
Organometallic Compounds in the Environment

Second edition

Edited by P.J. Craig

School of Molecular Sciences,

De Montfort University,

Leicester, UK



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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 (organo-mercury or organotin compounds), gasoline additives (methyl- and ethylleads), polymers (organosilicons) 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. Equally, 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.

EDITOR'S ACKNOWLEDGEMENTS

I am delighted to thank the following, with whom I had helpful discussions or who have read parts of the text in the manuscript: Drs Richard Jenkins and Chris Harrington of De Montfort University, Dr Francesca Cima of the University of Padova, Italy and Dr Karl Ryder of Loughborough University of Technology. Any mistakes which remain are of course my own responsibility. I also thank Mrs Lesley Winder of De Montfort University for expert typing in connection with this work.

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. $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6(\eta\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3)$) 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).

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.

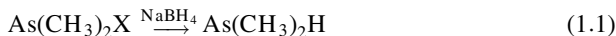
The main methods of separation are:

- (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 ($\text{NaB}(\text{C}_2\text{H}_5)_4$) or other alkyl group (e.g. from a Grignard reagent), e.g. Equation (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, $(\text{CH}_3)_3^+\text{AsCH}_2\text{COO}^-$). 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. $(\text{CH}_3)_4\text{Pb}$) 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 $\mu\text{g g}^{-1}$, 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. $\text{M}^{\delta+}-\text{C}^{\delta-}$). Polarizations vary and affect stabilities considerably. In general the $\text{M}-\text{C}$ 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 $\text{M}-\text{C}$ 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 ($\bar{E}_m \text{M}-\text{C}$) measurements; compounds with strong $\text{M}-\text{C}$ bonds are, not surprisingly, more stable than those with weaker $\text{M}-\text{C}$ bonds. Although not inherently weak, $\text{M}-\text{C}$ bonds are less strong than $\text{M}-\text{N}$, $\text{M}-\text{O}$ and $\text{M}-\text{X}$ ($\text{X} = \text{halogen}$) bonds. (Table 1.1). Free energies of formation (ΔG_f^0) are not usually known for organometallics as standard entropies are rarely known and so enthalpies of formation (ΔH_f^0) are usually used in comparing thermodynamic stabilities. Hence organometallic reactions are exothermic or endothermic (ΔH_f^0 is negative or positive), but free energies (ΔG_f^0) 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 ($\bar{E}(\text{M}-\text{C})$) 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

$$\bar{E} = \frac{1}{n} \sum_i^n D_i. \quad (\text{see Me}_2\text{Hg below, Equation 1.2, 1.3})$$

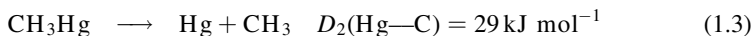


Table 1.1 Bond dissociation energies^a of diatomic molecules (in kJ mol⁻¹). From Kerr JA, 1983, Strengths of chemical bonds, *Handbook of Chemistry and Physics*, Chemical Rubber Company, 65 edn, F171–181 Reprinted with permission. Copyright CRC Press Inc, Boca Raton, Fla, USA

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* + X*, 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 $\bar{E} = 121.5 \text{ KJ mol}^{-1}$, 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 (CH₃)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), (CH₃)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 (CH₃)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 (CH₃)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_{δ}^0 (kJ mol⁻¹) and mean bond enthalpies, \bar{E} (M—C) (kJ mol⁻¹) of CH₃ derivatives in the gas phase^a

MMe ₂			MMe ₃			MMe ₄			MMe ₃		
M	ΔH_{δ}^0	\bar{E}	M	ΔH_{δ}^0	\bar{E}	M	ΔH_{δ}^0	\bar{E}	M	ΔH_{δ}^0	\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
			Tl	—	—	Ph	136	152	Bi	194	141

^a mean 'bond strengths'. $n\bar{E}(\text{M—CH}_3) = \Delta H_{\delta}^0 \text{M}_{(\text{g})} + n\Delta H_{\delta}^0(\text{CH}_3^0)_{\text{g}} - \Delta H_{\delta}^0(\text{M}(\text{CH}_3)_{n(\text{g})})$

Notes

- Some compounds are exothermic, some are endothermic with respect to decomposition to elements in the absence of air/water.
- \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.
- These bonds are weak compared to metal–oxygen, metal–halogen, carbon–oxygen bonds in weakness of organometallic to oxidation.
- Mean bond enthalpies can be misleading (see text).
- 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.
- Mode of decomposition is via homolytic breakage of the M—C bond to produce radical species.

