CHAPTER V

HYDROCARBON ACTIVATION BY METAL IONS, ATOMS, AND COMPLEXES IN THE GAS PHASE AND IN A MATRIX

Taking into account the experimental details of the reactions between metals and hydrocarbons in the gas phase and at low temperatures as well as their reactions in solutions, one will notice that they are very different. However it is reasonable to discuss such reactions of naked metal atoms in a special chapter of this book because the mechanisms of interaction between complexes in solutions and atoms or ions may have much in common. Again, from the experimental point of view, the chemistry of naked atoms at low temperature and the chemistry of gas phase reactions between ions and hydrocarbons are different, but the mechanisms are quite similar. In both cases the crucial step of such processes is oxidative addition of the C–H bond components to a metal atom or low-valent ion.

V.1. REACTIONS WITH METAL IONS, ATOMS, AND COMPLEXES IN THE GAS PHASE

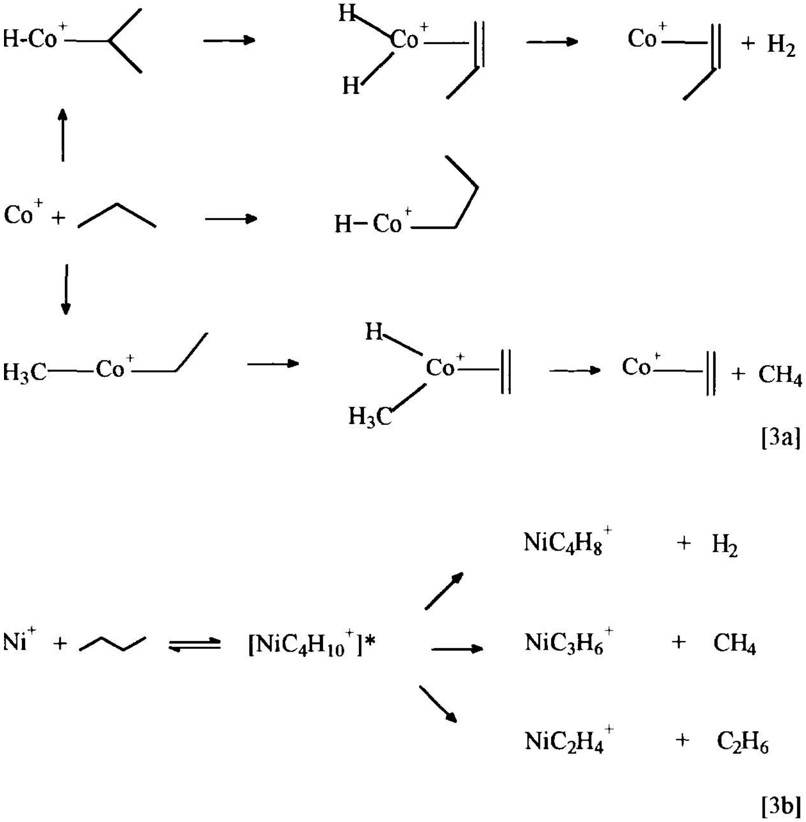
Metal ions are known to react with hydrocarbons, particularly alkanes, in the gas phase (see reviews [1]). A brief survey of these reactions will be given in the present section.

V. 1 .A THERMAL REACTIONS WITH NAKED IONS AND ATOMS

Alkanes

Usually oxidative addition of C–H and C–C bonds occurs at the first step of the reaction between metal ions and alkanes. The alkyl hydride or dialkyl derivative thus formed provides an entry to further transformations.

"Naked" metal ions (for example, Fe^+, Cr^+, Co^+, Ti^+, V^+) react with alkanes, alkanes bearing functional substituents, and silanes [2]. Some reactions of this type are shown in Scheme V. 1.



Scheme V.1. Examples of the gas-phase reactions between metal ions and simple alkanes. Reference numbers are in brackets.

Bare Pt^+ cations activate methane in the gas phase [4a,b] according to the equation:

$$Pt^+ + CH_4 \longrightarrow H\text{-}Pt\text{-}CH_3^+ \longrightarrow PtCH_2^+ + H_2$$

A cationic hydrido-methyl complex, $HPtCH_3^+$, is formed upon the almost barrierless insertion of a Pt^+ ion into a C–H bond of methane and then 1,2-migration of a hydrogen atom and subsequent elimination of H_2 from the transition-metal center gives the platinum carbene cation $PtCH_2^+$ with an apparent rate constant of $k = 8.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The reaction of ground-state platinum atoms produced by the photodissociation of $[PtMe_3(C_5H_4Me)]$ follows a termolecular mechanism [4c]:

$$Pt + CH_4 \; [Ar] \longrightarrow H\text{–}Pt\text{–}CH_3$$

The room-temperature limiting low-pressure third-order rate constant in argon buffer is $(2.1 \pm 0.9) \times 10^{-28}$ molecule^{-2} sm^6 s^{-1} and the limiting high-pressure second-order rate constant is $(6.3 \pm 0.3) \times 10^{-12}$ molecule^{-1} sm^3 s^{-1}.

