Organometallic Compounds in the Environment

Second edition

Edited by P.J. Craig
School of Molecular Sciences,
De Montfort University,
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DEDICATION

This book is dedicated to my wife Carole Ruth Craig

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PREFACE TO SECOND EDITION

The aims of this second edition are similar to those of the first, published in 1986. As well as the normal requirements of updating, the fundamental purpose of this edition is the same as that of the previous one.

Commercially, organometallic compounds have been used extensively over the past 50 years and in many of these uses there is a direct interaction with the natural environment. Some examples include their use as pesticides (organomercury or organotin compounds), gasoline additives (methyl- and ethylleads), polymers (organosicons) and other additives and catalysts. In addition there is an increasing realization that organometallics also exist as natural products in the environment (e.g. arsenic species). This has led to intensive research into their biological properties, toxicities, pathways and transformations in the environment and to their ultimate fate and disposal.

Although much material now exists in the literature, it is still often scattered or in large-scale form and can be rather inaccessible to the reader who needs to form an understanding of the topic as a whole. The present volume is designed as a single-volume source of information for this area.

The use of the term ‘organometallic’ is discussed in Chapter 1, but it is generally taken here for compounds with a direct metal to carbon sigma bond. The work also emphasizes the importance of as full an identification of the chemical substances present as possible, i.e. ‘speciation’. Uses, chemical reactions in the environment, environmental pathways (biogeochemical cycles), biological properties and toxicities are covered.

It is intended that the book is read either as a whole, or as a series of stand-alone chapters which cover organometallic compounds of a single element together. The purpose of Chapter 1 is to cover the underlying properties of organometallic molecules that are relevant to their environmental behavior. The reader can consider these aspects first and then go on to consider the role of compounds of individual elements in the environment. Euqually, s/he may consider the elements separately and then draw the topic area together by using Chapter 1.

In order to allow this flexible use of the book a certain amount of redundancy is built in to allow chapters to be meaningful on their own. This element of repetition is intentional and it is hoped that it is helpful.

Finally, some other useful sources of information are given at the end of the book.

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The Editor can testify personally that a great effort has been made to obtain copyright permission for anything we have reproduced here from other works. If there are any omissions we sincerely apologize.

1 Occurrence and Pathways of Organometallic Compounds in the Environment—General Considerations

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1.1 SCOPE OF THIS WORK

The compounds considered in this work are those having metal–carbon (normally metal–alkyl) bonds, and which have environmental implications or properties. There is limited reference to metal–carbon π systems (e.g. $Mo(CO)_6$, $W(CO)_6(\eta\text{-}CH_3C_5H_4Mn(CO)_3)$ and mechanistic discussion of metal hydrides and ethene (e.g. decomposition by β elimination). In terms of formation of organometallics, methyl groups predominate but there is also reference to other metal hydrocarbon compounds (e.g. ethyl or phenyl mercury, ethyl leads, butyl tins). However, much of this work refers to metal methyl compounds as these are formed naturally in the environment (biomethylation)

The thrust of the work involves a good deal of analytical chemistry, but that is not the prime focus of the book. However, without the modern developments in analytical chemistry of the past 50 years, knowledge of most of the chemistry described in this book would barely exist. The analytical work that has led to this chemistry is described in the appropriate chapter but it is not the main theme. Several recent and comprehensive works that focus on the analytical chemistry of the environment have recently appeared and the reader is referred to those for the technical details of the analytical chemistry (see Standard Reference Sources and References at the end of the book).

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Amongst these, the recent comprehensive work by Crompton [1] focuses almost exclusively on the analysis of metal cations with minor consideration of organometallic compounds, and as its title denotes, is concerned with analysis from aqueous media. Similarly the work of Ure and Davidson [2] is mainly directed towards metal cations. The recent work edited by Ebdon *et al.* [3] also focuses more on analytical chemistry but takes full account of the complete molecular identity of the metallic compounds present (not focusing exclusively on organometallic compounds), i.e., speciation. (The importance of speciation is discussed later.)

