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Synthesis and mass spectrometry of halide and oxide halide (F and Cl) vapor species of technetium, tantalum and tungsten

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Abstract

Transition metal solids have been exposed to fluorine, chlorine trifluoride and/or oxygen at temperatures up to 800 °C, and the volatile reaction products analyzed by mass spectrometry. Reported here are the results of the reactions of the metals (sometimes partially oxidized) technetium, rhenium, tantalum and tungsten. The following vapor species have been identified: TcF_5, TcO_3F, $TcOF_4$, TcO_2F_3, TcO_3Cl, $TcOCl_3$, TcO_2Cl_x ($x=2$ or 3), $TcOF_2Cl$, $TcOFCl_2$, ReF_6, ReO_3F, ReO_2F_3, $ReOF_4$, WF_6, WO_2F_2, WOF_4, WO_2Cl_2, WF_5Cl, TaF_5, $TaOF_3$, $TaOCl_3$ and TaF_xCl_{5-x} ($x=1$–4). The conditions under which these species were formed and their relevance to conventional condensed phase chemistry are discussed.

Introduction

A wide variety of transition metal halides and oxide halides have been synthesized and characterized in the solid state. Additionally, there have been reported several studies of the products of the vaporization and/or decomposition of such solid compounds. However, there has been less investigation of vapor species which may be produced at high temperature in an oxidizing atmosphere. The study of this aspect of the chemistries of these systems may demonstrate different relative stabilities of compounds than is typically observed, and may even reveal new molecular species not obtained as condensed materials.

We have developed a system which allows the oxidation of transition metal solids at high temperatures and the performance of *in-situ* mass spectrometric analysis of volatile reaction products. This analysis is sensitive to very low partial pressures and it has thus proved possible to identify exotic halides and oxide halides present only as minor constituents of complex gas mixtures.

Experimental

The configuration of the reactor is shown schematically in Fig. 1. The entire Knudsen cell assembly is constructed of platinum. The 6 mm outside

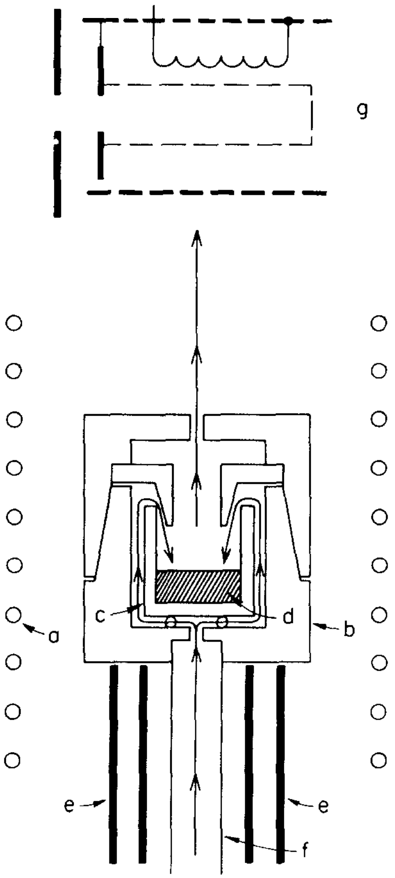

Fig. 1. Schematic diagram (not to scale) of Knudsen cell assembly: (a) Ta heater; (b) Pt Knudsen cell; (c) Pt cup; (d) condensed sample; (e) Pt vs. Pt/10%Rh (type-S) thermocouple; (f) Pt tube for oxidant; and (g) electron impact ionizer. Arrows show the direction of flow of the oxidant and volatile reaction products.

diameter cell has a 0.5 mm diameter effusion orifice in its removable, tight-fitting lid and an internal baffle to direct the reactive gas flow over the condensed sample, which is contained inside a removable cup. A platinum tube welded into the bottom of the cell supplies the reactive gas, which enters the cell through an orifice beneath the sample cup; the arrows indicate the flow of the reactive gas and of any volatile reaction products. Platinum and Pt/10%Rh wire pairs welded to the bottom of the cell provide intrinsic type-S thermocouples; one couple is in use while the other is a spare. The cell is surrounded by a helically wound resistance heater made of 1 mm diameter, high-purity Ta wire. The electron impact ion source for the quadrupole mass spectrometer is located ~5 cm above the top of the cell.

