NATURE OF THE SPECIES RESPONSIBLE FOR THE HIGH ACTIVITY OF $RCOX \cdot 2A1X_3$ COMPLEXES IN REACTIONS WITH ALKANES AND CYCLOALKANES

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The reasons for the high reactivity of aprotic organic superacids (AOS) containing an acyl halide and a double molar excess of Lewis acid in reactions with saturated hydrocarbons are studied. The synthesis and spectral properties of two pairs of acyl salts are studied: $MstCO^+AlBr_4^-$ and $MstCO^+Al_2Br_7^-$ ($Mst = 2,4,6-Me_3C_6H_2$) and $Ac^+SbF_6^-$ and $Ac^+Sb_2F_{11}^-$. Comparison of the reactivities of these salts in cracking of alkanes and isomerization of trimethylenenorbornane demonstrated that the AOS activity is due to generation of acyl salts with a dimeric anion in the slightly polar solutions. Analysis of the ^{13}C NMR spectra suggests that the superacid properties of these salts are due to formation of species containing acyl cations coordinated to the Lewis acid.

The complexes $RCOX \cdot 2AlX_3$ (R = Alk, X = Cl, Br) (I), which we call aprotic organic superacids (AOS), are the most active catalysts for cracking n-alkanes and cycloalkanes at ~20°C [1]. As a rule, their reactivity is greater than that of the most active protonated superacids. They differ qualitatively from the equimolar complexes $RCOX \cdot AlX_3$ (II) and other catalysts based on aluminum halides that are unreactive toward paraffins under such mild conditions.

In order to understand the reason for the unusually high activity of (I), we studied the structure of complexes (I) and (II)* in the solid and in solution [2, 3]. It was found that certain complexes are ionic acyl salts in the solid that differ only in the anionic structure: $\text{RCO}^+\text{Al}_2X_7^-$ for (I) and $\text{RCO}^+\text{Al}X_4^-$ for (II) (R = Me). In CH_2X_2 solution the former are an equilibrium mixture of acyl salts $\text{RCO}^+\text{Al}_2X_7^-$ and donor-acceptor complexes $\text{RC}(X)=0 \rightarrow \text{Al}_2X_6$ whereas the latter exist exclusively as coordination complexes $\text{RC}(X)=0 \rightarrow$ $\text{Al}X_3$ [1, 3]. This agrees with the literature [4, 5]

$$RCOX + AIX_3 \rightleftharpoons RC(X) = 0 \rightarrow AIX_3 \rightleftharpoons RCO^*AIX_4^-$$

in CH_2X_2 solution

$$\operatorname{RCOX} + 2\operatorname{AlX}_3 \rightarrow \operatorname{RC}(X) = 0 \rightarrow \operatorname{Al}_2 X_6 \simeq \operatorname{RCO}^* \operatorname{Al}_2 X_7^-$$

We note that the possibility of generating acyl salts in such slightly polar solvents as CH_2X_2 was first observed by us [3]. Thus, only (I) (R = Alk), which are reactive toward paraffins, are capable of effectively generating acyl cations in slightly polar solutions. This distinguishes them in principle from (II).

However, it remains to be seen whether any acyl salt being generated in solution can react at ~20°C with paraffins or whether the activity of these salts is due to the presence in them of the dimeric anion Al_2X_7 . In the present work, we attempted to answer this question by comparing the activities of several acyl salts with monomeric and dimeric anions

*The structure of complexes $RCOX \cdot AIX_3$ in the solid and in solution is the subject of many publications (for example, see reviews [5, 6]). However, data on the structure of complexes $RCOX \cdot AIBr_3$ in the solid and in CH_2Br_2 have not been reported.

