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Gas-Phase Chemistry of the Dimethylaluminum Oxide Ion and Related Aluminum Oxide Ions: Comparison of Reactivity with Siloxide Ions

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Abstract: The anion $[(CH_3)_2AlO]^-$ (**1**) has been prepared in a flowing afterglow selected ion flow tube (FA-SIFT) by ion selection from the reaction mixture of trimethylaluminum dimer and hydroxide. This unusual ion is quite reactive and has been extensively studied. It reacts with halogen-containing compounds of several types, including fluorobenzene, chlorobenzene, bromofluorobenzene, acetyl chloride, and HF, to give $[(CH_3)_2Al(OH)X]^-$, where X = F, Cl, and Br. Its chemistry with hexafluorobenzene and silicon tetrafluoride has also been detailed as have a number of reactions with carboxylic acids, esters, anhydrides, sulfur-containing neutrals, alcohols, water, and ammonia. The dominant reaction pattern of **1** involves six-centered processes which require a relatively acidic hydrogen and a lone pair donor atom in the neutral reactant. In these reactions, ion **1** abstracts a proton as the lone pair atom adds to aluminum, often with concomitant extrusion of a small, neutral molecule. We have compared the reactivity of **1** with that of $[(CH_3)_3SiO]^-$ and briefly examined other aluminum oxide ions. The kinetics of several reactions as well the thermochemical relationships among some of these ions have also been studied. Acidity studies coupled with thermochemical analysis establish that the conjugate acid of $[AlO]^-$ is AlOH, not HAlO. Computational studies have been carried out to probe both the reaction of trimethylaluminum and hydroxide, and the acidities and stabilities of AlOH and HAlO.

Introduction

Organoaluminum compounds have been known since late in the last century although their vast chemistry was not systematically studied until the early 1950's.[1] Primarily because of the pioneering work of Ziegler, studies of organoaluminum chemistry have had a fundamental effect on the development of organometallic chemistry, transforming it "from an arcane science into a mainstay of industrial research."[1] Many organoaluminum compounds have unusual properties. For example, trimethylaluminum is a dimer in both condensed and gas phases while trimethylborane is not.[1] Contributions to the theory of bonding have resulted from such structural information. The ease with which aluminum hydrides add to alkenes to produce a variety of alkylaluminum compounds, the ease of addition of trialkylaluminum compounds to alkenes to form polymers, and the catalytic nature of many of these processes have greatly contributed to the current importance of organoaluminum chemistry.[1]

Much of the structural complexity of aluminum chemistry results from the electron deficiency of aluminum. This is also important in explaining the reactivity of aluminum compounds. Thus, not only are a wide variety of structurally complex aluminum compounds known, but the tendency of aluminum to act as a Lewis acid is common. Complexes between organoaluminum compounds and almost every possible neutral Lewis base have been reported. Similarly, organoaluminum compounds react with a variety of anions to give anionic aluminates.[1]

We have for some time been interested in the gas-phase ion-molecule chemistry of anions derived from unusual neutral compounds.[2] In particular, we have concentrated on organosilicon chemistry because of its tremendous practical importance and the extremely interesting current questions concerning the nature of a variety of high-energy species. We have studied several silicon-containing anions and explored the relationships to their corresponding neutrals: $[CH_3Si(CH_2)_2]^-$, related to dimethylsilene;[2a] $[CH_3SiCH_2]^-$, related to dimethylsilylene;[2b] $[HCSi]^-$, related to silaacetylene;[2c] $[HSiO]^-$, related to silaformaldehyde;[2d] and $[RSiO]^-$ with R = CH_3 and OCH_3, related to silaacetaldehyde and methyl silaformate, respectively.[2e]

Our work has been carried out using evolving flowing afterglow (FA) technology.[2] Early FA studies required that ions be cleanly prepared since there was no means of separating one ion from another. Such studies led to many interesting results, but were limited because complex mixtures of ions could never be studied. The recent introduction of tandem flowing afterglow selected ion flow tube (FA-SIFT) technology has greatly simplified studies of complex mixtures by allowing the mass selection of an individual ion for study.[3] For example, $[HCSi]^-$ can be selected from a mixture of some 20 ions that results from electron impact on methylsilane.[2c] After selection, the ion can be injected into the second flow tube for further study. One added benefit of this new methodology is that some ions undergo collision-induced decomposition (CID) during the injection process. In some cases, CID gives a single ionic product which can be studied further.[2d,e]

One of the most important advantages of this new technology is that ions corresponding to highly reactive neutrals can be selected. The result of studying such ions is that information on the neutrals, which otherwise might be impossible to obtain, becomes available. Having used this attribute of the technology to good advantage in organosilicon chemistry, we have turned our attention to the chemistry of organoaluminum compounds. In a preliminary communication,[4] we have reported on the chemistry of $[(CH_3)_2AlO]^-$. We report here in greater detail on this ion as well as on related aluminum oxide ions and on the reactions leading to them. We will also compare the chemistry of these ions with that of $[(CH_3)_3SiO]^-$.

Experimental Section

All experiments were carried out at room temperature in a tandem flowing afterglow selected ion flow tube (FA-SIFT) which has been described in detail previously.[3] A brief description of the technique follows. The FA-SIFT consists of four sections: a source (first) flow tube for ion preparation, an ion separation and purification region, a second

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flow tube for studying the chemical reactions of the selected ions, and an ion detection region.

In the typical experiment to be described in this paper, hydroxide ions are generated in the first flow tube from oxide ions (O^-) which can be prepared by electron ionization of small amounts of N_2O (0.01 Torr) entrained in a rapidly flowing helium stream (0.4 Torr). The oxide ions are rapidly converted to hydroxide by hydrogen atom abstraction from 0.02 Torr of methane also entrained in the helium. Trimethylaluminum dimer is added downstream through a movable inlet where rapid reaction ensues producing a variety of ionic products. At the end of the first flow tube these ions are sampled through an orifice into the ion separation region. The helium and other neutrals are removed by pumping, while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole can be tuned to an appropriate *m/z* and the desired ion (for example, $[(CH_3)_2AlO]^-$) can be injected into the second flow tube, where it is entrained in helium (0.5 Torr). The reaction chemistry of the injected ion can then be probed by the addition of a variety of neutral reactants in the second flow tube. At the end of the second flow tube, the ionic products are sampled through an orifice, mass analyzed, and detected by an electron multiplier. It is important to recognize that the product ions which we assume are based on a recording of their *m/z* and chemical intuition. Neutral products are not detected, but are assumed based on mechanistic rationale. In most equations we have shown the assumed neutral product(s); however, in eq 11, 12, 13, and 18c, where the reactions are not well understood, we have not speculated on possible neutral products.

A wide variety of reactions between selected ions and neutrals have been used to characterize ions. Among the most important of these are reactions with reference acids. These, in essence, characterize the conjugate acid of the ion under study, giving a determination of the gas-phase acidity of that parent. For example, a typical anion is reacted with a series of reference acids to determine whether the anion abstracts a proton from the reference acid. Such determinations allow us to bracket an acidity between two reference acids, one from which the anion can abstract a proton and another from which it cannot. The reference acids are selected so that the narrowest possible acidity range is bracketed. Among the inherent difficulties of this approach are that (1) sometimes only a limited number of reference acids is available for the acidity region under study, (2) some reference acids, particularly C–H and N–H acids, undergo slow proton transfer, and (3) a reference acid whose acidity is close to that of the conjugate acid under study gives proton transfer which is a sensitive function of the amount of reference acid added. Recognizing these difficulties, we have carefully selected our reference acids. Although some of the bracketing acids we report in this work are N–H acids, we have been limited by the availability of suitable references in the acidity region in question (see footnote 23 and Table II for more details).

