Novel Sulfur-Containing Inorganic Aprotic Superacids as Effective Initiators of Low-Temperature Cracking and Isomerization of Alkanes

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Abstract: A novel family of inorganic aprotic superacids has been found. Oxochlorides and chloride of sulfur combined with aluminium halides ($\mathrm{SOCl_2}\cdot n\mathrm{AlX_3}$, $\mathrm{SO_2Cl_2}\cdot n\mathrm{AlX_3}$, $\mathrm{MeSO_2Cl}\cdot n\mathrm{AlX_3}$, $\mathrm{CF_3SO_2Cl}\cdot n\mathrm{AlX_3}$, $\mathrm{S_2Cl_2}\cdot n\mathrm{AlX_3}$; $n = 2$ or 3, X = Br or Cl) are found to be effective promoters for the cracking and isomerization of alkanes at room temperature.

Keywords
alkanes · cracking · isomerizations · sulfur compounds · superacids

Introduction

The award of the Nobel Prize for Chemistry to George Olah in 1994 for his work on the activation of alkanes by protic superacids not only acknowledged his basic contribution to alkane chemistry, but also demonstrated how topical this field of chemistry is. Olah categorized Lewis superacids as being stronger than anhydrous aluminium chloride.[1] Until recently inorganic aprotic superacids have been restricted exclusively to salt systems.[2] We have recently shown that halogens in the presence of aluminium halides should also be referred to as inorganic aprotic superacids, because of their high activity in initiating alkane cracking under mild conditions.[3] Our studies of systems based on aluminium halides, in which cationic or even multicharged positive species are thought to be generated, has led to a novel group of inorganic aprotic superacids, which are not only more active than aluminium chloride in initiating cracking of *n*-alkanes, but also than the markedly more reactive aluminium bromide.

Results and Discussion

In the presence of superacids $\mathrm{SOCl_2}\cdot n\mathrm{AlX_3}$, $\mathrm{SO_2Cl_2}\cdot n\mathrm{AlX_3}$, $\mathrm{MeSO_2Cl}\cdot n\mathrm{AlX_3}$, $\mathrm{CF_3SO_2Cl}\cdot n\mathrm{AlX_3}$ or $\mathrm{S_2Cl_2}\cdot n\mathrm{AlX_3}$ (X = Cl, Br; $n = 2$ or 3), 60–96% of the octane is converted into cracked products after 10–30 min at 20°. Under similar conditions, $\mathrm{AlCl_3}$ as well as the corresponding equimolar (1:1) complexes are inactive, and conversion of *n*-octane by $\mathrm{AlBr_3}$ does not exceed 20% (Table 1).

The main products from the cracking of octane, as in other reactions catalyzed by aprotic superacids,[4] are low $\mathrm{C_4}$–$\mathrm{C_6}$ isoalkanes [Eq. (1)]. In addition, a mixture of sulfur-containing oligomers are formed.

Table 1. Activity of sulfur-containing aprotic inorganic superacids in initiating octane cracking (20°, [RH]:[S] = 10:1 in $\mathrm{CH_2Cl_2}$).

