CHAPTER I

PROCESSES OF C–H BOND ACTIVATION

This chapter is devoted to some general problems which should be discussed before consideration of the reactions of alkanes and other hydrocarbons with non-metal and metal-containing substances. First of all we will consider general chemical properties of hydrocarbons and principle mechanisms of reactions with participation of these compounds.

I.1. CHEMICAL REACTIVITY OF HYDROCARBONS

Chemical inertness of alkanes is reflected in one of their old names, "paraffins", from the Latin *parum affinis* (without affinity). However, saturated hydrocarbons can be involved very easily in a total oxidation with air (simply speaking, burning) to produce thermodynamically very stable products: water and carbon dioxide. It should be emphasized that at room temperature alkanes are absolutely inert toward air, if a catalyst is absent. At the same time, some active reagents, e.g., atoms, free radicals, and carbenes, can react with saturated hydrocarbons at room and lower temperatures. These compounds are easily transformed into various products under elevated (above 1000 °C) temperatures, in the absence of other reagents.

Some important reactions of alkanes have been developed, e.g., autoxidation by molecular oxygen at elevated temperatures, which proceeds via a radical chain mechanism. The main feature of this and many other reactions is a lack of selectivity. Reactions with radicals give rise to the formation of many products; all possible isomers may be obtained. As far as burning is concerned, this process can be very selective, producing solely carbon dioxide, but apart from being an important source of energy, is useless from the viewpoint of the synthesis of valuable organic products. Chemical inertness of alkanes is due to

very high values of C–H bond energies and ionization potentials. Proton affinities are far lower than for unsaturated hydrocarbons (see Table I.1). Alkane acidities are much smaller than those of other molecules listed in Table I.1.

Table I.1. Characteristics of some hydrocarbons.

RH	$\longrightarrow$	R•	D(R–H) [a] kcal mol^{-1}	I.P. [b] eV	E.A. [c] eV	P.A. [d] eV	pK$_a$ [e]
CH_4		CH_3•	104	12.7		5.3	40
C_2H_6		C_2H_5•	98	11.5		5.6	42
C_3H_8		n-C_3H_7•	97	11.1		6.1	
		iso-C_3H_7•	94				44
C_4H_{10}		$tert$-C_4H_9•		10.6			
$cyclo$-C_6H_{12}		$cyclo$-C_6H_{11}•	94	9.9			45
C_6H_6		C_6H_5•	109	9.2	−1.1	7.5	37
$CH_2=CH_2$		$CH_2=CH$•	106	10.5	−1.8	6.9	36
$CH\equiv CH$		$CH\equiv C$•	120	11.4			25
$C_6H_5CH_3$		$C_6H_5CH_2$•	85	8.8	−1.3	7.3	35
CH_3CN		$NCCH_2$•	79	12.1		8.1	24
H_2		H•	104	15.4	−3.6	4.4	25
H_2O		HO•	118	12.6	1.8	7.1	16

[a] Energy of C–H bond.
[b] Ionization potential.
[c] Electron affinity.
[d] Proton affinity.
[e] Acidity.

Thus, we should conclude, that alkanes are extremely inert toward "normal" (i.e., not very reactive) reagents in reactions that proceed more or less selectively. In many respects, alkanes, especially lower ones (methane, ethane) are similar to molecular hydrogen. Indeed, like alkanes, dihydrogen while being inert towards dioxygen at ambient temperatures can be burned in air to produce thermo-dynamically stable water. The values of the C–H and H–H dissociation energy

for methane and dihydrogen molecules are almost exactly equal (104 kcal mol^{-1}).
Like methane, dihydrogen is relatively unreactive with respect to many reagents.
Ethylene, acetylene and benzene, compounds with stronger C–H bonds (106, 120
and 109 kcal mol^{-1}) in contrast to methane, are known to exhibit much higher
reactivity. This is due to the fact that both methane and dihydrogen are comple-
tely saturated compounds, i.e., contain neither π- nor n-electrons. Therefore, it is
not surprising that most reactions with unsaturated hydrocarbons proceed as
addition, followed in some cases by elimination. In the last decades, the reactions
involving metal complex activation of C–H bonds in unsaturated hydrocarbons
were described that do not involve the addition to a double or triple bond. These
reactions proceed via oxidative addition of C–H bonds to metal centers. Using
the term "the activation" of a molecule, we mean that the reactivity of this
molecule increases due to some action. In contrast to saturated compounds (and
saturated bonds), the activation of the unsaturated species (or their fragments)
may be induced by coordination of a particle followed by the addition to this
bond or by the rupture of the unsaturated bond. For example, for olefins and
arenes such activation can be caused by π-complexation. It is known that π-
coordination of the olefinic double bond with some metal ion gives rise to the
enhanced reactivity of the organic fragment in its interaction with nucleophiles
[1a,b]. Carbonyl group, CO, when coordinated to a metal, becomes reactive with
nucleophilic reagent [1a, c–f].

