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# Aspects of Methane Chemistry

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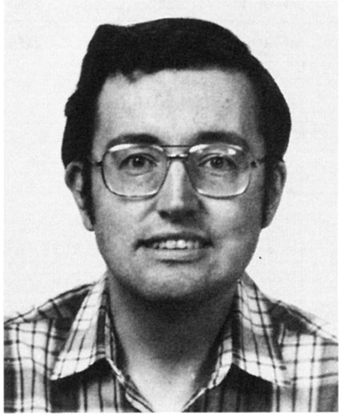
## Contents

## I. Introduction

As the simplest hydride of carbon and the major constituent of natural gas, methane has attracted increased attention in recent years. An important factor has been the recognition of the significance of world natural gas reserves to energy and chemicals production in the 21st century.[1] This expectation is linked to the gradual depletion of oil reserves and to the possible influence of any greenhouse global warming effect on energy policy. The combustion of fossil fuel has caused a rise in the $CO_2$ level in the atmosphere from an estimated preindustrial level of 280 ppm to the current 360 ppm. If current climate models are correct, this may cause a global warming trend in the next few decades. If public resistance to nuclear energy remains strong, natural gas is likely to become a more important energy source. The low C:H ratio of $CH_4$ means that on combustion it can furnish a much larger amount of energy per $CO_2$ molecule released than can oil (approximate ratio, $CH_2$) or coal (approximate ratio, CH).



Born in London in 1948, Robert Crabtree was educated at Oxford, worked from 1973 for the Centre Nationale de la Recherche Scientifique at Gif, near Paris, and moved to Yale in 1977, where he is now a Professor of Chemistry. He started his work on alkane functionalization on first moving to the United States, and has been involved in catalytic alkane conversion by oxidative addition, radical, and most recently, electrophilic routes. He has also worked in the areas of hydride chemistry, the complexation of $\sigma$-bonds to metals, hydrogen bonding, and the development of metal complexes as catalysts for enzyme reactions. He is author of an organometallic chemistry text and has awards in the area from the American Chemical Society and Royal Society of Chemistry.

Earlier reviews of different aspects of alkane activation[2] in general are cited below and duplication is avoided here.

## II. Occurrence, Production, and Origin

### A. Natural Gas

"Dry" natural gas, largely methane (Table 1), is a growing factor in world primary energy production, accounting for 18.4% in 1980 and 21.5% in 1991 (heat content basis). World production (Table 2) is currently rising at 2% per year and reserves (Table 3) constitute >60 years of current production versus 44 years for crude oil.[3] In the US, natural gas supplies 24.7% of energy consumption (1991). In addition to dry gas, gas can also be found with petroleum ("associated gas") in which case it often contains $C_2$–$C_4$ hydrocarbons; this heavy fraction is known as LPG, liquid petroleum gas. This gas was once flared at the well head but increasingly it is reinjected or recovered for use.

Natural gas reserves are currently estimated at $1.4 \times 10^{11}$ $m^3$ or 4900 TCF (trillion cubic feet). Much of it is nonassociated gas in remote locations where transport to the market poses problems. The largest reserves are found in the ex-USSR and the Middle East, but substantial reserves are present elsewhere.[4] Methane can also be released from subsurface rocks and landfills, in which case it can cause mine and other underground explosions.[5]

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**Table 1. Typical Composition of Natural Gas (% vol)**

| Gas | $H_2$ | CO | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $CO_2$ | $N_2$ |
|---|---|---|---|---|---|---|---|---|
| West Sole | 0 | 0 | 94.1 | 3.2 | 0.6 | 0.2 | 0.5 | 1.2 |
| Hewitt | 0 | 0 | 81.8 | 6.0 | 2.5 | 0.4 | 0.1 | 9.0 |
| Algerian LNG | 0 | 0 | 87.7 | 8.6 | 2.3 | 0.9 | 0 | 0.4 |
| Lacq[a] | 0 | 0 | 82.1 | 3.3 | 1.0 | 0.7 | 11.6 | 0.2 |
| Eurofisk[b] | 0 | 0 | 85.2 | 8.6 | 2.9 | 0.9 | 1.7 | 0.5 |
| Coal Gas[c] | 51.0 | 14.6 | 19.1 | 1.7 | 0 | 0 | 3.6 | 6.0 |

[a] France. [b] Norway. [c] For comparison.

**Table 2. Production of Natural Gas in 1990[a]**

| country | production ($\times 10^9$ $m^3$) | % of total | country | production ($\times 10^9$ $m^3$) | % of total |
|---|---|---|---|---|---|
| USSR | 844.8 | 33.6 | Mexico | 37.7 | 1.5 |
| Algeria | 126.6 | 5 | Norway | 37.0 | 1.5 |
| Netherlands | 72.4 | 2.9 | Romania | 29.5 | 1.2 |
| Indonesia | 58.7 | 2.3 | Nigeria | 27.7 | 1.1 |
| UK | 57.7 | 2.3 | Argentina | 23.1 | 0.9 |
| Saudi Arabia | 49.3 | 2 | Australia | 20.7 | 0.8 |
| Iran | 46.3 | 2 | Abu-Dhabi | 19.8 | 0.8 |
| Venezuela | 40.5 | 1.6 | Malaysia | 18.8 | 0.8 |

[a] Source: US Department of Energy, *International Energy Annual*, 1990.

**Table 3. World Proven Reserves by Region for 1988[a]**

| region | reserves ($\times 10^9$ $m^3$) | % of total | region | reserves ($\times 10^9$ $m^3$) | % of total |
|---|---|---|---|---|---|
| North America | 7994 | 7.2 | Africa | 7337 | 6.6 |
| Latin America | 7090 | 6.3 | Middle East | 31235 | 28.0 |
| Western Europe | 5512 | 4.9 | Asia | 7694 | 6.9 |
| Eastern Europe & USSR | 42396 | 40.0 | Japan & Oceania | 2420 | 2.2 |

[a] Source: Cedigaz, *Le Gaz Naturel dans le Monde en 1988.*

As a permanent gas, methane cannot be liquefied by pressure alone, but refrigeration is possible and liquified natural gas (LNG) has been transported by ship since 1959. Today about 4% of world energy demand is supplied by LNG; Japan (69%) and Western Europe (25%) are the chief importers and Indonesia (41%) and Algeria (25%) the chief LNG exporters. Indeed, Exxon and the Indonesian oil company Pertamina have recently signed an agreement to develop Natuna Field, a huge Indonesian offshore natural gas deposit. A $40 million investment is anticipated, including an LNG plant and marine terminal which are to be built on Natuna Island to allow gas delivery to East Asian markets.

Other than LNG transport, pipelines can be used for gas distribution, but compression to ca. 80 bars is required. In contrast with oil, where the cost of transport is a minor factor, the costs of gas transport are high so most gas is consumed in the region of its production.[6] Transport would be facilitated if it were possible to transform gaseous methane into a liquid fuel that would not need refrigeration or compression; hence the current interest in methane conversion. Of world production, about a one-quarter of it goes into each of the following uses: power generation, residential and commercial use, industrial use; and miscellaneous other uses.

"Sweetening" or removal of sulfur compounds such as $H_2S$, MeSH, and COS is usually necessary before distribution to the user.[7] Methane also occurs naturally as a hydrate, as discussed in the next section.

### *Origin of Natural Gas*

It used to be thought that natural gas originates along with petroleum from the pyrolysis of sedimentary organic matter, such as kerogen, and that the temperature determined the oil-to-gas ratio in the products: the higher the temperature, the more methane that was formed.[8a] The discovery of petroleum deposits lying deeper than would have been expected on the basis of this idea,[8b] together with the failure of pyrolysis experiments to yield a gas fraction with a sufficiently high methane content,[8c] has cast doubt on this picture, and a range of alternate ideas are now under discussion,[8b] without any clear consensus having yet emerged. It is likely that different types of kerogen deposits may give rise to substantially different ratios of gas to oil, independent of the thermal history of the deposit.

At least some of the methane in natural gas deposits is likely to be of biological origin and thermophilic methanogenic bacteria (see section IV.N) have been suggested as a possible source.[8d] Mango[8e] suggested that the hydrogen and α-olefins formed by kerogen pyrolysis might react with transition metal catalysis to yield methane. This idea has been supported by his[8f] experimental demonstration that an Eocene carbonaceous (C analysis, 14%) rock from the Monterey Formation (CA) converts hydrogen and α-olefins at 190 °C over 1 year into a gas fraction indistinguishable in molecular and isotopic composition from typical natural gas. The rock contains both Ni (350 ppm) and V (560 ppm), and these are suggested as the most probable catalysts. Recent reviews are available.[8g] $CH_4$ is a significant "greenhouse effect" gas.[8h]

## B. Methane Hydrate

Methane forms two hydrates[9] that are clathrate complexes in which the methane is trapped as a guest in an ice-like lattice as host and the water molecules are held together by H-bonds. The largest void is formed by a pentagonal dodecahedron ($5^{12}$ polyhedron) consisting of a cage of 20 hydrogen-bonded water molecules. Hydrates tend to form at temperatures below 300 K and gas pressures above 5 kPa. Idealized formulae for the two forms are $\{CH_4\}_9\cdot\{H_2O\}_{46}$ and $\{CH_4\}_{24}\cdot\{H_2O\}_{136}$, but real samples are nonstoichiometric. Formation of the hydrate can be a significant problem when natural gas is pumped in undersea pipelines. It is believed that substantial quantities of methane may be trapped as natural gas hydrates in marine sediments and, in cold climates, in subsurface deposits.[10] Methane hydrate has been detected, for example, under the Black Sea at 2000 m.[11] In such deposits methane can be the almost exclusive hydrocarbon present; in such a case, ethane and higher alkanes are usually present only at the ppm level. The isotope compositions suggest that much of this marine methane hydrate may be derived from biological methanogenesis, discussed in section IV.O, rather than from other sources.[12]

Arctic islands have significant deposits of methane hydrate, and these deposits have been considered as a potential fuel source. Methane being a greenhouse gas, concern has been expressed that any global warming might melt some of the hydrate and release

**Table 4. Some Physical Properties of Methane**

| property | value | ref |
|---|---|---|
| mp | −182.6 °C | *a* |
| bp | −161.6 °C | *a* |
| density (at bp) | 0.4240 | *a* |
| critical temperature | −82 °C | *a* |
| critical pressure | 45.8 atm | *a* |
| first ionization potential | 13.16 eV | *c* |
| second ionization potential | 19.42 eV | *c* |
| viscosity (gas, 35 °C) | $1.12 \times 10^{-4}$ g $cm^{-1}$ $s^{-1}$ | *d* |
| first BDE | 105.1(2) kcal/mol | *e* |
| proton affinity | 130.5(±1) kcal/mol | *g* |
| $pK_a$ (estd) | ca. 40 | *g* |
| $\Delta H^\circ_f$ | −17.889 kcal/mol | *h* |
| | Structure | |
| C−H bond length (e diff) | 1.1068(10) Å | *b* |
| H⋯H distance | 1.8118(70) Å | *b* |
| | Spectroscopy | |
| C-13 NMR shift | −2.3 ppm | *f* |
| $J$(C−H) | 125 Hz | *f* |
| vibrational frequencies[g] | 1306,[k] 1534[k]<br>2917, 3020[k] $cm^{-1}$ | *i* |

[a] Coffey, S., Ed. *Rodd's Chemistry of Carbon Compounds*; Elsevier: New York, 1964; p 367, et seq. [b] Bartell, L. S.; Kuchitsu, K.; de Neui, R. *J. Chem. Phys.* **1961**, *35*, 1211. [c] Frost, J.; McDowell, P. *Proc. Roy. Soc. A* **1957**, *241*, 194. [d] Lambert, J. *Proc. Roy. Soc. A* **1955**, *231*, 280. [e] Cohen, N.; Benson, S. W. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992; Chapter 6. [f] Berger, S. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992; Chapter 7. [g] Hopkinson, A. C. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1992; Chapter 11. [h] Rossini, F. D. *Selected Values of Chemical Thermodynamic Properties*; US Department of Commerce: Washington, DC, 1952. [i] Schrader, B. *Raman and IR Atlas of Organic Compounds*; VCH: Weiheim, 1989. [j] Relative to TMS as internal standard. [k] Active in IR spectrum.

