

J. R. Blackborow D. Young

Metal Vapour Synthesis in Organometallic Chemistry



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With 36 Figures and 32 Tables



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Reactivity and Structure Concepts in Organic Chemistry

Volume 9

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For Hilary and La Tendre Poulet

Preface

Metal Vapour Synthesis (MVS) can be defined as; "The use in synthesis of high temperature gaseous species such as metal atoms by their reactions with themselves or other materials in a condensed phase." This short book, covering the literature up to the middle of 1979, describes MVS in organic chemistry; i.e. the reactions of metal atoms with various, predominantly organic, substrates in the synthesis and reactivity studies of organic and organometallic compounds. In order to effectively describe all the underlying principles and to present a coesive picture of pertinent metal atom processes in condensed organic phases, some inorganic substrates such as rare gases, dinitrogen, dioxygen, dihalogens, and inorganic halides have been included. For similar reasons, we have used, where relevant, information provided by the closely related technique of Matrix Isolation Spectroscopy (MIS).

After an introductory chapter which gives the basis principles and includes a brief critique of the technique, the book is divided into three further chapters dealing respectively with

- (a) experimental techniques,
- (b) behaviour of metal atoms in matrices, and
- (c) results of preparative experiments.

While not being encyclopaedic the book describes or refers to all noteworthy areas if not in the deliberately short text in the many tables and figures. Therefore we hope that chemists, fresh or experienced, will find this book useful as a comprehensive introduction to the technique, a starting point for the setting up of MVS equipment, a guide to the metal atom processes, and a synopsis of metal atom reactions to date.

On the present evidence we can see a considerable future for MVS both in the research laboratory and in the commercial production of catalysis and related metal coated systems.

J. R. Blackborow
D. Young

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Abbreviations

Ac	acetyl	Hal	halogen
acac	acetylacetone	Hex	hexyl
acacH	acetylacetone	I.P.	ionisation potential
An	acrylonitrile	ir	infrared (spectroscopy)
Bd	buta-1,3-diene	L	2-electron ligand
bipy	dipyridyl	Me	methyl
bp	boiling point	Mht	methylheptatriene
Bu	Butyl	MIS	matrix isolation spectroscopy
Bu ⁿ	n-butyl	M.O.	molecular orbital
Bu ⁱ	iso-butyl	mp	melting point
Bu ^s	sec-butyl	MVS	metal vapour synthesis
Bu ^t	tert-butyl	Nbd	norbornadiene
c	cis	Nbe	norbornene
Cdt	cyclododeca-1,5,9-triene	nmr	nuclear magnetic resonance
Cht	cycloheptatrienyl	Ot	octatriene
ChtH	cycloheptatriene	Pbd	polybutadiene
ChtH ₂	cycloheptadienyl	pes	photoelectron spectroscopy
ChtH ₃	cycloheptadiene	Ph	phenyl
Cod	cyclooctadiene	PhH	benzene
Cot	cyclooctatetraene	PhMe	toluene
Cp	cyclopentadienyl	Pr	propyl
CpH	cyclopentadiene	Pr ⁿ	n-propyl
Cy	cyclohexyl	Pr ⁱ	iso-propyl
CyH	cyclohexane	py	pyridine
Db	dibenzylideneacetone	t	trans
Ddt	dodecateraene	TCNQ	tetracyanoquinodimethane
dec	decomposition	thf	tetrahydrofuran
diphos	1,2-bis(diphenylphosphino)ethane	uv	ultraviolet (spectroscopy)
e	electron	uv-vis	ultraviolet-visible (spectroscopy)
esr	electron spin resonance	X	1-electron ligand
Et	ethyl	xs	excess
glc	gas liquid chromatography	Δ	heat, warm

Reactivity and Structure

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1 The Basic Principles

1.1 Introduction

It is now possible to use vapours such as atoms of transition metals^{1, 2)}, carbon atoms³⁾, and molecules which may only exist in the gaseous state, e.g. SiF_2 ⁴⁾, Cr-Fe ⁵⁾, or TiO ⁶⁾ as routine reagents in synthesis^{1, 2)}, catalysis⁶⁾, or other reactivity studies⁷⁾. Recent research has already shown that interesting and novel compounds such as $(\text{Cod})_2\text{Fe}$ ⁸⁾, $(\text{Bd})_3\text{Mo}$ ⁹⁾, $(\text{PhH})_2\text{Ti}$ ¹⁰⁾, and $\text{C}_6\text{F}_5\text{PdBr}$ ¹¹⁾, which have not been prepared by conventional methods may be readily made by vapour synthesis.

