respectively. The salting-out coefficients, k_s, are equal to slopes, 0.284 ± 0.003 and 0.214 ± 0.005 dm^3 mol^{-1}, respectively. The former value is the same as that for Cr(acac)$_3$,[10] and it is nearly equal to 1.5 times the value for Be(acac)$_2$.[4] It may be assumed that each acetylacetonate ligand in the molecule of coordinatively saturated chelate contributes the same share into the total salting out of the molecule, independently of the central metal ion.

The greater salting-out effect exerted on Co(acac)$_3$ than on Co(Sacac)$_3$ reflects stronger outer-sphere hydration of the former chelate. The difference, Δk_s = 0.070 dm^3 mol^{-1}, is comparable with the respective difference for acetylacetonates of zinc and beryllium,[4,27] Δk_s = 0.077 dm^3 mol^{-1}. The latter difference can be attributed to the inner-sphere hydration of Zn(acac)$_2$, which engages a number of water molecules per chelate molecule.[27]

Therefore, both the differences in the respective functions of transfer and the differences in salting-out coefficients for Co(acac)$_3$ and Co(Sacac)$_3$ are not only the evidence for a stronger outer-sphere hydration of the former chelate, but they also make it possible to estimate the magnitude of the hydration. It may be expected that similar contributions to thermodynamic functions of transfer and to salting coefficients should be observed in the case of extraction of other metal complexes with organic ligands containing sulfur as donor atoms.

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Gaseous Species in the Ti–Al–Cl System and Reaction with H_2O

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Chemical species in the Ti–Al–Cl system at elevated temperatures were studied by effusion-beam mass spectrometry up to 1400 K. Gaseous TiAlCl$_5$ and TiAlCl$_6$ were identified as products of the reaction of TiCl$_4$(g) and a Ti–Al mixture above about 900 K, for which AlCl$_3$, TiCl$_2$, and TiCl$_3$ were also present. No evidence was found for TiAlCl$_7$. When gaseous TiCl$_4$, AlCl$_3$, and H$_2$O and admitted simultaneously, TiOCl$_2$, Al(OH)Cl$_2$, and TiAl(OH)Cl$_5$ were observed. All ion species showed the correct isotopic distribution. The results confirm earlier indications that AlCl$_3$ forms gaseous complexes with divalent and trivalent Ti, but not with tetravalent Ti.

Introduction

The gaseous complexation of the titanium chlorides with AlCl$_3$ was studied by Sorlie and Oye[1] by means of absorption spectroscopy at temperatures of 500–900 K. Samples of TiCl$_3$(s) and TiCl$_2$(s) were contained in sealed tubes with AlCl$_3$ at pressures ranging from 0.3 to 4 atm; under these conditions the dimer Al$_2$Cl$_6$ is the major Al–Cl species present. From measurements of the absorption spectra as a function of temperature, reaction stoichiometric coefficients were obtained and were used in identifying the gaseous complexes formed. Complexation was observed with gaseous TiCl$_2$ and TiCl$_3$, but not with TiCl$_4$. However, the derived stoichiometric coefficients were nonintegral, indicating the possibility of more than one complex for each Ti–Cl species. With TiCl$_3$, the dominant gaseous complex was assumed to be TiAlCl$_6$, with a smaller amount of TiAl$_2$Cl$_9$, while, for TiCl$_2$, the results indicated TiAl$_3$Cl$_{11}$ was dominant, with a possible contribution from TiAl$_4$Cl$_{14}$.

Our interest in the high-temperature chemistry of the Ti–Al–Cl system and the products of reaction with H$_2$O led us to investigate this system by a more direct method, effusion-beam mass spectrometry. Use of a molecular effusion source necessarily limits the total pressure to the region below 10^{-5} atm, but it does provide a direct sampling method that eliminates secondary reactions with surfaces and other gas molecules, thereby giving unambiguous information about vapor composition. In this work, the gaseous products generated by reaction of TiCl$_4$ with a Ti–Al mixture and by direct reaction of TiCl$_4$, AlCl$_3$, and H$_2$O were examined by mass spectrometry, with the results reported below.

