CHAPTER II

HYDROCARBON TRANSFORMATIONS THAT DO NOT INVOLVE METALS OR THEIR COMPOUNDS

In this chapter we will briefly survey the main types of hydrocarbon transformations that occur without the participation of solid metals or oxides and metal complexes. The alkane transformations described here should be taken into consideration for comparison when discussing the metal complex activation.

II. 1. Transformations Under the Action of Heat or Irradiation

Under the action of heat or irradiation, alkanes decompose to produce free radicals which further form stable products. Such processes, especially pyrolysis, are of practical importance.

II. 1.A. PYROLYSIS

Heating alkanes [1a-c] at temperature 900-2000 °C gives rise to the formation of radicals:

$$CH_4 \rightleftharpoons CH_3\bullet + H\bullet$$

$$CH_3\bullet + CH_4 \rightleftharpoons C_2H_6 + H\bullet$$

$$H\bullet + CH_4 \rightleftharpoons CH_3\bullet + H_2$$

$$2\,H\bullet \rightleftharpoons H_2$$

$$2\,CH_3\bullet \rightleftharpoons C_2H_6$$

$$H\bullet + CH_3\bullet \rightleftharpoons CH_4$$

and carbenes:

$$CH_4 \rightleftharpoons :CH_2 + H_2$$
$$:CH_2 + CH_4 \longrightarrow C_2H_6$$
$$C_2H_6 \longrightarrow CH_2{=}CH_2 + H_2$$
$$CH_2{=}CH_2 \longrightarrow CH{\equiv}CH + H_2$$
$$CH{\equiv}CH \longrightarrow 2\,C + H_2$$

In accordance with these equations, ethane, ethylene, acetylene and elemental carbon are produced by the cracking of methane. Activation energy of this process is 76 kcal mol^{-1}. The formation of acetylene starting from methane or ethane are endothermic processes:

$$2\,CH_4 \rightleftharpoons CH{\equiv}CH + 3\,H_2 \qquad -\Delta H_{298}^{0} = -90 \text{ kcal mol}^{-1}$$
$$C_2H_6 \rightleftharpoons CH{\equiv}CH + 2\,H_2 \qquad -\Delta H_{298}^{0} = -74 \text{ kcal mol}^{-1}$$

The equilibrium in these reactions is shifted to the right at temperatures >900 °C for ethane and > 1100 °C for methane. Higher alkanes are formed from methane via a recombination of methyl radicals [1d].

High-temperature pyrolysis of methane is very important since it is a main source of raw material (e.g., acetylene) for chemical industry. Cracking of higher alkanes gives a wider set of products. For example, pyrolysis of propane (activation energy is 64 kcal mol^{-1}) yielding ethylene, methane, propene, hydrogen and ethane consists of the following stages:

$$C_3H_8 \longrightarrow CH_3\bullet + C_2H_5\bullet$$
$$CH_3\bullet + C_3H_8 \longrightarrow CH_4 + n\text{-}C_3H_7\bullet$$
$$CH_3\bullet + C_3H_8 \longrightarrow CH_4 + iso\text{-}C_3H_7\bullet$$
$$n\text{-}C_3H_7\bullet \longrightarrow CH_2{=}CH_2 + CH_3\bullet$$

$iso\text{-}C_3H_7\bullet \longrightarrow CH_3CH{=}CH_2 + H\bullet$

$H\bullet + C_3H_8 \longrightarrow H_2 + n\text{-}C_3H_7\bullet$

$H\bullet + C_3H_8 \longrightarrow H_2 + iso\text{-}C_3H_7\bullet$

$2\,H\bullet \longrightarrow H_2$

$H\bullet + CH_3\bullet \longrightarrow CH_4$

$H\bullet + n\text{-}C_3H_7\bullet \longrightarrow C_3H_8$

$H\bullet + iso\text{-}C_3H_7\bullet \longrightarrow H_2 + CH_3CH{=}CH_2$

$H\bullet + iso\text{-}C_3H_7\bullet \longrightarrow C_3H_8$

$CH_3\bullet + n\text{-}C_3H_7\bullet \longrightarrow CH_4 + CH_3CH{=}CH_2$

$CH_3\bullet + n\text{-}C_3H_7\bullet \longrightarrow C_4H_{10}$

$CH_3\bullet + iso\text{-}C_3H_7\bullet \longrightarrow CH_4 + CH_3CH{=}CH_2$

$CH_3\bullet + iso\text{-}C_3H_7\bullet \longrightarrow C_4H_{10}$

$2\,CH_3\bullet \longrightarrow C_2H_6$

$2\,n\text{-}C_3H_7\bullet \longrightarrow C_3H_8 + CH_3CH{=}CH_2$

$2\,n\text{-}C_3H_7\bullet \longrightarrow C_6H_{14}$

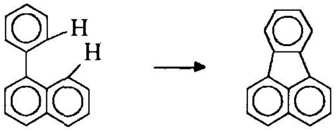
$2\,iso\text{-}C_3H_7\bullet \longrightarrow C_3H_8 + CH_3CH{=}CH_2$