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Table 1.3 E_{298}^0 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

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

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

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

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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		

Taken with permission from Ref. 9

Table 1.5 Decomposition of $(\text{CH}_3)_4\text{Pb}$

Decomposition route	ΔH^0	ΔH per $\text{M}-\text{C}^+$
(1) $\text{Pb}(\text{CH}_3)_{4(\text{g})} \rightarrow \text{Pb}_{(\text{s})} + 4\text{C}_{(\text{s})} + 6\text{H}_{2(\text{g})}$	-136	-34
(2) $\text{Pb}(\text{CH}_3)_{4(\text{g})} \rightarrow \text{Pb}_{(\text{s})} + 2\text{C}_2\text{H}_{6(\text{g})}$	-307	-76.75
(3) $\text{Pb}(\text{CH}_3)_{4(\text{g})} \rightarrow \text{Pb}_{(\text{s})} + 2\text{CH}_{4(\text{g})} + \text{C}_2\text{H}_{4(\text{g})}$	-235	-58.75
(4) $\text{Pb}(\text{CH}_3)_{4(\text{g})} \rightarrow \text{Pb}_{(\text{s})} + 2\text{H}_{2(\text{g})} + 2\text{C}_2\text{H}_{4(\text{g})}$	-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)



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—CH₃ bond) then a thermodynamically unstable compound ($\Delta G^\theta - \text{ve}$) 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

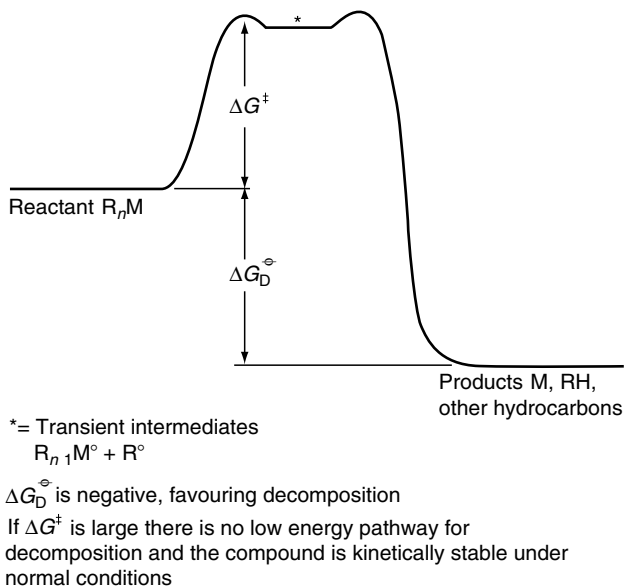
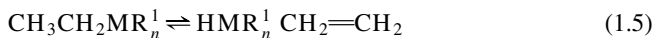


Figure 1.1 Activation energy and decay of compounds.

Taken from this work, first edition, with permission

with metal alkyl groups other than methyl are susceptible to an important route to decomposition and on this ground alone should be less stable and less observed than metal methyls. This route is termed β elimination and occurs by migration of a hydrogen atom attached to a carbon atom at a remove of one other carbon atom from the metal (e.g. in an $M-CH_2-CH_3$ grouping but not limited to ethyl). The products are a metal hydride and ethenes (ethylene). That ethene is frequently observed in the natural environment may be related (Equation 1.5). Blockage of β elimination by alkyl groups not having a β hydrogen atom (e.g. $-CH_2C(CH_3)_3$, $-CH_2CF_3$, etc.) is not relevant to the environment.

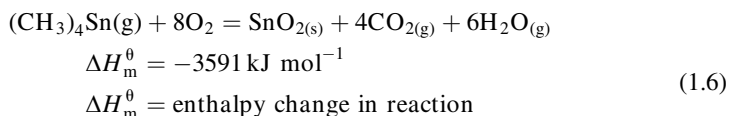


β elimination proceeds more rapidly down the groups in the periodic table because at the intermediate stage the metal is, in effect, increasing its coordination number. It may be assumed that β elimination could be involved (even when accompanied by hydroxide attack) in decay routes for compounds where decay is known to occur (e.g. butyltins) in compounds inputted into the environment, and why few ethyls and no higher alkyl species appear to be *formed* and stable in the environment. β elimination requires an empty valence metal orbital on M to interact with the electron pair on the $C_{\beta}-H$ bond. Hence β elimination is more important for groups 1, 2 and 13 than for groups 14, 15 and 16. Empty orbitals can be blocked by ligands to increase stability. Two other processes are feasible but have never been investigated as environmental routes.