Experimental Section

All measurements were made with the magnetic deflection mass spectrometer system and experimental techniques described in previous publications.[2,3] For studies of the Ti–Al–Cl system alone, TiCl$_4$(g) was admitted to a graphite effusion cell containing pieces of Ti and Al wire. To provide inert conditions with gas mixtures containing H$_2$O, a platinum effusion cell with two concentric gas-inlet tubes was utilized. In order to prevent prereactions in the inlet system, H$_2$O was added through the small central Pt inlet tube extending into the cell hot region, while TiCl$_4$ and AlCl$_3$ were admitted through the annular space between the inlet tubes. The Pt cell contained pieces of Ti wire supported on a Pt screen, giving a less reducing environment than that of the Al/Ti sample in the graphite cell. Each reagent gas was added from a separate reservoir containing the solid or liquid, and the flows were controlled with precision leak valves.

Ionization efficiency curves were recorded automatically,[3] and threshold appearance potentials were evaluated by the vanishing-current method. All reported ion intensities were subjected to the beam-defining slit test to eliminate potential background contributions. Temperatures were measured by optical pyrometry, sighting on a blackbody cavity in the cell lid; for the Pt cell, a graphite cover containing the cavity was placed over the cell body.

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TABLE I: Ions, Appearance Potentials, and Neutral Precursors from Mass Spectra of the Ti-Al-Cl System

ion	AP, eV[a]	neutral precursor	approx T, K
$TiCl_4^+$	11.9	$TiCl_4$	400
$TiCl_3^+$	13.1	$TiCl_4$	400
	9.1	$TiCl_3$	900
$TiCl_2^+$	16.5	$TiCl_4$	400
	12.5	$TiCl_3$	900
	8.2	$TiCl_2$	1100
$TiCl^+$	20.8	$TiCl_4$	400
	17.1	$TiCl_3$	900
	12.0	$TiCl_2$	1000
$AlCl_3^+$	12.5	$AlCl_3$	900
$AlCl_2^+$	13.0	$AlCl_3$	900
$AlCl^+$	18.2	$AlCl_3$	900
	9.9	AlCl	1100
Al^+	6.1	Al	1100
$Al_2Cl_5^+$	12.7	Al_2Cl_6	900
$TiAlCl_5^+$	11.4	$TiAlCl_6$	1100
$TiAlCl_4^+$	11.7	$TiAlCl_5$	1100

[a] Uncertainty ±0.3 eV.

The $TiCl_4$, $AlCl_3$, Ti, and Al samples were reagent grade materials obtained from commercial suppliers. $AlCl_3$ was further purified by dehydration in a stream of Cl_2 at 450 K, followed by vacuum sublimation. Laboratory deionized H_2O was frozen and then held under vacuum to remove dissolved gases. The $TiCl_4$ and H_2O liquid samples had sufficient vapor pressure at room temperature to maintain the desired gas flow rates, while the solid $AlCl_3$ was heated to about 340 K with a water bath; the $AlCl_3$-inlet line was warmed with a heating tape up to the point where it passed through the molecular-source flange to prevent condensation.

Results

A. $TiCl_4$ + Ti-Al. In Table I are listed the ions observed in the mass spectra of the effusing gas generated by the reaction of $TiCl_4(g)$ with the Ti-Al mixture for various cell temperatures. Also shown are the measured threshold appearance potentials (AP's) of the ions and the assigned neutral precursors. At 400 K, only unreacted $TiCl_4$ is observed; the measured AP's of the Ti-Cl ions are in good agreement with those reported in the mass spectrum of $TiCl_4$.[4] At 900 K, the AP($TiCl_3^+$) dropped to 9.1 eV, signaling the presence of molecular $TiCl_3$. The AP's of $TiCl_2^+$ and $TiCl^+$ also fell by about 4 eV, consistent with expectations for $TiCl_3$. Also appearing at 900 K were the parent ion $AlCl_3^+$, with the $AlCl_3$ fragments $AlCl_2^+$ and $AlCl^+$, and the fragment $Al_2Cl_5^+$ from Al_2Cl_6, all with AP's in accord with literature values.[4]