However, what is "the activation of ordinary σ-bond"? It is reasonable to
propose that the activation of, for example, the C–H bond, is the increasing of
the reactivity of this bond toward a reagent. As a consequence, such a bond is
capable of splitting, thus producing two particles instead of one initial species. In
many cases such a rupture of a saturated bond is implied when the term
"activation" is used. However, strictly speaking, the splitting of the bond is in
fact a consequence of its activation. It seems that in some respects the term
"splitting of C–H bond" would be more correct. It is noteworthy that in the last
years examples of coordination between some particles (and metal complexes
also) and saturated hydrocarbons or their fragments were demonstrated [2]. In
the present monograph, we will consider all processes of splitting C–H bonds in
hydrocarbons by metal complexes as well as the problem of coordination of
alkanes or alkyl groups (from various organic compounds) with metal
complexes. To concern this problem is important when we discuss the possible

mechanisms of the C–H bond splitting, because such adducts of alkanes with metal complexes can lie on the reaction coordinate. It should be noted that the term "the activation of C–H bond" is noticeably more narrow than that of "the activation of hydrocarbons". Indeed, the activation of alkanes may also involve the splitting of C–C bonds. As for unsaturated hydrocarbons, their activation is outside the content of this book. Nevertheless, some reactions of formal substitution at aromatic C–H bond which proceed as addition followed by elimination (e.g., electrophilic metalation) will be surveyed. Metal complex activation of C–H bond in unsaturated hydrocarbons which does not involve the addition to double or triple bond (proceeding usually as oxidative addition) will also be a topic of this monograph.

I.2. Cleavage of the C–H Bond Promoted by Metal Complexes

Bearing in mind a mechanistic consideration, we propose to divide all the C–H bond splitting reactions promoted by metal complexes into three groups. This formal classification is based on the reaction mechanisms.

I.2.A. THREE TYPES OF PROCESSES

In the previous section, we discussed the term "activation" when applied to saturated compounds and concluded that the cleavage of an ordinary bond (e.g., C–H) can be a result of such activation, and in many cases, we might consider the activation and splitting as synonymous. We wish to describe here the classification that is based on types of interaction between the alkane and metal complex.

First Type: "True" (Organometallic) Activation

Processes where organometallic derivatives, i.e., compounds containing an M–C σ-bond (M = metal), are formed as an intermediate or as the final product, can be conveniently assigned to the first type. The σ-ligand in the resulting compound is an organyl group, i.e., alkyl, aryl, vinyl, acyl, etc. (all these groups

are bound to M via a carbon atom). Subsequently, the M–C σ-bond can be cleaved; naturally, in catalytic processes the dissociation of this bond is inevitable. The cleavage of the C–H bond with direct participation of a transition metal ion proceeds via the oxidative addition mechanism:

$$RH + M^{n+} \longrightarrow R-M^{(n+2)+}-H \qquad\qquad (I.1)$$

or an electrophilic substitution:

$$RH + M^{n+} \longrightarrow R-M^{n+} + H^{+} \qquad\qquad (I.2)$$

Conventionally speaking, metals in low and high oxidation state respectively take part in these reactions. In the case of electrophilic metalation of the aromatic nucleus, the reaction proceeds in two stages, the electrophilic species adding to the arene in the first step with the formation of a Wheland intermediate [3]. An analogous intermediate, which might be formed in the interaction of a saturated hydrocarbon with an electrophilic metal-containing species, should be much less stable. Much more probable is that this structure is a transition state corresponding to a maximum on the energy diagram (Figure I.1).

It is therefore not surprising that the reactivities of arenes and alkanes in electrophilic substitution reactions are very different, with the former being much more active. At the same time, the mechanism of the interaction (oxidative addition) of both saturated and aromatic hydrocarbons with complexes of metals in a low oxidation state is in principle the same. The reactivities of arenes and alkanes in oxidative addition reactions with respect to low-valent metal complexes therefore usually differ insignificantly. Furthermore, a metal complex via the oxidative addition mechanism can easily cleave the C–H bond in olefin or acetylene.