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Salt	δ, ppm rel. to TMS			
	C'H3	¹³ CH ₃	13CO	
$CH_{3}CO+SbF_{6}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_{3}CO+Sb_{2}F_{11}-CH_$	$4,24 \\ 4,24$	6,4 5,9	151,0 151,0	

TABLE 1. Chemical Shifts in PMR and $^{13}\rm C$ NMR Spectra of $Ac^+SbF_6^-$ and $Ac^+Sb_2F_{11}^-$ in SO_2 Solution

TABLE 2. Comparision of the Activities of Acyl Salts with Monomeric and Dimeric Anions in Cracking of n-Alkanes and Isomerization of Trimethylenenorbornane (TMNB)

Hydrocarbon (RH)	Acyl salt (A)	RH : A	Time,	Con- ver- sion of RH,	Products (mass % of RH)
n-Octane*	Ac+SbF6-	1:1	3.0	0	
n-Octane [*]	Ac+Sb ₂ F ₁₁ -	1:1	3.0	100	$i-C_{4}II_{10}$ (31)
n-Octane	$\Lambda c^+ Sb_2 F_{11}^-$	1:1	1.0	100	$i-C_4H_{10}$ (36)
-Dodecane*	Ac+Sb ₂ F ₁₁ =	1:1	2,0	85	Oligomer (50)
n-Octane***	MstCO+AlBr ₁ =	1:4	0,5	- 0	
n-Octane***	MstCO+Al ₂ Br ₇ =	1:4	0,5	100	**
n-Dodecane***	MstCO ⁺ Al ₂ Br ₇ ⁺	1:2	0,5	100	**
IMNB	MstCO+AlBr ₄ -	1:10	5.0	0	(27)
TMNB	MstCO+Al ₂ Br ₇ -	1:10	<u>5,0</u>	37	Adamantane (3/)
TMNB	$ $ MSICO ⁺ Λ_{12} Br_7	1.10	1 0,0	00	Audiantiane (54)

*SO₂ solvent. **Not determined. ***CH₂Br₂ solvent.

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in model cracking of octane and dodecane (the cracking of n-alkanes by AOS is described in detail in [7]) and in isomerization of trimethylenenorbornane into adamantane.

Since acyl salts with a monomeric anion cannot be generated in slightly polar CH_2Br_2 solutions, we initially studied the complex $AcF \cdot SbF_5$, which exists exclusively as the salt $Ac^+SbF_6^-$ in SO_2 solution according to ${}^{13}C$ NMR spectra [8] (Table 1). As it turned out, the complex $AcF \cdot 2SbF_5$ in SO_2 solution also exists exclusively as an ionic acyl salt (cf. Table 1). In fact, as seen from Table 1, adding another mole of SbF_5 to the complex $AcF \cdot 2SbF_5$ has practically no effect on the ${}^{1}H$ and ${}^{13}C$ NMR spectra. The ${}^{19}F$ NMR spectrum of $AcF \cdot 2SbF_5$ exhibits one broad signal at 37 ppm. The absence of signals corresponding to uncoordinated SbF_5 is evidence for formation of the salt $Ac^+Sb_2F_{11}^-$, the chemical shifts of which are very close to those of $Ac^+SbF_6^-$ (cf. Table 1).

The complexes $Ac^+Sb_{6}^-$ and $Ac^+Sb_{2}F_{11}^-$ had different reactivities as judged from the conversion of the starting hydrocarbon. Whereas in the presence of $Ac^+Sb_{6}^-$ octane remained unchanged, in the presence of $Ac^+Sb_{2}F_{11}^-$ it was cracked (Table 2). Although the difference in activities of the complexes was conditional (cf. Table 2), the fact that the reactions were carried out in the two-phase system SO_2 -alkane hindered an unambiguous interpretation of the observed difference.

An unambiguous conclusion about the dependence of the reactivity of the acyl salts on the anion structure suggested a study of the complexes of mesitoylbromide with AlBr₃ of composition MstCOBr·AlBr₃ and MstCOBr·2AlBr₃ (Mst = 2,4,6-Me₃C₆H₂). Substituents in the 2- and 6-positions of an aromatic ring prevent formation of coordination complexes ArC(X)=O \rightarrow MX_n with an sp²-hybridized carbonyl C atom on steric grounds. They have practically no effect on formation of ArCO⁺ cations with an sp-hybridized carbonyl C atom containing the linear fragment Ar-C-O [5, 6]. As a result, formation of acyl salts MstCOX·MX_n is favored even with weak Lewis acids (MX_n). Thus, TiCl₄ and even AlCl₃ form only coordination complexes with PhCOX whereas replacing PhCOX by MstCOX leads to formation of mixtures of coordination and ionic complexes [6].