The technique owes its origins to experiments conducted by Pimentel¹²⁾ and others in the late 1950s who showed that highly reactive species such as radicals could be trapped in rare gas matrices at liquid H_2 (20 K) and liquid He (4 K) temperatures, and their spectroscopic properties determined at leisure. Following this, Linevsky¹³⁾ and others showed that species generated only at high temperatures could be similarly trapped, while Skell¹⁴⁾ and collaborators found that species such as carbon atoms when trapped in reactive matrices at liquid N_2 temperatures (77 K) formed compounds in gram quantities. Timms logically extended the scope to syntheses using transition metal atoms^{15, 16)}.

The highly reactive atoms or molecules are generated at high temperatures in a vacuum and then brought together with the chosen coreactants on a cold surface. The use of species such as atoms can provide synthetic advantage from both kinetic and thermodynamic considerations. Indeed atoms have virtually no kinetic barrier towards ligand addition whereas, even for a spontaneous reaction, the massive metal may be inert due to a relatively low surface area, inhibition by thin oxide films, or the strong cohesive forces of the metal lattice. Figure 1.1 shows the synthetic advantages of metal atoms compared with the solid metal. For example gaseous Cr or Ti atoms with benzene form bis(η -benzene) chromium in 60% yield¹⁶⁾ or bis(η -benzene)titanium in 40% yield¹⁰⁾. These compounds cannot be made directly from the solid metal: $(\eta\text{-PhH})_2\text{Cr}$ must be synthesised by a circuitous route¹⁷⁾, while $(\eta\text{-PhH})_2\text{Ti}$ cannot even be similarly prepared¹⁸⁾.

It is not firmly known at what stage the isolated products are formed, but the generally held belief is that there is some initial reaction between atom and coreactant in the nascent cocondensate, otherwise solid metal will be formed. Reaction is presumed to continue through a series of non-isolable intermediates, either at the cocondensation temperature or on warming, till sufficiently inert or stable products are formed which are then extracted. These points are considered in further detail in Chap. 4.

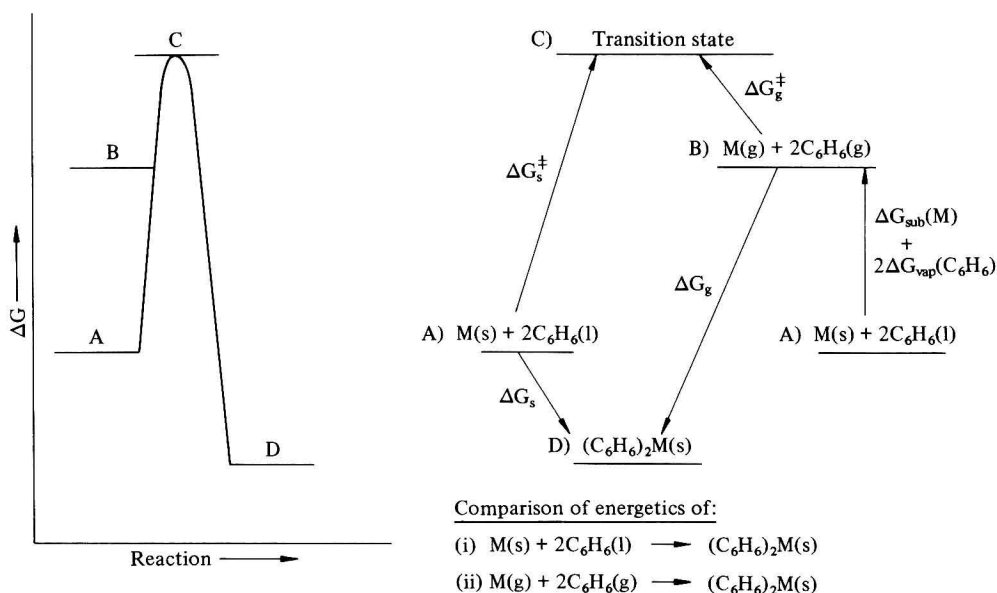


Fig. 1.1. Synthetic advantage of metal atoms

ΔG_s^\ddagger is the energy required to activate reaction (i).

ΔG_g^\ddagger is the energy required to activate reaction (ii).

$\Delta G_g^\ddagger < \Delta G_s^\ddagger$ therefore reaction (ii) is more favourable kinetically.

ΔG_s is the energy gained by forming $(C_6H_6)_2M(s)$ in reaction (i).

