Translated from *Uspekhi Khimii* 59 1906–1930 (1990) U.D.C. 541.128:547.21+547.51

Activation of C–C bonds in unsaturated hydrocarbons by metal complexes

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ABSTRACT. The current position of the problem of the activation of C–C bonds in alkanes and cycloalkanes is examined. The two main routes for the cleavage of unactivated single C–C bonds—metal-complex cleavage on an unsaturated coordinate metal site and electrophilic cleavage—are discussed. The literature data on the development of catalysts for the "low-temperature" cleavage of C–C bonds in alkanes are correlated.

The bibliography includes 158 references

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I. Introduction

A new stage in the chemistry of alkanes that could be called "the low-temperature chemistry of paraffins" began in the 1970s.

Activation of the C–H bonds of saturated hydrocarbons by transition metal complexes in solution[1] was discovered in 1969 and thus new possibilities for selective conversions of alkanes, including methane, under mild conditions were demonstrated. This area is undergoing rapid development at the present time.[2–15] In his introduction to the recently published issue of *New Journal of Chemistry* that is devoted to problems concerning the activation and functionalisation of alkanes, Hill writes that there are few problems in chemistry which would have stimulated greater interest during the last ten years than the selective conversions of alkanes. The reasons for this are clear. Alkanes constitute "the ultimate feedstocks for production of a myriad of organic products from pharmaceuticals and fibres to new and innovative materials".[15]

The second important milestone in the development of the low-temperature chemistry of alkanes is mainly connected with the discovery of new proton superacids whose acidity is greater than that of sulphuric acid by a factor of 10^7-10^{19}.[16–20] Because of the exceptionally high electrophilicity of the unsolvated proton in superacid media it was possible for the first time to carry out conversions of alkanes effectively at room temperature and lower temperatures.[16–26] Until recently proton superacids were the only reagents capable of cleaving not only the C–H bonds but also the more inert C–C bonds in alkanes under mild conditions.[27,28] By using superacid media it was possible to observe experimentally for the first time alkyl cations formed from alkanes,[16,21,22] which had previously been postulated as intermediates in organic reactions.

Another important contribution to the problem of the activation of alkanes has been made by the concept of the "pentacoordinate carbonium ion", which plays a key role in electrophilic attack on C–H and C–C σ-bonds.[19] Superacid activation of alkanes, to which a large number of publications have been devoted, will not be specifically examined in this review. We should only mention that the use of proton superacids is severely restricted by their limited availability, toxicity, and corrosive nature, and the difficulties in using them.

We also do not have the opportunity to dwell on the impressive progress achieved in a traditional area such as the gas-phase reactions of alkanes on heterogeneous metal and oxide catalysts, which as usual has played a leading role in industrial processes (see, for example, several studies).[29–40]

Table 1. Logarithms of equilibrium constants of the cracking reactions of alkanes and the dimerisation of olefins.*

Reaction	$\log K_p$, at T, K		
	300	500	700
$C_6H_{14} \rightleftarrows C_4H_{10}+C_2H_4$	−8.230	−2.230	+0.172
$C_7H_{16} \rightleftarrows C_5H_{12}+C_2H_4$	−7.846	−1.908	+0.608
$C_8H_{18} \rightleftarrows C_4H_{10}+C_4H_8$	−3.583	+0.367	+2.025
$C_8H_{18} \rightleftarrows C_5H_{12}+C_3H_6$	−5.442	−0.301	+1.853
$C_{10}H_{22} \rightleftarrows C_4H_{10}+C_6H_{12}$**	−5.758	−0.676	+1.468
$2C_4H_8 \rightleftarrows C_8H_{16}$**	+6.631	+0.915	−1.481
$2C_5H_{10} \rightleftarrows C_{10}H_{20}$**	+6.434	+0.736	−1.657

* Calculated from the results of Zhorov.[45]
** Alkene-1.

The aim of this review is to cover the recent progress in the low-temperature activation of the C–C bonds of alkanes by metal complexes.

It is well known that the carbon–carbon bond of paraffins is amongst the most passive of bonds of one of the most inert classes of organic compounds. Not long before the discovery of the metal-complex activation of the C–H bonds of alkanes, Halpern wrote that this problem presents a challenge to chemists.[41,42] This can apply even more to the activation of C–C bonds.

The ever increasing interest in a solution to this problem is governed by the key role of reactions involving cleavage of C–C bonds in industrial processes for the treatment of hydrocarbon raw materials (isomerisation, cracking, hydrocracking, etc.).

Cleavage of the thermodynamically stable non-polar C–C σ-bonds in paraffins, which do not have either free electron pairs or low-lying vacant orbitals, usually takes place effectively at high temperatures (300–1000 °C) in the gas phase.[43,44]

It follows from Table 1 that the cracking of alkanes at a low temperature is thermodynamically unfavourable. Only at elevated temperatures is the thermodynamic restriction lifted, but high-temperature processes consume considerable energy and are generally not very selective.

On the other hand the oligomerisation of olefins at low temperatures is accompanied by the liberation of sufficient heat to compensate the energy of cleaving the C–C bonds. Therefore the low-temperature cracking of alkanes is thermodynamically possible if it occurs with the formation of lower alkanes and oligomers.

At the present time it would appear that two routes for the activation of C–C bonds in alkanes resulting in their cleavage are of the greatest significance. The first is an electrophilic route which either involves the direct cleavage of C–C bonds by treatment with an electrophile E^+

$$R_3C{-}CR_3 + E^+ \rightarrow R_3CE + \overset{+}{C}R_3 \qquad (1a)$$

or the initial cleavage of C–H bonds to form carbocations or cation-like intermediates, which subsequently undergo intramolecular reactions with cleavage of C–C bonds:†

$$RH \xrightarrow[-EH]{E^+} R^+ \rightleftarrows (R')^+ + \quad \diagup C{=}C \diagdown \qquad (1b)$$

The second route for activating C–C bonds involves their interaction with unsaturated coordinate transition metal complexes, which can formally be represented as occurring via the insertion (oxidative addition) of complex M into the C–C bond:

$$\diagup C{-}C \diagdown + M \rightarrow \diagup C{-}M{-}C \diagdown \rightarrow \text{products.} \qquad (2a)$$

In this case as in the electrophilic cleavage of C–C bonds, 2 routes are actually possible. The first involves the direct insertion of the metal complex into the C–C bond [scheme (2a)], similar to that which occurs with the covalent bonds: H–H,[48–50] R–X,[48] Si–H,[51–53] and C–H.[2,5–7,9,10,54–62]

The second route involves the oxidative addition of C–H bonds to the metal complex followed by cleavage of the C–C bond in the resulting σ-alkylhydride complex:

$$R{-}CH_2{-}CH_3 + M \rightleftarrows RCH_2CH_2{-}M{-}H \qquad (2b)$$

α-elimination | β-elimination

$$\begin{array}{ll} H & CH_2{=}CH_2 \\ | & | \\ CH_2{=}M{-}CH_2R & R{-}M{-}H \\ \downarrow\uparrow & \uparrow\downarrow \\ CH_3{-}M{-}CH_2R & CH_3CH_2{-}M{-}R \end{array}$$

As will be demonstrated below, scheme (2b) is not just speculative.

† The formation of carbocations from hydrocarbons may possible occur in stages. Initially one electron is transferred to the electrophile to form E, then the transfer of $H^{\cdot}$ occurs.[46,47]

II. Cleavage of C–C bonds in alkanes on a metal site

During the last thirty years significant progress has been made in the use of transition metal complexes for activating inert covalent bonds,[48–64] and C–H bonds in paraffins. However, all of the known catalytic conversions of unactivated alkanes and cycloalkanes by transition metal complexes in the liquid phase relate only to C–H bonds and not C–C bonds. Cleavage of C–C bonds only occurs in strained cycloalkanes and in energy-rich polyhedranes (see the review of Crabtree).[6]

What is the reason for the high degree of inertness of C–C bonds compared to C–H bonds in alkanes? The energies of σ-bonds (in kcal mol^{-1}) are given below:[65,66]

H–H	C–H	C–C
104	96–105	87–90

It follows from this that the C–C bond is appreciably less stable than the C–H and H–H bonds. However, their reactivity increases in reverse order. Thus, molecular hydrogen is fairly readily activated by a large number of metal complexes while examples of the activation of C–H bonds in alkanes and cycloalkanes are quite well known although comparatively rare. On the other hand the catalytic cleavage of C–C bonds in paraffins by metal complexes in the liquid phase has until recently not been reported at all:

