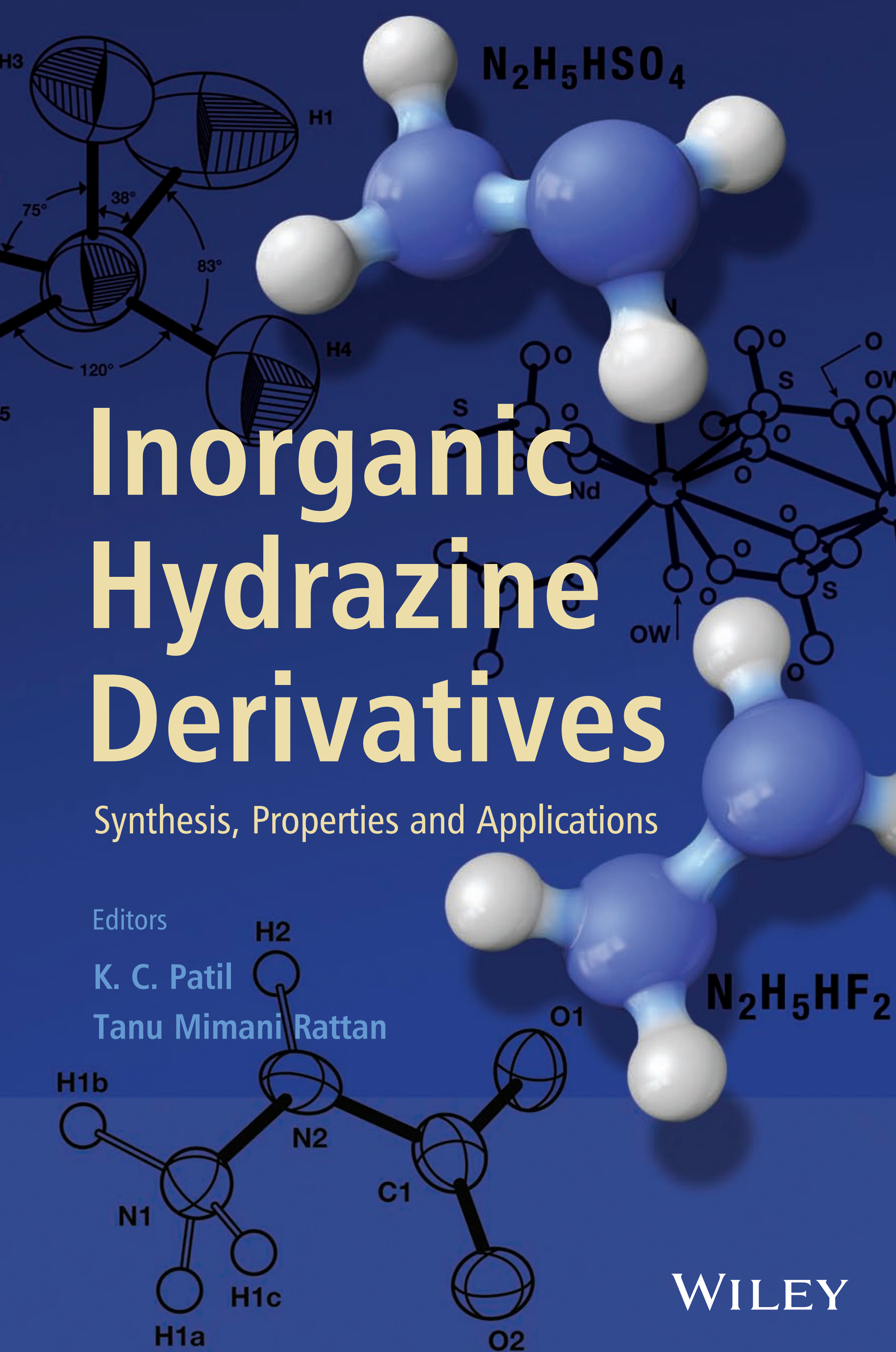

Inorganic Hydrazine Derivatives

Synthesis, Properties and Applications

Editors

K. C. Patil

Tanu Mimani Rattan

WILEY

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Synthesis, Properties and Applications

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WILEY

This edition first published 2014
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Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Inorganic hydrazine derivatives : synthesis, properties, and applications /
edited by K.C. Patil and Tanu Mimani Rattan.
pages cm
Includes index.
Includes bibliographical references.
ISBN 978-1-118-71513-0 (hardback)
1. Hydrazines. 2. Hydrazines–Industrial applications. I. Patil, K. C.,
editor of compilation. II. Rattan, Tanu Mimani, editor of compilation.
QD181.N1I57 2014
661–dc23
2013037822

A catalogue record for this book is available from the British Library.

