

# CHEMISTRY OF FREE ATOMS AND PARTICLES

Kenneth J. Klabunde

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## Preface

Studies of the chemical reactions of high-temperature species began in the 1920s and 1930s with the investigations of gas-phase sodium organohalide flames. In the early 1960s a new era opened with the studies of  $C_1$ ,  $C_2$ , and  $C_3$  as *macroscale* ( $> 50$  mg) synthons. The carbon vapor work represented the first examples of how new and interesting molecules could be prepared incorporating the high-temperature species. Also in the 1960s, *microscale* ( $< 50$  mg) matrix isolation spectroscopy techniques for investigating "frozen" high-temperature species were developed. New chemistry, but not new syntheses, has resulted.

In the 1970s the field of "metal atom" or "vapor synthesis" chemistry has grown tremendously. Hundreds of macroscale and microscale studies on the chemistry of reactive high-temperature atoms and particles have appeared. And, although there have been a variety of reviews published, there is a definite need for a complete work with proper organization. This book attempts to fill such a need.

The coverage of this volume is as follows. First, metal atoms and metallic molecules or fragments are considered. The chemistry of  $H\cdot$ ,  $O\cdot$ ,  $S\cdot$ , organic free radicals and carbenes, and halogen atoms is not covered. A separate volume would be needed for  $H\cdot$  and  $O\cdot$  chemistry alone; and these do not fit particularly well into the present work whose main theme is the use of high-temperature species to prepare novel molecules, on either a macro- or a microscale. Essentially, the entire remaining portions of the periodic chart are covered. This includes all the available metals, as well as B and C. Then, the literature is covered exhaustively (or nearly so) up through 1978 and the early part of 1979. Vaporization properties of the elements, oxides, sulfides, etc., are covered through 1977. A great deal of original literature is referenced regarding vaporization properties and vapor compositions of various materials.

A variety of needs surfaced as the literature search was made. For example, very little is known about vapor compositions for many elements and compounds at high temperature. This is especially true for "free vaporizations" from a normal surface (as opposed to Knudsen cell

studies). Also, there is a great need for microscale studies for gaining mechanistic information about macroscale syntheses using high-temperature species.

Grateful acknowledgment must be made at this time to the author's students who carried out a great deal of the work described herein. In addition to this, they provided help in organization and reading of the manuscripts and continued their work quite independently as much of the author's time was expended on the manuscript. These students are James Y. F. Low, Curt White, Howard F. Efner, John S. Roberts, Bruce B. Anderson, Thomas Murdock, William Kennelly, Thomas Groshens, Richard Kaba, Steve Davis, Dan Ralston, Russell Morris, William Martin, Robert Gastinger, and Robert Zoellner. The author also most gratefully acknowledges the agencies that have supported much of his research, especially the National Science Foundation, but also Research Corporation, the Petroleum Research Fund, and the Department of Energy.

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*To Sara*

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# CHAPTER 1

## Introduction

The book deals with the chemistry of free atoms and coordination-deficient molecules. Included are such species as free metal atoms (e.g., V or Ni atoms), molecular salts (e.g.,  $\text{MgF}_2$  or  $\text{NiCl}_2$ ), and molecular subhalides, oxides, and sulfides (e.g., BF or CS). Generally, high temperature is needed to generate these particles, so the chemistry investigated is necessarily that of high-temperature species. However, the reaction chemistries of these high-temperature atoms and molecules are usually studied at extremely low temperatures.

How many reactive high-temperature particles exist? Counting the atoms of the elements, clearly more than 100. If we then narrowly define a reactive high-temperature molecule (or particle) as something that possesses no more than three atoms (in a few cases, four and five atoms must be considered) and that is coordination or bond deficient, we must in the first analysis consider diatomics and triatomics of all the elements. The number of possible reactive particles becomes astonishingly high. Species such as  $\text{Mn}_2$ ,  $\text{V}_3$ ,  $\text{MgO}$ ,  $\text{CaCl}$ ,  $\text{BCl}$ , and CS are typical examples. Even in the second analysis, after we consider experimental feasibility, the number of reactive particles studied or to be studied is very large indeed.

The chemistry of these reactive species is a rather young field in that experimental advances in vacuum technology, high-temperature ceramics, and cryochemical techniques have been absolutely necessary. These advancements have only come in recent times, and have thus allowed a major new chemical research field to develop.

### I. Extremes in Temperatures, Energies, and Chemistry

In order to generate free atoms of most of the elements, a great deal of energy is required. Simple vaporization of nickel for example requires at least 100 kcal/mole. This energy is required to break the neighboring Ni—Ni bonds and allow Ni atoms to escape, and this requires temperatures in excess of  $1400^\circ\text{C}$  under vacuum. Many other elements require much larger



energies, for example W or Pt. Figure 1-1 shows a periodic chart of the elements and the approximate energies required for their vaporization. Further vaporization data and information can be found in the respective chapters covering the element in question.