Up to 900 K then, the species $TiCl_4$, $TiCl_3$, $AlCl_3$, and Al_2Cl_6 were identified in the cell beam. At about 1100 K, AP($TiCl_2^+$) dropped still further to 8.2 eV, close to the expected ionization potential (IP) of molecular $TiCl_2$, and the parent ions Al^+ and $AlCl^+$ appeared with characteristic AP's close to 6 and 10 eV, respectively.[4] Thus, the conditions were sufficiently reducing at the higher temperature to generate gaseous $TiCl_2$, Al, and AlCl. Near 1100 K, somewhat weaker ion signals also appeared at the mass positions corresponding to $TiAlCl_5^+$ and $TiAlCl_4^+$; both ions showed isotopic spectra in close agreement with those calculated from the natural abundances of the elements. No ion signals corresponding to $TiAlCl_6^+$ were observed. It is highly unlikely that $TiAlCl_5^+$ and $TiAlCl_4^+$ can be parent ions, since the corresponding open-shell neutrals would be expected to have IP's of 8-9 eV. However, the observed AP's are reasonably consistent with those anticipated for the common halide fragmentation processes

$$TiAlCl_6 + e \rightarrow TiAlCl_5^+ + Cl + 2e \qquad (1)$$

and

$$TiAlCl_5 + e \rightarrow TiAlCl_4^+ + Cl + 2e \qquad (2)$$

involving the neutral complexes $TiCl_3{\cdot}AlCl_3$ and $TiCl_2{\cdot}AlCl_3$. From bond energy considerations, one estimates $D(TiAlCl_5{-}Cl)$ and $D(TiAlCl_4{-}Cl)$ to be about 3.5 eV, and with IP ~8.5 eV for $TiAlCl_5$ and $TiAlCl_4$, the threshold AP's of processes 1 and 2 would be about 12 eV, in accord with the observed values of 11.4 and 11.7 eV. The parent ions of such halides are frequently unstable and dissociate to fragment products before reaching the ion collector.

TABLE II: Relative Abundances of Ion Species in Mass Spectra of the Ti-Al-Cl System

		ion intensity[a]	
ion	neutral	1100 K	1400 K
$TiCl_4^+$	$TiCl_4$	183	0.23
$TiCl_3^+$	$TiCl_3$	26.7	9.72
$TiCl_2^+$	$TiCl_2$	0.11	0.93
$Al_2Cl_5^+$	Al_2Cl_6	1.3	4.89
$AlCl_3^+$	$AlCl_3$	103	89.7
$AlCl^+$	AlCl	1.6	124
Al^+	Al	0.11	15.0
$TiAlCl_5^+$	$TiAlCl_6$	0.05	0.02
$TiAlCl_4^+$	$TiAlCl_5$	0.34	0.87

[a] Arbitrary units.

$TiCl_4{\cdot}AlCl_3$ would be expected to yield the major ion $TiAlCl_6^+$, but none was observed. In fact, no Ti-Al complex-ion signals were seen at lower temperatures where $TiCl_4$ and $AlCl_3$ alone were present; the complex-ion signals were observed only when $TiCl_3$ and $TiCl_2$ were present. Furthermore, the fragmentation process

$$TiAlCl_7 + e \rightarrow TiAlCl_5^+ + 2Cl + 2e \qquad (3)$$

has an estimated AP of 15.5 eV, well above the observed value for $TiAlCl_5^+$; even if Cl_2 were the product of reaction 3, the predicted AP of 13 eV would still be significantly larger than the experimental value. Thus, the mass spectrometric evidence is consistent with the complexes $TiAlCl_6$ ($TiCl_3{\cdot}AlCl_3$) and $TiAlCl_5$ ($TiCl_2{\cdot}AlCl_3$). No heavier complexes were observed under these experimental conditions.

In Table II are listed the intensities of the major ion species associated with the neutrals identified from the mass spectra at two temperatures; in all instances, intensities were measured at 3 eV above the respective ionization thresholds to avoid overlapping fragmentation effects. Increasing the temperature from 1100 to 1400 K led to a substantial depletion of $TiCl_4$ due to chemical reduction by Al and emergence of AlCl as a major species. The decline in the abundance of $TiCl_3$ led to the expected decrease in that of $TiAlCl_6$, while the sharp rise in $TiCl_2$ abundance was consistent with the observed increase in that of $TiAlCl_5$.