Branching ratios for the reaction of trimethylaluminum dimer and hydroxide were determined by injecting hydroxide into the second flow tube and adding the dimer at various points along the second tube. These ratios were determined as a function of reaction distance and are reported as extrapolations to zero reaction distance to eliminate any effects of secondary reactions or differential diffusion among the ions. Mass discrimination corrections were not made since in most of the cases studied the range of masses was small. The one exception was that mass discrimination measurements were made in the trimethylsilyl acetate studies.

To inject ions from the low-pressure (10^{-6} Torr) region of the SIFT quadrupole into the higher pressure region of the second flow tube, they must be extracted by an electrical potential which imparts kinetic energy to them. Multiple collisions with the helium buffer gas generally cool such ions; however, if the potential is made sufficiently high, ions can often undergo collision-induced dissociation (CID), forming new ions. In a field-free region, the resulting ions can subsequently undergo multiple collisions with helium where they are usually cooled to room temperature before being allowed to react with neutral reagents. The injection potential leading to decomposition of ions is the potential difference between the ion source and the injector plate. The exact resulting kinetic energy of the ions is a sensitive function of a variety of factors and is not well characterized.

All reactions were studied at a flow of 250 STP $cm^3\ s^{-1}$. Gases were obtained from commercial sources and were of the following purities: He (99.995%), N_2O (99.99%), O_2 (99.95%), CH_4 (99.99%), CO_2 (99.5%), SO_2 (99.9%), and COS (97.7%). $(CH_3)_6Al_2$ (>99.9%) was obtained from Band Gap Technology. Other reagents also were obtained from commercial sources and were purified as necessary before use. The helium buffer gas was passed through a liquid nitrogen cooled molecular sieve trap before entering the flow tubes.

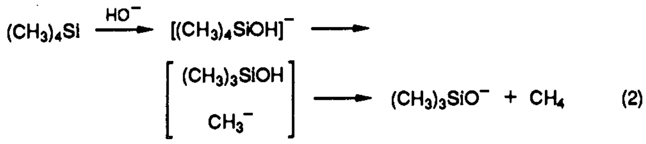
The computational results presented were obtained by standard methods. All stationary points were located at the RHF/6-31G* level[5] and were characterized as minima or transition states by computation of the energy hessian. The energies reported for these stationary points were obtained at the MP2/6-31++G** level[6,7] and were corrected with RHF/6-31* zero-point energies to correspond to enthalpies at 0 K. Addition of the diffuse functions at the RHF level has a somewhat larger effect than inclusion of electron correlation by MP2 although both are important. The energy results presented are probably accurate to 10 kcal/mol. All calculations presented were performed with the GAMESS program.[8] G1 calculations[9] were used to determine the acidities and heats of formation for AlOH and HAlO. This method is discussed in more detail in the Results and Discussion section.

Results and Discussion

Preparation of Aluminum Oxide Anions. Hydroxide reacts with a wide variety of alkyl-substituted silanes to give alkyl cleavage products (eq 1).[10] The alkyl cleavage reaction has been studied

$$(CH_3)_4Si \xrightarrow{HO^-} (CH_3)_3SiO^- + CH_4 \qquad (1)$$

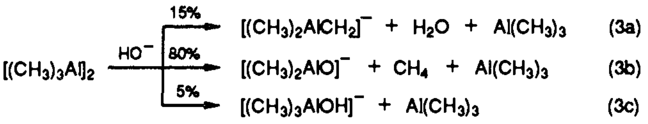
in detail and is the basis of a method to determine the acidity of weakly acidic hydrocarbons.[11] Cleavage is thought to involve attack of hydroxide on silicon to form a pentacoordinate intermediate (siliconate) which cannot be detected. Rather, the siliconate loses an alkyl anion, which, because of its proximity to the newly formed neutral silanol, abstracts a proton to give the observed products (eq 2).[11] Although many alkyl anions are



$$(CH_3)_4Si \xrightarrow{HO^-} [(CH_3)_4SiOH]^- \longrightarrow \begin{bmatrix} (CH_3)_3SiOH \\ CH_3^- \end{bmatrix} \longrightarrow (CH_3)_3SiO^- + CH_4 \qquad (2)$$

unstable with respect to their corresponding radical and an electron, the cleavage process shown in eq 2 is thought to operate because it involves not a free alkyl anion, but one stabilized by silanol solvation.[11]

The analogous reaction between hydroxide and trimethylaluminum dimer has been carried out.[4] The primary reaction products determined from branching ratios are an M – 1 ion (15%) (eq 3a), an alkyl cleavage (80%) product (eq 3b), and an adduct



$$[(CH_3)_3Al]_2 \xrightarrow{HO^-} \begin{cases} \xrightarrow{15\%} [(CH_3)_2AlCH_2]^- + H_2O + Al(CH_3)_3 & (3a) \\ \xrightarrow{80\%} [(CH_3)_2AlO]^- + CH_4 + Al(CH_3)_3 & (3b) \\ \xrightarrow{5\%} [(CH_3)_3AlOH]^- + Al(CH_3)_3 & (3c) \end{cases}$$

(aluminate) (5%) (eq 3c) which corresponds to the intermediate in reaction 2. Secondary reactions lead to a variety of other interesting ions as illustrated in eq 4. It is important to emphasize

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(5) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Standard polarization exponents were used: H(p = 1.1), C(d = 0.8), O(d = 0.8), and Al(d = 0.325).

(6) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Carsky, P.; Hess, B. A.; Schaad, L. J. *J. Comput. Chem.* **1984**, *5*, 280.

(7) Standard diffuse exponents were used: H(s = 0.0360), C(l = 0.0438), O(l = 0.0845), and Al(l = 0.0318), where l means sp shell. See: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, *4*, 294. Footnote 13 of: Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Phys. Chem.* **1984**, *80*, 3265.

(8) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

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$$[(CH_3)_3Al]_2 + HO^- \xrightarrow[\text{processes}]{\text{secondary}} [(CH_3)_3AlCH_2Al(CH_3)_2]^- + [(CH_3)_3AlOAl(CH_3)_3]^- + [(CH_3)_3Al(OH)Al(CH_3)_3]^- + [(CH_3)_4Al]^- + [(CH_3)_2Al(OH)_2]^- \quad (4)$$

that flowing afterglow studies, like other mass spectroscopic ones, lead to m/z information only. As a result, the structures given in the equations are assumed ones based on the m/z and chemical intuition. The rate coefficient of reaction 3 is 3.3×10^{-9} cm^3 molecule^{-1} s^{-1} and the efficiency assuming dimeric character for trimethylaluminum is 1.2.[12] The reaction efficiency, which is the ratio of the experimental rate coefficient to the theoretical collision rate coefficient, is a measure of the fraction of collisions actually leading to reaction. Although we have made but a crude estimate of the theoretical collision rate based on the polarizability of the trimethylaluminum dimer (from its refractive index),[12,13] nevertheless, it seems likely that this reaction occurs with every collision. As a result, it is likely the trimethylaluminum dimer is the reactive neutral. If the monomer present was the reactive neutral, it would react with a much smaller efficiency since most of the collisions would be with dimer. (We estimate that about 8% of the monomer is present at room temperature and 0.5 Torr.)[14]