The analogous reaction of metastable $Mo(^5S_2s^1d^5)$ with methane, which has been studied using the method of crossed molecular beams [5], proceeds via insertion of Mo into CH_4 with potential energy barrier less than or equal to 7.2 kcal mol^{-1}:

$$Mo + CH_4 \longrightarrow H\text{–}Mo\text{–}CH_3 \longrightarrow MoCH_2 + H_2$$

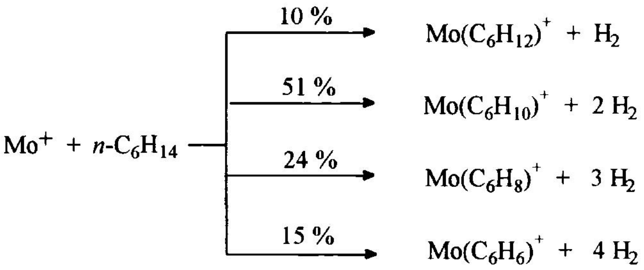
Reactions of methane with metal ions, M^+, can lead to oligomerization products as follows [6]:

$$M^+ + n\,CH_4 \longrightarrow \;\longrightarrow MC_nH_{2n}^+ + n\,H_2$$

For example, the cation $PtCH_2^+$ reacts with an excess of methane to produce species $Pt(C_2H_4)^+$ and higher ions $Pt(C_nH_m)^+$.

The interaction of higher alkanes with metal ions also induces dehydrogenation and affords various π-complexes (Schemes V.2 and V.3) [7]. The activation of various alkanes (as well as some unsaturated and aromatic hydrocarbons) by ions W^+ is shown in Table V. 1 [8].

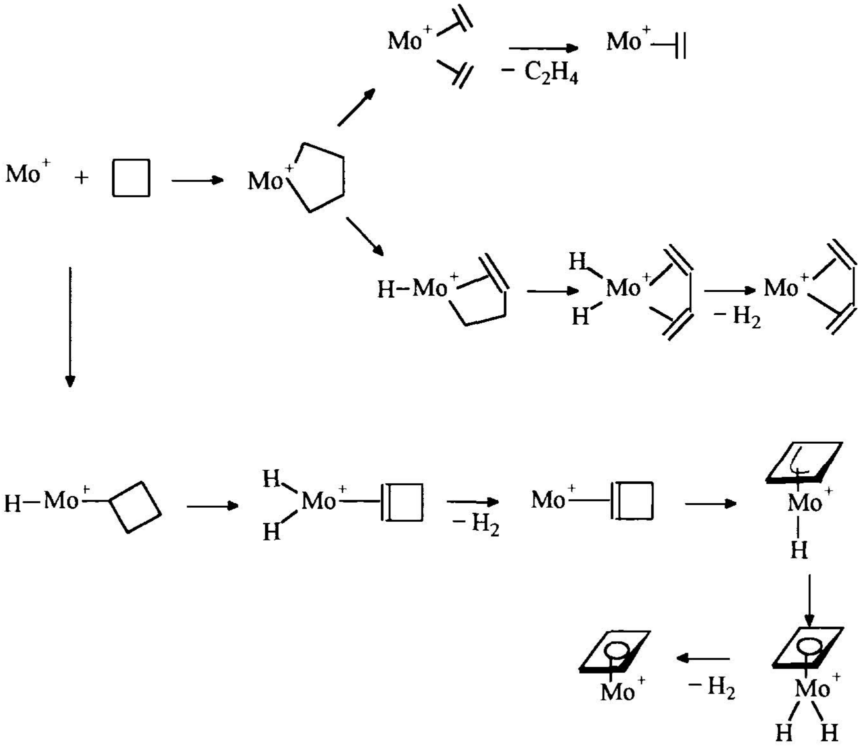
It is noteworthy that while ground state rhodium atoms insert into methane molecules [9a], there is no evidence of chemical reaction for the ground state of rhenium with CH_4 up to a temperature of 548 K [9b]. Reactions of metal cluster ions, for example, $MgFe^+$ [10a], Pt_n^+ [10b], Nb_n^-, and Rh_n^- [10c] with saturated and aromatic hydrocarbons in the gas phase have been recently described.



Scheme V.2. Dehydrogenation of *n*-hexane under the action of Mo^+.

Table V.1. Reaction of W^+ with hydrocarbons.

Hydrocarbon	Products	Comments
CH_4	$WCH_2^+ + H_2$	
C_2H_2	No reaction	
C_2H_4	$WC_2H_2^+ + H_2$	
C_2H_6	$WC_2H_4^+ + H_2$	
	$WC_2H_2^+ + 2\ H_2$	
C_3H_6	$WC_3H_2^+ + 2\ H_2$	
$c\text{-}C_3H_6$	$WC_3H_2^+ + 2\ H_2$	major
	$WC_2H_2^+ + CH_4$	minor
C_3H_8	$WC_3H_4^+ + 2\ H_2$	major
	$WC_2H_2^+ + CH_4 + H_2$	minor
$n\text{-}C_4H_{10}$	$WC_4H_6^+ + 2\ H_2$	
	$WC_4H_4^+ + 3\ H_2$	
	$WC_3H_4^+ + CH_4 + H_2$	
	$WC_3H_2^+ + CH_4 + 2\ H_2$	
$i\text{-}C_4H_{10}$	$WC_4H_6^+ + 2\ H_2$	major
	$WC_3H_2^+ + CH_4 + 2\ H_2$	minor
	$WC_3H_4^+ + CH_4 + H_2$	minor
C_6H_6	$WC_6H_4^+ + H_2$	
$c\text{-}C_6H_{12}$	$WC_6H_6^+ + 3\ H_2$	
$n\text{-}C_6H_{14}$	$WC_6H_8^+ + 3\ H_2$	major
	$WC_6H_6^+ + 4\ H_2$	
	$WC_5H_6^+ + CH_4 + 2\ H_2$	minor



Scheme V.3. Reaction of Mo^+ with cyclobutane.

