, *sec*-butylamine, *tert*-butylamine, diisopropylamine and di-*sec*-butylamine do not form addition compounds under the conditions of our experiment. It has been demonstrated<sup>3</sup> that these amines undergo a pronounced steric interaction with the reference acid trimethyl-

(5) H. C. Brown and H. Pearsall, *J. Am. Chem. Soc.*, **67**, 1765 (1945); H. C. Brown, M. D. Taylor and Sei Sujishi, *ibid.*, **73**, 2404 (1951); H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953).

boron. It is proposed that a similar steric interaction toward the  $N_2O_2$  group prevents the formation of stable adducts with these amines. Small amounts of the alkyl ammonium nitrites are obtained instead.

Some definite trends in the stability of the amine-nitric oxide products have been noted. The ammonium salts of the straight chain primary amines show a stepwise increase in stability from methylamine through *n*-butylamine. The *n*-amylamine product is comparable in stability to that of methylamine. Isopropylamine and cyclohexylamine form compounds which are more stable than those of the straight chain primary amines. The stability difference of the *sec*-butylamine and isopropylamine product is surprising.

The nitric oxide products of symmetrical, straight chain secondary amines exhibit a steady increase in stability from the diethylamine through the di-*n*-hexylamine products; relatively, the latter two members of the series are very stable. Two branched-chain analogs, diisopropylamine and di-

*sec*-butylamine do not form product but give very low yields of the alkylammonium nitrites.

These observations on "stabilities" are purely qualitative and are based upon visual observation of the ease of decomposition of the material. It has not been possible to correlate all of the "stabilities" described above with any single property of the amine donor. The basicity of the amine, crystal lattice effects, steric effects and volatility of the amine are all important considerations. With few exceptions, the stability of the products parallel the basicity of the amines as measured by the heat of formation of the trimethylboron adducts. There are some exceptions to this general rule in instances where one or more of the above factors become controlling.

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## Stability of the Chloro-complexes of Iodine in Aqueous Solution<sup>1</sup>

BY D. L. CASON AND H. M. NEUMANN<sup>2</sup>

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Spectrophotometric measurements have been used to study the stability in aqueous solution of the chloro-complexes of iodine in the (0), (I) and (III) oxidation states. The ion  $I_2Cl^-$  is characterized by absorption maxima at 248 and 437  $m\mu$ . Qualitative observations were made on the conditions necessary for disproportionation of  $I_2Cl^-$  to  $I^-$  and  $ICl_2^-$  and for the air oxidation of  $I_2Cl^-$  to  $ICl_2^-$ . The dissociation constant for  $I_2Cl^-$  was determined by a spectrophotometric method, and the value so obtained was compared with the variety of values in the literature. The most probable value is 0.60. The ion  $ICl_2^-$  is characterized by absorption maxima at 224 and 343  $m\mu$ , and the spectral data on its dissociation are consistent with the work of Faull. Spectral evidence for  $ICl_1^-$  could not be found, either in solutions prepared from  $ICl_3$  or from  $KI$ ,  $KIO_3$  and  $HCl$ . Solutions equivalent to iodine (III) in terms of oxidation were found to be equimolar mixtures of  $ICl_2^-$  and  $IO_3^-$ .

The existence of chloro-complexes of iodine in the (0), (I) and (III) oxidation states has been well established. However, there are a number of conflicting statements in the literature as to the stability of these complexes in aqueous solution. The purpose of this work is to determine the conditions under which these complexes exist in aqueous solution. It was hoped that this evidence would aid in interpreting the behavior of astatine in chloride solutions. Evidence for the existence of a chloro-complex of astatine has been presented,<sup>3</sup> but it has been difficult to make arguments about the oxidation state without further information about the behavior of iodine.

The work reported here has established the nature and amount of the iodine species in chloride solutions where the iodine concentration is in the range  $10^{-5}$  to  $10^{-3}$  *M*. In addition to the experimental work, which has principally involved spectrophotometric measurements, the earlier data in the literature has been evaluated.

### Experimental

**Materials.**—A sample of commercial iodine was ground into powder and treated with successive portions of water to

dissolve salts. It was then thoroughly dried and purified by sublimation.

Iodine monochloride was made by treating the purified iodine with condensed chlorine according to the method of Cornog and Karges.<sup>4</sup> It was purified by two or three recrystallizations.

A modification of the method of Booth and Morris<sup>5</sup> was used for the preparation of iodine trichloride. Small amounts of liquid  $ICl$  were added, a drop or two at a time, to condensed chlorine. After all the  $ICl$  was added, most of the excess chlorine was allowed to evaporate from the solid  $ICl_3$ . When solutions of  $ICl_3$  were desired some  $ICl_3$  crystals would be shaken out onto a piece of paper, allowed to stand for a few seconds to let the excess  $Cl_2$  escape and then added to the solvent without further delay.

All other chemicals were commercial materials of reagent grade. The concentrations of stock solutions were determined by the standard iodometric method.

**Spectral Measurements.**—The absorption spectra were determined with either a Beckman Model DU spectrophotometer or a Beckman Model DK-1 spectrophotometer. Most of the measurements were made with matched, fused silica cells having a light path of  $1.000 \pm 0.003$  cm. A water jacket was used to keep the cells at a constant temperature of  $25.0 \pm 0.5^\circ$ . Even though the cells were cleaned repeatedly, fluctuations in readings occasionally appeared due to impurities in the cells. This difficulty with iodine solutions has been observed and discussed by other workers.<sup>6</sup>

(1) Taken in part from a thesis submitted by Dennis Lamar Cason in partial fulfillment of the requirements for the M.S. degree, June 1959.

(2) Requests for reprints should be addressed to this author.

(3) H. M. Neumann, *J. Inorg. Nuclear Chem.*, **4**, 349 (1957).

(4) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 165.

(5) H. S. Booth and W. C. Morris, *ibid.*, p. 167.

(6) J. H. Wolfenden, *Anal. Chem.*, **29**, 1098 (1957).