A free atom or particle is extremely reactive because it carries a high kinetic energy and orbitals poised for reaction without steric restrictions. Therefore, a high-temperature particle will usually react at very *low* temperature with a substrate of interest. Therefore, temperatures low enough to moderate reaction rates are often desired, and these temperatures are usually in the  $-50$  to  $-200^{\circ}\text{C}$  range. Low temperatures also serve to hold down the vapor pressures for incoming reactants, which is a necessity, since almost all reactants of interest must not be allowed to contact the hot source generating the high-temperature species. A variety of experimental techniques have been devised to study the "chemistry of high-temperature species at low temperature"; they are outlined in Table 1-1 with page references to

TABLE 1-1

Techniques Employed for the Study of the Chemistry of High-Temperature Species

Technique	Temperatures involved ( $^{\circ}\text{C}$ )	Comments	Page
(1) Diffusion flame	100–500	Gas-phase reactions	9
(2) Life period	100–500	Gas-phase reactions	9
(3) Gas phase flow (macroscale)	200–400	Gas-phase reactions	10
(4) Rotating cryostat (microscale)	500–1500	Cocondensation reactions	10
(5) Stationary codeposition (microscale)	500–2000	Cocodensation reactions	10
(6) Stationary codeposition (macroscale)	300–2000	Cocondensation reactions	35
(7) Rotating codeposition (macroscale)	500–2000	Cocondensation reactions	62
(8) Rotating solution	300–1500	Solution-phase reactions	84
(9) Resistive heating vaporization	25–2000	Used in methods 1–8 above	a
(10) Electron beam vaporization	1000–2500	Used in methods 6 and 7 above	51, 52
(11) Laser vaporization	1000–2000	Used in method 6 above	53, 54
(12) High-temperature disproportionation processes	800–1500	Used for preparation of $\text{BF}$ and $\text{SiF}_2$ for method 6 above	172
(13) Discharge processes		Used for preparation of $\text{CS}$ for method 6 above	191
(14) Electric arc processes		Used for graphite vaporization	179
(15) High-temperature fast flow reactor	25–1400	Gas-phase reactions	156

<sup>a</sup> Ref. 6.

TABLE 1-2

## High-temperature Species of Greatest Interest to Date

Species	Method of generation (from Table 1-1)
Chapter 2	
Li, Na, K, Rb, Cs atoms	1, 2, 3, 4, 5, 6, 7, 8, 9
LiF, NaF, KF, RbF, CsF vapors	5, 9
LiCl, NaCl, KCl, RbCl, CsCl vapors	5, 9
LiBr, NaBr vapors	5, 9
Chapter 3	
Be, Mg, Ca, Sr, Ba atoms	5, 6, 9
BeF <sub>2</sub> , BeCl <sub>2</sub> , BeBr <sub>2</sub> vapors	5, 9
MgF <sub>2</sub> , MgCl <sub>2</sub> , MgBr <sub>2</sub> vapors	5, 9
CaF <sub>2</sub> vapors	5, 9
SrF <sub>2</sub> vapors	5, 9
BaF <sub>2</sub>	5, 9
Chapter 4	
Ti, V, Cr, Mn atoms	5, 6, 7, 9, 10, 11
Zr, Nb, Mo atoms	5, 6, 7, 9, 10, 11
Hf, Ta, W, Re atoms	5, 6, 7, 9, 10, 11
Chapter 5	
Fe, Co, Ni atoms	5, 6, 7, 8, 9, 10, 11
Pd, Pt atoms	5, 6, 7, 8, 9, 10, 11
CoF <sub>2</sub> , NiF <sub>2</sub> vapors	6, 9
NiCl <sub>2</sub> vapors	6, 9
NiBr <sub>2</sub> vapors	6, 9
Chapter 6	
Cu, Zn atoms	5, 6, 7, 8, 9
Ag, Cd atoms	5, 6, 7, 8, 9
Au atoms	5, 6, 7, 8, 9
CuF <sub>2</sub> , CuCl vapors	6, 9
Chapter 7	
B, Al, Ga, In atoms	5, 6, 7, 9, 11, 12
BF, AlF	6, 12
BCl, AlCl	6, 12
Chapter 8	
C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> vapors	6, 9, 11, 14
Si, Ge, Sn, Pb atoms	5, 6, 9, 10
Carbenes (not included)	
CS	6, 13
SiF <sub>2</sub> , SiCl <sub>2</sub>	6, 12
Chapter 9	
Se, Te vapors	6, 9
Chapter 10	
Pr, Nd, Sm, Eu, Dy, Ho, Er atoms	6, 9

detailed descriptions throughout this book. Excellent earlier reviews<sup>1-6</sup> are helpful in this area, especially a recent article by Timms.<sup>4</sup>

Studies on the chemistry of the high-temperature species has indicated that a wealth of new reactions and products are available through such pursuits, and that a wide variety of studies await us. Thus, each high-temperature species examined exhibits its own rich and varied chemistry.