Very interesting alkane functionalizations in the presence of metal ions in the gas phase have also been reported. Schwarz *et al.* have described recently [11a] a gas-phase model for the platinum-catalyzed coupling of methane and ammonia. Endothermic by 61 **kcal** $\mathbf{mol^{-1}}$ reaction

$$CH_4 + NH_3 = HCN + 3\,H_2$$

can be an economically attractive basis for industrial synthesis of hydrogen cyanide as well as molecular hydrogen. In the Degussa process, the reaction is performed at ca. 1500 K while in the Andrussow synthesis, added molecular oxygen transformed hydrogen atoms from methane into water. Both processes use platinum catalysts [12]. In the model study, the reaction of atomic platinum cations with methane and ammonia has been examined using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Mass-selected ion $PtCH_2^+$, formed in the reaction between Pt^+ and methane, reacts rapidly with ammonia ($k = 6.2 \times 10^{-10}$ sm^3 molecule^{-1} s^{-1}) to generate three different products in a ratio of 70 : 25 : 5 as shown below:

$$\begin{aligned}
&PtCH_2^+ + NH_3 \longrightarrow CH_2NH_2^+ + [PtH]\\
&PtCH_2^+ + NH_3 \longrightarrow [Pt,C,N,H_3]^+ + H_2\\
&PtCH_2^+ + NH_3 \longrightarrow NH_4+ + [PtCH]
\end{aligned}$$

The sequence of all steps leading to the final product, hydrogen cyanide, includes the dehydrogenation of CH_2NH:

$$\begin{aligned}
&Pt^+ + CH_4 \longrightarrow PtCH_2^+ + H_2\\
&PtCH_2^+ + NH_3 \longrightarrow CH_2NH_2^+ + [PtH]\\
&CH_2NH_2^+ + NH_3 \longrightarrow NH_4^+ + CH_2NH\\
&CH_2NH \longrightarrow HCN + H_2\\
&[PtH] + NH_4^+ \longrightarrow Pt^+ + NH_3 + H_2
\end{aligned}$$

Taking into account the results on gas-phase reaction between methane and ammonia, a working model for the heterogeneous catalysis has been proposed (Figure V.1) [11a].

The oxidation of methane with molecular oxygen is catalyzed by the atomic platinum cation [11b]. A key step in the catalytic cycle is the reaction of $PtCH_2^+$ with molecular oxygen to mainly (70%) regenerate Pt^+ via liberation of neutral species $[C,H_2,O_2]$ which either represents vibrationally excited formic acid and/or its decomposition products $(CO+H_2O)$ and (CO_2+H_2). Final oxygenates are methanol, formaldehyde as well as higher oxidation products (Scheme V.4). Experimentally determined reaction energies for the elemental steps are summarized in Table V.2 [11b]. The coupling of carbon dioxide and aromatic C–H bonds mediated by ion SiF_3^+ has also been observed [11c].

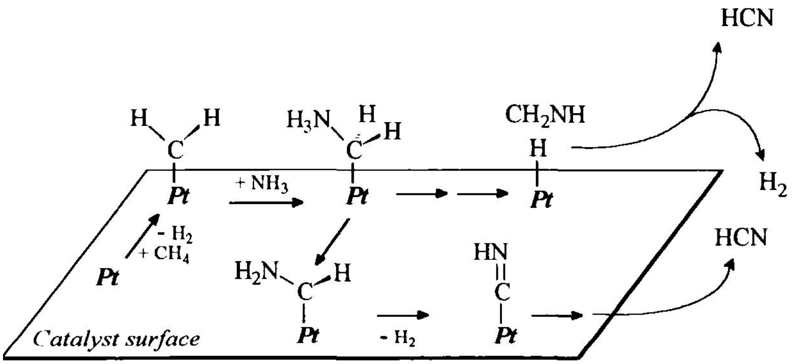
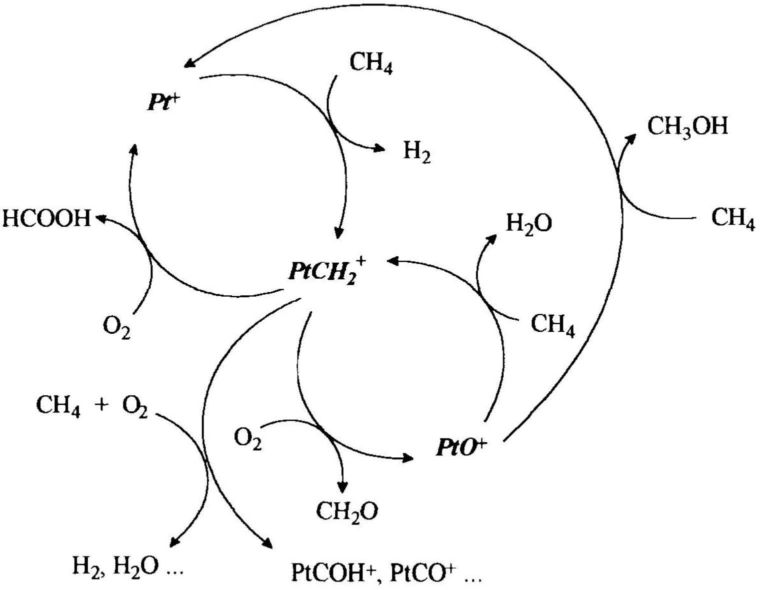


Figure V.1. Proposed mechanism for the methane–ammonia coupling catalyzed by a platinum surface.



