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# Halogens ($Cl_2$, $Br_2$, $I_2$) Activated by Aluminium Halides – Effective Initiators for Low-temperature Alkane Cracking

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The $Br_2{\cdot}nAlX_3$, $Cl_2{\cdot}nAlX_3$ and $I_2{\cdot}nAlBr_3$ systems (X = Cl, Br, $n$ = 1,2) have been found to actively catalyse cracking of $C_5$–$C_{12}$ $n$-alkanes at room temperature.

Halogens in the presence of Lewis acids are widely used for electrophilic halogenation of unsaturated compounds. In elaborating our approach to novel aprotic superacids for low-temperature alkane transformations[1,2] we have found a quite new area for application of these systems.

The $Br_2{\cdot}nAlX_3$, $Cl_2{\cdot}nAlX_3$ (X = Cl, Br; $n$ = 1,2) and $I_2{\cdot}2AlBr_3$ systems turned out to be the active catalysts for $C_5$–$C_{12}$ $n$-alkane cracking. Indeed, at 20 °C for 10–20 min octane is converted almost completely into cracked products by $X_2{\cdot}2AlBr_3$ systems (X = Cl, Br, I). The turnover numbers

**Table 1** Transformations of *n*-alkanes by inorganic superacids at 20 °C.

| Superacid | *n*-RH | RH:Cat (mol) | Conversion of RH, % (mol/mol cat) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 10 min | | 20 min | | 30 min | | 60 min | |
| | | | *a* | *b* | *a* | *b* | *a* | *b* | *a* | *b* |
| $Br_2 \cdot 2AlBr_3$ | $C_8H_{18}$ | 10:1 | 93(9.3) | 57(5.7) | | 76(7.6) | | | | 87(8.7) |
| $Br_2 \cdot AlBr_3$ | $C_8H_{18}$ | 20:1 | 57(11.4) | | 71(14.2) | | | | 73(14.6) | |
| $Br_2 \cdot 2AlBr_3$ | $C_8H_{18}$ | 40:1 | 36(14.2) | | 39(15.6) | | | | 48(19.0) | |
| $Br_2 \cdot AlBr_3$ | $C_8H_{18}$ | 10:1 | 42(4.2) | 34(3.4) | | 35(3.5) | | | | 55(5.5) |
| $Br_2 \cdot 3AlBr_3$ | $C_8H_{18}$ | 10:1 | | 90(9.0) | | | | | | |
| $Br_2 \cdot 2AlCl_3$ | $C_8H_{18}$ | 10:1 | | 38(3.8) | | 80(8.0) | | | | 82(8.2) |
| $Cl_2 \cdot 2AlCl_3$ | $C_8H_{18}$ | 10:1 | | | | 21(2.1) | | | | 72(7.2) |
| $I_2 \cdot 2AlBr_3$ | $C_8H_{18}$ | 10:1 | 79(7.9) | 21(2.1) | 90(9.0) | 32(3.2) | | | | 68(6.8) |
| $I_2 \cdot 2AlCl_3$ | $C_8H_{18}$ | 10:1 | 9(0.9) | 3.5(0.4) | | | | | | 16(1.6) |
| $Br_2 \cdot 2AlBr_3$ | $C_5H_{12}$ | 40:1 | | | | | 44(18) | 33(13.2) | 81(32.6)[c] | |
| $Br_2 \cdot 2AlBr_3$ | $C_{12}H_{26}$ | 5:1 | | 36(1.8) | | 70(3.5) | 96(4.8) | | | 85(4.3) |
| $AlBr_3$ | $C_8H_{18}$ | 5:1 | 28(1.4) | 17(0.85) | | | | | 34(1.7) | |
| $AlCl_3$ | $C_8H_{18}$ | 5:1 | | 8(0.4) | | | | | | 16(0.3) |

[a] In the presence of $CH_2Br_2$ (1 ml per 1.5–2.3 mmol of $AlBr_3$). [b] Without solvent. [c] For 90 min conversion of $C_5H_{12}$ is 96% (38 mol/mol cat).

reach 1.42 $min^{-1}$ (Table 1). The $X_2 \cdot 2AlCl_3$ (X = Br, Cl) systems are less active than the systems based on $AlBr_3$. However, even with these systems octane conversions reach 80% (20 min, X = Br) and 72% (60 min, X = Cl). On the contrary, the activity of $I_2 \cdot 2AlCl_3$ does not surpass that of $AlCl_3$. Dodecane also undergoes rapid cracking by these systems but the number of catalytic cycles is lower in comparison with octane cracking as in other acid-catalysed cracking reactions.[1]

The products of alkane cracking are mainly low $C_4$–$C_6$ isoalkanes and oligomers (Scheme 1, Table 2).[†]

$$RH \xrightarrow[20\,^\circ C]{Cat} i\text{-}C_4H_{10} + i\text{-}C_5H_{12} + i\text{-}C_6H_{14} + \text{oligomers}$$

