Reviews

Novel superelectrophilic complexes for low-temperature alkane and cycloalkane transformations*

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The results of studies on the elaboration of new superelectrophilic complexes and their use for efficient low-temperature transformations of alkanes and cycloalkanes, such as cracking, isomerization, alkylation, and single-step functionalization (acylation, carbonylation, ionic monobromination, sulfurization, thioacylation, *etc.*), are summarized. The activity of new aprotic organic and inorganic superacids is compared to that of known electrophilic systems, including protic superacids. The reasons for the superelectrophilic properties of new active systems are considered.

Key words: aluminum halides, superelectrophiles; transformations of alkanes and cycloalkanes.

Introduction

The activation of alkanes and their involvement in selective transformations is one of the fundamental problems of organic chemistry. On the one hand, alkanes and cycloalkanes, which are the main components of oil and natural gas, still remain the most promising starting compounds for organic synthesis. On the other hand, industrial processing of hydrocarbon raw materials requires perfecting due to the continuous depletion of world oil reserves, which are not limitless.

In early 70s, the discovery of principally new types of systems which can activate alkanes under mild conditions dispelled the myth that compounds belonging to this class are absolutely inert under ordinary conditions and revealed new prospects for the elaboration of the low-temperature chemistry of alkanes. At about the same time, the first transition metal complexes activating alkane C—H bonds in solutions under mild conditions were described,[1] and activation of alkanes with protic superacids was discovered.[2,3] The reactivity of the weakly solvated proton turned out to be so high that efficient transformations of non-activated alkanes under mild conditions in the medium of protic superacids became possible for the first time.[4,5]

Among the most significant achievements of organic chemistry are Olah's concept of the electrophilic activation of σ-bonds, based on the formation of a two-electron three-centered transition state, and the discovery and study of long-lived intermediates of electrophilic reactions, *viz.*, carbenium alkyl ions, which have previously been only postulated as reaction intermediates,

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* This review, which was initiated by Mark Efimovich Vol'pin, is a tribute of our memory and gratitude to him.

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and carbonium ions, *i.e.*, compounds of hypervalent carbon.[4,6] The nontraditional approaches gave a powerful impetus to the development of this field, to organic, organometallic, and coordination chemistry, as well as to catalysis in general. Over a quarter of the century, a huge number of complexes of transition metals, lanthanides, and actinides have been reported[7—10] (including metalloenzymes[11]) which activate C—H bonds in alkanes; the mechanisms of reactions of alkanes on a metallic center in solutions have been described; examples of stoichiometric and catalytic reactions have been reported.[7—12] During this period, studies of gas-phase reactions of alkanes and cycloalkanes with metal ions,[13—15] metals,[16,17] and small metal clusters[18—20] were developing successfully.

In parallel with the development of new fields, a renaissance of traditional directions occurred: considerable success was achieved in studies of alkane reactions on heterogeneous catalysts[21—25] and transformations involving radical reagents.[26,27] During the recent 20—25 years, the number of publications dealing with alkane reactions redoubled each three to four years.[8] Award of the 1994 Nobel prize in chemistry to G. Olah for fundamental studies in alkane chemistry is an indication of the current interest in this field. Although the possibility of direct functionalization of alkanes and cycloalkanes exists, and a number of examples of selective stoichiometric and even catalytic reactions are available, only a small amount of saturated hydrocarbons is used in organic synthesis even now. Alkanes and cycloalkanes still offer huge unrealized resources for organic synthesis.

It should be noted that, while the discovery of homogeneous activation by complexes of transition metals initiated an avalanche-like increase in the number of activating metal complexes, superacids active in alkane reactions have long been represented exclusively by proton-containing systems, which differed in their position on the Hammett acidity scale,[4] and some salt systems.[28—34] Almost ten years had passed before a new type of superacids, *viz.*, aprotic organic superacids, which have extremely high activity in initiating transformations of alkanes and cycloalkanes, was discovered. Surprisingly, these were not some exotic systems but complexes of acyl halides with aluminum halides known in organic chemistry for over a century. The discovery of the acylation of aromatic hydrocarbons in the presence of aluminum halides by Friedel and Crafts[35] was the beginning of an intense development of organic synthesis. However, the application of acyl halide—aluminum halide complexes was long limited to aromatic and unsaturated compounds only.[36] Their application for reactions with saturated hydrocarbons has not met with any considerable success. The first studies into the reactions of alkanes and cycloalkanes with Friedel—Crafts complexes started as early as in the 30s[37—40] (a description of these works can be found in monographs[36] and reviews[41,42]).

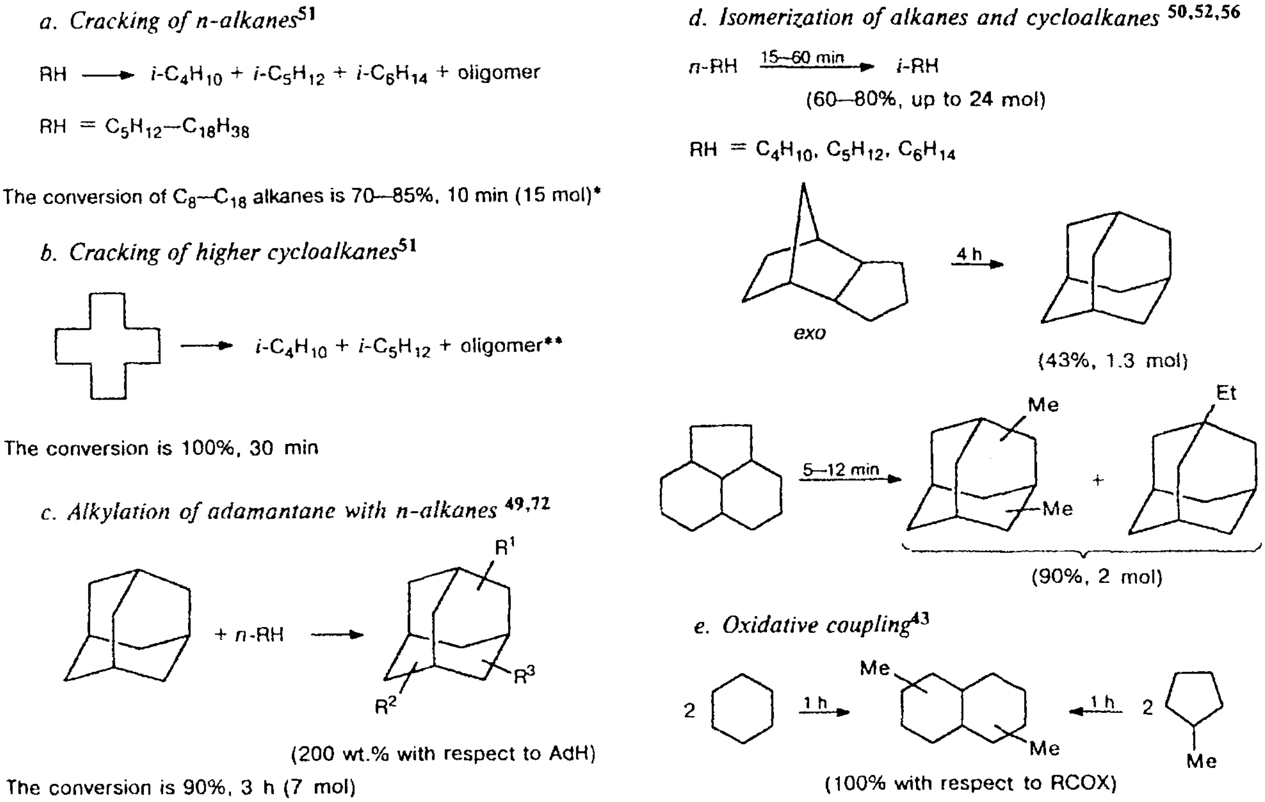
$RCOX \cdot 2AlX_3$ complexes as a new type of aprotic superacids

In the early 80s, the authors of the present review found that the addition of 1 mol of an aluminum halide to classical Friedel—Crafts equimolecular complexes $RCOX \cdot AlX_3$ abruptly changed their properties. The complexes, which are inactive toward alkanes, are transformed into highly-active systems, whose activity exceeds that of all hitherto known protic and aprotic acids, generally including even the strongest protic superacids. Because of the unusually high activity in reactions with alkanes, $RCOX \cdot 2AlX_3$ systems were named aprotic organic superacids.[42,43]

A strong effect of an excess of $AlBr_3$ on the reactivity of the $PhCOBr \cdot nAlBr_3$ complexes in the benzoylation of arenes was observed back in 1959.[44] On passing from $PhCOBr \cdot AlBr_3$ to $PhCOBr \cdot 2AlBr_3$, the benzoylation rate constant increased by a factor of 320. A further increase in the amount of $AlBr_3$ increased the rate only slightly. The authors of the work cited[44] could not explain the phenomenon they observed and only stated that the electrophilicity of $PhCOBr \cdot nAlBr_3$ at $n = 2$ was higher than that at $n = 1$. A short time later, an assumption was made on the important role of the $AlX_3 \leftarrow X(R)C{=}O \rightarrow AlX_3$ complexes, which are formed with participation of two Lewis acid molecules and one acyl halide molecule, in arene acylation.[45] This hypothesis acquired an experimental confirmation in 1971 in a kinetic study.[46] On the contrary, a different conclusion was made in another study[47] also dealing with benzene acylation with the $RCOX \cdot AlCl_3$ complex. It should be noted that studies on the enhanced reactivity of complexes of acyl halides with an excess of aluminum halides did not acquire due importance in the literature, and the superelectrophilic properties of $RCOX \cdot 2AlX_3$ systems toward one of the most inert class of organic compounds, alkanes, were not discovered until the 80s. Reactions of alkanes and cycloalkanes initiated by aprotic organic superacids $RCOX \cdot 2AlX_3$ have been considered in a number of papers.[42,43,48—62] Therefore, we will just briefly summarize the types of reactions studied. Tables 1—3 compare the activity of $RCOX \cdot 2AlX_3$ complexes with that of other previously known strong electrophilic systems (E) in some reactions of alkanes. Scheme 1 presents transformations of alkanes or cycloalkanes at 20 °C, in which $RCOX \cdot 2AlX_3$ systems act as initiators (*b*, *e*) or as catalysts (*a*, *c*, *d*).

It is noteworthy that the high activity of aprotic organic superacids in the alkylation of adamantane with alkanes at 20 °C (see Table 3) makes it possible to synthesize mixtures rich in higher alkyladamantanes.[61c,d,72] The latter are not formed in reactions which occur at high temperatures or on prolonged heating of reaction mixtures in the presence of an electrophile at 60 °C due to secondary dealkylation processes. In addition to high rates and high yields, the advantages of the

Scheme 1



a. Cracking of n-alkanes[51]

$RH \longrightarrow i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + i\text{-}C_6H_{14}$ + oligomer

$RH = C_5H_{12}$—$C_{18}H_{38}$

The conversion of C_8—C_{18} alkanes is 70—85%, 10 min (15 mol)*

b. Cracking of higher cycloalkanes[51]

$\longrightarrow i\text{-}C_4H_{10} + i\text{-}C_5H_{12}$ + oligomer**

The conversion is 100%, 30 min

c. Alkylation of adamantane with n-alkanes[49,72]

(200 wt.% with respect to AdH)

The conversion is 90%, 3 h (7 mol)

d. Isomerization of alkanes and cycloalkanes[50,52,56]

$n\text{-}RH \xrightarrow{15-60\ \text{min}} i\text{-}RH$

(60—80%, up to 24 mol)

$RH = C_4H_{10}, C_5H_{12}, C_6H_{14}$

(43%, 1.3 mol)

(90%, 2 mol)

e. Oxidative coupling[43]

(100% with respect to RCOX)

method involving aprotic organic superacids include the possibility of controlling the composition of the alkyladamantane mixture by changing the content of higher and lower homologs and the ratio of mono- and polyalkyladamantanes.[61c,d,72] The properties of the resulting alkyladamantane mixtures (low glass transition temperatures, high densities, chemical and thermal stability, good lubricating characteristics)[61,72] give reasons to hope that they will find practical application in the future.

Scheme 2 presents reactions of alkane and cycloalkane functionalization with $RCOX \cdot 2AlX_3$ complexes as sources of an acyl group or a halogen atom. The acylation of linear alkanes and cyclopentane in satisfactory and good yields and the transformation of trimethylenenorbornane to 1-bromoadamantane in one step have been carried out for the first time. The reactions occur at 20 °C in 1—2 h.

In reactions of the latter type (Scheme 3), functionalizations require a third component which is added to the reaction mixtures (either as the single source of the functional group or in parallel with inclusion of the acylating group of $RCOX \cdot 2AlX_3$ complexes in the molecule formed). Of the transformations shown in Scheme 3, carbonylation (*d*) has previously been carried out in the HF—SbF_5 system.[76] However, in contrast to a reaction occurring with an excess of a protic superacid, the carbonylation initiated by $RCOX \cdot 2AlX_3$ [60] occurs without a solvent or in CH_2X_2 and is completed within a considerably shorter time. Ionic bromination of *n*-alkanes was not reported before 1988.[53] Reactions of isoalkanes and cyclohexane with Br_2 in the presence of $AgSbF_6$ resulted in small yields of monobromides (2—27% with respect to $AgSbF_6$) and were complicated by polybromination.[77] Reactions of isoalkanes with Br_2 in the HSO_3F—SbF_5 system were also inefficient and nonselective.[78]

The first examples of benzene alkylation with isoalkanes and cycloalkanes on treatment with the $AlCl_3$—$CuCl_2$ salt mixture were reported in 1973.[28] The reaction of benzene with isopentane gave a mixture of pentylbenzenes in 20% overall yield with respect to the starting copper salt. Additionally, ethylbenzene, isopropylbenzene, 1,2-diphenylethane, and *p*-polyphenylene were formed as side products. The reaction of cyclohexane with benzene resulted in *p*-polyphenylene as the main product (60%), while alkylation products were present in trace amounts only. The addition of isopentane increased the yield of cyclohexylbenzene to 20%. We

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* Here and below, the number of moles of the product (indicated in parentheses) is given per one mole of the superelectrophile.