The close proximity of the Knudsen cell vapor source to the ion source maximizes the analytical sensitivity and allows the detection of vapor species produced in low concentrations. This compact geometry precluded inclusion of extensive heat shielding around the furnace, and the maximum attainable cell/sample temperature was limited to ~800 °C. To provide some indication of the reliability of the measured temperatures in relation to the actual sample temperature, the melting point of lead metal contained in a Ta cup placed in the Knudsen cell (without lid) was determined by observation through a viewport using a microscope; it was found with two different cells that the measured melting point was about 40 °C below the actual value of 327 °C. The temperature deviation is likely to be even greater at higher temperatures. The reported temperatures have not been corrected and the actual cell temperatures were probably somewhat higher than indicated.

All of the gases used (F_2, ClF_3 and O_2) were of at least 97% (in-cylinder) purity; no attempts were made at further refinement. The gases were supplied to the inlet in the bottom of the Knudsen cell through a manifold constructed primarily of stainless steel. The gases were handled in the manifold at pressures of ~25 Torr, with further pressure reduction prior to the cell inlet achieved by a fine metering needle valve. In addition to the inherent impurities in the oxidant gases, mass spectra obtained for the residual oxidizing gases effusing from the cell under a variety of conditions (empty cell, cell with sample, room temperature, high temperatures) indicated that reaction with impurities in the gas handling system and with the platinum cell assembly (especially at high temperatures) often resulted in substantial oxidant depletion, decomposition and/or the introduction of impurities (e.g., HF, ClF, Cl_2, O_2, etc.). The reactivity of platinum at high temperatures (generating PtF_4 to ~600 °C and PtF_2 at higher temperatures) made complete passivation by fluorine pre-treatment impossible. Based upon the observed increase in the vacuum chamber pressure, it was estimated that the net pressure in the cell was ~0.1 Torr at room temperature; however, due to the gettering effect of the platinum, the F_2 and ClF_3 pressures decreased at higher temperatures.

The tungsten and rhenium metals were of >99.9% purity and were in the form of 0.25 and 0.10 mm diameter wires, respectively. The heater (>99.9% wire) served as the tantalum source. The technetium was the isotope Tc-99, supplied by the ORNL Isotopes Department as a metal powder of >99% radiochemical purity; this isotope undergoes β-decay with $t_{1/2} = 2 \times 10^5$ years. Although the technetium was nominally in the form of a metal, it was a fine powder which had been stored in air for ~30 years and its dark appearance indicated extensive oxide formation. No effort was made to reduce the technetium oxide and some of the most interesting technetium results were due to the presence of the oxide. It should be noted that the compositions of the reactant solid samples may have changed during the course of the high-temperature oxidation experiments and the same sample was frequently used for several experiments; interpretation of the solid reactivities based upon the nominal sample compositions are thus limited.

The Knudsen cell reactor assembly and mass analyzer were located inside of a turbomolecular-pumped high vacuum chamber. The chamber was maintained at background pressures of 10^{-6} Torr (measured with a nude ionization gauge), but pressure increases to about 10^{-5} Torr were observed upon admission of the reactive gas to the cell. The vacuum chamber is mounted inside of an air-atmosphere glove box designed for the handling of highly radioactive materials, making studies of the β-emitting ^{99}Tc especially convenient.

The mass analyzer was a 2–400 amu quadrupole mass filter (UTI model 100C), incorporating a Channeltron electron multiplier as the positive ion detector. The electron impact ion source for the mass spectrometer is of a design which provides ionizing electrons only down to energies of ~20 eV; this limitation precluded the lower energy appearance potential determinations which might have been used for more direct assignment of certain precursor molecules. Although the ion source and its tungsten (thermal emission) filaments were oriented so as to minimize exposure to and reaction with the effusing oxidant, WF_6 so derived could occasionally be identified in spectra. The resolution of the spectrometer was maintained high enough to achieve at least unit mass discrimination throughout. The computer control and data acquisition system could acquire spectra with a wide dynamic intensity range using automatic picoammeter switching, a particularly useful feature for the identification of the most dilute and exotic vapor components.