Thus according to our classification, the first group includes reactions involving "true", "organometallic" metal complex activation of the C–H bonds. We call this type of activation "true", because only in this case, the closest contact between metal ion and the C–H bond (i.e., normal σ-bond between M and C) is realized. A molecule of C–H compound enters in the form of an organyl σ-ligand into the coordination sphere of the metal complex.
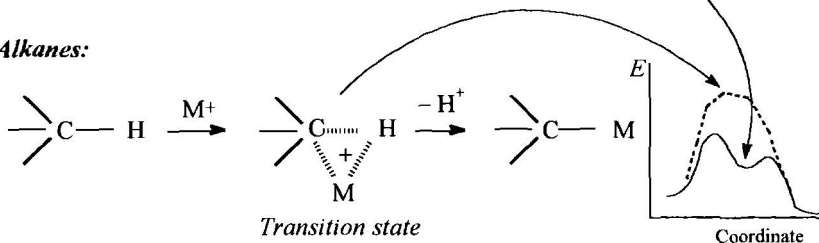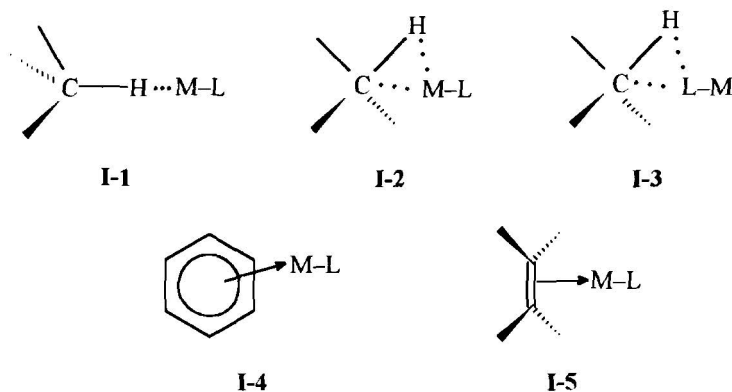
Arenes:

Wheland intermediate

Alkanes:

Transition state

Figure I.1. Schematic representation of routes for the interactions of arenes and alkanes with electrophilic transition metal complex, M.


I-1   I-2   I-3

I-4   I-5

Very weak adducts of metal complexes with alkanes (or alkyl groups), in which the C–H bond is directly coordinated to the metal (**I-1, I-2**) or its ligands (**I-3**), do not necessarily lead to subsequent cleavage of the C–H bond. However,

in some cases, compounds like **I-1, I-2** or **I-3** can be intermediate species lying on the reaction coordinate, which leads to σ-organyl products. These intermediates are analogous in some respects to much more stable π-complexes, (e.g., **I-4** and **I-5**) which are known to be formed by unsaturated hydrocarbons. This coordination of the metal complex to the C–H bond may be referred to as preactivation of the compound's C–H bond.

Second Type: Interaction of the Complex and the C–H Bond only via the Ligand

In the second group, we include reactions in which the contact between the complex and the C–H bond is only via a complex' ligand during the process of the C–H bond cleavage and the σ-C–M bond is not generated directly at any stage. The function of the metal complex usually consists under these conditions in abstracting an electron or a hydrogen atom from the hydrocarbon, RH. The radical-ions $RH^{+}\bullet$ or radicals $R\bullet$ which are formed, then interact with other species present in solution, for example, with molecular oxygen. One of the ligands of the metal complex can also serve as a species of this sort. An example is provided by the hydroxylation of an alkane by an oxo complex of a high-valent metal:

$$RH + O{=}M^{n+} \longrightarrow R\bullet + HO{-}M^{(n-1)+} \longrightarrow ROH + M^{(n-2)+} \quad (I.5)$$
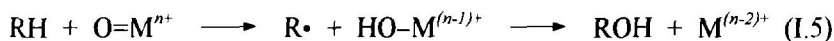
In this reaction, the oxo complex is an oxidant of the type CrO_4^{2-} or MnO_4^{-} and also, for example, one of the states of the cytochrome P450 enzyme – an oxoferryl species containing the $Porph^{+\bullet}Fe^{V}{=}O$ species.