Given that the stability, transport and toxicities of organometallic compounds depends on the number and type of the metal alkyl or aryl groups present, and that different compounds of the same or different metals may coexist at the same location in the environment, then separate detection of each species (speciation) is necessary. Separation and detection go together in so-called interfaced or hyphenated analytical systems. This is of particular importance because such species, although having real environmental and/or toxicity *effects*, often occur at very low concentrations in the environment (ppb, ppm—see later for definitions).

Nevertheless a broad statement on analysis needs to be made. There are two considerations:

(i) The metal, organometallic fragment or full compound needs to be *detected* by a sufficiently sensitive method (e.g. Hg, CH_3Hg^+, CH_3HgCl respectively), and
(ii) as a variety of organometallic compounds of the same element may be present together in the same matrix (e.g. butyltins, butyl/methyltins) and they each have different toxicity and environmental properties, then they must be *separated* before individual detection.

The main methods of detection are as follows:

(i) Atomic absorption spectroscopy (flame, graphite furnace, Zeeman, hydride generation/quartz furnace),
(ii) atomic fluorescence spectroscopy (alone or via hydride generation),
(iii) atomic emission spectroscopy (usually inductively coupled plasma),
(iv) voltammetry,
(v) mass spectrometry (conventional or chemical ionization, electrospray, tandem, isotope dilution, plasma),
(vi) X-ray and neutron methods.

The main methods of separation are:

(i) Gas chromatography (conventional or capillary),
(ii) thermal desorption methods (which depend on boiling points),
(iii) high performance liquid chromatography,
(iv) flow injection methods,

(v) ion exchange chromatography,
(vi) ion chromatography.

Many organometallic compounds, or cations are insufficiently volatile to undergo gas chromatography, but may be induced to do so by *derivatization.*

This is generally achieved by (formally) SN_2 attack by hydride (from $NaBH_4$), ethyl ($NaB(C_2H_5)_4$) or other alkyl group (e.g. from a Grignard reagent), e.g. Equation (1.1)

$$As(CH_3)_2X \xrightarrow{NaBH_4} As(CH_3)_2H \tag{1.1}$$

X = environmental counter ion (in this case not riboside—see Chapter 5)

This has been widely achieved, even in the case of mercury where it had been thought that mercury hydrides were too unstable for use in analysis [4].

Coupling of these separation and detection techniques is now ubiquitous and provides an intensive battery of techniques for analytical work, well described in Reference [3]. Without these, little knowledge of organometallic compounds in the environment would be possible.

The present work is also not primarily a work of toxicology although the toxicity properties of the compounds are discussed in the chapters element by element. The reader is referred to several excellent works specifically dedicated to toxicity studies of organometallic compounds [5].

The present work is a consideration of the inputs (natural and anthropogenic) and/or formation of organometallic compounds in the natural environment (sediment, water and atmosphere), their properties and behaviour there, and their ultimate fate. Although much of our understanding in this field is derived from analytical chemistry and the methods are described where needed, the theme of the work is the overall behaviour of organometallics in the environment, not their analysis. Compounds are covered by chapters on an element-by-element basis.

Organometallic species (i.e. compounds, complexes or ions) may be found in the natural environment either because they are *formed* there or because they are *introduced* there. To date, the behaviour of the latter group is better understood, and their environmental impact has been assessed by studies of their direct toxicities, their stabilities and routes to decay, and by toxicity studies of their decay products. Organometallic compounds entering the environment may be deliberately introduced as products whose properties relate to the environment (e.g. biocides) or they may enter peripherally to a separate, main function (e.g. gasoline additives, polymer stabilizers). Compounds of arsenic, mercury, tin and lead have important uses as organometallic compounds. Their role and behaviour in the environment are covered in the appropriate chapters of this work (Chapters 2 to 5). The behaviour of other organometallic species in the natural environment is also covered (Chapters 6 to 10). However, not all organometallics found in the environment are introduced—some are *formed* after entry as inorganic species and constitute the organometallic components of global biogeochemical cycles. This process of environmental methylation is usually termed biomethylation and is, as the name implies, almost exclusively concerned with formation of metal–methyl bonds (although ethyl mercury has been found in the environment in circumstances removed from likely input as a product). Recent work has demonstrated the occurrence of transition metal carbonyls, likely to have been formed in the environment (see below).