Unless otherwise specified, all mass spectral results were obtained with a nominal ionizing electron energy of 70 eV, allowing for direct comparison with literature results obtained with typical electron energies in the range of 50–120 eV. Mass spectral intensities were not corrected for the mass variation of the transmission efficiency of the quadrupole mass filter but this effect should have been relatively minor over the mass ranges of the spectra considered here.

Results and discussion

Although the most simple relevant mass spectra available have been utilized to establish the products of these oxidations, the nature of the reaction system generally introduced simultaneous contributions from several species containing the element of immediate interest in addition to contributions from species generated by unavoidable secondary reactions (e.g., by oxidation/fluorination of the Pt cell, Ta heater or W filaments). Deconvolution of the mass spectra and assignment of the neutral precursor molecules has required consideration of the chemistry and molecular ion fragmentation behavior of these and similar systems. Although oligomer formation in many transition metal halide and oxide halide systems is an important and interesting feature of their gas-phase chemistries [1], the monomer species are generally dominant and reveal the essential high-temperature vapor chemistry (though not necessarily reflecting the conventional condensed phase chemistry). Our search for dimers and larger oligomers was limited by the mass range of the quadrupole and we discuss here solely the monomers which were observed.

Technetium

(a) $TcF_x(g)$ and $TcO_xF_y(g)$

In Fig. 2 are shown typical mass spectra of the volatile products from the reaction of technetium (oxide) with fluorine. Although the shown spectra extend only to 205 amu, no additional $TcO_xF_y^+$ peaks were observed to 235 amu (as noted above, heavier oligomers were not searched for). The only ion definitively derived solely from a binary fluoride was TcF_5^+ (194 amu). As suggested by the temperature dependence of its intensity, this fluoride ion was apparent upon reaction of technetium with fluorine above

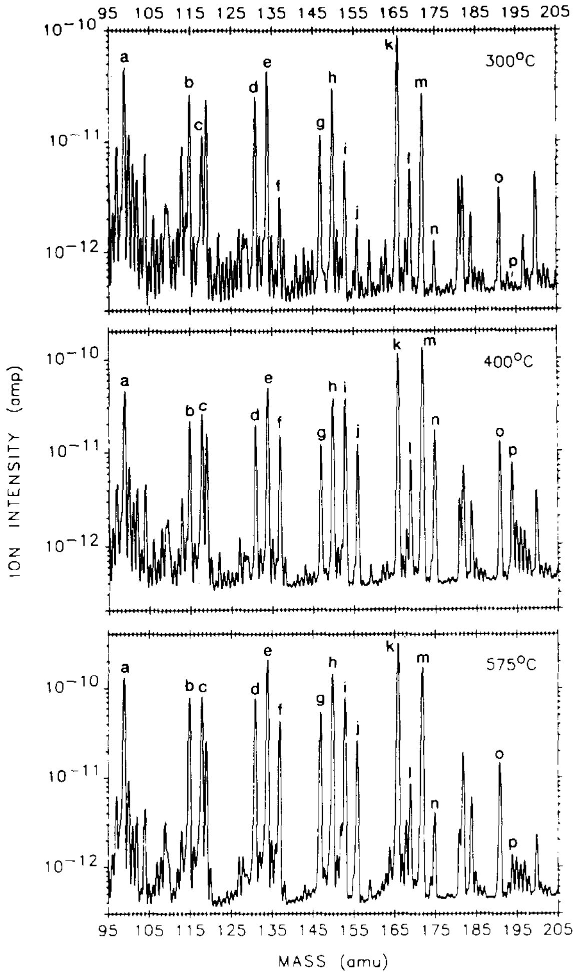

Fig. 2. Mass spectra of volatile products of the reaction, $Tc+F_2$, at 300 °C (top), 400 °C (middle) and 575 °C (bottom). Peaks due to $TcO_xF_y^+$ have been assigned as follows: (a) Tc^+; (b) TcO^+; (c) TcF^+; (d) TcO_2^+; (e) $TcOF^+$; (f) TcF_2^+; (g) TcO_3^+; (h) TcO_2F^+; (i) $TcOF_2^+$; (j) TcF_3^+; (k) TcO_3F^+; (l) $TcO_2F_2^+$; (m) $TcOF_3^+$; (n) TcF_4^+; (o) $TcOF_4^+$; and (p) TcF_5^+. Other peaks include $C_2F_5^+$ (from C_8F_{14} residue), Ta^+, TcO_3Cl^+, Pt^+, $TaOF^+$ and TaF^+.