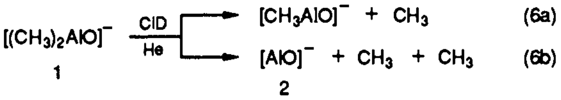
The primary products in reaction 3 can be considered in a mechanistic framework similar to the silicon reaction (eq 2). In addition to the proton abstraction channel (eq 3a), which is not observed in the silicon case, we believe the dimer reacts with hydroxide to give $[(CH_3)_3AlOH]^-$ and $(CH_3)_3Al$. The driving force to break up the strong trimethylaluminum dimer[14] is the dimer–hydroxide ion–dipole attraction[15] and the probable exothermicity of the subsequent reaction. The resulting aluminate either undergoes methide loss followed by proton transfer to give the products of channel 3b (eq 5) or is cooled by collisions with He to give the products of channel 3c. The proton abstraction product (3a) may result directly or by prior formation of the aluminate (3c).

$$[(CH_3)_3Al]_2 \xrightarrow{HO^-} [(CH_3)_3AlOH]^- + (CH_3)_3Al \longrightarrow \begin{bmatrix} (CH_3)_2AlOH \\ CH_3^- \end{bmatrix} \longrightarrow (CH_3)_2AlO^- + CH_4 \quad (5)$$

The nature of the secondary reactions of the trimethylaluminum dimer is more complex. Five additional products have been detected (eq 4). In the formation of $[(CH_3)_3AlCH_2Al(CH_3)_2]^-$, $[(CH_3)_3AlOAl(CH_3)_2]^-$, and $[(CH_3)_3Al(OH)Al(CH_3)_3]^-$, it is reasonable to assume that reaction between the primary products and excess trimethylaluminum dimer occurs. The other two products, $[(CH_3)_4Al]^-$ and $[(CH_3)_2Al(OH)_2]^-$, must result in more complicated processes.

When both hydroxide and trimethylaluminum dimer are introduced in the plasma of the first flow tube, all of the products just discussed as well as $[CH_3Al(OH)O]^-$ are formed. Although each of these ions has been selected and injected into the second flow tube for additional study, this paper will concentrate on the chemistry of $[(CH_3)_2AlO]^-$ (**1**) selected from that mixture. Since flowing afterglow is a mass spectroscopic technique, it provides us with m/z information only. In many cases such information is ambiguous, corresponding to more than one possible structure. Isotopic labeling is often used to distinguish between isomeric possibilities. We have formulated **1** as $[(CH_3)_2AlO]^-$ rather than $[CH_3Al(OH)CH_2]^-$ based on such isotopic studies as well as its reaction chemistry. Thus, when trimethylaluminum dimer reacts with DO^-, the corresponding ion we observe does not contain deuterium, a result consistent with the oxide but not the carbanion formulation.

During the course of its injection, **1** can undergo collision-induced decomposition (CID) if given sufficient kinetic energy. Both $[CH_3AlO]^-$ and $[AlO]^-$ (**2**) result (eq 6), presumably by a process



involving methyl radical loss. $[AlO]^-$ (**2**) will be considered in more detail in the discussion on thermochemistry.

Two other aluminum oxide anions have been selected and briefly studied. $[CH_3Al(OH)O]^-$ (**3**), which is prepared in the plasma of the first flow tube as already mentioned, undergoes CID to give $[AlO_2]^-$. Interestingly, $[CH_3Al(F)O]^-$ (**4**) can be prepared in the first flow tube by a complex series of reactions involving the addition of F^- and water to trimethylaluminum dimer. We believe that trimethylaluminum dimer and F^- react to give $[(CH_3)_3AlF]^-$, that this ion loses methane giving $[CH_3Al(F)CH_2^-]$, and that this reacts with water to give **4**. Both the reaction chemistry and thermochemistry of **3** and **4** will be discussed subsequently.

Computational Studies of $[(CH_3)_3AlOH]^-$ Decomposition. Ab initio calculations have been performed to further investigate the formation of **1**. In the results presented below, the "reactant" energy will be for the monomer $(CH_3)_3Al$ plus hydroxide although the experimental results suggest it is the dimer which reacts. We have studied the monomer for computational simplicity.

Assigning the reactants $(CH_3)_3Al$ plus hydroxide a relative energy of zero, the tetracoordinate aluminate ion, $[(CH_3)_3AlOH]^-$, is at −83 kcal/mol. As noted experimentally, this ion can decompose by methane loss. The proton abstraction product, $[(CH_3)_2AlCH_2]^-$, could also arise from the tetracoordinate aluminate although a direct hydrogen abstraction process could also occur. We have computationally examined the decomposition of the aluminate by both methane and water loss. Other decompositions, such as H_2 loss, are not considered here.

The elimination channel preferred by far is that of methane loss. The transition state for this elimination lies at −35 kcal/mol, with the products methane and **1** at −53 kcal/mol. The structure of the transition state resembles a leaving CH_3^- group which abstracts a proton from the OH as it departs. The OH and CH bond distances at the transition state are both long, namely, 1.26 and 1.42 Å, respectively. The OHC angle is 164°, and the imaginary transition frequency is large at 1929i cm^{-1}. The Mulliken charge on the methyl group is −0.83 with the abstracted hydrogen having a +0.40 charge. Thus, this transition state strongly resembles that involved in the decomposition of pentacoordinate siliconates[16] such as $[(CH_3)_4SiOH]^-$. Such a process has been termed dissociative anionic proton transfer.

The elimination of water is a considerably higher energy process. Here the barrier to elimination from $[(CH_3)_3AlOH]^-$ is at −17 kcal/mol, with the products $[(CH_3)_2AlCH_2]^-$ and water lying at −5 kcal/mol. There is, in addition, a long-range water–$[(CH_3)_2AlCH_2]^-$ solvation complex at −17 kcal/mol. While the transition-state geometry looks as if the leaving hydroxide can abstract a proton from methyl, the bond distances more closely resemble the final products than the methyl elimination case just considered. The breaking CH bond is long at 1.82 Å, while the forming HO bond is short at 1.04 Å. The CHO angle is more bent at 144° and the transition frequency is much smaller at 233i cm^{-1}. The charge on the abstracted carbon is +0.38 while that on the hydroxide is −0.39. The more complete proton transfer

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(12) Reaction efficiencies have been calculated from ion–neutral collision rates using the Langevin (k_L) and the variational transition state theory (VTSTR) (k_{var}) models depending on the particular reaction: (a) Langevin, P. M. *Ann. Chem. Phys.* **1905**, *5*, 245. (b) Chesnavich, W. J.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1980**, *72*, 2641. Such calculations have been applied to the reaction of hydroxide and trimethylaluminum dimer (k_L since the trimethylaluminum dimer has no dipole moment) and to a series of reactions of $(CH_3)_2AlO^-$ (**1**). The data on **1** are collected in Table I.

(13) *Handbook of Organometallic Compounds*; Hagihara, N., Kumada, M., Okawara, R., Eds.; W. A. Benjamin: New York, 1968; p 171.

(14) The enthalpy of dissociation for gaseous trimethylaluminum dimer is 20.5 kcal/mol (Hendrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461). See ref 1a for a comprehensive discussion of dissociation thermodynamic and kinetics, particularly as these relate to monomer–dimer reactivity.

(15) DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science* **1982**, *218*, 955.

(16) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056.