Run	Superacid	Octane conversion/%			
		10 min	20 min	30 min	60 min
1	$2\,\mathrm{AlCl_3}$		0	3	2
2	$3\,\mathrm{AlCl_3}$			0	
3	$\mathrm{SOCl_2}\cdot\mathrm{AlCl_3}$		0	2	
4	$\mathrm{SOCl_2}\cdot 2\,\mathrm{AlCl_3}$		58	71	79
5	$\mathrm{SOCl_2}\cdot 3\,\mathrm{AlCl_3}$		86	93	
6	$\mathrm{SO_2Cl_2}\cdot\mathrm{AlCl_3}$			6	
7	$\mathrm{SO_2Cl_2}\cdot 2\,\mathrm{AlCl_3}$			34	49
8	$\mathrm{SO_2Cl_2}\cdot 3\,\mathrm{AlCl_3}$			96	
9	$\mathrm{MeSO_2Cl}\cdot 2\,\mathrm{AlCl_3}$			44	
10	$\mathrm{MeSO_2Cl}\cdot 3\,\mathrm{AlCl_3}$			77	92
11	$\mathrm{CF_3SO_2Cl}\cdot 2\,\mathrm{AlCl_3}$			59	
12	$\mathrm{CF_3SO_2Cl}\cdot 3\,\mathrm{AlCl_3}$			68	94
13	$\mathrm{S_2Cl_2}\cdot 2\,\mathrm{AlCl_3}$				31
14	$\mathrm{S_2Cl_2}\cdot 3\,\mathrm{AlCl_3}$			67	
15	$\mathrm{S_8}\cdot 3\,\mathrm{AlCl_3}$				0
16	$2\,\mathrm{AlBr_3}$	17	20		
17	$\mathrm{SOCl_2}\cdot 2\,\mathrm{AlBr_3}$	68	74		
18	$\mathrm{SO_2Cl_2}\cdot 2\,\mathrm{AlBr_3}$	66	72		
19	$\mathrm{S_2Cl_2}\cdot 2\,\mathrm{AlBr_3}$	38	40		

$$n\mathrm{C_8H_{18}} \xrightarrow[-\mathrm{H^-}]{+\mathrm{E}} \mathrm{C_8H_{17}^+} \longrightarrow i\mathrm{C_4H_{10}} + i\mathrm{C_5H_{12}} + i\mathrm{C_6H_{14}} + \text{oligomers} \qquad (1)$$

$\mathrm{E} = \mathrm{SOCl_2}\cdot n\mathrm{AlX_3}, \mathrm{RSO_2Cl}\cdot n\mathrm{AlX_3}, \mathrm{S_2Cl_2}\cdot n\mathrm{AlX_3}$

R = Cl, Me, $\mathrm{CF_3}$; X = Cl, Br; $n = 2$ or 3

The oligomer mixture of composition $\mathrm{(CH_{1.8})_{17}SO_{1.75}}$ with $M \approx 500$ (ebullioscopy), obtained by reaction of $\mathrm{SOCl_2}\cdot 2\,\mathrm{AlCl_3}$ with octane (run 4, Table 2), is made up of bulky unsaturated hydrocarbons with a small number of sulfur-containing groups ($\mathrm{SO_2}$, SO, -S-). As follows from Table 1, the activity of the systems based on $\mathrm{SO_2Cl_2}$, $\mathrm{MeSO_2Cl}$ and $\mathrm{S_2Cl_2}$ changes abruptly on moving from the $\mathrm{A}\cdot 2\,\mathrm{AlCl_3}$ to the $\mathrm{A}\cdot 3\,\mathrm{AlCl_3}$ systems (A is a sulfur-containing compound), while for the corresponding systems based on $\mathrm{SOCl_2}$ and $\mathrm{CF_3SO_2Cl}$ this change is less sub-

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Table 2. Products of cracking and isomerization of C_5-C_{12} alkanes by sulfur-containing inorganic aprotic superacids at 20°

1	C_5H_{12}	$SOCl_2 \cdot 2AlCl_3$	40:1	3	73	17.4	31.6	10.7	4
2	C_5H_{12}	$SOCl_2 \cdot 2AlCl_3$	200:1	20	42	3.0	39.1	2.6	0.5
3	C_5H_{12}	$2AlCl_3$	200:1	20	23	31.5	41.8	2.2	0.2
4	C_8H_{18}	$SOCl_2 \cdot 2AlCl_3$	10:1	0.5	62	34.5	56.2	4.7	10
5	C_8H_{18}	$SO_2Cl_2 \cdot 3AlCl_3$	10:1	0.5	69	40.2	52.5	4.8	17
6	C_8H_{18}	$MeSO_2Cl \cdot 2AlCl_3$	10:1	0.5	44	53.6	38.9	4.6	14
7	C_8H_{18}	$CF_3SO_2Cl \cdot 2AlCl_3$	10:1	0.5	59	24.9	44.3	12.6	26
8	$C_{10}H_{22}$	$SOCl_2 \cdot 2AlCl_3$	10:1	0.5	46	42.6	47.5	5.4	17
9	$C_{12}H_{26}$	$SOCl_2 \cdot 2AlCl_3$	10:1	0.5	41	64.7	27.8	4.4	48