$2\,iso\text{-}C_3H_7\bullet \longrightarrow C_6H_{14}$

$n\text{-}C_3H_7\bullet + iso\text{-}C_3H_7\bullet \longrightarrow CH_3CH{=}CH_2 + C_3H_8$

$n\text{-}C_3H_7\bullet + iso\text{-}C_3H_7\bullet \longrightarrow C_6H_{14}$

Plasma reforming of methane can be efficiently used to produce hydrogen-rich gas (50-75% H_2, 25-50% CO) [1e}. Methane has also been converted to higher hydrocarbons (including ethylene and acetylene) by a microwave plasma [1f]. Heating induces important transformations not only in alkanes, but also in aromatic hydrocarbons, for example [1g]:



II.1.B. PHOTOLYSIS

Analogous transformations of alkanes may be induced by light irradiation under ambient temperature [2]. When irradiated with light λ = 121.6 nm, methane (which absorbs light $\lambda < 143$ nm) decomposes to generate the following species (Φ is quantum yield):

$$CH_4 \longrightarrow {}^1{:}CH_2 + H_2 \qquad \Phi = 0.4$$

$$CH_4 \longrightarrow {}^1{:}CH_2 \ (\text{or } {}^3{:}CH_2) + H\bullet + H\bullet \qquad \Phi = 0.5$$

$$CH_4 \longrightarrow CH + H\bullet + H_2 \qquad \Phi = 0.08$$

Then the following stable products are formed:

$${:}CH_2 + {:}CH_2 \longrightarrow HC{\equiv}CH + H\bullet + H\bullet$$

$$CH + CH_4 \longrightarrow CH_2{=}CH_2 + H\bullet$$

$${:}CH_2 + H_2 \longrightarrow CH_3\bullet + H\bullet$$

$$CH + H_2 \longrightarrow CH_3\bullet$$

$${:}CH_2 + CH_3\bullet \longrightarrow CH_2{=}CH_2 + H\bullet$$

$$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$$

$$CH_2 + HC{\equiv}CH \longrightarrow CH_3C{\equiv}CH$$

II. 1. C. RADIOLYSIS

The interaction of high-energy irradiation with alkanes leads, at the first stage of the process, to the excitation of the hydrocarbon molecule [3a]. Furthermore, the excited molecule decomposes to generate free radicals and carbenes. Radiolysis of methane produces ethane, ethylene, and higher hydrocarbons:

$$CH_4 \rightsquigarrow CH_4^{+} + e\text{–}\ CH_4 \rightsquigarrow CH_4^{+*} + e^{-}$$

$$CH_4 \rightsquigarrow CH_4^* \qquad CH_4^* \longrightarrow CH_3^+ + H\bullet$$

$$CH_4^{+*} \longrightarrow CH_2^+ + H_2 \qquad CH_4^{+*} \longrightarrow CH^+, C^+, H_2, H$$

$$CH_4^* \longrightarrow CH_3\bullet + H\bullet$$

$$CH_4^* \longrightarrow CH_2 + H_2$$

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3\bullet$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_7^{+*}$$

$$C_2H_7^{+*} \longrightarrow C_2H_5+* + H_2$$

$$CH_2^+ + CH_4 \longrightarrow C_2H_6^{+*} \qquad C_2H_6^{+*} \longrightarrow C_2H_4^+ + H_2$$

$$CH_2 + CH_4 \longrightarrow C_2H_6^*$$

$$C_2H_6^* \longrightarrow 2\, CH_3\bullet$$

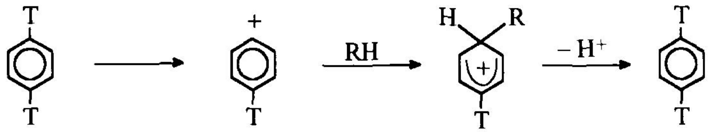
$$C_2H_6^* + M \longrightarrow C_2H_6 + M$$

$$CH_5^+ + C_2H_6 \longrightarrow CH_4 + C_2H_7^{+*} \qquad C_2H_7^{+*} \longrightarrow C_2H_5^+ + H_2$$

Pulse radiolysis of N_2O-saturated methylcyclohexane (MCH) gives rise to the formation of the solvent radical cation, MCH^+, but in argon-saturated MCH, the olefinic fragment cation (methylcyclohexene)$^+$ is obtained [3b].

