were washed with cold ethyl acetate and dried. ^{13}C NMR spectra of the products in solution in D_2O were recorded. The bromides were converted into hydroxides with Ag_2O to produce mildly acidic or neutral gels. These were prepared by the addition of aluminum hydroxide hydrate ($Al(OH)_3 \cdot xH_2O$, Aldrich), magnesium acetate tetrahydrate, orthophosphoric acid, and the diquinuclidinium hydroxide to distilled water in the molar ratio of 0.9:0.1:1.0:0.4:40. The gels were heated without stirring at 190 °C for 48 h in a stainless steel, PTFE-lined autoclave. The MgAPOs were characterized by X-ray powder diffraction with a STOE STADIP automated diffractometer and analyzed thermogravimetrically. The density of STA-1 was determined with the aid of a variable mixture of diiodomethane (3.325 $g\,cm^{-3}$) and 1-bromobutane (1.276 $g\,cm^{-3}$). ^{31}P, ^{27}Al and ^{13}C MAS-NMR spectra were obtained with a Bruker 400 MSL spectrometer. The ^{13}C NMR spectrum of the template within STA-1 in the solid state (δ = 65.4, 56.1, and a broad envelope of peaks between 30 and 20, maximum at 24.5, for the n = 8 template) corresponded closely with that in solution with higher resolution (δ = 64.31, 54.64, 27.73, 25.51, 23.40, 21.36, 19.10). Chemical analysis was performed by EDX of X-rays emitted in an electron microscope.

Single-crystal diffraction data were collected on the Materials Science Beamline (ID-11, BL2) at the ESRF, Grenoble [10]. A crystal of approximate dimensions 30 × 30 × 30 µm was glued to a fine glass fiber and mounted on the three-circle fixed kappa Siemens diffractometer fitted with a Siemens SMART CCD detector and cooled to 200 K. The wavelength was calibrated prior to the experiment as 0.484 Å. Individual frames (1250) were collected at ω intervals of 0.1°, during which the detector covered $8^{\circ} < 2\theta < 28^{\circ}$, corresponding to a d-spacing range $1.000 < d < 3.469$ Å. Normalization and integration of the data carried out with Siemens SAINT software gave refined lattice parameters of $a = 13.620(4)$ and $c = 21.649(5)$ Å for 411 contributing reflections. A total of 2097 reflections were processed, of which 954 were unique and 845 considered observed ($I > 3\sigma(I)$). The space group was identified as $P\bar{4}n2$ from the systematic absences and intensity statistics. The framework structure was solved with SIR92 and refined with the teXsan suite [11] to final agreement factors R = 0.059, Rw = 0.076. The positions of the template molecules could not be determined from the single crystal data, presumably due to disorder, and the simulated powder diffraction pattern calculated from the single-crystal data closely matched the observed pattern measured over the same range, although the intensities of reflections with higher d-spacings were very different, due to the presence of extra-framework scattering. Atomic coordinates of STA-1 are given in Table 1. At 200 K the structure has a cell volume of 4016 Å and a calculated density, including template molecules and water, of 1.815 $g\,cm^{-3}$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405444.

Table 1. Atomic coordinates and equivalent isotropic temperature factors for STA-1 at 200 K.