Table I. Rate Coefficients and Efficiencies for Reactions of $[(CH_3)_2AlO]^-$ and $[(CH_3)_3SiO]^-$

ion	neutral	dipole moment of neutral (Debye units)	$k_{expt} \times 10^9$ (cm^3 molecule^{-1} s^{-1})	k_{expt}/k_X[a]
$[(CH_3)_2AlO]^-$	C_6H_5F	1.60[b]	0.48	$k_{expt}/k_{var} = 0.26$
$[(CH_3)_2AlO]^-$	C_6F_6	0	1.0	$k_{expt}/k_L = 1.0$
$[(CH_3)_2AlO]^-$	SiF_4	0	0.78	$k_{expt}/k_L = 0.93$
$[(CH_3)_2AlO]^-$	CH_3CH_2Cl	2.05[b]	0.66	$k_{expt}/k_{var} = 0.30$
$[(CH_3)_2AlO]^-$	CH_3CH_2Br	2.03[b]	1.2	$k_{expt}/k_{var} = 0.58$
$[(CH_3)_2AlO]^-$	$(CH_3)_3SiCl$	2.70[c]	1.6	$k_{expt}/k_{var} = 0.61$
$[(CH_3)_2AlO]^-$	CH_3CO_2H	1.74[b]	2.3	$k_{expt}/k_{var} = 1.2$
$[(CH_3)_2AlO]^-$	F_2CHCO_2H	~2.5[d]	2.0	$k_{expt}/k_{var} = 0.88$
$[(CH_3)_2AlO]^-$	CH_3COSH	2.12[e]	1.7	$k_{expt}/k_{var} = 0.76$
$[(CH_3)_2AlO]^-$	$CH_3CO_2SiMe_3$	1.85[f]	1.5	$k_{expt}/k_{var} = 0.73$
$[(CH_3)_2AlO]^-$	$(CH_3CO)_2O$	3.10[g]	2.53	$k_{expt}/k_{var} = 0.91$
$[(CH_3)_2AlO]^-$	CS_2	0	0.58	$k_{expt}/k_L = 0.51$
$[(CH_3)_2AlO]^-$	OCS	0.712[b]	0.96	$k_{expt}/k_{var} = 0.73$
$[(CH_3)_2AlO]^-$	$C_6H_5OCH_3$	1.38[b]	0.41	$k_{expt}/k_{var} = 0.22$
$[(CH_3)_2AlO]^-$	$(CH_3)_3SiOCH_3$	1.20[h]	1.2	$k_{expt}/k_{var} = 0.69$
$[(CH_3)_2AlO]^-$	H_2O	1.85[b]	2.0	$k_{expt}/k_{var} = 0.77$
$[(CH_3)_3SiO]^-$	C_6F_6	0	0.88	$k_{expt}/k_L = 0.93$
$[(CH_3)_3SiO]^-$	CS_2	0	0.14	$k_{expt}/k_L = 0.13$
$[(CH_3)_3SiO]^-$	OCS	0.712[b]	0.65	$k_{expt}/k_{var} = 0.52$
$[(CH_3)_3SiO]^-$	SiF_4	0	0.68	$k_{expt}/k_L = 0.86$

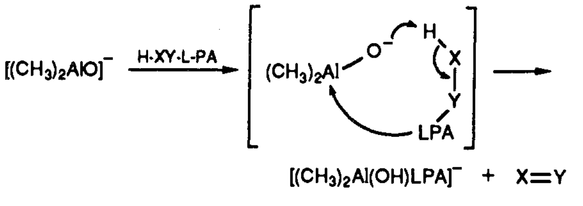
[a] References to the calculation of k_L or $k_{Langevin}$ and k_{var} are given in ref 17. [b] *CRC Handbook of Physics and Chemistry*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1978. [c] Dewar, M. J. S.; Jie, C. *Organometallics* **1987**, *6*, 1486. [d] Estimated. [e] Prezhdo, V. V.; Tarasova, G. V.; Ivanova, A. V. *Zh. Obshch. Khim.* **1983**, *53*, 406. [f] Varlamov, A. V.; Papouskova, Z.; Pola, J.; Trska, P.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1977**, *42*, 489. [g] Borgen, G. *Acta Chem. Scand., Ser. B.* **1974**, *28*, 13. [h] Nagy, J.; Ferenczi-Gresz, S.; Farkas, R.; Barta, I.; Borbely-Kuszmann, A. *Acta Khim.* (*Budapest*) **1971**, *69*, 397.

is thus reflected in the charge on hydroxide compared to that on methyl in the methyl elimination.

Although the water elimination channel is not as energetically feasible as the methane elimination, both paths are possible. The distribution of products shown in eq 3 is consistent with these results, viz. 5% undecomposed aluminate, 15% water elimination, and 80% methane elimination products. The possibility that $[(CH_3)_2AlCH_2]^-$ arises by direct proton abstraction without formation of the aluminate intermediate has not been considered computationally.

Some bond distances obtained for the ions just considered are given as follows: (1) Al–C bonds are between 2.03 and 2.05 Å and Al–O bond is 1.79 Å for $[(CH_3)_3AlOH]^-$; (2) Al–C bond is 2.03 Å and Al–O bond is 1.62 Å for $[(CH_3)_2AlO]^-$; and (3) Al–CH_3 bonds are 2.03 Å and Al–CH_2 bond is 1.83 Å for $[(CH_3)_2AlCH_2]^-$.

Reactions of Aluminum Oxide Ions. Ion **1** has been studied in detail and reacts with a wide variety of molecules including halogen-containing compounds of several types, carboxylic acids, esters, anhydrides, sulfur-containing molecules, alcohols, water, and ammonia.[4] We believe that the reactivity of **1** is dominated by six-centered transfers of both a proton and a lone pair bearing atom from its neutral reactants. Equation 7 is a generalized depiction of such a transformation.



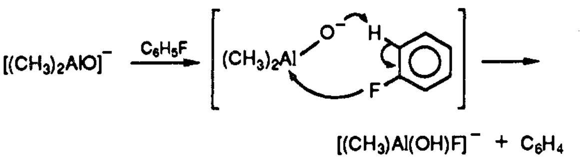
(7)

LPA = lone pair bearing atom

Reactions with Halogen-Containing Neutrals. Some of the most striking chemistry which $[(CH_3)_2AlO]^-$ (**1**) undergoes occurs with halogen-containing aromatics, particularly fluoroaromatics. With fluorobenzene, it removes HF to give $[(CH_3)_2Al(OH)F]^-$ and presumably benzyne (eq 8). Since **1** is too weak a base (vide infra)

$$[(CH_3)_2AlO]^- \xrightarrow{C_6H_5F} [(CH_3)_2Al(OH)F]^- + C_6H_4 \quad (8)$$

to abstract a proton from fluorobenzene, this reaction is best considered as a concerted process in which the oxygen atom of **1** abstracts a proton from fluorobenzene simultaneously with benzyne formation caused by the loss of fluoride which bonds to aluminum (eq 9). This mechanism is the simplest one in terms



(9)

of the information currently available and is consistent with many of the other reactions that **1** undergoes. Since so little is known about the bond energies of aluminum-containing species, it is impossible to assess the energetics of this reaction or any of the others to be discussed.[17] Suffice it to say that HF is commonly removed from fluoroaromatics of several types, that the reactions cleanly give $[(CH_3)_2Al(OH)F]^-$, and that, therefore, the energetics must be favorable.