II.2. REACTIONS WITH ATOMS, FREE RADICALS AND CARBENES

Atoms and free radicals are very reactive species toward all organic substances including hydrocarbons, even saturated ones. Reactions of alkanes with atoms



$R = CH_3, C_2H_5, C_3H_7$

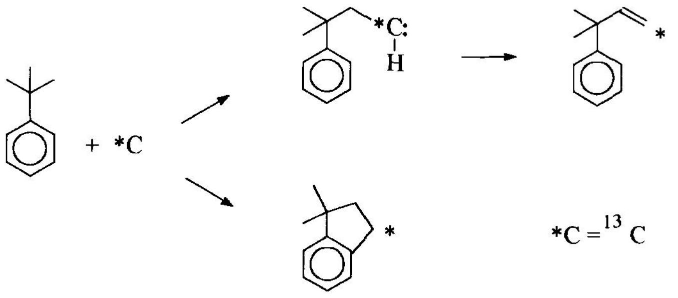
Scheme II.1. The interaction of 1,4-T_2-benzene with light alkanes.

and radicals (see, for example, [4]) are stages of various chain-radical processes, occurring both in the gas phase [5] and in solution [6]. Interactions of hydrocarbons with ions in the gas phase are also known; for example, phenylium ion formed from 1,4-T_2-benzene reacts with methane and other lower alkanes to give tritiated alkylbenzene (Scheme II. 1) [7].

A carbon atom inserts into C-H bond of methane to produce a species which is transformed into ethylene and some other hydrocarbons [8a]:

$$C + CH_4 \longrightarrow$$
$$C_2H_2 + C_2H_4 + C_2H_6 + CH_2{=}C{=}CH_2 + HC{\equiv}C{-}C{\equiv}CH$$

In one of the stages of the reaction between carbon atoms and *tert*-butyl-benzene, a carbon atom inserts into a methyl C-H bond to give a carbene followed by a 1,2-hydrogen shift (Scheme II.2) [8b].



Scheme II.2. Reaction of arc generated carbon atoms with *tert*-butylbenzene.

The electronically excited oxygen atom reacts with alkanes, the dominant reaction mechanism being the insertion of this atom into the C-H bond, thus yielding chemically activated alcohol followed by fragmentation [8c,d].

$$O(s) + CH_4 \longrightarrow CH_3OH$$

The same species in triplet state reacts with alkanes similarly to free radicals since the insertion is a spin-forbidden reaction for a triplet to form a singlet state molecule. Investigation of the singlet state oxygen $O(^1D_2)$ reaction with alkanes in the gas phase has revealed that two distinct channels exist for these reactions. They were interpreted as insertion into C–H bond and H atom abstraction. The insertion component dominates for small molecules (CH_4, C_2H_6) with strong C–H bonds, while the abstraction component is the dominant mechanism for formation of OH radical in the cases of larger molecules $[C_3H_8, C(CH_3)_4]$ with stronger steric hindrances and weaker C–H bonds. An insertion mechanism of the interaction of singlet state oxygen with methane was confirmed in *ab initio* theoretical calculations [8e]. The minimum energy path of the reaction was found to be an almost collinear approach of $O(^1D)$ to one of the hydrogen atoms of methane to the distance of 1.66 Å, and then oxygen atom migrates off-axis.

We will see that similar conclusions with respect to the mechanism (possibility of insertion as well as hydrogen atom abstraction) may be made for reactions of oxygen atoms bound to metal ("oxenes") with alkanes in enzymatic and model chemical reactions. The excited nitrogen atom, $N(^2D)$, reacts analogously [8f,g].

The most usual reaction of alkanes and other C–H compounds with atoms and free radicals is the hydrogen atom abstraction [9]:

$$\mathrm{Rad}\bullet + \mathrm{R'H} \longrightarrow \mathrm{RadH} + \mathrm{R'}\bullet$$

The activation energy of this reaction is usually low. To estimate the activation energy (E) as the function of the reaction heat (Q), one may use a simple approximate equation (so called Polanyi-Semenov rule) [10]:

$$E = A - \alpha Q$$

Here A and α are constants approximately equal to 11.5 and 0.25, respectively. Modern theoretical analysis gives more complicated and more precise, but also approximate formulae. According to Denisov [11], the dependence of the activation energy on enthalpy (ΔH) is expressed by the formula:

$$\Delta \mathrm{E}_H = [\alpha'/(1 + \alpha')]\,\Delta H_\mathrm{e} + (\alpha'\Delta H_\mathrm{e}/2br_\mathrm{e})^2.$$

Here α' is a coefficient which is constant for each pair of fixed bonds, the one being cleaved, and the other being formed; br_e is a parameter also constant for a given series of reactions and not very different for different classes of reactions. The latter formula gives non-linear dependence of activation energy on the reaction's enthalpy; whereas, less precise Polanyi-Semenov rule predicts a linear dependence:

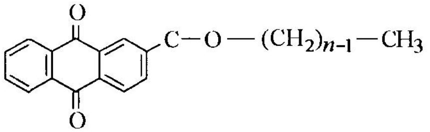
$$\Delta E = \alpha \Delta \Delta H.$$

Nevertheless, the thermodynamics of these reactions remain an important basis for their kinetic characteristics. Polar factors, while they should not be completely neglected, are not of great importance in reactions of neutral free radicals with molecules. If we have a series of substrates reacting via C–H homolytic cleavage, we can then expect that as a rule, the stronger the C–H bond, the smaller the rate constant.