~350 °C, and was evident to ~550 °C; the conclusion is that the parent fluoride was thermally unstable above this latter temperature. Note that since the thermal energies involved are minuscule ($kT \sim 0.1$ eV at 1000 K) relative to the ionizing electron energy (70 eV), the possibility of the thermal instability of the electron-impact-generated TcF_5^+ ion (rather than of the neutral precursor) can be discounted. This TcF_5^+ ion is ascribed to the parent species $TcF_5(g)$, rather than to $TcF_6(g)$, based primarily upon comparison with the mass spectra of the binary fluorides of homologous rhenium and other transition metals. For rhenium fluoride, as well as for most other transition metal fluorides, MF_x, the dominant peak in the mass spectrum corresponds to the single-fluorine-detachment ion, MF_{x-1}^+ [1]. In accord with this generalization, we were able to synthesize ReF_6 by the reaction of Re^0 with F_2 at 360 °C in the Knudsen cell reactor and found from its mass spectrum that $I[ReF_6^+]/I[ReF_5^+]=0.11$ and $I[ReF_4^+]/I[ReF_5^+]=0.37$. In the case of the binary technetium fluoride, the mass spectrum showed that $I[TcF_4^+]>I[TcF_5^+]$ (it was difficult to quantify these relative intensities due to the concurrent contribution to $I[TcF_4^+]$ from fragmentation of $TcOF_4(g)$; this relation indicates that TcF_5 is the neutral precursor, and TcF_4^+ the most intense ion fragment. For comparison, Falconer *et al.* [1] found that $I[ReF_5^+]$ was approximately 18% of $I[ReF_4^+]$ in the ReF_5 mass spectrum. The relatively large (11%) intensity of the ReF_6^+ parent ion in the ReF_6 mass spectrum compares, for example, with much smaller (<1%) contributions of WF_6^+, UF_6^+ and SF_6^+ to the respective MF_6 electron-impact mass spectra [2]. This can be interpreted in terms of the availability of a higher (+7) oxidation state in the case of rhenium, since the metal is nominally +7 in the hexafluoride parent ion, MF_6^+; technetium also has available a +7 oxidation state, and the degree of fragmentation (or, alternatively, cohesion) of TcF_6 upon electron-impact ionization should be comparable to that of ReF_6. We were not able to detect TcF_6^+ to 2% of the intensity of TcF_5^+ (interference from $^{194}PtF^+$, also at 213 amu, precluded an even more sensitive detection limit for TcF_6^+), providing additional evidence for TcF_5 as the precursor.

The mass spectra from reaction of the technetium (oxide) with fluorine (e.g., Fig. 2) were generally dominated by oxide fluoride vapor species. The ions TcO_3F^+, $TcOF_4^+$ and $TcO_2F_2^+$ were the heaviest oxide fluoride ions detected and are considered to derive from the parent vapor species, $TcO_3F(g)$, $TcOF_4(g)$ and $TcO_2F_3(g)$, respectively. Although the first of these neutral precursors represents technetium in its highest (+7) oxidation state and the assignment of TcO_3F^+ as a parent ion is thus virtually certain, assignment of the origins of the latter two ion fragments is less straightforward. In particular, it is conceivable that $TcOF_4^+$ derived from the +7 oxide fluoride $TcOF_5$, and that $TcO_2F_2^+$ was a parent ion from TcO_2F_2. Because it can be assumed that the fragmentation patterns of the analogous Tc and Re oxide fluorides are at least similar, comparison with the corresponding rhenium oxide fluoride mass spectra reported by Sunder and Stevie [3] is useful for assignment of the neutral precursors. Their mass spectra for both $ReOF_4$ and $ReOF_5$ show dominance by the single F-detachment ion, as is typical of binary fluorides and fluorine-rich oxide fluorides. The observed intensity ratio, $I[TcOF_3^+]/I[TcOF_4^+]$, and the absence of any TcF_5^+ peak in conjunction with $TcOF_4^+$, is entirely consistent with a $TcOF_4$ precursor and inconsistent with the spectrum expected for $TcOF_5$. Although assignment of the origin of the observed $TcO_2F_2^+$ peak is complicated by contributions to other, related peaks from ion fragments of TcO_3F and/or $TcOF_4$, it is possible to assign this ion to TcO_2F_3 with some confidence. The mass spectrum of ReO_2F_2 has not been reported (this compound has not been identified), but that of ReO_2F_3 shows $ReO_2F_2^+$ to be the dominant ion fragment, with only a 2% relative intensity for the parent ion, $ReO_2F_3^+$. It is thus consistent that we were unable to detect the parent ion fragment, $TcO_2F_3^+$.