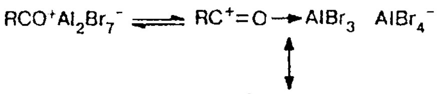
** Along with Bu^iAc and $C_8H_{15}Ac$ (1 : 1).

ied in the solid state and in solutions using ^{81}Br NQR, ^{1}H, ^{13}C, ^{27}Al, and ^{17}O NMR, IR, and Raman spectroscopy.[93,94] It was found that in the solid state, both types of complexes are ionic acylium salts differing only in anion composition, *viz.*, $RCO^+Al_2X_7^-$ in the case of $RCOX \cdot 2AlX_3$ and $RCO^+AlX_4^-$ for $RCOX \cdot AlX_3$. In solutions in CH_2X_2, the former are equilibrium mixtures of acylium salts $RCO^+Al_2X_7^-$ and donor-acceptor complexes $RC(Cl)=O \rightarrow Al_2X_6$, while the latter are exclusively donor-acceptor complexes $RC(Cl)=O \rightarrow AlX_3$.

$$RCOX + 2\,AlX_3 \xrightarrow{CH_2X_2} RC(X)=O \rightarrow Al_2X_6 \rightleftharpoons RCO^+\,Al_2X_7^-$$

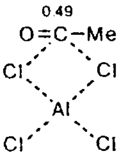
$$RCOX + AlX_3 \xrightarrow{CH_2X_2} RC(X)=O \rightarrow AlX_3 \cancel{\rightleftharpoons} RCO^+\,AlX_4^-$$

The difference in the activity of $RCOX \cdot 2AlX_3$ and $RCOX \cdot AlX_3$ systems can be explained by the assumption that it is only systems with an excess of an aluminum halide that can generate acylium ions in solution. It remained unclear whether any acylium salt existing in solution can react with alkanes under mild conditions, or the activity of $RCOX \cdot 2AlX_3$ complexes originates from the presence of dimeric ions $Al_2X_7^-$ in them. In order to answer this question, it was necessary to synthesize two acylium salts differing only in the anion structure (monomeric or dimeric) and to compare their activity toward saturated hydrocarbons. Since $RCO^+AlX_4^-$ salts (R = Alk) could not be generated in low-polarity solvents, we resorted to complexes of mesitoyl bromide and $AlBr_3$: $MstCOBr \cdot AlBr_3$ and $MstCOBr \cdot 2AlBr_3$ (Mst = 2,4,6-$Me_3C_6H_2$). In this case, we were able to obtain two different individual mesitoylium salts as solutions in CH_2Br_2:[95] one with monomeric $AlBr_4^-$ anion and another with dimeric $Al_2Br_7^-$ anion. This unique case of the existence of acylium tetrabromoaluminate in a low-polarity solution is explained by steric hindrance created by the substituents at positions 2 and 6 of the aromatic ring, which impedes the formation of donor-acceptor complexes. The addition of an alkane to solutions of both the $MstCO^+AlBr_4^-$ and $MstCO^+Al_2Br_7^-$ salts resulted in homogeneous solutions, in which the structure of the original salt was maintained. This circumstance made it possible to make a correct comparison of reactivity of the $MstCO^+AlBr_4^-$ and $MstCO^+Al_2Br_7^-$ salts toward saturated hydrocarbons. The difference in activity of the mesitoylium salts in the cracking of *n*-octane and *n*-dodecane and in the isomerization of trimethylenenorbornane to adamantane was as great as that in the case of the $MeCOX \cdot AlX_3$ and $MeCOX \cdot 2AlX_3$ systems. Mesitoylium tetrabromoaluminate was inert, whereas the corresponding heptabromodialuminate initiated the cracking of alkanes and the isomerization of trimethylenenorbornane. A similar result was observed for the $AcF \cdot SbF_5$ and $AcF \cdot 2SbF_5$ complexes, which form two different acetylium salts when dissolved in SO_2, *i.e.*, $Ac^+SbF_6^-$ and $Ac^+Sb_2F_{11}^-$, respectively.[95] However, the ^{1}H and ^{13}C NMR spectra of the $MstCO^+AlBr_4^-$ and $MstCO^+Al_2Br_7^-$ salts with such a different activity, as well as those of the other pair, $Ac^+SbF_6^-$ and $Ac^+Sb_2F_{11}^-$, were found to be virtually identical. This gave us a reason to assume that the acylium salts themselves are not responsible for the superelectrophilic properties of $RCOX \cdot 2AlX_3$ systems. We assumed that active systems exist in equilibrium, which is strongly shifted to the left, between acylium salts and more electrophilic complexes, in which an acylium cation (RCO^+) is coordinated to a Lewis acid.[42,62] Obviously, this coordination should lead to the formation of more electrophilic complexes, which in the limiting case can be represented as dicationic complexes:



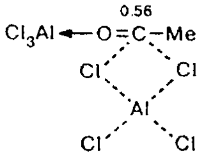
$$RCO^+Al_2Br_7^- \rightleftharpoons RC^+=O \rightarrow AlBr_3\;\; AlBr_4^- \;\longleftrightarrow\; [RCO^{2+}\text{—}OAlBr_3^-]AlBr_4^-$$

Probably, such highly electrophilic cations are present in very small concentrations and cannot therefore be detected experimentally. Semiempirical quantum-chemical calculations of $MeCOCl \cdot nAlCl_3$ complexes (n = 1—3) are consistent with this conclusion.[96] MNDO calculations showed that in systems containing an excess of $AlCl_3$ (n = 2 or 3), the formation of complexes **2** and **3**, which have a larger positive charge on the C atom of the carbonyl group than in the acetylium cation **1**, is possible. Complex **2** is analogous to the postulated acylium cation coordinated to AlX_3. Complex **3** can be represented as dicationic complex $Cl_2Al—O—C^{2+}Me(AlCl_4^-)_2$.



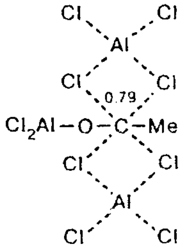
1

(H_f = −185 kcal mol^{-1})



2

(H_f = −322 kcal mol^{-1})



3

(H_f = −423 kcal mol^{-1})

Importantly, the formation of complex **2** from MeCOCl and the Al_2Cl_6 dimer is accompanied by a small release of energy. Conversely, the formation of complex **3** from MeCOCl and Al_2Cl_6 occurs with energy consumption.

$$MeCOCl + Al_2Cl_6 \longrightarrow \underset{\mathbf{2}}{[MeCO \rightarrow AlCl_3]^+AlCl_4^-}$$

(ΔH = −4.4 kcal mol^{-1})

$$\mathrm{MeCOCl + 3/2\,Al_2Cl_6 \longrightarrow \underset{\mathbf{3}}{[MeC^{2+}OAlCl_2]\,(AlCl_4^-)_2}}$$

(ΔH = 75.4 kcal mol^{-1})

$$\mathrm{MeCOCl + 3\,AlCl_3 \longrightarrow \underset{\mathbf{3}}{[MeC^{2+}OAlCl_2]\,(AlCl_4^-)_2}}$$

(ΔH = −2.3 kcal mol^{-1})

The conclusion on the important role of dicationic complexes in reactions of alkanes with $RCOX \cdot 2AlX_3$ systems is in agreement with the data[71] on the transfer of a hydride ion to the acetylium cation in the HF—BF_3 system. This reaction with acetylium fluoroborate does not occur in the absence of protic superacids.[97]

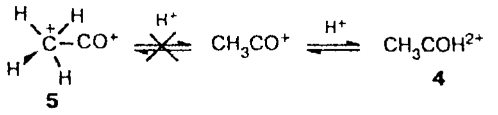
$$\mathrm{MeC^+{=}O + H^+ \rightleftharpoons \underset{\mathbf{4}}{MeC^+{=}O^+H}}$$

$$\mathrm{Me_3CH + MeC^+{=}O^+H \rightleftharpoons Me_3C^+ + MeCH{=}O^+H}$$

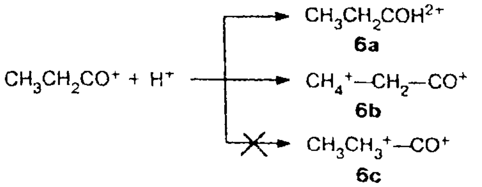
$$\mathrm{Me_3CH + MeC^+{=}O \;\cancel{\xrightarrow{SO_2}}\; Me_3C^+ + MeCHO}$$

Quantum-chemical calculations (by the HF/6-31G* method) showed that protonated acetylium, *i.e.*, dication **4** analogous to cation **2**, corresponds to a global minimum on the potential energy surface (PES).[98,99] The formation of dication $C_2H_4O^{2+}$ in the gas phase was confirmed by mass spectrometry.[100]

The possibility of *O*- or *C*-protonation of acylium cations in DF—SbF_5 was recently studied by ^2H NMR spectroscopy and quantum-chemical methods.[101] The absence of H/D-exchange in the acetylium methyl group indicates that protonation of the methyl group with formation of five-coordinate carbonium ion does not occur.



Calculations showed[101] that ion **5** corresponds to a minimum on the PES, but it is less energetically favorable (by 18.8 kcal mol^{-1}) than *O*-protonated acetylium ion **4**. Conversely, the methyl group hydrogen in the $CH_3CH_2CO^+$ cation is slowly exchanged for deuterium in DF—SbF_5 (2.5% of deuterium in the CH_3 group after 12 days), which allowed the conclusion on the *C*-protonation of the $CH_3CH_2CO^+$ cation to be made.[101]



It follows from quantum-chemical calculation data that the global minimum on the PES of $C_3H_6O^{2+}$ dications corresponds to *C*-protonated isomer **6b**, which is more stable (by 20.4 kcal mol^{-1}) than *O*-protonated acylium ion **6a**. No minimum at all is observed on the PES of methylene-protonated isomer **6c**.[101]

It has been convincingly proven by Japanese authors[102] that protonated acylium and aroylium cations play the key role in the acetylation and benzoylation of benzene and chlorobenzene with $MeCO^+SbF_6^-$ and $PhCO^+SbF_6^-$ in protic media. For example, the rate of benzene acetylation increases tenfold, while the concentration of $MeCO^+$ changes only from 60 to 75% on passing from a solvent with $H_0 = -12$ to one with $H_0 = -14$. Calculations showed that if acetylium cations were the reacting particles, the acetylation rate would increase by a factor of less than two on passing from $H_0 = -12$ to $H_0 = -14$. The formation of H_4O^{2+}, H_4S^{2+}, and other dications has been proven clearly.[98] There is growing evidence of the important role of multicharged particles in electrophilic organic reactions[98—104] (this problem has been considered in most detail in Refs. 99 and 104).

The conclusion on the key role of dicationic particles in reactions of alkanes with $RCOX \cdot 2AlX_3$ complexes motivated the search for new superelectrophilic complexes which would be more readily accessible and more convenient to work with than complexes based on acyl halides and would open up possibilities for new types of functionalization of alkanes and cycloalkanes. Testing a number of system, which are potentially capable of generating cations and even dicationic species, led to the elaboration of new types of aprotic organic and inorganic superacids. Of these, systems based on polyhalomethanes and aluminum halides proved to be the most promising.

Aprotic organic superacids based on polyhalomethanes and aluminum halides as initiators of selective and efficient transformations of alkanes and cycloalkanes

Cracking and isomerization of alkanes

The ionization of CCl_4 upon the action of $AlCl_3$ has been known for a long time. In particular, it has been shown back in 1950 [105] that exchange between CCl_4 and $Al^{36}Cl_3$ exists at −20 °C. However, the superelectrophilic properties of polyhalomethanes in the presence of aluminum bromide in reactions with alkanes have been discovered only in 1993. It was found that $CBr_4 \cdot nAlBr_3$, $CHBr_3 \cdot nAlBr_3$ (where n = 1 or 2), $CCl_4 \cdot 2AlBr_3$, and $CHCl_3 \cdot 2AlBr_3$ systems efficiently initiate the isomerization of *n*-alkanes to isoalkanes, the cracking of *n*-alkanes into lower isoalkanes and oligomers, and other low-temperature transformations of alkanes and cycloalkanes (Scheme 5).[106]

The turnover number of the catalyst in the cracking of pentane in the presence of superelectrophilic systems

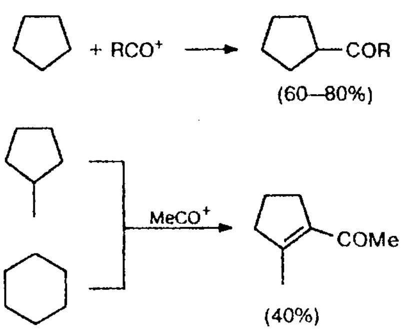
Scheme 2

a. Acylation and dehydroacylation of alkanes[51]

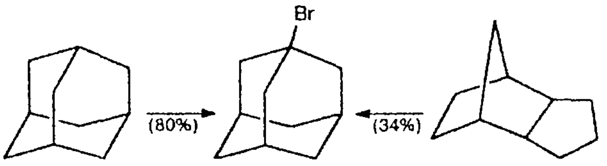
$n\text{-}C_nH_{2n+2} + RCO^+ \longrightarrow i\text{-}C_nH_{2n+1}COR + i\text{-}C_nH_{2n-1}COR$ (20—60%)

R = Me, Pr; n = 4—6

b. Acylation and dehydroacylation of cycloalkanes[43]



c. Halogenation with the RCOX · 2AlBr₃ complex[72]



were the first to perform the direct alkylacylation of benzene and bromobenzene (see Scheme 3, *a*) with alkanes (cycloalkanes) as alkylating agents and RCOX · 2AlX$_3$ complexes as acylating systems. It is important that the products are formed in good yields and, in some cases, selectively and regioselectively. Reaction *b* in Scheme 3 is the first example of sulfurization of alkanes and cycloalkanes with elemental sulfur under mild conditions. The previously reported transformations of alkanes and cycloalkanes upon the action of sulfur occur at enhanced temperatures; they are nonselective and have low efficiency.[79,80]

Obviously, the reactions of alkanes and cycloalkanes presented in Schemes 1—3 have one common step, namely, the generation of a carbenium ion from the saturated hydrocarbon and the reduction of the acyl halide:

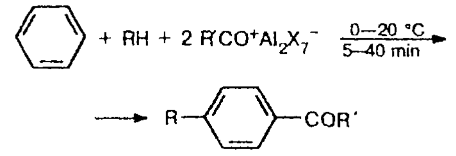
$$RH + RCO^+ \rightleftharpoons R^+ + RCHO.$$

The formation of aldehydes on treatment of alkanes with AlkCO$^+$ · Al$_2$Br$_7^-$ has not been detected, probably due to the high reactivity of the latter toward superelectrophiles. However, benzaldehyde was detected[49] in the reaction of adamantane with the PhCOCl · 2AlBr$_3$ complex.

$$AdH + PhCOCl \xrightarrow{2\ AlBr_3} AdBr + PhCHO$$

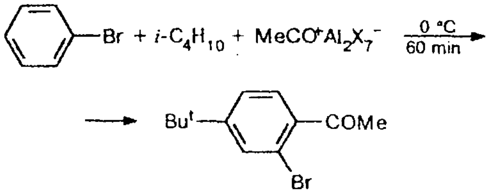
Scheme 3

a. Alkylacylation of arenes [58,59]



(65—87% with respect to ArH)

R = Bu^i, Bu^n, n-C$_5$H$_{11}$, 2,3-Me$_2$C$_5$H$_9$, *cyclo*-C$_5$H$_8$Me;
R′ = Me, Pr, Ph; X = Cl, Br



(82% with respect to ArH)

b. Thioacylation (0—20 °C, 2—4 h)[57]

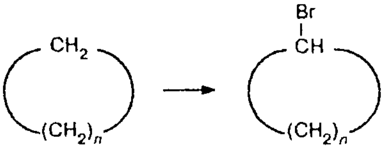
$RH + S + R'CO^+Al_2X_7^- \longrightarrow s\text{-}RSCOR'$

(29—60% with respect to S)

R = Pr^i, Bu^n, n-C$_5$H$_{11}$, *cyclo*-C$_5$H$_9$, *cyclo*-C$_6$H$_{11}$;
R′ = Me, Pr, Ph

c. Catalytic ionic bromination
(−20÷+20 °C, 0.5—3.0 h)[53,54]

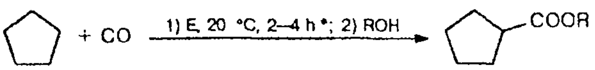
$$RH + Br_2 \longrightarrow RBr$$



(55—370% with respect to AcCl · AlCl$_3$;
110—910% with respect to AcBr · 2AlBr$_3$)

RH = C$_3$H$_8$—C$_7$H$_{16}$, *cyclo*-C$_5$H$_{10}$, *cyclo*-C$_6$H$_{12}$, *etc.*

d. Carbonylation[60]



(53—93%)

E = MeCOBr · nAlBr$_3$ (n ≥ 1.8)

Selectivity 90—99%

---

* Without a solvent.