These are α hydrogen elimination (clearly possible with metal–methyl groupings) and orthometallation (where a nearby *ortho* aromatic hydrogen is transferred to the metal). Methyl and phenyl mercury species do decay in the environment and may do so by these routes. However in the presence of air, water and microbes, the above routes are likely to be minor ones.

1.6 STABILITY OF ORGANOMETALLIC COMPOUNDS TO ATMOSPHERIC OXIDATION

All organometallic compounds are thermodynamically unstable to oxidation because of the much lower free energy of the products of oxidation (metal oxide, carbon dioxide, water). Equation 1.6 gives an example.



Here again, we rely on ΔH not ΔG values because of lack of knowledge of ΔS ; however, in view of the liberation of gaseous molecules, $T\Delta S$ will be an overall positive input into $\Delta G = \Delta H - T\Delta S$. This is very exothermic, but $(\text{CH}_3)_4\text{Sn}$ is quite stable in air. Some, but not all, organometallic compounds however are spontaneously inflammable. Others, although thermodynamically unstable ($(\text{CH}_3)_4\text{Sn}$) still do not oxidize in this way for kinetic reasons, as discussed in Section 1.5 above. Interestingly and relevant, compounds which *in bulk* may spontaneously oxidize (burn; ignite) may be stable or decay much more slowly when they are attenuated (in dilute form, e.g. ppm or ppb in air). $(\text{CH}_3)_3\text{Sb}$ has been noted in this respect.

Greater stability on attenuation follows from a consideration of the collision theory of gases. The rate constant is related to a collision number Z (the number of reactant molecules colliding per unit time) and the activation energy E , the Arrhenius equation (Equation 1.7),

$$k = Z \exp(-E/RT) \quad (1.7)$$

where k = rate constant, E = activation energy, R = gas constant and T = absolute temperature.

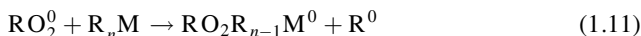
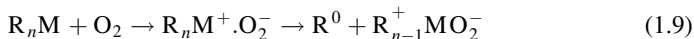
Z can be derived from classical gas kinetic theory as (Equation 1.8)

$$Z = \sigma_{\text{AB}}^2 \left[8\pi kT \frac{m_{\text{A}} + m_{\text{B}}}{m_{\text{A}}m_{\text{B}}} \right]^{\frac{1}{2}} n_{\text{A}} \cdot n_{\text{B}}. \quad (1.8)$$

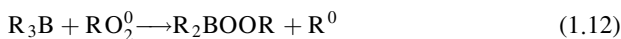
σ_{AB} is the collision cross section of A and B molecules with masses m_{A} and m_{B} and, crucially, concentrations n_{A} and n_{B} atoms as molecules per unit volume. Where reaction depends on collision between two molecules then it is quicker as concentration increases. This aspect is well discussed in Reference [10].

For these reasons, organometallics which, by their pyrophoric nature, alarm the laboratory chemist, may be much more stable in the environment.

The initial process of oxidation of organometallics by O₂ is a rapid charge transfer interaction that occurs, involving electron donation from the organo-metallic to oxygen [11]. This is shown in Equations 1.9–1.11.



The species R_nM⁺.O₂⁻ may decay by various routes, and peroxides may be formed or coupling of the alkyl ligands may occur. Organocarbon and -mercury compounds are oxidized by radical chain SH₂ processes as exemplified below, following the initial charge transfer processes, (Equations 1.12 and 1.13); [11]



The comparative susceptibilities of some metal–carbon bonds to oxidation to metal oxides are demonstrated in Tables 1.6 and 1.7. For main group elements they suggest increasing liability to oxidation as the group is descended.

Atmospheric oxidation will tend to occur rapidly:

- (i) Where metal–carbon bonds are very polar, the partial charges on M(δ +) or C(δ –) may facilitate attack by external reagents including oxygen. This can be observed indirectly by considering electronegativity values (Table 1.8). Electronegativity is the ability of an atom in a molecule to attract a shared

Table 1.6 Comparative bond enthalpy terms for metal–carbon and metal–oxygen bonds^a (in kJ mol⁻¹). Data gives an assessment of comparative bond strengths. (Reproduced with permission Johnson DA 1982 *Some Thermodynamic Aspects of Inorganic Chemistry* (2nd edn). Cambridge University Press, pp 201–2).