ISBN: 9781118715130

Set in 10.5/13pt, SabonLTStd-Roman by Thomson Digital, Noida, India.

1 2014

Dedicated To
“Eckart W. Schmidt – The Hydrazine man”

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Foreword

Of the two dozen or so known binary compounds of nitrogen and hydrogen, only three are economically significant. Arranged in descending order of importance these are ammonia, hydrazine, and hydrazoic acid. The discovery of phenylhydrazine (1875) and other substituted hydrazines by Fischer preceded that of hydrazine itself by several years. Curtius first prepared hydrazine from ethyl diazoacetate following a circuitous route (1887). Serious research on the structure and reactivity of hydrazine could begin only after its ready availability was assured by Raschig's discovery of its simple and effective synthesis via oxidative coupling of ammonia (1907). A relatively weak N–N bond, two nucleophilic nitrogen sites, multiple replaceable hydrogen atoms, variable reducing power, endothermicity, and high heat of combustion are among the factors that have added unique features to the chemistry of hydrazine. These in turn have prompted extensive uses of hydrazine and its derivatives in the chemical industry, encompassing polymers, agriculture, pharmaceuticals, explosives, water-treatment, and more. Hydrazine and its derivatives also feature in space missions, where the versatility and reliability of hydrazine-powered propellant systems have performed a signal role.

An account of the state of hydrazine chemistry preceding the middle of the last century was chronicled by Audrieth and Ogg in their book *The Chemistry of Hydrazine* (1951). Nearly three decades later, Schmidt's compendium *Hydrazine and its Derivatives, Preparation, Properties, Applications* appeared in 1984. The explosion in hydrazine literature (4400 references) was apparent and in the second edition (2001) of this authoritative book the number of references nearly doubled! Hydrazine and its derivatives very much remains a living arena for continued scrutiny and practical use.

Patil and his students have been intimately associated with several facets of hydrazine chemistry for many years at the Indian Institute of Science, Bangalore. They have enriched the basic chemistry by developing newer methods of preparing hydrazinium salts and by exploring the synthesis and structure of hydrazinium complexes of metal salts. They were also deeply involved with applied aspects such as in the development of energetic oxidizers for solid propellants and of detonators, some of which have commercial success stories to tell. The group also succeeded in preparing technologically important transition metal oxide nanomaterials utilizing combustible carboxylic metal hydrazine salts as starting materials.

The rich contributions of the group to both basic and applied inorganic chemistry of hydrazine have been documented in the literature over the years. Patil and Rattan have now carried out a commendable service by organizing the material into a logical and connected account laid out against the broader background of hydrazine chemistry. The outcome is the present monograph, which has six chapters and is appropriately titled *Inorganic Hydrazine Derivatives: Synthesis, Properties and Applications*. The chapters are divided into sections and subsections for both basic and applied activities and include recent work on these topics by other groups. I expect this book to become a must for all those with direct interest in hydrazine chemistry and technology. It should also arouse considerable general interest in the inorganic chemistry and material science communities. I feel very pleased to write this Foreword for a work that highlights the noteworthy contributions to the pure and applied chemistry of hydrazine derivatives from India in the last few decades. On visits to Bangalore I had the opportunity to watch Patil *et al.* making progress in silent dedication. It is now time for me to congratulate them as I browse through their text.