∑ _____1 CO+A1Br₄~ -CO+Al2Br-Assignment 27 A1 чC ъC 27 Al 21,4 $C^2 - CH_3$ 21.723,7 $C^4 - CH_3$ 24.279,4 85,3 ${}^{{\rm C}^{1}}_{{\rm C}^{2}}$ 84.6 93,0 $(\Delta = 12 \text{ Hz})$ 153,7153,9 $(\Delta = 930 \text{ Hz})$ \mathbb{C}^3 130,9 131.5 162.1C4 163,1159,2ĊO 159.7

TABLE 3. ¹³C and ²⁷Al NMR Spectra of MstCO⁺ Salts with AlBr₄⁻ and Al₂Br₇⁻ Anions (δ , ppm)

We demonstrated that using AlBr₃ as Lewis acid increases the tendency toward formation of ionic complexes since MstCOBr·AlBr₃ and MstCOBr·2AlBr₃ in CH_2Br_2 solution are exclusively ionic salts MstCO⁺AlBr₄⁻ and MstCO⁺Al₂Br₇⁻, respectively. This is confirmed unambiguously by the ¹³C and ²⁷Al NMR spectra (Table 3). Signals of one carbonyl group lying in the range characteristic for acyl salts are observed in the spectra of each complex [9]. The chemical shifts of the signals of C¹ aryl atoms are also very characteristic and agree with those described for ArCO⁺MX_{n+1}⁻ [9].

The constancy of the ¹³C NMR spectra on lowering the temperature provides independent confirmation of the ionic structure of the complexes. In fact, the o-C atoms of the aromatic ring are equivalent in the MstCO⁺ cations. On the other hand, we observed broadening of the signals of the o-C atoms due to nonequivalency arising as the free rotation about the Ph-CO bond slowed with decreasing temperature in the coordination complexes PhC(Br)=O \rightarrow AlBr₃ and PhC(Br)=O \rightarrow Al₂Br₆ in CH₂Br₂ solution (δ = 190 and 192 ppm, respectively).

The structure of the anions in the mesitoylium salts was determined using ²⁷Al NMR spectra. The ²⁷Al chemical shift of AlBr₄⁻ from Pr₄N⁺AlBr₄⁻ in CH₂Br₂ (δ = 79.6 ppm) has been reported [10]. We obtained the value (δ = 79.4 ppm, Δ = 12 Hz) for a saturated solution of BuEt₃N⁺AlBr₄⁻ in CH₂Br₂. The ²⁷Al spectrum of an equimolar solution of the complex MstCOBr·AlBr₃ contains a single signal (cf. Table 3) whose position and width are consistent with the proposed structure of the salt MstCO⁺AlBr₄⁻. The ²⁷Al spectra of salts with the dimeric anion Al₂Br₇⁻ have not been described. Therefore, we recorded the spectrum of BuEt₂N⁺Al₂Br₇⁻ in CH₂Br₂. The structure of the anion in this solution was confirmed using Raman spectra^{*} (ν_1 = 200 cm⁻¹) [11]. A single broad (Δ = 930 Hz) signal with δ = 93 ppm is seen in the ²⁷Al NMR spectrum of this salt. As seen from Table 3, this same signal is observed in the spectrum of MstCOBr·2AlBr₃. This is consistent with a dimeric anion in the mesitoylium salt formed.

Thus, an acyl salt with the monomeric anion $AlBr_4$ and the discrete dimeric anion Al_2Br_7 could be prepared for the first time as complexes of MstCOBr with $AlBr_3$. It is important that adding saturated hydrocarbon in both cases does not disturb the homogeneity of the solutions in which the ionic structure of the starting salts is preserved according to NMR data.