stantial. Similarly to octane, the nC_5-C_{12} alkanes also undergo cracking under the action of these superacids to form a mixture of low isoalkanes and oligomers, which qualitatively resembles that obtained with octane (Table 2). In the presence of catalytic amounts of $SOCl_2 \cdot 2AlCl_3$, a rather selective isomerization of *n*-pentane into isopentane can be achieved: with 1 mol of the superacid, ca. 80 mol of isopentane is formed after 20 h with a selectivity of 88% (run 2, Table 2). Under similar conditions, isomerization of pentane with Al_2Cl_6 is noticeably less effective and selective. On increasing the molar ratio of hydrocarbon to catalyst, the conversion of *n*-pentane increases, albeit with simultaneous decrease in the selectivity of isomerization (run 1, Table 2).

This is the first time that the action of the above-considered systems on alkanes has been studied. Stetter has reported that refluxing of adamantane with an excess of $SOCl_2$ in the presence of $AlCl_3$ leads to the formation 1,3,5-trichloroadamantane;[5] the interaction at −15° gives AdSOCl (Ad = adamantyl) in high yields. The proposed mechanism of chlorosulfination of adamantane[5] does not involve the participation of a $SOCl_2 \cdot AlCl_3$ complex. Asinger has described radical chlorosulfonation and chlorination of alkanes by SO_2 and Cl_2 under irradiation.[6]

Some complexes of sulfur oxochlorides and chlorides with aluminium halides have been studied,[7–12] however, data on the systems considered here are very scarce. Heating of aluminium chloride with an excess of $SOCl_2$ has been shown to result in formation of the $SOCl_2 \cdot 2AlCl_3$ complex (**I**), an oily liquid with a boiling point of 214–215 °C.[7] Heating of this complex in vacuo leads to the solid equimolar complex $SOCl_2 \cdot AlCl_3$ (**II**).[8] The structure $Cl_2S{=}O \rightarrow AlCl_3$ has been assigned to complex **II** on the basis of its Raman spectrum.[8] As to the structure of **I**, the conclusion of authors was not so definite.[8] The insignificant shift of the S–O band in the spectrum of **I** in comparison with that of **II** has been interpreted in terms of a weak bonding of **II** with the second molecule of $AlCl_3$ (the specific atom involved in bonding is not identified). The potentiometric and conductometric studies on solutions of $AlCl_3$ in $SOCl_2$ have shown that complex **II** is formed, and dissociates to a very small degree [Eq. (2)].[9]

$$\underset{\textbf{II}}{SOCl_2 \cdot AlCl_3} \rightleftharpoons SOCl^+ AlCl_4^- \quad K = 1 \times 10^{-4} \tag{2}$$

The complex $S_2Cl_2 \cdot 2AlCl_3$ reported earlier, which was prepared in SO_2Cl_2,[10] has been reinvestigated[11] and shown to be the known ionic salt $SCl_3^+ AlCl_4^-$.[12]

At present we are engaged in elucidation of the structure of the active complexes and the nature of their activity. We tentatively propose that species whose limiting forms may be presented as the ions **III**, **IV** and **V** [Eq. (3–5)] are responsible for the

$$SOCl_2 \overset{AlCl_3}{\rightleftharpoons} Cl_2S{=}O \rightarrow AlCl_3 \overset{AlCl_3}{\rightleftharpoons} \underset{\textbf{III}}{SOCl^+ Al_2Cl_7^-} \tag{3}$$