When a branched alkane is used as the substrate, a radical usually attacks the C–H bonds in accordance with "normal" selectivity, i.e., the reactivity of C–H bonds decreases in the following order:

tertiary > *secondary* > *primary* (or in another notation 3° > 2° > 1°).

The hydrogen abstraction process by photo-excited ketones and some other organic compounds have been thoroughly investigated [12a–f]. The rates of intramolecular hydrogen atom abstraction from methylene groups of anthraquinone-2-carboxylic acid derivatives have been measured [12a]. For n = 9, the abstraction constant is $k = 10^4\ s^{-1}$. Each methylene group added to the alkyl chain increases k by approximately $1.5 \times 10^4\ s^{-1}$.



Alkyl radicals formed via abstraction of the hydrogen atom may react with molecular oxygen present in the solution; if dioxygen is replaced with carbon monoxide, carbonylation of the alkane occurs to produce an aldehyde or a ketone

[12d]. A theoretical study of H-abstraction from aliphatic alcohols was carried out [12f]. The atomic oxygen anion, O^- [12g], reacts with alkanes via the mechanism of hydrogen atom transfer [12h]:

$$O^- + C_nH_{2n+2} \longrightarrow HO^- + C_nH_{2n+1}^\bullet$$

$$O^- + C_nH_{2n+2} \longrightarrow H_2O + C_nH_{2n} + e^-$$

Table II.1 presents total rate constants and HO^- branching percentages for the reactions of O^- with various straight-chain and branched alkanes [12h].

Table II.1. Reactions of the oxide anion O^- with alkanes at 300 K

Alkane	$k \times 10^{-9}$, $cm^3 s^{-1}$	% HO^-
Methane	0.088	100
Ethane	0.59	60
Propane	1.2	50
n-Butane	2.0	27
2-Methylpropane	1.9	32
n-Pentane	2.1	21
2-Methylbutane	2.2	25
2,2-Dimethylpropane	2.1	97
n-Hexane	2.3	17
n-Heptane	2.4	10
n-Octane	2.6	9
n-Decane	2.8	4

Unsaturated hydrocarbons and even alkanes are capable of formation of weak complexes with various radicals [13]. A theoretical consideration of a model system $H_2NO \cdots HCH_3$ (by method INDO UHF) showed that the stabilization energy of this complex at the equilibrium distance $r(O \cdots H) \cong 2$ Å is <1 kcal mol^{-1}. One may suggest that complexes of such type are intermediate species in alkane reactions with radicals.

II.2.A. HALOGENATION

Halogenation and especially chlorination of alkanes is a very important process as it gives halogenated alkyls [14]. If the temperature of chain radical chlorination of methane is high, and time of contact between hydrocarbon and chlorine is short, in addition to chlorinated hydrocarbons, large amounts of ethane (at ~1000 K) or ethylene and hydrogen (at ~2000 K) are formed (Benson's process [15]). Thus the content of ethylene, propylene and acetylene is up to 77% at 1273 K. The radical chain process includes the following stages:

I:

$$CH_4 \longrightarrow CH_3\bullet + H\bullet$$
$$Cl_2 \longrightarrow 2\,Cl\bullet$$
$$CH_4 + H\bullet \longrightarrow CH_3\bullet + H_2$$
$$Cl_2 + H\bullet \longrightarrow Cl\bullet + HCl$$
$$CH_4 + Cl\bullet \longrightarrow CH_3\bullet + HCl$$
$$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$$
$$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$$
$$CH_3\bullet + H\bullet \longrightarrow CH_4$$

II:

$$\bullet CH_2Cl + RH \rightleftharpoons CH_3Cl + R\bullet$$
$$\bullet CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl\bullet$$
$$C_2H_5\bullet \longrightarrow CH_2{=}CH_2 + H\bullet$$
$$C_2H_5\bullet + RH \rightleftharpoons C_2H_6 + R\bullet$$
$$C_2H_5\bullet + Cl_2 \longrightarrow C_2H_5Cl + Cl\bullet$$
$$CH_3\bullet + \bullet CH_2Cl \longrightarrow C_2H_5Cl$$
$$\bullet CH_2Cl + \bullet CH_2Cl \longrightarrow ClCH_2CH_2Cl$$

