

THE
INORGANIC CHEMISTRY
OF NITROGEN

WILLIAM L. JOLLY

**THE
INORGANIC CHEMISTRY
OF NITROGEN**

WILLIAM L. JOLLY
University of California, Berkeley

W. A. BENJAMIN, INC.
1964 New York Amsterdam

THE INORGANIC CHEMISTRY OF NITROGEN

Copyright © 1964 by W. A. Benjamin, Inc.
All rights reserved

Library of Congress Catalog Card Number 63-19981
Manufactured in the United States of America

*Final manuscript was received on March 20, 1963;
this volume was published on January 30, 1964*

*The publisher is pleased to acknowledge the assistance
of Oren Hunt, who produced the illustrations, and
William Prokos, who designed the dust jacket*

W. A. BENJAMIN, INC.
New York, New York

Editors' Foreword

In recent years few fields of chemistry have expanded at a rate to match that of inorganic chemistry. Aside from the stimulus afforded by the demand for new materials, a primary cause for the resurgence has been the application of physics and physical chemistry concepts to inorganic problems. As a result, both researchers active in the field and students entering the field need to become as thoroughly familiar with physical concepts as with descriptive information. However, there is presently no single point of view sufficiently general to organize the entire discipline. Instead, various points of view have arisen corresponding to the most powerful methods of attack in each research area. The synthesis of these different points of view constitutes the present series of monographs. Each monograph is contributed by an inorganic chemist active in a particular research area and reflects the methods of approach characteristic to that area. The operational procedure has been to invite able scientists to write where their interests lead them.

The series fulfills several functions. Through flexible selection of several of the monographs to supplement the introductory volume, it can be used as a textbook for an advanced inorganic chemistry course that makes full use of physical chemistry prerequisites. As a series in total, it is a reference treatise of inorganic chemistry systematized by

vi—EDITORS' FOREWORD

physical principles. Finally, each monograph by itself represents a specialist's introduction to a specific research field.

It is hoped that the authors contributing to this series have succeeded in directing attention to unsolved problems and that their efforts will be repaid by continued research advances in inorganic chemistry.

M. J. SIENKO
R. A. PLANE

Ithaca, New York
February 1963

Preface

Among the innumerable compounds of nitrogen, one finds a wide variety of molecular structures and properties. Many of these compounds have practical importance. A few important categories are: biochemically significant compounds (such as proteins, porphyrins, alkaloids, vitamins, drugs, and fertilizers), nitrogen oxides (important in air pollution, atmospheric physics, and astrophysics), explosives (mostly nitro compounds), fuels (substituted hydrazines), and plastics (e.g., Nylon).

Even if there were no useful nitrogen compounds, chemists would still find nitrogen chemistry quite fascinating. This fascination is attributable to the fact that the chemical reactions of nitrogen compounds are seldom thermodynamically controlled. Therefore it is possible to prepare compounds that are thermodynamically unstable but that decompose at a negligible rate. In this respect we are quite fortunate, because almost all the compounds mentioned above are thermodynamically unstable. Whenever a nitrogen compound can react to form several alternative products, it is quite commonly observed that the most thermodynamically stable product does not form at all, or that several products form simultaneously. For this reason, nitrogen compounds form a

viii—PREFACE

happy hunting ground for kineticists, who attempt to unravel and systematize the mechanisms of the reactions.

WILLIAM L. JOLLY

Berkeley, California
October 1963

Contents

Editors' Foreword	v
Preface	vii
Chapter 1 THE UNIQUE FEATURES OF NITROGEN	1
1-1 Comparison with Carbon	1
1-2 Comparison with Phosphorus	2
1-3 Comparison with Oxygen	3
Chapter 2 ELEMENTARY NITROGEN	4
2-1 Sources and Preparation	4
2-2 Bonding	5
2-3 Physical Properties	8
2-4 Atomic Nitrogen	10
2-5 The Nitrogen Nucleus	13
Chapter 3 AMMONIA	19
3-1 Preparation	19
3-2 Structure	20
3-3 Physical Properties	24