The last condition enables a valid comparison of the reactivities of the acyl salts $MstCO^+AlBr_4^-$ and $MstCO^+Al_2Br_7^-$ relative to saturated hydrocarbons to be made in model reactions.

As seen in Table 2, $MstCO^+AlBr_4^-$ is completely inert toward craking of octane and dodecane under the conditions studied. On the other hand, $MstCO^+Al_2Br_7^-$ initiates this reaction. Quantitative cracking of octane and dodecane with formation of the same principal products that result from cracking catalyzed by a complex of type (I) with R = Me is observed with $MstCO^+Al_2Br_7^-$ after 30 min [7].⁺

^{*}The intense coloration of the mesitoylium salt solutions prevented us from identifying the anions using Raman spectroscopy.

⁺The lower activity of $MstCO^+Al_2Br_7^-$ compared to $Ac^+Al_2Br_7^-$ is due to charge delocalization in the mesitoyl cation.

The same qualitative difference in activities of the two mesitoylium salts is seen in the reaction with trimethylenenorbornane. In the presence of $MstCO^+AlBr_4^-$ the reaction does not occur whereas $MstCO^+Al_2Br_7^-$ initiates formation of adamantane (cf. Table 2).

Thus, the data obtained indicate that only the acyl salt with the dimeric anion is active toward saturated hydrocarbons whereas salts with the monomeric anion AlX_4^- are inactive toward paraffins at ~20°C.

So the question of which type of complex generates the superacid properties in the $RCOX \cdot 2AlX_3$ systems is answered. However, it is still unclear whether the $RCO^+Al_2X_7^-$ salts themselves are active toward paraffins or whether they are sources of still more electrophilic complexes responsible for the high activity observed for $RCOX \cdot 2AlX_3$ systems. In other words, can the distinct difference in activities of $RCO^+AlBr_4^-$ and $RCO^+Al_2Br_7^-$ be related only to the different degree of screening of the positive charge by the counterion? Finally, $AlBr_4^-$ is more nucleophilic than $Al_2Br_7^-$ [12]. However, in our opinion the qualitative difference in activities should also be accompanied by a noticeable difference in $^{1.3}$ C NMR spectra, which are very sensitive to a change in electron density. However, the $^{1.3}$ C NMR spectra of these salts (cf. Table 3) are practically identical. This makes the hypothesis about the different electrophilicity of the acyl cations with monomeric and dimeric anions doubtful.

We think that the hypothesis about the existence in solutions of $RCO^+Al_2X_7^-$ of an equilibrium strongly shifted to the left between these salts and the more electrophilic complexes in which the RCO^+ cation is coordinated to the Lewis acid deserves serious consideration. It is obvious that such coordination should cause more electrophilic cations to appear. In the limiting case, these can be represented as acyl dications with structures (III) or (IV).



The latter probably occur in very small concentrations and cannot be identified by ordinary spectral methods. However, they most likely are responsible for the unusually high activity of $RCOX \cdot 2AIX_3$, AOS.

The important role of acyl halide complexes with two moles of AlX₃ of the type RC(X \rightarrow AlX₃)=O \rightarrow AlX₃ in acylation of arenes was first proposed by Fillet [13]. It was reported recently [14] that formation of the complex MeC(Cl \rightarrow AlCl₃)=O \rightarrow AlCl₃ in the system AcCl - n moles AlCl₃ in SO₂ solution could be detected by NMR. However, the assignment of spectral data from this work contradict those commonly accepted [5, 6] and seem erroneous to us. Thus, complexes of the type (III) or (IV) have not yet been observed experimentally.

Apparently, a direct analogy exists between complexes of type (III) or (IV) and the protonated form of the acetylium cation (V) postulated by Olah [15] to form in protic super-acid.