$[(CH_3)_2Al(OH)F]^-$ is also the major ionic product in reactions of **1** with 1,2,4-trifluorobenzene, pentafluorobenzene, 2-fluoropyridine, 3-bromofluorobenzene, and 4-bromofluorobenzene. These last two cases are particularly interesting since small amounts of $[(CH_3)_2Al(OH)Br]^-$ resulting from HBr loss are detected in both as well. The generality of HX loss is also demonstrated by HBr loss from bromobenzene and HCl loss from both chlorobenzene (eq 10) and 1,3-dichlorobenzene. Perhaps surprisingly, acetyl chloride and vinyl chloride react to give $[(CH_3)_2Al(OH)Cl]^-$ as well, along with neutrals ketene and acetylene, respectively. Consistent with the behavior of **1**, ion **3**, $[CH_3Al(OH)O]^-$, reacts with pentafluorobenzene to give $[CH_3Al(OH)_2F]^-$ in addition to other ionic products.

$$[(CH_3)_2AlO]^- \xrightarrow{C_6H_5Cl} [(CH_3)_2Al(OH)Cl]^- + C_6H_4 \quad (10)$$

The rate coefficient of reaction of **1** with fluorobenzene is given in Table I[12] as are a number of other rate coefficients for reactions discussed subsequently.

The reactivity of $[(CH_3)_2AlO]^-$ (**1**) with haloaromatics appears governed by two factors: (1) the availability of both a hydrogen and halogen atom in the halo compound and (2) the aromatic

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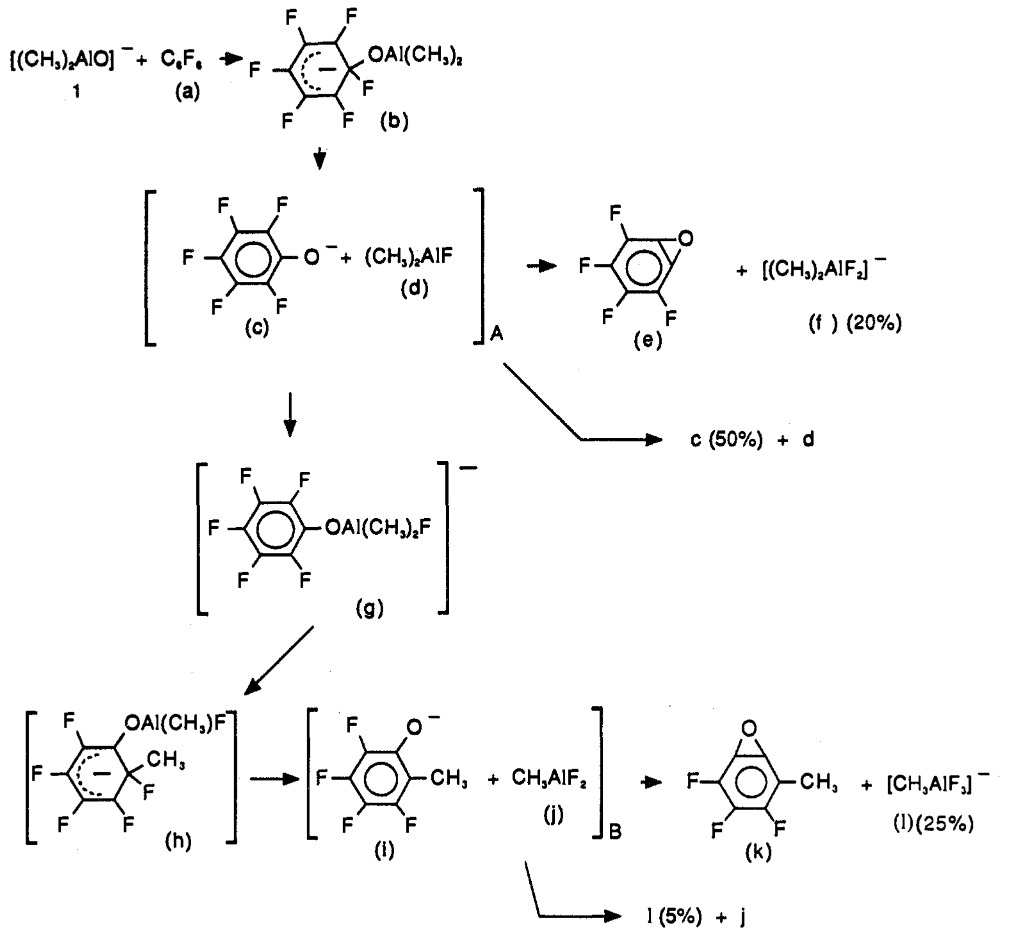
(17) Estimates of the relative bond strengths of Al–X bonds are based on reported data on the corresponding diatomics: Al–F ~160 kcal/mol, Al–O ~120 kcal/mol, Al–Cl ~120 kcal/mol, and Al–S ~87 kcal/mol. From: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

Scheme I



nucleus itself. To assess the importance of structure on reactivity, we have studied other halogen-containing compounds with variable structural features. The reaction of **1** with HF, which has been studied only briefly, examines a case where both a hydrogen and halogen atom are present, but where there is no aromatic nucleus. Here, only a small amount of $[(CH_3)_2Al(OH)F]^-$ is detected, but large amounts of two methyl cleavage products, believed to be secondary reactions products, form as well (eq 11). As we will

$$[(CH_3)_2AlO]^- \xrightarrow{HF} \underset{\text{small amount}}{[(CH_3)_2Al(OH)F]^-} + [F_2AlO]^- + [F_3AlOH]^- \quad (11)$$

see in other reactions, there is a strong tendency for aluminum to form bonds to fluorine, undoubtedly driven by a very strong aluminum–fluorine bond.[17] Hexafluorobenzene, a system having both the aromatic nucleus and a halogen atom, but lacking a hydrogen atom, has a remarkable chemistry (eq 12). Not only

$$[(CH_3)_2AlO]^- \xrightarrow[20\%]{C_6F_6} [(CH_3)_2AlF_2]^- \quad (12a)$$
$$\xrightarrow{25\%} [(CH_3)AlF_3]^- \quad (12b)$$
$$\xrightarrow{50\%} C_6F_5O^- \quad (12c)$$
$$\xrightarrow{5\%} C_6F_4(CH_3)O^- \quad (12d)$$

are two aluminate ions formed, one where methyl cleavage has occurred, but two phenoxide ions, one containing a methyl group, result as well. We believe these products are formed by the mechanism shown in Scheme I. The major features of this scheme include (1) ipso attack of a and g to give Meisenheimer intermediates b and h, (2) four- and five-centered fluoride migrations of b and h to give ion–molecule product complexes A and B, and (3) fluoride transfer from c and i to d and j, respectively, in ion–molecule product complexes A and B. That complexes A and B have lifetimes sufficiently long to involve further reaction of their ionic and neutral component is not surprising in view of a number of examples of hydrogen-exchange reactions in ion–molecule product complexes.[18] Two other important features of this reaction are worth mentioning: (1) we believe this to be the first example in the gas phase of an alkyl transfer reaction (g to h);[19] and (2) the formation of the strained benzoepoxides e and k, although unusual, is not without precedent since benzocyclopropene is known.[20] Finally, we have studied SiF_4 as an example of a halogen-containing compound having neither an aromatic nucleus nor a hydrogen atom and have observed another very complex reaction with considerable methyl cleavage (eq 13). The

$$[(CH_3)_2AlO]^- \xrightarrow[65\%]{SiF_4} [F_3SiO]^- \quad (13a)$$
$$\xrightarrow{25\%} [CH_3Si(F)_2O]^- \quad (13b)$$
$$\xrightarrow{10\%} [CH_3AlF_3]^- \quad (13c)$$

rate coefficients of both reactions 12 and 13 have been determined to be fast (Table I). The reaction of $[(CH_3)_3SiO]^-$ and SiF_4 has been studied as well (eq 14). A single ionic product, $[F_3SiO]^-$,

$$[(CH_3)_3SiO]^- \xrightarrow{SiF_4} [F_3SiO]^- + (CH_3)_3SiF \quad (14)$$

is observed; the rate of this reaction is fast as well. In contrast to the above variations, we find that fluoromethane does not react with **1**. Ethyl chloride, ethyl bromide, and trimethylchlorosilane, which might be expected to lose HX forming $[(CH_3)_2Al(OH)X]^-$, instead lose halide ion. The rate of each of these reactions is given in Table I where we see that ethyl chloride has a rate coefficient

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(18) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384.