Group 14	M—C	M—O	Group 15	M—C	M—O	Group 16	M—C	M—O
C	347	358	N	314	214	O	358	144
					632(NO)			
Si	320	466	P	276	360	S	289	522(S=O)
Ge	247	385	As	230	326	Se	247	
Sn	218		Sb	218		Te		
Pb	155		Bi	141		Po		
<hr/>								
B—C	= 364	C—H = 413	O—H = 464	N—H = 391				
B—O	= 520	H—H = 436	Cl—H = 432	C—Cl = 346				

^a From thermodynamic data on the decomposition of the molecules, e.g. C₂H₆. Calculated from thermodynamic cycles

Definitions as in Table 1.3. M = elements listed

Table 1.7 Stability of methylmetals to oxygen^a

Stable	Unstable ^b
(CH ₃) ₂ Hg	CH ₃ PbX ₃
(CH ₃) ₄ Si, [(CH ₃) ₂ SiO] _n , (CH ₃) _n Si ⁽⁴⁻ⁿ⁾⁺ , (CH ₃) ₆ Si ₂	CH ₃ Tl ⁺
(CH ₃) ₄ Ge, (CH ₃) ₄ Ge ⁽⁴⁻ⁿ⁾⁺ , (CH ₃) ₆ Ge ₂	(CH ₃) ₂ Zn(CH ₃ Zn ⁺ also)
(CH ₃) ₄ Sn	(CH ₃) ₂ Cd(CH ₃ Cd ⁺ also)
(CH ₃) ₄ Pb ^c	(CH ₃) ₃ B
CH ₃ HgX(C ₆ H ₅ and C ₂ H ₅ also stable)	(CH ₃) ₃ Al
(CH ₃) _{4-n} SnX _n	(CH ₃) ₃ Ga
(CH ₃) ₃ PbX	(CH ₃) ₃ In
(CH ₃) ₂ PbX ₂	(CH ₃) ₃ Tl
π(CH ₃ C ₅ H ₄ Mn(CO) ₃) ^c	(CH ₃) ₅ As
CH ₃ Mn(CO) ₄ L ^d	(CH ₃) ₃ As ^e
(CH ₃) ₂ AsO(OH)	(CH ₃) ₃ Sb ^e
CH ₃ As(O)(OH) ₂	(CH ₃) ₃ Bi
(CH ₃) ₂ S	(CH ₃) ₂ AsH
(CH ₃) ₂ Se	CH ₃ AsX ₂
CH ₃ HgSeCH ₃	CH ₃ SbX ₂
CH ₃ COB ₁₂ (solid state)	(CH ₃) _{4-n} SnH _n ^e
(CH ₃) ₃ SbO	(CH ₃) ₆ Sn ₂ (At RT gives [(CH ₃) ₃ Sn] ₂ O)
(CH ₃) ₂ SbO(OH)	(CH ₃) ₆ Pb ₂ (to methyl lead products)
CH ₃ SbO(OH) ₂	(CH ₃) ₅ Sb
(CH ₃) ₂ Tl ⁺ , (CH ₃) ₂ Ga ⁺	(CH ₃) ₃ AsO
(CH ₃) ₃ S ⁺	(CH ₃) ₃ P
(CH ₃) ₃ Se ⁺	(CH ₃) ₄ SiH _{4-n}
(CH ₃) ₃ PO	(CH ₃) ₄ GeH _{4-n}

^a At room temperature in bulk (assume similar but lesser environmental stability for ethyls). As against rapid (seconds, minutes) oxidation. Table to be read in conjunction with Table 1.6. Not necessarily stable against water (see Table 1.9)

^b Variously unstable because of empty low lying orbitals on the metal, polar metal-carbon bonds and/or lone electron pairs on the metal.

^c Gasoline additive.

^d To exemplify ligand-complexed transition metal organometallics. Many of these synthetic compounds are oxygen stable but none have been found in the natural environment.

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^e But stable in dilute form and detected in the environment (Ch.3).

