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FeAlCl₆, a Volatile Molecule Formed by the Reaction of Aluminum Chloride with Ferric Chloride¹

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In a series of experiments to determine whether the reaction with chlorine gas could be used to separate tin from the steel and aluminum in bimetallic cans, a volatile iron compound was formed only when aluminum was present. The nature of this compound was of interest because of the role it could play in the corrosion of steel by chlorine.

Two types of volatile iron compounds seemed possible: an oxochloride and an aluminum chloride complex. Though volatile oxohalides have been observed for most transition metals, none have been reported for iron.² Volatile aluminum chloride complexes have been reported for NaCl,³⁻⁵ CaCl₂,⁶ CoCl₂,⁶ MgCl₂,⁶ PbCl₂,⁶ CrCl₃,⁷ NdCl₃,⁸ and UCl₄.⁹ These compounds have been made by heating a solid mixture of the chlorides or by passing aluminum chloride vapor over the metal halide at an appropriate temperature.

Experimental Section

Materials and Apparatus. High-purity chlorine and prepurified nitrogen gases (Matheson), practical grade anhydrous aluminum chloride and anhydrous iron(III) chloride (Eastman Kodak), and reagent grade metallic aluminum and iron (J. T. Baker) were used without further purification.

Flow system experiments were carried out with (1) bimetallic cans, chlorine, and nitrogen carrier gas, (2) metallic aluminum and iron, chlorine, and nitrogen carrier gas, and (3) anhydrous aluminum and iron(III) chlorides and nitrogen carrier gas. The apparatus for this work consisted of a glass inlet bulb where gases were mixed, a 1 in. × 14 in. mullite tube (Coors) where solid materials were held in 1/4 × 4 in. unglazed ceramic boats, and a series of glass traps where the products were collected. A Model 167 Lindberg furnace was used to heat the mullite tube. After 4-5 g of reactants were placed in the boats, the system was flushed with nitrogen (40 cm³/min) at room temperature for 10 min. For the first two types of reactions, the furnace was then rapidly heated to 175°C and chlorine (10 cm³/min) was passed over the boats for 15 min; the tube was then flushed with nitrogen gas until the furnace cooled to room temperature and the product was analyzed. The third reaction differed in that the temperature of the furnace was slowly increased to 200°C and no chlorine gas was added.

In another set of experiments, various ratios of anhydrous iron(III) and aluminum chlorides were sealed in an evacuated Pyrex tube that had two or three constrictions in it. This tube was placed in the furnace so that approximately one-third of it extended outside the furnace. The reactants, in the opposite end of the tube, were heated at 175°C for 2-8 h; the compounds that collected in different parts of the tube were analyzed when the tube cooled to room temperature.

Analysis. Standard qualitative analysis procedures were used to determine the presence of iron, aluminum, and chloride ions.

Infrared studies were made with KBr pellets on a Perkin-Elmer Model 337 spectrometer.

Mass spectrometric studies were made with a Perkin-Elmer Model 270B G.C.-M.S. Samples were introduced into the spectrometer via Pyrex capillary tubes in a solids probe. Normal operating conditions for the mass spectrometer were electron voltage 80 eV, accelerating voltage 2 kV, electron multiplier 2 kV, and emission current 100 μA. Minimum temperature for the background spectra was about 50°C. Because of the high vapor pressure of the sample, the first spectra were frequently taken at pressures as high as 1 or 2 × 10⁻⁵ Torr.

Results

A moisture-sensitive orange compound that turned yellow when exposed to the atmosphere was formed in all of the reactions described above. In the anhydrous chlorides reaction, however, a yellow compound collected in the traps unless a

fast (100 cm³/min) flow rate was used. The analysis for iron¹⁰ in the orange compounds ranged from 1 to 12%. In the sealed-tube experiments, a yellow-orange compound collected in the tube outside of the furnace and long, thin crystals of a lustrous black-purple solid collected in the coolest portion of the evacuated tube still within the furnace. Chemical analysis^{10,11} of this dark material gave 32.5% Fe and 0.5-1.0% Al; iron(III) chloride should have 34.4% Fe.

More complete ir data can be found in the supplementary material which separately lists the bands observed for various orange and yellow compounds and for the starting materials. Qualitatively the infrared absorptions (cm⁻¹) found for KBr pellets of the orange compound were 1100 (s, br), 975 (w), 850 (m), 705 (s, br), 610 (m, br), and 500 (m, br); those for the yellow compound, 850 (vs, br), 610 (vs, br), and 540 (w, sh). Anhydrous AlCl₃ showed essentially the same absorptions as the yellow compound and FeCl₃ showed no distinct bands in 1300-400 cm⁻¹ range. The orange compounds from all reactions gave several of the same extra bands that were not observed for the pure compounds or for a simple mixture of these compounds with KBr that was pressed for short periods of time.

