A Novel Family of Aprotic Organic Superacids for Low-temperature Alkane and Cycloalkane Transformations

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The $CBr_4 \cdot nAlBr_3$, $CHBr_3 \cdot nAlBr_3$, $CCl_4 \cdot 2AlBr_3$, $CHCl_3 \cdot 2AlBr_3$ and $CH_2Br_2 \cdot nAlBr_3$ (n = 1,2) systems have been found to catalyse various transformations of alkanes and cycloalkanes under mild conditions.

Recently, we have found that aprotic organic superacids (AOSs)—complexes of acyl halides with aluminium halides (2 mol) $RCOX \cdot 2AlX_3$ (X = Br, Cl; R = alkyl, Ar)—display high activity in the low-temperature transformations of n-alkanes and cycloalkanes including cracking, isomerization, alkylation and functionalization reactions.[1]

In our search for new AOSs and in attempts to find effective and simple catalysts for alkane transformations under mild conditions we focused our attention on systems formed by the

combination of $AlBr_3$ with compounds containing several nucleophilic centres.

We have found that the $CBr_4 \cdot nAlBr_3$, $CHBr_3 \cdot nAlBr_3$ (n = 1,2), $CCl_4 \cdot 2AlBr_3$ and $CHCl_3 \cdot 2AlBr_3$ systems, under mild conditions, effectively initiate isomerization of n-alkanes into isoalkanes, cracking of alkanes into C_4–C_6 isoalkanes as the main products as well as bromination of alkanes and cyclo-alkanes (Table 1). The $CH_2Br_2 \cdot nAlBr_3$ systems are markedly less active. Scheme 1 demonstrates the transformations of

Table 1 Some examples of alkane and cycloalkane reactions by the polyhalomethane $\cdot nAlBr_3$ superacids at 20 °C

RH	Superacid (SA)	RH : SA (mol)	t/h	Conversion of RH (%)	Conversion of RH mol per mol SA	Products of RH transformations
$C_2H_6^a$	$CHBr_3 \cdot 2AlBr_3$	3.7 : 1	10	7	0.27	$EtBr(3)$, i-$C_4H_{10}(5.3)^b$
C_3H_8	$CHBr_3 \cdot 2AlBr_3$	2 : 1	0.66	50	1	$Pr^iBr(50)$, $Pr^nBr(7)^c$
C_3H_8	$CBr_4 \cdot AlBr_3$	10 : 1	10	7	0.7	i-$C_4H_{10}(4)$, n-$C_4H_{10}(1)$, i-$C_5H_{12}(2)^d$
n-C_4H_{10}	$CBr_4 \cdot 2AlBr_3$	35 : 1	6	72	25	i-$C_4H_{10}(65)$, i-$C_5H_{12}(7)^d$
n-C_5H_{12}	$CHCl_3 \cdot 2AlBr_3$	40 : 1	3	65	26	i-$C_5H_{12}(51)$, i-$C_4H_{10}(5)$, i-$C_6H_{14}(9)^d$
n-C_5H_{12}	$CCl_4 \cdot 2AlBr_3$	200 : 1	20	89	178	i-$C_4H_{10}(37)$, i-$C_5H_{12}(28)$, i-$C_6H_{14}(24)^{d,e}$
n-C_8H_{18}	$CCl_4 \cdot 2AlBr_3$	10 : 1	0.17	71	7.1	i-$C_4H_{10}(12)$, i-$C_5H_{12}(8)$, i-$C_6H_{14}(8)$, i-$C_7H_{16}(5)$, i-$C_8H_{18}(7)$, oligomers(15)^b
n-$C_{12}H_{26}$	$CCl_4 \cdot 2AlBr_3$	5 : 1	0.17	62	3.1	i-$C_4H_{10}(9)$, i-$C_5H_{12}(6)$, i-$C_6H_{14}(3)$, i-C_7H_{16}–i-$C_{10}H_{22}(7)$, oligomers(18)^b
Adamantane	$CHBr_3 \cdot 2AlBr_3$	2 : 1	1	50	1	1-Bromoadamantane(80), 2-bromoadamantane(5)^c

^{a} At 50–55 °C. ^{b} Weight(%) based on initial RH. ^{c} Mol.(%) on SA. ^{d} Composition of main voltaile products. ^{e} Small amounts of C_7–C_{12} isoalkanes, isomeric $C_6H_5C_3H_7$ and $C_6H_5C_4H_9$ alkylbenzenes are also formed as well as the CBr_4 reduction products, alkylbenzenes are also formed as well as the CBr_4 reduction products, viz. $CHBr_3$ and traces of CH_2Br_2.