- (ii) electron pair to itself, forming a polar covalent bond. The values of electronegativity computed by Pauling (Table 1.8) still remain the best indicator of polarity, as dipole moments apply to the molecular as a whole, not just to the bond (whose dipole may therefore only be estimated indirectly).
- (ii) Where empty low lying (valence) orbitals on the metal exist, or where the metal has a lone electron pair (non-bonding pair), then this also facilitates kinetic instability to oxidation. The oxygen molecule (a diradical) can attack empty orbitals on M, e.g. d orbitals.
- (iii) Where the compound is thermally (thermodynamically) unstable anyway.
- (iv) Where full coordination complexation with stabilizing ligands is not occurring.

Table 1.8 Some electronegativity values relative to carbon

Group 13	Group 14	Group 15	Group 16	Group 17
B 2.0				F 4.0
Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Ln 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

Notes

1. The C—S bond is non-polar. The electrons are distributed midway between C and S.

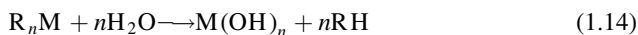
2. For the other environmental main group elements (E) the electrons are closer in the covalent bond to carbon (i.e. $M^{\delta-}-C^{\delta-}$).

Taken from standard data in texts.

Conversely complexation requires available empty orbitals on the metal. It is a competition between available ligands and atmospheric oxygen. $(CH_3)_4Sn$ is quite stable in air (fully coordinated) whereas $(CH_3)_2Zn$ is pyrophoric (empty orbitals, coordinatively unsaturated).

1.7 STABILITY OF ORGANOMETALLICS TO WATER

The first step in the hydrolysis of an organometallic compound is usually nucleophile attack of the lone electron pair on the water oxygen atom to an empty metal orbital on the organometallic. Hence hydrolytic instability is also connected with empty low-lying orbitals on the metal and on the ability to expand the metal coordination number. The rate of hydrolysis is connected with the polarity of the metal–carbon bond; strongly polarized ($M^{\delta-}-C^{\delta-}$) bonds are unstable to water. These are found for example in groups I and II organometals and for those of zinc and cadmium. The influence of polarity is shown for alkylboron compounds which have low polarity and are water stable although unstable to air. Low polarity compounds which cannot easily expand their coordination number are expected to be water stable. Most metal alkyls and aryls are thermodynamically unstable to hydrolysis to metal hydroxide and hydrocarbon (Equation 1.14). Many, though, are kinetically stable. Examples are given in Table 1.9.



To illustrate, $SiCl_4$ is easily attacked by water, owing to the low lying 3d orbitals on silicon being polarized ($\delta+$) by the electron attracting chloride ligands. $(CH_3)_4Si$ is kinetically inert to hydrolysis at room temperature because the Si—C bonds are less polarized than the Si—Cl bonds.

Table 1.9 Stability of organometallic species to water

Organometallic	Stability, comments
R_2Hg , R_4Sn , R_4Pb	Only slightly soluble, stable, diffuse to atmosphere. Higher alkyls less stable and less volatile. Species generally hydrophobic and variously volatile
CH_3HgX $(CH_3)_nSn^{(4-n)+}$	Stable, slightly soluble depending on X Soluble, methyltin units stable but made hexa- and penta-coordinate by H_2O , OH^- . Species are solvated, partly hydrolysed to various hydroxo species. At high pH polynuclear bridged hydroxo species form for $(CH_3)_2Sn^{2+}$
$(CH_3)_3Pb^+$	Soluble, hydrolysis as methyltins above. Also dismutates to $(CH_3)_4Pb$ and $(CH_3)_2Pb^{2+}$ at $20^\circ C$
$(CH_3)_2Pb^{2+}$	Soluble as for $(CH_3)_3Pb^+$ above. Disproportionates to $(CH_3)_3Pb^+$ and CH_3^+ slowly. These reactions cause eventual total loss of $(CH_3)_3Pb^+$ and $(CH_3)_2Pb^{2+}$ from water.
$(CH_3)_2As^+$	Hydrolyses to $(CH_3)_2AsOH$ then to slightly soluble $[(CH_3)_2As]_2O$
CH_3As^{2+} $(CH_3)_2AsO(OH)$	Hydrolyses to $CH_3As(OH)_2$, then to soluble $(CH_3AsO)_n$ Stable and soluble (330 g dm^{-3}). Acidic $pK_a = 6.27$, i.e. cacodylic acid, dimethylarsonic acid. Detected in oceans
$CH_3AsO(OH)_2$	Stable and soluble. Strong acid $pK_1 = 3.6$, $pK_2 = 8.3$ —methylarsinic acid. Detected in oceans
$(CH_3)_3S^+$, $(CH_3)_3Se^+$ $(CH_3)_nSiCl_{4-n}$	Stable and slightly soluble Hydrolyse and condense but methylsilicon groupings retained
$(CH_3)_nGe^{(4-n)+}$	Stable, soluble, have been discovered in oceans. Hydrolyse but $(CH_3)_nGe$ moiety preserved
$(CH_3)_2Tl^+$	Very stable, soluble, but not been detected as a natural environment product
$(CH_3)_3AsO$, $(CH_3)_3SbO$	Stable and soluble
$(CH_3)AsH$, $(CH_3)AsH_2$	Insoluble, diffuse to atmosphere, air unstable
$(CH_3)SbO(OH)$	Stable and soluble. Detected in oceans
$CH_3SbO(OH)_2$	Stable and soluble. Detected in oceans