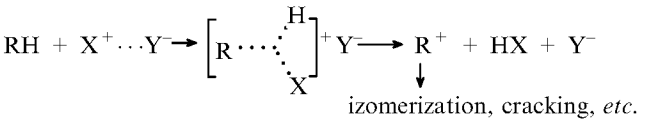
RH = $C_5$–$C_{12}$ alkanes

Cat = $Hal_2 \cdot nAlX_3$ (Hal = Cl, Br, I; X = Cl or Br, $n$ = 1–2)

**Scheme 1**

It is to be noted that the bromo-containing compounds are practically absent in the volatile alkane transformation products of the reaction with $Br_2 \cdot 2AlBr_3$. The bromine content in oligomers is also low (~7.5%). At the same time the main part of bromine (92–98% of the total initial content in $AlBr_3 + Br_2$) was found in water solution after hydrolysis of the reaction mixture. Thus, it is important that the components of this system are hardly involved in the products of alkane conversion, contrary to the $RCOX \cdot 2AlX_3$ complexes.[1]

The most probable reaction path postulated for these reactions is the electrophilic attack of alkane by a positive halogen species resulting in alkane hydride ion abstraction and formation of $R^+$ which further undergoes isomerization and fragmentation reactions (Scheme 2).




**Scheme 2**

The remarkable feature of these reactions is that generated HX is formally formed by $H^-$ (from RH) and $X^+$ (from $X_2$).

Alternative schemes with participation of radical cations or radicals in these and other superacid initiated alkane reactions can not be ruled out although at present there are no reliable data for elucidation of this problem.

The nature of positive halogen species generated under the action of Lewis acids on halogen molecules is not clear in spite of extensive investigations devoted to this problem.[3–10] The $X^+ \cdots Y^-$ species, often postulated for electrophilic halogenation and, in particular, for ionic halogenation of alkanes and cycloalkanes in the presence of protic[11,12] and aprotic[13] superacids have no experimental evidence. On the contrary, the salts of halonium cations $X_3^+$ have been prepared under special conditions as long-lived species and convincingly characterized.[9] The results of their quantum chemical calculations have been reported.[5,10]

The linear dependence of activity of the $Br_2 \cdot nAlBr_3$ systems in octane cracking on the $AlBr_3$ concentration (Fig. 1) shows the probable importance in these reactions of ions containing several molecules of $AlX_3$. The halonium cations $X{-}X^+{-}X$ coordinated with one (Scheme 3, complex **1**, $[AlX_3]:[X_2]$ = 1.5) or two (complex **2**, $[AlX_3]:[X_2]$ = 2) molecules of Lewis acid seem to be the probable candidates for the role of the key super-electrophiles in alkane reactions with the $X_2 \cdot nAlX_3$ systems (Scheme 3).

$$X_2 + AlX_3 \rightleftharpoons [X^+ \cdots AlX_4^-] \overset{X_2}{\rightleftharpoons} X{-}X^+{-}X]AlX_4^- \overset{AlX_3}{\rightleftharpoons}$$

$$[X{-}X^+{-}X]Al_2X_7^- \overset{AlX_3}{\rightleftharpoons} \underset{\mathbf{1}}{[X{-}X^+{-}X{\rightarrow}AlX_3]Al_2X_7^-} \overset{AlX_3}{\rightleftharpoons}$$

$$\underset{\mathbf{2}}{[X_3Al{\leftarrow}X{-}X^+{\rightarrow}AlX_3]Al_2X_7^-}$$

**Scheme 3**

[†] The composition of reaction products was estimated by GLC and GLC-MS. Typical procedures:
(i) Molecular bromine (0.089 ml, 0.278 g, 1.74 mmol) was added at room temperature to powdered anhydrous $AlBr_3$ (0.93 g, 3.48 mmol) and stirred for 5 min in a closed glass flask. Octane (2.82 ml, 1.98 g, 17.4 mmol) and $CH_2Br_2$ (1.5 ml) were then added at once in one portion. The reaction mixture was stirred for 10 min, then hydrolysed with water, extracted with diethyl ether, washed and dried. *n*-Octane conversion (1.84 g, 93%) was measured by GLC. To determine the yields in a special experiment the volatile reaction products were completely transferred from the closed flask into an evacuated vessel of known volume and analysed by GLC. Treatment of the residue in the flask with water followed by extraction with ether and removal of the solvent gave the oligomers.
(ii) Liquid molecular chlorine (0.8 g, 11.3 mmol) was added to powdered anhydrous $AlCl_3$ (2.99 g, 22.8 mmol) in a glass flask, cooled by mixture of dry $CO_2$ and acetone. The reaction mixture was stirred in a closed flask for 10 min until the yellow colour of $Cl_2$ disappeared. Octane (18.3 ml, 12.88 g, 113 mmol) was then added and the reaction mixture was allowed to warm up to room temperature. After stirring for a further 20 min the mixture was hydrolysed and traces of $Cl_2$ were removed by $Na_2SO_3$. After the above treatment octane conversions were 21% for 20 min and 72% for 1 h.
(iii) Solid $I_2$ (0.436 g, 1.72 mmol) was stirred with $AlBr_3$ (0.92 g, 3.44 mmol) for several minutes. Octane (2.78 ml, 1.96 g, 17.2 mmol) was then added, and the mixture was stirred for 2 h. After the above treatment conversion of octane was 89%.