Increase in reactivity ←

H–H C–H C–C

→ Decrease in bond strength

The theory that the metal-complex cleavage of a C–C bond to form two weak C–M bonds, the energy of which does not compensate the energy of cleavage of the C–C bond, is thermodynamically unfavourable has been made widely known.[5,6] Thus, it follows from the experimental results of Halpern[5] that the energy of the Co–R bond in dimethylglyoximate complexes $RCo(dmg)_2$ and the R–Mn bond in the complexes $RMn(CO)_5$ and $RMn(CO)_4(PPh_3)$ is in the range 18–25 kcal mol^{-1}. Halpern assumes that for other metals of the 3*d* series (end of the period) the same order of magnitude of M–C bond energy is typical. At the same time the energies of the corresponding M–H bonds are 52–80 kcal mol^{-1}. It was concluded from this that the oxidative addition of the H–H bond to the metal site of a complex is exothermic while addition of C–H bonds is an endothermic process. The oxidative addition of C–C bonds to a metal complex is thought to be even more thermodynamically unfavourable. However, this does not appear to be a general conclusion. Judging by the small amount of data on the M–C bond energies in solution for certain transition metals of the 3*d* series (beginning of the period), 4*d* and 5*d* series, lanthanides, and actinides, these values are considerably higher than those quoted (see Tables 2 and 3). We should note that the energies of M–C bonds in cationic complexes is higher than in neutral complexes and is approximately equal to the energies of M–H bonds (Table 3). As will be demonstrated below, the energies of $M^+{-}CH_3$ bonds in the gas phase are higher than the energies of the corresponding $M^+{-}H$ bonds. Thus, the thermodynamic restrictions on the cleavage of C–C bonds with metal complexes are not obligatory. The thermodynamics of these reactions also depend to a large extent on the characteristics of the metal complex and in certain cases they can be exothermic.[74]

Table 2. Energies of M–Alk bonds.

Complex	M–C	Bond energy, kcal mol^{-1}	Refs.
RCoL(L')[a,b]	Co–CHR_2	28–25	[5]
Ado-B_{12}[c]	Co–CH_2R	32	[67]
$CH_3Mn(CO)_5$	Mn–CH_3	37	[68]
$(CH_3)_3PtCp$	Pt–CH_3	38	[69]
$CH_3IrClI(CO)(PMe_3)_2$	Ir–CH_3	46	[69]
$CH_3Re(CO)_5$	Re–CH_3	53	[70]
$(CH_3)_2TiCp_2$	Ti–CH_3	60	[71]
$(CH_3)_2ZrCp_2$	Zr–CH_3	66	[71]
$(C_4H_9)_2ThCp_2'$[d]	Th–C_4H_9	73	[72]
Alk(Alk')UCp_2'[d]	U–Alk	60–85	[72]

[a] L = pyridine, imidazole, PR_3; L' = dimethylglyoxime.
[b] L = pyridine; L' = *N,N'*-disalicylidene-*o*-phenylenediamine.
[c] Ado-B_{12} = adenosylcobalamine.
[d] Cp' = pentamethylcyclopentadienyl.

Table 3. Calculated energies of the M–C and M–H bonds in transition metal carbonyl complexes[73].

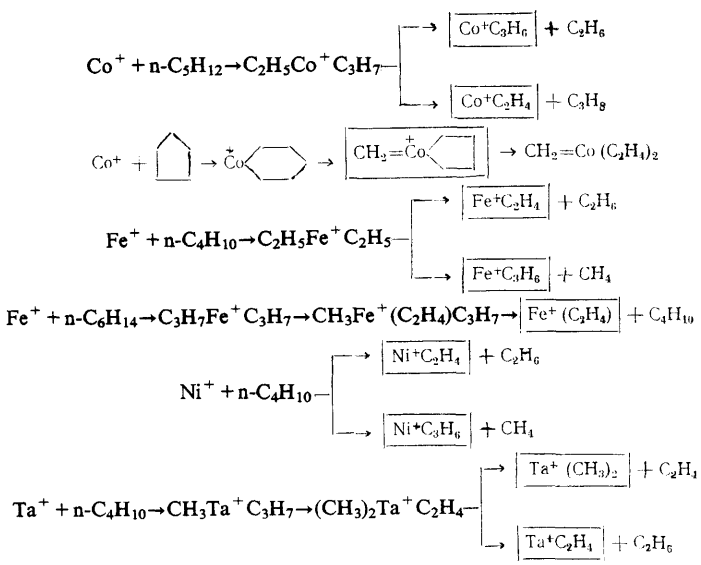
Complex	Energy of M–X bond, kcal mol^{-1}		Complex	Energy of M–X bond, kcal mol^{-1}	
	X=CH_3	X=H		X=CH_3	X=H
$XMn(CO)_5$	37	54	$XIr(CO)_4$	51	68
$XRe(CO)_5$	48	67	$XRe(CO)_5^+$	57	60
$XCo(CO)_4$	38	55	$XNi(CO)_4^+$	60	62
$XRh(CO)_4$	45	61			

These conclusions are supported by the literature data on the cleavage of C–C bonds in alkanes and cycloalkanes on a "ligand-free" metal site. These data will be examined below. On the other hand, all of the experimentally obtained material indicates the outstanding importance of steric factors in the attack by a metal complex or metal on a C–C bond.

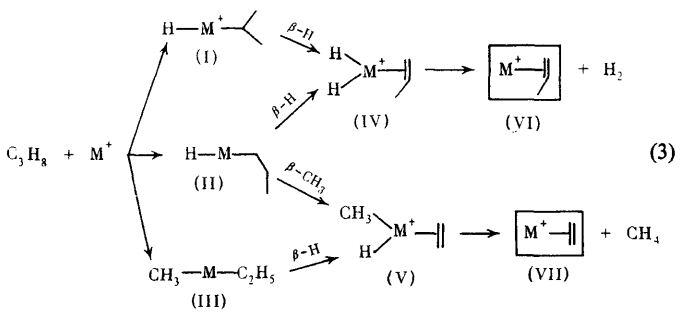
1. Cleavage of C–C bonds by metal ions in the gas phase

Alkanes and cycloalkanes can react with Fe^+, Ni^+, Co^+, Ta^+ and other ions in the gas phase.[75–92] The reactions are accompanied by cleavage of not only C–H but also C–C bonds. Furthermore, the cleavage of C–C bonds is frequently an exothermic process and constitutes the predominant conversion route of paraffins.

Examples of the cleavage of C–C bonds in alkanes and cycloalkanes by metal ions in the gas phase are given below (the observed reaction products are enclosed in boxes):



The proposed mechanism for the interaction of alkanes with Co^+, Ni^+, Fe^+, and other ions (for the reaction with propane) is shown in scheme (3):[86–89]

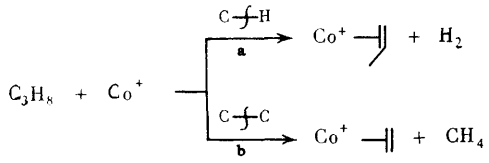


(3)

Scheme (3) involves the oxidative addition of C–H and C–C bonds of the alkane to M^+ to form intermediates (I), (II), and (III), the intramolecular transfer of β-H and β-CH_3 groups to the metal, resulting in the formation of dihydride (IV) and alkylhydride (V) olefin complexes, and elimination of H_2 from intermediate (IV) and CH_4 from intermediate (V) to give the observed olefin complexes (VI) and (VII).

Recently the reaction of alkanes with Co^+ and Ni^+ ions was made the subject of a more thorough investigation.[89] In this case an unusual feature of the reaction between propane and Co^+ was detected, which lay in the fact that of the two parallel reactions for cleavage of a C–H bond (4a) and a C–C bond (4b), the first predominates at low energies (0.1 eV) and the second predominates

at high energies (1 eV). The ratio of yields of $Co^+C_2H_4$:$Co^+C_3H_6$ was 1:2 in the first case and 3:1 in the second case.



(4)

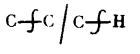
Georgiadis et al.[89] assumes that cleavage of the C–C bond (4b) at a low energy occurs to a lesser degree because the overall reaction (4b) includes the endothermic elimination of methane from intermediate (V) [(V)→(VII) in scheme 3)], the energy barrier of which is 1.6 ± 0.7 kcal mol^{-1}. According to estimates, on going from methane to heavier homologues with the number of carbon atoms not less than 3, this barrier decreases from 19 to only a few kcal mol^{-1}. Since there is an endothermic stage, the overall exothermic‡ reaction (4b) [(II) or (III)→(V)→(VI) in scheme (3)] occurs with greater difficulty than reaction (4a), in which there is no endothermic stage [(I) or (II)→(IV)→(VI) in scheme (3)].

The two alternative mechanisms given in scheme (3) were examined[89] in order to explain why the C–C bond is preferentially cleaved as a result of the reaction between propane and Co^+ at high energies and also as a result of a wide range of reactions between alkanes and Ni^+, Fe^+, and Co^+ at all energies.

In accordance with the first mechanism, cleavage of the C–C bond occurs solely as a result of the insertion of M^+ into this bond [via intermediate (III)]. On the other hand, the transfer of the β-CH_3 group (III)→(V) does not occur. In this case the ratio of yields of products $M^+C_2H_4$:$M^+C_3H_6$ is determined completely by the ratio of probabilities of the oxidative addition of M^+ to the C–C and C–H bonds. The predominance of C–C clevage is due to thermodynamic factors—a weaker bond (compared to C–H) is broken and a stronger M^+–C bond (compared to M^+–H) is formed (Table 4).