Other species

Stable and insoluble: R_4Si , $(R_2SiO)_n$, $CH_3\dots H_3HgSeCH$, most C_6H_5Hg derivatives, $(CH_3)_2S$, $(CH_3)_2Se$, $(CH_3)_2Ge$, $(CH_3)_3B$

Unstable: CH_3Pb^+ (has not been detected in the environment), R_2Zn , R_2Cd , R_3Al , R_3Ga , $(CH_3)_6Sn_2$, $(CH_3)_6Pb_2$, $(CH_3)_5Sb$, CH_3Tl^{2+} , CH_3Cd^+ , $(CH_3)_2Cd$, $(CH_3)_2Sb^+$, CH_3Sb^{2+} .

Solubility here refers to *air-free* distilled water, no complexing ligands. Range of solubilities is from $mg\text{ dm}^{-3}$ to $g\text{ dm}^{-3}$. Data from references.

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1.8 STABILITY OF ORGANOMETALLICS TO LIGHT AND ATMOSPHERIC REAGENTS

The primary radiolytic decomposition process for organometallic compounds is electronic absorption leading to organic radical formation. The absorption may lead to d-d electronic transitions in the case of transition elements, or to charge transfer to or from metal orbitals. The former often causes the dissociation of

metal–ligand bonds, and hence coordinative unsaturation, and the latter may facilitate nucleophilic attack at the metal. For organometallic compounds photo properties are more dependent on the wavelength of excitation radiation than is the case for organic compounds. Light stability is more relevant for volatile, i.e. R_nM , species as it is they that enter the atmosphere, and not the organometallic cationic derivatives that are complexed in sediments, water, etc. The most important of these are $(CH_3)_2Hg$, R_4Pb , R_4Sn , $(CH_3)_3As$, $(CH_3)_3Sb$, and $(CH_3)_2Se$.

Photolysis of $(CH_3)_2Hg$ at 254 nm in the gas phase produces CH_3Hg^0 and CH_3^0 radicals, further reactions producing ethane and methane by hydrogen abstractions. At normal temperatures ethene is formed; methane occurs at higher temperatures. CH_3HgI in organic solvents at 313 nm forms CH_3^0 by breaking of the mercury–carbon bond. In the gas phase, however, the mercury–halogen bond breaks. Diphenylmercury in organic solvents is photolysed to $C_6H_5^0$ and also decomposes thermally [12].

Degradation of methyltin halides in water at about 200 nm was observed to produce inorganic tin via sequential degradation, [13] and irradiation of alkyl-lead compounds at 254 nm also leads to breakdown [14]. These wavelengths exist in the homosphere (see below) and hence these materials would be expected to decay if they volatilize to the atmosphere. Atmospheric fates are discussed in detail in the appropriate chapters.

Processes in the real atmosphere are more complex and, in general, lead to much reduced stability from that suggested by laboratory experiments. There is the additional presence of oxygen, other free radicals and surfaces on which enhanced decomposition will take place. Where this has been measured the lifetime of organometallics in the atmosphere may be in terms of hours or days, rather than years. The lifetime of $(CH_3)_4Pb$ in the atmosphere, for example, has been estimated as several days [15].