X—CONTENTS

3-4	Liquid-Ammonia Solutions	25
3-5	Metal-Ammonia Solutions	30
3-6	Amides, Imides, and Nitrides	34
3-7	Ammonia Hydrates and Aqueous Ammonia	38
3-8	Ammonium Salts	40
3-9	Ammonium Amalgams	43
3-10	Ammoniates and Ammines	43
Chapter 4	NITROGEN-HALOGEN COMPOUNDS	47
4-1	Nitrogen-Fluorine Compounds	47
4-2	Nitrogen-Chlorine Compounds	52
4-3	Nitrogen-Bromine Compounds	54
4-4	Nitrogen-Iodine Compounds	55
Chapter 5	THE HYDRONITROGENS AND HYDROXYL-AMINE	56
5-1	Hydrazine, N_2H_4	56
5-2	Hydrazoic Acid, HN_3	62
5-3	Miscellaneous Hydronitrogens	64
5-4	Organosubstituted Free Radicals	65
5-5	Hydroxylamine, NH_2OH	66
Chapter 6	NITROGEN OXIDES AND OXY-ACIDS	69
6-1	Nitrous Oxide, N_2O	70
6-2	Hyponitrous Acid, $H_2N_2O_2$	71
6-3	Nitramide, NH_2NO_2	72
6-4	Nitric Oxide, NO	73
6-5	The Nitrosyl Cation, NO^+	75
6-6	Some Unusual Oxy-acids and Oxy-anions of Nitrogen	76
6-7	Dinitrogen Trioxide, N_2O_3	77
6-8	Nitrous Acid and Nitrites, HNO_2 and NO_2^-	78
6-9	Peroxynitrous Acid, $HOONO$	80
6-10	Dinitrogen Tetroxide and Nitrogen Dioxide, N_2O_4 and NO_2	80
6-11	Dinitrogen Pentoxide, N_2O_5	83
6-12	Nitric Acid, HNO_3	83
6-13	Peroxynitric Acid, HNO_4	85
6-14	Nitrogen Trioxide, NO_3	85
6-15	Structural Correlations	86

Chapter 7	SULFUR-NITROGEN COMPOUNDS	89
7-1	Sulfur Nitrides	89
7-2	Sulfur-Nitrogen-Oxygen Compounds	91
7-3	Sulfur-Nitrogen-Halogen Compounds	92
7-4	Imides and Amides of Sulfur Oxy-acids	94
Chapter 8	PHOSPHORUS-NITROGEN COMPOUNDS	98
8-1	Phosphorus Amides and Nitrides	98
8-2	Amido Derivatives of Phosphoric Acid	99
8-3	Phosphonitrilic Compounds	101
Chapter 9	CARBON-NITROGEN COMPOUNDS	103
9-1	Cyanogen, $(\text{CN})_2$	103
9-2	Cyanide, CN^- , and Hydrogen Cyanide, HCN	104
9-3	Cyanate, OCN^-	104
9-4	Thiocyanate, SCN^-	105
9-5	Cyanamide and its Isomers	106
Chapter 10	BORON-NITROGEN COMPOUNDS	109
10-1	Boron Nitride, BN	109
10-2	The Reaction of Boron Halides with Ammonia and Amines	110
10-3	Borane Ammoniates	111
10-4	Borane-Amine Coordination Compounds	112
10-5	Borazine	113
Chapter 11	THERMODYNAMICS OF NITROGEN COMPOUNDS	115
11-1	Thermodynamic Functions at 25°	115
11-2	Bond Energies and Dissociation Energies	118
Index		121

I

The Unique Features of Nitrogen

The unique features of nitrogen chemistry may be emphasized by comparing nitrogen with the three elements that are adjacent to it in the periodic table: carbon, phosphorus, and oxygen.

1-1 COMPARISON WITH CARBON

Whereas carbon atoms readily link together to form long chains (as in hydrocarbons), very few nitrogen compounds contain chains of more than two consecutive nitrogen atoms. This striking difference between carbon and nitrogen is a manifestation of the very weak N—N single bond, which is probably a consequence of the repulsion of the lone-pair electrons on the nitrogen atoms.