Aom	x	y	z	B(eq) [Å^2]
P(1)	0.3905(2)	0.1197(2)	0.1332(1)	1.60(7)
P(2)	0.1100(2)	0.1207(2)	0.1892(1)	1.69(7)
P(3)	0.2094(2)	−0.1143(2)	0.0563(1)	1.70(7)
P(4)	0.2953(2)	−0.2047(2)	0.2500	1.73(5)
Al(1)	0.2022(3)	0.1119(3)	0.0597(1)	1.76(8)
Al(2)	0.1156(3)	−0.1114(3)	0.1885(1)	1.85(8)
Al(3)	0.3900(3)	−0.1082(3)	0.1346(1)	1.96(8)
Al(4)	0.2950(2)	0.2050(2)	0.2500	1.57(5)
O(1)	0.3220(6)	0.1410(7)	0.0821(3)	3.0(2)
O(2)	0.3706(6)	0.1832(7)	0.1872(4)	3.3(2)
O(3)	0.3763(6)	0.0132(5)	0.1538(4)	2.4(2)
O(4)	0.4928(5)	0.1360(70	0.1110(4)	2.5(2)
O(5)	0.1959(8)	−0.0099(5)	0.0369(4)	3.7(2)
O(6)	0.1260(6)	0.1403(6)	0.1220(3)	2.6(2)
O(7)	0.1812(6)	0.1848(6)	−0.0039(3)	3.1(2)
O(8)	0.1737(6)	0.1878(6)	0.2267(3)	2.5(2)
O(9)	0.1332(6)	0.0152(5)	0.2036(4)	2.5(2)
O(10)	0.3141(6)	−0.1304(7)	0.0715(4)	3.8(2)
O(11)	0.1439(6)	−0.1372(6)	0.1105(3)	2.9(2)
O(12)	0.0057(4)	0.1434(7)	0.2061(4)	2.5(2)
O(13)	0.1906(5)	−0.1879(7)	0.2353(3)	2.8(2)
O(14)	0.3577(6)	−0.1789(7)	0.1965(4)	4.0(2)

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Probing Gaseous Ion–Molecule Complexes with Chiral Agents: The Reaction of Arenium Ions with (*R*)-(–)-*s*-Butyl Chloride**

Massimiliano Aschi, Fulvio Cacace,* and Anna Troiani

Gaseous ion-neutral complexes (INC) are currently the focus of active interest, owing to the increasing recognition of their role in a variety of ionic processes.[1, 2] Crucial questions concern the chemical identity and the relative spatial arrangement of the reactants confined in the complex, two features of paramount importance to assess the kinetic and mechanistic role of the INC. Direct experimental information on these points is very scarce, which accounts for the recourse to theoretical approaches in systems of particular interest.[3, 4]

We report here the first use of a chiral reagent in the characterization of gaseous INCs. A class of aromatic substitutions that do not conform to the conventional mechanism but follow the route delineated in Equation (a), in which ArH_2^+ denotes the

$$\begin{array}{ccccccc} ArH_2^+ + P & \longrightarrow & [ArH_2^+, P] & \xrightarrow[\text{transfer}]{H^+} & [ArH, E^+] & \longrightarrow & ArHE^+ \\ & & \text{INC 1} & & \text{INC 2} & & \sigma\text{-Complex} \end{array} \qquad (a)$$

arenium ions and P a proelectrophile, that is, a neutral molecule whose protonation within the complex generates the electrophile E^+, have been studied. The quite general reaction has been nicknamed a 'Crafts–Friedel' reaction in the specific case of alkylation to underline the exchange of roles relative to the conventional course.[5–7] Among other examples, aromatic s-butylation has been demonstrated to occur according to sequence (a) within the INC formed upon addition of the benzenium ion to s-butyl chloride. Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometry shows that the alkylation takes place at 300 K with a rate constant of about $5 \times 10^{-11}\,cm^3\,s^{-1}$ per molecule, corresponding to a collision

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efficiency of about 2.5%. In these low-pressure experiments the $C_{10}H_{15}^+$ ion ($m/z = 135$), that is, protonated *s*-butylbenzene, is accompanied by minor fragments, namely, the $C_4H_9^+$ ($m/z = 57$) and the $C_{10}H_{13}^+$ ions ($m/z = 133$).[7] The FT-ICR results provide no information on the electrophile responsible for the intracomplex alkylation—which could be either a halonium (INC **2a**) or a carbenium ion (INC **2b**)—nor on its relative

$[C_6H_6, s\text{-}C_4H_9ClH^+]$ **2a** $[C_6H_6, s\text{-}C_4H_9^+, HCl]$ **2b**

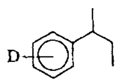
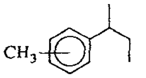
spatial juxtaposition with the arene. In particular this concerns the mechanistically relevant question whether the complex has a definite structure, that is whether the arene and the electrophile are in a fixed geometrical arrangement.