Table 1-2 lists the atoms and particles that have been seriously investigated and that are covered in this book. Other species that obviously await study are included throughout the book, to the extent that methods for their generation (usually vaporization properties) are included. The only limitations imposed are that usually only species of one, two, or three atoms are included, and only metal atoms, metal halides or subhalides, metal oxides or suboxides, or metal sulfides or subsulfides (boron and carbon are included). In a practical sense, these limitations on coverage are not detrimental since essentially all of the species that have been studied or that appear experimentally feasible fall into these categories.

## II. Organization of the Book

This book is organized on the basis of the Periodic Chart. Each group of elements is separated into a discussion of first the free atoms, followed by a discussion of reactive molecular forms of metal halides, oxides, and sulfides. These sections are further broken down into subsections on "Occurrence, Properties, and Techniques" followed by "Chemistry." This organizational pattern is shown in the Table of Contents. The "Chemistry" sections are further divided into several of the following headings, shown below with explanation and examples. If specific headings are not applicable to a certain group of high temperature species, then that heading is not included in that chapter, e.g., if no Oxidative Addition Processes were found for Alkali Metal Atoms, then that heading is not included, or a brief statement about the absence of work in the area is made.

## III. Chemistry

### A. Abstraction Processes

A fragment of a molecule is removed by the reactive species in question:



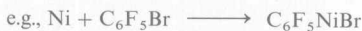
### B. Electron-Transfer Processes

A nearly complete transfer of an electron, generally from the reactive species to the substrate, takes place:



### C. Oxidative Addition Processes

An oxidative insertion of the reactive species into a  $\sigma$ -bond of the substrate takes place:



### D. Simple Orbital Mixing Processes

A  $\pi$ - or  $\sigma$ -complex is formed by mixing of  $\pi$ - or nonbonding electrons with the available orbitals of the metal atom or other reactive species. No  $\sigma$ -bonds are made or broken in the substrate:



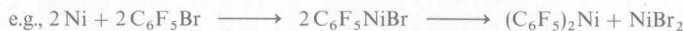
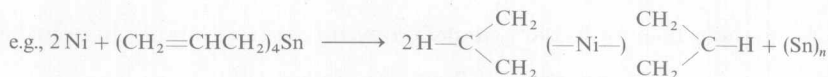
### E. Substitution Processes

A high-temperature species displaces a fragment of a substrate molecule. Usually two high-temperature species are required for this to occur:



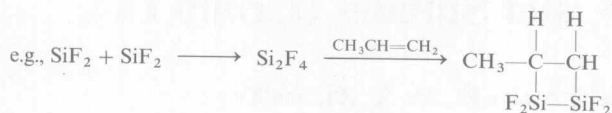
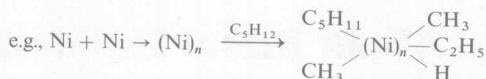
### F. Disproportionation and Ligand Transfer Processes

Groups attached to the substrate or an intermediate product are transferred to the reactive species in question:



### G. Cluster Formation Processes

The reactive species in question begins re-forming bonds with itself, but only small clusters form, not bulk material, since the small clusters react in their own way:



### References

1. P. L. Timms, *Adv. Inorg. Chem. Radiochem.* **14**, 121 (1972).
2. P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Acc. Chem. Res.* **6**, 97 (1973).
3. K. J. Klabunde, *Acc. Chem. Res.* **8**, 393 (1975).
4. P. L. Timms, in "Cryochemistry", (M. Moskovits and G. Ozin, ed.), p. 61. Wiley (Interscience), New York, 1976.
5. M. Moskovits and G. Ozin, in "Cryochemistry", (M. Moskovits and G. Ozin, eds.), p. 9. Wiley (Interscience), New York, 1976.
6. K. J. Klabunde, in "Reactive Intermediates", (R. A. Abramovitch, ed.), Plenum, New York, 1979.