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Indian Association for the Cultivation of Science
Kolkata, India
August 2013

Preface

The chemistry of hydrazine and its derivatives continues to be of interest to chemists, material scientists, and engineers due to their applications in propellants, explosives, polymers, pharmaceuticals, medical, and agricultural fields. Although there are several reviews on this subject there are very few books devoted to the chemistry of hydrazine. The latest voluminous work on hydrazine authored by Eckart W. Schmidt – the hydrazine man – was published over a decade ago in 2001. It contains a wealth of information, citing nearly 8400 references, signifying the importance of hydrazine and its derivatives. The research work of the authors has been cited in this book.

The present monograph, *Inorganic Hydrazine Derivatives: Synthesis, Properties and Applications*, is a compendium of the research work carried out during the last four decades by the authors at the Indian Institute of Science, Bangalore. An attempt has been made to present the work on inorganic hydrazine derivatives over six chapters. Details of the synthesis, spectra, thermal analysis, crystal structure, and applications of inorganic derivatives of hydrazine such as hydrazine salts, metal hydrazines, metal hydrazine carboxylates, and hydrazinium metal complexes are expounded in a systematic manner. Recent contributions by other groups working in similar areas have also been examined. The monograph also highlights current developments and applications of inorganic hydrazine derivatives, including the synthesis of nanostructured materials.

Chapter 1 – Hydrazine and its Inorganic Derivatives briefly describes the chemistry of hydrazine, its physical and chemical properties. A clear distinction is made between hydrazine and hydrazine hydrate in terms of structure and properties. Since there is hardly any difference in the chemical properties of the two, a case is made for the use of hydrazine hydrate instead of the hazardous and toxic anhydrous hydrazine. A brief literature survey on the synthesis and crystal structure of various hydrazine salts and metal hydrazine complexes is presented. Various thermoanalytical and spectroscopic techniques used in the characterization of hydrazine compounds and metal complexes are discussed.

Chapter 2 – Hydrazine Salts discusses the synthesis and characterization of the inorganic salts of hydrazine. A novel and simple method of preparing hydrazinium salts by the heterogeneous reaction of solid ammonium salts with hydrazine hydrate is presented. The preparation and characterization of numerous N_2H_5A salts, where $A = $ halide, NO_3^-, ClO_4^-, N_3^-, SCN^-, acetate, and so on, are profiled. The formation of $N_2H_5HF_2$ and $N_2H_5HSO_4$ by this method is reported for the first time. These salts are characterized by infrared spectroscopy and differential thermal analysis (DTA), and their properties compared with those of $N_2H_6F_2$ and $N_2H_6SO_4$, respectively. Interestingly, few hydrazine salts form hydrates: for example, $N_2H_5ClO_4{\cdot}0.5H_2O$ and $N_2H_6X{\cdot}2H_2O$, $X = ClO_4^-$. Infrared spectroscopy, thermal analysis, and conductivity measurements show that the water in these compounds is partially present as oxonium ion (H_3O^+) and is involved in hydrogen bonding with N_2H_4.

Chapter 3 – Metal Hydrazines presents the synthesis and properties of metal hydrazine complexes. These compounds are of interest from the point of view of bonding, structure, and reactivity. The hydrazine molecule with its two free electron pairs can coordinate to a metal ion either as a monodentate or bridged bidentate ligand. Several metal hydrazine complexes containing different anions, such as oxalate, perchlorate, nitrate and azide, sulfate, sulfite, hydrazine carboxylate, and so on, are prepared and investigated. In all these complexes hydrazine is usually present as a bridged bidentate and, occasionally, as a monodentate ligand. The thermal reactivity of these metal hydrazines varies from explosion → deflagration → decomposition, depending upon the anion. Transition metal perchlorate, nitrate, and azide hydrazines are primary high energy materials (HEMs). Non-transition metal hydrazines of Li, Mg, and Al perchlorate, nitrate and azide, and so on, and transition metal hydrazine complexes of oxalate, sulfite, and hydrazine carboxylate, deflagrate. The rest simply decompose, with the loss of hydrazine.