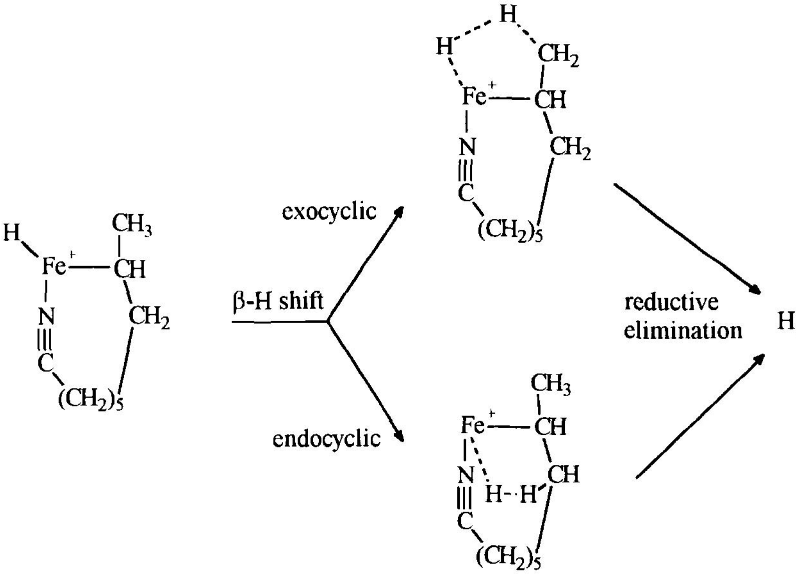
Scheme V.4. The catalytic cycle proposed for the Pt^+-catalyzed oxidation of methane in the gas phase.

Table V.2. Energies of steps of the Pt^+-catalyzed methane oxidation.

No	Reaction	ΔE, kcal mol^{-1}
1	$Pt^+ + CH_4 \longrightarrow Pt(CH_2)^+ + H_2$	-2.9
2	$Pt(CH_2)^+ + O_2 \longrightarrow PtO^+ + CH_2O$	-24.1
3	$Pt(CH_2)^+ + O_2 \longrightarrow Pt^+ + HCOOH$	-71.1
4	$Pt(CH_2)^+ + O_2 \longrightarrow Pt^+ + CO + H_2O$	-65.1
5	$Pt(CH_2)^+ + O_2 \longrightarrow Pt^+ + CO_2 + H_2$	-75.1
6	$PtO^+ + CH_2O \longrightarrow Pt^+ + HCOOH$	-47
7	$PtO^+ + CH_2O \longrightarrow Pt^+ + CO + H_2O$	-41
8	$PtO^+ + CH_2O \longrightarrow Pt^+ + CO_2 + H_2$	-51
9	$PtO^+ + CH_4 \longrightarrow Pt(CH_2)^+ + H_2O$	-46
10	$Pt^+ + O \longrightarrow PtO^+$	-77
11	$Pt^+ + CH_2 \longrightarrow Pt(CH_2)^+$	-112.5
12	$CH_4 \longrightarrow CH_2 + H_2$	-109.6
13	$O_2 + 2\,CH_4 \longrightarrow H_2 + CH_2O + CH_3OH$	-38.3
14	$O_2 + CH_4 \longrightarrow 2\,H_2 + CO_2$	-78.0
15	$O_2 + CH_4 \longrightarrow H_2 + H_2O + CO$	-68.0
16	$O_2 + CH_4 \longrightarrow H_2 + HCOOH$	-74.4

Remote Functionalization of Substituted Alkanes

In remote functionalization of alkanes bearing various groups, a bare transition-metal cation is first complexed to the functional group and then directed toward a certain region of the aliphatic backbone of the substrate [13]. For example, in the reaction of Fe^+ and Co^+ with nonanitrile, decanitrile, and undecanitrile [13d], both metal ions exhibit an overall similar reactivity pattern Molecular hydrogen, methane, and small olefins are formed as major neutral products. According to the theoretical study, the most favorable pathway of bond activation proceeds via initial insertion into the C–H bond at position C(8), followed by exocyclic activation of a C–H bond and reductive elimination of H_2 via a multicentered transition structure (Scheme V.5).



Scheme V.5. Remote functionalization of nonanitrile by Fe^+.

Aromatic and Other Hydrocarbons

Thorium and uranium metal and oxide ions react with several arenes (benzene, naphthalene, toluene, mesitylene, hexamethylbenzene) in the gas phase [14]. For M^+ ions, C–H and/or C–C bond activation was observed in the primary reactions for all the arenes.