## CHAPTER 2

# Alkali Metals and Alkali Metal Halides, Oxides, and Sulfides (Group IA)

### I. Alkali Metal Atoms Li, Na, K, Rb, and Cs

#### A. Occurrence, Properties, and Techniques

The natural occurrence of these vapors in the atmosphere, in flames, and in stars is intriguing. There are numerous reports of Li, Na, and K vapor in the twilight sky<sup>1,1a</sup> or twilight airglow (Li 6707 Å absorption, Na 5890 Å, K 7665 Å and 7699 Å). These atoms appear to be responsible for some of the beautiful colors observed in twilight airglow from the upper atmosphere. Donahue<sup>2</sup> has spectroscopically measured the Li atom/Na atom ratio in the upper atmosphere; he has discussed their atmospheric origin in detail and favors a marine origin, based on the ratios of Li/Na in seawater as compared with the Li/Na ratio in the upper atmosphere. Similarly, Lytle and Hunten<sup>2a</sup> have measured the Na/K ratio in the upper atmosphere at 30/1, which compares with 47/1 in seawater, and has concluded that the source of Na and K in the upper atmosphere is marine. However, both of these studies, especially the Li/Na study, were disputed and later work seems strongly to indicate an extraterrestrial source for Li and Na in the upper atmosphere. Thus, Kvifte<sup>1a</sup> found a Na/K ratio of 50/1 at 85–130 km and believes meteorites are the source. Gadsden and Salmon<sup>1</sup> made absolute measurements of Li and found  $3 \times 10^8$  atoms/cm<sup>3</sup> at one level in the upper atmosphere. Ghosh<sup>3</sup> found 900 atoms Na/cm<sup>3</sup> at 93 km and calculated that about 550 Na atoms/cm<sup>3</sup>/sec are deposited extraterrestrially in the upper atmosphere.

So what is the source of Li, Na, and K in the upper atmosphere, marine or extraterrestrial? There are a number of authors who now believe neither of these sources can satisfactorily explain recent data. At 80–90 km over a Pacific island, Delannoy<sup>4</sup> measured Li/Na ratios of  $7 \times 10^{-4}$  to  $8 \times 10^{-3}$  and attributed the origin to meteorites and thermonuclear explosions in the upper atmosphere over the Pacific. And indeed, Gadsden<sup>5</sup> found Li/Na ratios of 1.5 and 1.1 shortly after two such explosions. Apparently, a large amount of Li was generated in the upper atmosphere by these blasts.



TABLE 2-1

Vaporization Data for Alkali Metals

Element	mp (°C)	bp (°C)	Vap temp <sup>a</sup> under vac (°C)	Vap method <sup>b</sup>	Vapor composition	References
Li	180	1347	535	Resistive heating of crucibles or Knudsen cell	Li	8c,d
Na	98	883	289	Resistive heating of crucibles or Knudsen cell	Na	8c,d
K	64	774	208	Resistive heating of crucibles or Knudsen cell	K, K <sub>2</sub> (small)	8a–d
Rb	39	688	173	Resistive heating of crucibles or Knudsen cell	Rb	8c,d
Cs	28	678	145	Resistive heating of crucibles or Knudsen cell	Cs	8c,d

<sup>a</sup> Vapor pressure of the metal is approximately 10  $\mu$ m at this temperature.<sup>b</sup> Stainless steel crucibles, Al<sub>2</sub>O<sub>3</sub> crucibles, and Knudsen cell have all been used satisfactorily.

Alkali metal atoms have also been observed in abundance in stars,<sup>6,6a</sup> star dwarfs,<sup>6a</sup> and flames.<sup>7</sup> Actually, the spectral lines for Li and Na in flames can be used to determine flame temperature.<sup>7</sup>

In the laboratory, alkali metal atoms are readily prepared by thermal vaporization of elements, yielding mainly monoatomic species.<sup>8</sup> However, significant portions of M<sub>2</sub> have been detected, for example 5% K<sub>2</sub> in K vapor at 935°C.<sup>8a,b</sup> Mixed dimers can also be detected spectroscopically when alkali metal alloys are vaporized.<sup>8a</sup> Table 2-1<sup>8a–8d</sup> summarizes some of the vaporization data for the alkali metals.

The vaporizations can be readily carried out in stainless steel crucibles or Al<sub>2</sub>O<sub>3</sub>–W crucibles by resistive heating methods. Therefore, the production and study of these atoms is experimentally trivial, and they can be conveniently produced even at pressures of several torr. Accordingly, studies have been carried out in flow systems as well as in high vacuum. These techniques are now described.

#### 1. DIFFUSION FLAME METHOD AND LIFE-PERIOD METHOD<sup>9–10</sup> (MACROSCALE)

Hot liquid Na (about 300°C) can be slowly vaporized by passing an inert carrier gas over it and transporting the Na vapor to a spray nozzle. The Na