1.2 GENERAL APPROACH: SPECIATION, CONCENTRATIONS AND TERMINOLOGY

This work considers those organometallic compounds that have relevance to the natural environment. It is concerned with compounds that are found there, or which may be formed there, or which may react or be transported within the environment. Accordingly we discuss inputs, formation, transportation and decay. The approach is to consider these processes element by element in each chapter. The present chapter links the work by considering those fundamental aspects of organometallic chemistry that are relevant to the environmental chemistry of the elements discussed in each chapter, including stabilities, and mechanisms of environmental formation and decay.

It is at this point that further consideration of the term 'speciation' should be made. A generation ago, and indeed much legislation concerning pollution, etc. still occurs in this context, chemists had to be content with discussing a contaminant by its defining *element* (e.g. total arsenic, mercury concentrations, etc.). In parallel with many chemists becoming environmental chemists, technology and necessity prompted further identification into partial or complete molecular identification of the contaminant (e.g. methylmercury, CH_3Hg^+, arsenobetaine, $(CH_3)_3^+AsCH_2COO^-$). Such full operational identification of a compound within a larger matrix is now commonly termed 'speciation'. Where possible, to accord with a speciation approach, we will discuss the chemistry in terms of compounds.

Additionally of course, speciation is now not only more possible, it is essential. The main toxicity and environmental properties depend markedly on what compound is present, not on what metal. Some arsenic compounds are notoriously toxic (e.g. As_2O_3), but some are effectively non-toxic (e.g. arsenobetaine). Toxicity also depends on the degree of alkyl substitution of a metal and the identity of the organic (alkyl) group, and it varies also for the same compound towards different (biological) species. Residence times may also vary with species (e.g. CH_3Hg^+ (long) and Hg^{2+} (shorter) in biological tissue), and this can determine toxic impact. In addition to toxicity, transportation parameters also vary for the same element with its speciation, e.g. partition to atmosphere or water. Organometallic cations (e.g. Bu_3Sn^+) tend to be more water soluble and non-volatile, but saturated compounds (e.g. $(CH_3)_4Pb$) are hydrophobic and volatile.

Additionally, a generation ago analytical chemists had generally to accept quantitative limits for their work of parts per thousand (ppt or mg g^{-1}) e.g. for arsenic in a matrix (containing medium). At the time of the first edition of the present work (1986) parts per million or billion (ppm, ppb or μg g^{-1}, ng g^{-1}) were being achieved. The standard now is commonly ppb (or ng g^{-1}; the quantity present in 10^9 parts of the matrix), but parts per 10^{-12} (ppt or pico grams per gram (fg g^{-1})) are now commonly reported. It should always be borne in mind how relevant in practical terms such extreme measures of dilution might be, and analytical and environmental chemists should pause on occasion to consider which chemical species may *not* be present in a matrix at fg g^{-1} or more dilute levels. Chemical analysis is usually targeted towards the species of interest and much else present may be missed or ignored. The question is, 'if the level of a certain species is of the order of 10^{-12} parts per gram, does it *matter* and if so, to *whom*?'

The above considerations also bring forward another point of terminology. Laboratory chemists usually express concentrations in molar terms, i.e. mol dm^{-3}. At greater levels of dilution parts per million (ppm) and similar terms are often used. These terms are less precise, often because the matrix in which the species of interest is present is not water or a similar solvent. It is often a wet, amorphous sediment. Hence 'ppm' can mean one of the following:

(i) grams of the relevant atom present in 10^6 grams of the matrix,
(ii) grams of a defined part of the molecule in 10^6 grams of the matrix,
(iii) grams of the whole molecule in 10^6 grams of the matrix.