In radiolytic experiments mixtures containing CD_4 as the bulk component are irradiated together with traces of $^{12}C_6H_6$[8] and (*R*)-(−)-*s*-butyl chloride (Table 1). Ionization of CD_4 gives $C_nD_5^+$ ions ($n = 1, 2$), which undergo exothermic deuteron transfer to C_6H_6 to give $C_6DH_6^+$ ions. Following collisional thermalization and intramolecular isotopic randomization, the benzenium ions interact with $s\text{-}C_4H_9Cl$ promoting sequence (a) whose product, the $s\text{-}C_4H_9C_6DH_5^+$ ion, is deprotonated by a gaseous base, eventually yielding $s\text{-}C_4H_9C_6DH_4$.[9] It should be noted that conventional alkylation promoted by deuteron transfer to *s*-butyl chloride [Eq. (b)] does occur as well, but yields

$$C_nD_5^+ + s\text{-}C_4H_9Cl \longrightarrow C_nD_4 + DCl + s\text{-}C_4H_9^+ \xrightarrow{+C_6H_6} s\text{-}C_4H_9C_6H_6^+ \qquad \text{(b)}$$

unlabeled *s*-butylbenzene. The neutral products have been analyzed by GC-MS on a capillary column coated with a chiral stationary phase. The results, illustrated in Table 1, show that sequence (a) is moderately efficient, characterized by a $s\text{-}C_4H_9C_6DH_4$ G_{+M} value of 0.12. This corresponds to a 10% abundance of deuterated molecules in the *s*-butylbenzene formed, which allows reliable enantiomeric analysis. The paramount result is that complete racemization is observed, as illustrated in the typical chromatogram of Figure 1. In an ancillary experiment methylbenzenium ions were formed by methylation of C_6H_6 with $(CH_3)_2F^+$ ions, generated by irradiating CH_3F.[9] The yields of $s\text{-}C_4H_9C_6H_4CH_3$ isomers from $CH_3C_6H_6^+$ are much lower than those of $s\text{-}C_4H_9C_6DH_4$ from $C_6DH_6^+$, owing to the higher basicity of $CH_3C_6H_5$ than of C_6DH_5, which makes intracomplex proton transfer energetically more unfavorable. Nevertheless, also in this case the enantiomeric analysis of the *meta* and *para* isomers, the only ones amenable to chiral resolution by the column employed, show complete racemization (Figure 2).

Table 1. Aromatic alkylation in the gaseous complexes formed upon addition of $C_6DH_6^+$ and $CH_3C_6H_6^+$ ions to (*R*)-(−)-*s*-butyl chloride.

Composition [Torr] [a]	Product	G_{+M}[b]
CD_4:700, $^{12}C_6H_6$:6.7, (*R*)-(−)-$s\text{-}C_4H_9Cl$:1.8		0.12
CH_3F:750, C_6H_6:4.1, (*R*)-(−)-$s\text{-}C_4H_9Cl$:2.8	 (43% *o*, 27% *m*, 30% *p*)	2.2×10^{-2}

[a] Irradiation performed at 25 °C. All systems contained O_2 (10 Torr) as a radical scavenger. [b] Number of molecules formed per 100 eV absorbed by the gas. The estimated uncertainty of the G_{+M} values is ±20%.