Table 1. Activity of electrophilic systems (E) in the cracking of alkanes

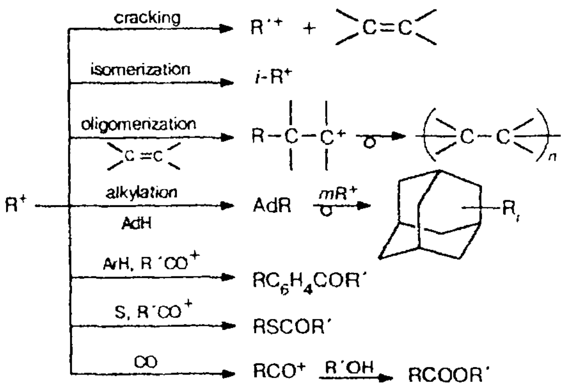
n-RH	E	RH : E	*T*/°C	*t*/h	Conversion (%)
C_5H_{12}—C_8H_{18}	$AcBr \cdot 2AlBr_3$	1 : 1	20	0.5	98—100[51]
C_8H_{18}—$C_{18}H_{38}$	$AcBr \cdot 2AlBr_3$	10 : 1	20	0.16	70—85[51]
C_8H_{18}—$C_{18}H_{38}$	$AcCl \cdot 2AlCl_3$	10 : 1	20	0.33	57—70[51]
C_5H_{12}	$AcCl \cdot AlCl_3$	1 : 1	60	5.0	0[63]
C_7H_{16}	$AlBr_3$	5 : 1	35	2.0	Traces[64]
C_7H_{16}	CF_3SO_3H—SbF_5	1 : 1	30	3.0	40[65]
C_6H_{14}	CF_3SO_3H—SbF_5	1 : 3	20	2.0	Traces[66]
C_5H_{12}	HSO_3F—SbF_5		20	0.7	1[67]

Table 2. Activity of electrophilic systems (E) in the isomerization of *n*-butane at 20 °C

E	n-C_4H_{10} : E	*t*/h	Content of i-C_4H_{10} (%) [mol per 1 mol of E]
$AcBr \cdot 2AlBr_3$	11 : 1	3	78 [9][50]
$AcBr \cdot 2AlBr_3$	34 : 1	6	80 [27][50]
$AcCl \cdot 2AlCl_3$	7 : 1	7	35 [3][50]
$AlBr_3$	20 : 1	1000	73 [15][68]
HCl—$AlCl_3$	9 : 1	64	21 [2][69]
$TfOH_2^+[B(OTf)_4]^-$[a]	1 : 1	24	40 [0.4][70]
$MeCO^+BF_4^-$		72	<1 [71]

[a] Tf = CF_3SO_2.

Scheme 4



Other examples of the reduction of acyl halides in reactions with alkanes in the presence of $AlBr_3$ are also known.[55,62] Subsequently, the carbenium ions formed undergo fragmentation and isomerization; they alkylate olefins that are in equilibrium with them. In the presence of traps for carbenium ions, they are transformed to products of alkane and cycloalkane functionalization (Scheme 4).

It was very important to understand the origin of the superelectrophilic properties of $RCOX \cdot 2AlX_3$ systems, which are so different from inactive Friedel—Crafts equimolecular complexes.

As a result of studies started at the beginning of the century and developed most intensely in the 60s and 70s, the structure of classical Friedel—Crafts $RCOX \cdot MX_n$ complexes (R = Alk, Ar; X = Cl, F) in the crystal and in solutions has been well studied by now.[36b,81—86] The first reliably characterized acylium complex was obtained in 1943 [87] by the reaction of AcF with BF_3. In the crystalline state, the $RCOX \cdot AlCl_3$ complexes exist as ionic acylium salts or as donor-acceptor complexes.[84] The structures of ionic acylium salt[88] $MeCO^+AlCl_4^-$ (**1**) and donor-acceptor complexes $RC(Cl){=}O{\rightarrow}AlCl_3$ (R = Et,[89] Ph,[90] *o*- and *p*-MeC_6H_4 [91]) were determined by X-ray diffraction studies. On the contrary, data[92] on $RCOX \cdot 2AlX_3$ * were scant and uncertain before our works.[93,94] The structure of $MeCOX \cdot AlX_3$ and $MeCOX \cdot 2AlX_3$ complexes was stud-

Table 3. Activity of electrophilic systems (E) in the alkylation of adamantane (AdH)

RH	E	RH : AdH : E	*T*/°C	*t*/h	Conversion of AdH (%)	Yield of alkyladamantane (wt.%)[a]
C_6H_{14}	$AcBr \cdot 2AlBr_3$ [49,72]	10 : 1 : 1	20	0.3	95	—
C_8H_{18}	$AcBr \cdot 2AlCl_3$ [72]	25 : 5 : 1	20	3.5	96	171
C_8H_{18}	$AcBr \cdot 2AlCl_3$ [72]	40 : 8 : 1	20	3.5	86	156
$C_{12}H_{26}$	$AcBr \cdot 2AlCl_3$ [72]	17 : 5 : 1	20	3.5	96	206
C_9H_{20}	$AlBr_3$ [73]	3 : 1 : 1.5	160	2.5	60	—
C_7H_{16}	$AlCl_3$ [74]	9 : 1 : 1	75	5.0	30	—
C_9H_{20}	HCl—$AlCl_3$ [75]	3 : 1 : 1.5	60	30.0	100	50

[a] With respect to the reacted AdH.

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* The conclusions of the authors of Ref. 92 are believed to be doubtful (see the comments in Ref. 84).

Scheme 5

$$n\text{-}C_nH_{2n+2} \xrightarrow[20\ ^\circ C]{E}$$

$$\longrightarrow i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + i\text{-}C_6H_{14} + \text{oligomers}$$

$[RH] : [E] = 10 : 1; n = 5 \div 12;$

$E = CX_4 \cdot mAlBr_3, CHX_3 \cdot mAlBr_3; X = Cl, Br; m = 1, 2$

The conversion of C_8—C_{12} alkanes is 70—80%, 10—20 min

$$n\text{-}RH \xrightarrow[20\ ^\circ C,\ 3\text{—}6\ h]{E} i\text{-}RH$$

(51—65%, 20—25 mol)

$RH = C_4H_{10}, C_5H_{12}; E = CBr_4 \cdot 2AlBr_3, CHCl_3 \cdot 2AlBr_3$

$$C_3H_8 \xrightarrow[20\ ^\circ C]{E} i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + \text{oligomer}$$

The conversion is 0.7 mol per 1 mol of E, 10 h

based on polyhalomethanes reaches 200. The higher catalytic activity of these systems in comparison with $RCOX \cdot 2AlX_3$ systems is explained by two reasons. First, the catalyst components are not involved in the formation of products with alkanes, in contrast to the $RCOX \cdot 2AlX_3$ complexes, which produce a noticeable amount of carbonyl-containing compounds. Reactive bromides are the only functional alkane derivatives formed on treatment with polyhalomethane—$AlBr_3$ systems. The second reason is that $CBr_4 \cdot nAlBr_3$ systems are reduced with alkanes to give $CHBr_3 \cdot nAlBr_3$ complexes, which, in turn, display activity (although smaller) in initiating the reactions of alkanes and cycloalkanes. The next reduction step gives $CH_2Br_2 \cdot nAlBr_3$ systems, which are also active but to a much smaller extent.

In contrast to $RCOX \cdot nAlX_3$ complexes, which are active at $n = 2$ and totally inert at $n = 1$, both types of complexes (1 : 1 and 1 : 2) with polyhalomethanes are active in many alkane reactions.[106] The effect of excess $AlBr_3$ on the initiating ability of polyhalomethanes is not uniform. In transformations involving low-reactivity alkanes, the 1 : 2 systems are noticeably more active than the corresponding 1 : 1 systems (the latter sometimes do not promote alkane transformations at all). Conversely, there is no noticeable difference in the activity of 1 : 1 and 1 : 2 systems in reactions with more reactive alkanes and cycloalkanes.

The order of catalytic activity of superelectrophilic systems in transformations of n-pentane is as follows (C_5H_{12} : E = 40 : 1, 20 °C, 3 h; degree of conversion shown in parentheses):[106]

$$\underset{(89\%)}{CBr_4 \cdot 2AlBr_3} > \underset{(77\%)}{CHCl_3 \cdot 2AlBr_3} \geq \underset{(73\%)}{CBr_4 \cdot AlBr_3} >$$

$$> \underset{(50\%)}{CHBr_3 \cdot 2AlBr_3} \geq \underset{(47\%)}{CHBr_3 \cdot AlBr_3} > \underset{(30\%)}{CH_2Br_2 \cdot 2AlBr_3} \cdot$$

Despite the high activity of the complexes in question in the initiation of alkane cracking, this process can be suppressed and functionalization of alkanes and cycloalkanes can be carried out under certain conditions. It is important that in some cases the reactions occur selectively and give high yields of the products.

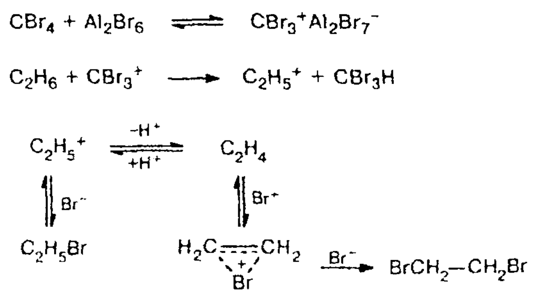
Ionic bromination of alkanes and cycloalkanes

Similarly to aprotic superacids $RCOX \cdot 2AlX_3$, polyhalomethanes in the presence of aluminum halides initiate or catalyze the bromination of alkanes or cycloalkanes.[107] Ethane efficiently reacts with Br_2 at 50—60 °C in the presence of $CBr_4 \cdot 2AlBr_3$. This reaction occurs both in CH_2Br_2 and in the absence of a solvent (a homogeneous solution is formed at 60 °C and with $[Br_2] > [CBr_4 \cdot 2AlBr_3]$). 1,2-Dibromoethane is the main product; a small amount of ethyl bromide is also formed.

$$C_2H_6 + Br_2 \longrightarrow C_2H_4Br_2 + C_2H_5Br$$

In the stoichiometric reaction in the absence of a solvent ($[Br_2] : [CBr_4 \cdot 2AlBr_3] = 1 : 1$) in a tube at 50—60 °C, bromine is consumed completely within 18 h. 1,2-Dibromoethane is formed in 100% yield with respect to the starting Br_2. The yield of 1,2-dibromoethane over 6 h is 84%. At 50—60 °C under atmospheric pressure, the reaction of ethane with bromine for 3 h results in a mixture of ethyl bromide, 1,2-dibromoethane, and 1,1,2,2-tetrabromoethane (in 1 : 3 : 5 ratio) in 73% overall yield with respect to Br_2. At the same temperature, ethane does not react with Br_2 in the presence of the $CBr_4 \cdot AlBr_3$ and $MeCOBr \cdot 2AlBr_3$ complexes or $AlBr_3$ in CH_2Br_2. Thus, the $CBr_4 \cdot nAlBr_3$ system ($n \geq 2$) is the most active of those mentioned above, and the differentiation of superelectrophiles toward low-reactivity ethane is quite pronounced. The reactions can be explained by Scheme 6. The key step is the abstraction of a hydride ion from ethane upon the action of a tribromomethyl cation. The ethyl cation that forms is in equilibrium with ethylene. Ionic bromination of ethylene results in 1,2-dibromoethane, while the addition of Br^- to the ethyl cation gives ethyl bromide.

Scheme 6



The dibromination of ethane could not be carried out in the catalytic mode, which can be explained by the absence of superelectrophile regeneration step and the inactivity of the weaker electrophile $CHBr_3 \cdot 2AlBr_3$ in accepting a hydride ion from ethane. The alternative Scheme 7, which involves the abstraction of a hydride ion from ethane by Br^+, is not realized in this case.

Scheme 7

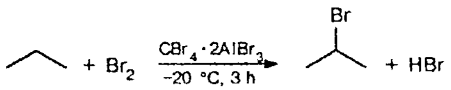
$$Br_2 + CBr_3^+ \rightleftharpoons [Br^+] + CBr_4$$

$$C_2H_6 + [Br^+] \not\longrightarrow C_2H_5^+ + HBr$$

The inactivity of the $Br_2 \cdot nAlBr_3$ systems in ethane bromination and the complete transformation of CBr_4 to the reduction product $CHBr_3$ are consistent with this viewpoint.

The deep bromination of ethane under atmospheric pressure can be explained by its small steady-state concentration in solution, which is the reason why the bromination of the 1,2-dibromoethane formed initially becomes the main direction of the reaction.

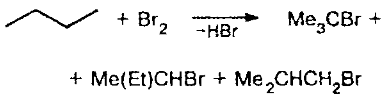
Unlike with ethane which does not react with Br_2 at room temperature, bromination of the more reactive propane in the presence of $CBr_4 \cdot 2AlBr_3$ occurs even at −20 °C. In this case, isopropyl bromide is the only reaction product.