In contrast to the sharp response to movement of the beam-defining slit shown by all other species, the $TiAlCl_5^+$ and $TiAlCl_4^+$ signals exhibited only a partial reduction in intensity and a gradual increase in background level; this behavior suggests that a volatile Ti-Al-Cl condensed phase deposited on the cooler parts of the chamber and was responsible for the background pressure of the species in the ion source. Sorlie and Oye[1] reported a relatively volatile $TiAl_2Cl_8$ liquid phase that could account for this behavior.

B. $TiCl_4$ + $AlCl_3$ + H_2O. When the three reagent gases were added to the platinum cell, the ions with the threshold AP's shown in Table III were observed. Below 900 K, when only $TiCl_4$ and $AlCl_3$ were admitted, no mixed complex ions were found, again showing that there is no evidence for the existence of $TiAlCl_7$ ($TiCl_4{\cdot}AlCl_3$). With the appearance of $TiCl_3$ at about 1000 K, the complex ion $TiAlCl_5^+$ was again observed with the same AP. And since neither parent $TiCl_2^+$ nor $TiAlCl_4^+$ appeared under these conditions, the ion/neutral precursor assignments $TiAlCl_5^+/TiAlCl_6$ and $TiAlCl_4^+/TiAlCl_5$ are fairly certain.

When H_2O was admitted, the additional ions $TiOCl_2^+$, $Al(OH)Cl_2^+$, and $TiAl(OH)Cl_4^+$ appeared above 1000 K. The threshold AP of $TiOCl_2^+$ is close to that of $TiCl_4$ and is a reasonable IP for the closed-shell $TiOCl_2$. Likewise, $Al(OH)Cl_2^+$, with an AP of 11.2 eV, is considered to be a parent ion. For reasons similar to those stated above the $TiAlCl_5^+$ and $TiAlCl_4^+$, $TiAl(OH)Cl_4^+$ is taken to be a fragment from the open-shell

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TABLE III: Ions, Appearance Potentials, and Neutral Precursors from Mass Spectra of the Ti–Al–Cl–O–H System

ion	AP, eV[a]	neutral precursor	approx T, K
$TiCl_4^+$	11.9	$TiCl_4$	400
$TiCl_3^+$	13.1	$TiCl_4$	400
	9.1	$TiCl_3$	1000
$TiCl_2^+$	12.6	$TiCl_3$	1000
$AlCl_3^+$	12.5	$AlCl_3$	900
$TiAlCl_5^+$	11.4	$TiAlCl_6$	1000
$TiOCl_2^+$	12.2	$TiOCl_2$	1050
$Al(OH)Cl_2^+$	11.2	$Al(OH)Cl_2$	1050
$TiAl(OH)Cl_4^+$	11.3	$TiAl(OH)Cl_5$	1050
$TiAlO^+$	9.4	TiAlO?	1600
$TiAlOCl^+$	11.1	?	1600

[a] Uncertainty ±0.3 eV.

TABLE IV: Relative Abundances of Ion Species in Mass Spectra of the Ti–Al–Cl–O–H System

ion	neutral	ion intensity[a]		
		950 K	1200 K	1400 K
$TiCl_4^+$	$TiCl_4$	60.9	116	130
$TiCl_3^+$	$TiCl_3$	0.03	3.4	7.6
$TiOCl_2^+$	$TiOCl_2$	0.53	1.6	1.0
$AlCl_3^+$	$AlCl_3$	3.7	1.7	3.7
$TiAl(OH)Cl_4^+$	$TiAl(OH)Cl_5$	1.0	1.9	2.8

[a] Arbitrary units.

species $TiAl(OH)Cl_5$ ($TiCl_3 \cdot Al(OH)Cl_2$), with an AP very close to those of the other complex fragment ions.

At the highest temperatures, the smaller mixed ions $TiAlOCl^+$ and $TiAlO^+$ were observed, but the assignment of neutral precursors is problematical. The AP of $TiAlO^+$ is perhaps consistent with formation from the parent neutral Ti–O–Al, but $TiAlOCl^+$ is most likely a fragment, of uncertain origin.