**Table 5. Thermodynamics of Some Methane Reactions[a]**

| reaction | $\Delta G^\circ$ (kcal/mol) 400 K | $\Delta G^\circ$ (kcal/mol) 1000 K |
|---|---|---|
| $2CH_4 \rightarrow C_2H_4 + 2H_2$ | 18.9 | 9.5 |
| $2CH_4 \rightarrow C_2H_6 + H_2$ | 8.6 | 8.5 |
| $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ | −34.6 | −36.4 |
| $2CH_4 + O_2 \rightarrow C_2H_6 + H_2O$ | −18.4 | −14.5 |
| $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ | −26.0 | −27.8 |
| $CH_4 + Br_2 \rightarrow CH_3Br + HBr$ | −8.4 | −10.3 |
| $CH_4 + I_2 \rightarrow CH_3I + HI$ | 12.5 | 9.0 |
| $CH_4 + {}^1/_2O_2 \rightarrow CH_3OH$ | −25.4 | −18.0 |
| $CH_4 + O_2 \rightarrow CH_2O + H_2O$ | −69.0 | −71.2 |
| $CH_4 + S \rightarrow CH_3SH$ | −6.4 | −7.8 |
| $CH_4 + CO \rightarrow CH_3CHO$ | 16.0 | 33.6 |
| $CH_4 + CO_2 \rightarrow CH_3COOH$ | 19.2 | 35.5 |
| $CH_4 + CO + {}^1/_2O_2 \rightarrow CH_3COOH$ | −40.0 | −10.0 |
| $CH_4 + H_2O \rightarrow CO + 3H_2$ | 28.6 | −6.5 |

[a] Data are from ref 15.

large amounts of the gas into the atmosphere, which would give rise to positive feedback by encouraging further warming. A number of recent papers have examined the kinetics of hydrate formation.[13] Computational work has shown that a solvent-separated methane pair and a contact methane pair are both stable configurations in the system $CH_4$−$H_2O$.[14]

## III. Physical Properties, Structure, and Bonding and Their Influence on Reactivity

The chief physical properties of methane are reported in Table 4. Exhaustive listings of thermodynamic properties are available.[15] Table 5 gives $\Delta G^\circ$ values for some common methane reactions,[16] and the thermochemistry of hydrocarbon activation has been reviewed in detail.[17]

Methane has a tetrahedral geometry with four equivalent C−H bonds (see Table 2), as expected from the $sp^3$ hybridization of carbon. The molecular orbital description of $CH_4$ involves a $1t_2$ triply degenerate HOMO formed from the combination of the three p orbitals of carbon with pairs of H(1s) orbitals, together with a totally symmetric $1a_1$ orbital formed from a combination of C(2s) and the four H(1s) orbitals.[18] Many high-level quantum calculations have been performed on methane,[19a] and alkane activation,[19b] including the theoretical aspects,[19c] has been reviewed.

Compared with other alkanes, methane has an unusually high C−H bond strength, which means that it is normally the least reactive alkane in reactions that involve H atom abstraction by a radical reagent. Methyl cation is one of the least stable carbenium ions, so methane is also the least reactive alkane in reactions involving hydride abstraction by an electrophile. Alkyl substitution stabilizes both C-radicals and carbenium ions, so in both radical and electrophilic reactions, the reactivity of different types of C−H bonds is tertiary > secondary > primary > $CH_4$. $CH_4$ also has a very high ionization potential, so it is very unreactive in electron transfer reactions. Only if steric hindrance plays a decisive role, as it appears to do in some cases of oxidative addition (section IV.E), can methane be the most reactive alkane. A sufficiently hindered reagent should in general be selective for reaction with methane.

Kinetic and thermodynamic factors in alkane activation, including a comparison[19b] with $H_2$ and XH bonds ($X \neq C$), are discussed in detail in earlier reviews.[2,19d] Although hydrogen has a bond dissociation energy essentially the same as that of methane, it is very much more reactive. This is usually ascribed to the nondirectional character of hydrogen 1s orbitals, which allows them to form strong partial bonds to the reagent in the transition state for a reaction. In contrast, the $sp^3$ bonding orbital of a $CH_3$ group is directed and so is less well-adapted to forming bonds in a transition state, so barriers to reaction are higher. Alkane C−C bonds, having two directed $sp^3$ bonding orbitals, are even less reactive.

## IV. Chemical Reactivity of Methane

### A. Early Alkane Conversion Reactions

The earliest application of transition metal compounds to alkane chemistry was an 1881 study by Etard on the reaction of $CrO_2Cl_2$ with cyclohexane.[20] In 1898, Fenton[21] reported the $Fe^{2+}/H_2O_2$ hydroxylation system that bears his name (Fenton reagent). The latter still attracts interest in connection with continuing discussions about the mechanism of biochemical C−H oxidation (section IV.O). Apart from these rare cases, alkanes have generally been considered to be among the most difficult substrates for selective functionalization, and even today, very few synthetically useful reactions are known.

## B. High-Temperature Methane Conversion

Methane is very stable and only begins to decompose into the elements at 785 °C.[22] Above 1250 °C, acetylene is formed and does not decompose if the gas mixture is rapidly quenched. Hüls has operated such a process with electric arc heating,[23] in which the resulting acetylene can be oligomerized to aromatic compounds.[24] Methane and steam at 1000–1100 °C give acetylene, ethylene, and ethane.[25] These processes have proved too energy intensive for general application.

### *Methane Oxidation via Syngas*

For the reasons discussed above, methane conversion to a transportable liquid such as MeOH, $Me_2O$, or hydrocarbons is of intense current interest. In either case, the classical route involves initial conversion of methane to synthesis gas ($H_2$ + CO, otherwise known as "syngas"), which can subsequently be converted to methanol or to liquid hydrocarbons in a second step. The most important high-temperature reaction of methane is therefore "reforming" to synthesis gas, which is the only method in current commercial use for the large scale synthesis of fuels and chemicals from methane. Among the disadvantages of reforming are high capital costs, however.[26a] Several variants are known, but the simplest is steam reforming, shown in eq 1.

$$CH_4(g) + H_2O(g) \xrightarrow{\text{Ni catalyst, heat}} CO(g) + 3H_2(g) \quad (1)$$

$$\Delta H^\circ = 49.3 \text{ kcal/mol}$$

$$CO(g) + 2H_2(g) \xrightarrow{\text{zeolite catalyst, heat}} CH_3OH(g) \quad (2)$$

$$\Delta H^\circ = -21.7 \text{ kcal/mol}$$

$$nCO(g) + (2n + 1)H_2(g) \xrightarrow{\text{Fe catalyst, heat}} C_nH_{(2n+2)} + nH_2O(g) \quad (3)$$

$$\Delta H^\circ = \text{ca. } -50 \text{ kcal/mol}$$

The resulting CO/$H_2$ mixtures are then converted either to methanol with a zeolite catalyst or to higher paraffins by Fischer–Tropsch (FT) catalysts.[26b] The latter process is long established: the first plant, built by Ruhrchemie in 1936, was producing 600 000 tons of FT products per year by 1944. From 1955 to the present, Sasol has operated FT plants in South Africa. The product normally follows the Schultz–Flory distribution and typically consists of linear paraffins in the $C_6$–$C_{30}$ range.

$CO_2$ can partially or completely replace the steam in steam reforming and syngas is then produced with a lower $H_2$/CO ratio, which can be useful, but carbon deposition via CO disproportionation to C + $CO_2$ often becomes a serious problem.[27a] Several strategies have been used to mitigate this problem: (i) operating with a noble metal catalyst, which tends to show lower carbon-formation rates; (ii) using partly S-poisoned Ni, the basis of the SPARG process;[27b] and (iii) including oxygen in the mixture, which has been achieved using a special burner in the Topsoe Process.[27a] A recent contribution combines strategies i and iii by using a 1% $Ir/Al_2O_3$ catalyst to convert a $CO_2$–$O_2$–$CH_4$ mixture at 1050 K, which gives a 90% selectivity for syngas.[27c] Catalytic partial oxidation of methane to synthesis gas takes place at 700 °C over $Ni/Al_2O_3$, $Re/Al_2O_3$, and related catalysts.[27c−e]

In spite of the inherent inefficiency of oxidizing methane to the CO level in the reforming step only to reduce it again in the second step, these processes are still the only ones which are close to being economically viable[27f] for wide application. The first generation of new methane conversion plants that begin operation early in the next century are likely to employ these routes, but some workers in the field generally believe that a direct process may well replace the syngas route in the longer term.

### *Methane Oxidation via Direct Routes*

Direct conversion of methane to methanol (or any other useful product)[28a] would reduce the number of steps required and thus save greatly on capital costs in a commercial plant. For this reason, a large number of studies have been reported in the area of direct conversion. For the moment, none has succeeded in demonstrating the required combination of high conversion, yield, and catalyst stability that would be required to make direct conversion competitive with the classical reforming route.

Simple pyrolysis of $CH_4$ in air or oxygen does give methanol, but the short survival time of methanol in the system requires that conversion be kept low. For example, Newitt and Haffner[28b] found up to 22% selectivity for methanol at 1.6% conversion of methane at 380 °C and 100 atm. Better results can be obtained in a flow system in which the products are rapidly cooled.[29] For example, Newitt and Szego[30] saw MeOH (51%) and $CH_2O$ (4.1%) on heating $CH_4$–$O_2$–$N_2$ (90:3:7) at 430 °C for 5 s, but conversion was again low. Catalysts such as copper improve the reaction, which can give up to 51% MeOH at 3.7% conversion.[31] A more recent study of the effect of reactant ratios, pressure, temperature, and flow rate has given an optimum 81% selectivity for MeOH at 450 °C, 50 atm, and a $CH_4/O_2$ ratio of 20, but conversion was still only 8%.[26] Recent improvements include the use of staged $O_2$ injection along a membrane reactor.[32] The kinetics for the combustion of methane has been examined in great detail.[33a] From theoretical studies the activation energy for H abstraction from $CH_4$ by $O_2$ is believed to be ca. 60 kcal/mol.[33b]

Combustion can be catalyzed; for example, silica catalysts, which can also be doped with transition metal , can give formaldehyde and methanol at 600 °C with good yields at low conversion.[34a] $MoO_3$ can also be used as a catalyst for conversion of methane–$N_2O$ to formaldehyde; 3.5% of MeOH + $CH_2O$ is seen at 5% conversion.[34b] Ethylene has also been formed with relatively good selectivity at 775 °C over Mg–Li–$Mo/Al_2O_3$ catalyst; ethane and $CO_2$ are byproducts; oxidative coupling is covered in section IV.J.[34c] Methane is converted (0.5%) over $FePO_4$ to MeOH (26%) and HCHO (46%) by $H_2/O_2$ at 673–723 K.[34d] Methane also reacts with an oxygen–ammonia mixture at 800–1100 °C to give HCN; Pt catalysts improve the rate.[35] Cyanogen reacts at 700 °C to give HCN and $CH_3CN$:

$$CH_4 + (CN)_2 \rightarrow CH_3CN + HCN \qquad (4)$$

Methane/chlorine at very high temperatures (1500 °C) gives a mixture containing ethane, ethylene, $H_2$, and HCl.[36a] Dehydrodimerization–aromatization has been reported on amorphous pyrolitic carbons obtained from a number of organic precursors, including $n$-$Pr_3P$. For this case, at 1323 K, the methane conversion was 41% and the selectivity for benzene was 56%.[36b]

Diamond can be produced from methane–hydrogen at 1900–2300 °C and 20–100 Torr by filament-assisted chemical vapor deposition (FACVD); the mechanisms involved are not well-understood.[36c]

Unless a new concept is developed, the efficiency of the processes discussed in this section is unlikely to be greatly improved in the near future, so attention has turned to other areas.

### Methane Homologation on Heterogeneous Catalysts

In a new development that holds promise for possible future commercial applications, methane can be converted to $C_2$ and higher hydrocarbons in a two-step process.[37] In the first step, methane chemisorbs on any of a number of supported metal catalysts at a temperature of around 700 K to give carbidic carbon. In the second step, carried out at a much lower temperature, this carbidic carbon is hydrogenated to give $C_2^+$ hydrocarbons. The two-step nature of the process is made necessary by the thermodynamics, which indicate that the methane activation step is only favorable at >600 K but carbide hydrogenation to give $C_2^+$ hydrocarbons is only favorable below 350 K.[37a] Three types of absorbed carbon are recognized, carbidic ($C_\alpha$), amorphous ($C_\beta$), and graphitic ($C_\gamma$). The carbidic form is most desirable because it hydrogenates below 400 K to give $C_2^+$ hydrocarbons; the amorphous type only reacts around 500 K and gives only trace $C_2^+$ hydrocarbons; the graphitic type reacts only above 650 K and gives only methane.[37b] Typical catalysts ($Co/Al_2O_3$, Co/C, $Ni/Al_2O_3$) resemble those useful for the related Fischer–Tropsch process (see below) and a similar mechanism involving oligomerization of surface-bound $CH_x$ intermediates is proposed.[37c] In the case of Pt, products up to $C_6$ have been detected,[37d] and in the case of single crystal ultrahigh vacuum work on Pt, $C_6H_6$ was formed selectively.[37e] A three-step variant has also been studied in which the carbide intermediates first react with added $C_2H_4$, $C_2H_2$, or $C_3H_6$, before undergoing hydrogenation to $C_1$–$C_5$ products.[37f]

## C. Commercial Applications of Methane Conversion

Mobil commercialized a methane to gasoline process in New Zealand in 1986. The process starts with a reforming step to give $H_2$/CO, followed by catalytic conversion to methanol and then conversion to gasoline range hydrocarbons on a zeolite catalyst. The Mossgas plant run by Sasol at Mossel Bay in South Africa uses Lurgi's $CH_4$ reforming process to produce syngas, together with Sasol's own Fischer–Tropsch process to convert the syngas to fuel hydrocarbons.[38] In Bintulu, Sarawak, Malaysia, Shell has commercialized its Middle Distillate Synthesis (SMDS) in which the syngas is generated by partial methane oxidation, followed by a Fischer–Tropsch synthesis of hydrocarbons.[39a] Exxon has announced its AGC-21 process in which syngas is formed from natural gas, oxygen, and steam. In this way the exothermicity of partial oxidation is compensated by the endothermicity of the concurrent steam reforming pathway. A Fischer–Tropsch synthesis of relatively high molecular weight hydrocarbon wax is followed by a hydroisomerization step to produce a liquid hydrocarbon, which can be used as a feedstock in a conventional refinery. A small scale unit is operating at Baton Rouge, LA.[39b] In contrast to most petroleum-derived liquid fuels, these products are clear and colorless liquids with a very slight but agreeable odor. Clearly, the syngas route is technically viable; the only issue at present is the economics of these processes. This is largely determined by the crude oil price which is probably currently too low ($18/barrel) to make any of the natural gas-based processes economically viable in other than special situations.