The gas-phase reactions of bare lanthanide monocations Ln with fluorobenzene occur with C–F bond activation to produce LnF^+ and phenyl radical [15]. The reactions of various fluorocarbons with calcium monocation proceed according to the following equations [16]:

$$Ca^+ + CH_3F \longrightarrow Ca^+\text{–}F + CH_3\bullet$$

$$Ca^+ + CH_3CHF_2 \longrightarrow Ca^+\text{-}F + CH_3CHF\bullet$$

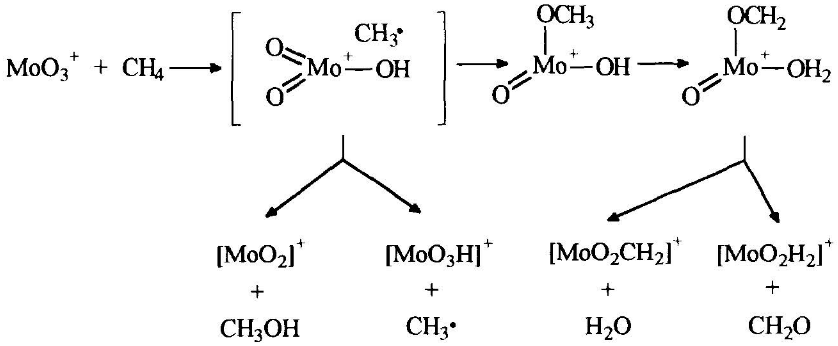
$$Ca^+ + C_6H_5F \longrightarrow Ca^+\text{-}F + C_6H_5\bullet$$

$$Ca^+ + CHF_3 \longrightarrow Ca^+\text{-}F + CHF_2\bullet$$

$$Ca^+ + CF_4 \longrightarrow Ca^+\text{-}F + CHF_3\bullet$$

V.1.B. THERMAL REACTIONS WITH LIGATED METAL IONS

Reactions of oxometal cations (e.g., CoO^+, ScO^+, FeO^+, ThO^+, UO^+, CeO_2 [17]) and positively or even negatively charged complex ions, for example, $Co_4(CO)_n^+$ [18] and $(OC)_2Fe^-$ [19], with various hydrocarbons in the gas phase have been described. The reaction between MoO^+ and methane is presented in Scheme V.6 [17j].



Scheme V.6. Reaction between MoO^+ and methane in the gas phase.

The following gas-phase reactions of metal derivatives with alkanes have also been described:

$$Sc(CH_3)_2^+ + c\text{-}C_6H_{12} \longrightarrow CH_3\text{-}Sc^+\text{-}c\text{-}C_6H_{11} + CH_4 \qquad [20a]$$

$$Sc(CH_3)_2^+ + c\text{-}C_5H_{10} \longrightarrow CH_3\text{-}Sc^+\text{-}c\text{-}C_5H_9 + CH_4 \qquad [20a]$$

$$\begin{array}{llll}
FeCF_3^+ + n\text{-}C_4H_{10} & \longrightarrow F\text{–}Fe^+\text{–}(C_4H_{10}) + CF_2 & (92\%) & \\
 & \longrightarrow C_4H_9^+ + FeCF_3H & (8\%) & [20b] \\
CoCF_3^+ + n\text{-}C_4H_{10} & \longrightarrow CoCF_3(C_3H_6)^+ + CH_4 & (75\%) & \\
 & \longrightarrow CoF(C_4H_{10})^+ + CF_2 & (18\%) & \\
 & \longrightarrow CoCF_3(C_4H_{10})^+ & (7\%) & [20b]
\end{array}$$

The gas-phase reactions of ligated iron ions $Fe(CH_2X)+$ with alkanes give different products depending on X [20c], Thus like bare Fe, C–C insertion, particularly terminal C–C insertion, is predominant for the reactions of $Fe(CH_2O)^+$, while C–H insertion is preferred for $Fe(CH_2S)^+$.

V.1.C REACTIONS WITH PHOTOEXCITED METAL IONS

Vapors of mercury, cadmium and zinc sensitize photochemical alkane transformations [21]. Thus, irradiation of propane with light of $\lambda = 307.6$ nm at 633 K and pressure 67–40000 Pa in the presence of zinc vapor gives rise to the formation of hydrogen, methane, ethylene and dimethylbutane [21a]. The first step in the reaction is a hydrogen atom transfer from the alkane to the excited zinc atom:

$$Zn^* + RH \longrightarrow Zn\cdots H\cdots R \longrightarrow ZnH + R\bullet$$

Alkane functionalization on a preparative scale by mercury-photosensitized C–H bond activation has been recently developed by Crabtree [22], Mercury absorbs 254-nm light to generate a $^3P_1$ excited state which homolyzes a C–H bond of the substrate with a 3° > 2° > 1° selectivity. Radical disproportionation gives an alkene, but this intermediate is recycled back into the radical pool via H-atom attack, which is beneficial in terms of yield and selectivity. The reaction gives alkane dimers and products of cross-dehydrodimerization of alkanes with various C–H compounds:

$$R'\text{–}H \xrightarrow{Hg^*} R'\bullet + H\bullet$$

$$R''\text{-}H \xrightarrow{Hg^*} R''\bullet + H\bullet$$

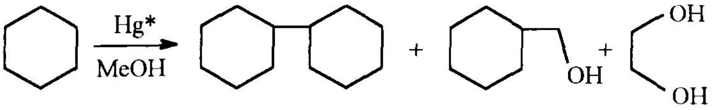
$$R'\bullet + R''\text{-}H \longrightarrow R''\bullet + R'\text{-}H$$

$$2\,R'\bullet \longrightarrow R'\text{-}R'$$

$$2\,R''\bullet \longrightarrow R''\text{-}R''$$

$$R'\bullet + R''\bullet \longrightarrow R'\text{-}R''$$

For example, the interaction between cyclohexane and methanol proceeds according to the equation:



When a mixture of alkane and ammonia containing a trace of mercury vapor was exposed to UV light, an oligomeric high-boiling liquid containing C, H, and N was formed. The authors proposed that imines are produced in the reaction:

$$RCH_3 + NH_3 \xrightarrow{h\nu} RHC{=}NH + 2\,H_2$$

Here **R** = **H** and CH_3. The analogous dehydrodimerization of aromatic substrates proceeded with the formation of an organometallic exciplex, $^3[Hg(\eta^2\text{-}C_6H_6)]$

