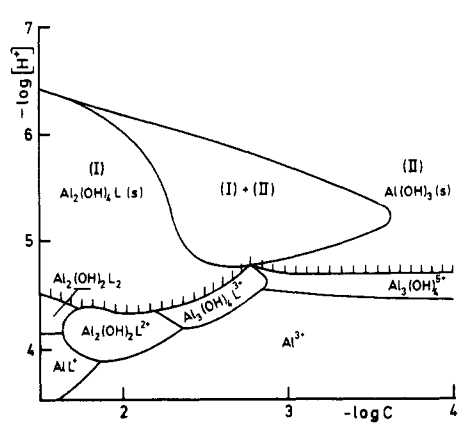

Figure 7. Predominance area diagram of $-\log [H^+]$ vs $(-\log C)_B$ for $B = 10$ mmol dm^{-3}. The diagram shows the predominating Al species as well as the stable ranges of solid phases.

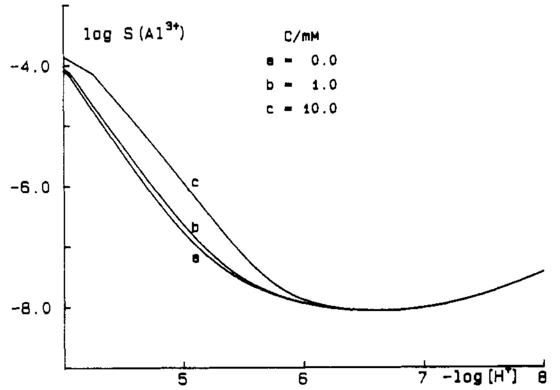

Figure 8. Solubility of kaolinite ($Al_2(OH)_4Si_2O_5$) (with respect to Al) in the presence of phthalate at different concentrations. The formation constant for kaolinite is according to Helgeson.[23]

The phthalate phase can be regarded as a hydrolysis product of the complexes $Al_2(OH)_2L^{2+}$ and $Al_2(OH)_2L_2$:

$$Al_2(OH)_2L^{2+} + 2H_2O \rightleftarrows Al_2(OH)_4L(s) + 2H^+$$

$$Al_2(OH)_2L_2 + 2H_2O \rightleftarrows Al_2(OH)_4L(s) + L^{2-} + 2H^+$$

On further hydrolysis this solid phase is transformed to aluminum hydroxide and $Al(OH)_4^-$ ions.

Modeling Calculations. It has been shown earlier that pyrocatechol[19] and salicylic acid[18] both enhance the dissolution of the clay mineral kaolinite ($Al_2(OH)_4Si_2O_5$). With pyrocatechol this influence was found in slightly alkaline solutions, whereas in the presence of salicylic acid the main influence was found at $-\log [H^+] \approx 5$. In the present work a similar model calculation was performed with phthalate. However, due to the weak Al complexation the dissolution of kaolinite in the presence of phthalate was less extensive (cf. Figure 8) than in the case of pyrocatechol and salicylic acid. A similar effect was observed on dissolution of δ-Al_2O_3 in the presence of salicylate, phthalate, and benzoate by Furrer and Stumm.[22]

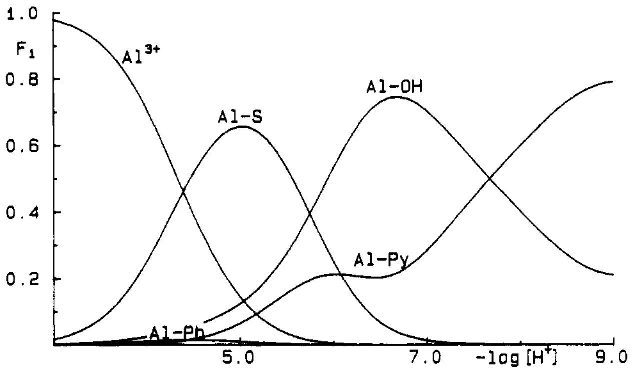

Figure 9. Distribution diagram of F_i vs $(-\log [H^+])_{BC}$ showing the sum of distribution coefficients, F_i, for aluminum phthalates (Al–Ph), aluminum salicylates (Al–S), aluminum pyrocatecholates (Al–Py), and aluminum hydroxides (Al–OH) as well as $F_{Al^{3+}}$. The total concentration of each ligand is equal to 0.1 mmol dm^{-3}. Kaolinite is the stable solid phase.

When these three aromatic bidentate ligands are regarded as possible binding sites in natural organic material, Figure 9 shows the complexation features of these sites to be quite different. *O*-dicarboxylic and *O*-carboxylic phenolic compounds are active in slightly acidic solutions, while *O*-diphenolic compounds are much more active in neutral and slightly alkaline solutions. As seen, the relative importance of aluminum bound to phthalate is negligible unless high (unnatural) concentrations are considered. It must also be noted that pure Al hydrolysis is predominating the speciation at neutral pH.