It is noteworthy that the reaction with the intermediate participation of radicals can result in the formation of alkyl σ-complexes, for example via the following mechanism

$$RH + M^{n+} \longrightarrow R\bullet + M^{(n-1)+} + H^{+} \longrightarrow \sigma\text{-R-M}^{n+} + H^{+} \quad (I.6)$$
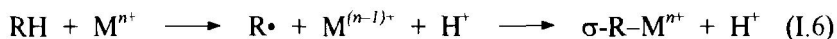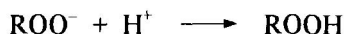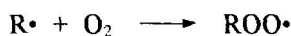
and the reaction should then be assigned to the first type. Since the alkyl σ-derivative is usually unstable, it is difficult to demonstrate its intermediate formation. The mediated (i.e., without contact with metal center of the metal

complex) splitting of the C–H bond in the hydrocarbon, RH, by a complex can be apparently effected also via a molecular mechanism, where RH is in direct contact only with a ligand of the complex. In some cases, the metal complex is capable of activating not only as a hydrocarbon but also as another reactant. Thus, for example, the active center of cytochrome P450 initially causes the transition of the oxygen molecule to a reactive state (one or the two atoms of dioxygen is coordinated to the iron ion, forming an oxo ligand). After this, the same active center activates the hydrocarbon molecule (with the participation of the oxo ligand).

Third Type: Metal Complex Generates an Independent Reactive Species Which Then Attacks the C–H Bond

Whereas the reactions included in the second group require direct contact between a molecule of the C–H compound and the metal complex (albeit via the ligand). In the processes belonging to the third type, the complex activates initially not the hydrocarbon but the other reactant (e.g., H_2O_2 or O_2). The reactive species formed (a carbene or radical, e.g., hydroxyl radical) attacks then the hydrocarbon molecule without any participation in the latter process of the metal complex which has generated this species. Oxidation of alkanes by Fenton's reagent [4a–c] is an example of a such type process:

$$H_2O_2 + Fe^{2+} \longrightarrow HO\bullet + HO^- + Fe^{3+}$$

$$HO\bullet + RH \longrightarrow H_2O + R\bullet$$

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + Fe^{2+} \longrightarrow ROO^- + Fe^{3+}$$

$$ROO^- + H^+ \longrightarrow ROOH$$

It should be mentioned that this is only a simplified scheme. Actual mechanism of this reaction is much more complex.

The Ishii oxidation reaction uses a combination of *N*-hydroxyphthalimide (NHPI, **I-7**) and cobalt derivative, e.g., Co(acac)₂, as a catalyst in the transformation of alkanes, RH, and other compounds into oxygenates under the action of

molecular oxygen [4d]. The reaction proceeds, though much less efficiently, in the absence of a metal compound. It is assumed that the role of metal complex is to facilitate conversions between NHPI and phthalimide *N*-oxyl (PINO, I-6) under the action of molecular oxygen.
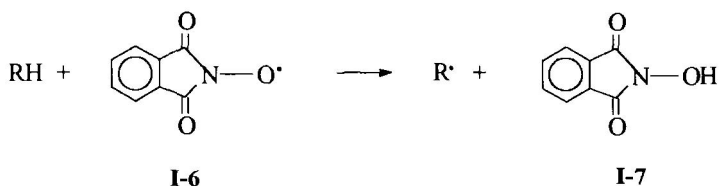
It is evidently that the metal catalyst does not take part in the direct "activation" of the alkane C–H bond by the radical.

I.2.B. MECHANISMS OF THE C–H BOND CLEAVAGE

The classification described above is an approximate subdivision of all reactions known in accordance with their mechanisms. One example was given in eq. (I.6). Such process can proceed with participation of ligands of metal complex. Photochemical reaction between, for example, alkane, RH, and $PtCl_6^{2-}$ [5], depicted by eq. (I.7) and initiated via mechanism of the third type can lead to the formation of an σ-organyl derivative of the metal and the entire process then belongs to the first type.

$$RH + [M{-}Cl] \xrightarrow{h\nu} R{\cdot} + M + H^+ + Cl^- \longrightarrow$$
$$\sigma{-}R{-}M + H^+ + Cl^- \qquad (I.7)$$
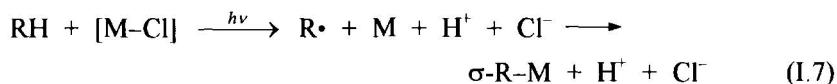
Evidently the unambiguous assignment of a process to a particular type requires a detailed knowledge of the reaction mechanism. However, at the present time the mechanisms of many processes have not been elucidated even in a broad outline. For example, organomagnesium compounds formed by co-condensation of magnesium and aryl halides from the gas phase are capable of catalyzing

alkane transformations at room temperature [6], Thus *n*-hexane can be converted into a mixture of saturated and unsaturated hydrocarbons C_4–C_8, with the conversion reaching 75%. The mechanism of this very interesting reaction seems to be unclear.

