

respectively. The salting-out coefficients, k_s , are equal to slopes, 0.284 ± 0.003 and $0.214 \pm 0.005 \text{ dm}^3 \text{ mol}^{-1}$, respectively. The former value is the same as that for $\text{Cr}(\text{acac})_3$,¹⁰ and it is nearly equal to 1.5 times the value for $\text{Be}(\text{acac})_2$.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 $\text{Co}(\text{acac})_3$ than on $\text{Co}(\text{Sacac})_3$ reflects stronger outer-sphere hydration of the former chelate. The difference, $\Delta k_s = 0.070 \text{ dm}^3 \text{ mol}^{-1}$, is comparable with the respective difference for acetylacetonates of zinc and beryllium,^{4,27} $\Delta k_s = 0.077 \text{ dm}^3 \text{ mol}^{-1}$. The latter difference can be attributed to the inner-sphere hydration of $\text{Zn}(\text{acac})_2$, 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 $\text{Co}(\text{acac})_3$

and $\text{Co}(\text{Sacac})_3$ 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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(27) Narbutt, J. To be published.

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 $\text{TiCl}_4(\text{g})$ 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_2O and admitted simultaneously, TiOCl_2 , $\text{Al}(\text{OH})\text{Cl}_2$, and $\text{TiAl}(\text{OH})\text{Cl}_5$ 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 Oye¹ by means of absorption spectroscopy at temperatures of 500–900 K. Samples of $\text{TiCl}_3(\text{s})$ and $\text{TiCl}_2(\text{s})$ were contained in sealed tubes with AlCl_3 at pressures ranging from 0.3 to 4 atm; under these conditions the dimer Al_2Cl_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_2Cl_9 , while, for TiCl_2 , the results indicated $\text{TiAl}_3\text{Cl}_{11}$ was dominant, with a possible contribution from $\text{TiAl}_4\text{Cl}_{14}$.

Our interest in the high-temperature chemistry of the Ti-Al-Cl system and the products of reaction with H_2O 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_2O 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, $\text{TiCl}_4(\text{g})$ was admitted to a graphite effusion cell containing pieces of Ti and Al wire. To provide inert conditions with gas mixtures containing H_2O , a platinum effusion cell with two concentric gas-inlet tubes was utilized. In order to prevent prereactions in the inlet system, H_2O 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 ₂ Cl ₅ ⁺	12.7	Al ₂ Cl ₆	900
TiAlCl ₅ ⁺	11.4	TiAlCl ₆	1100
TiAlCl ₄ ⁺	11.7	TiAlCl ₅	1100

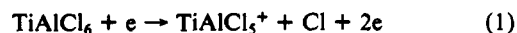
^a Uncertainty ± 0.3 eV.

The TiCl₄, AlCl₃, Ti, and Al samples were reagent grade materials obtained from commercial suppliers. AlCl₃ was further purified by dehydration in a stream of Cl₂ at 450 K, followed by vacuum sublimation. Laboratory deionized H₂O was frozen and then held under vacuum to remove dissolved gases. The TiCl₄ and H₂O liquid samples had sufficient vapor pressure at room temperature to maintain the desired gas flow rates, while the solid AlCl₃ was heated to about 340 K with a water bath; the AlCl₃-inlet line was warmed with a heating tape up to the point where it passed through the molecular-source flange to prevent condensation.

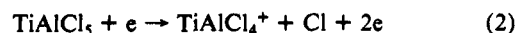
Results

A. TiCl₄ + Ti-Al. In Table I are listed the ions observed in the mass spectra of the effusing gas generated by the reaction of TiCl₄(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 TiCl₄ is observed; the measured AP's of the Ti-Cl ions are in good agreement with those reported in the mass spectrum of TiCl₄.⁴ At 900 K, the AP(TiCl₃⁺) dropped to 9.1 eV, signaling the presence of molecular TiCl₃. The AP's of TiCl₂⁺ and TiCl⁺ also fell by about 4 eV, consistent with expectations for TiCl₃. Also appearing at 900 K were the parent ion AlCl₃⁺, with the AlCl₃ fragments AlCl₂⁺ and AlCl⁺, and the fragment Al₂Cl₅⁺ from Al₂Cl₆, all with AP's in accord with literature values.⁴

Up to 900 K then, the species TiCl₄, TiCl₃, AlCl₃, and Al₂Cl₆ were identified in the cell beam. At about 1100 K, AP(TiCl₂⁺) dropped still further to 8.2 eV, close to the expected ionization potential (IP) of molecular TiCl₂, 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 TiCl₂, Al, and AlCl. Near 1100 K, somewhat weaker ion signals also appeared at the mass positions corresponding to TiAlCl₅⁺ and TiAlCl₄⁺; both ions showed isotopic spectra in close agreement with those calculated from the natural abundances of the elements. No ion signals corresponding to TiAlCl₆⁺ were observed. It is highly unlikely that TiAlCl₅⁺ and TiAlCl₄⁺ 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



and



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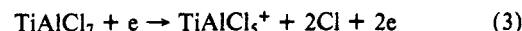
TABLE II: Relative Abundances of Ion Species in Mass Spectra of the Ti-Al-Cl System

ion	neutral	ion intensity ^a	
		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 ₂ Cl ₅ ⁺	Al ₂ Cl 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.

involving the neutral complexes TiCl₃·AlCl₃ and TiCl₂·AlCl₃. From bond energy considerations, one estimates $D(\text{TiAlCl}_5\text{--Cl})$ and $D(\text{TiAlCl}_4\text{--Cl})$ to be about 3.5 eV, and with IP ~ 8.5 eV for TiAlCl₅ and TiAlCl₄, 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.