In some published work, 'ppm' is not even defined as above. To add to the imprecision, the matrix (which may be a sediment or biological tissue) may be taken as wet (heavier) or dried (lighter)—giving two possible figures for the same measurement. Clarity of definition is not always present in quantitative work in this field, and the matrix is rarely the simple defined volume of known solvent that occurs in laboratory chemistry.

With regard to atmospheric or liquid measurements, terms such as ppm could mean:

(i) grams of the molecule (or relevant atom) present in 10^6 cm^3 of atmosphere (at STP?) or water, or
(ii) volume (cm^3) of the molecule (or relevant atom) present in 10^6 cm^3 of atmosphere or water.

Care therefore needs to be taken when results from different laboratories or groups are compared. Consistency is often absent (even orthodox molar concentrations are sometimes used, even at extremes of dilution).

To put this field into perspective—although ppm, ppb and similar concentrations can be of major physiological, toxicological or environmental significance, it will do little harm to repeat the comparison given in the first edition of this work—a ppm is equivalent to a needle in a haystack; a ppb is equivalent to a grain of sand in an Olympic-sized swimming pool (in checking the calculation the reader is also invited to consider this as a not completely outlandish example of the use of imprecise concepts to register concentrations).

Within the present work, full standardization of terms is not possible owing to wide differences in practice, methods, matrices and analytical feasibility. To overcome this as far as possible, a basic attempt at standardization has been made and cross-referencing will then be used to clarify detailed points.

1.3 TYPES OF ORGANOMETALLIC COMPOUND

Most, but not all, organometallic compounds of environmental interest are covalent, bound by a σ bond from a single carbon atom, to a main group element. The term 'organometallic' is generally defined as a compound with a bond (M—C) polarized $M^{\delta+}$—$C^{\delta-}$ i.e. the metal is less electronegative than carbon. A compound containing carbon atoms, but where the bonds to the metal are not directly to the carbon atom (but may be via oxygen, nitrogen or halogen atoms instead), is not considered to be organometallic, although such a compound may be referred to as 'metal organic'. In general then, the compounds discussed in this book will involve carbon bound to a main group metal via a single carbon atom—these are referred to as 'monohapto' compounds. Despite the polarization above, in this work metal–carbon bonds are usually shown as R_nM to accord with common practice.

A vast organometallic chemistry of interest to synthetic and mechanistic organometallic chemists exists outside the definition above, which is of little significance (so far as is known) in an environmental context, other than by way of input from manufacture or use, in which case the pollutant is a decomposition product that is usually non-organometallic. (Transition metal organometallics have hugely important uses as synthetic and catalytic intermediates, but there is usually little pollution owing to the high cost of the metals concerned, e.g. rhodium, ruthenium, etc.) Within the context of these transition-metal compounds there are actually some instances of environmental significance, for example, (λ-$CH_3C_5H_4Mn(CO)_3$) is used as an anti-knock agent in gasoline (Chapter 9) and $Mo(CO)_6$ and $W(CO)_6$ have been detected in the environment (Chapter 9).

Most of the 'metals' in the present work are clear cut main group elements (mercury, tin, lead, etc.) but certain 'metalloidal' elements are included because their environmental properties have so much in common (arsenic, antimony, etc.). Some elements generally considered to be non-metallic have strong interactions with this area of work and are mentioned as needed (e.g. sulphur, selenium). Polymeric organometallic compounds are covered in the chapters relating to siloxanes (Chapter 8) and tin (Chapter 3).