Finally, it was concluded that the phthalate phase $Al_2(OH)_4L{\cdot}4H_2O$ is too soluble to be a likely precipitate in the environment. This is different from findings in the corresponding oxalate system.[2]

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Registry No. Al, 7429-90-5; $C_8H_6O_4$, 88-99-3; $Al_2(OH)_4L{\cdot}4H_2O$, 112816-48-5.

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Preparation and Characterization of Chlorodifluorosulfur(IV) Hexafluoroarsenate

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The stable salt $[SF_2Cl]^+[AsF_6]^-$ was prepared and isolated in good yield from the reaction of *trans*-CF_3SF_4Cl and AsF_5. The identity and ionic nature of this salt were established by its elemental analysis and by ^{19}F NMR, IR, and mass spectral studies. Redistribution of the halogen atoms in the cation of $[SF_2Cl]^+[AsF_6]^-$ to form $[SF_3]^+[AsF_6]^-$ and $[SCl_3]^+[AsF_6]^-$ in liquid SO_2 occurred at ambient temperature. In the presence of NaF or NaCl, $[SF_2Cl]^+$ was converted to $[SF_3Cl]$ or $[SF_2Cl_2]$, respectively, at low temperature, where redistribution occurred to form SF_4 and $[SCl_4]$.

Salts that contain the $[SF_3]^+$ cation are formed readily by fluoride ion transfer reactions between sulfur tetrafluoride (SF_4) and fluorine-containing Lewis acids.[1,2] The lack of an appropriate precursor, e.g., SF_3Cl, has precluded the formation of $[SF_2Cl]^+$

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salts from similar fluoride ion donor–acceptor reactions. However, recently SCl_3F, SCl_2F_2, and $SClF_3$ have been observed by using matrix isolation techniques.[3] Although $[SCl_3]^+[AsF_6]^-$[4,5] and $[SBr_3]^+[AsF_6]^-$[6] are known, no mixed-halide cation of sulfur(IV) has been reported. Cations that contain a trifluoromethyl group and fluorine or chlorine are also known, viz.

$$CF_3SF_3 + AsF_5 \rightarrow [CF_3SF_2]^+[AsF_6]^{-\,7}$$

or

$$CF_3SCl + 3AsF_5 + Cl_2 \xrightarrow{SO_2} 2[CF_3SCl_2]^+[AsF_6]^- + AsF_3{}^8$$

Recently preliminary evidence was presented for the existence of the rather unstable salt $[Ir(CO)ClF(PEt_3)_2SF_2]^+[BF_4]^-$, detected by ^{19}F and ^{31}P NMR measurements.[9] In this paper we now report the preparation of a simple, stable compound, $[SF_2Cl]^+[AsF_6]^-$, formed from the reaction of CF_3SF_4Cl with AsF_5 either as a neat mixture or in CH_2Cl_2.

The salt $[CH_3SF_4]^+[AsF_6]^-$, formed from the reaction of CH_3SF_5 and AsF_5 in SO_2, decomposed rapidly above −80 °C to form CH_3F and $[SF_3]^+[AsF_6]^-$.[10] A similar decomposition with the (dialkylamido)tetrafluorosulfur(VI) cation does not occur, and $[(CH_3)_2NSF_4]^+[AsF_6]^-$ has been isolated at room temperature.[11] However, the corresponding monoalkylamido derivatives, e.g., $[CH_3NHSF_4]^+[AsF_6]^-$, are unstable with respect to loss of HF.[11]

The compound $[SF_2Cl]^+[AsF_6]^-$ can be prepared as shown in eq 1. The yield is ~70% when the reaction mixture is warmed slowly from −78 to +25 °C over a period of 12–16 h. Rapid warmup results in reduction in yields of ~50%. The yield is based on the amount of CF_3SF_4Cl consumed and by weighing the solid $[SF_2Cl]^+[AsF_6]^-$ formed. Carbon tetrafluoride was identified by its known IR[13] and ^{19}F NMR spectra.[14] The Lewis acid catalyzed elimination of CF_4 has been observed earlier in the case of CF_3NF_2.[15]

$$trans\text{-}CF_3SF_4Cl^{12} + AsF_5 \xrightarrow[\text{or } CH_2Cl_2]{\text{neat}} [SF_2Cl]^+[AsF_6]^- + CF_4 \qquad (1)$$

The molecular composition is supported by elemental analysis data (Anal. Calcd for $SAsF_8Cl$: F, 51.61; Cl, 12.04; S, 10.89. Found: F, 51.3; Cl, 12.03; S, 10.73). The negative chemical ionization mass spectrum had peaks at *m/e* 189 ($[AsF_6]^-$, 41%) and 151 ($[AsF_4]^-$, 100%). In the EI mass spectrum peaks at *m/e* 105 ($[SF_2Cl]^+$, 1.2%) and 86 ($[SFCl]^+$, 1.6%) were observed. The ^{19}F NMR spectrum of $[SF_2Cl]^+[AsF_6]^-$ in anhydrous SO_2 at −70 °C has a singlet at ϕ 18 ($[SF_2Cl]^+$) and another slightly broad single peak ($^1/_2\Delta \approx 25$ Hz) at ϕ −55 ($[AsF_6]^-$) with an area ratio of 1:3.[16] Although, in general, the fluorine resonances in metal fluorides shift to lower field when fluorine is substituted by a less electronegative atom or group,[17] the fluorine resonance assigned to $[SF_2Cl]^+$ is shifted upfield from that of $[SF_3]^+$ (ϕ 30.5 in anhydrous HF).[18] This anomalous behavior has also been observed for molecules that are isoelectronic with $[SF_3]^+$ and $[SF_2Cl]^+$, e.g., PF_3 (ϕ −33.1),[19] PF_2Cl (ϕ −36.6)[20] and NF_3 (ϕ 146.9),[21] NF_2Cl (ϕ 140.6).[22]