The alternative mechanism is based on the assumption that both reactions for cleavage of the C–H and C–C bonds start with a common stage involving insertion of M^+ into C–H bonds. Insertion of M^+ into the C–C bond does not occur because of steric hindrance. The cleavage of the C–C bond occurs through the successive reactions (II)→(V)→(VII) [scheme (3)]. In this case preferential cleavage of the C–C bond may occur because transfer of the β-CH_3 group [(II)→(V)] predominates over transfer of β-H [(I) or (II)→(IV)] since formation of a stronger $M-CH_3$ bond is more favourable. In this case the ratio of $M^+C_2H_4$:$M^+C_3H_6$ or

must be equal to the ratio of the number of primary to secondary C–H bonds in propane, i.e., 3:1. This ratio actually occurs in the reaction of propane with Fe^+.[90] In the reaction of propane with Ni^+ the ratio of



increases to 3.5–4.0:1, which in the opinion of Schultz et al.,[90] could indicate a certain contribution from the mechanism for insertion of Ni^+ into a C–C bond. This reaction is exothermic, in contrast to the competing reaction for insertion of Ni^+ into a C–H bond (Table 4). Houriet et al.[91] have also shown that Ni^+ is mainly inserted into a C–C bond in reactions with linear alkanes.

Table 4. Energies of $M-CH_3$ and M–H bonds in the gas phase (kcal mol^{-1})*.

M	M+–H	M+–CH_2	M–H	M–CH_3
Ti	60	65		
Cr	35±4	37±7	—	—
Mn	53±3	71±7		
Fe	49.8±1.4 53.2	57.9 54.6	46±3 38.7	37±37 34±9
Co	46.6±1.4 51±5 45.4	49.1±3.5 61±4 >56, <68 57±7 46±14	46±3 39±6 45±3 42±3 54±10	46±3 41±10 39.9
Ni	39.5±1.8 41.9 43±2	45.0±2.4 41.3 48±5 <56	58±3 62.1 59±2 65±2 65±6	55±3 53.7 60
Ru Rh Pd Ta	41±3 42±3 45±3 54±5	54±5 47±5 59±5 65±5	—	—

*The results of different authors cited in two studies[88,89] are summarised.

The ease of cleavage of the C–C bonds of alkanes by Fe^+, Ni^+, and Co^+ ions is due to the high energy of the M^+-CH_3 and $M-CH_3$ bonds in the gas phase. These energies are similar to the corresponding values of M^+–H and M–H and even exceed them (Table 4). Thus, the ratio of energies of these bonds in the gas phase is the opposite of what appears in solution. The difference in the strength of the bonds in the gas and condensed phases is attributed to the effect of steric factors in saturated systems (solution), resulting in a weakening of M–C bonds,[93] and also to the possibility of stabilisation of charge by the more polarisable alkyl group compared to H in ionic species in the gas phase.[83,86,89]

It should be emphasised that in all cases addition of a ligand to the metal inhibits cleavage of C–C bonds even in the gas phase. For example, replacement of Fe^+ by $Fe(CO)^+$ [77] and $Fe(CH_2)^+$ [84] is accompanied by a decrease in the proportion of C–C cleavage. The more shielded $Fe(CH_3)^+$ ion is completely inactive towards

‡ The energy of the $Co^+-C_2H_4$ bond (46 ± 8 kcal mol^{-1}) is 26 ± 8 kcal mol^{-1} greater than that needed for cleavage of the C–C bond.

aliphatic hydrocarbons.[85] In reactions of FeH^+, CoH^+, NiH^+, and $Co(CH_3)^+$ ions with alkanes only C–H bonds participate.[85,92] In contrast to the Ni^+ ion, the 14-electron complex $(\eta^5\text{-}C_5H_5)Ni^+$ does not cleave C–C bonds in hydrocarbons.[86]

Thus, the greater the steric hindrance, the lesser is the ability of the attacking species to cleave C–C bonds.

2. Cleavage of C–C bonds with small metal clusters

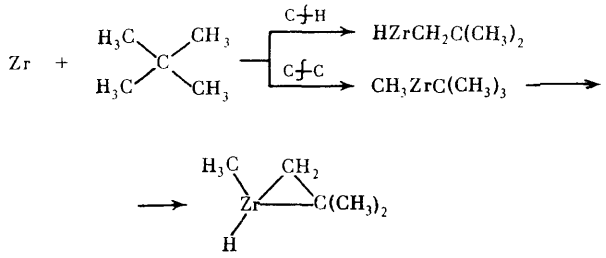
It was first shown in a study by Davis and Klabunde[91] that when atomic Ni and pentane are co-condensed at a low temperature very active small Ni clusters are formed, reacting with pentane even at −130 °C. In this case oxidative addition of the C–H and C–C bonds of the alkane to the Ni atoms occurs:

$$m\ Ni + n\ C_5H_{12} \xrightarrow{-196\,^\circ C} Ni_m(C_5H_{12})_n \xrightarrow[C\not\leftarrow H,\ C\not\leftarrow C]{-130\,^\circ C} \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!(Ni)_m\!<\!\!\begin{matrix} R^3 \\ R^4 \end{matrix}$$

R^1, R^2, R^3, R^4 = Alk, H.

The organic groups on the Ni atom inhibit the further agglomeration of clusters.

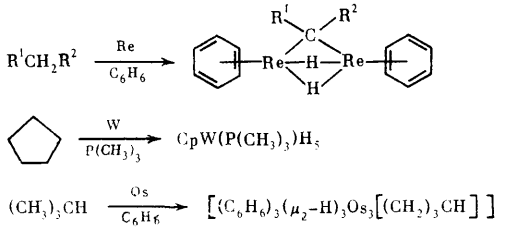
A similar pattern was observed in the co-condensation of Zr atoms with neopentane or isobutane.[95] Reaction of Zr with the alkane resulted in the formation of heterogeneous organozirconium surface complexes, to which Remick et al.[95] have attributed the following structure:



At the present time quite a few different examples of the vapour-phase synthesis of systems of a similar type are known.[96–101] They have various names in the literature: SMAD (Solvated Metal Atom Dispersion), obtained by dispersion of solvated metal atoms;[33,99–102] pseudo-organometallic powders;[33] ultradispersed metals;[103] ligand-free clusters;[103] metal microcrystals;[104] and others. In our opinion the most apt name is "low-ligand clusters",[105] reflecting the main characteristic of these systems.

Low-ligand clusters (LLCs) are intermediate between a compact metal and molecular clusters, being distinguished from both by the high percentage of surface atoms with low coordination numbers. In a bulk metal there are no ligand but the proportion of surface atoms is small while in molecular clusters all of the metal atoms are essentially saturated with ligands. The high percentage of surface atoms with low coordination numbers also governs the potentialities for using LLCs in catalysts, in particular for the cleavage of C–C bonds. The LLCs of nickel obtained by vapour-phase synthesis at normal temperatures are particles with a diameter of 25–36 Å or more (depending on the conditions of synthesis).[96] In terms of their catalytic activity they are superior to traditional Ni hydrocracking catalysts.[99,101] These systems can be used both in a pure form and in the form of particles deposited LLCs being the absence of a deactivating effect from the support.[102] The reasons for the increased activity of LLCs are discussed by Matsuo and Klabunde.[99] Bimetallic LLCs exhibit a particularly high activity.[100,101,106] For example, the presence in Co/SiO_2 of 2.5 at.% Mn–metal, which in itself is inactive in the hydrocracking of saturated hydrocarbons, increases the activity of the catalyst by a factor of 10^2.[100] It should be noted that the promotion of heterogeneous platinum catalyst with rhenium is widely used in industry.[107]

If the co-condensation of an atomic metal with an alkane takes place in the presence of a ligand [$P(CH_3)_3$, benzene], the reaction route changes considerably. In this case the conversions of alkanes take place solely with the participation of C–H bonds. On the other hand, the stabilising effect of the ligand hinders the agglomeration of the organometallic particle being formed. This method has been used for the synthesis of organometallic compounds:[108,109]



A serious disadvantage of the vapour-phase method for synthesising LLCs (in particular heavy metals, which are the most promising as catalysts) is the necessity to use special high-vacuum equipment. Therefore an attempt was made to synthesise catalysts for the cleavage of C–C bonds of alkanes based on LLCs by the conventional reduction of a transition metal compound in solution under conditions that excluded the deactivation of the LLC being formed.[105] It was shown that the reduction of OsO_4 in an alkane or arene with molecular hydrogen at 100–150 °C for 3–15 h or at 20 °C for 3 days resulted in the formation of active catalysts for the hydrocracking of paraffins:

$$OsO_4 + 4\,H_2 \xrightarrow[-4H_2O]{} \ll Os \gg \xrightarrow{RH} Os_{2.5-1.5}C_1H_{2-0}$$

An analysis of the EXAFS spectra showed that the pyrophoric osmium catalysts obtained in this way are actually Os LLCs with a particle diameter of 7–12 Å (if the synthesis is carried out at 20 °C) or 12–20 Å (at 150 °C). The combined data on hydrogenation and deuteration of the dry catalyst and other material suggest that the clusters are stabilised by carbon-containing ligands (probably CH_3, CH_2, CH, and C≡). It was established using EXAFS and XANES§ that for every surface Os atom there were 0.39–0.64 C atoms and the Os–C distance was 2.11–2.19 Å.[110]

The LLCs of Os obtained by a chemical method have similar properties to the LLCs of Ni and Co that are synthesised by a vapour-phase method (Table 5). The main product of the hydrogenation of all of these LLCs is methane.