Of historical interest is the partial oxidation of methane to formaldehyde with $O_2/HNO_3$ at 400 °C developed in Germany in the 1940s and once operated at Copsa Mica in Romania.[16]

## D. σ-Complexes

In a σ-complex, a σ-bond is bound to an electrophile via a two-electron, three-center bond, as in the triangular species, $H_3^+$, formed from $H_2$ and $H^+$ in the gas phase. An important development was the idea that carbonium ions, such as $C_2H_7^+$, have nonclassical bridged structures with two-electron, three-center bonds.[40]

With the discovery of the $H_2$ complex, $[W(H\text{-}H)(CO)_3(PC_6H_{11})_2]$ (**1**), by Kubas[41] in 1984, the area of σ-bond complexation[42] gained prominence in transition metal chemistry. The bond between a Lewis base ligand and a Lewis acid metal ion consists of a shared electron pair. Traditional ligands like ammonia use their lone pair to bind to a metal ion, but π-bonding ligands like $H_2C{=}CH_2$ have no lone pair and must therefore use their π-bonding electrons, which come to be shared between three centers in the complex; in the $M(H_2C{=}CH_2)$ case, these are the two carbons and the metal. Strong binding requires the presence of some back-donation, in this case from the filled $M(d_\pi)$ into the empty $C_2H_4(\pi^*)$ orbital.

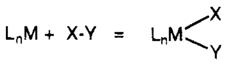
In σ-complexes, this idea is taken one step further. $H_2$ lacks both lone pairs and π-bonding electrons and must use its σ-bonding electrons to form a bond with the metal. As before, this electron pair comes to be shared between three centers in the complex, the two hydrogens and the metal. Back bonding is once again required for stability, in this case from the filled $M(d_\pi)$ into the empty $H_2(\sigma^*)$ orbital. An important point is that back-donation has different effects in a σ-complex than in a π-complex like $M(H_2C{=}CH_2)$, where the two carbons are held together by a C–C σ-bond that is unaffected by binding. In a σ-complex

**Table 6. Thermodynamics of Alkane Binding to $W(CO)_5$[a]**

| alkane | $\Delta G°$ (kcal/mol) | IP (eV) of HOMO[b] | alkane | $\Delta G°$ (kcal/mol) | IP (eV) of HOMO[b] |
|---|---|---|---|---|---|
| $CH_4$ | <5 | 14.33 | $n$-$C_4H_{10}$ | 9.1(±2) | 11.66 |
| $C_2H_6$ | 7.4(±2) | 12.35 | c-$C_5H_{10}$ | 10.2(±3) | 11.01 |
| $C_3H_8$ | 8.1(±2) | 11.51 | c-$C_6H_{12}$ | 11.6(±3) | 10.32 |

[a] From ref 39b. [b] The highest lying filled C−H σ-orbital in free alkane.

such as **1**, the σ-electrons are the only ones holding the two H atoms together. Although the $H_2(\sigma)$ to $M(d_\sigma)$ electron donation weakens but does not break the H−H bond, the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation, if sufficiently strong, can break the H−H bond to give a dihydride, H−M−H, the oxidative addition product. The formation of a σ-complex is therefore an initial stage of oxidative addition. Many σ-complexes (including **1**[41]) are in equilibrium with their oxidative addition products. Alternate ways of representing σ-complexes are shown as **1′** and **1″**.

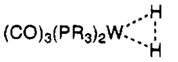


(5)

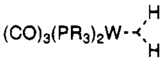
($L_n$ = ligand set; X, Y = H, halogen, alkyl...)

(6)

**1**



**1′**

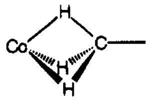


**1″**

### *Alkane Complexes*

Although many $H_2$ σ-complexes have been detected, a similar series of stable, isolable species has so far not been reported for methane of the other alkanes. The key differences may be the lack of full availability of the carbon lobe of the C−H σ* for back-donation, as a result of the steric inhibition of strict side-on binding, possible for $H_2$ but not for $CH_4$, and the lower basicity of the C−H σ-bond as a result of the higher electronegativity of C versus H. σ-Complexes of alkanes have been proposed from kinetic studies, however.[43]

The photogenerated $\{M(CO)_5\}$ (M = Cr, Mo, W) fragment has long been known to complex alkanes in matrix.[44] Unexpectedly, the measured M−alkane bond strengths (Table 6)[45] increase with the size of the alkane. As they correlate quite well with the IP of the alkane C−H bond, it was suggested that the M−alkane bond strength simply depends on the basicity of the alkane. A σ-complex has been detected in the reaction of $CH_4$ with Co atoms in a solid argon matrix. Of the possible structures, the IR data definitely indicate a $C_{3v}$ symmetry, but the $\eta^4$-structure shown below was preferred over the alternative $\eta^2$-structure [By an $\eta^n$-structure, we mean that $n - 1$ hydrogens are bound to the metal]. An additional argument in favor of the $\eta^4$-assignment is that a $C_{3v}$ $\eta^2$-structure would have to have a linear C−H··M group, inconsistent with the usual side-on arrangement favored by the bonding model described above.[46]



ESR data shows that the $RhH_2$ fragment forms a complex with methane in an argon matrix at 4 K.[47] Isotope exchange evidence shows that even in solution at room temperature alkane complexes are stable enough to show H/D exchange between alkyl and hydride in a number of species of type $L_nM(CD_3)H$.[48,49]

Metal ions in the gas phase also form methane complexes, such as $[Fe(CH_4)_n]^+$ ($n$ = 1−4), for which collision-induced dissociation MS studies indicate the following dissociation energies: first, 17.6(±1.5); second, 23.6(±1.4); third, 23.3(±1.0); fourth, 13.7(±0.8) kcal/mol; in a related study, $[Co(CH_4)]^+$ was shown to have a dissociation energy of 22.9 kcal/mol. Ab initio theoretical studies suggest a $[Co(\eta^2\text{-}CH_4)]^+$ structure with a Co−H distance of 1.94 Å. The $[Co-CH_4]^+$ bond strength is a result of ion polarization of the $CH_4$ and donation of electron density from the C−H(σ) to the $Co^+$, but $Co^+$ to C−H(σ*) back-donation is negligable.[50]

The formation of C−H··M σ-complexes has also been seen in many theoretical studies on the interaction of methane and other light alkanes with metal atoms or ions.[51] Theoretical studies (MCPF) on the oxidative addition of methane to the second row bare metal (=M) atoms from Y to Pd and their $MH_x$ hydrido metal fragments have shown that the reaction is exothermic in many cases (e.g., Y, Zr, Nb, Rh). When the atomic electron configuration and the product electron configuration are different, the resulting promotion energy term was found both to raise the barrier and to make the reaction less exothermic (or more endothermic). The transition states identified showed considerable structural differences, depending on the metal. The reaction with $H_2$ is always more exothermic (or less endothermic) as a result of M−H bonds being stronger than $M-CH_3$ bonds.[52]

Silane Si−H bonds are much better ligands than alkane C−H bonds and numerous examples[53a] of ($\eta^2$-$R_3Si-H$) coordination have been observed, even, most recently, for the case of $SiH_4$ itself.[53b]

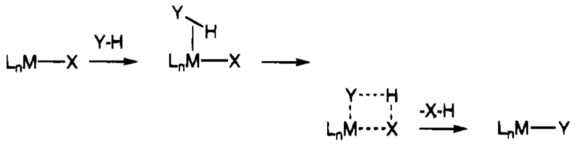
### *Agostic Complexes*

Although methane itself does not bind strongly enough to transition metal fragments for complexes to be isolable, there are a large number of stable C−H··M adducts in which a C−H bond of a ligand binds to the metal. These "agostic" compounds[42,53c] help us learn something about the properties of methane σ-complexes, which are the presumed intermediates in a variety of reactions. An important result of agostic binding is that the C−H bond becomes a very much better proton acid than in the free state. Loss of a proton to yield the isolable metal alkyl has been established most clearly for an agostic complex of Co(III).[54]

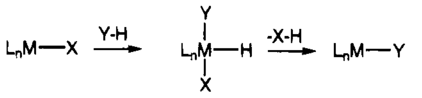
## E. σ-Bond Metathesis

σ-Bond metathesis is the process shown below (eq 7), in which an M−X bond is cleaved by a Y−H bond, where X and Y are monovalent fragments such as $R_3C$, $R_3Si$, and H. This pathway can normally only be unambiguously distinguished from the alternative oxidative addition/reductive elimination route (eq 8) in the case of a $d^0$ system where oxidative addition is forbidden, but it may also be possible in $d^n$ systems ($n \neq 0$) as well. An $L_nMX(CH_4)$ $\sigma$-complex is a plausible intermediate in eq 9 because such binding makes the bound proton acidic and therefore more likely to be transferred to any anionic cis X group. Theoretical studies of the reaction by density functional theory (DFT) find this type of intermediate adduct.[55] There is also theoretical evidence that the reaction trajectory for oxidative addition and $\sigma$-bond metathesis are quite similar up to the transition state but tend to deviate thereafter.[56] In oxidative addition it is back-donation of the $M(d_\pi)$ electrons into C−H ($\sigma^*$) that cleaves the C−H bond. In a $d^0$ system there are no $M(d_\pi)$ electrons and so only the M−X bonding electrons are left to cleave the C−H bond.

The reaction of $Cp_2Sc{-}H$ with methane to give $Cp_2Sc{-}Me$ and $H_2$ has been shown computationally (HFS-LCAO, A-MOL) to have an endothermicity of 42 kJ/mol, largely because the Sc−H bond is 45 kJ/mol stronger than the $Sc{-}CH_3$ bond. In the early stages of the reaction, an $\eta^2$-methane $\sigma$-complex is formed which has a binding energy of 25 kJ/mol.[57a] Reactions of alkanes with complexes of lanthanides and actinides[57b] and of early transition metals[57c] have been reviewed.



(7)



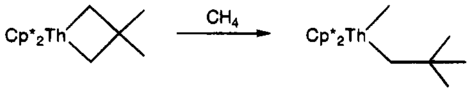
(8)

As early as 1975, Grigorjan et al.[58] found H/D isotope exchange between $CD_4$ (0.3−4 atm) and Ziegler−Natta catalysts of the type $Cp_2TiCl_2/AlMe_2Cl$ at 20−50 °C and between $CH_4$ and $D_2$ catalyzed by $Cp_2V$ at 70°. An alternative mechanism was proposed, however, because $\sigma$-bond metathesis was not recognized at that time.

In 1983, Watson[59] showed that isotopically labeled methane could exchange with a methyl group in $Cp^*_2LuCH_3$ and, faster, with $Cp^*_2YCH_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$). Part of the reaction goes via direct reaction of the $Y{-}CH_3$ bond with $CH_4$ and part via initial cyclometalation of the Cp* group.

$$Cp^*_2LuCH_3 + {}^{13}CH_4 = Cp^*_2Lu^{13}CH_3 + CH_4 \quad (9)$$

Marks et al. showed ring opening of a thorium complex in a similar type of reaction,[60] which is assisted by release of the ring strain energy of the metallacycle.



(10)

Ethane reacts more slowly and cyclohexane fails to react at all, so it can be used as a solvent. $CD_4$ gives the expected $Cp^*_2ThCD_3(CH_2CMe_2CH_2D)$ product with a $k_H/k_D$ of 6 ± 2 at 60 °C. Thermochemical work shows that metal−alkyl bond strengths in these systems are 70−80 kcal/mol, somewhat larger than found in the later d block.[61] Catalytic addition of methane across the ethylene double bond to give propane is catalyzed by $Ti(Ot\text{-}Bu)_4/AlEt_3$; 15% yield based on ethylene was reported.[62] Grigorjan also observed catalytic methane addition across the ethylene double bond, catalyzed by $Ti(Ot\text{-}Bu)_4/AlEt_3$, and the acetylene triple bond, catalyzed by Fe, Ni, and Pt complexes, to give propane and propene, respectively, in modest yields.[62]

Bercaw et al. find H/D exchange between $CH_4$ and $D_2$, catalyzed by $[Cp^*_2ScH]_n$. $Cp^*_2ScMe$ also reacts with $^{13}CH_4$ by a bimolecular pathway.[63]

### *Addition across M=N Bond*

In an unusual variant that may be best described as a 1,2-addition across a Zr=N bond, the transient zirconium imido intermediate of eq11, reacts with

$$[\{t\text{-}Bu_3SiNH\}_2Zr(CD_3)NHSi(t\text{-}Bu)_3] \xrightarrow{\text{heat, }-CD_3H} [\{t\text{-}Bu_3SiNH\}_2Zr{=}NSi(t\text{-}Bu)_3] \xrightarrow{CH_4} [\{t\text{-}Bu_3SiNH\}_2Zr(CH_3)NHSi(t\text{-}Bu)_3] \quad (11)$$

methane as shown. Cyclohexane is an inert solvent, presumably for steric reasons, and Ta gives similar chemistry.[64]

### *Late Metal Chemistry*

In a rare example of a $\sigma$-bond metathesis route being proposed for a late metal species,[65] $[Cp^*Ir(PMe_3)(CH_3)(OTf)]$ reacts at 45 °C with a variety of hydrocarbons, RH, including $^{13}CH_4$, to give $Cp^*IrL(R)OTf$ and $CH_4$. A $\sigma$-bond metathesis route is indeed very likely, although an Ir(V) intermediate cannot be completely eliminated in view of the stability of such species as $IrH_5L_2$.