To establish whether the observed ion, $TcOF_3^+$, derives solely from $TcOF_4(g)$, or whether $TcOF_3(g)$ was also simultaneously produced, it is useful to consider the ion intensity ratio, $I[TcOF_4^+]/I[TcOF_3^+]$, as a function of the variable experimental parameters. At temperatures from 300 °C to 700 °C and under atmospheres of both ClF_3 and F_2, this ratio remains nearly constant at 0.12(3) (compared with 0.19 for the corresponding ratio in the $ReOF_4$ mass spectrum [3]). As it is unlikely that $P[TcOF_3(g)]/P[TcOF_4(g)]$ would remain so constant under such varied conditions, we conclude that both of these ions derive predominantly from $TcOF_4(g)$. In contrast, for example, the ratios of the intensities of TcO_3F^+, $TcO_2F_2^+$ and $TcOF_4^+$ were seen to vary by a factor of four or more over this same temperature range. As a further indication that $TcOF_4^+$ is the parent ion, the ratio $I[TcOF_4^+]/I[TcOF_3^+]$ doubled (to 0.24) when 'softer', 30 eV rather than 70 eV, ionizing electrons were used.

For comparison with the observed oxidation behaviour of technetium, mass spectra of the volatile products of the comparable treatment of rhenium were also obtained. Except for the significant ReF_6^+ peak [from $ReF_6(g)$] as noted above, the results were quite similar for Tc and Re. For example, the reaction of rhenium with fluorine (with oxygen/oxide impurity present) at 350 °C resulted in the following terminal oxide fluoride ions (with proposed parent vapor species indicated in squared brackets): ReO_3F^+ [$ReO_3F(g)$], $ReO_2F_2^+$ [$ReO_2F_3(g)$] and $ReOF_4^+$ [$ReOF_4(g)$].

Our findings on the technetium fluoride and oxide fluoride systems may be summarized as follows: (1) TcF_5 was generated under ~0.1 Torr F_2, but only up to ~550 °C; and (2) the three oxide fluorides, TcO_3F, TcO_2F_3 and $TcOF_4$, were generated over a wider temperature range. The observed co-existence of $Tc^{VII}O_3F$, $Tc^{VII}O_2F_3$, $Tc^{VI}OF_4$ and $Tc^{V}F_5$ (e.g., at 400 °C: Fig. 2, middle) is a good example of the well-known tendency for oxygen to stabilize the higher metal oxidation states in such compounds. The qualitative trend in ease of formation of these compounds under the conditions used here was TcO_3F (most easily produced and generally present at the highest partial pressure) $> TcOF_4 > TcO_2F_3 > TcF_5$. Although previous study of such Tc-containing vapor-phase species has been limited, all of these compounds have been reported to have been isolated and identified in a condensed phase [4, 5] (indeed, the vapor species reported here comprise all of the known technetium oxide fluorides), and our observations regarding the relative difficulties with which these vapors were generated are generally consistent with descriptions of the condensed phase syntheses [4]. It is particularly noteworthy to have identified TcO_2F_3 here; although its rhenium analogue is well known, there has been only one report of the possible existence of this particular technetium oxide fluoride [5].

(b) $TcO_xCl_y(g)$ and $TcO_xF_yCl_z(g)$

In Fig. 3 are shown mass spectra of products generated from the reaction of technetium with chlorine trifluoride at representative temperatures of 300 °C and 650 °C. As in the case of the oxide fluoride system discussed above, the heavier Tc-containing ions are emphasized as they can be more definitively ascribed to a given neutral precursor vapor species; thus, although such highly fragmented ions as Tc^+, TcO^+ and TcF^+ were evident at lower masses, only the spectra above 130 amu are shown. Although the spectra shown extend only to 230 amu, no additional $TcO_xF_yCl_z{}^+$ peaks were observed to 260 amu.