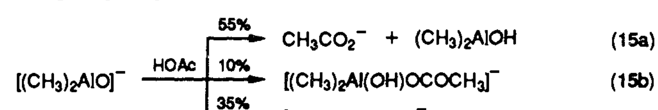
(19) Alkyl transfers from *tert*-butoxide to trimethylaluminum have been observed earlier, but this reaction chemistry was not pursued because of the complicated nature of the reaction mixtures: Professor Steven Kass, personal communication, March 1990.

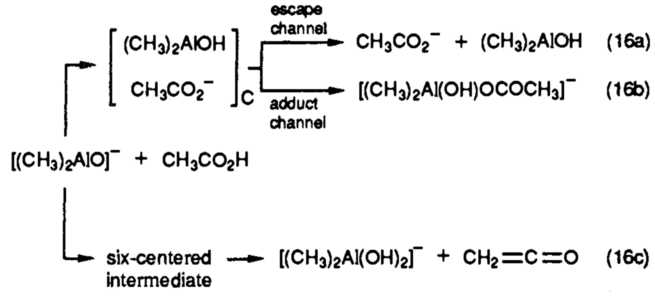
(20) March, J. *Advanced Organic Chemistry*; John Wiley: New York, 1985.

about one-half that of ethyl bromide (efficiencies of 0.30 and 0.58, respectively) and of trimethylchlorosilane (efficiency of 0.61).

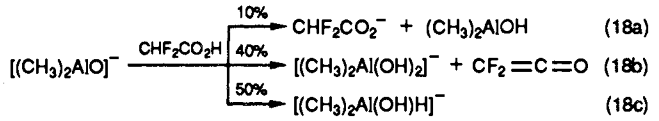
Although it is difficult to confidently rationalize these reactions of halogen-containing compounds without thermochemical groundings, it seems clear that the most unusual reactions of **1** require a reactant with either a relatively acidic hydrogen and an atom with lone pair electrons or one which is a strong Lewis base (eq 8, 10,12, and 13). When these features are absent, **1** reacts as a nucleophile and displaces halide.

Reactions with Carboxylic Acids and Their Derivatives. The reactions of $[(CH_3)_2AlO]^-$ (**1**) with acetic acid, difluoroacetic acid, and trifluoroacetic acid, thioacetic acid, trimethylsilyl acetate, and acetic anhydride have been studied in some detail. The carboxylic acids studied react to form several types of products. Among these are (1) adducts of **1** and RCO_2H, (2) the corresponding acetates, RCO_2^-, and (3) $[(CH_3)_2Al(OH)_2]^-$. The relative amounts of these depends on the structure of a particular carboxylic acid. For example, acetic acid reacts with **1** as shown in eq 15 giving 55% of the acetate ion, 10% of the adduct, $[(CH_3)_2Al(OH)OCOCH_3]^-$, and 35% of $[(CH_3)_2Al(OH)_2]^-$. The first two products can result from an ion-molecule complex C as shown (eq 16), although the acetate ion could as well result from a direct reaction without the formation of C. The second product forms from C by addition of acetate at aluminum. We suggest that $[(CH_3)_2Al(OH)_2]^-$ forms by a concerted extrusion of ketene in a manner analogous to the depictions in eq 7 and 9. The six-centered process depends on the enhanced kinetic acidity of the C-H in acetic acid. Indeed, recent studies of acetic acid have uncovered such unexpected reactivity.[21] The rate coefficient for reaction 15 is given in Table I; the reaction occurs at the collision rate. In contrast, the far more acidic trifluoroacetic acid gives only trifluoroacetate ion on reaction with **1** (eq 17), while difluoroacetic acid gives several products (eq 18).



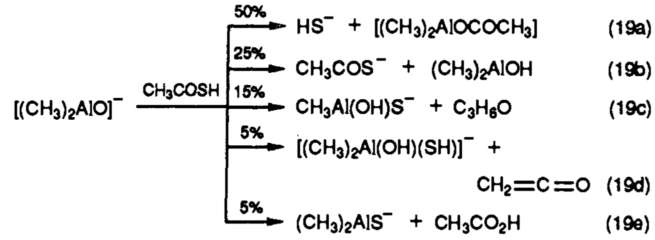


$$[(CH_3)_2AlO]^- \xrightarrow{CF_3CO_2H} (CH_3)_2AlOH + CF_3CO_2^- \quad (17)$$

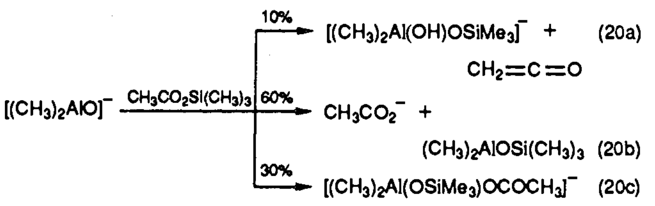


It is easy to explain the single product with trifluoroacetic acid because of its high acidity. The trifluoroacetate ion again could form either directly or from the decomposition of a complex analogous to C in eq 16. A concerted process is impossible here because trifluoroacetic acid has no α-hydrogen. More challenging is the difluoroacetic acid reaction where both the difluoroacetate ion and $[(CH_3)_2Al(OH)_2]^-$ are detected, but where, in addition, a large amount of $[(CH_3)_2Al(OH)H]^-$ results. It is likely that the first two of these form by processes analogous to their counterparts in eq 15; however, we are unable to explain how the aluminate (18c) forms and thus have not speculated about the nature of the neutral products. Finally, we have observed that the related ion **4**, $[CH_3Al(F)O]^-$, reacts with acetic acid to give acetate ion, $[CH_3Al(OH)_2F]^-$, and an adduct formulated as $[CH_3Al(F)(OH)OCOCH_3]^-$. The products observed here are analogous to those seen in reaction with **1**.

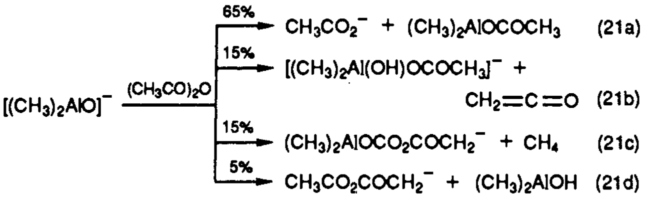
The reaction of thiolacetic acid with **1** (eq 19) is complex although some of it can be understood in light of the discussion of acetic acid. The thioacetate ion (eq 19b) and the ketene extrusion (eq 19d) products occur by analogous processes to those in acetic acid. In contrast, the HS^- product (eq 19a) results from direct displacement when **1** attacks the carbonyl carbon of thiolacetic acid. If HS^- reacts with $(CH_3)_2AlOCOCH_3$ in the resulting ion-molecule product complex, attack by HS^- at aluminum, transfer of a methyl group from aluminum to the carbonyl carbon, and carbonyl carbon-oxygen bond scission lead to $CH_3Al(OH)S^-$ and acetone (eq 19c). Finally, HS^- attack at aluminum in the same ion-molecule product complex can lead to aluminum-oxygen bond cleavage giving, after proton transfer, $(CH_3)_2AlS^-$ and acetic acid (eq 19e). The rate coefficient for eq 19 is given in Table I.