**Table 2** Examples of reactions of alkanes at 20 °C initiated by $Br_2 \cdot 2AlBr_3$ [a].

| *n*-Alkane | RH:Cat (mol) | *t*/min | Conversion (%) | Products, composition in wt.% | | | | |
|---|---|---|---|---|---|---|---|---|
| $C_5H_{12}$ | | | | *i*-$C_4H_{10}$ | *i*-$C_5H_{12}$ | *i*-$C_6H_{14}$ | *i*-$C_7H_{16}$ | oligomers |
| | 40:1 | 30 | 44.2 | 19.60 | 14.31 | 8.00 | 2.82 | 1.5[b] |
| | 40:1 | 60 | 81.4 | 22.78 | 28.76 | 22.75 | 6.91 | |
| | 40:1 | 90 | 95.0 | 39.77 | 22.08 | 25.57 | 7.55 | |
| $C_8H_{18}$ | | | | *i*-$C_4H_{10}$ | *n*-$C_4H_{10}$ | *i*-$C_5H_{12}$ | *i*-$C_6H_{14}$ | oligomers |
| | 20:1 | 30 | 67.0 | 46.22[b] | 6.60[b] | 5.97[b] | | 19.01[b] |
| | | | | (0.91) | (0.10) | (0.12) | | (0.39) |
| $C_{12}H_{26}$ | | | | *i*-$C_4H_{10}$ | *i*-$C_5H_{12}$ | | | oligomers |
| | 5:1 | 30 | 95.5 | 58.00[b] | 8.59[b] | | | 38.70[b] |
| | | | | (1.69) | (0.22) | | | (1.16) |

[a] In the presence of $CH_2Br_2$ (1 ml per 0.7 g of $AlBr_3$). [b] The production yields in wt.% (mol.%) on converted RH.

In apparent contrast with our data concerning the cracking activity of the above systems towards $C_5$–$C_{12}$ alkanes, Sommer and coworkers have found that in the presence of bromide anion or bromine the direct cleavage of the C–C bonds in propane carbonylation in proton superacid media ($HF$–$SbF_5$) was surpassed in favour of hydride abstraction from the secondary C–H bond resulting in isopropyloxocarbenium ion formation.[14] This effect was ascribed to the higher rate of hydride transfer from alkane to the bromocarbonyl cation $BrCO^+$ (formed by addition of CO to the positive bromine) compared with much lower rates of protolytic cleavage of the C–C and C–H bonds.[14,15] The difference between the behaviour of $C_3$ and $C_5$–$C_{12}$ alkanes is probably due to the higher stability of *iso*-$Pr^+$ cation towards C–C scission compared with higher alkyl cations generated from $C_5$–$C_{12}$ alkanes as well as the dissimilarity of species acting in the presence or absence of CO. Thus, a novel field of employment of halogens activated by aluminium halides was found. Due to their high activity in alkane cracking under mild conditions, the systems $Hal_2 \cdot nAlX_3$ can be referred to as aprotic inorganic superacids.

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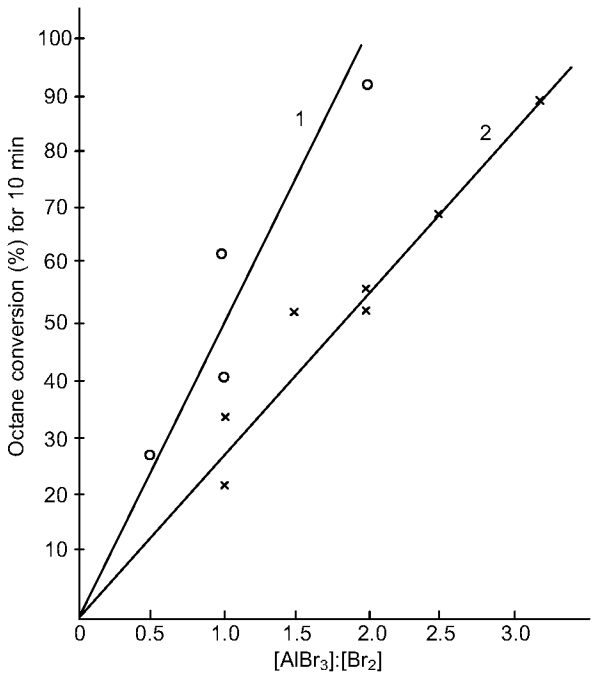


**Fig.1** Dependence of activity of the $Br_2 \cdot nAlBr_3$ systems on the $AlBr_3$ content at 20 °C ([RH]:[Cat] = 10:1; 1, in the presence of $CH_2Br_2$ (1 ml per 0.7 g $AlBr_3$); 2, without solvent.

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