Functionalization of the resulting M−Me group has yet to be achieved in these systems, which are also often air and water sensitive, at least in the early metal cases.

## F. Electrophilic and Superacid Reactions

The recent award of the Nobel Prize to G. A. Olah[66−75] emphasizes the importance of reactions of alkanes with electrophiles and superacids, which are not only themselves interesting but also have great commercial significance. Sufficiently strong Lewis and Bronsted acids can both protonate alkanes, but only in the absence of basic solvents, which otherwise level the acidity to that of the protonated solvent, hence the importance of non-nucleophilic solvents in this area. Alkane C−H and C−C bonds can both act as electron donors to the proton to give carbocations, of which $CH_5^+$ is the parent.[83d,e] The relative rates of attack follow the C−H bond basicity order: tertiary C−H > secondary C−H > primary C−H > $CH_4$.

Protonation of higher alkanes gives rise to carbenium ions and can hence cause skeletal rearrangements of linear to branched alkanes,[76a] often more useful in fuel applications. Modern versions of this reaction are practiced commercially on a very large scale in petroleum refining. Applications of electrophilic activation to methane conversion have been discussed by Olah.[67a] Initial protonation gives a species such as $CH_5^+$, for which two of the three most stable minima on the potential energy surface have one close H···H distance and can be considered as different rotamers of an $H_2$ complex of the methyl cation, although the molecule is so fluxional that it has been considered as not having a definite structure.[67b,c] H/D exchange to give deuterated alkanes is the simplest subsequent reaction.[68] In the presence of alkenes, alkylation is observed[71,72] with superacids such as $TaF_5$ or $SbF_5$/graphite, as for example in eq 12, which is thought to occur via the steps shown in eqs 13 and 14.

$$CH_2{=}CH_2 + {}^{13}CH_4 \xrightarrow{H^+} CH_3CH_2{}^{13}CH_3 \quad (12)$$

$$CH_2{=}CH_2 \xrightarrow{H^+} CH_3CH_2^+ \quad (13)$$

$$CH_3CH_2^+ + {}^{13}CH_4 \xrightarrow{-H^+} CH_3CH_2{}^{13}CH_3 \quad (14)$$

It is difficult to avoid oligocondensation of the alkene in these reactions, but a 60% selectivity for $C_3$ products was seen with $HF/TaF_5$.[72] More recently, $^{13}CH_4$ has been shown to give propane which is 96% monolabeled with $^{13}C$ for $SbF_5$/graphite.[76b]

Condensation of methane to give ethane and $H_2$ is endothermic at room temperature and pressure; for example eq 15 is endothermic by 16 kcal/mol. Condensation can still be achieved with superacids that are also mild oxidants; for example, at 50–60 °C, homologation of $CH_4$ to $C_2$–$C_6$ hydrocarbons can take place.[67] In this case, the medium must also act as oxidant (eq 18) to remove the $H_2$ as HF.[69]

$$2CH_4 \rightarrow C_2H_6 + H_2 \quad (15)$$

$$\Delta H = +16 \text{ kcal/mol}$$

The probable overall mechanism is:

$$CH_4 + HF + SbF_5 \rightarrow [CH_5][SbF_6] \quad (16)$$

$$[CH_5][SbF_6] \xrightarrow{-H_2} [CH_3][SbF_6] \xrightarrow{CH_4} [C_2H_7][SbF_6] \quad (17)$$

$$H_2 + SbF_5 \rightarrow 2HF + SbF_3 \quad (18)$$

Deliberate addition of oxidants such as $O_2$, $S_x$, or Se in superacid media also leads to homologation.[69] A heterogeneous version of this reaction is known on acid zeolites.[70] Oxidative oligomerization of $CH_4$ to an oil (MW = ca. 700) was found with $HSO_3F/SbF_5$[71a] and to $C_2$–$C_5$ hydrocarbons is also known on Zn–ZSM5 zeolite.[71b] Zeolites are useful in this area because they are heat-stable acids and the cavity size of the internal pore structure limits the amount of oligomerization that can take place.

### Functionalization Pathways

Other oxidants lead to the formation of oxygenated products. For example,[73] $H_2O_2$ gives methyl alcohol, which is protected from further oxidation by conversion to the protonated form, $MeOH_2^+$, in the superacid medium. Product protection is an important issue in alkane reactions in general; otherwise overoxidation is the usual result. Ozone gives formaldehyde as the predominant product in a superacid medium.[74]

Halogenation is also possible in superacids: chlorine shows high (80–98%) selectivity for $CH_3Cl$ at conversions of 7–34%, in contrast to the low selectivity seen for the usual radical reactions involving $Cl_2$. In the superacid medium, the formation of $[MeClMe]^+$ protects the product and prevents overoxidation; Pt/$Al_2O_3$ and zeolites are also effective catalysts for this reaction.[75] With 20% $SbOF_3$ on $Al_2O_3$, 99% selectivity for MeBr formation was observed at 20% conversion in methane bromination.[75] Subsequent hydrolysis[67a] of the methyl halide is required if MeOH is the desired product, followed by reoxidation of the hydrogen halide back to the elemental halogen to make the system catalytic. A combined halogenation–hydrolysis–reoxidation process using $Br_2/H_2O/O_2$ has been described, but conversion is modest.[67a] Recently, $N_2F^+$ and $NF_4^+$ have been shown to be $F^+$ equivalents capable of selective fluorination of methane to $CH_3F$. In HF or pyridine/HF at 20 °C, $N_2F^+$ gives predominantly $CH_3F$ and $NF_4^+$ gives exclusively $CH_3F$. $F^+$ attack on a C–H bond is proposed and calculations suggest that the proposed intermediate $CH_4F^+$ may have a structure analogous to an HF complex of $CH_3^+$.[67d]

Cold, fuming sulfuric acid reacts slowly with methane to give methyl bisulfate,[78] and $NO_2BF_4$ in $HSO_3F$ converts methane to $CH_3NO_2$.[79a] In both cases overoxidation is minimal as a result of the deactivating effect of the $OSO_3H$ and $NO_2$ groups in the product on the remaining C–H bonds. A mechanism has been proposed involving the formation of a $\sigma$-complex between the alkane C–H bond and the protonated form of $NO_2$, $NO_2H^+$, which has been called a "superelectrophile".[79b] Calculations by Schreiner, Schleyer, and Schaefer on $NO^+ + CH_4$, however, suggest that $NO^+$ directly attacks the carbon to give $CH_4NO^+$, which can be regarded as a methylene group complexing an $H_2$ and $NO^+$.

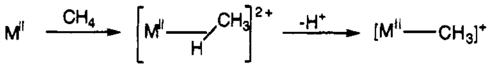
### Solid Superacids

In recent years, acidic solid state materials have tended to replace simple acids as reagents. Zeolites are the most common such materials, and USY and ZSM-5 have been used in catalytic cracking, ZSM-5 has also been used in arene alkylation, and Y-zeolite, erionite and mordenite have been used in hydrocracking. The advantages are very high thermal stability and high internal surface area. Variation of the pore size can also lead to control of reactant and product selectivities by molecular sieving effects. The acid form of the zeolite is often formed by cation exchange with an ammonium salt followed by pyrolytic expulsion of the amine or amine fragments, leaving the proton trapped within the zeolite cavities.[80] Fluorinated resins such as Nafion can be useful solid acids in this context.[79d]

## G. Shilov Chemistry and Related Systems

Methane is an extremely poor acid, so it loses a proton only with difficulty. By analogy with the very large acidification that can be achieved when $H_2$ binds to metal ions in the form of an $H_2$ complex, if the electrophile forms a $\sigma$-bond complex with methane, the proton acidity of the methane should be greatly enhanced (section IV.D). We commonly find soft electrophiles (Pt(II), Hg(II)) involved in such reactions probably because (a) they bind methane transiently even in aqueous solution, hence we can have superacid catalysis in a conventional acid medium, and (b) they can hold the product $CH_3^-$ group in the form of an alkyl.

Consensus has not yet been reached on the mechanistic aspects; however, Shilov[19b] does not consider that the Pt(II) system has predominant electrophilic character and prefers a pathway in which the C–H bond oxidatively adds to the metal with concerted loss of a proton.[81] This is less likely for Hg(II), where a Hg(IV) transient would be required.


(20)

(e.g., M = Hg, Pt)

Once the alkyl has formed, it may be cleaved with protons, in which case we can have H/D exchange. More interestingly, it can also undergo nucleophilic attack by $Cl^-$ or $H_2O$ with reduction of the metal to give a functionalized $CH_3X$ derivative. In catalytic systems, a metal reoxidation step is required, which may precede or follow the nucleophilic attack step.

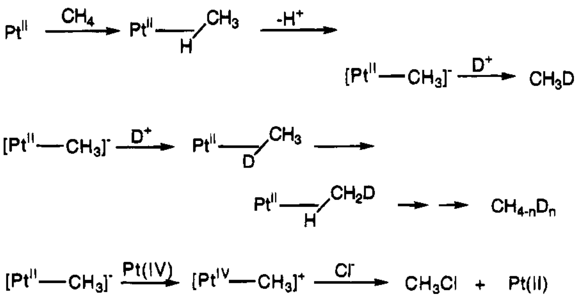
$$M^N-CH_3 \xrightarrow{Nu^-} M^{(N-2)} + CH_3Nu \qquad (21)$$

(e.g., $M^N = Hg^{II}, P^{IV}; Nu^- = Cl, H_2O, HSO_3^-$)

The overall process is loss of one proton and two electrons from $CH_4$ to give the methyl cation, which is trapped by the nucleophile. It is likely that different mechanisms are possible in which the order of events differs. Two or more of these steps may also be concerted.

### *Platinum Chemistry*

In very important work since the 1970s, Shilov and co-workers[81] have found that alkanes including methane can undergo both H/D exhange and functionalization with a number of transition metal electrophiles, of which $Pt(II)Cl_4^{2-}$ was the most intensively studied. For example, $K_2PtCl_4$ in $D_2O/CH_3COOH/DClO_4$ gave deuterated methane at 100–120°. A Taft correlation using substituted alkanes gives a $\varrho$ value of −1.4 for the reaction, consistent with Pt(II) having some electrophilic character.[82]


(22)

(23)

(24)

The reactions probably go via eqs 22–24, in which deprotonation of a $\sigma$-complex leads to an alkylplatinum (II) species. It is known[42] that $\sigma$-complexation causes a very large acidification of the coordinated $\sigma$-bond, explaining the facile proton loss from this intermediate. If this reacts with $D^+$, the result is deuteration of the alkane. Multiple H/D exchanges occur without dissociation of methane, which was originally explained on the basis of formation of $Pt{=}CH_2$, but with our improved understanding of $\sigma$-complexation, the intermediacy of a methane complex now gives a plausible alternative pathway.

In the presence of Pt(IV) as oxidant, methane can be converted to MeOH and MeCl; Pt(II) is still required as catalyst. This result is most easily explained if the Pt(II) alkyl is oxidized to the Pt(IV) alkyl by added Pt(IV). This is followed by nucleophilic attack by $Cl^-$ or $OAc^-$, which can lead to functionalization of the alkyl group to give $CH_3X$, the Pt(IV) being reduced to Pt(II) in the process. The similarity of the relative rates and the selectivity patterns for the H/D exchange and the oxidation reactions found for higher alkanes is consistent with both reactions going through the same initial Pt(II) alkyl.[83] Pt(II) halo and aqua species are in equilibrium in aqueous $PtCl_4^{2-}$ and the rate dependence with chloride concentration suggests that species such as $[PtCl_2(OH_2)_2]$ have the highest activity.

In one case an intermediate Pt–Me complex was detected by NMR in the reaction of $H_2PtCl_6$ with $CH_4$ (100 atm) at 120 °C; addition of $PPh_3$ allowed isolation of $PtMeCl(PPh_3)_2$.[84] In more recent work on the Pt(II)/Pt(IV) system, Labinger and Bercaw[85a–e] found 60% selectivity for MeOH at 5% conversion. Analysis of the data[85a] suggests that methane was 6 times *more reactive* than methanol, in contrast to the situation for most oxidants. Recent work on Pt(II) by Sen[87] also shows that methane is less reactive than methanol.