In all cases, the mass spectra for the reaction products were complex and corresponded to more than one compound. To determine which ion peaks arose from the same neutral progenitor, series of spectra were taken at increasing temperatures of the probe; ions which showed similar increasing and decreasing ion intensities were grouped together as probably arising from the same neutral species. When ions were present in only one or two series of spectra, this behavior was used to relate ions formed from the same molecule. The chemical composition of the ions was assigned on the basis of mass number, differences between mass numbers, and isotopic abundance ratios. In addition, mass spectra of anhydrous iron(III) chloride, anhydrous aluminum chloride (Baker, reagent), and of aluminum chloride vaporizing through iron(III) chloride in the probe capillary were taken to help clarify the analysis.

Abbreviated mass spectra observed for AlCl₃, FeCl₃, and mixed species of them are given in Table I; more complete spectra are given in the supplementary material; FeAlCl_x⁺ (x = 4-6) ions were observed in at least one spectrum for all the different types of experiments carried out in this work. FeAl₂Cl₇⁺ and FeAl₂Cl₈⁺ ions, however, were observed only in spectra from the sealed-tube experiments and the reaction of the chlorides in the mass spectrometer. The spectrum given for FeAlCl₆ in Table I, therefore, is not the result of fragmentation of the higher molecular weight ions. Some of the AlCl_x⁺ and FeCl_y⁺ (y = 0-3) ion intensity, however, does arise from the fragmentation of these mixed species; this is shown by the very different distribution of ion intensity for a typical reaction mixture compared with the distribution for the pure compounds. This molecule has a remarkably similar fragmentation pattern to that of the iron chloride dimer; FeAlCl₄⁺ and Fe₂Cl₄⁺ ions are the principal peaks; the FeAlCl₅⁺ and Fe₂Cl₅⁺ ions are about 50% as intense and the parent peaks are both about 6% as intense. Because the ions from FeAlCl₆ were frequently observed only in the first spectra taken, the compound appears to have a volatility similar to that of AlCl₃.

Although ions for HCl, Cl₂, and H₂O were found in almost all spectra, the amount of water in the sample was normally negligible. Large Na⁺ ion intensity, observed in most spectra including those of the pure compounds, apparently arose from the ion fragmentation of NaAlCl₄ and NaFeCl₄, which possibly formed in a reaction with the Pyrex capillary. Fragmentation of these species would be expected to contribute some AlCl_y⁺ and FeCl_y⁺ (y = 0-3) ion intensity as well. Suitable assignment for a number of ions observed in the range

Table I. Mass Spectra of AlCl_3 , FeCl_3 , and FeAl_xCl_y ($x = 1$ or 2 , $y = 4-8$)

| Ion | m/e | Rel % | |
|----------------------------|-------|------------------------|-----------------------------|
| | | AlCl_3 (pure) | AlCl_3 3-18-75-III |
| Al_3Cl_9^+ | 398 | 0.22 | |
| Al_3Cl_8^+ | 365 | 16 | |
| Al_3Cl_7^+ | 328 | 0.29 | |
| Al_2Cl_6^+ | 266 | 0.37 | |
| Al_2Cl_5^+ | 231 | 96 | 13.3 |
| Al_2Cl_4^+ | 196 | 1.24 | |
| AlCl_3^+ | 132 | 27 | 100 |
| AlCl_2^+ | 99 | 67 | 99 |
| AlCl^+ | 62 | 23 | 12 |
| Al^+ | 27 | 11 | 12 |

| Ion | m/e | Rel % | |
|----------------------------|-------|------------------------|-----------------------------|
| | | FeCl_3 (pure) | FeCl_3 3-18-75-III |
| Fe_3Cl_9^+ | 452 | 0.20 | |
| Fe_3Cl_7^+ | 415 | 0.62 | |
| Fe_2Cl_6^+ | 324 | 6.9 | 3.2 |
| Fe_2Cl_5^+ | 289 | 57 | 20 |
| Fe_2Cl_4^+ | 254 | 100 | 40 |
| Fe_2Cl_3^+ | 219 | 11.3 | 6.8 |
| FeCl_3^+ | 161 | 15 | 63 |
| FeCl_2^+ | 126 | 66 | 100 |
| FeCl^+ | 91 | 81 | 92 |
| Fe^+ | 56 | 60 | 49 |

| Ion | m/e | Rel % of FeAl_2Cl_y 4-7-75 | | Ion | m/e | Rel % of FeAlCl_y 3-18-75 | |
|------------------------------|-------|--|--|---------------------|-------|------------------------------------|--|
| | | | | | | | |
| $\text{FeAl}_2\text{Cl}_8^+$ | 394 | 32 | | FeAlCl_6^+ | 295 | 6.2 | |
| $\text{FeAl}_2\text{Cl}_7^+$ | 357 | 100 | | FeAlCl_5^+ | 260 | 51.5 | |
| | | | | FeAlCl_4^+ | 225 | 100 | |

of m/e 300–600 mass units could not be made.