Chapter 4 – Metal Hydrazine Carboxylates gives an account of the preparation of various metal hydrazine carboxylate complexes such as $M(N_2H_3COO)_2{\cdot}xH_2O$, $M = $ Ca, Mg, Mn, Cu, and Cr; $Ln(N_2H_3COO)_3{\cdot}3H_2O$, $Ln = $ rare earth ion; $M(N_2H_3COO)_2(N_2H_4)_2$ and $N_2H_5M(N_2H_3COO)_3{\cdot}H_2O$, $M = $ Mn, Fe, Co, Ni, and Zn. These complexes are investigated by infrared spectroscopy and thermal analysis. The characteristic N–N stretching frequency is used to distinguish between monodentate N_2H_4 (ν_{N-N} 930 cm^{-1}), ionic $N_2H_5^+$ (ν_{N-N} 965 cm^{-1}), and $N_2H_3COO^-$ (ν_{N-N} 990–1005 cm^{-1}) species. Transition metal hydrazine carboxylates decompose in air at low temperatures (75–200 °C) to yield nanosize oxide materials. The decomposition is autocatalytic; once initiated it is accompanied by swelling due to the evolution of large amounts of gases like NH_3, H_2O, H_2, and CO_2.

Chapter 5 – Hydrazinium Metal Complexes highlights the coordinating ability of the hydrazinium cation, $N_2H_5^+$. The synthesis and structure of several hydrazinium metal sulfate and oxalate complexes are presented. Single-crystal structures are showcased of $N_2H_5M(SO_4)_2$ where, M = Mn, Fe, and Cd; $N_2H_5Nd(SO_4)_2{\cdot}H_2O$, $(N_2H_5)_2Cu(C_2O_4)_5{\cdot}2H_2O$, $(N_2H_5)_6(UO_2)_2(C_2O_4)_5{\cdot}2H_2O$, $(N_2H_5)_2(UO_2)_2(C_2O_4)_2{\cdot}H_2O$, and so on. Interestingly, $N_2H_5^+$ ion coordinates to the metal ion in sulfate complexes but is outside the coordination sphere of the metal ion in oxalate complexes.

Several hydrazinium metal chloride complexes $(N_2H_5)_2MCl_4{\cdot}2H_2O$, where M = Fe, Cu, Co, Ni, Pt, and Pd, $N_2H_5CuCl_3$, $(N_2H_5)_2ZnCl_4$, $(N_2H_5)_3MnCl_5$, and $(N_2H_5)_4FeCl_6$ have been synthesized and investigated for their crystal structure. Single-crystal structures presented are of $(N_2H_5)_2MCl_4{\cdot}2H_2O$, M = Fe and Pt, $(N_2H_5)_3MnCl_5$, and so on. In all these complexes $N_2H_5^+$ ions are coordinated to the metal ion. Hydrazinium metal thiocyanates $(N_2H_5)M(NCS)_4{\cdot}2H_2O$, where M = Co and Ni, have been prepared and the single-crystal structure of the cobalt compound is shown.

Chapter 6 – Applications of Inorganic Hydrazine Derivatives summarizes the uses of inorganic hydrazine derivatives. Some interesting properties and reactions of hydrazine salts have emerged from these investigations. These include flame retardancy of hydrazinium phosphates, solid-state rearrangement of hydrazinium thiocyanate to thiosemicarbazide ($N_2H_5SCN \rightarrow N_2H_5CSNH_2$), and the use of N_2H_5SCN as an analytical reagent for the quantitative estimation of copper. Hydrazinium hydrazinecarboxylate formed by the reaction of commercial ammonium carbonate with hydrazine hydrate reacts with acetonitrile at room temperature to give a triazole compound. Triazoles find applications in a wide variety of agrochemicals and medicine. The perchlorate, nitrate, and azide salts of hydrazine, $N_2H_5NO_3$, $N_2H_5N_3$, $N_2H_5ClO_4{\cdot}0.5H_2O$, $N_2H_6(ClO_4)_2{\cdot}2H_2O$, and so on, are potentially energetic oxidizers and are being considered for use in solid propellant compositions. However, they are highly hygroscopic and incompatible with conventional polymeric fuels and in solid propellants. These problems have been overcome successfully by complexing both hydrazine perchlorates with ammonia as well as by doping with Mg^{2+} ions. Transition metal hydrazines containing anions like nitrate, azide, and perchlorates have been investigated as detonators. Surprisingly, the thermolysis of $Mg(N_3)_2(N_2H_4)_2$ gives a blue colored residue that shows strong IR absorption at $2100\,cm^{-1}$, which is characteristic of molecular nitrogen.