A particularly notable feature of the Shilov system is the use of aqueous acetic acid as solvent. An aqueous solvent is not tolerated by the superacid systems described above. This implies that the Pt(II) acts as a selective superacid toward the alkane but not toward the water. That is, the $pK_a$ of water is little affected by lone pair binding to Pt(II) compared with the large reduction of $pK_a$ when alkane binds as a $\sigma$-complex. The surprise is that alkane binds strongly enough to be competitive with water. Hence the importance of having a soft electrophile. The system uses robust ligands and only loses activity if metallic Pt is precipitated.

The functionalization of the newly formed $M-CH_3$ bond is a challenging step. The key feature of the Shilov system which allows this to happen is the presence of a redox-active Pt. The oxidation of Pt(II)–$CH_3$ to Pt(IV)–$CH_3$ allows the functionalization step to occur via nucleophilic attack on the methyl group with reduction of Pt(IV) to Pt(II).

Significant recent mechanistic work on the Pt(II)/Pt(IV) system has been reported by Labinger and Bercaw et al.[85] using both $CH_4$ itself and water-soluble substrates (RH). Initial formation of $Pt^{II}-R$

was proposed, although this step could not be studied directly. Subsequent oxidation of $Pt^{II}-R$ to $Pt^{IV}-R$ via electron transfer from the Pt(IV) oxidant was observed in a model system, $[PtMe(H_2O)(tmeda)]^+$. Evidence for nucleophilic attack of $Cl^-$ on the Pt(IV) alkyl was obtained from the stereochemical inversion observed at the α-carbon for erythro- and threo-$[PtCl_5(CHDCHDOH)]^{2-}$. A key feature is the selectivity of the system for basic C–H bonds, so reaction with $CH_4$ is competitive with reaction with $CH_3X$. This helps prevent overoxidation. Similarly, attack at the $CH_3$ group of EtOH is preferred. This selectivity is consistent with initial formation of a σ-complex because this is favored for basic C–H bonds.

Horvath[86] has studied $^{13}CH_4$ chlorination with the $PtCl_4^{2-}$ system in $D_2O$ at 125 °C by high pressure NMR and has found that most of the chloro intermediates are hydrolyzed in situ to form MeOH, $CH_2O$, HCOOH, and some $CO_2$.

### Palladium Chemistry

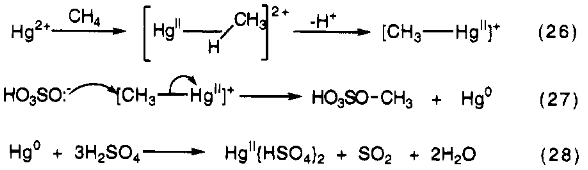
Work by Sen et al.,[87] has shown how Pd(II) can give a variety of methane functionalization reactions, for example, that shown in eq 25, where a 60% yield of

$$CH_4 + Pd(OAc)_2 \xrightarrow{CF_3COOH,\ 80\ °C} CH_3OCOCF_3 \quad (25)$$

the methyl ester based on Pd(II) was reported. In a related system, $H_2O_2$ oxidizes methane to the same ester in $(CF_3CO)_2O$ at 90 °C.

### Mercury Chemistry

In one of the most interesting developments of this type of chemistry, Periana et al.[88] showed that methane can be converted into $CH_3OSO_3H$ by heating methane with Hg(II) in concentrated $H_2SO_4$ at 180 °C. A mechanism was proposed of the type shown in eqs 26–28 with $H_2SO_4$ acting as reoxidant for the Hg(0) formed in the functionalization step is shown below. $MeOSO_3H$ was observed in the system by NMR. Alternative mechanisms have been proposed, however.[89]



In general, the systems in this section either involve the proton itself or a soft, redox-active electrophile, such as $SbF_5$ or Pt(II)/(IV). As electrophiles, they all tend to interact primarily with the C–H bonding electron pair. Their redox activity plays a variety of roles in allowing the functionalization step to take place.

### Related Systems

In the period from 1973 to 1980, Rudakov[81,90] looked at the oxidation of alkanes at 15–120 °C by a variety of oxidants in acid solution. Among the reagents studied were Hg(II), $H_2SO_4$, $NO_2^+$, Pd(II), Cr(VI), Ru(IV), and Mn(III). Some may go via the electrophilic pathway of the last section, others by oxidation, probably accompanied by concerted deprotonation of the resulting radical cation. The most readily available summary of the results appears in Shilov's book.[81] Kinetic isotope effects in the range of $k_H/k_D = 1.9–5.2$ show that C–H(D) bond breaking is involved in the transition state. Taft $\varrho$ values from −1.7 to −6.8 were found, together with tertiary > secondary selectivity ratios for alkane C–H bonds of 12–3000. The authors suggest that the proton-coupled electron transfer pathway of eq 29 may be important (*N* represents the oxidation state of the oxidant).

$$RH + L\text{-}M^N = R^{\bullet} + HL^+ + M^{N-1} \quad (29)$$

Certain powerful one-electron oxidants, such as $S_2O_8^{2-}$ and Ce(IV), can oxidize methane to $CH_3OSO_3H$ in sulfuric acid solutions. The intermediate radical cation is assumed to lose a proton to give the methyl radical, which is probably oxidized to the methyl cation, the solvolysis of which gives the observed product.[89]

$$CH_4 \xrightarrow{-e^-} CH_4^{\bullet+} \xrightarrow{-H^+} CH_3^{\bullet} \xrightarrow{-e^-} CH_3^+ \xrightarrow{HSO_4^-} CH_3OSO_3H \quad (30)$$

With ethane, the intermediate radical cation can undergo competitive C–C bond cleavage, leading to the formation of some $C_1$ products.

$$C_2H_6 \xrightarrow{-e^-} C_2H_6^{\bullet+} \rightarrow CH_3^+ + CH_3^{\bullet} \xrightarrow{-e^-} 2CH_3^+ \xrightarrow{HSO_4^-} CH_3OSO_3H \quad (31)$$

A similar cleavage has been found for the reaction of ethane with $NO_2PF_6$.[91]

Moiseev[92] reported methane conversion to $MeOCOCF_3$ in up to 90% selectivity by Co(III) complexes at 180 °C in a reaction which probably goes by a Shilov-type mechanism. König[93] described the oxidation of methane by aqueous $FeCl_3$ under anaerobic conditions in the presence of platinum black, a reaction recently studied by Kool and co-workers. Sen et al.,[95] have recently described the use of Pt(II)/Pt(0)/$O_2$ at 108–134 °C for the oxidation of ethane to acetic and glycolic acids; Pt(II) was proposed to carry out the initial CH activation step. Electrophilic alkane activation has been reviewed.[96]

The systems described up to this point in section IV.G are interesting in that they show useful chemical selectivity and many are very thermally robust and air- and water-stable. If their activity could be improved, they would be serious contenders for practical applications.

### Proton-Coupled Electron Transfer

Concerted loss of an electron and a proton from a molecule, or proton-coupled electron transfer (PCET), has been best characterized[97,98] in electrochemical studies, but it is likely to be common in chemical redox reactions. As applied to methane, the result of PCET is equivalent to H atom abstraction in that a radical is formed.

$$CH_4 \rightarrow CH_3^{\bullet} + H^+ + e^- \quad (32)$$

The PCET process has a number of advantages for reactions of alkanes. Incipient proton loss from $CH_4$ facilitates electron transfer from the developing $CH_3^-$ carbanion. The proton acceptor and the electron acceptor can be separate centers in the reagent. Although the reagent causes net H atom loss, it does not need to be a radical.

In an important paper, Cook and Mayer[98] have pointed out how the diamagnetic nonradical species $CrO_2Cl_2$ can abstract an H atom from cyclohexane. In this case, Cr(VI) accepts the electron and the oxo group accepts the proton in a PCET. For the related reagent $MnO_4^-$, figures are available which allow estimation of the $\Delta G°$ for H atom addition (eq 33).

$$Mn^{VII}O_4^- + H^{\bullet} = HMn^{VI}O_4^- \qquad (33)$$

$$\Delta G° = -79 \text{ kcal/mol}$$

The value for $CrO_2Cl_2$ is expected to be similar and both are high enough to be consistent with the observed rate of H atom abstraction from hydrocarbon C−H bonds.

Oxygens having "radical character" have been widely postulated as the active H-abstraction intermediates in metal−oxo chemistry, heterogeneous catalysts, and alkane oxidizing enzymes, but eq 18 shows how PCET allows net H abstraction in the absence of radical character ($CrO_2Cl_2$ and $Mn^{VII}O_4^-$ are diamagnetic). The PCET concept therefore needs more careful consideration by workers in the area.

The potential availability of a range of mechanisms, both concerted and nonconcerted, may help explain the wide variations of $k_H/k_D$ and tertiary: secondary selectivity found in alkane reactions of this type, depending on whether deprotonation or electron transfer is kinetically dominant.

## H. Oxidative Addition

A number of reactive transition metal species, bare atoms, ions, or complex fragments give oxidative additions to alkane C−H bonds. The fragments in question tend to be thermodynamically and kinetically unstable carbenoids, which, like $CH_2$ itself, can insert into C−H bonds.

### *Bare Metal Atoms*[99]

Billups et al.[100] found that bare Fe atoms in a $CH_4$ matrix can give $H-Fe-CH_3$ when irradiated at 300 nm; Ozin et al.[101] later showed that subsequent irradiation at 400 nm reverses the reaction.[102] Copper and even main group atoms such as Al can give the same type of reaction.[102] Excited state mercury ($^3P_1$, Hg*) in the vapor phase has long been known to homolyze alkane C−H bonds in a reaction that is also applicable in synthetic work.[103] Siegbahn et al.[104] have shown that the reaction involves formation of an exciplex, $[Hg(CH_4)]^*$, followed by insertion of Hg into the C−H bond (oxidative addition) with concerted release of R radicals.

### *Bare Metal Ions*

Armentrout and Beauchamp[105] have looked at the reactions of first row transition metal monocations such as $V^+$ with methane in a mass spectrometer. A variety of species including $MH^+$ and $MCH_n^+$ ($n$ = 1−3) are observed depending on the metal, the energy of the ions, and their electronic state. The reactions are often endothermic, in which case only electronically or translationally excited $M^+$ ions bring about reaction. Oxidative addition to give $H-M-CH_3^+$ has been suggested as the first step of the reaction. This work also allows good estimates of $M-CH_3^+$ bond strengths; for example, the bond dissociation energy (BDE) is 57.9 ± 2.4 kcal/mol for $Fe-CH_3^+$. A useful review has appeared.[105] More recently, third row (5d) transition metals have been shown to dehydrogenate methane and, for certain metals after long reaction times, even polymerize methane to give $C_2-C_8$ fragments bound to the metal ion.[106] This implies that Fischer−Tropsch type polymerization of $CH_2$ can occur even on a monometallic site.

$$M^+ + nCH_4 \rightarrow\rightarrow MC_nH_{2n}^+ + nH_2 \qquad (34)$$

$$(n = 1-8)$$

### *Isolable Complexes*[107]

The first examples in which the alkyl hydride products of alkane oxidative addition were directly observed were Bergman's[108] photochemical $Cp^*Ir(PMe_3)H_2$ system, which reacts with linear and cyclic alkanes, and Graham's[109] $CpIr(CO)_2/h\nu$, which, in a perfluorocarbon solvent, also reacts with methane (8 atm). The role of the light is to expel $H_2$ or CO to give a reactive intermediate, CpML, which then inserts into alkane C−H bonds. The Graham system gave reaction with $CH_4$ in a matrix even at 12 K, showing how low the barrier for CH oxidative addition is in this case.[110] In the Bergman system, methane activation was observed thermally, after prior loss of $C_6H_{12}$ from the cyclohexyl hydride.

$$Cp^*Ir(PMe_3)(C_6H_{11})H \xrightarrow{150\ °C,\ CH_4\ (20\ bar)} Cp^*Ir(PMe_3)(CH_3)H + C_6H_{12} \qquad (35)$$

Extensive efforts[111] to observe the presumed CpML intermediate by Bergman and Moore et al. were always thwarted by the formation of adducts CpML(S), where S could be the alkane solvent or even Xe, when liquid Xe is used as solvent. Good spectroscopic evidence for the formation of the alkane and rare gas complexes was obtained in fast kinetic studies. Recent theoretical work has probed the electronic structure of the presumed CpML intermediate.[112]

Related chemistry has been seen in the case of $(Me_3P)_4OsH(CH_2tBu)$, which loses neopentane at 80 °C under $CH_4$ to give a mixture of the methyl hydride and the product of Os insertion into the C−H bond of the phosphine. Intermediacy of the 14-electron species $(Me_3P)_3Os$ was proposed.[113] Photolysis of $[FeH_2(Me_2PCH_2CH_2PMe_2)_2]$ with methane in xenon at −100 °C also gives the methyl hydride.[114]

Oxidative addition of $H_2$ is common, but that of $CH_4$ is very rare. This is not so much a result of the greater kinetic reactivity of $H_2$ (section III) but that the $L_nM(H)_2$ adduct, having two strong M−H bonds (bond strength of ca. 60 kcal/mol) is much more likely