In the elementary state, carbon is a giant molecule (graphite or diamond), whereas elementary nitrogen exists as a diatomic molecule. Of course, carbon cannot form a stable diatomic molecule $\text{C}\equiv\text{C}$ because of the extreme electron repulsion that would

exist in the quadruple bond. Or to put it another way, the tetrahedrally directed valences of carbon prohibit the formation of a quadruple bond.¹

The simple hydrides methane and ammonia differ enormously in their physical and chemical properties. Methane forms an unassociated, low-boiling liquid and is a rather chemically inert material. Ammonia forms an associated, relatively high-boiling liquid and is a reactive, basic material. These differences are again due to the lone pair of electrons on the nitrogen atom that causes the ammonia molecule to have an electric dipole moment in contrast to the completely symmetric methane molecule.

1-2 COMPARISON WITH PHOSPHORUS

The single-bonded structures of white and red phosphorus contrast with the triple-bonded nitrogen molecule. The difference here is probably directly related to the difference in the sizes of the atoms. The lone pair-lone pair repulsion in a P—P bond is not as important as it is in an N—N bond. And because of inadequate overlap of the appropriate *p* orbitals, the π bonds in P_2 are not as strong as the corresponding bonds in N_2 .

Nitrogen in the +5 oxidation state forms only one oxy-acid, HNO_3 . On the other hand, phosphorus forms a whole series of phosphates in which each phosphorus atom is surrounded by four oxygen atoms. Phosphorus forms the compounds PCl_5 and PF_5 and the ion PF_6^- , whereas nitrogen forms no analogous species.

These differences can largely be ascribed to the relative sizes of the phosphorus and nitrogen atoms. The nitrogen atom is apparently too small to coordinate more than three oxygen atoms or fluorine atoms. In order to maintain an octet of electrons around the nitrogen atom, we must ascribe double-bond character to the N—O bonds in HNO_3 and NO_3^- . The *3d* orbitals of phosphorus are of only slightly higher energy level than the *3s* and *3p* orbitals and are probably involved in the bonding of the phosphorus compounds mentioned above. Of course, nitrogen has no comparable *2d* orbitals available for bonding.

Phosphine, PH_3 , is a much weaker base than ammonia and has H—P—H bond angles of 93° in contrast to ammonia's H—N—H

¹ The C_2 gaseous molecule has a double bond and is extremely unstable with respect to graphite.

bond angles of $106^{\circ} 47'$. Both of these features correspond to a greater degree of *s* character in the lone pair of phosphine (and consequently more *p* character in the bonds to hydrogen), an effect which may again be ascribed to the larger size of phosphorus compared to that of nitrogen.

The four pairs of electrons (three bonding pairs and one lone pair) around the nitrogen atom in ammonia are quite crowded, and although there is appreciable repulsion between the lone pair and the bonding pairs, the H—N—H bond angle cannot decrease far below the tetrahedral value because of the repulsion between bonding pairs that sets in at lower bond angles. In phosphine, however, repulsion among the bonding pairs of electrons becomes important only at much smaller bond angles. The bond angles in phosphine, arsine, and stibene are all slightly greater than 90° and correspond to the use of practically pure *p* orbitals in bonding.

1-3 COMPARISON WITH OXYGEN

Because of its smaller size and higher nuclear charge, oxygen is more electronegative than nitrogen. Thus although water, alcohols, and ethers have two lone pairs of electrons on their oxygen atoms in contrast to the single lone pair in ammonia and amines, ammonia and amines are much stronger bases than the corresponding oxygen compounds.²

The greater electronegativity of oxygen perhaps also explains why water is a much more hydrogen-bonded liquid than is liquid ammonia. The hydrogen ion in water migrates by a very rapid mechanism involving a shift of hydrogen bonds. In ammonia, the corresponding process involves the diffusion of ammonium ions and is a much slower process.