V.2. REACTIONS WITH METAL ATOMS IN A MATRIX

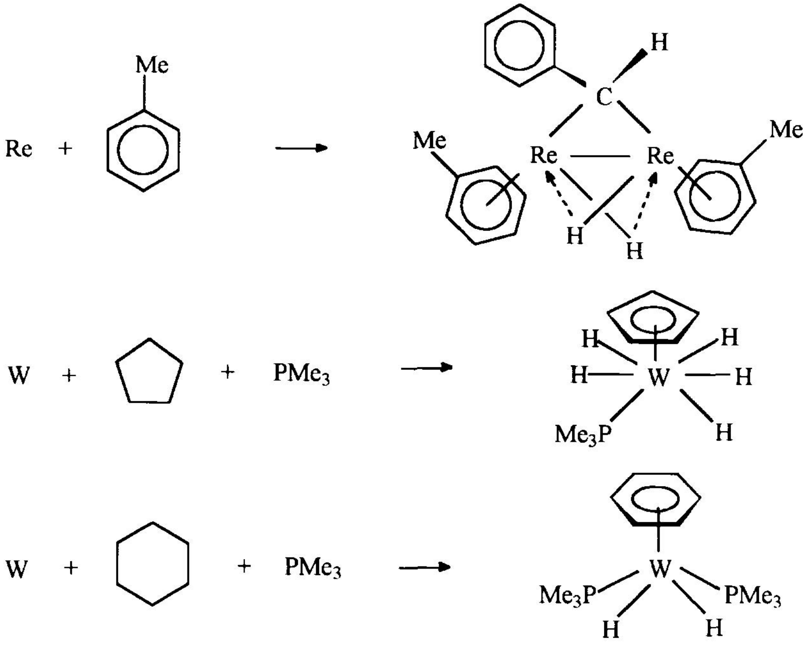
At high temperature metals react with alkanes. For example, at temperatures > 1600 °C, tungsten interacts with methane [23] according to the equation:

$$W + CH_4 \longrightarrow W_2C + WC + H_2$$

It is interesting that in recent decades the numerous reactions of metal atoms with hydrocarbons occurring at very low temperatures have been discovered and thoroughly studied [24]. A method of cocondensing metal atoms with various compounds has been used for instance in order to investigate the reaction of zirconium atoms with isobutane and neopentane at 77 K [25]. Metal atoms insert into both the C–H and C–C bonds:

$$Zr + C(CH_3)_4 \longrightarrow HZrCH_2C(CH_3)_3 + H_3CZrC(CH_3)_3$$

The reaction of Fe_2 dimers with methane in a matrix at 77 K gives rise to the formation of species **$H{-}FeFe{-}CH_3$** or **$FeFe{-}CH_3$** [26a]. Analogously, the C–H bond in alkanes is cleaved by nickel clusters [26b]. Methane activation has also been detected during the co-condensation of methane with aluminum atoms at 10 K [26c]. It is noteworthy that under the same conditions, atoms of Mg, Ti, Cr, Fe, Ga, Pd and some other metals do not react with methane.



Scheme V.7. Synthesis of organometallic compounds by the co-condensation of metals with hydrocarbons.

Various organometallic compounds can be prepared by the co-condensation of transition metals with some hydrocarbons (for examples, see Scheme V.7) [27].

In the cases when metal atoms in their ground state do not react with alkane at low temperature, an active species may be generated by photoexcitation of metal atoms. The excited atoms which are formed are capable of inserting into the C–H bond of alkane [28]. For example, irradiated ($\lambda < 360$ nm) iron atoms react with methane to produce the species CH_3–Fe–H. Analogously, atoms of Mn, Co, Cu, Zn, Ag and Au insert into the C–H bond of methane. However, atoms of Ca, Ti, Cr and Ni are inactive in this reaction [29]. Species containing M–C bonds can be detected by IR spectroscopy (Table V.3) [29].

Table V.3. IR spectra of species formed in the photolysis of metal atoms in a methane matrix at 15 K.

	ν, cm^{-1}				
Atom	C–H	M–H	CH_3		M–C
Mn	2932.9	1582.6	1142.3	550.3	500.7
Fe	2933.5	1653.1	1153.4	548.8	521.1
	2908.6	–	–	545.9	–
Co	–	1699.5	–	585.4	527.5
	–	–	–	576.7	–
Cu	–	1855.7	1200.1	613.8	433.9
	–	–	–	–	417.4
Zn	–	1845.8	1069.5	689.1	447.1
Ag	2907.6	1725.8	1232.4	6144.7	–
	2900.1	–	–	–	–
Au	–	2195.8	1202.8	610.9	–

Photoexcited particles Cu and Cu_2 can also activate methane [30]. An investigation of the reactions of excited gallium atoms with methane in Ar, Kr, and neat CH_4 matrices has shown that H–Ga–CH_3 was the only photoreaction product [31]. Activation of methane in a matrix by atoms of Zn, Cd, Hg, Mg, Ca, and Be has been reported [32]. Co-condensation of beryllium atoms produced by laser ablation with methane-argon mixtures onto a substrate at 10 K gave the following organoberrylium products: CH_3BeH, CH_3BeCH_3, CH_3Be, H_2CBeH., HCBeH. It is interesting that in the analogous reaction of magnesium or calcium atoms, only CH_3MH was identified [32d]. Theoretical investigations of reactions between photoexcited metal atoms and alkanes have been carried out [33].