ΔG_g is the energy gained by forming $(C_6H_6)_2M(s)$ in reaction (ii).

$\Delta G_g > \Delta G_s$ therefore reaction (ii) is more favourable thermodynamically.

$-(\Delta G_g^\ddagger - \Delta G_s^\ddagger) \simeq \Delta G_g - \Delta G_s \simeq \Delta G_{\text{sub}}$, the sublimation energy of the metal (to a reasonable approximation) and is a reflection of the synthetic advantage of the metal atom over the massive metal

1.2 The Method

The principle of the technique is simple. The metal atoms (e.g., Cr atoms) are brought into contact with the other reactants (e.g., PF_3 molecules) at a reaction site where the product (i.e. $Cr(PF_3)_6$)¹⁶ is formed and extracted. This is shown in Fig. 1.2.

1.2.1 Metal Atom Source

The most convenient and attractive source of metal atoms is a furnace inside a vacuum system. The furnace is heated to the required vaporisation temperature and in the low pressure environment (pressure lower than 10^{-3} to 10^{-4} torr) the metal atoms will proceed by essentially collision-free paths from the furnace to the reaction site. Furnaces which have been successfully used in vapour synthesis include electron beam guns^{6, 10, 20},

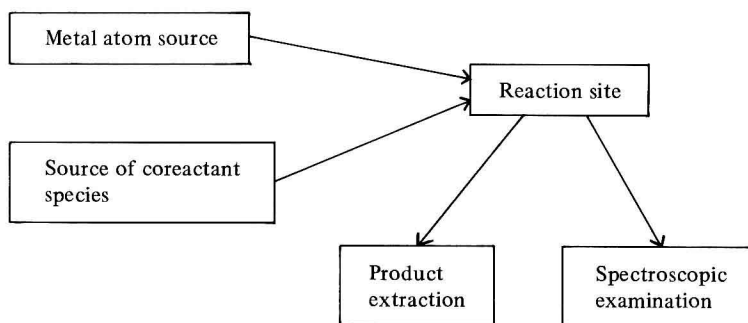


Fig. 1.2. The principal requirements of the method

resistance heated furnaces^{1, 21, 22}), laser beam heating^{23, 24}), hot filaments (resistance heating)^{19, 22}), electric arcs^{3, 25}), and sputtering²⁶). Each source may have special advantage for a particular situation but the first two methods are likely to prove to be the most versatile and convenient. A fuller discussion can be found in Chap. 2.

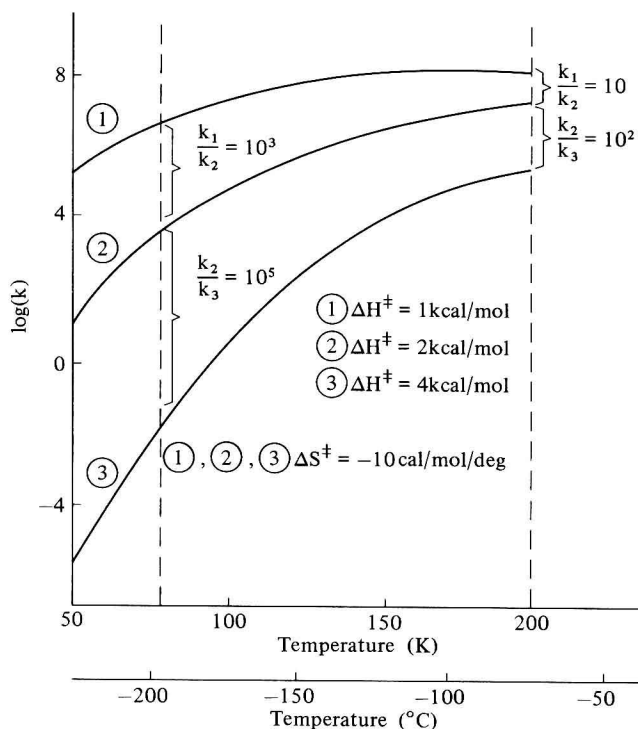


Fig. 1.3. Variation of reaction velocities with temperature

$$k \text{ (reaction velocity)} = \text{const.} \cdot e^{-\Delta G^\ddagger/RT} = \text{const.} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

$$= \text{const.} \cdot e^{-\Delta H^\ddagger/RT} \text{ (at constant } \Delta S^\ddagger \text{)}$$

$$k_1/k_2 = \text{const.} \cdot \exp [(\Delta H_2^\ddagger - \Delta H_1^\ddagger)/RT]$$

as T increases, k_1/k_2 decreases