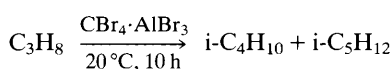alkanes and cycloalkanes by the polyhalomethane-nAlBr$_3$ superacids.†

$$nC_nH_{2n+2} \xrightarrow[20\,°C]{Cat} \text{i-}C_4H_{10} + \text{i-}C_5H_{12} + \text{i-}C_6H_{14} + \ldots \text{oligomers}$$
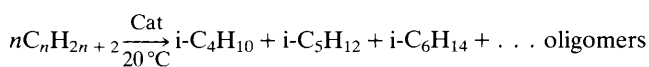
n = 5–12; Cat = CX$_4$·nAlBr$_3$, CHX$_3$·nAlBr$_3$ (X = Cl, Br, n = 1 or 2)

(conversion of C$_8$–C$_{12}$ alkanes 70–80% for 10–20 min)

$$nRH \xrightarrow[20\,°C,\ 3\text{–}6\,h]{Cat} \text{i-RH}$$
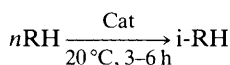
Yield 51–65% (20–25 mol per mol Cat) RH = C$_4$H$_{10}$, C$_5$H$_{12}$; Cat = CBr$_4$·2AlBr$_3$, CHCl$_3$·2AlBr$_3$

$$C_3H_8 \xrightarrow[20\,°C,\ 10\,h]{CBr_4 \cdot AlBr_3} \text{i-}C_4H_{10} + \text{i-}C_5H_{12}$$

(conversion 0.7 mol per mol Cat)

$$C_2H_6 + CHBr_3 \xrightarrow[50\text{–}55\,°C,\ 10\,h]{2AlBr_3} C_2H_5Br + \text{i-}C_4H_{10} + CH_2Br_2$$
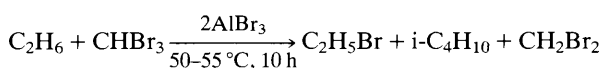
(conversion 0.27 mol per mol Cat)

$$RH + CHBr_3 \xrightarrow[20\,°C,\ 40\,min]{2AlBr_3} RBr + CH_2Br_2$$
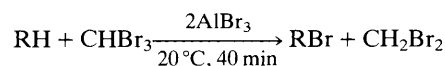
Yield: RBr 60–80%, CH$_2$Br$_2$ 100%
RH = C$_3$H$_8$, AdH (adamantane)

Scheme 1

Contrary to the RCOX·nAlX$_3$ complexes, whose activity is extremely high at n = 2 and completely absent at n = 1,[1] both 1:1 and 1:2 polyhalomethane-nAlBr$_3$ systems display high activity. The influence of an AlBr$_3$ excess on activity of polyhalomethanes is not uniform. In some cases the 1:2 polyhalomethane–AlBr$_3$ systems are more active than the 1:1 systems but in other cases such dependence is not seen.

The order of catalytic activity for pentane transformations [C$_5$H$_{12}$:Cat = 40:1, 20°C, 3 h, conversion in (%)] is as follows:

CBr$_4$·2AlBr$_3$ > CHCl$_3$·2AlBr$_3$ ≥ CBr$_4$·AlBr$_3$ >
  (89)   (77)   (73)
    CHBr$_3$·2AlBr$_3$ ≥ CHBr$_3$·AlBr$_3$ > CH$_2$Br$_2$·2AlBr$_3$.
      (50)   (47)   (30)