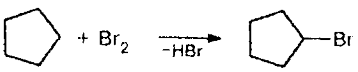
(48%, 0.96 mol with respect to E)

Propane is brominated completely both at −10 °C and at 0 °C. However, an increase in the temperature causes an increase in the dibromide content in the product mixture. The $Pr^iBr : C_3H_6Br_2$ ratio is 2 : 1 at 0 °C after 2 h.

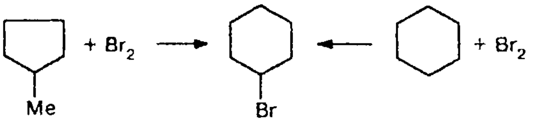
In the reaction with butane, bromine is consumed completely at −20 °C in 2 h to give a mixture of three isomeric monobromides, $Bu^tBr + \{Bu^iBr + Bu^sBr\}$, in 1.0 : 0.4 ratio.



Cyclopentane, methylcyclopentane, and cyclohexane efficiently react with Br_2 at −20 °C in the presence of a catalytic amount of a superacid. The yields of monobromides reach 76% with respect to bromine and 600% with respect to the catalyst. Polybromides are either absent or present as traces. The reaction with cyclopentane gives cyclopentyl bromide.



The bromination of methylcyclopentane and cyclohexane at −40 °C and −20 °C results in the same product, *viz.*, cyclohexyl bromide. This result can be explained by the instability of 1-bromo-1-methylcyclopentane, which is initially formed from both cycloalkanes and then irreversibly transformed into the more stable cyclohexyl bromide.



The order of catalytic activity of superelectrophiles in cyclohexane bromination at −20 °C is as follows (the yields of cyclohexyl bromide with respect to Br_2 (mol.%) at *cyclo*-C_6H_{12} : Br_2 : Cat = 10 : 4 : 1 and the duration of reactions are given in parentheses):

$$\underset{(75\%,\ 1\ h)}{CBr_4 \cdot 2AlBr_3} > \underset{(50\%,\ 1\ h)}{CHBr_3 \cdot 2AlBr_3} > \underset{(36\%,\ 2\ h)}{C_6F_5CF_3 \cdot 2AlBr_3} >$$

$$> \underset{(29\%,\ 2\ h)}{CCl_4 \cdot 2AlBr_3} > \underset{(22\%,\ 3\ h)}{CH_2Br_2 \cdot AlBr_3}$$

The difference between ethane and higher alkanes (cycloalkanes) in reactions with Br_2 are as follows. The bromination of ethane occurring at a higher temperature is a stoichiometric reaction, whereas the brominations of higher alkanes and cycloalkanes occur as catalytic reactions. Ethane forms a dibromide, whereas higher hydrocarbons give monobromides. Higher homologs of ethane (but not ethane itself) are brominated with the $CH_2Br_2 \cdot AlBr_3$ system, although not as actively as with CX_4-based systems.

Two possible bromination schemes of higher alkanes and cycloalkanes were considered.[107] The first includes generation of a carbenium ion from a saturated hydrocarbon (RH) upon the action of a superelectrophile (Scheme 8). The subsequent reaction of the carbenium ion with Br_2 gives a monobromide and a particle containing a positively charged bromine atom, which then reacts with a new RH molecule.

Scheme 8

$$RH + CBr_3^+ \longrightarrow R^+ + CHBr_3$$

$$R^+ + Br_2 \longrightarrow RBr + [Br^+]$$

$$RH + [Br^+] \longrightarrow R^+ + HBr$$

$$R^+ + Br_2 \longrightarrow RBr + [Br^+]$$

According to this scheme, the starting superelectrophilic complex initiates the reaction, while the $[Br^+]$ electrophile serves as a catalyst. It should be noted that the $CHBr_3 \cdot 2AlBr_3$ and $CH_2Br_2 \cdot AlBr_3$ systems also initiate this reaction, although much less actively. The alternative Scheme 9 starts from initial superelectrophilic attack on the Br_2 molecule to give a reactive bromine-containing particle, which is the catalyst of bromination.

Scheme 9

$$Br_2 + CBr_3^+ \rightleftharpoons [Br^+] + CBr_4$$

$$RH + [Br^+] \longrightarrow RBr + H^+$$

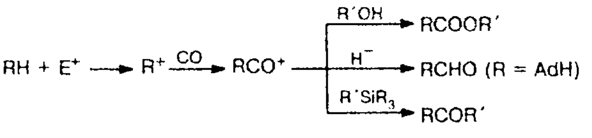
$$RH + Br_2 \longrightarrow RBr + HBr$$

It can be stated that Scheme 9 is never realized purely, since bromination is invariably accompanied by reduction of the starting polyhalomethane. However, the contribution of this mechanism to reactions of activated alkanes is probably more significant than in the case of low-reactivity alkanes, whose activation requires strong electrophiles.

Selective functionalization of alkanes and cycloalkanes with CO

Polyhalomethanes in the presence of aluminum halides initiate efficient and selective reactions of alkanes and cycloalkanes with CO. Probably, electrophilic carbonylation of saturated hydrocarbons occurs by the Koch—Haaf mechanism,[108] which includes generation of a carbocation from a saturated hydrocarbon followed by CO addition and acylium cation formation. In the presence of traps of acylium cations (water or alcohols), carboxylic acids or their esters are formed. The presence of a hydride ion donor (adamantane, methylcyclopentane) results in the formation of an aldehyde. The use of silanes as sources of alkyl (aryl) groups gives ketones (Scheme 10).[60,109–111]

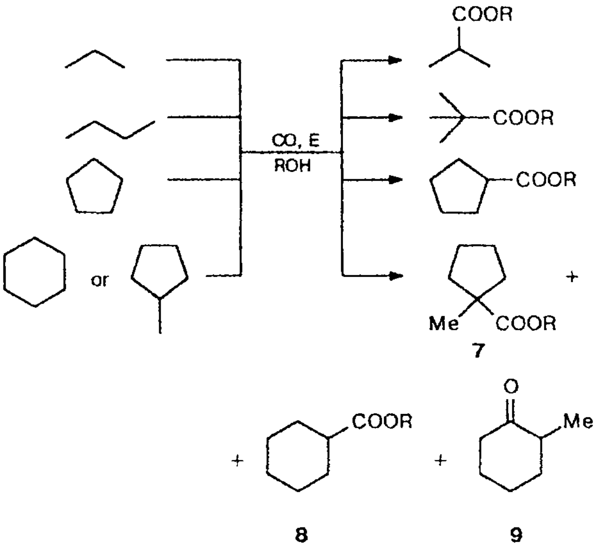
Scheme 10



Transformation of alkanes or cycloalkanes to carboxylic acids and their esters. Scheme 11 presents examples of the carbonylation of alkanes and cycloalkanes to give carboxylic acids or their esters (after treatment with water or an alcohol).[60,109–111]

These reactions occur under mild conditions under atmospheric pressure of CO, at temperatures from −20 to +20 °C, in a short time (1—4 h), in solutions in CH_2X_2 (X = Br, Cl) or without a solvent. $CBr_4 \cdot n AlBr_3$, $CCl_4 \cdot n AlBr_3$, $CHBr_3 \cdot n AlBr_3$ (n = 1 or 2), and other systems can be used as catalysts.[109–111] The reactions are selective, each giving a single product in 80—150% yield with respect to the superelectrophile. The formation of products in yields above 100% indicates that the reduction of $CBr_4 \cdot 2AlBr_3$ with alkanes gives the $CHBr_3 \cdot 2AlBr_3$ complex, which is also capable of accepting a hydride ion, although less readily, from new alkane molecules. This fact has been confirmed experimentally. In other words, along with the main reaction (Scheme 12, *a*), some contribution comes from the transformation according to Scheme 12, *b*.

Scheme 11



Scheme 12

$$RH + CO + CBr_3^+ \xrightarrow{a} RCO^+ + CHBr_3$$

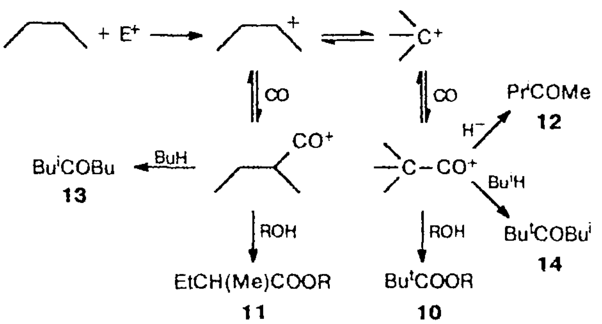
$$RH + CO + CBr_2H^+ \xrightarrow{b} RCO^+ + CH_2Br_2$$

Depending on the temperature, the reactions of methylcyclopentane or cyclohexane can result in preferred or exclusive formation of products **7** or **8** in yields above 80%. At −45 °C, compound **7** is formed from both cycloalkanes; at 0 °C, compound **8** is formed, while at −23 °C, a mixture of compounds **7** and **9** is formed in 74 and 80% yields, respectively.[111]

Previously, the carbonylation of methane,[112] propane,[113] C_5—C_9 alkanes,[114] cyclopentane, cyclohexane, methylcyclopentane,[76,115] and adamantane[116] has been carried out in the HF—SbF_5 system.[5] The carbonylation of propane in protic media is non-selective and inefficient.[113] It was found[113] that the addition of polyhalomethanes or halogens and, most surprisingly, even sodium bromide increases noticeably the selectivity of Pr^iCO^+ formation and the carbonylation efficiency.

We were the first to perform the selective carbonylation of *n*-butane.[111] It is interesting that this reaction, which is initiated by $CBr_4 \cdot 2AlBr_3$ or $CCl_4 \cdot 2AlBr_3$, affords (after hydrolysis or alcoholysis of the reaction mixture) the valuable pivalic acid or its esters. Product **10** is formed in 80% yield in 1 h at −20 °C or 0 °C. The yield of isomeric product **11** is 10—25% (Scheme 13).

Scheme 13



It was reported in previous papers that reactions of butane and isobutane with CO in the presence of $AlCl_3$ or $HCl—AlCl_3$ at 20—40 °C under 100—130 atm CO pressure for 20—36 days gave mixtures of products **11**, **12**, and **13** (for *n*-butane) and **10**, **12**, and **14** (for isobutane).[117,118] In both cases, the overall yields of the carbonylation products were very small. The successful use of very strong superelectrophilic systems for the selective carbonylation of butane to give pivalic acid is explained by their ability to catalyze rapidly the generation and isomerization of butyl cations under very mild conditions. As a result, the most stable *tert*-butyl cation, which is 10 kcal mol^{-1} more favorable than the *sec*-butyl cation,[119] is accumulated. The Bu^tCO^+ formed subsequently is sufficiently stable to decarbonylation at −20 °C to 0 °C. The carbonylation and decarbonylation rate constants for secondary and tertiary cations, including butyl cations, are available in a review (see Ref. 119).

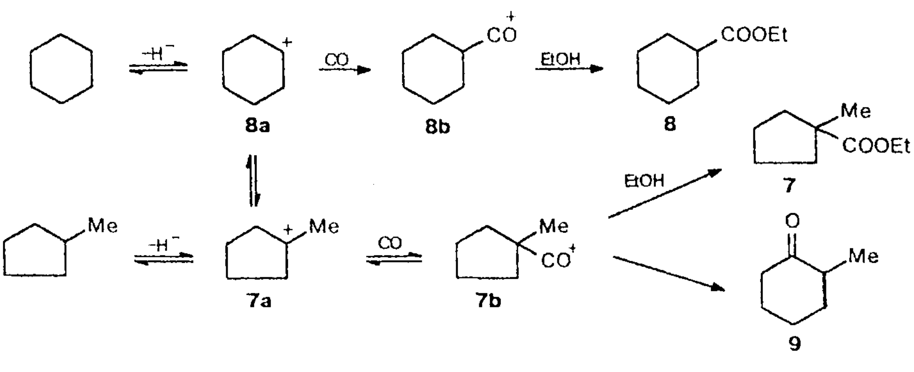
The carbonylation of cyclopentane, cyclohexane, and methylcyclopentane in the $HF—SbF_5$ system has been reported.[76,115] The scheme of cyclohexane and methylcyclopentane carbonylation[110] in the presence of $CBr_4 \cdot 2AlBr_3$ (Scheme 14) is generally similar to those suggested[76,115] for the carbonylation in the $HF—SbF_5$ system.

Both in protic and aprotic media at low temperature, the two cycloalkanes produce the same tertiary cation **7a**. The latter adds CO to give acylium cation **7b**, which is stable at low temperatures, and ester **7** as the final product. At higher temperatures, the decarbonylation of cation **7b** makes the reaction involving the secondary cation, **8a** → **8b** → **8**, the main pathway. The formation of 2-methylcyclohexanone (**9**), which has not been observed in the $HF—SbF_5$ system,[76,115] is an exception. Product **9** was also detected in the reaction of cyclohexane with $HCl—AlCl_3$ under 150 atm CO pressure.[120] It was shown that ketone **9** is formed from acylium ion **7b** in the presence of methylcyclopentane as the hydride ion donor. It should also be noted that the carbonylation of cyclohexane in a protic superacid was not very efficient,[76] as opposed to the reactions with $CBr_4 \cdot 2AlBr_3$. In addition, the reactions in protic media were always carried out with an excess of the superacid and for markedly longer periods of time.

The simple method for the synthesis of acids and esters from alkanes and cycloalkanes in the presence of $CX_4 \cdot 2AlBr_3$ (particularly with X = Cl) appears to show considerable promise. It is worthwhile mentioning here the catalytic carbonylation of methane, ethane, propane, and cyclohexane in CF_3COOH in the presence of the $Pd(OAc)_2+Cu(OAc)_2$ mixture and $K_2S_2O_8$ as the reoxidant. These reactions are carried out at 80 °C for 20 h and require large amounts of $K_2S_2O_8$ and CF_3COOH. For example, 40—100 g of $Pd(OAc)_2$, 30—150 g of $Cu(OAc)_2$, 7—8 kg of $K_2S_2O_8$, and 14—17 L of CF_3COOH are needed in order to obtain 1 kg of $C_6H_{11}COOH$ or EtCOOH. The reaction with propane in the presence of a $Pd^{2+}+Cu^{2+}+K_2S_2O_8$ mixture in CF_3COOH is nonselective.[12]

Formylation of adamantane. All of the known reactions of alkanes and cycloalkanes with CO initiated by protic or aprotic superacids give, after treatment with water or an alcohol, carboxylic acids or their derivatives.