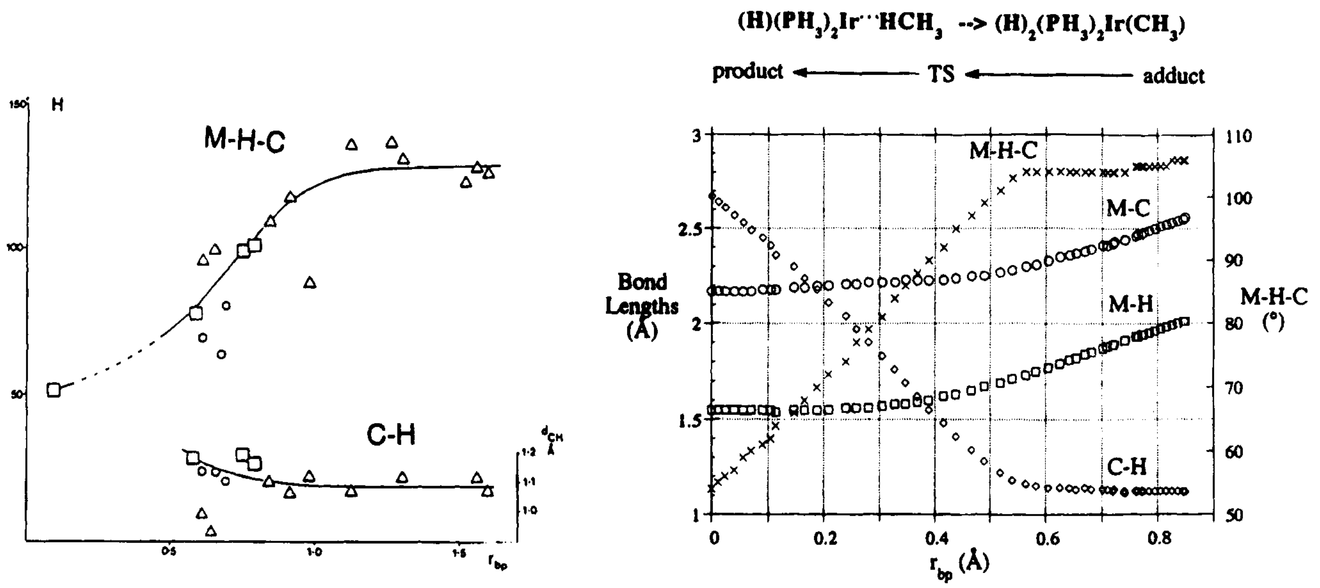


**Figure 1.** Calculated and experimental C−H + M → C−M−H reaction trajectory, showing the good agreement obtained between theory and experiment.[56,118] The experimental data, derived from the results of a series of crystal structures of agostic complexes, is shown on the left and the theoretical trajectory is shown on the right. [Reproduced from refs 56 and 118 by kind permission of the American Chemical Society.]

to be thermodynamically stable toward $H_2$ loss than the $L_nM(H)(CH_3)$ adduct, because $M-CH_3$ bond strengths are commonly 10−15 kcal/mol less than for M−H.

Certain systems are selective for the oxidative addition of methane over other alkanes. In some cases a kinetic preference has been established, for example, in H/D exchange between arenes and alkanes with $CpReH_2(PPh_3)_2$ as photocatalyst, as reported by Jones and Maguire,[115] in which $CH_4$ reacts twice as fast as EtH. In this air-stable system, loss of phosphine rather than $H_2$ has been identified as the photoinduced step. A thermodynamic preference has also been shown in other cases, however. For example, in the Tp′Rh(CO)(R)H system of Ghosh and Graham,[116] the cyclohexyl hydride converts to the methyl hydride in the presence of methane at 1 atm as a result of the greater strength of M−Me versus $M-C_6H_{11}$ bonds. Selectivity for methane seems to be most marked for bulky metal complexes. For example, in the case of $[Os(PP_3)H_2]$ ($PP_3 = P(CH_2PPh_2)_3$), Perutz et al.[117] have shown that for the presumed $\{Os(PP_3)\}$ intermediate formed by laser photolysis at 7−52 °C in the almost inert solvent, cyclohexane, the rate constant for reaction with methane is 4.3 times that for reaction with *n*-pentane. The very much slower reaction with cyclohexane suggests that primary attack takes place in pentane.

These data suggest that the bulk of the metal complex is important in determining the $CH_4$:primary C−H:secondary C−H selectivity and that the transition state for the reaction therefore involves significant steric effects. This is consistent with the side-on three-center transition state that has been proposed for C−H oxidative addition.

Information about the nature of the transition state was obtained from a detailed structural comparison of a number of agostic species, in which C−H bonds interact with 16 valence electron metal fragments to give C−H···M bridges having different CH···M interaction strengths.[118] By the Bürgi−Dunitz postulate this series of structures constitutes a model for the reaction trajectory for the C−H + M → C−M−H reaction. The results showed that the C−H bond approaches the metal so that the C−H bond points toward M with an M−H−C angle of about 150° until the H−M distance is relatively short (ca. 1.8 Å for Ir). The $CH_4$ group then rotates to bring the C−H carbon close to the metal. This rotation means that the $CH_3$ group is also brought close to the other ligands on the metal, leading to potential steric interference. The situation is worse if the carbon bears non-hydrogen substituents. Cundari[56] has calculated a theoretical reaction trajectory (Figure 1, right) for $\{IrH(PH_3)_2\} + H_3C-H \rightarrow [(H_3C)IrH_2(PH_3)_2]$ by RHF methods, which closely resembles the experimental one (Figure 1, left) and has the advantage of referring to an unconstrained C−H bond and the same metal and substrate combination, rather than to a variety of chelating agostic species as in the experimental work. The $r_{bp}$ variable is effectively the reaction coordinate for the process; it decreases from 1.0 to 0 Å as the reaction goes to completion.

The primary and secondary equilibrium deuterium isotope effects for $H_2(D_2)$ and $H-CH_3(D-CD_3)$ addition to *trans*-$[Ir(PR_3)_2(CO)X]$ have been determined by a statistical mechanical and theoretical study. For $H_2$ addition an inverse primary isotope effect of 0.46 (X = Cl) is found, and for $H-CH_3(D-CD_3)$, a value of 3.64.[119]

### *Catalytic Systems*

Although higher alkanes can be dehydrogenated and carbonylated by related systems involving oxidative addition as the first step,[120,121] functionalization of the methyl hydrides resulting from oxidative addition of methane has proved difficult in these systems. A problem with some of these catalysts is that they tend to degrade rapidly by attack of the metal on its own ligands.

A catalytic reaction of the oxidative addition type was established for methane as early as 1969 by Shilov et al.,[81] H/D exchange with $D_2$ catalyzed by $CoH_3(PPh_3)_2$, but the area was not further developed at that time. $IrH_5(PPh_3)_2$ is known to catalyze isotope exchange between $C_6D_6$ and methane at 80 °C; up to 40 turnovers were observed. Small amounts of ethane, toluene, and biphenyl were observed as byproducts. The presence of $tBuCH{=}CH_2$, is required to remove hydrogen from the catalyst, and so activate it.[122]

Lin and Sen[123] have shown that methane (56 atm) can be converted to acetic acid by reaction with $CO/O_2$ (3:1, 20 atm) at 100–150 °C over 10 days with aqueous acidic $RhCl_3$ (10 mM), containing iodide ion as promoter. A likely route involves formation of $[Rh(CO)_2I_2]^-$, the same intermediate as is proposed in the well-known conversion of MeOH and CO to MeCOOH in the Monsanto process.[124a] In the latter case, MeOH is first converted by HI to give MeI, which oxidatively adds to Rh(I) to give a Rh(III) methyl species. By analogy, in the Lin and Sen case, methane may oxidatively add to Rh(I) to give a closely analogous Rh(III) methyl; subsequent carbonylation and hydrolysis would be expected to give acetic acid. Neither acetaldehyde nor methanol is believed to be an intermediate. Fujiwara et al. also have a methane carbonylation, discussed in section IV.J.

### Theory

Theoretical studies on oxidative addition have shown how both a $\sigma$- and a $\pi$-effect operate. The metal generally has an empty orbital capable of accepting electrons from a C–H $\sigma$-bond. In the early stages of the reaction, this is dominant, the C–H bond is not broken, and a $\sigma$-complex results. Transfer of metal electron density into a $CH(\sigma^*)$, dominant in the latter stages of the reaction, cleaves the CH and forms the M–C and M–H bonds. A $d^8$-$ML_3$ fragment is particularly appropriate for this process.[56,124b,125a] The theoretical picture for single atoms has also been studied.[125b]

### Binuclear Oxidative Addition

Sherry and Wayland[126a] have found that the bulky monomer of $[Rh(TMP)]_2$ (TMP = tetramesitylporphyrin) reacts selectively with methane.

$$[Rh(TMP)]_2 + CH_4 \rightarrow [HRh(TMP)] + [CH_3Rh(TMP)] \quad (36)$$

The kinetic isotope effect is 8.6 (296 K) and negative $\Delta S^{\ddagger}$ (−37 eu) is consistent with an ordered linear transition state: $Rh\cdots H_3C{-}H\cdots Rh$. The sum of the Rh–H and Rh–Me bond energies must be a very high 117 kcal/mol, implying a Rh–Me bond strength of nearly 60 kcal/mol. This is perhaps a result of the absence of a trans ligand and minimal steric interference close to the Rh–Me group. Related systems having two porphyrins linked together give faster reactions with $H_2$ and methane.[126b]

**Table 7. Bond Dissociation Energies for H–Q**

| Q | BDE (kcal/mol) | Q | BDE (kcal/mol) | Q | BDE (kcal/mol) |
|---|---|---|---|---|---|
| F | 135 | $NH_2$ | 108 | H | 104 |
| OH | 118 | $CF_3$ | 106 | Cl | 103 |
| CN | 111 | $C_6H_5$ | 105 | t-BuO | 102 |

## I. Hydrogen Atom Abstraction and Radical Pathways

### Classical Radical Reactions

H atom abstraction from methane has a low barrier (>5 kcal/mol),[127] so in the reaction of a radical, $Q^\bullet$, with $CH_4$, the abstraction reaction will generally proceed rapidly if eq 37 is exothermic. This will

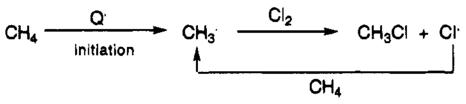
$$Q^\bullet + CH_4 \rightarrow QH + {}^\bullet CH_3 \quad (37)$$

generally be the case for N, O-centered radicals, and Cl and F atoms, where, as shown in Table 7, the bond dissociation energy of the new Q–H bond formed exceeds that of the $CH_3$–H bond broken. The OH radical is capable of abstraction from methane and this is believed to be a key step in removal of methane from the atmosphere, where OH is a trace constituent. Since methane is a greenhouse gas, the kinetics of its removal are of importance in atmospheric chemistry.[128]

Overoxidation tends to occur in any such reaction because the initially formed $CH_3X$ product tends to have weaker C–H bonds than $CH_4$ itself and so is selectively oxidized.

In using radical reagents in synthesis, an important limitation is that there must be no weak (≤100 kcal/mol) X–H bonds in the reagents or solvent; otherwise, abstraction may occur at those X–H bonds instead.

In a series of classical radical chain reactions of methane, electronegative radicals, principally Cl and RO (=Q), give H atom abstraction, followed by functionalization of the resulting $CH_3$ radical by atom abstraction, leading to regeneration of the reactive Q radical. The general scheme is shown below for the case of $Cl_2$.[129]



(38)

Initiation can be thermal or, more commonly, photochemical. The chief problem is the ease of overoxidation, as discussed above. All the halomethanes, $CH_{4-n}Cl_n$, are therefore formed, but the chlorination of methane is still commercially useful. Selectivity for MeCl is improved by carrying out the reactions in a superacid medium, but the mechanism changes from radical chain to electrophilic under these circumstances (see section IV.G). Similar pathways are believed to operate for the other halogens,[130,131] and other typical halogenating agents such as $AgF_2$ or $SO_2Cl_2$ can also be used.

Oxidative fluorination of methane at 700 °C gives mainly fluoroform,[132] and the industrially important oxychlorination reaction gives a mixture of halomethanes.[133]

$$CH_4 + 3HF + {}^3/_2O_2 \xrightarrow{HF,\ O_2,\ chromia/alumina} CHF_3 + 3H_2O \quad (39)$$

In the oxyfluorination case, full oxidation is disfavored by the progressive increase in C−H bond strength of the remaining C−H bonds as the molecule is fluorinated.

The fact that the reaction of C-centered radicals with $SO_2$ is very fast allows rapid chlorosulfonation[134] via the following sequence:

$$CH_4 + Cl^\bullet \rightarrow CH_3^\bullet + HCl \quad (40)$$

$$CH_3^\bullet + SO_2 \rightarrow CH_3SO_2^\bullet \quad (41)$$

$$CH_3SO_2^\bullet + Cl_2 \rightarrow CH_3SO_2Cl + Cl^\bullet \quad (42)$$

The product is then hydrolyzed and oxidized to yield the sulfonic acid. A number of commercial plants use this process.