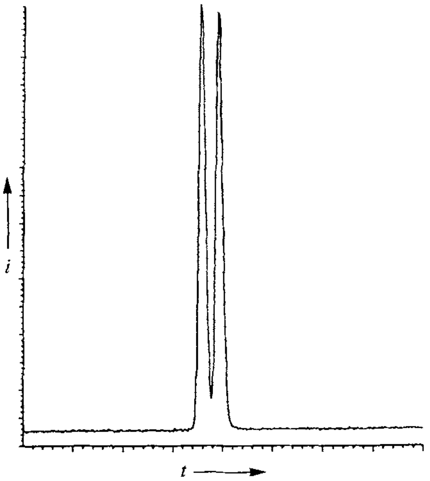


Figure 1. Enantiomeric resolution by GC/MS of racemic $s\text{-}C_4H_9C_6DH_4$ from the reaction of $C_6DH_6^+$ with (*R*)-(−)-$s\text{-}C_4H_9Cl$. Time profile of the intensity of the molecular ion at $m/z = 135$.

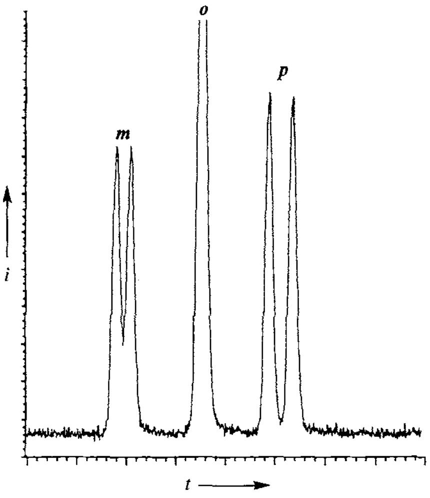


Figure 2. Partial enantiomeric separation by GC/MS of the $CH_3C_6H_4\text{-}s\text{-}C_4H_9$ isomers from the reaction of $C_7H_9^+$ with (*R*)-(−)-$s\text{-}C_4H_9Cl$. Time profile of the intensity of the molecular ion at $m/z = 148$.

The result elucidates the nature of the electrophilic reagent: the nucleophilic attack of the arene on optically active $s\text{-}C_4H_9ClH^+$ would be expected to be stereoselective and to lead to inversion rather than to the observed racemization.

A recent theoretical analysis of the other candidate, the *s*-butyl cation, is consistent with the results of NMR, ESCA,[10–13] and solvolytic studies[14] and has identified several species of comparable stability, namely, a *cis* and *trans* H-bridged ion, a CH_3-bridged ion, and two classical ions whose energies are very close (within a 2.3 kcal mol⁻¹ range).[15] Interconversion of relevant structures, allowed by the relatively flat energy hypersurface of this region of the $s\text{-}C_4H_9^+$ system, and possibly catalyzed by the neutrals present in the complex, may well account per se for the observed racemization. Even if one assumes that differential solvation effects stabilize the classical *s*-butyl cation within the INC, racemization can occur as well, provided that internal rotation of the electrophile with respect to the arene is allowed. In summary, the results deny any role for $s\text{-}C_4H_9ClH^+$ and identify $s\text{-}C_4H_9^+$ as the electrophile responsible for the intracomplex alkylation.

Another relevant point concerns the spatial correlation of the reactants. Should the electrophile be generated in a fixed geometrical position relative to the aromatic ring ("structured" complex) and retain the position until substitution takes place, for example according to a concerted mechanism, pronounced stereoselectivity would be expected in contrast to the experimental results. Instead, the picture emerging from the present study is consistent with a model in which the reagents confined in INC **2b** are not constrained in a fixed geometrical arrangement ("loose" complex).

Despite its preliminary nature, this study shows that the use of chiral reagents can probe gaseous INCs, in particular with regard to the identity of the reacting species and the structure of the complex ("loose" vs "structured"). Further work along these lines is in progress, and the results will be reported in a full paper.