Scheme 14

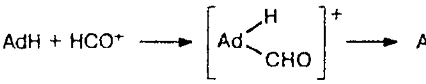


Conversely, formylation, which is quite common in the aromatic series,[121] has been carried out only for one hydrocarbon, namely, adamantane.[122,123]

$$\text{AdH} + \text{CO} \longrightarrow \text{AdCHO}$$

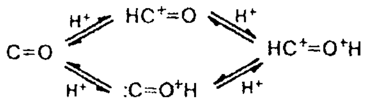
G. Olah *et al.* were the first to report that in protic media of various acidities[122] or on treatment with $AlCl_3$ in dichloromethane,[123] adamantane reacts with CO to give, in addition to the usual carbonylation products such as 1-AdCOOH (60—75%) and 1-AdOH (1—7%), a small amount of 1-AdCHO (0.2—21%). The reaction with 1,3,5,7-tetradeuterioadamantane showed that formylation of adamantane in a protic superacid involves the formyl cation.[122]

$$\text{CO} + \text{H}^+ \longrightarrow \text{HCO}^+$$



$$\text{AdH} + \text{HCO}^+ \longrightarrow \left[\text{Ad}\begin{smallmatrix}\text{H}\\ \text{CHO}\end{smallmatrix}\right]^+ \longrightarrow \text{AdCHO} + \text{H}^+$$

Quantum-chemical calculations confirmed that two forms of protonated carbon monoxide, *viz.*, the formyl and isoformyl cations,[124] and a diprotonated form of CO^{99} can exist.

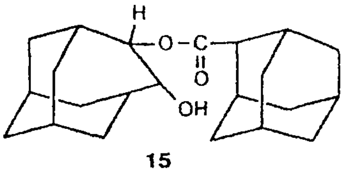


It is important that the formation of the formyl cation HCO^+ and of the less stable (by 38 kcal mol^{-1}) isoformyl cation ^+COH is exothermic. Both cations have a high energy barrier for deprotonation;[124] their existence in the gas phase has been proven.[125] However, none of the protonated forms of carbon monoxide has ever been observed in solutions.[122]

A different mechanism is more probable for the formylation of adamantane initiated by $AlCl_3$ in CH_2Cl_2.[123] It is a three-step process, in which the initially formed acylium cation abstracts a hydride ion from a saturated hydrocarbon to give an aldehyde and a new carbocation. The final formylation step is the same as the key step in the reactions of saturated hydrocarbons with aprotic organic superacids $RCOX \cdot 2AlX_3$ discussed above.

$$\text{RH} \xrightarrow{E^+} \text{R}^+ \xrightarrow{\text{CO}} \text{RCO}^+ \xrightarrow{\text{R'H}} \text{RCHO} + \text{R'}^+$$

Although the principal possibility of electrophilic formylation of adamantane was shown, the yields of AdCHO and the selectivity of its formation were very low. Furthermore, a detailed study of reactions of the Ad^+ cation (obtained from 1-AdOTf and from other sources) with CO in the presence of AdH (as the hydride donor) in the CF_3SO_3H—CCl_4 system at 30 °C did not reveal even traces of AdCHO. After treatment with water, homoadamantane derivative **15** was obtained in 70% yield instead of the aldehyde.[126]



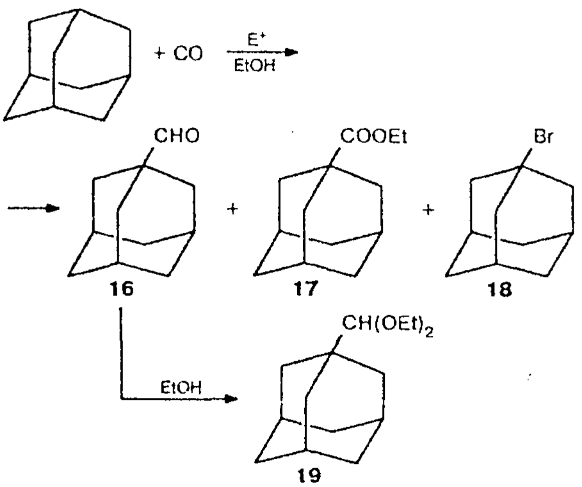
15

The fact that authentic 1-AdCHO added to the reaction mixture was transformed into compound **15** and other products allowed the authors[126] to conclude that it is unstable in strong protic acids.

The use of polyhalomethanes in combination with aluminum halides for adamantane formylation was found to be much more successful. The reaction of adamantane with CO in the presence of $CX_4 \cdot 2AlX_3$ and $CH_2X_2 \cdot 2AlX_3$ (X = Cl, Br) in CH_2X_2 was studied by us in detail[127,128] in the temperature range from −45 to +20 °C.

It was shown that functionalization of adamantane (Scheme 15) occurs even at −45 °C to give, after hydrolysis, products **17** and **18** in 80% overall yield with respect to $CBr_4 \cdot 2AlBr_3$.

Scheme 15



The products of the reactions at −45 °C and −23 °C contain only traces of 1-AdCHO (**16**). An increase in temperature and the use of an excess of adamantane with respect to the superelectrophile favors the formation of the aldehyde. At 0 °C and with molar ratio AdH : $CBr_4 \cdot 2AlBr_3$ = 4, the yield of aldehyde **16** is 45%, and the selectivity is 50% (treatment with ethanol sometimes results in a mixture of products **16** and **19**). At equimolar AdH : $CBr_4 \cdot 2AlBr_3$ ratio, the yields of compound **16** decrease and are as low as 8 and 32% at 0 and

20 °C, respectively. At 20 °C, the alcoholysis products contain 2-AdCOOR (**20**) along with 1-substituted adamantane derivatives (1-AdCOOR : 2-AdCOOR = 2), indicating that not only the 1-AdCO$^+$ cation but also 2-AdCO$^+$ are formed. This fact seems unexpected, considering the tendency of 2-AdCO$^+$ to decarbonylation, as opposed to 1-AdCO$^+$.[119]

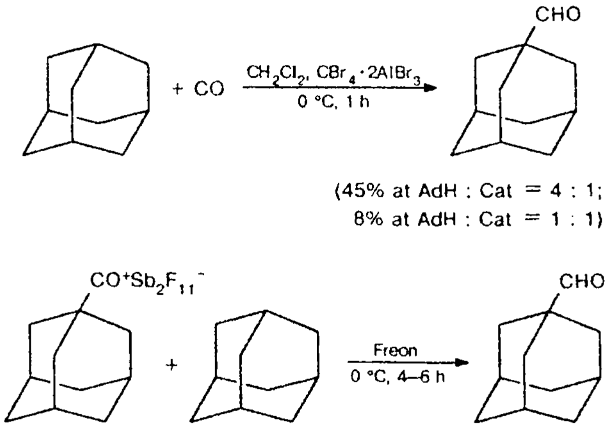
As usual, $CX_4 \cdot nAlX_3$ complexes are more active than $CH_2X_2 \cdot nAlX_3$ systems. However, even the latter weak electrophiles can provide comparable or higher yields of AdCHO after a longer period of time.[127,128]

The reactions occurring at 20 °C give a small amount of products of further reduction of the aldehyde, *viz*., alcohol **21** and bromide **22**.

$$\mathrm{AdCHO} \xrightarrow{E^+} \mathrm{AdC^+H{-}OE} \xrightarrow{H^-} \underset{\mathbf{21}}{\mathrm{AdCH_2OH}} \xrightarrow{HBr} \underset{\mathbf{22}}{\mathrm{AdCH_2Br}}$$

A comparison of the two reactions shown in Scheme 16 indicates a considerably higher efficiency of the three-step adamantane formylation[128] in the presence of the $CBr_4 \cdot 2AlBr_3$ complex in CH_2Cl_2 in comparison with direct acceptance of a hydride ion from AdH by the $AdCO^+Sb_2F_{11}^-$ salt in Freon-113.[122]

Scheme 16



(45% at AdH : Cat = 4 : 1;
8% at AdH : Cat = 1 : 1)

(0.2—1.1%)

On the other hand, the higher efficiency of relatively inactive $CH_2X_2 \cdot nAlX_3$ systems in the adamantane formylation in comparison with the strongest electrophilic systems $CBr_4 \cdot nAlBr_3$ can be explained by the following reasons. It is known that adamantane does not require a strong electrophile to generate the Ad$^+$ cation. For example, adamantane carbonylation occurs successfully even in sulfuric acid.[108,129] In addition, the highly active $CBr_4 \cdot nAlBr_3$ systems remove adamantane from the reaction zone too quickly, whereas electrophiles of medium strength, which generate Ad$^+$ relatively slowly, create more favorable conditions for the reaction of AdCO$^+$ with adamantane. The assumed pattern of the reaction between adamantane and CO is shown in Scheme 17.

Scheme 17

$$\mathrm{AdH} + E^+ \longrightarrow \mathrm{Ad}^+ + \mathrm{EH}$$

$$\mathrm{Ad}^+ + \mathrm{CO} \longrightarrow \mathrm{AdCO}^+$$

$$\mathrm{AdH} + \mathrm{AdCO}^+ \longrightarrow \mathrm{AdCHO} + \mathrm{Ad}^+$$

$$2\,\mathrm{AdH} + E^+ + \mathrm{CO} \longrightarrow \mathrm{AdCHO} + \mathrm{Ad}^+ + \mathrm{EH}$$

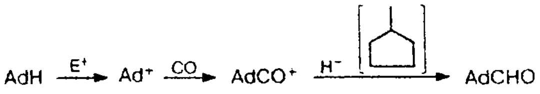
Since Ad$^+$ can accept CO, and in turn, AdCO$^+$ can abstract a hydride ion from AdH, it would seem possible to perform chain formylation:

$$\mathrm{AdH} + \mathrm{CO} \xrightarrow{E} \mathrm{AdCHO}.$$

However, the chain process does not really occur, and the maximum yield of AdCHO is 50% with respect to the catalyst. The reason is that the formation of AdCO$^+$ cation is a rapid reaction, while acceptance of a hydride ion from adamantane by this cation occurs slowly. Therefore, at [AdH] = [E], the reaction mixture is deficient in a hydride ion source, while at [AdH] > [E], the accumulation of AdCHO, which can coordinate to the superelectrophile, leads to deactivation of the system.

The efficiency and selectivity of adamantane formylation can be increased markedly if another hydride ion donor, methylcyclopentane, is added to the reaction mixture. In this case, adamantane can be quantitatively transformed to AdCHO. In may be assumed that in the presence of methylcyclopentane, in parallel with the reaction according to Scheme 17, another process (Scheme 18) occurs, in which the cycloalkane serves as the source of the hydride ion for AdCO$^+$.

Scheme 18



Importantly, the products of methylcyclopentane carbonylation are either absent completely or are found as traces.[128]

The overall reaction of adamantane formylation is exothermic (ΔH = −20.7 kcal mol^{-1}). However, the transfer of a hydride ion from a saturated hydrocarbon to AdCO$^+$ is accompanied by energy consumption (the values of E/kcal mol^{-1} are given in parentheses):

$$\underset{(17.0)}{cyclo\text{-}C_6H_{12}} > \underset{(15.7)}{\mathrm{AdH}} > \underset{(8.2)}{i\text{-}C_4H_{10}} > \underset{(5.5)}{cyclo\text{-}C_5H_9Me}$$

Methylcyclopentane is the best hydride ion donor of the hydrocarbons listed, and the transfer of a hydride ion from methylcyclopentane is more favorable (by 10.2 kcal mol^{-1}) than that from adamantane.[128]

Direct synthesis of ketones from alkanes (cycloalkanes), CO, and silanes. The addition of a hydride ion donor for the acyl cation formed has made it possible to convert adamantane to an aldehyde in quantitative yield. Likewise, the use of silanes as sources of alkyl and aryl groups for acyl cations provided the possibility of elaborating efficient and selective syntheses of ketones directly from alkanes and cycloalkanes.

$$RH \xrightarrow{E^+} R^+ \xrightarrow[0\ ^\circ C]{CO} RCO^+ \xrightarrow[0\ ^\circ C]{R'SiR'_3} RCOR'$$

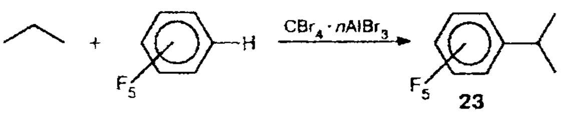
(60—97%)

The formation of ketones from acyl halides and silanes in the presence of $AlCl_3$ was reported in the literature.[130—132] The specific feature of this method is that alkanes or cycloalkanes and CO are used as the starting compounds for the synthesis of ketones. This reaction was considered in detail in our paper (see this issue of the journal).[133] It is believed that acylium cations obtained *in situ* from alkanes (cycloalkanes) and CO can also be widely used in other acylation reactions.

Alkylation of deactivated arenes with alkanes and cycloalkanes

Like superelectrophilic complexes $RCOX \cdot 2AlX_3$, the $CX_4 \cdot nAlBr_3$ systems initiate the alkylation of aromatic compounds with alkanes and cycloalkanes. However, in reactions with $RCOX \cdot 2AlX_3$, the first alkylation step is followed by acylation of alkylated arenes to give eventually alkylated aromatic ketones. On the contrary, the action of $CX_4 \cdot nAlBr_3$ exclusively gives alkylated products. The second difference is the possibility of alkylation of deactivated arenes.[134,135] Thus far, the alkylation of aromatic compounds even with traditional alkylating agents has mainly been limited to weakly passivated arenes (monohalobenzenes) and fluoroarenes[136] that display specific properties. The alkylation of deactivated arenes with alkanes and cycloalkanes has been carried out for the first time.

It was found that propane alkylates pentafluorobenzene in the presence of $CBr_4 \cdot nAlBr_3$ (n = 1 or 2) at 0 °C in 1.5 h to give pentafluoroisopropylbenzene (**23**) in almost quantitative yield.[134]

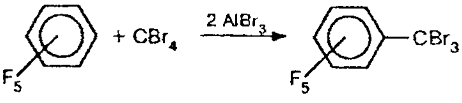


23

(90—94% with respect to C_6F_5H)

n = 1, 2; C_6F_5H : CBr_4 = 1 : 4

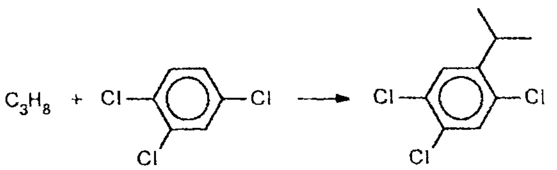
In this unusual reaction, the $CBr_4 \cdot 2AlBr_3$ and $CBr_4 \cdot AlBr_3$ complexes display high and similar activity. The $CCl_4 \cdot 2AlBr_3$ complex is markedly less active (the yield is 27% under the same conditions), whereas the corresponding equimolecular complex is not active at all. At 20 °C, the reaction promoted by $CBr_4 \cdot 2AlBr_3$ is completed within 10 min to give product **23** in 60% yield, while CBr_4 disappears completely to give $CHBr_3$ in 68% yield. In the absence of propane at 20 °C, the $CBr_4 \cdot 2AlBr_3$ complex slowly reacts with pentafluorobenzene to give $C_6F_5CBr_3$ in 40% after 24 h.