Assignments of the infrared vibrational spectral data for $[SF_2Cl]^+[AsF_6]^-$ were made by comparison with the isoelectronic species PF_2Cl[23] and with values previously assigned to $[AsF_6]^-$ (cm^{-1}):[24] 935 w ($\nu_{as}(SF_2)$), 888 w ($\nu_s(SF_2)$), 701 s ($\nu_3(AsF_6^-)$), 690 sh ($\nu_1(AsF_6^-)$), 605 w ($\nu(SCl)$), 561 w ($\nu_2(AsF_6^-)$), 393 m ($\nu_4(AsF_6^-)$) (w, weak; s, strong; sh, shoulder; m, medium).

Pure $[SF_2Cl]^+[AsF_6]^-$ is stable for at least 1 week at 25 °C in a Kel-F tube under anhydrous conditions. While it is insoluble in CH_2Cl_2, it is soluble in liquid SO_2, where it is stable at −60 °C. However, when it is warmed (−30 °C) in SO_2, redistribution occurs (eq 2). A ^{19}F NMR spectrum (−70 °C) of the yellowish SO_2 solution showed two resonances at ϕ 31 [$([SF_3]^+)$][15] and ϕ −57 ($[AsF_6]^-$) in a ratio of ~1:3 (one extra AsF_6^- from $[SCl_3]^+[AsF_6]^-$). The Raman spectrum of this solution displays peaks assigned to $[SCl_3]^+$,[25] $[SF_3]^+$,[26] and $[AsF_6]^-$.[26]

$$3[SF_2Cl]^+[AsF_6]^- \rightarrow 2[SF_3]^+[AsF_6]^- + [SCl_3]^+[AsF_6]^- \qquad (2)$$

It is possible that $[SF_2Cl]^+[AsF_6]^-$ is formed via the very unstable intermediate $[CF_3SF_3Cl]^+[AsF_6]^-$. We attempted to observe this species by monitoring the ^{19}F NMR spectrum of an equimolar mixture of CF_3SF_4Cl and AsF_5 in liquid SO_2 at −70 °C. The spectrum contained a quartet at ϕ 101.2 ($J_{SF-CF_3} = 19.5$ Hz), as well as the quartet at ϕ 102.6 ($J_{SF-CF_3} = 22$ Hz) for the SF fluorine atoms of CF_3SF_4Cl. The former can be assigned to the SF resonance of the probable intermediate $[CF_3SF_3Cl]^+$. However, the corresponding quartet for the CF_3 group of the intermediate was not observed perhaps because of overlapping of this signal with that of the starting material. When the mixture was warmed to −65 °C, signals attributed to $[SF_2Cl]^+[AsF_6]^-$ were observed and the quartet at ϕ 101.2 had disappeared.

When $[SF_2Cl]^+[AsF_6]^-$ was reacted with anhydrous NaF in liquid SO_2 at −65 °C for 1 h, the ^{19}F NMR spectrum (−72 °C) contained a single broad peak ($^1/_2\Delta \approx 550$ Hz) at ϕ 41. When the mixture was warmed to −30 °C and then to 25 °C over 1 h, it became yellow. Its ^{19}F NMR spectrum (−72 °C) showed peaks assignable to SF_4 (a_2b_2 spin system, $\phi(F_a)$ 32.4, $\phi(F_b)$ 86, $J_{F_a-F_b} = 77.5$ Hz).[27] This result supports a metathesis reaction followed by the formation of SF_4 (eq 3). The fine structure of the broad peak at ϕ 41 could not be observed most likely because of fluoride exchange of the highly reactive SF_3Cl. Similarly, reaction of NaCl with $[SF_2Cl]^+[AsF_6]^-$ in SO_2 at −65 °C resulted in a broad peak ($^1/_2\Delta \approx 340$ Hz) in the ^{19}F NMR spectrum at ϕ 37. On further warming to −30 °C over 1 h, resonances due to the presence of SF_4 appeared.

$$\begin{array}{lcl} 4[SF_2Cl]^+[AsF_6]^- + 4NaF & \longrightarrow & 4[SF_3Cl]^3 + 4NaAsF_6\downarrow \qquad (3) \\ & & \quad\downarrow \\ & & 3SF_4 + [SCl_4] \end{array}$$

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Registry No. $[SF_2Cl]^+[AsF_6]^-$, 113250-69-4; CF_3SF_4Cl, 42179-04-4; AsF_5, 7784-36-3; NaF, 7681-49-4; NaCl, 7647-14-5.

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