III:

$$CH_3\bullet + CH_2{=}CH_2 \rightleftharpoons CH_3CH_2CH_2\bullet$$

$$C_2H_5\bullet + CH_2{=}CH_2 \rightleftharpoons CH_3CH_2CH_2CH_2\bullet$$
$$CH_3CH_2CH_2\bullet \longrightarrow CH_3CH{=}CH_2 + H\bullet$$
$$CH_3CH_2CH_2CH_2\bullet \longrightarrow CH_3CH_2CH{=}CH_2 + H\bullet$$
$$R\bullet + CH_2{=}CH_2 \longrightarrow RH + C_2H_3\bullet$$
$$C_2H_3\bullet \longrightarrow HC{\equiv}CH + H\bullet$$

IV:

$$CH_3\bullet + HC{\equiv}CH \rightleftharpoons CH_3CH{=}CH\bullet$$
$$R\bullet + CH_3CH{=}CH_2 \longrightarrow RH + \bullet CH_2CH{=}CH_2$$
$$R\bullet + HC{\equiv}CH \longrightarrow RH + HC{\equiv}C\bullet$$
$$CH_3C{=}CH\bullet \longrightarrow CH_3C{\equiv}CH + H\bullet$$
$$HC{\equiv}C\bullet \longrightarrow 2\,C + H\bullet$$
$$\bullet CH_2CH{=}CH_2 \longrightarrow CH_2{=}C{=}CH_2 + H\bullet$$

Chlorine atoms can also be generated at ambient temperature by light irradiation of molecular chlorine mixed with hydrocarbon [14a, 16]. The following scheme describes the process in the liquid phase:

$$Cl_2 \overset{h\nu}{\rightleftharpoons} [2\,Cl\,]_S \longrightarrow 2\,Cl\bullet$$
$$Cl\bullet + RH \xrightarrow{k_1} R\bullet + HCl$$
$$R\bullet + Cl_2 \longrightarrow RCl + Cl\bullet$$
$$2\,Cl\bullet \longrightarrow Cl_2$$
$$R\bullet + Cl\bullet \longrightarrow RCl$$
$$2\,R\bullet \longrightarrow R_2$$

For ethane at 293 K lg k_1 = 7.6 dm^3 mol^{-1} s^{-1}. Chlorination of alkanes also occurs if solutions of metal chlorides (for example, $AuCl_4^-$ or $PtCl_6^{2-}$; see [17]) are irradiated in the presence of an alkane. Bromination of alkylaromatic hydrocarbons with anion Br^- in the presence of cerium ammonium nitrate proceeds as a radical reaction [18a]:

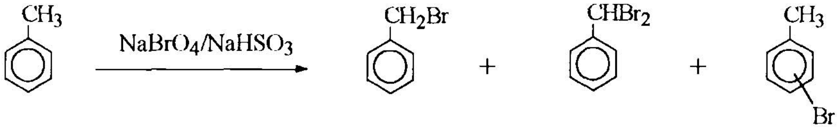
$$Ce^{IV}NO_3 + Br^- \longrightarrow Ce^{IV}Br + NO_3^-$$

$$Ce^{IV}Br \longrightarrow Ce^{III} + Br\bullet$$

$$Br\bullet + C_6H_5CH_3 \longrightarrow HBr + C_6H_5CH_2\bullet$$

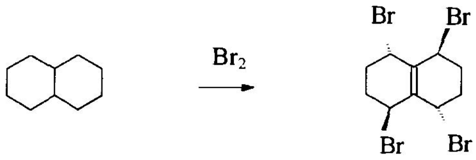
$$C_6H_5CH_2\bullet + Ce^{IV}Br \longrightarrow C_6H_5Br + Ce^{III}$$

Bromination of toluene by the system $NaBrO_3$ – $NaHSO_3$ gives three main products:

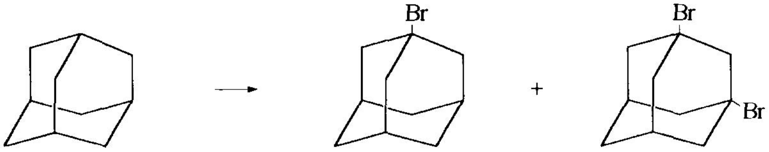


The free-radical bromination by $Br\bullet$ occurs in ethyl acetate yielding **α-bromotoluene** and **α,α′-dibromotoluene**, while the ring-bromination by Br^+ occurs in aqueous acetonitrile [18b].

Photochemical reaction of 4-*tert*-butyltoluene with HBr/H_2O_2 gives benzyl bromide easily hydrolyzed to 4-*tert*-butylbenzaldehyde [18c]. Thermal and photochemical bromination of decalin gives mainly tetrabromooctalin [18d]:



Adamantane has been brominated with the system $CBr_4/NaOH$ under phase transfer catalysis conditions [18e]:



The reaction is believed to be initiated by single-electron oxidation of **HO^-** by CBr_4:

$$CBr_4 + HO^- \rightleftharpoons CBr_4\bullet^- + HO\bullet$$
$$CBr_4\bullet^- \longrightarrow \bullet CBr_3 + Br^-$$
$$RH + \bullet CBr_3 \longrightarrow R\bullet + HCBr_3$$
$$R\bullet + CBr_4 \longrightarrow RBr + Br_3C\bullet$$

The behavior of 1-adamantyl radical in chlorine atom abstraction has been investigated recently [18f]. Initiators of radical reactions and some metal complexes induce dark chlorination of saturated hydrocarbons with Cl_2 or CCl_4 [19].