Osmium LLCs have considerably higher activity than that of both cellular osmium and osmium black. The latter even at 180 °C is appreciably less active than osmium LLCs at 100 °C. At the same time fine LLCs (10 Å) exhibit higher activity than the coarser forms.[105] Hydrocracking of alkanes and cycloalkanes in the

§ X-Ray Absorption Near-Edge Structure.

presence of osmium LLCs takes place effectively at 100–150 °C at an initial H_2 pressure of 50 atm. Under these conditions 1 mole of catalyst has converted hundreds of moles of hydrocarbon after 5–15 h, and the catalyst can be used repeatedly without loss of activity.

Table 5. Certain properties of LLCs of osmium,[105] nickel, and cobalt[96].

LLC	Overall composition	Specific surface $m^2 g^{-1}$	Particle size, Å
Os (20° C)*	$Os_{1,5}CH_{0-2}$	34	7–12
Os (150° C)*	$Os_{2,3-2,5}CH_{0-2}$	46	12–20
Ni**	$Ni_{2-9}CH_{2-3}$	37–40	25–36
Co**	Co_4CH_2	—	18–21

* Obtained by chemical synthesis.
** Obtained by gas-phase synthesis.

We can illustrate the composition of the products from the hydrocracking of certain alkanes and cycloalkanes (in moles per mole of converted RH) on osmium (LLCs) with a particle size of 10 Å (Os-I) and 20 Å (Os-II) (initial H_2 pressure 50 atm., reaction time 15 h):[105]

$$n\text{-}C_5H_{12} + H_2 \xrightarrow[89\%\ \text{conversion of RH}]{\text{Os-I, 120° C}} \underset{0.06}{C_4} + \underset{0.31}{C_3} + \underset{0.71}{C_2} + \underset{2.20}{C_1}$$

$$n\text{-}C_6H_{14} + H_2 \xrightarrow[60\%]{\text{Os-II, 150°}} \underset{0.10}{C_5} + \underset{0.04}{C_4} + \underset{0.11}{C_3} + \underset{0.50}{C_2} + \underset{3.29}{C_1}$$

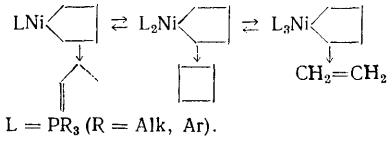
$$cyclo\text{-}C_5H_{10} + H_2 \xrightarrow[94\%]{\text{Os-II, 120° C}} \underset{0.88}{C_5} + \underset{0.04}{C_4} + \underset{0.07}{C_3} + \underset{0.09}{C_2} + \underset{0.22}{C_1}$$

$$cyclo\text{-}C_6H_{12} + H_2 \xrightarrow[89\%]{\text{Os-II, 150°C}} \underset{0.25}{C_6} + \underset{0.10}{C_5} + \underset{0.11}{C_4} + \underset{0.14}{C_3} + \underset{0.24}{C_2} + \underset{0.44}{C_1}$$

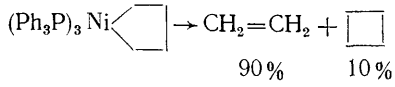
The conversion products of n-alkanes containing 5, 6, 8, or 18 carbon atoms (120–150 °C, 15 h) are represented by the complete range of lower alkanes from C_1 to C_{n-1}, with 80–97% of this being made up as a rule by methane, ethane, and propane. All of the products of cracking of n-alkanes have a linear structure. Cyclopentane and methylcyclopentane undergo hydrogenolysis to an appreciable extent at 100 °C. At 100–120 °C the hydrogenolysis of cyclopentane is effective and takes place selectivity to give n-pentane—a product of ring-opening. Selective opening of the ring also occurs in methylcyclopentane with cleavage of the least shielded bonds and formation of 2- and 3-methylpentanes.

3. Cleavage of C–C bonds in alkyl complexes of transition metals

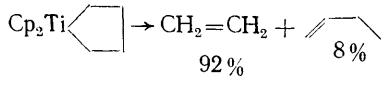
By assuming that C–C bonds are cleaved in intermediate alkyl complexes of transition metals in the gas phase (see Section II), it is possible effectively to elucidate the large quantity of experimental material on the reactions of alkanes and cycloalkanes with metal ions. The reactions of this type could be observed directly in solution. Thus, phosphine complexes of nickel metallocyclopentanes undergo reductive elimination, β-hydride elimination, and C–C cleavage.[111] The contribution of each of these processes depends on the coordination number of the Ni atom:



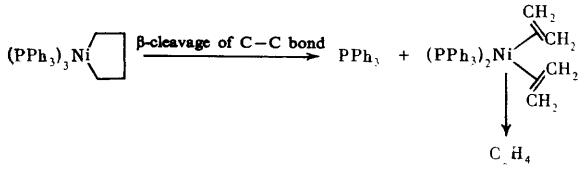
The Ni triphenylphosphine complex with the highest coordination number decomposes to form ethylene and cyclobutane;



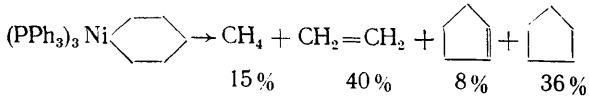
Ethylene is also formed as the main product from a titanocyclopentane complex:



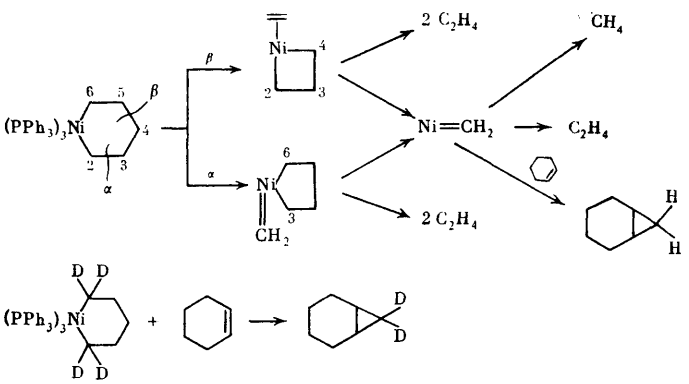
In both cases reaction takes place with the formation of intermediate bis(ethylene) complexes:[112]



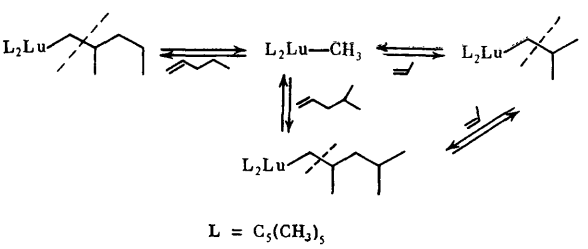
Cleavage of C–C bonds also occurred in Ni-cyclohexane:[111]



It was possible to demonstrate using complexes labelled with deuterium and with the use of traps (cyclohexene) that of the two possible routes for cleavage of C–C bonds α-elimination predominates.

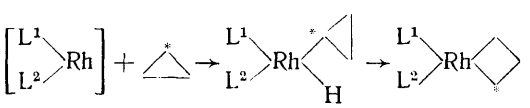


The β-cleavage [sic] of C–C bonds was observed in lutetium alkyl complexes.[113] In this case the cleavage and formation of C–C bonds are reversible:



These reactions, which take place in solution, represent the α- and β-cleavage of C–C bonds in alkyl complexes of transition metals. The proposed cleavage of C–C bonds according to scheme (2b) is thus confirmed experimentally.