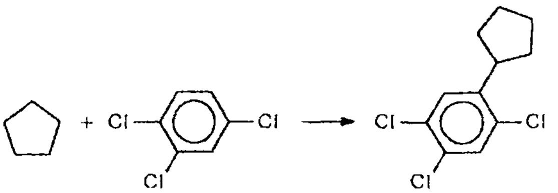
The above reaction is the first example of a superelectrophilic complex ($CBr_4 \cdot 2AlBr_3$) participating in the formation of a product of hydrocarbon functionalization. Previously, reduction was the only known direction of transformation of these complexes in reactions with alkanes and cycloalkanes.

Let us note an example of the very slow alkylation of pentafluorobenzene upon the action of CF_3H in the presence of an excess of SbF_5. At 0 °C, a mixture of $(C_6F_5)_2CFH$ and $(C_6F_5)_3CH$ in 2 : 1 ratio formed in 50 h.[136a] It was also reported that pentafluorobenzene reacted with CH_2Cl_2 or $CHCl_3$ in the presence of $AlCl_3$ at 150 °C to give $(C_6F_5)_2CH_2$ and $(C_6F_5)_3CH$ in 4.5—8 h in 77 and 92% yields, respectively.[136b]

It was found that other passivated arenes (trichlorobenzene, dichloro- and dibromobenzenes, acetophenone, benzophenone, methyl benzoate) are also alkylated with propane, butane, and cyclopentane at −40 to 0 °C in the presence of $CBr_4 \cdot 2AlBr_3$ complexes in solutions in CH_2Br_2.[135] Each of the reactions of propane and cyclopentane with 1,2,4-trichlorobenzene at −20 °C for 30 min gives a single alkylation product in high yield.



(86%)



(77%)

The alkylation of dihalobenzenes occurs less selectively. The reaction of *p*-dibromobenzene is accompanied by disproportionation to give mono- and tribromobenzene derivatives. Dichlorobenzenes do not undergo disproportionation but form mixtures of mono- and dialkylated products. Since mono- and dialkylated products can be separated, it is felt that some of these reactions (Scheme 19) will be of interest for the synthesis.

The reaction with alkanes and cycloalkanes in the presence of excess arene and CH_2X_2 as the solvent can follow a different pathway to give alkylated diarylmethane derivatives.[133]

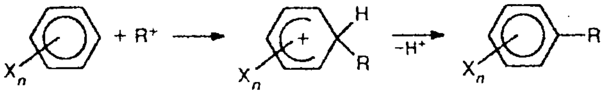
$$2\ C_6H_5Cl + CH_2X_2 + C_5H_{10} \xrightarrow{20\ ^{\circ}C}$$

$$\longrightarrow ClC_6H_4CH_2C_6H_3(Cl)R + ClC_6H_4CH_2C_6H_2(Cl)R_2$$

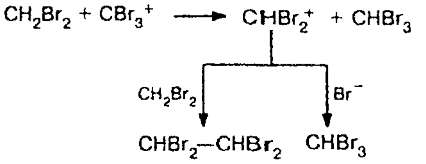
$R = C_5H_9,\ C_5H_7$

Most likely, the alkylation of arenes with alkanes occurs according to the usual scheme of electrophilic substitution.[135]

$$RH \xrightarrow{E^+} R^+$$

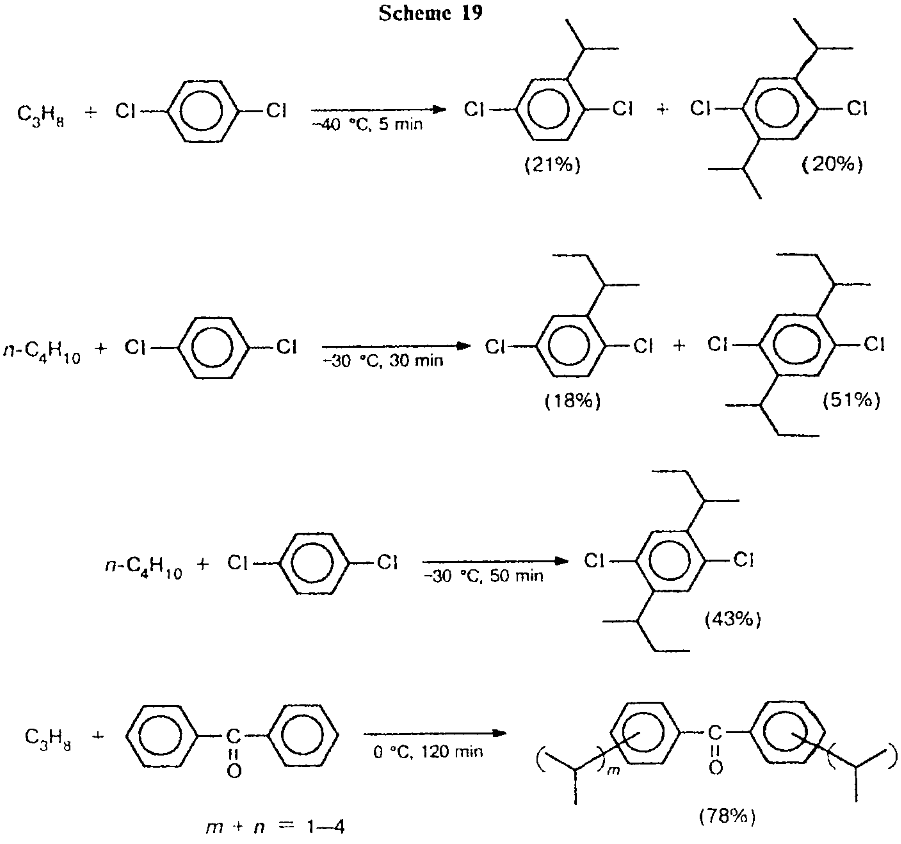


The alternative mechanism analogous to reactions of superelectrophiles with alkanes, in which the superelectrophile accepts a hydride ion from the arene to give an Ar^+ cation,[137] can be ruled out. In fact, when an alkane was absent, not even traces of $CHBr_3$ were detected upon treatment of C_6F_5H or $C_6H_4Br_2$ with $CBr_4 \cdot 2AlBr_3$ in CH_2Br_2. It is interesting that in the absence of an arene, reduction of the $CBr_4 \cdot 2AlBr_3$ with dibromomethane to give $CHBr_3$ in 20% yield was observed under the same conditions.[135]



The explanation for the suppression of hydride transfer from CH_2Br_2 to the cation by arenes is probably that the electrophilic attack of the cation on the arene with formation of Wheland σ-complexes is the dominating process. Thus, arenes are poorer hydride ion donors than alkanes and dihalomethanes. The results of alkylation of passivated arenes with alkanes dispel the idea that arenes more passivated than monohalobenzenes cannot be alkylated in the presence of electrophiles.[138]

Scheme 19

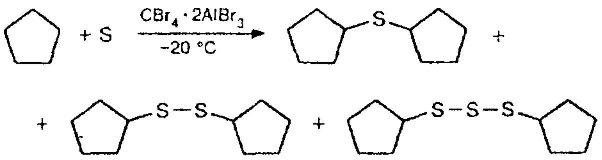


Facile sulfurization of propane and cycloalkanes with elemental sulfur

Propane reacts with sulfur at 20 °C in the presence of $CBr_4 \cdot 2AlBr_3$ in CH_2Br_2 to give diisopropyl sulfide in 2 h in 60% yield with respect to sulfur.[139] A small amount of the corresponding disulfide is also formed.

$$C_3H_8 + S \longrightarrow Pr^i{-}S{-}Pr^i + Pr^i{-}S{-}S{-}Pr^i$$

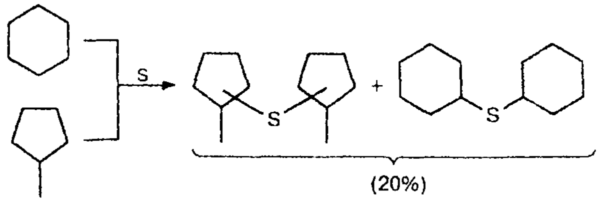
The reaction of cyclopentane with elemental sulfur in the presence of $CBr_4 \cdot 2AlBr_3$ occurs particularly readily. At −20 °C, dicyclopentyl sulfide is formed in 71% yield with respect to sulfur even in 5 min, and it is formed in nearly quantitative yield in 20 min. The reaction is selective: the corresponding di- and trisulfides are either completely absent or formed in an overall yield no more than 6%.



The equimolecular $CBr_4 \cdot AlBr_3$ complex is noticeably less active in this reaction, while the CH_2Br_2—$AlBr_3$ system is totally inert. The yield of the sulfide is as small as 30% in the presence of $CCl_4 \cdot 2AlBr_3$, as opposed to the 99% yield when the reaction is initiated with $CBr_4 \cdot 2AlBr_3$ under the same conditions. In addition to a threefold decrease in the sulfide yield, the use of $CCl_4 \cdot 2AlBr_3$ markedly increases the content of di- and trisulfides. On the contrary, $CCl_4 \cdot nAlBr_3$ systems ($n \geq 3$) can be used successfully instead of $CBr_4 \cdot 2AlBr_3$. The yields of dicyclopentyl sulfide decrease abruptly with an increase in the S : $CBr_4 \cdot 2AlBr_3$ ratio (m): at m = 1.2, the yield is 72%, while at m = 2.0, it is only 8% (in parallel with the decrease in the yield, the selectivity of monosulfide formation also decreases).

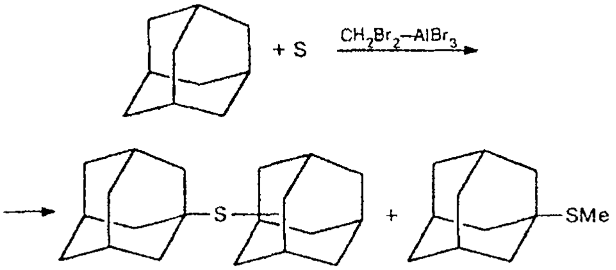
It was shown that in the absence of a saturated hydrocarbon, sulfur reacts with the $CBr_4 \cdot 2AlBr_3$ (or $CCl_4 \cdot 3AlBr_3$) complex in CH_2Br_2 with liberation of molecular bromine. It is this reaction of sulfur with the superelectrophilic system that suppresses the sulfurization of saturated hydrocarbons. For example, sulfur pretreated with the $CCl_4 \cdot 2AlBr_3$ system in CH_2Br_2 at 20 °C for 20 min is inactive in the reaction with cyclopentane.

The reaction of cyclohexane or methylcyclopentane with sulfur in the presence of the $CCl_4 \cdot 3AlBr_3$ (or $CBr_4 \cdot 2AlBr_3$) system at −20 °C results in a small amount of di(methylcyclopentyl) sulfide or a mixture of the latter with dicyclohexyl sulfide in an overall yield not exceeding 20%. These transformations occur with low selectivity.



Thus, the difference between the behavior of cyclopentane and cyclohexane (or methylcyclopentane) in the reaction with sulfur is quite significant (as opposed to their similar reactivity in other transformations initiated by superelectrophiles).

Adamantane does not form a sulfur-containing product in the presence of $CBr_4 \cdot 2AlBr_3$ at −20 °C. However, the action of a much weaker electrophilic system, CH_2Br_2—$AlBr_3$, at room temperature for 20 h gives a mixture of isomeric 1,1- and 1,2-diadamantyl sulfides (in the 4 : 1 ratio) and methyl adamantyl sulfide in 60% overall yield.

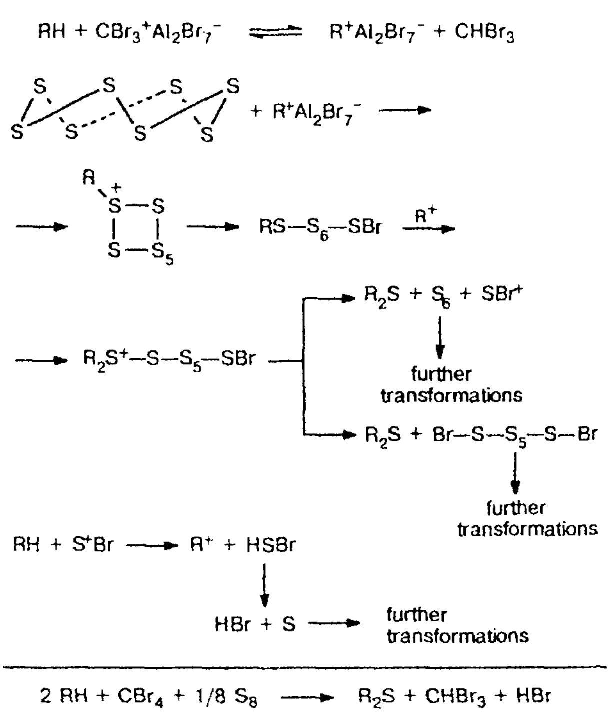


Two alternative reaction mechanisms of saturated hydrocarbons with elemental sulfur in the presence of complexes of polyhalomethanes with aluminum halides have been considered in our recent work.[139] The first presumes the initial generation of a carbocation, which alkylates the S_8 cycle with its subsequent opening (Scheme 20). The carbocation then attacks the sulfur atom of the S—R fragment, since the electron-donating properties of this atom are enhanced in comparison with those of nonalkylated S atoms. The final reaction products include R_2S, HBr, and the reduced polyhalomethane. Exhaustive reduction of CX_4 to $CHBr_3$ is actually observed during the sulfurization of hydrocarbons.

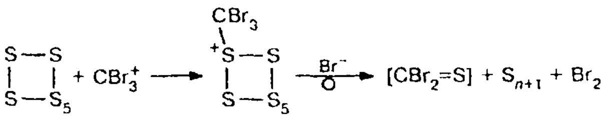
The second mechanism involves the initial attack of the sulfur cycle by the superelectrophilic complex. It is possible that this pathway transforms sulfur to an inactive compound through an irreversible redox process (Scheme 21).

The difference in the behavior of cyclopentane and cyclohexane (or methylcyclopentane) may be explained by quicker alkylation of sulfur by secondary cyclopentyl cation in comparison with tertiary methylcyclopentyl cation, which is formed from both C_6 cycloalkanes at low temperature. At +20 °C, the competing reaction of sulfur with a superelectrophilic system occurs very

Scheme 20



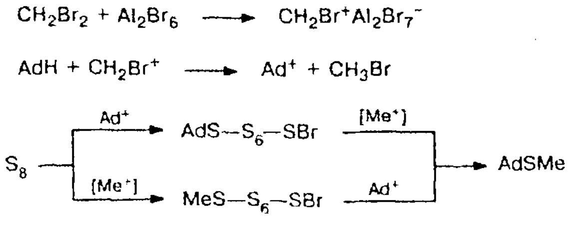
Scheme 21



quickly, as well as transformations of cyclohexane (or methylcyclopentane) without the participation of sulfur to give dimethyldecalins, bromides, and other products.