We may note that the mechanisms of reactions included in the last two types are, in general, not the same for paraffins, on the one hand, and aromatic hydrocarbons, on the other hand, even if the products of these reactions are of the same type. For example, alcohols and phenols may be obtained from alkanes and arenes respectively by the reaction in air with hydroxyl radicals generated by the action of a metal complex. However, in the case of alkane, an alcohol can be formed by the reduction of alkyl peroxide, whereas hydroxyl is added to an arene with subsequent oxidation of a radical formed. Hence follows the possibility that arenes and alkanes may exhibit different reactivities in each specific reaction.

I.3. BRIEF HISTORY OF METAL-COMPLEX ACTIVATION OF C–H BONDS

Although first metal-containing systems capable of reacting with hydrocarbons and other C–H compounds such as Fenton's reagent (hydroxylation) and mercury salts (direct mercuration) were discovered as early as the end of nineteenth century, the 1930s should apparently be regarded as the start of investigations into activation of C–H compounds with participation of transition metal complexes. During this period, the reaction involving the electrophilic auration of arenes was described [7a], the radical chain autoxidation of hydrocarbons initiated by metal derivatives was developed [7b], and the method was proposed for the oxidation of alkenes and arenes by hydrogen peroxide promoted by oxo-complexes [7c].

A second spurt in pioneering research into this field occurred in the 1960s. Reactions involving the cyclometalation (i.e., the cleavage of a C–H bond in the ligand linked to the metal via an atom of nitrogen, phosphorus etc.) of the aromatic nucleus [8a] and of a sp^3-hybridized carbon atom [8b] were found. It was demonstrated that palladium(II) derivatives induce the oxidative coupling of arenes [9a] and also the arylation of alkenes [9b], while platinum(II) salts catalyze the H–D exchange between benzene and D_2O [9c]. In 1969 the first

reactions involving activation of C–H bond in alkanes were discovered [10]: it was found that platinum(II) salts catalyze the H–D exchange between methane or its analogs and D_2O at 100 °C and the complex $CoH_3(PPh_3)_3$ induces the deuteration of methane by D_2 at room temperature. It has now become evident that, as expected, organometallic derivatives are formed as intermediates in all these instances. It was shown in the 1970s that alkanes are oxidized by platinum(IV) [11a], palladium(II) [11b], ruthenium(IV) [11c], and cobalt(III) [11d,e] compounds, and that complexes of iridium(III) [11f] and titanium(II) [11g] catalyze the H–D exchange.

The next decade was marked by a vigorous development of studies on the activation of alkanes and arenes by low-valent metal complexes via an oxidative addition mechanism with the formation of alkyl and aryl derivatives of metals (or alkenes) [12]. The number of known examples of the activation of the C–H bond by complexes of metals in a high oxidation state with formation of organometallic compounds is so far much less. Thus, the methyllutetium σ-complex, which enters into an exchange reaction with $^{13}CH_4$ presents another case of C–H bond activation by high-valent metal complex [13]. Ion $PtCl_6^{2-}$ metalates arenes similarly to palladium(II). However, unlike palladium(II) σ-aryl complexes of Pt(IV) are stable compounds and have been isolated [14]. The $PtCl_6^{2-}$ ion easily platinates arenes under the action of light [14] (or γ-irradiation [14]) giving the first example of photo-electrophilic substitution of arenes. Under the same conditions, alkanes are dehydrogenated to afford π-olefin complexes of platinum(II).

At the end of the 1980s and during 1990s, the intensity of investigations of the C–H bond activation by low-valent metal' complexes began to diminish somewhat and interest gradually shifted to the field involving the oxidation of hydrocarbons by high-valent metal oxo-compounds and oxygen (e.g., [4d, 15]). Attention is being especially concentrated nowadays on biological oxidation and its chemical models. Studies on the modeling of cytochrome P450 were stimulated by the use of iodosyl benzene and some other compounds as the donors of an oxygen atom in catalytic oxidation reactions and of metalloporphyrin as a model of the active center of the enzyme (e.g., [16]).

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