Table IV shows the temperature dependences of the major ion intensities in the mass spectra of the $TiCl_4$–$AlCl_3$–H_2O system. As expected, the abundance of $TiAl(OH)Cl_5$ increased in step with that of $TiCl_3$. $TiAlCl_5^+$ and $TiAl(OH)Cl_4^+$ were not observed simultaneously; when H_2O was admitted, the signals from the former decreased to the background level as those of the latter increased.

Discussion

In accord with the findings of Sorlie and Oye,[1] we obtained no evidence for the formation of the mixed complex $TiCl_4 \cdot AlCl_3$, where both Ti and Al are in their highest oxidation states. Mixed Ti–Al–Cl complexes were observed only in the presence of gaseous $TiCl_3$ and $TiCl_2$, with the stoichiometries $TiAlCl_6$($TiCl_3 \cdot AlCl_3$) and $TiAlCl_5$ ($TiCl_2 \cdot AlCl_3$). In their work at higher pressures, Sorlie and Oye[1] also inferred the existence of $TiAlCl_6$, but in contrast to our observation of $TiAlCl_5$, they identified $TiAl_3Cl_{11}$ ($TiCl_2 \cdot 3AlCl_3$) as the major complex involving divalent Ti. The abundances of higher order complexes would increase more rapidly with pressure, so that $TiAl_3Cl_{11}$ could well predominate near 1 atm.

From their evaluation of the apparent vapor pressures of the complexes, Sorlie and Oye[1] concluded that $AlCl_3$ enhances the stability of divalent Ti to a much greater degree than the trivalent state. The observed intensities in Table II, where $TiAlCl_5^+/TiCl_3^+ \sim 0.002$ and $TiAlCl_4^+/TiCl_2^+ \sim 1$, are in accord with this concept.

From the temperature dependence of the absorption spectrum, Sorlie and Oye[1] deduced for the reaction

$$TiCl_3(s) + \tfrac{1}{2}Al_2Cl_6(g) = TiAlCl_6(g) \qquad (4)$$

$\Delta H^\circ = 77.3 \pm 2.6$ kJ mol^{-1}. With the aid of auxiliary tabulated data,[5] one can derive for the reaction

$$TiCl_3(g) + AlCl_3(g) = TiAlCl_6(g) \qquad (5)$$

$\Delta H^\circ = -133$ kJ mol^{-1} using the result from reaction 4. One-to-one complexes such as $TiAlCl_6$ are thought to have chlorine-bridged structures between adjacent –Ti–Cl and Cl–Al–groups, and as such, similar complexes with $AlCl_3$ might be expected to have comparable entropy changes. For reactions such as

$$MCl(g) + AlCl_3(g) = MAlCl_4(g) \qquad (6)$$

Schafer[6] estimated $\Delta S^\circ_{298} = -151$ J K^{-1} mol^{-1} and $\Delta C_p^\circ = 12$ J K^{-1} mol^{-1}. Assuming the same value of ΔS° for reaction 5 and estimating the equilibrium constant $K^\circ(5) \sim 100$ atm^{-1} from the intensities in Table II and an approximate pressure calibration, one calculates the third-law enthalpy change $\Delta H^\circ \sim -230$ J K^{-1} mol^{-1}. This latter value is much more negative than the one obtained from absorption spectroscopy,[1] -133 kJ mol^{-1}, but is in line with an enthalpy change of -219 kJ mol^{-1} obtained for the reaction

$$NaCl(g) + AlCl_3(g) = NaAlCl_4(g) \qquad (7)$$

from equilibrium measurements.[7] However, the enthalpies of $AlCl_3$ complexation can vary widely, depending on the coordination of the metal ions and the strength of the acid–base interaction,[6] so that further studies are needed to define the stabilities of the $TiCl_x$–$AlCl_3$ complexes and particularly the dependence on the Ti valence state.

Although the species $TiOCl_2$ has been postulated as an intermediate in the chlorination of titania[8] and several infrared bands have been reported,[9] to our knowledge it has not been directly identified previously. The mass spectral results show that gaseous $TiOCl_2$ could be an important intermediate in the oxidation of $TiCl_4$, as well as in the chlorination of TiO_2.

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