As regards adamantane, it has already been noted above that generation of the Ad^+ cation does not require a strong electrophile. Possibly, the failure to carry out the sulfurization of adamantane on treatment with the $CBr_4 \cdot 2AlBr_3$ superelectrophilic system is explained by the instability of Ad_2S in the presence of strong electrophiles. The formation of AdSMe can be demonstrated by Scheme 22.

Scheme 22



The difference in the structure of products of sulfurization of alkanes and cycloalkanes with the $RCOX \cdot 2AlX_3$ and $CBr_4 \cdot 2AlBr_3$ systems is probably caused by the relative stability of S—COR bonds in comparison with the $S—CBr_3$ bond.

The nature of active complexes generated in polyhalomethane—AlX_3 systems

There are no spectroscopic data for polyhalomethane—AlX_3 systems. On the contrary, complexes formed from polyhalomethanes on treatment with SbF_5 have been studied in solutions[140] and in the solid state.[141] The formation of trihalomethyl cations was first observed upon the action of an excess of SbF_5 on tetrahalomethanes.[140] In all cases, the ^{13}C NMR spectrum contained the only resonance signal shifted downfield by 159—235 ppm relative to the signal of the corresponding CX_3H (X = Cl, Br, I).

$$CX_4 \xrightarrow[-70\ ^\circ C,\ SO_2ClF]{nSbF_5} CX_3{}^+Sb_nF_{5n}X^-$$

Based on NMR spectra, the observed complexes were assigned an ionic structure.[140] The thermodynamic stability of $CX_3{}^+$ cations, as distinct from the methyl cation which does not exist as a long-lived particle in solutions, was explained by efficient p—π interaction of free electron pairs with the positively charged carbon atom. Cocondensation of CCl_4, as well as $CHCl_3$ and CH_2Cl_2, with SbF_5 at 77 K on CsF-glasses followed by increasing the temperature to 150 K resulted in ionic complexes of $CCl_3{}^+$, $CHCl_2{}^+$, and $(ClCH_2)_2Cl^+$, respectively, with $Sb_2F_{10}Cl^-$ anions, which were characterized by IR spectra.[141] It was also shown that the $CCl_3{}^+$ cation readily abstracts a hydride ion from alkanes and cycloalkanes, generating the corresponding carbocations.[141]

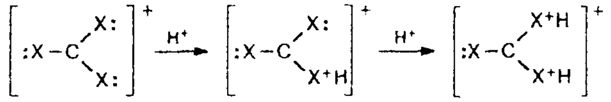
In order to find the reasons of the superelectrophilic properties of polyhalomethanes in the presence of strong Lewis and protic acids, quantum-chemical calculations were carried out.[142—144] Semiempirical and nonempirical calculations of $CCl_4 \cdot nAlCl_3$ (n = 2 or 3) and $CBr_4 \cdot 2AlBr_3$ complexes and $CX_3{}^+$, $CHX_2{}^+$, CHX^{2+}, and $CX_2{}^{2+}$ cations (X = Cl, Br, I, but not F) showed[142,143] that, strictly speaking, polyhalomethyl cations, both free and those included in cationic and dicationic complexes $CX_3{}^+Y^-$ and $CX_2{}^{2+}Y_2{}^-$ (Y = $AlBr_4$ or Al_2Br_7), are not carbenium ions. Rather, they are halenium cations or cationic complexes containing monocoordinate, positively charged halogen atoms directly bound to an electron-deficient carbon atom in $X_2C=X^+$ or $X^+=C=X^+$. To put it another way, transfer of electron density from free electron pairs of the halogen to the carbocation is so significant that a large positive charge is localized on the halogen atoms, whereas the carbon atoms bear only a very small positive or zero charge, or even a considerable negative charge. Halenium

Table 4. Distribution of charge (q) on atoms in polyhalomethyl cations and dications[142]

Particle	q/au			Particle	q/au		
	q_X	q_C	q_H		q_X	q_C	q_H
CF_3^+	0.09	0.71		$HCBr_2^+$	0.46	−0.17	0.25
CCl_3^+	0.32	0.02		HCI_2^+	0.53	−0.29	0.23
CBr_3^+	0.43	−0.28		CF_2^{2+}	0.47	1.06	
CI_3^+	0.51	−0.52		CCl_2^{2+}	0.94	0.12	
HCF_2^+	0.07	0.54	0.31	CBr_2^{2+}	1.04	−0.07	
$HCCl_2^+$	0.35	0.04	0.25	CI_2^{2+}	1.04	−0.08	

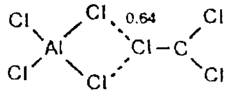
cations differ fundamentally from the known halonium cations.[145] Some data on the charge distribution in polyhalomethyl cations[142] are presented in Table 4. Similar results were obtained by other authors as well.[146,147]

The question arises whether the superelectrophilic properties of the systems in question are related to the formation of halenium cations, or if there are other, more electrophilic cations that determine their specific features. One might expect that protonation (or formation of donor-acceptor complexes with Lewis acids) of halomethyl cations would increase the electrophilicity of cationic particles, and that it is these multicharged particles that are responsible for the superelectrophilic properties of polyhalomethanes in the presence of protic and aprotic superacids, as is the case in systems containing acylium salts in the presence of strong protic and aprotic acids.[144]



Calculations showed that the monoprotonation of trihalomethyl cations requires 70—84 kcal mol^{-1}, while their diprotonation requires 150—170 kcal mol^{-1}. However, both cations are stable to deprotonation. For example, the deprotonation barriers for CBr_3H^{2+}, $CBr_3H_2^{3+}$, and $CBr_3H_3^{4+}$ are 74, 37, and 8 kcal mol^{-1}, respectively, *i.e.*, at least the di- and trications, once formed, are rather stable. Hence, the calculations support the possible formation of multicharged ions from polyhalomethanes in protic superacids.[144]

Conversely, semiempiric and nonempiric calculations did not confirm the possibility of existence of the $CCl_3^+ \rightarrow AlCl_3$ cation.[143] Instead, two very weak complexes can exist. The first can be considered as the $^+Cl_3C...ClAlCl_2$ solvate. In the second complex, $AlCl_3$ does not play its usual role of a Lewis acid. Instead, it has the function of a donor of Cl^- toward the positively charged chlorine atom of the trichloromethyl cation: $Cl_2CCl^+...Cl^-AlCl_2$. Bidentate complex **24** with a large positive charge on the nodal chlorine atom (0.64 au (*ab initio*), 0.54 au (AM1), while in the free CCl_3^+ cation, the charge of the Cl atom is 0.51 au (*ab initio*) and 0.33 au (AM1)) is assumed[143] to be the most likely candidate for the role of a superelectrophile.

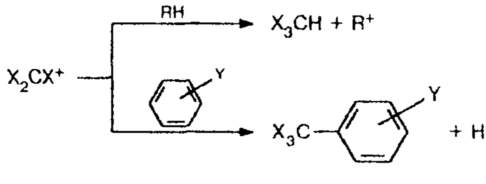


24

The formation of this complex requires 33 kcal mol^{-1} (*ab initio*) or 53 kcal mol^{-1} (AM1). The fact that CX_3^+ cations extremely easily and irreversibly accept a hydride ion from nonactivated alkanes and cycloalkanes indicates that halenium cations are more powerful superelectrophiles than alkyl cations.

$$CX_3^+ + RH \longrightarrow CHX_3 + R^+$$

Further studies are necessary in order to decide conclusively on the nature of active particles generated from polyhalomethanes on treatment with strong acids. It is also essential to study the mechanism of hydride ion transfer from an alkane (or an aromatic fragment from an arene) to the carbon atom of the trihalomethyl cation, which bears no positive charge.



The unusual order of activity of polyhalomethanes in the presence of protic and aprotic superacids[106,144,148] also deserves explanation.

Decrease in cation stability

$$\longrightarrow$$
$$CX_3^+,\ CHX_2^+,\ CH_2X^+$$
$$\longleftarrow$$

Increase in reactivity

In accordance with the expected order of stability of halomethyl cations, which decreases as the number of halogen atoms decreases, $CCl_3^+Y^-$ is stable at temperatures below −50 °C, $CHCl_2^+Y^-$ is stable at 150 K, while $CH_2Cl^+Y^-$ ($Y = Sb_2F_{10}Cl$) is not observed at all. Instead, cationic complex $(ClCH_2Cl^+CH_2Cl)Y^-$ is formed.[140] The methyl cation, which is the final member of this sequence, also does not exist under the conditions where CX_3^+ and CHX_2^+ were observed. It is possible that the highly reactive CHX_2^+ and CH_2X^+ complexes react very quickly with the starting polyhalomethanes, and one has actually to compare the reactivity of a series different from the one shown above:

$$CX_3^+,\ X_2CHX^+CHX_2,\ XCH_2X^+CH_2X$$
$$\longleftarrow$$

Increase in reactivity

Scheme 23 summarizes the types of reactions of alkanes and cycloalkanes initiated by complexes of polyhalomethanes with aluminum halides.

Scheme 23

a. Catalytic cracking

$n\text{-}C_nH_{2n+2} \longrightarrow i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + i\text{-}C_6H_{14}$ + oligomer

The conversion is up to 200 mol

b. Catalytic isomerization

$n\text{-}RH \longrightarrow i\text{-}RH$

(26 mol)

$RH = C_4H_{10}, C_5H_{12}$

c. Sulfurization of alkanes and cycloalkanes

$2\,RH + S \longrightarrow R_2S$

(20—100%)

d. Bromination (stoichiometric and catalytic reactions)

$RH + CHBr_3 \xrightarrow{2\,AlBr_3} RBr + CH_2Br_2$

(60—80%)

$RH = C_2H_6, C_3H_8$, *cyclo*-C_5H_{10}, AdH

$C_2H_6 + Br_2 \longrightarrow 1,2\text{-}C_2H_4Br_2$

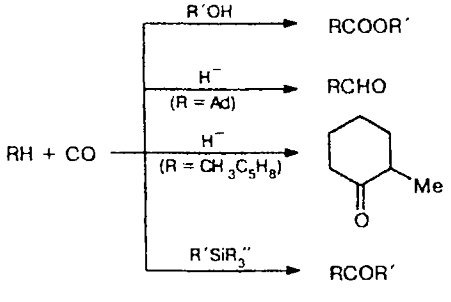
(100% with respect to Br_2)

$RH + Br_2 \longrightarrow RBr + HBr$

(6 mol)

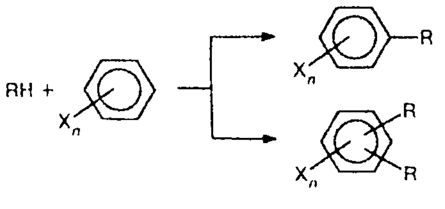
$RH = C_3H_8, C_4H_{10}$, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, *etc.*

e. Reactions with CO



(Yields 60—150%)

f. Alkylation of deactivated arenes with alkanes and cycloalkanes



Novel inorganic aprotic superacids for low-temperature transformations of alkanes and cycloalkanes

Olah classified aprotic superacids as Lewis acids stronger than anhydrous aluminum chloride.[149] Until recently, inorganic aprotic superacids were restricted exclusively to salt systems.[28—34] New types of such systems have been discovered in recent years.

Sulfur-containing inorganic aprotic superacids

It was shown[150] that in the presence of the $SOCl_2 \cdot nAlX_3$, $SO_2Cl_2 \cdot nAlX_3$, $MeSO_2Cl \cdot nAlX_3$, $CF_3SO_2Cl \cdot nAlX_3$, and $S_2Cl_2 \cdot nAlX_3$ systems (X = Cl, Br; n = 2 or 3) in a solution in CH_2Cl_2, octane is converted into cracked products, the conversion being 60—96% after 10—30 min (Table 5). Under similar conditions, both $AlCl_3$ and the corresponding equimolecular complexes (n = 1) are inactive, and the conversion of octane in the presence of $AlBr_3$ does not exceed 20%. Lower C_4—C_6 isoalkanes are the main cracking products. In addition, sulfur-containing oligomers, which are branched unsaturated hydrocarbons with molecular weights of *ca.* 500, are formed. It is important that not only systems based on $AlBr_3$ but also those containing $AlCl_3$ display high activity in the octane cracking. The initiating effect of SO_2Cl_2, $MeSO_2Cl$, and S_2Cl_2 changes dramatically on moving from the $A \cdot 2AlCl_3$ to the $A \cdot 3AlCl_3$ systems (where A is a sulfur-containing compound), whereas this difference is less pronounced in the corresponding systems based on $SOCl_2$ and CF_3SO_2Cl.

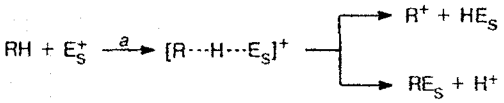
Table 5. Comparison of the activity of sulfur-containing inorganic aprotic superacids and aluminum halides (E) in octane cracking (20 °C, [octane] : [E] = 10 : 1, in CH_2Cl_2)[148]

E	Conversion of octane (%)			
	10 min	20 min	30 min	60 min
2 $AlCl_3$	—	0	3	2
3 $AlCl_3$	—	—	0	—
$SOCl_2 \cdot AlCl_3$	—	0	2	—
$SOCl_2 \cdot 2AlCl_3$	—	58	71	79
$SOCl_2 \cdot 3AlCl_3$	—	86	93	—
$SO_2Cl_2 \cdot AlCl_3$	—	—	6	—
$SO_2Cl_2 \cdot 2AlCl_3$	—	—	34	49
$SO_2Cl_2 \cdot 3AlCl_3$	—	—	96	—
$MeSO_2Cl \cdot 2AlCl_3$	—	—	44	—
$MeSO_2Cl \cdot 3AlCl_3$	—	—	77	92
$CF_3SO_2Cl \cdot 2AlCl_3$	—	—	59	—
$CF_3SO_2Cl \cdot 3AlCl_3$	—	—	68	94
$S_2Cl_2 \cdot 2AlCl_3$	—	—		31
$S_2Cl_2 \cdot 3AlCl_3$	—	—	67	—
$S_8 \cdot 3AlCl_3$	—	—	—	0
2 $AlBr_3$	17	20	—	—
$SOCl_2 \cdot 2AlBr_3$	68	74	—	—
$SO_2Cl_2 \cdot 2AlBr_3$	66	72	—	—
$S_2Cl_2 \cdot 2AlBr_3$	38	40	—	—

Like octane, *n*-alkanes C_5—C_{12} also undergo cracking to give qualitatively similar mixtures of lower isoalkanes and oligomers. Selective isomerization of *n*-pentane has also been carried out in the presence of a catalytic amount of $SOCl_2 \cdot 2AlCl_3$: at 20 °C, 1 mol of the superacid catalyzes the formation of 80 mol of isopentane with 88% selectivity.