References to Chapter V

1. (a) Beauchamp, J. L. In *High-Energy Processes in Organometallic Chemistry;* Suslick, K. S., Ed.; ACS: Washington, 1987, p. 11. (b) Dolgoplosk, B. A.; Oreshkin, I. A.; Soboleva, T. V. *Usp. Khim.* **1987**, *56,* 50 (in Russian), (c) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis;* Werner, H., Erker, G., Eds.; Springer: Heidelberg, 1989; Vol. 2, p. 203.(d) Schwarz, H. *Acc. Chem. Res.* **1989**, *22,* 282. (e) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22,* 315. (f) Eller, K.; Schwarz, H. *Chimia* **1989**, *43,* 371. (g) Armentrout, P. B. In *Gas Phase Inorganic Chemistry;* Russell, D. H., Ed.; Plenum: New York, 1989, p. 1. (h) Simões, J. A. M; Beauchamp, J. L. *Chem. Rev.* **1990**, *90,* 629. (i) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91,* 1121. (j) *Gas-Phase Metal Reactions;* Fontijn, A., Ed.; Elsevier: Amsterdam, 1992. (k) Eller, K. *Coord. Chem. Rev.* **1993**, *126***,** 93. (1) Freiser, B. S. *Acc. Chem. Res.* **1994**, *27,* 353. (m) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed Engl.* **1995**, *34,* 1973. (n) Schröder, D.; Heinemann, C.; Koch, W.; Schwarz, H. *Pure Appl. Chem.* **1997**, *69,* 273.
2. (a) Kickel, B. L.; Armentrout, P. B.. *J. Am. Chem. Soc.* **1995**, *117,* 764. (b) Schalley, C. A.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116,* 11089. (c) van Koppen, P. A. M.; Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1992**, *114,* 1083. (d) Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1992,** *114,* 2039. (e) Kickel, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 10742. (**f**) Carroll, J. J.; Haug, K. L.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1993**, *115,* 6962. (g) Noll, R. J.; Yi, S. S.; Weishaar, J. C. *J. Phys. Chem. A* **1998**, *1*02, 386. (h) Armentrout, P. B.; Tjelta, B. L. *Organometallics* **1997,** *16,* 5372. (i) Schroeter, K.; Schalley, C. A.; Schröder, D.; Schwarz, H. *Helv. Chim. Acta.* **1997**, *80,* 1205. (j) Hertwig, R. H.; Seemeyer, K.; Schwarz, H.; Koch, W. *Chem. Eur. J.* **997**, *3,* 1315.
3. (a) van Koppen, P. A. M.; Brodbelt-Lustig, J.; Bowers, M. T.; Dearden, D. V.; Beauchamp, J. L.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 2359. (b) Noll, R. J.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1994**, *116,* 10288.
4. (a) Irikura, K. K.; Beauchamp, J. L. *J. Phys. Chem.* **1991**, *95,* 8344. (b) Heinemann, C.; Wesendrup, R.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *239,* 75. (c) Campbell, M. L. *J. Chem. Soc., Faraday Trans.* **1998**, *94,* 353.

5. Willis, P. A.; Stauffer, H. U.; Hindrichs, R. Z.; Davis, H. F. *J. Chem. Phys.* **1998,** *108,* 2665.
6. Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1991**, *113,* 2769.
7. Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7,* 194.
8. Mourgues, P.; Ferhati, A.; McMahon, T. B.; Ohanessian, G. *Organometallics* **1997**, *16,* 210.
9. (a) Campbell, M. L. *J. Am. Chem. Soc.* **1997**, *119,* 5984. (b) Campbell, M. L. *J. Phys. Chem. A* **1998**, *102*, 892.
10. (a) Roth, L. M.; Freiser, B. S.; Bauschlicher, C. W., Jr.; Partridge, H.; Langhoff, S. R. *J. Am. Chem. Soc.* **1991**, *113,* 3274. (b) Jackson, G. S.; White, F. M.; Hammill, C. L.; Clark, R. J.; Marshall, A. G. *J. Am. Chem. Soc.* **1997**, *119,* 7567. (c) Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schattenburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1998**, *108,* 5398.
11. (a) Aschi, M.; Brönstrup, M.; Diefenbach, M.; Harvey, J. N.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed Engl.* **1998**, *37,* 829. (b) Pavlov, M.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Wesendrup, R.; Heinemann, C.; Schwarz, H. *J. Phys. Chem. A* **1997**, *101,* 1567. (c) Cecchi, P.; Crestoni, M. E.; Grandinetti, F.; Vinciguerra, V. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2522.
12. (a) Waletzko, N., Schmidt, L. D. *AIChE J.* 1988, 34, 1146. (b) Bockholt, A.; Harding, I. S.; Nix, R. M. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 3869.
13. (a) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7,* 2097. (b) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111,* 2857. (c) Hankinson, D. J.; Miller, C. B.; Allison, J. *J. Phys. Chem.* **1989**, *93,* 3624. (d) Holthausen, M. C.; Hornung, G.; Schröder, D.; Sen, S.; Koch, W.; Schwarz, *Organometallics* **1997**, *16,* 3135.
14. Marçalo, J.; Leal, J. P.; de Matos, A. P.; Marshall, A. G. *Organometallics* **1997**, *16,*4581.
15. Cornehl, H. H.; Hornung, G.; Schwarz, H. *J. Am. Chem. Soc.* **1996,** *118,* 9960.
16. Harvey, J. N.; Schröder, D.; Koch, W.; Danovich, D.; Shaik, S.; Schwarz, H. *Chem. Phys. Lett.* **1997**, *278,* 391.
17. (a) Schröder, D.; Eller, K.; Schwarz, H. *Helv. Chim. Acta.* **1990**, *73,* 380. (b) Ryan, M. F.; Fiedler, A.; Schröder, D.; Schwarz, H. *Organometallics* **1994**, *13,* 4072. (c) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32,* 1420. (d) Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114,* 1215. (e) Ryan, M.F.; Stöckigt, D.; Schwarz, H. *J. Am. Chem. Soc.*