The deflagrating nature of metal hydrazines is used in the preparation of ferrites and cobaltites. Commonly used recording material like γ-Fe_2O_3 and Co-doped γ-Fe_2O_3, is prepared by the thermal decomposition of iron hydrazine carboxylates in a single step. Similarly, nano-size ferrites (MFe_2O_4, $Ni_xZn_{1-x}Fe_2O_4$, and $Mn_xZn_{1-x}Fe_2O_4$) and cobaltites (MCo_2O_4) are obtained at very low temperatures (300 °C) by the thermal decomposition/combustion in air of solid solution precursors of the type $N_2H_5M_{1/3}Fe_{2/3}(N_2H_3COO)_3{\cdot}H_2O$ and $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3{\cdot}H_2O$, where M = Mg, Mn, Fe, Co, Ni, and Zn.

Finally, the work carried out and presented in this monograph has been quite exciting, creative, and rewarding to the authors. It is hoped that it will inspire future researchers and entrepreneurs working in academic institutes and defense and space research laboratories.

Acknowledgments

We gratefully acknowledge the collaboration of the following colleagues: Professors C.C. Patel, V.R. Pai Vernekar, S.R. Jain, H. Manohar, and K. Kishore and Drs. Nethaji, Damodar Pujari, and I.I. Mathews (Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore), and Professor Zhu Shanguan (Nanjing University of Science and Technology, China).

We also acknowledge the valuable research contributions of former PhD students: Drs Jayant Budukuley, R. Soundara Rajan, M. Ramanath, J. J. Vittal, C. Nesmani, D. Gajapathy, S. Govindrajan, P. Ravindranathan, N.R.S. Kumar, M.M.A. Sekhar, S. Ekambaram, N. Arul Das, S.T. Aruna, S. Shanmugaraju, Arun Kumar Bar, and Mr. G.V. Mahesh.

We are grateful to Professor A.G. Samuelson, Chairman, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore for the support and co-operation extended. We thank Professor K. Venkataramaniah and Dr Siva Sankar Sai of Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam for their encouragement.

Our sincere thanks are to Sanjay Rattan for editing the manuscript. Finally, we are grateful to Professor Animesh Chakravorty for readily agreeing to write the Foreword to our book.

K. C. Patil

Tanu Mimani Rattan

1

Hydrazine and Its Inorganic Derivatives

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1.1 INTRODUCTION

The chemistry of hydrazine (N_2H_4) acquires significance due to the presence of two free electron pairs and four substitutable hydrogen atoms, in addition to a potent N–N bond (Figure 1.1). Hydrazine is an endothermic molecule ($\Delta H_f = 55.63\,\text{kJ mol}^{-1}$) with nitrogen in the −2 valence state. Nitrogen's natural tendency is toward the attainment of a zero valence state as in N_2 molecule ($N \equiv N$). As a result, it gives off nearly six times the energy as that stored in the N–N bond. A tremendous amount of energy (ca $-622\,\text{kJ mol}^{-1}$) is released during the decomposition of N_2H_4 to N_2. This important energetic property of hydrazine was first recognized by the Germans during World War II when they used it as a rocket fuel. Since then hydrazine has been extensively used as a fuel in rocket motors because of its suitable physical properties, endothermicity,

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Inorganic Hydrazine Derivatives: Synthesis, Properties and Applications, First Edition.
Edited by K. C. Patil and Tanu Mimani Rattan.