Sulfur-containing compounds are absent among volatile products of alkane transformations. However, one might assume that the reaction of saturated hydrocarbons, which are relatively resistant to cracking, with sulfur-containing superelectrophiles would lead to alkane sulfurization according to Scheme 24.

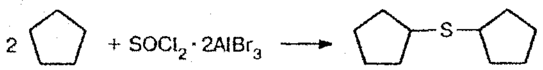
Scheme 24



$$R^+ + :Nu_S \xrightarrow{b} RNu_S^+ \longrightarrow \text{further transformations},$$

E_S^+ — sulfur-centered electrophile, $:Nu_S$ — sulfur-centered nucleophile.

In fact, it was shown that the action of $SOCl_2 \cdot 2AlBr_3$ on cyclopentane in CH_2X_2 (X = Cl, Br) at 20 °C for 2 h gives dicyclopentyl sulfide in 30% yield with respect to $SOCl_2 \cdot 2AlCl_3$.



25

The fact that the reactions of alkanes with $SOCl_2 \cdot 2AlX_3$ do not produce volatile sulfur-containing products (apart from SO_2) provides a reason to assume that reduction of $SOCl_2$ with a saturated hydrocarbon gives elemental sulfur as the final product, which then reacts with unsaturated cracking products. If this is the case, the role of the $SOCl_2 \cdot 2AlBr_3$ superelectrophilic complex in the reaction with cyclopentane is the generation of the cyclopentyl cation with simultaneous reduction of the sulfur-containing superelectrophile to elemental sulfur, which then reacts with the cyclopentyl cation (Scheme 25).

Scheme 25 is consistent with data on the instability of HSOX and SO,[151] slow accumulation of compound **25**, and its small yield with respect to $SOCl_2 \cdot 2AlBr_3$. According to this scheme, the maximum yield of R_2S is 50% with respect to the complex.

The action of sulfur chlorides and oxochlorides in the presence of aluminum halides on alkanes and cycloalkanes has not been studied. The reaction of adamantane with an excess of $SOCl_2$ in the presence of $AlCl_3$, which gives 1,3,5-trichloroadamantane at 20 °C and AdSOCl at −15 °C in a high yield, was reported.[152] The assumed scheme of adamantane chlorosulfinylation

Scheme 25

$$SOCl_2 \xrightarrow{AlBr_3} [SOX^+AlX_4^-] \xrightarrow{AlBr_3} [SOX^+Al_2X_7^-]$$

X = Cl, Br

$$\begin{array}{l} RH + SOX^+ \longrightarrow R^+ + [HSOX] \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad HX + SO \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad 1/2\ S + 1/2\ SO_2 \end{array}$$

$$2\ R^+ + S \longrightarrow R_2S$$

$$\overline{2\ RH + 2\ SOCl_2 \longrightarrow R_2S + 2\ HCl + SO_2 + Cl_2}$$

does not include the participation of the $SOCl_2 \cdot AlCl_3$ complex:

$$AdH \xrightarrow{AlCl_3} Ad^+,$$

$$Ad^+ + SOCl_2 \longrightarrow AdSOCl + Cl^+.$$

The radical chlorosulfinylation and chlorination of alkanes on treatment with SO_2 and Cl_2 under irradiation has also been studied.[153]

Some complexes of sulfur chlorides and oxochlorides with aluminum chloride have been described in the literature, although data for these compounds are very scarce.[154—159] It was shown[154] that refluxing $AlCl_3$ with an excess of $SOCl_2$ followed by removal of the latter gives the $SOCl_2 \cdot 2AlCl_3$ complex (**26**) as an oily liquid with m.p. 214—215 °C. Heating compound **26** gives the equimolecular complex, which was assigned the structure of a donor-acceptor complex $Cl_2SO{\rightarrow}AlCl_3$ (**27**) based on its Raman spectra.[155] The assumptions on the structure of complex **26** are less certain. It was assumed[155] that this complex is the donor-acceptor complex **27** weakly bound to an additional second molecule of $AlCl_3$. Potentiometric and conductometric studies indicate that the $SOCl_2 \cdot AlCl_3$ complex is dissociated very weakly:[156]

$$SOCl_2 \cdot AlCl_3 \overset{K}{\rightleftharpoons} SOCl^+AlCl_4^-$$

$$(K = 1 \cdot 10^{-4}).$$

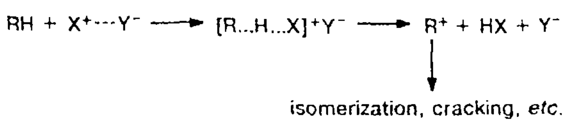
The structure of the $S_2Cl_2 \cdot 2AlCl_3$ complex obtained in SO_2Cl_2 [157] was later reconsidered.[158] It was found that in reality, it is the $SCl_3^+AlCl_4^-$ ionic salt.[159]

The $SOCl_2 \cdot nAlCl_3$ systems (*n* = 1 and 2) were studied by the *ab initio* method.[160] It was shown that at *n* = 1, the PES contains two minima corresponding to two complexes: $Cl_2SO \rightarrow AlCl_3$ and $Cl_3SOAlCl_2$. At $n = 2$, the PES has also two minima which correspond to analogous donor-acceptor complexes involving the Al_2Cl_6 dimer: $Cl_2SO \rightarrow Al_2Cl_6$ and $Cl_3SO(AlCl_2)_2Cl$. No energy minima corresponding to ionic complexes were found, which indicates their instability. However, calculations show that the formation of the $SOCl^+Al_2Cl_7^-$ complex at $n = 2$ is more favorable (by 17 kcal mol^{-1}) than that of the $SOCl^+AlCl_4^-$ complex at $n = 1$. At $n = 3$, the formation of the $Cl_2SOAlCl_2^+$ cation with two strong electrophilic centers (at the S and Al atoms) becomes more favorable than the formation of $SOCl^+$.[160]

Halogens in the presence of aluminum halides as initiators of cracking and isomerization of alkanes

It was found unexpectedly that halogens in the presence of aluminum halides also act as aprotic inorganic superacids. For example, $Br_2 \cdot nAlX_3$, $Cl_2 \cdot nAlX_3$ (X = Cl, Br; n = 1 or 2), and $I_2 \cdot 2AlBr_3$ are active catalysts of the cracking of C_5—C_{12} n-alkanes.[161] Octane is converted almost completely into cracked products at 20 °C in 10—20 min on treatment with $X_2 \cdot nAlBr_3$ systems (X = Cl, Br, I). The cracking occurs at high initial rate: the turnover number is 1.42 min^{-1}. Systems based on $AlCl_3$ are markedly less active. However, the degree of octane conversion into cracked products reaches 80% in 20 min even with these systems. Conversely, the activity of $I_2 \cdot 2AlCl_3$ is no higher than that of Al_2Cl_6.

It is interesting that these classical ionic halogenating systems behave as usual electrophilic cracking initiators giving lower alkanes and oligomers. Volatile products of reactions of alkanes and $Br_2 \cdot 2AlBr_3$ contain virtually no bromides, and the content of bromine in the oligomers is also small (8% with respect to the bromine contained in the $Br_2 \cdot 2AlBr_3$ system). The assumed reaction scheme involves the electrophilic attack of an alkane by a superelectrophilic complex containing a positively charged halogen.

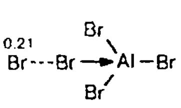


$$RH + X^+\cdots Y^- \longrightarrow [R...H...X]^+Y^- \longrightarrow R^+ + HX + Y^-$$

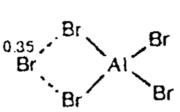
$$\downarrow$$

isomerization, cracking, *etc.*

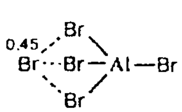
The nature of particles containing a positively charged halogen atom, which are formed on treatment of halogens with Lewis acids, is uncertain, despite the large number of papers on the subject.[162—169] The participation of Br^+ complexes in electrophilic reactions of Br_2 has been postulated by many authors. A quantum-chemical calculation of the $Br_2 \cdot AlBr_3$ system showed the possibility of formation of three complexes (**28a—c**), which can be considered as a Br^+ cation coordinated in a mono-, bi-, or tridentate way with $AlBr_4^-$ and in which the charges on the Br atom are +0.21, +0.35, and +0.45 au, respectively.[170,171]



28a



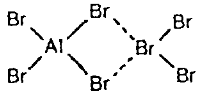
28b



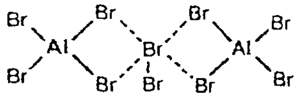
28c

The stability of tridentate complex **28c** with the highest positive charge on the Br atom is slightly smaller (by less than 10 kcal mol^{-1}) than that of the most stable monocoordinate isomer.[171]

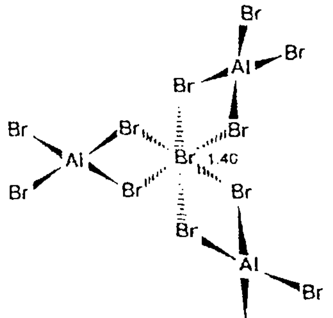
The assumption that two Br_2 molecules participate in the formation of active complexes in $mBr_2 \cdot nAlBr_3$ systems, *i.e.*, coordination is preceded by dimerization to give an angular or trigonal Br_4 molecule, revealed the principal possibility of generating new types of complexes with considerably higher positive charges on bromine atoms[170] (up to 1.40 au). These complexes may be regarded as Br^+ bound in a bidentate manner to one (**29a**), two (**29b**), or three (**29c**) $AlBr_4^-$ anions.



29a, $Br_4 \cdot AlBr_3$



29b, $Br_4 \cdot 2AlBr_3$



29c, $Br_4 \cdot 3AlBr_3$

Studying the mechanisms of alkane reactions with electrophiles **28** and **29** will make it possible to evaluate their role in reactions of alkanes with the $Br_2 \cdot nAlBr_3$ system.

Boron- and phosphorus-containing inorganic aprotic superacids

In continuation of works on the elaboration of new aprotic superacids for low-temperature transformations of alkanes and cycloalkanes, the activity of a series of systems containing halides of III—VI Group elements combined with aluminum halides was studied. The cracking of n-octane at 20 °C in a solution in CH_2Br_2 at a molar ratio octane : E system = 10 : 1 was chosen as the model reaction. The degree of octane conversion into cracked products over 10 min served as the measure of activity. The results obtained are listed below.

E	Conversion of octane (%)	E	Conversion of octane (%)
Al_2Cl_6	3	$SnCl_4 \cdot 2AlBr_3$	27
Al_2Br_6	18	$TiCl_4 \cdot 2AlBr_3$	36
$BBr_3 \cdot 2AlBr_3$	78	$PBr_3 \cdot 2AlBr_3$	77
$BBr_3 \cdot 2AlCl_3$	17	$PCl_3 \cdot 2AlBr_3$	9
$SiCl_4 \cdot 2AlBr_3$	28	$PBr_3 \cdot 2AlCl_3$	17
$GeCl_4 \cdot 2AlBr_3$	32		

The considerably higher activity of $BBr_3 \cdot 2AlBr_3$ and $PBr_3 \cdot 2AlBr_3$ in comparison with that of the CH_2Br_2—$AlBr_3$ superacid indicates that new superelectrophilic complexes are generated in these systems. The $AlCl_3$-catalyzed phosphorylation[172] of aromatic hydrocarbons with PCl_3 and their boration[173] with BCl_3 are well known.

The dichlorophosphorylation of saturated hydrocarbons on refluxing with PCl_3 in the presence of a small excess of $AlCl_3$ ($RH : PCl_3 : AlCl_3 = 1.0 : 1.1 : 1.3$) has been reported.[174]

$$RH \xrightarrow{1)\ PCl_3,\ AlCl_3;\ 2)\ H_2O} \underset{\mathbf{30}}{RPOCl_2}$$

The yields of product **30** were 40—60% over 16—24 h in the case of alkyladamantanes and diadamantanes, and 18 and 10% in the case of cyclopentane and isobutane, respectively. The authors[174] believe that the generation of a carbenium ion (or polarized RX), which then adds to PCl_3, from the saturated hydrocarbon upon the action of the CH_2Cl_2—$AlCl_3$ system, is the key stage of the reaction.

$$RH \xrightarrow{CH_2Cl_2-AlCl_3} RCl \xrightarrow{PCl_3-AlCl_3}$$

$$\longrightarrow RP^+Cl_3\ AlCl_4^- \xrightarrow{H_2O} \mathbf{30}$$

The formation of X_2P^+ and X_2B^+ in solutions has not been observed,[174—176] although Cl_2P^+ cation (the most intense fragment ion in the mass spectrum of PCl_3)[177] and $(NMe)_2B^+$, an analog of Cl_2B^+, have been reported.[176] The fact that the activity of CH_2X_2—AlX_3 systems increases strongly in the presence of phosphorus and boron halides probably indicates that new boron- and phosphorus-containing superelectrophiles are formed in these systems.

Conclusion

The approach to the development of superelectrophilic systems of the new type based on the activation of molecules with several nucleophilic centers upon the action of one or several molecules of an aluminum halide was found to be quite fruitful and led to the elaboration of new groups of highly active aprotic organic and inorganic superacids.

The discovery of new superelectrophilic complexes has enriched alkane chemistry considerably. Using these complexes, stoichiometric and catalytic transformations of alkanes and cycloalkanes have been carried out, such as cracking, isomerization, alkylation, and a broad spectrum of direct one-step functionalizations. It is important that most of the reactions are characterized by good yields, high selectivity, and higher efficiency than those with the most active electrophilic systems, including the strongest protic superacids. Some of the reactions present new types of alkane reactions. The high yields, good selectivity, and ease of performing one-step functionalization, as well as the accessibility of superelectrophilic complexes that can be obtained by simple mixing of the components, give us a reason to hope that some of the reactions found can be of interest as methods for the synthesis of organic compounds from alkanes. The elaboration of facile methods for the regeneration of aluminum halides would be a significant success for the development of organic synthesis on the basis of alkanes and cycloalkanes.

The chemical, physicochemical, and quantum-chemical studies have provided valuable data on the nature of new active superelectrophiles, revealed a remarkable diversity of superelectrophile types, and posed new fascinating problems in the field of superelectrophilic alkane chemistry.

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