Trimethylsilyl acetate reacts with **1** to give three anionic products (eq 20). One, $[(CH_3)_2Al(OH)OSi(CH_3)_3]^-$, arises from six-centered ketene extrusion, while both acetate and the adduct can result from initial nucleophilic attack of **1** at silicon in trimethylsilyl acetate. Thus, the resulting complex (analogous to C), $[(CH_3)_2AlOSi(CH_3)_3\cdots CH_3CO_2]^-$, can collapse to adduct or to acetate. The acetate ion can, of course, also be formed directly. Rate information is given in Table I.



Finally, we have examined the reaction of acetic anhydride and **1** (eq 21). Acetate (eq 21a) is the major product with $[(CH_3)_2Al(OH)OCOCH_3]^-$ (eq 21b), the conjugate base of acetic anhydride (eq 21d), and an ion formulated as $(CH_3)_2AlOCO_2COCH_2^-$ (eq 21c), all forming in small amounts.



The reactions of both acetic and thiolacetic acids with $[(CH_3)_3SiO]^-$ give only the corresponding conjugate base ions despite similar basicities for **1** and $[(CH_3)_3SiO]^-$ (see later discussion on thermochemistry). The reaction rate coefficients of acetic acid, thiolacetic acid, and trimethylsilyl acetate with **1** are 2.3×10^{-9}, 1.7×10^{-9}, and 1.5×10^{-9} cm^3 molecule^{-1} s^{-1} with reaction efficiencies of 1.2, 0.76, and 0.73, respectively.

Reactions of Sulfur-Containing Neutrals. Both CS_2 and OCS undergo sulfur-oxygen exchange reactions with **1** that are strikingly similar to their reactions with $[(CH_3)_3SiO]^-$ in terms of products formed and likely mechanism (eq 22 and 23). Thus,

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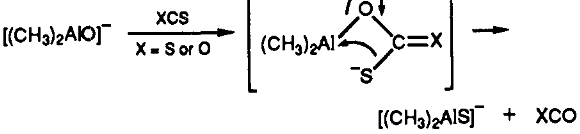
[21] (a) O'Hair, R. A. J.; Gronert, S.; DePuy, C. H.; Bowie, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 3105. (b) Grabowski, J. J.; Cheng, Z. *J. Am. Chem. Soc.* **1989**, *111*, 3106.

$$[(CH_3)_2AlO]^- \xrightarrow[\text{or OCS}]{CS_2} [(CH_3)_2AlS]^- + OCS \text{ or } CO_2 \quad (22)$$

$$[(CH_3)_3SiO]^- \xrightarrow[\text{or OCS}]{CS_2} [(CH_3)_3SiS]^- + OCS \text{ or } CO_2 \quad (23)$$

CS_2 and OCS convert both of these aluminum and silicon oxides to their corresponding thiol oxides in very clean reactions. The rate coefficients and efficiencies for these reactions are given in Table I. We consider these reactions as simple four-centered addition to the C=X (X = S or O) of CS_2 and OCS with the corresponding loss of OCS and CO_2, respectively, as we illustrate for the aluminum cases (eq 24). Ion **3**, $[CH_3Al(OH)O]^-$, also reacts with CS_2 to give $[CH_3Al(OH)S]^-$, but **4**, $[CH_3Al(F)O]^-$, gives no reaction.



(24)

Another remarkable extrusion reaction has been found with methyl disulfide which reacts with **1** cleanly giving $[(CH_3)_2Al(OH)SCH_3]^-$ and thioformaldehyde (eq 25). We again propose

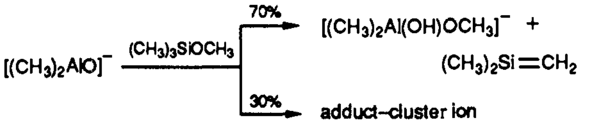
$$[(CH_3)_2AlO]^- \xrightarrow{CH_3SSCH_3} [(CH_3)_2Al(OH)SCH_3]^- + H_2C{=}S \quad (25)$$

a six-centered, concerted process to explain these products. A similar six-centered process is impossible for dimethyl sulfide, but could occur for diethyl sulfide. Indeed, we find that dimethyl sulfide gives only an adduct-cluster ion with **1**, while diethyl sulfide gives both an adduct-cluster ion and a small amount of $[(CH_3)_2Al(OH)SCH_2CH_3]^-$, which forms by extrusion of ethylene. The nature of the adduct-cluster ions is unclear.[22] They are probably weakly bound clusters of **1** and the neutral reactants. Some additional comments of the structure of such ions will be found in the section on other reactions.

Reactions of Ethers. Anisole undergoes benzyne extrusion with the formation of $[(CH_3)_2Al(OH)OCH_3]^-$ (eq 26). The rate

$$[(CH_3)_2AlO]^- \xrightarrow{C_6H_5OCH_3} [(CH_3)_2Al(OH)OCH_3]^- + C_6H_4 \quad (26)$$

coefficient for this reaction is given in Table I. Methoxytrimethylsilane gives this same aluminate (extrusion of dimethylsilene), with the formation of the corresponding adduct-cluster ion (eq 27). Its rate is much faster. In both reactions 26 and 27. we propose that the aluminate is formed by a concerted, six-centered process.



$$[(CH_3)_2AlO]^- \xrightarrow{(CH_3)_3SiOCH_3} \begin{cases} \xrightarrow{70\%} [(CH_3)_2Al(OH)OCH_3]^- + (CH_3)_2Si{=}CH_2 & (27a) \\ \xrightarrow{30\%} \text{adduct-cluster ion} & (27b) \end{cases}$$

Other Reactions. Many other neutrals react with $[(CH_3)_2AlO]^-$ (**1**) to give what we will loosely term adduct-cluster ions, that is, ions whose m/z is the sum of that of **1** and the neutral reactant. The ambiguity of having a signal at a particular m/z and knowing its structure has been discussed earlier in general terms.[2c] Adduct-cluster ions pose a special problem since they can be either covalently bonded ions or loosely bound complexes. For example, in the reaction of **1** and water, the adduct-cluster could be $[(CH_3)_2Al(OH)_2]^-$ or $[(CH_3)_2AlO\cdots H_2O]^-$. For many ions in the FA, we can distinguish between one or another isomeric structure by either isotopic labeling studies or by their reactivity; these approaches are generally not applicable to adduct-cluster ions. This problem is obvious in formulating many of the reactions of **1**. Our willingness to speculate on some adduct-cluster ions structures is based on our general understanding of the reactivity of **1**. We have already indicated that both hydrogen abstraction and lone pair atom attachment usually through a cyclic, six-centered transition state are among the important requisites for reaction of **1**. Also important is the tendency of trivalent aluminum neutrals to react with anions to give aluminates.[1] As a result, it seems sensible to formulate the 5% product of reaction **3** as an aluminate and to formulate the adduct in the trimethylsilyl acetate reaction as $[(CH_3)_2Al(OSiMe_3)OCOCH_3]^-$ (eq 20). It seems equally sensible to suggest that the adduct-cluster ion structures in the dimethyl sulfide and diethyl sulfide reactions are weakly bound clusters, since a covalent adduct formulation would require carbon bonding to aluminum.[17]

Table II. $\Delta G°_{acid}$ and $\Delta H°_{acid}$ for Aluminum and Silicon Compounds

conjugate acid	$\Delta G°_{acid}$, kcal/mol	$\Delta H°_{acid}$, kcal/mol
$(CH_3)_2AlOH$	352 ± 4	360 ± 5[a]
AlOH	352 ± 4	360 ± 6[a]
$CH_3Al(OH)_2$	352 ± 4	360 ± 5[a]
$CH_3Al(F)OH$	344 ± 4	351 ± 6[b]
$(CH_3)_3SiOH$	353 ± 4	361 ± 5[c]
$(CH_3)_2Si(F)OH$	348 ± 4	355 ± 5[d]

[a] Bracketed between pyrrole (+) and trifluoroethanol (−). [b] Bracketed between acetic acid (+) and *tert*-butylmercaptan (−). [c] Bracketed between pyrrole (+) and trifluoroethanol (−). [d] Between *tert*-butylmercaptan (+) and methylmercaptan (−). Note that plus (+) corresponds to the formation of the M − 1 ion and (−) corresponds to no M − 1 ion formation.