REFERENCES

- L. Pauling, *The Nature of the Chemical Bond*, 3d ed., Cornell University Press, Ithaca, N.Y., 1960.
- C. A. Coulson, *Valence*, 2d ed., Oxford University Press, London, 1961.
- H. A. Bent, "Distribution of atomic *s* character in molecules and its chemical implications," *J. Chem. Educ.*, **37**, 616 (1960).
- R. J. Gillespie, "Bond angles and spatial correlation of electrons," *J. Am. Chem. Soc.*, **82**, 5978 (1960).

² For similar reasons the methide ion CH_3^- is a stronger base than the amide ion NH_2^- .

2

Elementary Nitrogen

2-1 SOURCES AND PREPARATION

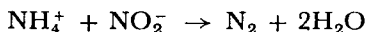
Dry air contains nitrogen to the extent of 78.09 per cent by volume. Practically all nitrogen of commerce is produced by the liquefaction and fractional distillation of air. The nitrogen in ordinary cylinders of compressed nitrogen usually has a guaranteed purity of 99.7 per cent and contains about 0.1 mole per cent of oxygen. However, specially purified nitrogen containing less than 0.0005 mole per cent of oxygen and hydrogen, less than 0.005 mole per cent of argon, and less than 0.0001 mole per cent of water is available in cylinders.

Oxygen (in small amounts) may be conveniently removed from nitrogen by passing the gas through either a tube containing copper wool heated to about 400° or a gas-washing bottle containing chromous chloride solution.¹ Residual water may be removed by passing the gas through an efficient trap cooled with

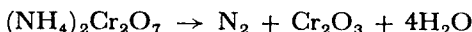
¹ When the scale letter is not supplied, a temperature should be taken as measured in degrees centigrade.

liquid nitrogen or through a tube containing a desiccant such as magnesium perchlorate or phosphorus pentoxide.

A variety of methods have been used to prepare nitrogen gas in the laboratory. Hot aqueous solutions of ammonium nitrite decompose to give nitrogen according to the reaction



Small amounts of nitric oxide and nitric acid are also formed, and they must be removed by suitable absorbents. Ammonium dichromate decomposes on heating to give nitrogen:



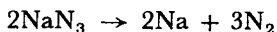
When ammonia is passed into bromine water, the principal reaction is the oxidation of ammonia to nitrogen:



Nitrogen may be prepared by the high-temperature reaction between ammonia and cupric oxide:

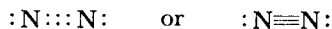


Extremely pure nitrogen may be prepared by the careful thermal decomposition of sodium azide:



2-2 BONDING

The bonding in molecular nitrogen may be satisfactorily explained in terms of the Lewis octet theory by formulas such as the following:



It is obvious that six of the valence electrons are engaged in bonding and that the other four valence electrons exist as lone pairs. A similar conclusion is reached by putting electrons into the molecular orbitals, which may be thought of as being formed from the overlap of atomic orbitals of the nitrogen atoms. There are many ways in which we may imagine these molecular orbitals being formed. Three ways are described below; each gives a satisfactory picture of the bonding in molecular nitrogen.

First, let us imagine that the *s* and three *p* orbitals of each nitrogen atom are so hybridized that all four orbitals are equivalent

and are directed toward the corners of a regular tetrahedron. If, as shown in Figure 2-1, three orbitals of one atom are made to overlap three orbitals of the other atom, three equivalent bonding molecular orbitals will form, with the lone pairs directed away from the molecule on the molecular axis.

Second, let us imagine that the s and a p orbital of each nitrogen atom are hybridized to two equivalent orbitals directed at 180° from the atom. The two remaining p orbitals will then be in a plane perpendicular to the axis of the sp hybrid orbitals. If, as shown in Figure 2-2, the atoms approach each other along an axis common to the sp hybrid orbitals, a bonding molecular orbital will form by the overlap of an sp hybrid orbital from each atom and two bonding molecular orbitals by the overlap of the p orbitals perpendicular to the molecular axis. Again the lone pairs will be directed away from the molecule that lies on the molecular axis.