1.4 THERMODYNAMIC STABILITIES OF ORGANOMETALLIC COMPOUNDS

As noted above, most of the organometallic compounds in the present work involve covalent bonds between a carbon atom (usually in a methyl, CH_3, group) and a main group (non-transition element). Such bonds may have little or much polarization (polarization is a measure of the drift in electronic charge in a covalent bond from, in this case, the metallic element to the carbon atom, viz. $M^{\delta+}$—$C^{\delta-}$). Polarizations vary and affect stabilities considerably. In general the M—C bonds can be considered as localized (albeit polarized) with conventional σ electron pair bonds similar to those occurring in organic chemistry.

In considering stability, we have to ask stability with respect to *what* phenomenon (hydrolysis, oxidation, thermal). We consider stability of a compound with respect to decomposition into its own elements (this doesn't usually happen) and towards external chemical attack (the norm), e.g. by atmospheric oxygen, water and microbial-mediated decay. We consider inherent (thermodynamic) stability first because the general approach is helpful. However, in general it can be said that where the compounds are unstable it is not because of weak M—C bonds (thermodynamic) but because there are low energy pathways to decomposition (kinetic). A component is thermodynamically unstable with respect to decay to elements if the standard Gibbs free energy for the process is negative. In certain equilibrium reactions where this equals zero, there can still be a driving force for the reaction.

Thermodynamic stabilities depend mainly on the strength of the bonds from metal to carbon. They can be estimated by bond enthalpy ($\bar{E}_m$ M—C) measurements; compounds with strong M—C bonds are, not surprisingly, more stable than those with weaker M—C bonds. Although not inherently weak, M—C bonds are less strong than M—N, M—O and M—X (X = halogen) bonds. (Table 1.1). Free energies of formation (ΔG_f^θ) are not usually known for organometallics as standard entropies are rarely known and so enthalpies of formation (ΔH_f^θ) are usually used in comparing thermodynamic stabilities. Hence organometallic reactions are exothermic or endothermic (ΔH_f^θ is negative or positive), but free energies (ΔG_f^θ) are not known other than that they are negative and hence, in a formal sense, neither are thermodynamic stabilities. For alkyl organometallics mean bond enthalpies for the whole molecule ($\bar{E}$ (M—C)) are usually quoted, but there is a problem here in that *stepwise* bond dissociation energies ($D_1 - D_n$) may deviate a lot from the mean values, viz

$\bar{E} = \frac{l}{n}\sum_{l}^{n} D_1$. (see Me_2Hg below, Equation 1.2, 1.3)

$$(CH_3)_2Hg \longrightarrow CH_3Hg + CH_3 \quad D_1(Hg—C) = 214\,kJ\ mol^{-1} \qquad (1.2)$$

$$CH_3Hg \longrightarrow Hg + CH_3 \quad D_2(Hg—C) = 29\,kJ\ mol^{-1} \qquad (1.3)$$

Table 1.1 Bond dissociation energies[a] of diatomic molecules (in kJ mol^{-1}). From Kerr JA, 1983, Strengths of chemical bonds, *Handbook of Chemistry and Physics*, Chemical Rubber Company, 65 edn, F171–181 Reprinted with permission. Copyright CRC Press Inc, Boca Raton, Fla, USA

Main group elements[b]											
Gp 13	M-C	M-O	Gp 14	M-C	M-O	Gp 15	M-C	M-O	Gp 16	M-C	M-O
B	449	806	C	605	1080	N	773	—	O	1080	500
Al	—	449	Si	437	790	P	517	596	S	701	521
Ga	—	299	Ge	462	660	As	—	479	Se	584	424
Ln	—	323	Sn	—	525	Sb	—	391	Te	—	382
Tl	—	—	Pb	—	416	Bi	—	302	Po	—	—

[a] $D(M—X) = M^\bullet + X^\bullet$, i.e. bond dissociation enthalpy; loosely, bond strength

[b] In kJ mol^{-1} measured spectroscopically (mass spectrum) from transient molecules as above, at 25 °C

Hence $\bar{E} = 121.5\,KJ\ mol^{-1}$, but this does not reflect the difficulty of breaking the *first* Hg—C bond [6].