$$S_2Cl_2 \overset{AlCl_3}{\rightleftharpoons} ClS{=}SCl \rightarrow AlCl_3 \overset{AlCl_3}{\rightleftharpoons} \underset{\textbf{IV}}{ClS{=}S^+ Al_2Cl_7^-} \tag{4}$$

$$\begin{aligned} RSO_2Cl &\overset{AlCl_3}{\rightleftharpoons} O{=}(R)S(Cl){=}O \rightarrow AlCl_3 \overset{AlCl_3}{\rightleftharpoons} \\ &AlCl_3 \leftarrow O{=}(R)S(Cl){=}O \rightarrow AlCl_3 \overset{AlCl_3}{\rightleftharpoons} \\ &\underset{\textbf{V}}{O{=}(R)S^+{=}O \rightarrow AlCl_3\, Al_2Cl_7^-} \end{aligned} \tag{5}$$

Editorial Board Member:[*] *Mark E. Vol'pin, born in Simferopol (USSR) in 1923, graduated from the Moscow State University in 1949 and received his Ph.D. in 1952. He obtained his D. Sc. in 1959 from the Institute of Organoelement Compounds (IOEC) of the Russian Academy of Sciences (RAS) in Moscow. He has been the Head of the Laboratory of Organometallic Catalysts since 1963 and the Director of the IOEC since 1988. He has been awarded the USSR Lenin Prize (1963), the Silver Medal of the Royal Society of Chemistry (1980), the Nesmeyanov Gold Medal and Prize of the RAS (1982), the USSR State Prize in Science (1982), and the "Maison de Chemie" prize (1993). He has been a Full Member of the USSR Academy of Sciences since 1987. He first reported the fixation of molecular nitrogen by transition metal complexes, did some pioneering research on carbon dioxide fixation, prepared graphite complexes with transition metals and elaborated new types of superacids for alkane activation.*

Abstract in Russian:

Открыта новая группа неорганических суперкислот. Оксохлориды и хлорид серы в комбинации с галогенидами алюминия ($SOCl_2 \cdot nAlX_3$, $SO_2Cl_2 \cdot nAlX_3$, $MeSO_2Cl \cdot nAlX_3$, $CF_3SO_2Cl \cdot nAlX_3$, $S_2Cl_2 \cdot nAlX_3$, n= 2 или 3, X= Br, Cl) оказались эффективными инициторами крекинга и изомеризации алканов при комнатной температуре.

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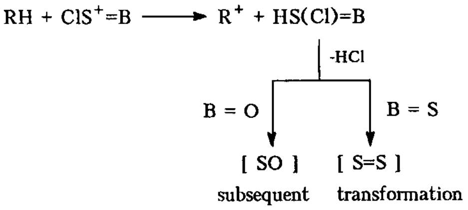

Scheme 1.

In this case the alkane hydride ion abstraction by $SOCl_2 \cdot n\,AlCl_3$ and $S_2Cl_2 \cdot n\,AlCl_3$ could be described by Scheme 1.

For all the systems studied, we were unable to observe any volatile sulfur-containing compounds (except SO_2 in the reaction of octane with $SOCl_2 \cdot 2\,AlCl_3$) after hydrolysis of the reaction mixtures. The absence of volatile sulfur-containing reduction products of oxochlorides and chlorides is probably due to their instability (for instance HCOCl and SO)[13] and high reactivity, in particular towards olefins generated in the course of cracking. Indeed, ca. 70% of the initial sulfur is transformed into oligomers. The presence of SO_2 fragments in oligomers prepared from octane with $SOCl_2 \cdot 2\,AlCl_3$ is probably due to facile oxidative–reductive transformations of sulfur-containing compounds in superacid media.[14]

Conclusion

Novel inorganic aprotic superacids for low-temperature alkane transformations have been found. The new sulfur-containing aprotic superacids have been used in novel alkane (cycloalkane) functionalization (sulfurization) reactions. The nature of active complexes, generated in the systems discussed above, has been elucidated, and the mechanisms of alkane reaction with aprotic superacids discussed. An important subject for future research is the application of these very active sulfur-containing systems to the transformation of other classes of inert molecules.