Methane (50 atm) reacts with sulfur at 550−625 °C either with or without catalysts to give $CS_2$ and $H_2S$, a reaction which has also been used commercially.[135] Nitration of methane is possible with nitric acid vapor at 475 °C.[136]

Many of the systems described above are unselective, but in recent years a number of new methods have been developed which although they still involve radicals give much improved selectivity, by using either low temperatures, rapid trapping of the radicals, or other strategies.

Fujiwara[137] observed acetic acid formation (40 turnovers in 45 h) from methane, $K_2S_2O_8$, and CO, at 80 °C catalyzed by Cu(II) or Pd(II). The proposed mechanism is thought to involve radical pathways for Cu(II), where an induction period is seen, and electrophilic attack for Pd(II), but more work is needed on the mechanistic aspects.

### *Mercury Photosensitized Reactions*

Photoexcited mercury can homolyze alkane C−H bonds as shown in extensive work in the period from 1950 to 1973.[138] Under the conditions employed, the reactions tend to be slow and unselective for $CH_4$. They are slow because the quantum efficiency is only high (0.2−0.8) for alkanes having C−H BDEs below ca. 97 kcal/mol. In addition, the initial products from methane, notably ethane and propane, are much more reactive than the starting alkane. This is a manifestation of the common problem of facile overoxidation of alkanes. The selectivity problem can be solved[103] by operating under conditions in which the initial products condense, because Hg photosensitization occurs only in the gas phase, provided a low pressure Hg lamp is used. The quantum efficiency problem can be solved[139,140] by using $NH_3$ as coreagent, because this molecule reacts very efficiently with Hg*, probably via lone pair binding to give an $[Hg-NH_3]^*$ exciplex, which subsequently breaks down to give H and $NH_2$ radicals. A special feature of $NH_3$ is that the N−H BDE of 107 kcal/mol is below the excitation energy of Hg*, so it is efficiently cleaved, but greater than the BDE of $CH_4$, so $NH_2$ can abstract H from $CH_4$. The sequence shown in eqs 43−46 operates to give $CH_2{=}NH$ as final product,

$$NH_3 \xrightarrow{Hg^*} H + NH_2 \quad (43)$$

$$NH_2 \xrightarrow{CH_4} CH_3 + NH_3 \quad (44)$$

$$CH_3 + NH_2 \rightarrow CH_3NH_2 \quad (45)$$

$$CH_3NH_2 \xrightarrow{2H} CH_2NH \quad (46)$$

and if this is condensed, and so removed from the system, subsequent reactions cannot occur.

If the residence time of the initial product is deliberately lengthened, higher imines such as $CH_3CH{=}NH$ are formed, presumably via $CH_3$ addition to $CH_2{=}NH$. If no attempt is made to remove the initial products, an oil is formed containing C, N, and H, probably a mixture of polymeric imines. Hg* can also photosensitize $N_2O$ to give $N_2$ and O atoms; the latter can abstract H from methane, but inefficiently.[141]

$$CD_3OD + CH_4 + N_2O \xrightarrow{Hg^*} CH_3CD_2OD + HD \quad (47)$$

## J. Metal and Metal Oxide Surfaces

Metal films, especially those of Pt and Rh, have long been known to carry out alkane reactions, such as isotope exchange. Metal oxides, such as $Cr_2O_3$, can also catalyze H/D exchange between $D_2$ and alkanes after activation by heating at 400−700 °C.[142] The reactivity of primary C−H bonds is found to be comparable with secondary C−H, and so a pure H abstraction mechanism is unlikely. One possibility is PCET (section IV.G) with a surface oxide acting as the proton acceptor and a redox active site as the electron acceptor.

### *Oxidative Coupling*

Lunsford and co-workers[143a] have described a series of heterogeneous catalysts (e.g., nontransition metal oxides such as $Li_2O/MgO$) for $O_2$ oxidation of $CH_4$ which are able to abstract H from methane to give gas-phase methyl radicals which then recombine to form ethane. This can in turn be dehydrogenated to give ethylene. A wide variety of oxide catalysts have proved to be active, and catalyst morphology has been shown to have a strong influence on the catalyst selectivity. This oxidative coupling reaction has attracted intense industrial and academic interest,[143b] but yields have generally been below 25% (typically, $C_2^+$ selectivities of ca. 80% at 20% conversion). With yields such as these, oxidative coupling cannot yet compete with syngas-based methods.[144] The high exothermicity of eq 48 also poses an engineering

$$CH_4 + O_2 = C_2H_4 + 2H_2O \quad (48)$$

$$\Delta H = -67\ \text{kcal/mol}$$

problem. In a recent suggestion, the energy output is used to generate electrical power along with $C_2$ products.[144]

A reduced surface oxide center having radical character ($O^{\bullet -}$) has been invoked to explain the H abstraction (but see section IV.G for an alternative possibility). A countercurrent-moving bed reactor has been introduced by Aris et al.[145a] which allows the rapid separation of the methane, oxygen, and $C_2$ products, as in a chromatographic experiment. With $Sm_2O_3$ catalyst at 1000 K, up to 60% selectivity for $C_2$ products has been obtained. Recently, a gas-recycle reactor has allowed high selectivity (88%) at high conversion (97%).[145b] The commercial viability of these improvements remains to be demonstrated.

### Other Systems

On a redox-active catalyst (e.g., molybdena/silica), partial methane oxidation yields MeOH and HCHO. Yields as high as 78% can be obtained, but at a conversion of only 3%. Methyl radicals are again proposed as the key intermediates and are thought to react with surface oxide to give methoxide, which can give MeOH by hydrolysis or formaldehyde by hydride transfer to the surface.[146] At high temperature and pressure (>500 °C, 580 kPa), gas phase radical chemistry has been shown to dominate the partial oxidation of methane and the catalyst has a minor contribution.[147]

Schwartz[148] has been able to graft the $(allyl)_2Rh-O-Si$ fragment on to a silica surface using $(allyl)_3Rh$ as the precursor. Hydrogenation seems to give $(allyl)HRh-O-Si$, which reacts with $^{13}CH_4$ to give labeled butane after protonation. The systems also catalyze H/D exchange and chlorination of methane.

## K. Electrochemistry

Electrochemical approaches to CH activation have been reviewed.[149a,150] As early as 1973, Fleischmann et al.[149b] found that the oxidation potential of alkanes became more cathodic in $HSO_3F$, where the alkane is protonated. Under certain conditions, separate cyclic voltammetry waves for RH and $RH_2^+$ can both be seen. The intermediate alkyl cation can be intercepted by CO to give carboxylic acids, by $RCO_2^-$ to give esters, or by alkanes to give oligomers. Electrochemical oxidation of methane to $CO_2$ is important in certain fuel cells but requires operating temperatures in excess of 900 °C for useful rates.[150] Under certain conditions, $C_2$ products can be formed in good yield, however.[150c] Another option is a reforming step external to the electrochemical reactor in which syngas is formed; this is an efficient fuel for fuel cells that operate at moderate temperature (25 −250 °C). A number of prototype reforming/fuel cell systems fueled by natural gas are in operation.[150b]

## L. Reactions in the Gas Phase and in Plasma

Alkane cations and dications such as $CH_4^+$ and $CH_4^{2+}$ have been formed[151a] in gas phase charge stripping experiments and studied theoretically by ab initio methods;[151b,c] a detailed review is available.[151d]

Unexpectedly stable carbon clusters, called metallocarbohedranes or met-cars, have been produced by exposing metal plasmas to methane or other light carbonaceous gases. $M_8C_{12}$ (e.g., M = Ti, Zr, Hf, V, Cr, Mo, Fe) seems to be particularly stable and dominates the mass spectrum of the products. So far these clusters have not been isolated in condensed phase, but the picture superficially resembles the situation early in the fullerene ($C_{60}$) story, so these species or their derivatives may eventually prove to be isolable.[152]

## M. Radiation Chemistry

Apart from the photosensitized reactions noted in section IV.I, direct photochemistry is also possible at vacuum UV wavelengths, but this is not a practically useful technique.[153] High-energy radiation can also cause ionization and fragmentation of methane.[154] Good recent reviews[153,154] are available for both areas, so we do not cover them in detail here.

## N. Chemical Aspects of Methanogenesis

Methane is one of the most important natural products, because as much as $10^9$ tons are estimated to be released each year as a result of bacterial methane production, and this release has implications for the greenhouse effect.[155] In certain situations, methane from fermentation of wastes can be useful as a fuel.[156]

Methanogenic bacteria, together with the halobacteria and the thermoacidophiles, constitute the archaebacteria. These have many unusual biochemical features, such as the occurrence of branched ethers as lipids and of a series of unusual cofactors. Because their ribosomal RNA sequences are distinct from those of other living things, they have been considered as evolutionarily very ancient organisms.[157]

Methanogenesis involves the biosynthesis of methane by anaerobic bacteria, a process in which $CO_2$ or CO are reduced to $CH_4$. Most methanogens are capable of growing on $H_2$ and $CO_2$ as their sole source both of carbon and of energy.[158] The overall reduction (eq 49) is exergonic and, accomplished stepwise,

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (49)$$

$$\Delta G^\circ = -138.8 \text{ kJ/mol}$$

provides the energy for the organism. The $H_2$ is harnessed by hydrogenase, a class of Ni/Fe or Fe enzymes that convert $H_2$ into protons and electrons.

$CO_2$ reduction occurs stepwise and the resulting $C_1$ fragments are bound to a series of cofactors unique to the methanogens: methanofuran, tetrahydromethanopterin, and factor F-430.[159]

The methanogenic bacteria are very rich in nickel and this element has been shown to play a role not only in $H_2$ activation by hydrogenases but also in the last step of methanogenesis (eq 50).

$$CH_3SCH_2CH_2SO_3^- + HSR \rightarrow CH_4 + RSSCH_2CH_2SO_3^- \qquad (50)$$

Coenzyme M, the unusual thioether cofactor shown in eq 50 carries the $C_1$ fragment in the form of an SMe group, the carbon of which is ultimately derived from $CO_2$. The thioether is hydrogenolyzed by a thiol cofactor RSH to liberate methane and the mixed disulfide $RSSCH_2CH_2SO_3^-$. This mixed disulfide is subsequently reduced to give the free cofactors in the thiol form.

Equation 50 is catalyzed by methyl-*S*-coenzyme M reductase, a nickel-dependent enzyme. Further work has shown that the nickel is present in the form of factor F-430, a nickel hydroporyrinoid cofactor bound to the reductase. F-430 is labile on removal from the enzyme and undergoes epimerization at the 12- and 13-positions to give an equilibrium mixture of F-430 (4%) itself and two epimers. The 12,13-diepi-form can be crystallized, and a crystal structure has allowed the structure of the native form to be deduced; this structure is shown in Figure 2.[160] One notable feature is the highly reduced porphyrinoid ring (corphin), which is very different from anything previously found in nature. While Ni porphyrin itself shows little tendency to bind exogenous ligands at the axial sites, Ni(II)–F-430 shows substantial axial reactivity and readily forms a 6-coordinate solvated high-spin species in solution. The flexibility of the corphin resulting from its partially reduced state may better enable the ring system to accommodate a 6-coordinate high-spin Ni(II) ion, larger than the 4-coordinate low-spin Ni(II) of the unsolvated cofactor.

The crystal structure also shows that there is a pronounced saddle-shaped out-of-plane deformation of the ring which is substantially larger than anything previously observed in a Ni hydroporphyrin. Molecular mechanics studies have shown that the ring can potentially distort so as to accommodate either trigonal bipyramidal or square pyramidal nickel and it has been suggested that such a distortion may have a role in the mechanistic pathway, especially if the nickel accepts either the methyl group or the thiolate of methyl-*S*-coenzyme M to give a 5-coordinate Ni–Me intermediate.[161]

Reduction of Ni(II) to Ni(I) in F-430 probably occurs during catalysis; this also leads to an expansion of the metal radius and may be favored by the flexibility of the ring. The nature of the hydroporphyrin ring system has also been shown to influence the location of the electron on reduction. In a Ni(II) chlorin, less reduced than F-430, reduction takes place on the ring, while in more reduced porphyrinoids such as Ni(II) isobacteriochlorin and F-430 itself, reduction takes place at the metal. The flexibility of the more reduced rings may allow the larger Ni(I) ion to fit more easily; in addition the more reduced the porphyrin, the less able the ring is to accept electrons.[162] The coordination number and geometry of F-430 under different circumstances has been probed by EXAFS: both 4- (Figure 2) and 6-coordinate solvated forms have been identified.[163]

The situation is complicated by the fact that the reduced form of F-430 in whole cells appears to have very different EPR characteristics than in the isolated enzyme or in free F-430. The activity of the enzyme also falls off very sharply on isolation for reasons that are not fully understood.[164] The detailed mechanism of the reduction is therefore still unclear, but Berkessel's suggestion,[164] shown in eqs 51–54, is the most persuasive to date because it shows why the heterodisulfide, $RSSCH_2CH_2SO_3^-$, is formed. In this mechanism, the thiol cofactor is oxidized by Ni(II) to the radical, which then adds to the thioether cofactor to give a thiyl radical. This is expected to methylate the Ni(I) form of F-430 by Me transfer.