What matters here is that some organometallic compounds are exothermic towards decomposition to their elements, and some are endothermic, but not all of the exothermic compounds decompose (kinetics again!). Also, when they do decompose on heating they usually do so to a mixture of hydrocarbons, hydrogen and the metal, not to the elements. Nevertheless, quantification information from such measurements is a useful guideline and, is usually all that is available. Data is given in Tables 1.2 to 1.4

The information in the tables relates to decomposition to the elements in their standard states, but this is not what usually happens. Taking $(CH_3)_4Pb$ for example (Table 1.5) it can be seen that there are other routes than those to elements. On this basis route 4 is apparently the most favoured.

Despite the apparent thermodynamics (we don't know the entropy values), $(CH_3)_4Pb$ is an important, readily available and commercial compound. The reason is, again, kinetic stability. The reaction pathway at room temperature does not have an activation energy low enough for it to happen at a measurable rate. The activation energy in such cases may depend on the inherent M—C bond strength and this appears to be strong enough to allow $(CH_3)_4Pb$ stored in an inert atmosphere to be indefinitely stable.

In practice, in the environment, decay mediated by oxygen, water, free radicals and biology is much more relevant. Many kinetically stable organometallics in these terms may be very unstable in the environment, including $(CH_3)_4Pb$ which decays in days in the atmosphere (Chapter 4).

So while all carbon compounds (including organometallics) are thermodynamically unstable owing to the stability of the products (again assuming entropy values), many are kinetically stable because there is no low energy route to decomposition. This may be associated with there being a closed shell of electrons, often of spherical symmetry, around the metal atoms, i.e. full use of

Table 1.2 Standard enthalpies of formation ΔH^0_δ (kJ mol^{-1}) and *mean* bond enthalpies, $\bar{E}$ (M—C) (kJ mol^{-1}) of CH_3 derivatives in the gas phase[a]

MMe_2			MMe_3			MMe_4			MMe_3		
M	ΔH^0_δ	$\bar{E}$	M	ΔH^0_δ	$\bar{E}$	M	ΔH^0_δ	$\bar{E}$	M	ΔH^0_δ	$\bar{E}$
Zn	50	177	B	−123	365	C	−167	358	N	−24	314
Cd	106	139	Al	−81	274	Si	−245	311	P	−101	276
Hg	94	121	Ga	−42	247	Ge	−71	249	As	13	229
			Ln	173	160	Sn	−19	217	Sb	32	214
			T1	—	—	Ph	136	152	Bi	194	141

[a] mean 'bond strengths'. $n\bar{E}(M—CH_3) = \Delta H^0_\delta M_{(g)} + n\Delta H^0_\delta(CH_3{}^0)_g - \Delta H^0_\delta(M(CH_3)_{n(g)})$

Notes

(i) Some compounds are exothermic, some are endothermic with respect to decomposition to elements n the absence of air/water.

(ii) $\bar{E}$ (M—C) decreases with increasing atomic number for main group elements (it is the opposite for transition metal–methyl compounds) due to increasing orbital dimensions on M and poorer covalent overlap.

(iii) These bonds are weak compared to metal–oxygen, metal–halogen, carbon–oxygen bonds in weakness of organometallic to oxidation.

(iv) Mean bond enthalpies can be misleading (see text).

(v) Analogous values of $\bar{E}$ for some transition metal carbonyls are $Cr(CO)_6$, $\bar{E} = 107$; $Mo(CO)_6$, $\bar{E} = 152$; $W(CO)_6$, $\bar{E} = 180$. Note *increasing* bond strength down the group.

(vi) Mode of decomposition is via homolytic breakage of the M—C bond to produce radical species.