From Figure 1.2, laboratory processes using wavelengths shorter than 340 nm might be thought to be less relevant under normal conditions for the lower atmosphere as radiation of these wavelengths hardly penetrates to the earth's surface [16]. However, at up to 85 km the atmosphere is homogeneous (homosphere) [17] and volatile materials released into it will, if stable, eventually circulate to that height and be subject to interaction with radiation penetrating to levels below 85 km. A wavelength of 120 nm is equivalent to 998 kJ mol^{-1} ; 240 nm is equivalent to 499 kJ mol^{-1} and 340 nm equals 352 kJ mol^{-1} . These are generally sufficient to homolyse metal–carbon bonds. The main absorbing medium at wavelengths below 340 nm is ozone, whose importance to biology is clear in view of the toxicity of short wavelength radiation. It might, therefore, be inferred that $(CH_3)_2Hg$, R_4Pb and R_4Sn , etc. will photolyse in the atmosphere to methyl radicals and $(CH_3)_nM^0$, and that further reactions to produce methane, ethane and other hydrocarbons will occur. However this is not the main decomposition process.

In addition to direct photolysis, reactions with other species produced by atmospheric photochemistry will also occur (e.g. OH^\bullet , O^3P and O_3). These

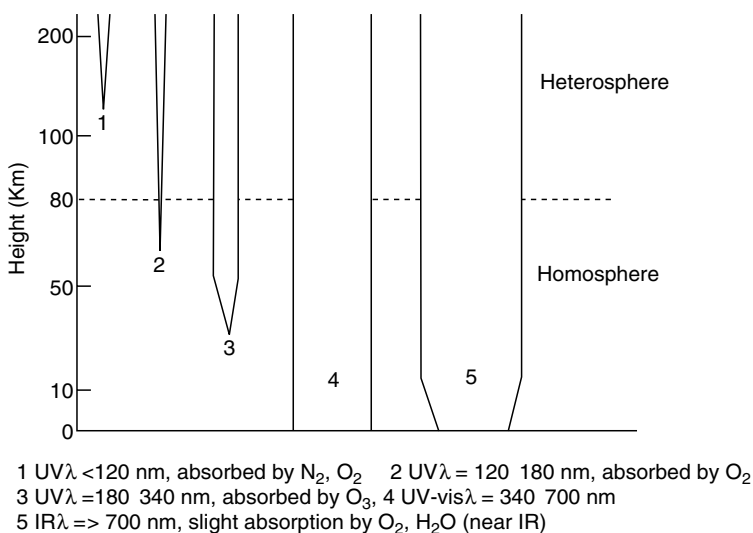
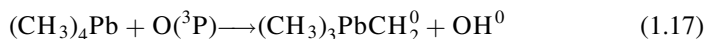


Figure 1.2 Absorption of light in the atmosphere

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occur faster than alternative heterogeneous processes available after adsorption on particles. (CH₃)₄Pb has been most thoroughly investigated [18] from this point of view (details are given in Chapter 4) but hydroxyl radical attack seems to be the most important first step reaction [19] here, viz. Equations (1.15–1.17). These chemical decomposition routes are much faster, in fact, than the photolytic decomposition processes described above when the real atmosphere is considered.



In view of these being reactions of a general nature, i.e. abstraction of hydrogen from a methyl group; insertion of ozone into a metal–carbon bond, it is likely that other volatile organometallics are decomposed chemically in the atmosphere this way, and similar mechanisms are likely to exist for R₄Sn, etc.

Thermal homolysis of metal alkyls leading initially to radical species (R_nM⁰ + R⁰) produces the radicals in their ground energy states. Photolysis produces products in higher excited energy states and, therefore, more energy is required to decompose compounds than is needed by the thermal route.

Photochemistry is, however, more effective than thermal decomposition in promoting permanent decomposition as the excited product fragments are less likely to recombine. The energy required for photochemical dissociation varies

but for relevant organometallic molecules it will be of the order of 100–120 kJ mol⁻¹ [20]. Taking D_1 values (Table 1.10) for mercury, tin and lead, we should expect energies around 320, 370 and 300 kJ mol⁻¹ to be required for the photochemical decompositions of (CH₃)₂Hg, (CH₃)₄Sn and (CH₃)₄Pb respectively. This is easily accomplished by, for example, 240 nm solar radiation (equivalent to 499 kJ mol⁻¹) which penetrates down to below 50 km altitude.

The volatile organometallics considered here are heavy molecules and their mixing ability in the atmosphere and consequent exposure to solar radiation must be considered. Higher diffusion into the atmosphere will give greater exposure to stronger intensities of radiation and faster photolysis. Higher energy radiation at greater height will also produced higher energy fragments, which are less likely to recombine. Mixing to cloud base level (varying from 0.5 to 12 km) is a rapid but complex phenomenon dependent on seasonal factors, temperature, inversions, maritime influence and the amount of atmospheric pollution in the area. Diffusion to greater heights is a slower process. For a fairly similar mass molecule CCl₃F (MW 137.5 versus 178.7 for (CH₃)₄Sn), it has been calculated that 50 to 80 years elapse between the release of CCl₃F at ground level and photochemical destruction at over 25 km altitude. (Boltzman distribution is assumed, leading to varied lifetimes for molecules.)