Olah proposed that these protonated acetylium cations (V) are responsible for transfer of hydride from isobutane to the acetylium cation in protic superacid. In an aprotic solvent (SO_2) , where the ion (V) cannot be formed, hydride transfer from isobutane is not observed [15]

$$CH_{3}C^{+} = O + H^{+} \rightarrow CH_{3}C^{+} = O^{+}H$$

$$i - RH + CH_{3}C^{+} = O^{+}H \rightarrow i - R^{+} + CH_{3}CH \stackrel{(V)}{=} O^{+}H$$

$$i - RH + CH_{3}C^{+} = O \xrightarrow{SO_{2}} i - R^{+} + CH_{3}CHO$$

Protonation of cations that have atoms with a free electron pair is rather common. Thus, formation of the dications H_4O^{2+} and H_4S^{2+} was recently reported [16, 17].

In spite of the analogy between complexes of type (III) or (IV) postulated by us and the protonated form of the acetylium cation (V), we emphasize that the substantial difference between them, namely the greater activity of (III) and (IV) should be noted. Complexes of type (V), as demonstrated in the literature [15], are inert toward n-alkanes whereas the systems $RC0.2AlX_3$ react with them at high rates [1]. Thus it can be confirmed that possible protic impurities in systems $RCOX.2AlX_3$ (due to traces of water or destruction of the complexes) cannot be responsible for the observed high activity of these systems, i.e., they should be viewed as AOS.

EXPERIMENTAL

Mesitoylbromide (MstCOBr) was prepared by reacting MstCOOH with PBr_5 according to [18] and was distilled twice under Ar, bp 82-83°C (1 mm). The compound $AlBr_3$ was distilled in vacuum and stored under Ar. Saturated hydrocarbons and CH_2Br_2 were purified and dried by standard methods. Chemically pure $BuEt_3NBr$ was thoroughly dried under vacuum over P_2O_5 .

Liquid reaction mixtures were analyzed by GLC on a Biochrom-1 chromatograph equipped with a glass capillary column 25 m \times 0.22 mm and an OV-101 stationary liquid phase. Gaseous products were analyzed on a Chrom-5 chromatograph (3 m \times 3 mm column, PAR-2 stationary phase).

NMR spectra were recorded on a Bruker WP-200 SY spectrometer at a working frequency of 200 MHz for protons. Raman spectra of $BuEt_3N^+Al_2Br_7^-$ were obtained on a Ramanor-2HG spectrometer.

The calculated amount of MstCOBr was added under Ar to AlBr₃ and then CH_2Br_2 until [A1] = 0.5 g-equiv/liter in order to prepare solutions of MstCOBr complexes with AlBr₃. Solutions of BuEt₃N⁺AlBr₄⁻ and BuEt₃N⁺Al₂Br₇⁻ were prepared by adding the calculated amount of BuEt₃NBr to AlBr₃ in CH_2Br_2 with [A1] = 0.5 g-equiv/liter. The solutions obtained were used for spectral studies. Slightly soluble BuEt₃N⁺AlBr₄⁻ that precipitated from solution was separated. The ²⁷Al NMR spectrum of its saturated solution was recorded.

Reactions of saturated hydrocarbons and MstCOBr complexes with $AlBr_3$ (cf. Table 2) were carried out using the following standard methods.

To 1.6 g (6 mmoles) $AlBr_3$ were added 0.68 g (3mmoles) MstCOBr and 2.5 ml CH_2Br_2 . After 5 min 0.086 g (0.75 mmole) n-octane was added to the dark-red solution at once. The homogeneous solution obtained was stirred for 30 min. Then gaseous products were transferred to an evacuated container and analyzed by GLC. The residue was hydrolyzed with ice, extracted with ether, and dried. The starting octane was absent. Conversion was 100%.

To 4.0 g (15 mmoles) $AlBr_3$ were added 1.7 g (7.5 mmoles) MstCOBr and 5 ml CH_2Br_2 and then 0.10 g (0.75 mmole) exo-TMNB. The reaction mixture was stirred for 5 h, after which it was treated as in the previous experiment. Yield 0.037 g adamantane (37%) and 0.063 g unreacted exo-TMNB (conversion 37%).

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