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Table 1.3 E^0_{298} Values for the first M—C bond in some polyatomic molecules (kJ mol^{-1})

$CH_3—Ge(CH_3)_3$	346 ± 17
$CH_3—Sn(CH_3)_3$	297 ± 17
$CH—Pb(CH_3)_3$	238 ± 17
$CH_3—As(CH_3)_2$	280 ± 17
$CH_3—Sb(CH_3)_2$	255 ± 17
$CH_3—Bi(CH_3)_2$	218 ± 17
$CH_3—CdCH_3$	251 ± 17
$CH_3—HgCH_3$	255 ± 17
$CH_3—SH$	312 ± 4.2
$CH_3—SCH_3$	272 ± 3.8

Notes

(i) Compare with Table 1.2. The above bonds are > $\bar{E}$ (M—C).

(ii) Measurement of bond strengths in polyatomic molecules is not straightforward, being hard to measure (usually by kinetic methods). Some can be calculated at 298 ° from the following equation:

$$E^0(R—X) = \Delta_\delta H^0(R^0) + \Delta_\delta H^0(X) - \Delta_\delta H^0(RX) \quad \text{or}$$

$$E^0(R—R) = 2\Delta_\delta H^0(R^0) - \Delta_\delta H^0(R—R)$$

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Table 1.4 Mean bond enthalpies ($\bar{E}$ (M—C)) for oxides and halides

B—O	526	Si—O	452	As—O	301
B—Cl	456	Si—Cl	381	Bi—Cl	274
Al—O	500	Si—F	565		
Al—Cl	420	Sn—Cl	(tin)323		

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Table 1.5 Decomposition of $(CH_3)_4Pb$

Decomposition route	ΔH^0	ΔH per M—C$^+$
(1) $Pb(CH_3)_{4(g)} \rightarrow Pb_{(s)} + 4C_{(s)} + 6H_{2(g)}$	−136	−34
(2) $Pb(CH_3)_{4(g)} \rightarrow Pb_{(s)} + 2C_2H_{6(g)}$	−307	−76.75
(3) $Pb(CH_3)_{4(g)} \rightarrow Pb_{(s)} + 2CH_{4(g)} + C_2H_{4(g)}$	−235	−58.75
(4) $Pb(CH_3)_{4(g)} \rightarrow Pb_{(s)} + 2H_{2(g)} + 2C_2H_{4(g)}$	−33	−8.25
+kJ mol^{-1}		

Taken with permission from Ref. 6

the metal orbitals allowing no easy access to attacking reagents. Where available empty orbitals do exist, the compound may still be kinetically stable unless the metal–carbon (M—C) bonds are strongly polarized allowing, for example, nucleophilic attack by an external reagent.

Organometallics are also thermodynamically unstable with respect to oxidation to MO_n, H_2O and CO_2. Again kinetic reasons may render such compounds inert. Very reactive are compounds with free electron pairs, low-lying empty valence orbitals and highly polar M—C bonds.

We now consider kinetic stability for organometallic compounds.

1.5 KINETIC STABILITY OF ORGANOMETALLIC COMPOUNDS

In order to decompose, homolytic breakage of the M—C bond must first occur (Equation 1.4)

$$MR_{n+1} \rightarrow MR_n + R \tag{1.4}$$

In isolation this process is thermodynamically controlled by bond strengths (or enthalpies)—see above. However, once the short lived and reactive radicals are formed, further rapid reaction takes place to produce thermodynamically stable final products. None the less an energy input is required to break the metal–carbon bond. If the input is large (i.e. for a strong M—CH_3 bond) then a thermodynamically unstable compound (ΔG^θ − ve) may be stable at room temperature. The required energy input is known as the activation energy ($G^\ddagger$). This is illustrated in Figure 1.1.

However, even when ΔG^θ is negative, $G^\ddagger$ may be large if the metal–carbon bond is strong. So thermodynamically unstable molecules may be kinetically stable, but when exposed to external attack, say by oxygen, water or microbes, they can soon decay. Strength of metal–carbon bonds is only a tendency towards environmental stability.

Some stability is dependent on molecular architecture other than metal–carbon bond strengths. Although many of the organometallics observed in the natural environment are metal methyls, others such as ethylleads and butyltins also exist and are observable in the environment. Organometallics