Together, the visual, analytical, and infrared data show that the reaction between ferric chloride and aluminum chloride produces a volatile complex, which transports iron from the reaction zone at temperatures as low as 50°C. This compound is moisture sensitive (shown by the color change when exposed to it) and is always found mixed with aluminum chloride (under our reaction conditions). Mass spectra indicate that this volatile complex is FeAlCl_6 ; the fragmentation pattern for this compound closely corresponds to those for the dimers Al_2Cl_6 and Fe_2Cl_6 , the predominant vapor species for the two chlorides at low temperatures.

Mass spectra suggest that the second mixed species observed is FeAl_2Cl_9 , even though a molecular ion is not observed; this molecule would be analogous to trimer species for the two chlorides. Small parent ions (7% or less) were observed for the dimers and even smaller ones (less than 0.3%) were observed for the analogous trimers of AlCl_3 and FeCl_3 . Hence a molecular ion for this compound would be small and difficult to detect. The 3:1 ratio of $\text{FeAl}_2\text{Cl}_7^+$ to $\text{FeAl}_2\text{Cl}_8^+$ is remarkably similar to that for Fe_2Cl_7^+ to Fe_2Cl_8^+ . This second complex is not the volatile carrier of iron because it was not observed for all reaction mixtures and the ions for it were much less intense than those for FeAlCl_6 .

Neither is NaFeCl_4 the volatile carrier. Sodium concentration in the mullite tube is less than 2% and the formation of this molecule should not depend on the presence of aluminum. The mass spectrometric data, however, suggest that this compound and the analogous aluminum one form readily at low temperatures and are volatile.

Discussion

Some Russian workers¹² have reported mass spectrometric identification of FeAlCl_6 in the vapor above melts of FeCl_3 and AlCl_3 . In the English translation, the ions they reported

are FeCl_4^{2+} and FeAlCl_5^+ ; the FeCl_4^{2+} ion was not observed in this present study while FeAlCl_6^+ and FeAlCl_4^+ were. They do not give the relative intensities for these ions or suggest the very volatile nature of the compound. They do suggest, however, that this molecule is the structural analogue of AlCl_3 and FeCl_3 dimers. Their hypothesis is supported by this study because these molecules have similar fragmentation patterns and because a second mixed species, analogous to the trimers was observed. The simple substitution of FeCl_3 into the AlCl_3 dimer would help explain the volatility of FeAlCl_6 .

The 1:1 ratio of FeCl_3 to AlCl_3 is interesting in that a 1:3 ratio was observed for CrCl_3 to AlCl_3 .⁷ For the latter complex, the authors postulated an octahedral arrangement of chlorine-bridged AlCl_3 around the chromium. Iron(III), also, normally shows octahedral coordination but a tetrahedral arrangement is possible because a high-spin d^5 ion would have no crystal field stabilization.

Because FeAlCl_6 forms readily and has about the same volatility, this work explains why it is so difficult to purify aluminum chloride when ferric chloride is the contaminant. Since reduction of the ferric ion with hydrogen or aluminum^{13,14} would preclude formation of FeAlCl_6 , this treatment is useful in aluminum chloride purification.

Although the mass spectrum for Fe_2Cl_6 given here agrees with the abbreviated one reported in the literature,¹⁵ fewer dimeric ions are observed in this work than are given in the published mass spectrum for Al_2Cl_6 .¹⁶ Different electron voltages and conditions of temperature and of vaporization in the sample inlet could be responsible for the discrepancy.

Relatively little work with the AlCl_3 complexes and even less with FeCl_3 complexes have been reported; perhaps this is because they have not been recognized since the condensed phase could often be nonstoichiometric. Yet, they could be important carriers of metals because of the enhanced volatility in the complexes. The apparent vapor pressure of NdCl_3 was increased by a factor of 10^{13} at 600°C in 1 atm of aluminum chloride.⁸ Mass spectrometric studies appear to be an excellent way to explore further the volatile complexes of both AlCl_3 and FeCl_3 .

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Registry No. AlCl_3 , 7446-70-0; FeCl_3 , 7705-08-0; FeAlCl_6 , 57606-43-6; FeAl_2Cl_9 , 12258-27-4.

Supplementary Material Available: Listings of the infrared absorptions and detailed mass spectra peaks (3 pages). Ordering information is given on any current masthead page.

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