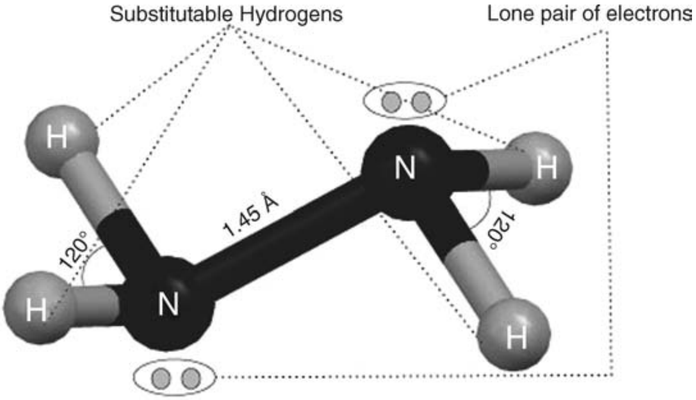

Figure 1.1 Structure of the hydrazine molecule.

and extremely high reactivity with various oxidizers. The ignition of anhydrous hydrazine is achieved simply by passing it through a catalyst bed, producing completely gaseous products, making it an excellent fuel for monopropellant rockets. The other advantage of using hydrazine and its derivatives [e.g., monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH)] as propellants stems from the fact that they ignite instantaneously. They are hypergolic on coming in contact with various liquid oxidizers such as HNO_3, N_2O_4, and so on. However, interest in hydrazine and its derivatives has now extended to applications in agriculture (pesticides and fungicides), blowing agents, boiler feed water treatment, pharmaceuticals, and in synthesizing nanostructures. The consumption of hydrazine produced for these latter applications far surpasses that used as rocket propellant.

1.1.1 Properties of Hydrazine

Hydrazine is a strong base, although slightly weaker than ammonia as evident from the respective dissociation constants (k_1 and k_2) in aqueous solution (1.1) and (1.2). It is a much stronger nucleophile than ammonia. The second ionization constant shown in (1.2) being very small, suggests that the $N_2H_6^{2+}$ cation exists at an extremely low pH:

$$N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-; k_1 = 8.5 \times 10^{-7} \tag{1.1}$$

$$N_2H_5^+ + H_2O \rightarrow N_2H_6^{2+} + OH^-; k_2 = 8.9 \times 10^{-16} \tag{1.2}$$

In aqueous solutions hydrazine largely exists as the hydrazinium cation ($N_2H_5^+$) while the hydrazonium cation ($N_2H_6^{2+}$) exists only in strong acidic conditions. $N_2H_6^{2+}$ ion reacts completely with solvent water to give back $N_2H_5^+$ in accordance with the equation:

$$N_2H_6^{2+} + H_2O \rightarrow N_2H_5^+ + H_3O^+ \qquad (1.3)$$

This suggests that the $N_2H_6^{2+}$ ion does not readily exist in aqueous solutions.

1.1.1.1 Redox Properties

Hydrazine has two lone pairs of electrons on its nitrogen atoms. This makes it a strong reducing agent since it can donate all four electrons. The hydrazinium cation ($N_2H_5^+$) also has a lone pair of electrons on its nitrogen atom and therefore acts as a reducing agent. However, as the hydrazonium cation ($N_2H_6^{2+}$) exists as hydrazinium cation in solution, it also acts as a good reducing agent.

The standard redox potentials of hydrazine and its cation are given below. Reaction 1.4 represents the half-reaction of the molecule as a reductant. It is much less of a reducer in acid medium, where it exists as the hydrazinium cation. As the redox potential (E_0) of hydrazine decreases by nearly 1 V, as shown by (1.5), it is a powerful reducing agent in basic solutions rather than in acidic solutions [1]:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \quad E_0 = +1.16\,V \qquad (1.4)$$

$$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^- \quad E_0 = +0.23\,V \qquad (1.5)$$

Nonetheless, hydrazine, like hydrogen peroxide, can also be an oxidizing agent (1.5) as well as reducing agent (1.4). It can therefore undergo redox reactions that are essentially electron-transfer reactions:

$$N_2H_4 + 2H_2O + 2e^- \rightarrow 2OH^- + 2NH_3 \quad E_0 = +0.1\,V \qquad (1.6)$$

Although reactions with hydrazine as an oxidant are possible, these are less frequent. Hydrazine is basically a strong reducing agent and as such reduces many ions to lower oxidation states or even to the bare metal and even beyond, to the hydride. The commonly encountered redox reactions of hydrazine are its autoxidation or atmospheric decay, oxidation in solution, and electro-oxidation. These redox reactions are governed by their reduction potentials and are responsible for its applications in fuel cells, electroless plating, or photographic processes.