II.2.B. REACTIONS WITH OXYGEN- AND NITROGEN-CONTAINING RADICALS

Reactions of alkanes with hydroxyl radicals, which take place in the atmosphere under the action of irradiation and occur as crucial stages in oxidation of hydrocarbons are of great importance and have been investigated in detail [20]. The data for reactions of **HO•** with some alkanes are summarized in Table II.2 [20f]. Reaction of alkanes with nitric acid occurs as a radical chain process with participation of radicals **HO•** and **NO_2•** [21]:

$$HNO_3 \longrightarrow HO\bullet + NO_2\bullet$$
$$RH + HO\bullet \longrightarrow R\bullet + H_2O$$
$$R\bullet + NO_2\bullet \longrightarrow RNO_2$$
$$R\bullet + HNO_3 \longrightarrow RNO_2 + HO\bullet$$

Table II.2. Rate constants, $k \times 10^{-13}$, $cm^3\ s^{-1}$, for the reaction of alkanes with radicals HO• at different temperatures

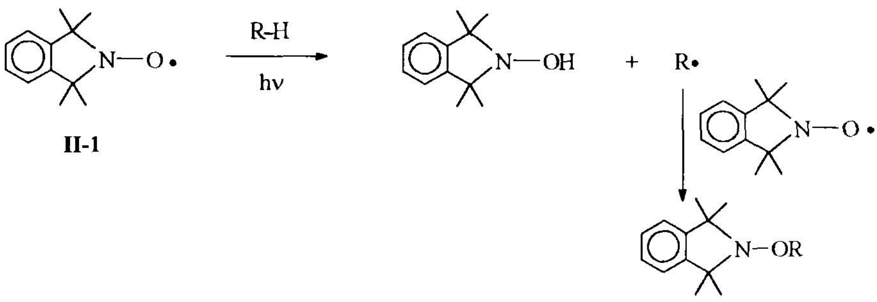
Alkane	300 K	340 K	390 K
Ethane	2.6	3.9	6.0
Propane	10.9	14.6	18.3
n-Butane	24.3	28.7	35.4
2-Methylpropane	20.9	24.7	27.2
n-Pentane	39.8	45.9	64.4
n-Hexane	54.5	62.3	72.9
Cyclopentane	58.9	61.8	75.3
Cyclohexane	76.6	78.4	103
Cycloheptane	120	133	164
Cyclooctane	134	149	191

Radical nitration of a hydrocarbon with cerium ammonium nitrate begins from the photohomolysis [22]:

$$Ce^{IV}NO_3 \xrightleftharpoons{h\nu} Ce^{III} + NO_3\bullet$$

$$RH + NO_3\bullet \longrightarrow R\bullet + HNO_3$$

The photochemically excited nitroxide **II-1** reacts with such alkanes as cyclohexane, isobutane and *n*-**butane** abstracting hydrogens and generating carbon-centered radicals which are trapped by ground state **II-1** [23]:



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II.2.C. REACTIONS WITH CARBENES

Singlet state carbenes produced in photo- or thermal decomposition of ketene or diazomethane

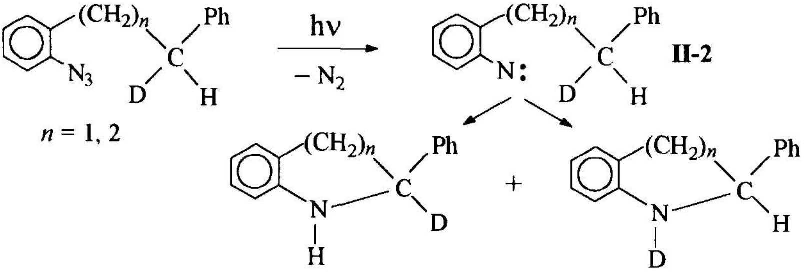
$$CH_2{=}C{=}O \longrightarrow CH_2 + CO$$

$$CH_2NN \longrightarrow CH_2 + N_2$$

are known to insert into the C–H bond of an alkane:

$$CH_2(s) + CH_4 \longrightarrow C_2H_6$$

Usually insertion of a simple carbene into the C–H bond of an alkane proceeds with retention of configuration. Some other carbenes react much more selectively than simple CH_2. For example, phenylcarbene reacts approximately eight times faster and species CHC1 twenty times faster with a secondary C–H bond of *n*-pentane than with a primary one. Diclorocarbene reacts even more selectively and inserts only into secondary and tertiary C–H bonds. Even secondary bonds are not affected if a tertiary bond is present. Calculations demonstrated that in the methylene insertion into the C–H bond, the hydrogen atom is first attacked to produce a complex similar to that which is formed in the recombination of two radicals [24]. Low stereoselectivities and a large deuterium isotope effect ($k_H/k_D = 4–8$) for the intramolecular insertion reaction of 2-alkoxyphenylcarbenes and 2-alkylphenylcarbenes led to the conclusion that a triplet state carbene was involved in the reaction [25a]. Even greater kinetic isotope effects ($k_H/k_D = 14.7$) have been measured for the intramolecular C–H insertion reaction of 2-alkylphenylnitrenes [25b]:



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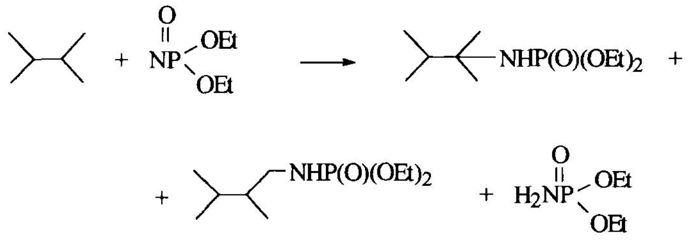
A large isotope effect supports the hydrogen abstraction–recombination mechanism involving the triplet state nitrene **II-2.**

The reaction of phosphorylnitrene species with alkanes gives a set of products [25c]:



Methylidyne and silylidyne insert into methane and silane (see [26]):

$$CH + CH_4 \longrightarrow CH_2CH_3$$
$$CH + SiH_4 \longrightarrow CH_2SiH_3$$
$$SiH + CH_4 \longrightarrow SiH_2CH_3$$
$$SiH + SiH_4 \longrightarrow SiH_3SiH_3$$

Processes with participation of methylidyne take place in combustion and planetary atmosphere chemistry, while silylidyne is an important intermediate in the chemical vapor deposition of amorphous silicon film from SiH_4.

II.2.D. REACTIONS WITH PARTICIPATION OF ION RADICALS

The interaction of arenes or alkylarenes, $ArCH_2R$, with some oxidants, Ox, [27] for example, with cerium(IV) salts [27c] or photoactivated quinones [27d], gives rise to the formation of the ion-radical pair:

$$ArCH_2R + Ox \rightleftharpoons [ArCH_2R^{+}\bullet, Ox^{-}\bullet]$$

which can subsequently undergo proton transfer to generate radical species:

$$[\mathrm{ArCH_2R^{+}\bullet},\ \mathrm{Ox^{-}\bullet}] \rightleftharpoons \mathrm{ArC{\bullet}H_2R} + \mathrm{Ox\bullet}$$

Carbon-centered arylalkyl radicals can then enter into various transformations, for example, can react with molecular oxygen (see next section).

It is interesting that in a similar reaction [27e] of perfluoroalkanes with the organometallic photosensitizer, decamethylferrocene, electron transfer leads to the formation of anion radical which is transformed further to a radical:

$$\mathrm{R^f{}_2CF{-}CF_2R^f} + e^{-} \longrightarrow [\mathrm{R^f{}_2CF{-}CF_2R^f}]\bullet^{-} \longrightarrow \mathrm{R^f{}_2C{\bullet}{-}CF_2R^f} + \mathrm{F^{-}}$$

Under the action of a reductant, Red, the radical produces an olefin

$$\mathrm{R^f{}_2C{\bullet}{-}CF_2R^f} + \mathrm{Red} \longrightarrow \mathrm{R^f{}_2C{=}CFR^f} + \mathrm{RedF}$$

II.3. OXIDATION BY MOLECULAR OXYGEN

The importance of chemical processes based on the oxidation of hydrocarbons by molecular oxygen is connected with the necessity of rational use of hydrocarbons from natural gas, petroleum and coal. Despite the great amount of work devoted to this problem, it is far from being completely solved. At present its significance, in terms of the urgent necessity of more economical consumption of natural resources, is increasing with time. Thermodynamically the formation of oxygen-containing products from saturated hydrocarbons and molecular oxygen is always favorable because oxidation reactions are highly exothermic. Nevertheless, it is this very fact that hinders the creation of selective processes, with the difficulty usually lying in the prevention of different parallel and secondary oxidation reactions.

II.3.A. HIGH-TEMPERATURE OXIDATION IN THE GAS PHASE

The complete oxidation of alkanes by air (burning) to produce water and carbon dioxide is a very important source of energy [28a-c]. There can also be partial oxidation of saturated hydrocarbons producing various valuable organic substances, e.g., alkyl hydroperoxides, alcohols and ketones or aldehydes [28a,b,d,e]. Oxidation of benzene and alkylbenzene under UV irradiation takes place in the atmosphere [29].