In this light, we can speculate about several other neutrals which react with **1** to give adduct-cluster ions. These include water, ammonia, methanol, 2,2,2-trifluorethanol, fluorotrimethylsilane, CO_2, SO_2, acetonitrile, and 2-butanone. We believe that of these, water, ammonia, methanol, and 2,2,2-trifluorethanol give true covalent adducts (aluminates) because their production is driven by the formation of a strong bond to aluminum.[17] We are less certain about whether the remaining four neutrals are weakly bound clusters or covalently bound although we favor the weakly bound cluster formulation. Additional studies are underway to attempt to unravel some of these structural problems.

Thermochemical Considerations. The gas-phase acidities corresponding to $[(CH_3)_2AlO]^-$ (**1**), $[AlO]^-$ (**2**), $[CH_3Al(OH)O]^-$ (**3**), and $[CH_3Al(F)O]^-$ (**4**), as well as those for two analogous silicon-containing ions $[(CH_3)_3SiO]^-$ and $[(CH_3)_2Si(F)O]^-$, are given in Table II. Gas-phase acidity is defined[23] as the standard free energy or enthalpy change for HA → $H^+ + A^-$. A weak acid corresponds to a large $\Delta G°_{acid}$ value.[24] We see that for both the aluminum and silicon oxides the strongest acid is the fluorine-containing one with a single fluorine substitution increasing acidity about 5–8 kcal/mol. By virtue of its high electronegativity, fluorine is expected to increase acidity, although the magnitude of these effects is difficult to assess since the corresponding

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(22) The question of the structural nature of a particular m/z is a vexing problem in ion–molecule chemistry. One way of obviating structural difficulties is to adapt a particular ion–molecule apparatus to detect and characterize neutral products. This has been accomplished with some success (see for example: Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 1645). We, on the other hand, use chemical intuition in discussing such structural ambiguities. This is not foolproof, but represents a choice we have made to study ion–molecule reactivity in broad terms rather than to specifically study individual structural problems.

(23) To determine gas-phase acidity, bases are reacted with a series of reference acids, and the acidity corresponding to their conjugate acid is determined by the so-called bracketing technique (see Experimental Section for further discussion). The aluminum-containing anions **1**–**4** have been bracketed as follows: **1**, **2**, and **3** between pyrrole (+) and trifluoroethanol (−) and **4** between acetic acid (+) and *tert*-butyl mercaptan (−). [Note that plus (+) corresponds to the formation of the M − 1 ion and (−) corresponds to no M − 1 formation.] Thus, although an N–H acid has been used for bracketing, it is one with which **1**, **2**, and **3** react. For the silicon-containing anions $(CH_3)SiO^-$ is bracketed between pyrrole (+) and trifluoroethanol (−), $(CH_3)_2Si(F)O^-$ is between *tert*-butylmercaptan (+) and methylmercaptan (−). In the latter of these cases, the unreactive bracket is an N–H acid. Unfortunately, we can not alter this result since we have found no other suitable reference acids in these acidity regions.

(24) All reference acidities are taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

gas-phase acidities of fluorine-substituted alcohols are unknown. It is surprising to us that the corresponding effect of OH-substitution is so small in the aluminum series.

In Table II we have listed the parent of $[\mathrm{AlO}]^-$ (**2**) as AlOH, not HAlO ($\Delta H^\circ_{\mathrm{acid}}$ = 360 kcal/mol). This structural assignment is based on the following analysis using the reported[17,24] experimental enthalpies of formation for AlOH, HAlO, $[\mathrm{AlO}]^-$, and H^+ (−43.0, 8.0, −67.4, and 365.7 kcal/mol, respectively). In considering eq 28–29, we see that $\Delta H^\circ_{\mathrm{acid}}$ can be calculated for

$$\Delta H^\circ_{\mathrm{acid[AlOH]}} = \Delta H_f^\circ{}_{[\mathrm{H}^+]} + \Delta H_f^\circ{}_{[\mathrm{AlO}]^-} - \Delta H_f^\circ{}_{[\mathrm{AlOH}]} \qquad (28)$$

$$\Delta H^\circ_{\mathrm{acid[HAlO]}} = \Delta H_f^\circ{}_{[\mathrm{H}^+]} + \Delta H_f^\circ{}_{[\mathrm{AlO}]^-} - \Delta H_f^\circ{}_{[\mathrm{HAlO}]} \qquad (29)$$

both AlOH and HAlO. Using the experimental literature values for the appropriate enthalpies of formation, we obtain calculated $\Delta H^\circ_{\mathrm{acid}}$ values of 341 and 290 kcal/mol for AlOH and HAlO, respectively. Clearly, the experimental value is more consistent with an AlOH formation. This analysis also points out that at least one of the heats of formation is in error, since our experimental determination is accurate to better than ±6 kcal/mol.

Recent AM1 computations using new parameters for Al report some very different heats of formation for AlOH, HAlO, and $[\mathrm{AlO}]^-$ than the experimental values reported (−40.1, −21.9, and −52.9 kcal/mol, respectively).[25] Using these computed ΔH_f° values, we obtain a computed acidity of 353 and 335 kcal/mol, respectively. These results are also best accommodated by AlOH. We have also used the relationship[26] between the $\Delta H^\circ_{\mathrm{acid}}$ of AlOH, the ionization potential of hydrogen, and the electron affinity of AlO to calculate the O–H bond dissociation energy. A surprisingly strong[27] bond dissociation energy (BDE) of 131 kcal/mol has been calculated.

To further probe the energetics of these molecules, we have carried out G1 theory[9] calculations on the gas-phase acidities and heats of formation of AlOH and HAlO. This level of theory uses extended basis sets, fourth-order perturbation theory (MP4),[28] and quadratically convergent configurational interaction (QCI)[29] calculations plus empirical corrections to predict heats of formation and energy differences to within 2 kcal/mol. We have calculated acidities of 363.2 and 337.7 kcal/mol for AlOH and HAlO, respectively, using this treatment. The first of these is in remarkable agreement with the experimentally measured value. In addition, enthalpies of reaction for eq 30 and 31 of −102.0 and

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{Al(g)} \rightarrow \mathrm{HAlO(g)} \qquad (30)$$

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{Al(g)} \rightarrow \mathrm{AlOH(g)} \qquad (31)$$

−127.5 kcal/mol at 0 K are obtained at the G1 level. Combining these with the experimental heat of formation of Al(g) (78.2 kcal/mol)[17] gives a heat of formation for AlOH(g) and HAlO(g) of −49.3 and −23.8 kcal/mol, respectively, at 0 °K. The former value is somewhat more negative than the experimental and AM1 values, while the latter is in good agreement with AM1. Finally, the G1 O–H BDE for AlOH is 136.4, in reasonable agreement with the value computed above.

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