1994, *116*, 9565. (f) Gibson, J. K. *Organometallics* **1997**, *16,* 4214. (g) Cornehl, H. H.; Wesendrup, R.; Diefenbach, M.; Schwarz, H. *Chem. Eur. J.* **1997**, *3,* 1083. (h) Heinemann, C.; Cornehl, H. H.; Dolg, M.; *Inorg. Chem.* **1996**, *35,* 2463. (i) Fiedler, A.; Kretzschmar, I.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 9941. (j) Kretzschmar, I.; Fiedler, A.; Harvey, J. N. Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1997**, *101*, 6252.

18. Pan, Y. H.; Sohlberg, K.; Ridge, D. P. *J. Am. Chem. Soc.* **1991**, *113*, 2406.
19. McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 476.
20. (a) Crellin, K. C.; Beauchamp, J. L.; Geribaldi, S.; Decouzon, M. *Organometallics* **1996**, *15*, 5368. (b) Chen, Q.; Freiser, B. S. *J. Phys. Chem. A* **1998**, *102*, 3343. (c) Chen, Q.; Chen, H.; Kais, S.; Freiser, B. S. *J. Am. Chem. Soc.* **1997**, *119*, 12879.
21. (a) Yamamoto, S.; Kozasa, M.; Sueishi, Y.; Nishimura, N. *Bull. Chem. Soc. Jpn.* 1988, *61,* 3439. (b) Yamamoto, S.; Hokamura, H. *Chem. Lett.* **1989**, 1429.
22. (a) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2935. (b) Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2946. (c) Muedas, C. A.; Ferguson, R. R.; Brown, S. H.; Crabtree, R. H. *J. Am. Chem. Soc.* **1991**, *113,* 2233. (d) Lee, J. C., Jr.; Boojamra, C. G.; Crabtree, R. H. *J. Org. Chem.* **1993**, *58,* 3895. (e) Ferguson, R. R.; Crabtree, R. H. *New J. Chem.* **1989**, *13,* 647. (f) Michos, D.; Sassano, C. A.; Krajnik, P.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32,* 1491. (g) Fowley, L. A.; Lee, J. C., Jr.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Organomet. Chem.* **1995**, *504,* 57. (h) Burdeniuc, J.; Chupka, W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 10119.
23. Kharatyan, S. L.; Chatilyan, A. A.; Merzhanov, A. G. *Khim. Fiz.* **1989**, *8,* 521 (in Russian).
24. (a) Power, W. J.; Ozin, G. A. *Adv. Inorg. Chem. Radiochem.* **1980**, *23,* 80. (b) Klabunde, K. J. *Chemistry of Free Atoms and Particles;* New York: Acad. Press. 1980.
25. Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101,* 1320.
26. (a) Barrett, P. H.; Pasternak, M.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 222. (b) Davies, S. C.; Severson, S. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 3024. (c) Klabunde, K. J.; Tanaka, Y. *J. Am. Chem. Soc.* **1983**, *105,* 3544.
27. (a) Green, M. L. H. *Pure Appl. Chem.* **1984**, *56*, 47. (b) Green, M. L. H.; O'Hare, D. In: *High-Energy Processes in Organometallic Chemistry;* Suslick, K. S., Ed.; ACS: Washington, 1987, p. 260.

28. (a) Ozin, G. A.; McCaffrey, J. G.; Mclntosh, D. F. *Pure Appl. Chem.* **1984**, *56,* 111. (b) Perutz, R. N. *Chem. Rev.* **1985**, *85*, 77. (c) Ozin, G. A.; McCaffrey, J. G.; Parnis, J. *M. Angew. Chem.* **1986**, *98,* 1076.
29. Billups, W. E.; Konarskii, M. M; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* 1980, *102,* 7393.
30. Ozin, G. A.; Mitchell, S. A.; Prieto, J. G. *Angew. Chem., Suppl.* **1982**, *369,* 798.
31. Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **1993**, *32,* 642.
32. (a) McCaffrey, J. G.; Parnis, J. M.; Ozin, G. A.; Breckenridge, W. H. *J. Phys. Chem.* **1985**, *89,* 4945. (b) Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117,* 8180. (c) Breckenridge, W. H. *J. Phys. Chem. A* **1996**, *100,* 14840. (d) Greene, T. M.; Lanzisera, D. V.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1998**, *120***,** 60097.
33. (a) Sevin, A.; Chaquin, P. *Nouv. J. Chim.* **1983**, *7,* 353. (b) Lefcourt, M. A.; Merritt, C. L.; Peterson, M. R.; Csizmadia, I. G. *J. Mot. Struct.* **1988**, *181,* 315. (c) Kolbanovskiy, Yu. A.; Gagarin, S. G. *Kinet. Katal.* **1988**, *29,* 88 (in Russian).