The oxidation of methane and other light alkanes in the gas phase at high temperature gives alcohols, aldehydes and ketones and occurs via a chain radical mechanism (for certain stages of the process, see recent publications [30]). The methane oxidation produces methanol and formaldehyde as main oxygenates. Due to the fact that both products are much more reactive than hydrocarbon, the yield of alcohol and aldehyde is only a few percents. Usually the reactions were

Table II.3. Partial non-catalyzed oxidation of methane with molecular oxygen.

Pressure, atm	Tempe-rature, °C	$[O_2]$, %	Reaction time, s	Conversion, of CH_4, %	S_{MeOH} [a]	S_{HCHO} [b]	Yield of MeOH, %
141	475	4.5	48	2.51	45.0	3.66	1.13
141	475	8.7	48	5.30	29.6	2.48	1.57
3500	264	7.9	600	6.29	40.1	0.64	2.52
40	455	2.04	~0.08	2.10	59.6	17.04	1.25
40	461	3.2	~0.08	2.90	54.4	17.0	1.58
40	483	7.2	~0.08	6.10	34.6	13.83	2.11
65	310	3.85	2–1000	7.5	95		6
65	410	7	2–1000	21	80		17
100	410–500	2.8	~1		46.0	9.1	2.8
65.3	456	5.1	~150	8.0	83.0		6.6
40	474–498	2.35–3.14	1.2–2.1	1.3–2.2	43.6	6.4	0.73–1.0
70	448	3.3	~2	3.9	67.5	1.8	2.56
20	400	5.0	10–100	>4.6	~32		
30	447	9.5		9.0	23.5		1.9–2.1
50	350–550	1.5	>10		44		1.1

[a] S_{MeOH} is the selectivity of the formation of methanol.

[b] S_{HCHO} is the selectivity of the formation of formaldehyde.

carried out in broad pressure (1–230 atm) and temperature (300–500 °C and higher) ranges. The reaction time varied from fractions of a second to tens of minutes. Some data on partial non-catalyzed methane oxidation are summarized in Table II.3 [28d].

The oxidation of ethane yields not only expected ethanol (and also less amount of acetaldehyde) but additionally large amounts of the **C–C** bond splitting products: methanol, formaldehyde, formic acid, as well as CO and **CO_2** [28d, 31a] (Table II.4).

Table II.4. The selectivity (products, % based on the combusted ethane) of the partial non-catalyzed ethane oxidation with molecular oxygen.

Pressure, atm	Temperature,°C	EtOH	MeOH	MeCHO	HCHO	AcOH	HCOOH	CO	CO_2
15[a]	315	16.0	19.4	1.9	4.5	0	0	–	–
50[b]	286	24.4	14.1	8.3	2.0	1.7	0.9	34.8	10.0
75[c]	279	18.0	16.6	6.8	0.4	3.6	0.6	–	–
100[d]	266.5	23.7	11.2	6.0	0.05	23.8	0.6	9.3	14.2

[a] Initial mixture composition: 88.2% ethane, 11.8% O_2; reaction time 3.0 min.

[b] Initial mixture composition: 88.4% ethane, 11.6% O_2; reaction time 10.7 min.

[c] Initial mixture composition: 88.2% ethane, 11.8% O_2; reaction time 2.5 min.

[d] Initial mixture composition: 88.4% ethane, 11.6% O_2; reaction time 34.5 min.

The composition of oxygenate mixture in the propane oxidation depends on the conditions (pressure and temperature of the process) [28d, 31b,c] (Table II.5).

Table II.5. The selectivity (products, %) of the partial non-catalyzed propane oxidation with air (propane : air = 1 : 3.6).

Products	1 atm, 373 °C	20 atm, 281 °C	60 atm, 252 °C	100 atm, 250 °C
The sum of aldehydes	20.5	21.8	13.5	13.7
The sum of normal alcohols	19.7	21.0	17.5	15.2
Isopropanol	1.3	2.8	6.2	16.0
Acetone	0.5	4.3	12.5	7.9
The sum of acids	4.3	17.0	19.0	18.9
CO_2	7.3	17.1	21.4	20.6
CO	21.3	16.0	9.9	7.7
Propene	25.1	0	0	0

Table II.6 demonstrates that the efficiency of oxidation of alkanes into useful products is much higher for propane and *n*-butane in comparison with light alkanes (ethane and especially methane) [28d].

Table II.6. The optimal parameters of the alkane oxidation.

Alkane	Pressure, atm	Temperature °C	Ratio alkane : O_2	Degree of conversion into useful products (%)
Methane	100	450	30	2
Ethane	50	360	10	5
Propane	20	280	1	20
n-Butane	9	260	1	20