Third, consider two nitrogen atoms each of which has one of its p orbitals on a common axis passing through the nuclei (see Figure 2-3). As these atoms approach one another, a σ -bonding molecular orbital will form as the result of the overlap of the two p orbitals that point toward each other. Two equivalent π -bonding molecular orbitals will form as the result of the overlap of the p orbitals that are perpendicular to the molecular axis. It will be noted that the three bonding orbitals and the two nonbonding

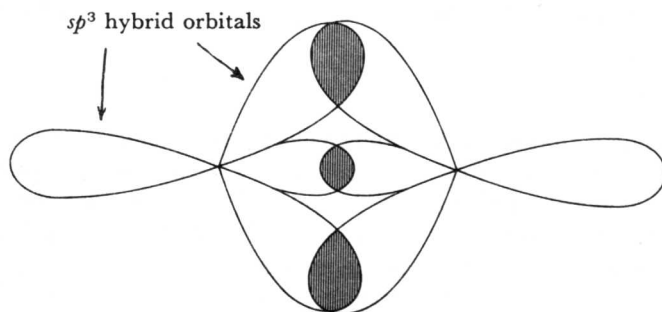


Figure 2-1 *Overlap of three pairs of sp^3 hybrid orbitals to form a triple bond. Each lobe represents an sp^3 hybrid orbital. This schematic diagram does not show the electron density of the resultant molecule, which has cylindrical symmetry.*

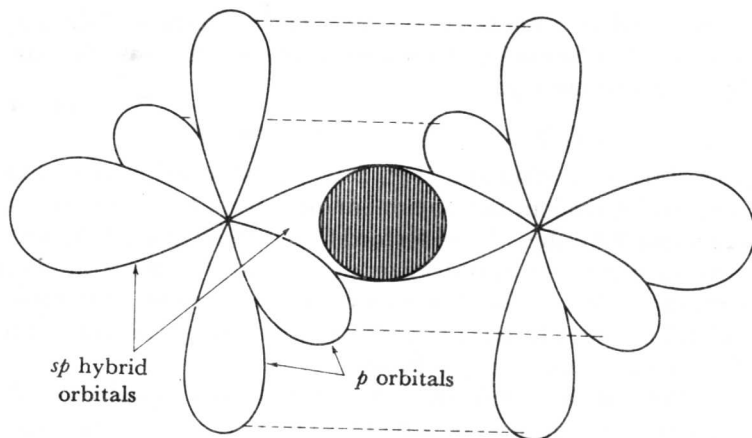


Figure 2-2 *Overlap of sp hybrid orbitals and p orbitals to form a triple bond. This schematic diagram does not show the electron density of the resultant molecule, which has cylindrical symmetry.*

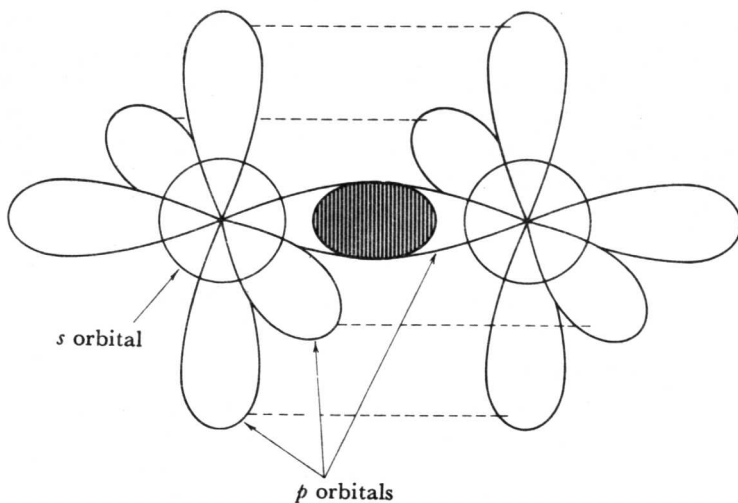


Figure 2-3 *Overlap of three pairs of p orbitals to form a triple bond. This schematic diagram does not show the electron density of the resultant molecule, which has cylindrical symmetry.*