It can be concluded that the photochemical processes alone would decompose organometallics into radical species and the metals but that this might take decades. However, it should also be considered that other processes are occurring in the atmosphere, particularly where it is polluted. Atmospheric chemistry is complex. Species involved include O₃, O (triplet³P), OH[°], ClO_x[°], HO_x[°], NO_x[°]. All of these are highly reactive radicals particularly able to abstract hydrogen atoms from hydrocarbons or organometallics. In addition, particle-based heterogeneous decomposition may occur. Radical or singlet oxygen attack on organometallic species in polluted atmospheres will actually decompose

Table 1.10 Bond energies in alkylmetal compounds (in kJ mol⁻¹)

Compound	Mean bond enthalpy, \bar{D}^a	D_1	D_2
(CH ₃) ₂ Hg	123	218	29
(C ₂ H ₅) ₂ Hg	101	179	25
(iC ₃ H ₇) ₂ Hg	88	113	63
(CH ₂ =CH) ₂ Hg	141	202	80
Hg(CN) ₂	302	517	94
	180	252	97 ^b
(CH ₃) ₄ Sn	218	270	
(CH ₃) ₄ Pb	155	205	
(CH ₃) ₂ Zn	172	197	147 ^c
(CH ₃) ₂ Cd	141	189	92 ^c

^a $\bar{D} = \frac{D_1 + D_2}{2}$ etc

^b Separate estimates

^c But note environmental instability despite \bar{D} and D_1 values compared to (CH₃)₂Hg
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these molecules rather than direct photochemical decomposition alone. It can be concluded that the lifetime of organometallic species in the atmosphere is of the order of hours or days rather than decades, with metals and hydrocarbons being produced. Actual measurements and estimates reinforce these conclusions (see, for example, Chapter 4).

Actual decay rates will vary widely and have been studied under environmental conditions, e.g. for lead where rates vary from 3 to 4% per hour in winter to 16 to 29% in summer for $(\text{CH}_3)_4\text{Pb}$ [15, 18, 19]. For $(\text{C}_2\text{H}_5)_4\text{Pb}$ the corresponding rates are 17–23 and 67–93%. These are upper limits but it can be seen that organometallics are not persistent in the atmosphere, with direct photolysis accounting for little of the decay. Even in the area of 340 nm radiation, where the atmosphere is fully transparent to light, the energy associated with the wavelength, (352 kJ mol^{-1}), is sufficient to break most metal–carbon bonds (Table 1.2) to produce ground energy state products. Shorter wavelengths are needed to produce higher energy state products, but normally *chemical* decomposition processes predominate [21].

For $(\text{CH}_3)_2\text{Hg}$ also, a relatively fast degradation by hydroxyl attack has been deduced, with elemental mercury being produced and the rate constant for hydroxyl attack calculated at $2 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [22]. Overall it should be assumed that the common organometallic species emitted to atmosphere degrade rapidly and cannot be considered a serious environmental contaminant in most locations owing to their low concentrations (see relevant chapters) and relatively rapid rates of decay. The role and fate of their non-organometallic products merges into the field of organic and metallic atmospheric chemistry in general. That organometallics have a source and a transport role for metals in the atmosphere is clear.

1.9 COORDINATION PREFERENCES OF ORGANOMETALLIC SPECIES IN THE ENVIRONMENT

The general coordination preferences for metal cations has been understood by the Hard and Soft Acid and Base Principle. Hard acid metals are small, have higher oxidation states and are not easily polarized—they bond preferably to hard donor bases. Soft acid metals are larger, have lower oxidation states and are more polarizable, and prefer to coordinate to soft donor bases.

Inorganic metals in the environment tend to follow this principle—hard acid metals such as magnesium, calcium, tin(IV), etc. are found in the earth's crust as oxides or carbonates, while softer metals such as mercury or lead are found in sulphides. Methyl groups are more electronegative than metals and generally withdraw electron density from metals (increasing hardness). Larger aliphatic groups are more electron releasing and polarizable than methyl groups and tend towards producing softer organometallic molecules overall, though the effect is small. Table 1.11 gives details.