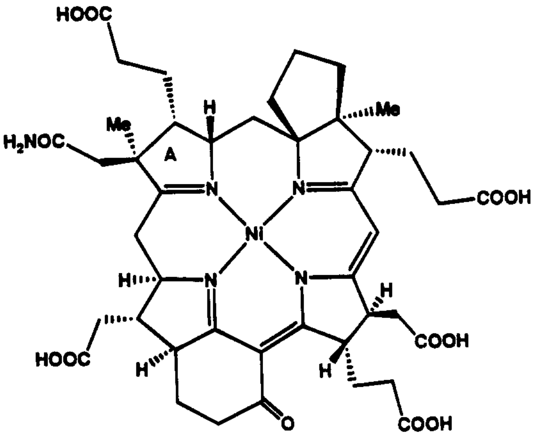


**Figure 2.** Structure of factor F-430, the unusual, partially saturated corrinoid ring unique to methyl-*S*-coenzyme M reductase in methanogenesis.[139]

$$\mathrm{Ni(II)} + \mathrm{HSR} \rightarrow \mathrm{Ni(I)} + {}^{\bullet}\mathrm{SR} + \mathrm{H}^+ \tag{51}$$

$$\mathrm{MeSCH_2CH_2SO_3^-} + {}^{\bullet}\mathrm{SR} \rightarrow \mathrm{RS{-}S(Me)CH_2CH_2SO_3^-} \tag{52}$$

$$\mathrm{RS{-}S(Me)CH_2CH_2SO_3^-} + \mathrm{Ni(I)} \rightarrow \mathrm{RS{-}SCH_2CH_2SO_3^-} + \mathrm{Me{-}Ni(II)} \tag{53}$$

$$\mathrm{Me{-}Ni(II)} + \mathrm{H}^+ \rightarrow \mathrm{MeH} + \mathrm{Ni(II)} \tag{54}$$

Subsequent protonation of the Ni–Me is proposed to lead to MeH.

## O. Chemical Aspects of Methane Monooxygenase

The great advantage of biochemical oxidation[165a] is that the reactivity is controlled by the molecular recognition and regulation characteristics of the enzyme. This allows essentially complete selectivity for methane conversion to methanol even when the radical chemistry involved is not intrinsically selective. Apart from the MMO case, another striking selectivity effect is shown by a monooxygenase from *Pseudomonas oleovorans*, which converts *n*-octane to 1-octanol by attacking one of the least reactive terminal C–H bonds.[165b]

Enzymes carry out a number of CH activation reactions.[165a] Methane monooxygenase, or MMO, is capable of converting methane into methanol using $O_2$ and two reducing equivalents. This provides methanotrophic bacteria with both energy and carbon. The best studied proteins have come from *Methylococcus capsulatus* (Bath)[165b] and *Methylosinus trichosporium* OB3b.

$$\mathrm{CH_4} + \mathrm{O_2} + \mathrm{NADH} + \mathrm{H}^+ = \mathrm{CH_3OH} + \mathrm{H_2O} + \mathrm{NAD}^+ \tag{55}$$

The $\alpha_2\beta_2\gamma_2$ hydroxylase component (251 kDa) directly responsible for methane oxidation contains four essential irons and binds methane and oxygen.

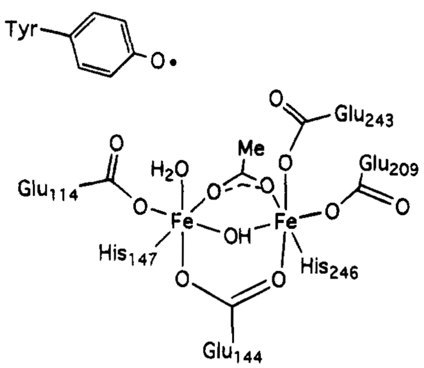


**Figure 3.** Schematic active site structure of MMO showing the dimeric iron site involved in dioxygen activation and substrate hydroxylation activity; the redox-active tyrosine residue is also shown.[148] The acetate ligand is an artefact of the isolation technique.

Results of EXAFS, Mössbauer, EPR, and X-ray crystallographic work[166-169] show that the the diiron site resembles that in hemerythrin and has a hydroxo and a carboxylato bridge. The Fe cluster has (II,II), (II,III), and (III,III) forms, of which the (II,II) state interacts with $O_2$. In addition to the hydroxylase, there is also a reductase (38.6 kDa) which accepts electrons from NADH and provides them to the hydroxylase. A third protein (15.5 kDa) regulates electron transfer between the two other components. This regulation ensures that the partial oxidation product, MeOH, leaves the site before a second oxidation event can occur.

The structure of the active site is shown schematically in Figure 3 and includes the mechanistically important tyrosine radical. The immediate environment of the site is strongly hydrophobic, no doubt in part to favor $CH_4$ binding over MeOH. Benzylic hydroxylation shows a substantial intramolecular $k_H/k_D$ isotope effect of 5.0–5.2, consistent with partial C–H bond cleavage being involved in the slow step of the reaction. Radical clock probes, compounds such as *trans*-2-(phenylmethyl)cyclopropane, which rearrange in defined ways when radical intermediates are formed, have shown that the radical rearrangements expected are indeed seen but only to a very small extent. This implies either that the reaction is too fast to allow complete rearrangement to occur or that the protein partly prevents the rearrangement. Probes with very fast radical rearrangement rates of up to $5 \times 10^{11}$ s$^{-1}$ were chosen to try to exclude the first possibility.[170] Spectroscopic signals have been detected in a transient from *M. trichosporium* MMO which have been tentatively identified[171] as arising from an Fe(IV)=O intermediate, and there is also EPR evidence[172] for the involvement of C-centered radicals.

The requirement for a coreductant when monoxygenases use $O_2$ as primary oxidant poses severe practical problems for commercial applications of this chemistry. A coreductant can often be avoided if a reduced form of $O_2$, for example $H_2O_2$, is used as primary oxidant. This is the reason that functional models often employ a peroxide.

### Functional Model Complexes

This work is still in its early stages in the case of MMO modeling. Better developed models involve a series of related CH activating enzymes, the cytochrome P-450 dependent monooxygenases, which have a heme group at the active site.[173,174] Reactive Fe=O species have been studied in the porphyrin (=L) series and shown to have the formulation $(L^{\bullet+})Fe^{IV}{=}O$. They oxidize methane via H atom abstraction by the oxo group consistent with the $k_H/k_D$ of ca. 13. Radical character was therefore associated with this oxo group (but see section IV.G). Radical abstraction of OH from the metal by the resulting radical (or "rebound" step) completes the cycle.

$$(L^{\bullet+})Fe^{IV}{=}O + RH \rightarrow (L)Fe^{IV}{-}OH + R^{\bullet} \rightarrow (L)Fe^{III} + ROH \quad (56)$$

The Fe=O species is thought to be originally formed from $O_2$ by coordination to the Fe(II), followed by two-electron reduction and loss of water.

$$(L)Fe^{II} + O_2 \rightarrow (L)Fe^{III}{-}O_2 \xrightarrow{e^-,\,2H^+} (L^{\bullet+})Fe^{IV}{=}O + H_2O \quad (57)$$

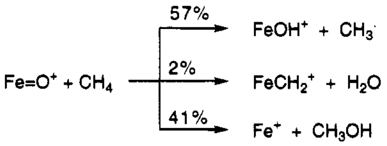
The situation for MMO is much less clear, but a $Fe^{IV}{=}O$ species or its equivalent is at least plausible. In this case, the iron is in a non-heme environment, where the inorganic chemistry involved is much less well-understood. In the absence of a porphyrin ring, the second iron or the tyrosine may carry an additional oxidizing equivalent. A variety of iron salts and their complexes have been shown to give CH oxidation reactions, including reactions with methane itself.[174] In the case of bis{(2-carboxy-6-carboxylato)pyridine}iron(II), $O_2$ was used as the oxidant, PhNHNHPh providing the reducing equivalents.[175]

The best known non-porphyrin iron catalyst to oxidize alkanes, the Gif system, has been reviewed recently.[176a] It uses iron salts or iron picolinate complexes and either $O_2$/Fe, $O_2$/Zn, or $H_2O_2$. The products are largely ketones, but in the presence of $CBrCl_3$, bromination is seen and with PhSSPh, the formation of RSPh. Its most interesting feature is the unexpectedly high selectivity for secondary over tertiary C–H bonds, thought to be inconsistent with simple H atom abstraction, which would normally favor the tertiary C–H bond. $H_2S$ does not inhibit the reaction in spite of being easily oxidized and having weak S–H bonds. In oxidation of secondary C–H bonds, radical products, such as alkylpyridine formation by $R^{\bullet}$ attack on the solvent pyridine, are not observed. A different mechanism is proposed involving addition of the C–H bond across the Fe=O bond of an iron ferryl species to give $R{-}Fe^{III}{-}OH$. The resulting functionalized products, RX, are thought to arise by subsequent reactions of the iron alkyl. The relation, if any, of the Gif system to MMO is still uncertain. An alternate metal for this type of chemistry seems to be copper: a membrane-bound copper-based MMO has recently been reported as well as a Cu-based version of the Gif system.[176b]

An interesting alternative interpretation of Gif chemistry has been devised by Minisci et al., at least for the peroxide-based versions.[176c] Pyridine is required as a solvent in the Gif system and t-BuOOH is expected to strongly hydrogen bond to the solvent. This is known to slow the rate of t-BuO$^{\bullet}$ attack on t-BuOOH to give tBuOO• with the result that t-BuO• does not decompose and becomes an important abstracting reagent from the substrate alkane in pyridine solvent. The steric bulk of this radical is believed to lead to the unusual selectivity pattern observed.

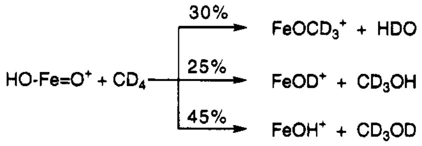
### Gas Phase Iron–Oxo Chemistry

In relation to the iron system, Schwarz[177] has reported a gas phase study of the reaction of $Fe{=}O^+$ with methane, where the following pathways were identified.



(58)

As a Fe(IV) species, the case of $O{=}Fe{-}OH^+$, also studied by Schwarz, is relevant. In each case, $H_3C{-}H$ addition across the $Fe{=}O$ group was proposed.



(59)

Whatever the details of the mechanism, these results do indicate that high-valent metal species can engage in unusual chemistry, suggesting that further work is needed in this area.

## P. Steric and Shape Selectivity Effects

Enzymes such as MMO combine a substrate recognition function with a catalytic oxidant to achieve exceptionally high chemical selectivity for alkane conversion. By analogy, a successful synthetic catalyst might incorporate a recognition site. Although zeolites embody some of these ideas, molecular recognition has otherwise only rarely been applied to catalysis. In one study, Suslick[178] looked at porphyrins that were substituted at the ortho positions of the *meso*-phenyl group in order to produce a pocket surrounding the catalytic site. In Mn(TTPPP)OAc {$TTPPPH_2$ = 5,10,15,20-tetrakis(2′,4′,6′-triphenyl)porphyrin}, this strategy had the additional advantage of increasing the oxidative stability of the porphyrin. The primary oxidant, PhIO, chosen to avoid the need for a coreductant, is believed to transfer an oxo group to Mn to give a species that hydroxylates alkanes as discussed in section IV.O. The shape selectivity effect proved to be insufficient to completely overcome the intrinsic selectivity of the chemistry because 1-pentanol was a very minor product from *n*-pentane, but the 2-ol/3-ol ratio was strongly enhanced from 0.9 in the MnTTPOAc system to 2.55 in the bulky system. For the more bulky substrate $t\text{-}BuCH_2CH_3$, the unhindered MnTTPOAc system gave <2% 1-ol, but the bulky catalyst gave as much as 63% of $t\text{-}BuCH_2CH_2OH$. Shilov incorporated an iron porphyrin bearing long tail groups into a vesicle bilayer and found strong enhancement of terminal hydroxylation of long chain alkanes.[179] The ordered arrangement of the vesicle is believed to give it its substrate recognition function.

Drago et al.[180] have studied the very crowded *cis*-$[Ru(2,9\text{-dimethyl-}1,10\text{-phenanthroline})_2(H_2O)_2](PF_6)_2$ catalyst with $H_2O_2$ as primary oxidant. At 75 °C in MeCN and at 4 atm pressure, 140 turnovers per day of a 4:1 ratio of MeOH to HCHO were observed. A Ru(VI) dioxo intermediate was proposed to abstract an H atom fom $CH_4$. The bulk of the system seems to prevent attack at the normally very sensitive ArMe groups of the ligand system. The opening of the thoracycle of eq 10 is faster for methane over ethane, and cyclohexane is unreactive, which may be a result of the very high steric hindrance in this system.

## V. Conclusion

Methane chemistry is likely to become more important in the coming decades as natural gas takes a larger role as an energy source. Methane conversion is already becoming a major commercial venture, but the current routes via syngas could be made obsolete if a practical direct partial methane oxidation should be discovered. Developing such a process poses difficult and as yet unsolved chemical and engineering problems. The biosynthesis of methane and its metabolism by MMO pose challenging mechanistic problems, and the latter may suggest biomimetic catalysts for methane conversion.

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