Experimental Procedure

All reagents were obtained from commercial sources or prepared according to standard procedures. CD_4 (99 atom% D) and $^{12}C_6H_6$ (99.9 atom% ^{12}C) were purchased from Cambridge Isotope Laboratories. *R*-(−)-*s*-butyl chloride was prepared from *S*-(+)-*s*-butanol (Aldrich) [16, 17] and its enantiomeric purity was checked by GC with the same column employed for the analysis of the radiolytic products (25-m long, 0.25 mm i.d. fused-silica capillary column coated with DACTBS-Beta-CDX chiral phase from Mega). The radiolysis was performed at 25 °C in a commercial γ-irradiation facility to a total dose of 2.5×10^4 Gy.

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On the Mobility of Trivalent Ions: Pr^{3+} in Pr^{3+}-β''-Al_2O_3**

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A growing number of reports on ion-conducting systems with trivalent ions as mobile charge carriers were published recently.[1–3] Indications for charge transport processes of that kind were found particularly in the lanthanide ion exchanged Na^+-β''-aluminas Na^+/Ln^{3+}-β''-Al_2O_3 (Ln = La,[4] Pr,[1,5,6,7] Gd,[3] Ho[2]), as well as in rare earth tungstates, for example $Sc_2(WO_4)_3$.[8]

From electrostatic considerations ions with a low charge are especially suitable for the transport of ionic current. Accordingly, numerous cationic ion-conducting systems with monovalent ions exist (for example α-AgI, Na^+-β''-Al_2O_3, and Li_3N). In contrast, only few compounds containing mobile divalent cations (for example M^{2+}-β''-Al_2O_3 where M = Ca, Sr, Pb) or trivalent charge carriers are known. Within these systems the ion transport is hindered by strong coulombic interactions between the polyvalent ions and the surrounding host lattice. In this report we present temperature-dependent, single-crystal X-ray diffraction[9] that confirms and substantiates the results concerning ion conduction by mobile trivalent cations obtained from impedance spectroscopic measurements on the Na^+/Pr^{3+}-β''-Al_2O_3[1,6] system.

Generally, the composition of the Mg^{2+}-stabilized superionic conductor Na^+-β''-Al_2O_3 is given by the formula $Na_{1+x}Mg_xAl_{11-x}O_{17}$ ($x = 0.24$–0.70). The layered crystal structure[10] consists of alternating sequences of close-packed spinel block layers and the "conduction planes" with loosely packed oxygen layers (three-quarters of the oxygen positions remain unoccupied). The spinel blocks are interconnected by covalent Al-O-Al bonds as well as by coulombic attractive forces between the Na^+ ions (which are located exclusively within the conduction planes) to adjacent oxygen ions. The lowered oxygen occupation facilitates a comparatively easy Na^+ migration generating the two-dimensional ionic conductivity. Due to the high mobility the Na^+ ions can be replaced by other mono-, di-, and trivalent cations, particularly by lanthanide ions (for example $Na_{1+x-y}Ln_{y/3}Mg_xAl_{11-x}O_{17}$).[11,12] These alumina compounds offer an easy opportunity to vary the conducting ion within an ion-conducting system and to investigate the dependence of the ionic conductivity on the type and concentration of the charge carrier.

An idealized representation of a conduction plane in Na^+-β''-Al_2O_3 (*ab*-plane) is given in Figure 1. Two different crystallographic positions within the planes are available to the cations: the Beevers–Ross (BR) position (C_{3v} symmetry) with a triply capped tetrahedron (4+3 coordination) and the eight-coordinate "mid-oxygen" (mO) position (C_{2h} symmetry, doubly capped octahedron). The height H_L of the conduction layers (extension in *c* direction) is determined through coulombic interactions by the type (size and charge) and concentration of the cations located within these planes. H_L decreases with increasing cation concentration as demonstrated recently by X-ray diffraction studies on Na^+-β''-Al_2O_3[6,13] and Pr^{3+}-β''-Al_2O_3.[14] In turn H_L influences the cation distribution within the planes as

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