TiCl₄·AlCl₃ would be expected to yield the major ion TiAlCl₆⁺, but none was observed. In fact, no Ti-Al complex-ion signals were seen at lower temperatures where TiCl₄ and AlCl₃ alone were present; the complex-ion signals were observed only when TiCl₃ and TiCl₂ were present. Furthermore, the fragmentation process



has an estimated AP of 15.5 eV, well above the observed value for TiAlCl₅⁺; even if Cl₂ 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 TiAlCl₆ (TiCl₃·AlCl₃) and TiAlCl₅ (TiCl₂·AlCl₃). 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 TiCl₄ due to chemical reduction by Al and emergence of AlCl as a major species. The decline in the abundance of TiCl₃ led to the expected decrease in that of TiAlCl₆, while the sharp rise in TiCl₂ abundance was consistent with the observed increase in that of TiAlCl₅.

In contrast to the sharp response to movement of the beam-defining slit shown by all other species, the TiAlCl₅⁺ and TiAlCl₄⁺ 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 Oye¹ reported a relatively volatile TiAl₂Cl₈ liquid phase that could account for this behavior.

B. TiCl₄ + AlCl₃ + H₂O. 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 TiCl₄ and AlCl₃ were admitted, no mixed complex ions were found, again showing that there is no evidence for the existence of TiAlCl₇ (TiCl₄·AlCl₃). With the appearance of TiCl₃ at about 1000 K, the complex ion TiAlCl₅⁺ was again observed with the same AP. And since neither parent TiCl₅⁺ nor TiAlCl₄⁺ appeared under these conditions, the ion/neutral precursor assignments TiAlCl₅⁺/TiAlCl₆ and TiAlCl₄⁺/TiAlCl₅ are fairly certain.

When H₂O was admitted, the additional ions TiOCl₂⁺, Al(OH)Cl₂⁺, and TiAl(OH)Cl₄⁺ appeared above 1000 K. The threshold AP of TiOCl₂⁺ is close to that of TiCl₄ and is a reasonable IP for the closed-shell TiOCl₂. Likewise, Al(OH)Cl₂⁺, with an AP of 11.2 eV, is considered to be a parent ion. For reasons similar to those stated above the TiAlCl₅⁺ and TiAlCl₄⁺, TiAl(OH)Cl₄⁺ is taken to be a fragment from the open-shell

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)Cl₅ (TiCl₃·Al(OH)Cl₂), 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 TiCl₄-AlCl₃-H₂O system. As expected, the abundance of TiAl(OH)Cl₅ increased in step with that of TiCl₃. TiAlCl₅⁺ and TiAl(OH)Cl₄⁺ were not observed simultaneously; when H₂O was admitted, the signals from the former decreased to the background level as those of the latter increased.

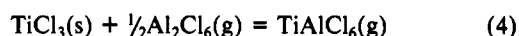
Discussion

In accord with the findings of Sorlie and Oye,¹ we obtained no evidence for the formation of the mixed complex TiCl₄·AlCl₃, where both Ti and Al are in their highest oxidation states. Mixed Ti-Al-Cl complexes were observed only in the presence of gaseous TiCl₃ and TiCl₂, with the stoichiometries TiAlCl₆(TiCl₃·AlCl₃) and TiAlCl₅ (TiCl₂·AlCl₃). In their work at higher pressures, Sorlie and Oye¹ also inferred the existence of TiAlCl₆, but in contrast to our observation of TiAlCl₅, they identified TiAl₃Cl₁₁

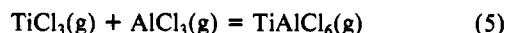
(TiCl₂·3AlCl₃) as the major complex involving divalent Ti. The abundances of higher order complexes would increase more rapidly with pressure, so that TiAl₃Cl₁₁ could well predominate near 1 atm.

From their evaluation of the apparent vapor pressures of the complexes, Sorlie and Oye¹ concluded that AlCl₃ enhances the stability of divalent Ti to a much greater degree than the trivalent state. The observed intensities in Table II, where TiAlCl₅⁺/TiCl₃⁺ ~ 0.002 and TiAlCl₄⁺/TiCl₂⁺ ~ 1 , are in accord with this concept.

From the temperature dependence of the absorption spectrum, Sorlie and Oye¹ deduced for the reaction



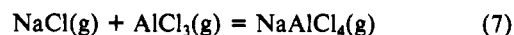
$\Delta H^\circ = 77.3 \pm 2.6$ kJ mol⁻¹. With the aid of auxiliary tabulated data,⁵ one can derive for the reaction



$\Delta H^\circ = -133$ kJ mol⁻¹ using the result from reaction 4. One-to-one complexes such as TiAlCl₆ are thought to have chlorine-bridged structures between adjacent -Ti-Cl and Cl-Al-groups, and as such, similar complexes with AlCl₃ might be expected to have comparable entropy changes. For reactions such as



Schafer⁶ 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



from equilibrium measurements.⁷ However, the enthalpies of AlCl₃ 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-AlCl₃ complexes and particularly the dependence on the Ti valence state.

Although the species TiOCl₂ has been postulated as an intermediate in the chlorination of titania⁸ 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 TiOCl₂ could be an important intermediate in the oxidation of TiCl₄, as well as in the chlorination of TiO₂.

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