Another form of cleavage of a C–C bond in a Rh cyclopropyl derivative has also been reported:[56]

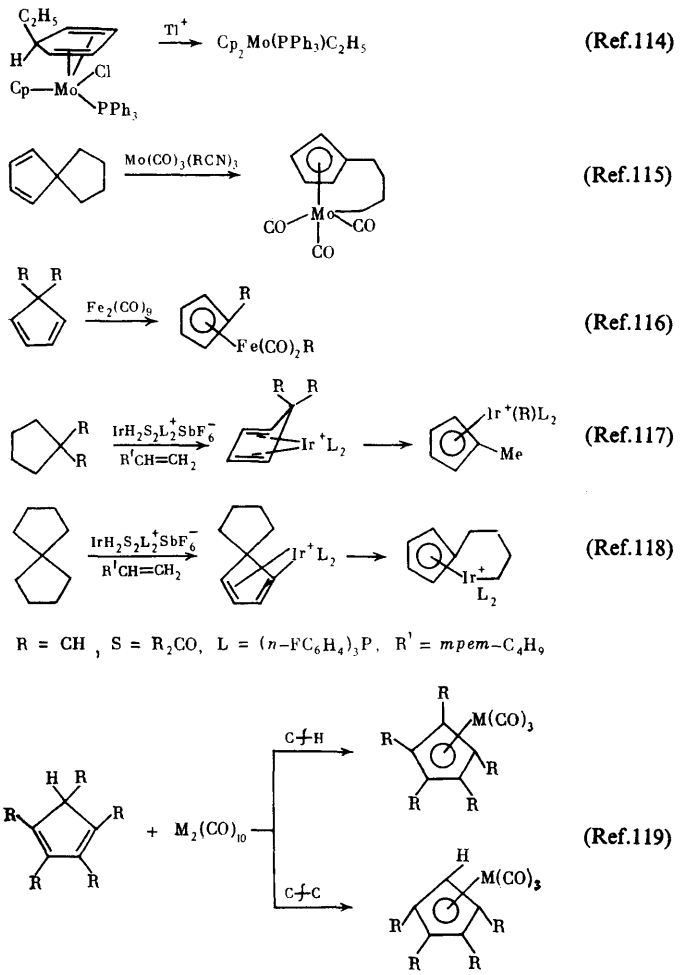


$L^1 = C_5(CH_3)_5$, $L^2 = P(CH_3)_3$.

4. Stoichiometric cleavage of C–C σ-bonds in hydrocarbons by transition metal complexes in solution

Because the cleavage of C–C bonds in alkanes by an attacking species is severely inhibited when steric hindrance increases, cases of the cleavage of single C–C bonds by transition metal complexes (even stoichiometric reactions) are extemely rare.

Examples of such reactions[114–119] are given below:



(Ref.114)

(Ref.115)

(Ref.116)

(Ref.117)

(Ref.118)

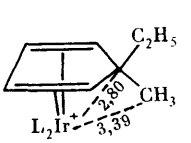
R = CH, S = R_2CO, L = $(n\text{-}FC_6H_4)_3P$, R' = *mpem*-C_4H_9

(Ref.119)

R = CH_3, when M = Mn
when M = Re the C–C bond is not cleaved.

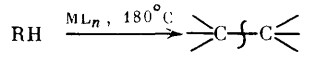
In these examples, as in other similar reactions, the driving force of the reaction is formation of the π-complex of a cyclopentadienyl aromatic system, which provides an additional energy gain of 25 kcal mol^{-1}.

It is interesting that an agostic C–C bond was first detected[18] in the complex



The reactions of alkanes and cycloalkanes with carbonyl and carbonylhydride clusters of osmium and iridium, "bare" clusters of bismuth, and other clusters[120] have also been studied. In all cases

cleavage of a C–C bond in RH ny ML_n at 180 °C was found not to occur



RH = n-C_6H_{14}, cyclo-C_5H_{10}, cyclo-C_5H_9R, cyclo-C_6H_{12} etc.,

ML_n = $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{12}$, Bi_4^{2-}, Bi_5^{3-} etc.

Muetterties came to the conclusion that the use of metal carbonyl clusters in reactions involving aliphatic hydrocarbons had no future potential.[120]

Table 6. Logarithms of equilibrium constants of the hydrocracking reactions of alkanes and cycloalkanes calculated from the data of Zhorov[45].

Reaction	K_p, at T, K		
	300	500	700
$C_2H_6+H_2 \rightleftarrows 2CH_4$	11.971	7.472	4.359
$C_6H_{14}+H_2 \rightleftarrows CH_4+C_5H_{12}$	10.267	6.399	4.634
$C_8H_{18}+H_2 \rightleftarrows C_2H_6+C_6H_{14}$	8.637	5.483	4.008
cyclo-$C_5H_{10}+H_2 \rightleftarrows C_5H_{12}$	7.157	3.374	1.341
cyclo-$C_6H_{12}+H_2 \rightleftarrows C_6H_{14}$	5.560	2.520	1.207

One report[121] states that the fragmentation of alkanes on exposure to γ-radiation is inhibited in the presence of $Co_2(CO)_8$ and at the same time there is the formation of $Co_3(CO)_9CR$ complexes, where R = CH_3, C_2H_5, and $CH(CH_3)_3$.

5. Catalytic cleavage of C–C bonds in alkanes and cycloalkanes by Ziegler-type systems

By taking into account the considerably steric shielding of the carbon atoms of a C–C bond, Akhrem et al.[122,123] formulated the requirements which must be satisfied by transition metal complexes that are capable of activating and cleaving such bonds:

a) the transition metal–carbon bond energy must be fairly high, which on the whole is typical for metals of the higher periods;

b) the degree of oxidation of the metal must be low, in other words, the metal must be capable of undergoing oxidative addition with ease;

c) the complex must have a low coordination number, which ensures the minimum steric hindrance in attack on the C–C bond;

d) ligands of a small size must be present on the metal atom, giving rise to the minimum steric hindrance (for example, H and CO).

Since conditions a–d will be conductive to activation of not only C–C bonds but also the more reactive C–H bonds, a shift in the equilibrium towards cleavage of C–C bonds according to scheme (5) could be assisted by inclusion into the reaction sphere of an additional reagent that reacts irreversible with the product of

Table 7. Hydrogenolysis of saturated hydrocarbons by systems based on rhenium carbonyl complexes and organoaluminium compounds[122].

RH	Catalyst[a]	RH : AlR_3 : Re_mL_n, mol	T, °C	Time, h	Conversion of RH		Products[b], mol per mol of reacted RH						
					%	mol per mol of Re_mL_n	C_1	C_2	C_3	C_4	C_5	C_6	C_7
C_6H_{14}	$Re_2(CO)_{10}$+A	100:6:1	180	3	77	77	2.81	0.53	0.28	0.17	0.16	—	—
C_6H_{14}	$Re_2(CO)_{10}$+A	100:6:1	150	3	16	16	1.39	0.28	0.15	0.21	0.57	—	—
C_8H_{18}	$Re_2(CO)_{10}$+A	100:6:1	180	5	65	65	1.56	0.30	0.16	0.16	0.18	0.18	0.22
C_8H_{18}	$Re_2(CO)_{10}$+B	190:10:1	180	15	48	91	2.00	0.46[c]	0.11	0.15	0.16	0.18	0.27
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:6:1	180	3	93	93	0.89	0.17	0.11	0.16	0.43	—	—
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:6:1	150	5	27	27	0.11	0.02	0.02	0.08	0.83	—	—
cyclo-C_5H_{10}	$Re_2(CO)_{10}$+A	100:9:1	180	15	94	94	0.61	0.12	0.08	0.14	0.46	—	—
cyclo-C_5H_{10}	$Re_4H_4(CO)_{12}$+A	200:12:1	180	15	84	168	0.98	0.16	0.13	0.07	0.58	—	—
cyclo-C_5H_9H*	$Re_4H_4(CO)_{12}$+A	200:12:1	180	15	82	164	0.94	0.10	0.04	0.07	0.19	0.50	—
cyclo-C_5H_9CH*	$Re_3H_3(CO)_{12}$+A	200:9:1	180	15	82	164	1.14	0.12	0.04	0.08	0.18	0.40	—
cyclo-C_6H_{12}	$Re_2(CO)_{10}$+A	100:6:1	180	3	22	22	0.85	0.11	0.05	0.09	0.22	0.30	—
cyclo-$C_{10}H_{20}$	$Re_2(CO)_{10}$+B	26:9:1	180	15	78	21	0.93	0.69[c]	0.06	0.06	0.05	0.04	0.04[d]

[a] A = iso-$(C_4H_9)_2AlH$, B = $(C_2H_5)_3Al$; [b] n-alkanes in every case except those marked with an asterisk; [c] $(C_2H_5)_3Al$ is a source of ethane in addition to the hydrocarbon; [d] C_8 (0.06), C_9 (0.14), and C_{10} (0.14) alkanes are also formed.

insertion of the metal complex into this bond. This type of reagent could be, for example, hydrogen:

$$\begin{array}{l} RCH_2CH_2{-}M{-}H \rightleftarrows RCH_2CH_3 + M \rightleftarrows RCH_2{-}M{-}CH_3 \\ \quad\downarrow H_2 \qquad\qquad\qquad\qquad\qquad\quad \downarrow H_2 \\ RCH_2{-}CH_3 + MH_2 \rightleftarrows M + H_2 + RC_2H_5\ RCH_3 + CH_4 + MH_2 \end{array} \quad (5)$$

It is significant also that the hydrocracking of saturated hydrocarbons is a thermodynamically favourable reaction (especially at lower temperatures, see Table 6).