Examples of the use of halomethanes for halogenation and carbonylation of alkanes in the presence of SbF$_5$ and HF·SbF$_5$ have been published. Olah et al.[2] have reported chlorination and bromination of alkanes and cycloalkanes by CH$_2$X$_2$ (X = Cl, Br) in the presence of SbF$_5$. Ionization of norbornane, adamantane and n-hexane in the SbF$_5$ matrix in the presence of CCl$_4$ at 150 K was found by Vancik et al.[3] Carbonylation of propane by an excess of HF–SbF$_5$ in the presence of CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$ has been studied by NMR spectroscopy.[4]

Special conditions are necessary for revealing the species responsible for the activity of the systems under consideration. Olah[5] prepared and fully characterized a large series of halonium ions formed under the action of strong protic and aprotic acids on organohalogen compounds; e.g. formation of the XCH$_2$X$^+$CH$_2$X Sb$_2$F$_{10}$X$^-$ salt from CH$_2$X$_2$ and SbF$_5$. On the other hand it has been reported[7] that trihalomethyl cations X$_3$C$^+$ were formed as long-lived species under the action of a fivefold excess of SbF$_5$ on CX$_4$ (X = Cl, Br, I) in SO$_2$FCl at −78°C. The proposed carbenium structure was based on a considerable downfield shift of its C-atom signal compared with the corresponding CX$_3$H in the ^{13}C NMR spectra.

Our recent AM1 calculations[8] show that the CBr$_3{}^+$, CHBr$_2{}^+$ and CH$_2$Br$^+$ cations represent ions of the 'bromenium' type, wherein, contrary to classic carbenium ions, the positive charge is localized exclusively on Br (and H) atoms whereas C atoms have zero or negative charges. According to the calculations 'bromenium' rather than carbenium cations seem to be responsible for the high activity of poly-halomethane-nAlBr$_3$ superacids. We also feel that in the reaction with CBr$_4$ in the presence of an excess of AlBr$_3$ the participation of 'dibromenium' Br$^+$=C=Br$^+$ dication may occur.

The key stage of alkane transformation seems to be hydride ion transfer from RH to species such as CX$_3{}^+$ or X$^+$=C=X$^+$ resulting in the corresponding carbocations (R$^+$) and the reduction of the initial halomethane. The subsequent transformations of R$^+$ lead to cracking, isomerization and other alkane conversion products.

These novel, available and non-toxic poly-halomethane-nAlBr$_3$ superacids exhibiting a markedly higher catalytic activity in comparison with proton superacids[9] and earlier studied AOSs[1] seem to be promising reagents for alkane and cycloalkane transformations under mild conditions.

† *Typical procedures*: (*i*) Octane (1.07 g, 9.4 mmol) was added at room temp. to a stirred mixture of powdered anhydrous AlBr$_3$ (0.5 g, 1.87 mmol) and CCl$_4$ (0.14 g, 0.9 mmol) in a flask equipped for removal of the gaseous reaction products; reaction started immediately. The heterogeneous reaction mixture was stirred for 5 min, hydrolysed with water, extracted with diethyl ether, washed and then dried. n-Octane conversion (0.53 g, 50%) was measured by GLC. (*ii*) A mixture of CCl$_4$ (0.023 g, 0.149 mmol) and pentane (2.18 g, 30 mmol) was added to anhydrous AlBr$_3$ (0.08 g, 0.3 mmol) and the reaction mixture was shaken in sealed-glass ampoule at 20°C for 20 h. Then the ampoule was opened under freezing and connected with an evacuated vessel to collect the volatile reaction products. The gaseous mixture analysed by GLC contained 0.79 g (37%) of isobutane, 0.60 g (28%) of isopentane, 0.52 g (24%) of isohexanes and 0.24 g (11%) of the initial n-pentane (conversion 89%, 178 mol per mol CCl$_4$). Treatment of the residue in the ampoule with water, followed by extraction with diethyl ether and removal of the solvent gave 0.07 g of a high molecular tar. (*iii*) Ethane, propane or butane were condensed on cooling into a glass ampoule containing AlBr$_3$ and halomethane. The sealed ampoule was shaken at room temp. or heated at 50–55°C. Then the volatile reaction products were completely transferred into an evacuated vessel and analysed by GLC.

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