Experimental Procedure

Aluminium halides, oxochlorides and chlorides of sulfur were distilled prior to use; dihalomethanes were refluxed with P_2O_5 and distilled. GC quantitative analyses of reaction mixtures was carried out by means a Model 3700 gas chromatograph equipped with an FID and a quartz capillary column (25 m × 0.23 mm, stationary phase of SE-54, $T = 80\,^{\circ}C$). GC-MS analyses were carried out with a VG-7070E instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP200SY.

Octane (1.2 g, 10.5 mmol) was added at room temperature to a stirred mixture of powdered anhydrous $AlCl_3$ (0.28 g, 3.1 mmol) and $SOCl_2$ (0.12 g, 1.05 mmol) in CH_2Br_2 (1.4 g, 8.1 mmol) or CH_2Cl_2 (0.7 g, 8.7 mmol) in a flask equipped for removal and collection of gaseous reaction products; the reaction started immediately. The two-layered reaction mixture was stirred for 30 min, hydrolysed with water, extracted with ether, mixed with nonane as a standard, washed and dried. In the course of the reaction gaseous products were collected in an evacuated vessel and analysed by GC or GC-MS. Octane conversion (70%) was measured by GC. The gaseous mixture, analysed by GC, contained isobutane (0.24 g, 34%), isopentane (0.38 g, 56.2%) and isohexanes (0.03 g, 4.7%). Removal of the volatile products and the solvent gave 0.2 g of oligomers as a dark viscous liquid, which was soluble in organic solvent. Found (%) C 68.61, H 10.44, S 10.65, Cl 1.0. M(ebul.) ≈ 500. IR (cm^{-1}): $\tilde{\nu}$ = 530, 580, 639, 666, 892, 1027, 1114, 1155, 1309, 1366, 1379, 1463, 2855, 2870, 2927, 2957. NMR (AMX-400, Bruker, C_6D_6, DEPT; I/% in parentheses): ^{13}C NMR: δ = 9.189 (1), 11.947 (1.5), 14.675 (2.9), 13.893–21.943 (4.0), 23.237 (2.0), 29.992 (1.4), 24.094–29.182 (3.1), 30.622–37.676 (3.9); ^1H NMR: δ = 1.0373–1.4276 (333.3, v br), 3.8923 (1.9), 5.3235 (1), 10.1813 (2.9). MS above 47 amu (EI, 300°, direct inlet) contains ions with m/z = 48–561; the most intense ions, m/z (I_{rel}, %): 57 (100), 55 (99), 69 (96), 56, 71 (92), 64 (91), 70 (88), 83 (87), 85 (85), 67 (81), 95, 53 (79), 81 (78), 109, 78 (77), 91 (72), 77 (68), 81 (61), 123 (59), 97 (58), 68 (51). In mass spectra there are signals corresponding to hydrocarbon fragments differing in the extent of unsaturation ($C_nH_{2n+1}^+$, $C_nH_{2n-1}^+$, $C_nH_{2n-3}^+$ etc.) and signals characteristic for sulfur-containing fragments (e.g. m/z 48, 60, 61, 62, 63, 64, 65, 75, 80, 94 etc.).

Pentane (1.84 g, 25 mmol) was added to the mixture of $SOCl_2$ (0.015 g, 0.12 mmol) and $AlCl_3$ (0.034 g, 0.25 mmol), and the reaction mixture was shaken in a sealed-glass ampoule at 20 °C for 20 h. The contents of the ampoule were frozen, and the ampoule was then opened and connected to an evacuated vessel to collect the volatile reaction products. The gaseous mixture was analysed by GC and found to contain 0.02 g (2.97%) of isobutane, 0.31 g (39.11%) of isopentane, 0.4 g (50.69%) of pentane and 0.02 g (2.55%) of isohexane. Treatment of the residue in the ampoule with water, followed by extraction with diethyl ether and removal of the solvent gave 0.01 g of a high molecular oligomer.

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