Thus, the problem could be stated as follows: to study the possibility of cracking paraffins with H_2 on catalysts which meet conditions a–d.

An experiment with a number of compounds of different transition metals, mainly from Groups VI–VIII (carbonyls, carbonylhydrides, oxides, halides) and systems based on them, showed that the rhenium carbonyl and carbonylhydride complexes $Re_2(CO)_{10}$, $Re_3H_3(CO)_{12}$, $Re_4H_4(CO)_{12}$ in combination with organoaluminium compounds [$Al(C_2H_5)_3$, $(iso\text{-}C_4H_9)_2AlH$] are actually capable of activating C–C bonds in alkanes and cycloalkanes such as hexane, octane, cyclopentane, methylcyclopentane, cyclohexane, and others, and of catalysing their hydrogenolysis. The reactions occur in the respective hydrocarbon at 150–180 °C and at an initial H_2 pressure of 50 atm. At 180 °C after several hours a conversion close to quantitative is achieved, 1 mole of rhenium compound catalysing the conversion of hundreds of moles of hydrocarbons (Table 7).

The activity of the catalytic system depends to a considerable extent on the ratio of the components. Thus, the activity of the catalyst formed by interaction of $Re_2(CO)_{10}$ with $(iso\text{-}C_4H_9)_2AlH$ reaches a maximum at an atomic ratio of Al:Re = 3:1, with an increase of this ratio to 5.5:1 or a decrease to 1.5:1 leading to complete loss of activity.

The catalyst remaining after removal of the gaseous and liquid reaction products retains its activity and can cause subsequent batches of hydrocarbon to undergo hydrogenolysis. Organoaluminium compounds used separately, in the same way as rhenium complexes [$Re_2(CO)_{10}$, $Re_3H_3(CO)_{12}$, $Re_4H_4(CO)_{12}$, $CpRe(CO)_3$, Na_2ReH_9, Na_2ReH_9 + 18-crown-6] in the absence of organoaluminium compounds, do not have any hydrocracking activity towards alkanes (the reaction was carried out at 180 °C for 40 h.[122,123]

The main conversion products of n-alkanes at the early stages of the reaction are methane and linear hydrocarbons that contain one carbon atom less than in the original paraffin. Thus, in paraffins initially it is mainly the terminal CH_2-CH_3 bonds that are cleaved:

$$R{-}CH_2CH_3 + H_2 \xrightarrow{[Re]} RCH_3 + CH_4$$
$$\downarrow [Re]H_2$$
$$C_1 + C_2 + C_3 + \text{etc.}$$

The primary products of the hydrocracking of unsubstituted cycloalkanes are mainly linear alkanes with the same number of carbon atoms:

$$\underset{(CH_2)_n}{\bigcirc} + H_2 \xrightarrow{[Re]} H{-}(CH_2)_n{-}H$$
$$\downarrow [Re]H_2$$
$$C_1 + C_2 + C_3 + \ldots \text{ etc.}$$

Also, in the conversion products of alkanes and cycloalkanes lower hydrocarbons formed through subsequent multistage hydrogenolysis are always present. The proportion of these increases with an increase in conversion of the initial paraffin.

The catalysts are X-ray-amorphous insoluble pyrophoric powders containing Re (70%), Al (16%), C (4–9%), and H (1–2%). Hydrogenation of the catalysts with hydrogen at 100–200 °C or protolysis of them (using aqueous H_2SO_4 and CH_3COOH) leads to the isolation of C_1-C_5 alkanes (mainly C_4-C_5).

In the IR spectra of the catalysts two weak absorption bands occur at 1900 and 2025 cm^{-1}, which are attributed to Re–H bond vibrations. Analysis of the EXAFS spectra of the L_{III} region of rhenium showed that each rhenium atom is bound to 2–3 carbon atoms (Re–C distance is equal to 2.18 Å) and to 1–2 metal atoms (Re–M bond length is 2.6–2.7 Å, M = Re or Al). Thus, there is reason to believe that the catalytic systems obtained are organometallic rhenium hydride complexes.[122,123]

III. Novel superacid complexes — effective reagents and catalysts of low-temperature conversions of alkanes and cycloalkanes

The basicity of alkanes is low and therefore the rate of their conversions by even strong proton and aprotic acids at 20 °C is extremely slow.[43,44,124–126]

In our research into effective electrophilic catalysts for conversions of paraffins we turned our attention to the well-known Friedel–Crafts complexes $RCOX.AlX_3$.[127–132] At room temperature, in the same way as aluminium halides, they are inactive in reactions with alkanes.[124] However, a molecule of acid chloride contains two potentially nucleophilic sites X–C(R)=O and only one of these participates in the formation of an $RCOX.AlX_3$ complex. It has transpired that addition of a further mole of AlX_3 to traditional $RCOX.AlX_3$ systems causes a rapid change in their properties, converting complexes that are inert towards paraffins into very active reagents which have higher reactivity than not only Lewis acids and systems based on them but also, as a rule, the strongest proton superacids. Complexes of this type have been called aprotic organic superacids (AOS).[27,28,133]

1. Cracking of n-alkanes

$RCOX.2AlX_2$ complexes (R = CH_3, R = C_3H_7, X = Br, Cl) react extremely readily with C_5-C_{18} n-alkanes. In this case the latter undergo cracking to form the same principal products.[133,134]

$$C_nH_{2n+2} \xrightarrow{RCOX_2AlX_2} iso\text{-}C_4H_{10} + iso\text{-}C_5H_{12} + iso\text{-}C_4H_9COR +$$
$$+ iso\text{-}C_4H_7COR + \text{oligomer}$$

For alkanes with *n* ranging from 5 to 18 conversion reaches 100% after 30 min at 20 °C. The resulting oligomers are branched polyunsaturated hydrocarbons with a molecular weight of 700–800.

Isobutane, isopentane, and oligomeric products are also formed when alkanes are treated with other catalysts based on aluminium halides, but these reactions occur under quite different conditions.[124–126]

The rate of catalytic cracking of n-alkanes in solution is especially high. Thus, in the presence of the complex $CH_3COBr.2AlBr_3$ (VIII) in CH_2Br_2 the conversions of C_8-C_{18} alkanes to cracked products

at room temperature reach 70–85% after only 10 min, and in the presence of the complex $CH_3COX.2AlCl_3$ (IX) there is 57–70% conversion after 20 min (Figs. 1 and 2). Such high rates of cracking do not occur even when the most active proton superacid systems are used, so that AOS, and primarily (VIII), can be classed as one of the most active catalysts for the fragmentation of n-alkanes. However, the number of catalytic cycles does not exceed 15 and decreases with an increase in length of the carbon chain of the alkane. Cyclododecane behaves similarly towards $RCOX.2AlX_3$ complexes. At room temperature it is cracked very readily to give the same principal products.

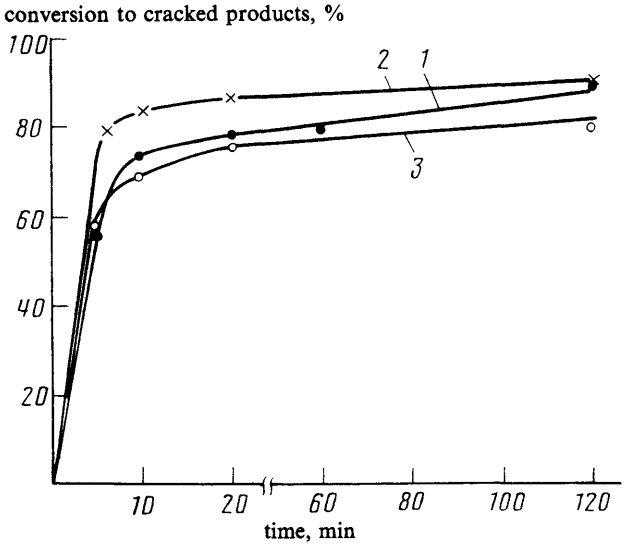
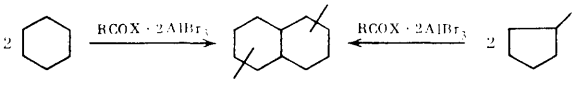


Figure 1. Cracking of C_8-C_{18} n-alkanes by the complex $CH_3COBr.2AlBr_3$ in CH_2Br_2 solution (20 °C, $[CH_3COBr]$ = 0.20 mol litre^{-1}) at the following ratios: *1*, $C_8H_{18}:CH_3COBr.2AlBr_3$ = 10:1; *2*, $C_{12}H_{26}:CH_3COBr.2AlBr_3$ = 5:1; *3*, $C_{18}H_{38}:CH_3COBr.2AlBr_3$ = 3:1.[133]

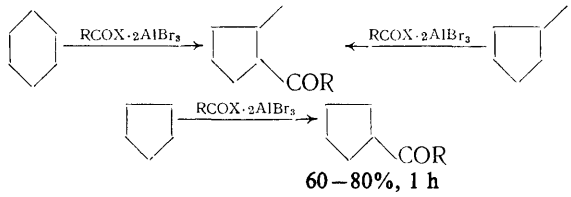
2. Oxidative combination and acylation of C_5-C_6 cycloalkanes

Aprotic organic superacids readily react with five- and six-membered cycloalkanes at 20 °C and lower temperatures.[27] The reactions occur by one of the three routes indicated below, and in certain cases the product yields are quite high. When there is excess cycloalkanes and in the absence of a solvent, cyclohexane or methylcyclopentane undergo oxidative coupling to form dimethyldecalins (mainly the 2,6- and 2,7-isomers):

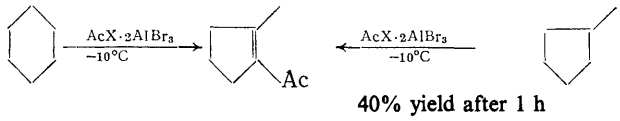


[the ratio of RH:(VIII) = 12:1; at 20 °C conversion is 100% after 1 h]. An increase in the concentration of electrophilic reagent suppresses this process and favours the acylation of cycloalkanes.

Acylation is the sole route for cyclopentane under all conditions.



On increasing further the concentration of acylating agent, namely, when it is in excess, when the temperature is lowered dehydroacylation of cyclohexane or methylcyclopentane can be achieved:



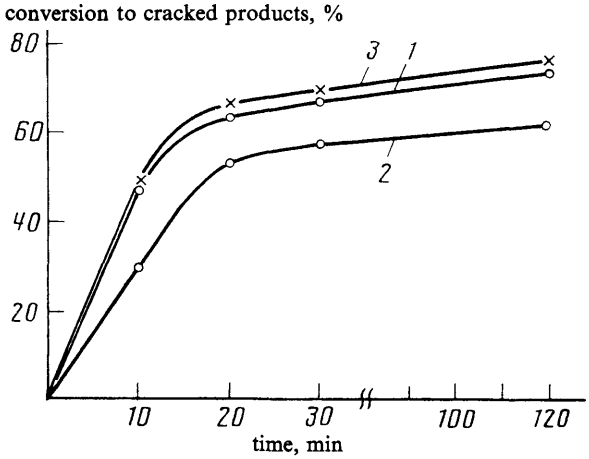


Figure 2. Cracking of C_8-C_{18} n-alkanes by the complex $CH_3COBr.2AlBr_3$ in CH_2Br_2 solution (20 °C, $[CH_3COBr]$ = 0.43 mol litre^{-1}) at the following ratios: *1*, $C_8H_{18}:CH_3COBr.2AlBr_3$ = 10:1; *2*, $C_{12}H_{26}:CH_3COBr.2AlBr_3$ = 5:1; *3*, $C_{18}H_{38}:CH_3COBr.2AlBr_3$ = 3:1.[133]

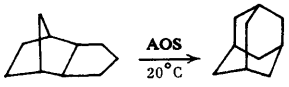
3. Isomerisation of C_4-C_6 n-alkanes to isoalkanes and saturated tricyclanes to adamantane and its homologues

Complex (VIII) catalyses the isomerisation of n-butane to isobutane at 20 °C.[134,135] At a ratio of n-C_4H_{10}:(VIII) = 11:1 the equilibrium concentration of isobutane is reached within 3 h, the selectivity of isomerisation being 90% (at the earlier stages it is about 100%). In terms of activity complex (VIII) has no equal amongst all of the known catalysts for the isomerisation of n-butane, including the strongest proton superacids. Complex (IX), although less active than (VIII), is also more active than known catalysts based on AlX_3.

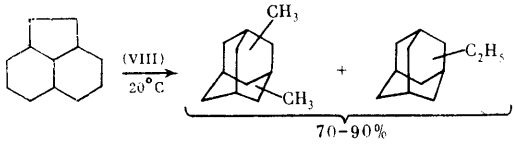
In contrast to higher alkanes, the cracking of n-pentane and n-hexane by aprotic organic superacids in CH_2Br_2 has an induction period during which there is a rapid and selective isomerisation of

n-pentane to 2-methylbutane, while n-hexane is isomerised to a mixture of all four possible isohexanes.[136] The yields of isoalkanes in the presence of (VIII) and (IX) reach 55–75% after 15–60 min and 50–60% after 90–120 min respectively with an almost complete absence of fragmentation.

Aprotic organic superacids effectively catalyse the synthesis of adamantane and its derivatives from isomeric saturated tricyclanes. Thus, they initiate the isomerisation of trimethylenenorbornane to adamantane:[13]

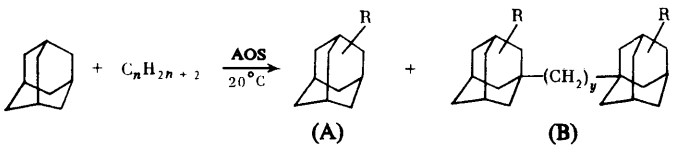


Complex (VIII) is also the most effective of all the known catalysts for isomerisation of perhydroacenaphthene or its isomeric $C_{12}H_{20}$ tricyclanes to a mixture of dimethyl- and ethyl-adamantanes in which 1-ethyladamantane predominates.[137] At 20 °C the initial hydrocarbons have already undergone quantitative conversion after only 5–12 min.



4. Alkylation of adamantane with n-alkanes

Alkylation of adamantane (AdH) with n-alkanes is a promising method for obtaining alkyladamantanes (AdAlk), whose use in the form of individual compounds or mixtures is of considerable interest.[138] The known methods for the alkylation of AdH are not very effective and are not at all suitable for the synthesis of higher AdAlk.[138–141] It was recently found that n-alkanes very readily alkylate AdH in the presence of AOS at 20 °C.[134,142] When stoichiometric quantities of complexes are used the conversion of AdH has reached 90–100% after 20 min. Under catalytic conditions [(AdH : (VIII)] = 8 : 1] the reactions with C_8–C_{18} alkanes are complete within 3 h, the total yield of AdAlk being 110–220 wt.% based on adamantane. The reaction products mainly comprise two types of compound—(A), which has a single adamantane ring with a total number of carbon atoms m ranging from 11 to 33, and (B) from m ranging from 23 to 51.



(A) (B)

$n = 6–18$; R—one or more groups

In addition to the high rates of alkylation and yields of AdAlk, the possibility of regulating the composition of the resulting mixture with respect to the content of higher and lower homologues and the ratio of mono- to poly-AdAlk should also be included amongst the merits of this method.

5. Functionalisation of alkanes and cycloalkanes

The single-state functionalisation of paraffins is a promising method for the direct synthesis of organic compounds based on readily available hydrocarbon feedstocks.[14,15] Complexes (VIII) and (IX) effectively catalyse the ionic bromination of C_4–C_7 n-alkanes, cyclopentane, cyclohexane, trimethylenenorbornane, and other compounds at −20 and +20 °C to give exclusively or principally monobromides in high yield—55–370 wt.% based on complex (IX) and 110–910 wt.% based on (VIII).[143]

$$RH + Br_2 \rightarrow RBr + HBr.$$

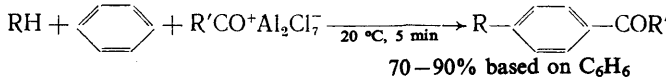
The maximum yield of RBr based on Br_2 is 75%, bromination is not complicated by fragmentation. The monobromides that are formed from alkanes comprise mixtures of isomers; pure alkylcyclobromides are formed from cyclohexane and cyclopentane, which may be of interest synthetically. Until the study of Akhrem et al. was published,[143] the ionic bromination of n-alkanes had not been reported, while for simple iso- and cyclo-alkanes it was ineffective.[144,145]

The considerable potentialities of AOS are indicated by other reactions for the functionalisation of alkanes which take place in their presence. One of these is the single-stage synthesis of organosulphur compounds from alkanes (or cycloalkanes) and elemental sulphur:

$$RH + S + R'CO^+Al_2X_7^- \xrightarrow[0-20\ ^\circ C]{} \underset{25-60\,\%}{\text{sec-RSCOR'}}$$

$RH = C_3H_8$, n-C_4H_{10}, n-C_5H_{12}, cyclo-C_5H_{10}, cyclo-C_6H_{12};
$R' = CH_3$, C_3H_7, Ph.

Another example is the alkylation and acylation of benzene in a single stage to form alkylated aromatic ketones. Isoalkanes and cycloalkanes with a tertiary carbon atom act as alkylating agents:



70–90% based on C_6H_6

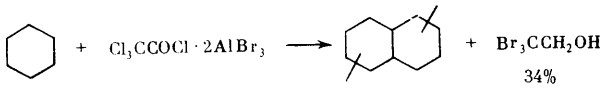
RH = iso-C_4H_{10}, iso-C_5H_{12}, iso-C_6H_{14}, cyclo-$C_6H_{11}CH_3$.

6. Saturated hydrocarbons as reducing agents of acyl halides in the presence of $AlBr_3$

In the reactions between $RCOX.2AlX_3$ complexes and saturated hydrocarbons the latter act as reducing agents, initially converting the acyl halides which form part of these complexes into aldehydes:

$$RH + R'COX \cdot 2\,AlX_3 \rightarrow R^+ \ldots\ Al_2X_7^- + R'COH.$$

Examples of the reduction of acyl halides by saturated hydrocarbons in the presence of aluminium halides (20 °C, 1 h) are given below. In certain cases halogen exchange occurs in parallel with reduction.[134,146]



$$AdH + PhCOCl \cdot 2\,AlBr_3 \rightarrow \underset{70\,\%}{1\text{-Br-Ad}} + \underset{82\,\%}{PhCHO} + 2\,AlBr_3,$$

$$ClCO(CH_2)_3COCl + RH \xrightarrow[2)\ H_2O/H^+]{1)\ AlBr_3} \underset{40\,\%}{BrCH_2CH(Br)CH_2CH_2COH}.$$

7. Nature of the superacidic properties of $RCOX.2AlX_3$ complexes

With the aim of trying to account for the unusually high activity of $RCOX.2AlX_3$ complexes, which clearly distinguishes them from the well established $RCOX.AlX_3$ complexes, the structure of $RCOX.2AlX_3$ complexes (VIII) and (IX) and $RCOX.AlX_3$ complexes (X) were studied in the solid state and solution using NQR, ^1H, ^{13}C, ^{27}Al, and ^{17}O NMR and vibrational spectroscopy.[134,147,148] It was established that in the solid state they all comprise ionic acylium salts which differ only according to the structure of the anion: $RCO^+Al_2X_7^-$ for (VIII) and $RCO^+AlX_4^-$ for (X). In solution (CH_2X_2) (VIII) and (IX) consist of equilibrium mixtures of acylium salts $RCO^+Al_2X_7^-$ and donor-acceptor complexes $RC(X)=O\rightarrow Al_2X_6$, while complexes (X) exist solely in the form of coordination complexes $RC(X)=O\rightarrow AlX_3$:

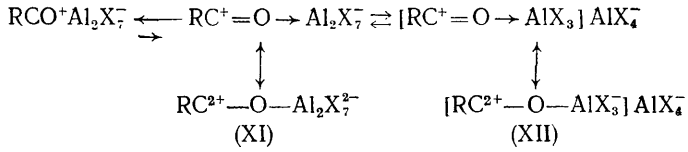
$$RCOX + 2\,AlX_3 \rightarrow RC(X)=O\rightarrow Al_2X_6 \rightleftarrows RCO^+Al_2X_7^-,$$
in CH_2X_2 solution

$$RCOX + AlX_3 \rightarrow RC(X)=O\rightarrow AlX_3 \rightleftarrows RCO^+AlX_4^-.$$

In order to answer the question as to whether any acylium salt being generated in solution is capable of reacting at 20 °C with paraffins or whether the activity of the $RCO^+Al_2X_7^-$ acylium complexes is due to the presence of the dimeric anion forming part of its structure, it was necessary to synthesise two acylium salts that differed only according to the anion (one with a monomeric anion and the other with a dimeric anion) and to compare their reactivity. This problem was resolved in the case of two pairs of complexes: 1) $AcF.SbF_5$ and $AcF.2SbF_5$ (forming the acylium salts $Ac^+ScF_6^-$ and $Ac^+Sb_2F_{11}^-$ respectively in SO_2 solution); and 2) $MesCOBr.AlBr_3$ and $MesCOBr.2AlBr_3$ [which exist in CH_2Br_2 exclusively in the form of the ionic salts $MesCO^+AlBr_4^-$ and $MesCO^+Al_2Br_7^-$ respectively, Mes = 2,4,6-$(CH_3)_3C_6H_2$].[134,149] Only acylium salts containing a dimeric anion exhibited superacidic properties in reactions with alkanes and cycloalkanes while acylium salts with a monomeric anion were inactive at 20 °C.

Is it possible to relate such a marked difference in activity of $RCO^+AlBr_4^-$ and $RCO^+Al_2Br_7^-$ salts with the different degree of electrophilicity of the acylium cations in them? On the one hand it is true that the nucleophilicity of the $AlBr_4^-$ anion is greater than that of the $Al_2Br_7^-$ anion.[150] On the other hand, a substantial difference in the reactivity of these salts should be accompanied by an appreciable difference in the ^{13}C NMR spectra, which are very sensitive to a change in electron density. However, the ^{13}C NMR spectra of these salts are virtually identical, which raises doubts about the theory of the different electrophilicity of the acylium cations bound to monomeric and dimeric anions.[134,149]

The idea that in solutions of $RCO^+Al_2X_7^-$ complexes an equilibrium that is very much shifted to the left exists between the acylium salts and more electrophilic complexes in which the RCO^+ cations are coordinated with a Lewis acid deserves serious consideration.[149] It is clear that this type of coordination should lead to the formation of more electrophilic cations, which in the limiting case can be represented as acylium dications with the structures (XI) or (XII):



The latter probably exist in very low concentrations and cannot be identified by conventional spectroscopic methods, but it is they that are very likely to be responsible for the unusually high activity of $RCO.2AlX_3$ complexes—aprotic organic superacids.[149]

The idea that acyl halide complexes with two moles of AlX_3 of the type $RC(X\rightarrow AlX_3)=O\rightarrow AlX_3$ played an important part in the acylation of arenes was first suggested in 1962.[151] A report was recently published[152] stating that it was possible to detect the formation of the complex $CH_3C(Cl\rightarrow AlCl_3)=O\rightarrow AlCl_3$ in the system $AcCl-n$ moles of $AlCl_3$ in SO_2 solution using NMR. However, the interpretation of the spectroscopic data made in this study is at variance with that generally accepted and appears to be erroneous. Thus is has so far not been possible to observe complexes of the type (XI) or (XII) experimentally.

There would appear to be a direct analogy between complexes of the type (XI) or (XII) and the protosolvated form of the acylium cation (XIII), which was postulated by Olah et al.[153] as being formed in a proton superacid. Olah et al. assume that it is the protosolvated acylium cations (XIII) which are responsible for the transfer of a hydride ion from isobutane to the acylium cation that occurs in a proton superacid. In an aprotic solvent (SO_2) where ion (XIII) cannot be formed, the transfer of hydride ion from isobutane does not occur:

$$CH_3C^+=O + H^+ \rightarrow \underset{\text{(XIII)}}{CH_3C^+=O^+H},$$

$$\text{iso-}RH + CH_3C^+=O^+H \rightarrow \text{iso-}R^+ + CH_3CH=O^+H,$$

$$\text{iso-}RH + CH_3C^+=O \xrightarrow{SO_2} \text{iso-}R^+ + CH_3CHO.$$

Proton solvation of cations which contain atoms with a free electron pair is quite a general phenomenon.[154–156] The formation of the dications H_4O^{2+} and H_4S^{2+} was recently reported.[155,156]

In mentioning the similarity between postulated complexes of the type (XI) or (XII) and the protosolvated form of the acetylium cation (XIII), we should draw attention to the considerably greater activity of the former. Complexes of the type (XIII) are inert towards n-alkanes,[157,158] whereas $RCOX.2AlX_3$ systems react with them at high rates. Therefore, the possible presence of small quantities of protonated compounds in $RCOX.2AlX_3$ systems (from

traces of water or the destruction of complexes) cannot be the reason for the high activity of these systems, i.e., they should actually be regarded as aprotic organic superacids.

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During the last 20 years the term "paraffins" has progressively lost its original meaning.

Metal-complex activation of inert σ-bonds (H—H, Si—H, Si—C, C—H) has provided a powerful stimulus for the development of the chemistry of inert molecules. At the present time there is the problem of the metal-complex activity of C—C bonds in alkanes. Although up to the present time there has been no single example of the cleavage of such bonds on well-characterised transition metal complexes, the data given in this review in conjunction with the preliminary results obtained on Ziegler-type systems would appear to suggest the possible occurrence of such reactions.

The development of "low-temperature" reagents and catalysts for the conversion of unactivated saturated hydrocarbons seems to indicate the considerable unexhausted possibilities in this area. There is future potential in the development of chemical methods for the synthesis of active catalysts for the cleavage of C—C bonds based on low-ligand clusters, and primarily heteronuclear LLCs on supports which retain all the advantages of Klabunde systems obtained by vapour-phase synthesis.

On the other hand, the availability of $RCOX.2AlX_3$ systems, the ease in working with them, and the possibility of carrying out a wide range of selective conversions of alkanes and cycloalkanes at room temperature in their presence give grounds for regarding the discovery of superacids of this type as a fundamentally new stage in the low-temperature chemistry of paraffins.

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