The low-temperature Tc + ClF_3 spectrum (Fig. 3, top) is dominated by ions derived from $TcO_3Cl(g)$ and $TcO_3F(g)$. The corresponding high-tem-

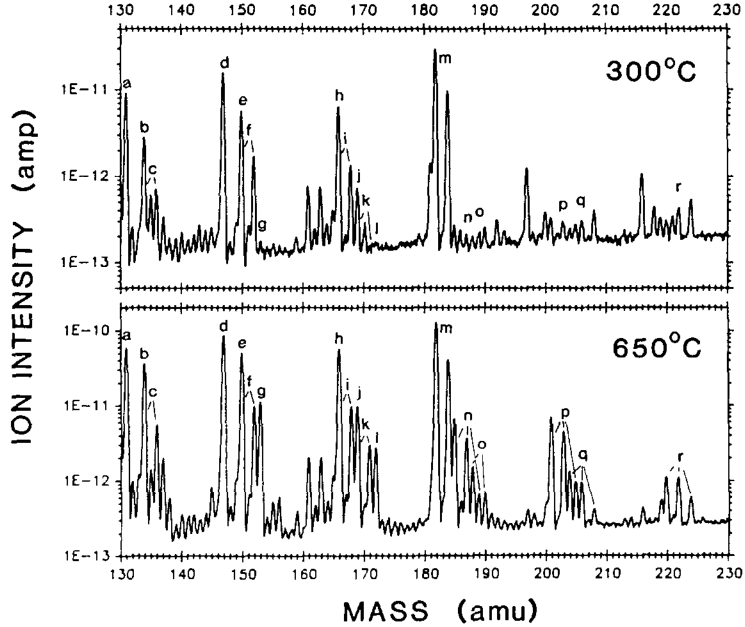

Fig. 3. Mass spectra of volatile products from the reaction, Tc + ClF_3, at 300 °C (top) and 650 °C (bottom). Peaks due to $TcO_xF_yCl_z{}^+$ have been assigned as follows: (a) $TcO_2{}^+$; (b) $TcOF^+$; (c) $TcCl^+$; (d) $TcO_3{}^+$; (e) TcO_2F^+; (f) $TcOCl^+$; (g) $TcOF_2{}^+$; (h) TcO_3F^+; (i) TcO_2Cl^+; (j) $TcO_2F_2{}^+$; (k) $TcOFCl^+$; (l) $TcOF_3{}^+$; (m) TcO_3Cl^+; (n) $TcOCl_2{}^+$; (o) $TcOF_2Cl^+$; (p) $TcO_2Cl_2{}^+$; (q) $TcOFCl_2{}^+$; and (r) $TcOCl_3{}^+$. Other peaks include $[56]Cl_3{}^+$ (56 amu component unidentified), Ta^+, TaO^+, TaF^+, $TaOF^+$ and $TaF_2{}^+$.

perature spectrum (Fig. 3, bottom) is relatively complex owing to simultaneous contributions from various ternary oxide fluoride vapor species, ternary oxide chloride species and quaternary oxide fluoride chloride species; it has nonetheless been possible to assign all of the significant peaks in this latter spectrum. The observed relative intensities within each of the assigned chloride peak manifolds are in good agreement with those predicted from the $^{35}Cl/^{37}Cl$ isotopic ratio.

In addition to the ternary ion, TcO_3Cl^+, the more chlorine-rich ion, $TcOCl_3^+$, is also evident at the higher temperature. Because of the relatively small intensity of the manifold due to this latter ion, it is only possible to set an upper limit of $<8\%$ on the relative intensity of the potential parent ion, $TcOCl_4^+$, which was not detected; this would compare with 12% $TcOF_4^+$ parent ion relative to the $TcOF_3^+$ ion fragment, as discussed above. Although is not possible to rule out the technetium(VI) oxide chloride vapor species $TcOCl_4(g)$, based upon this it is probable that we would have detected the parent ion of $TcOCl_4$, and that $Tc^{V}OCl_3(g)$ is thus the (primary) precursor of the $TcOCl_3^+$ peak. In support of this conclusion, a consideration of the fragmentation patterns of metal halide and oxide halide molecules suggests that the unfragmented parent ion in the case of a chloride should generally be at least as important as in the case of the analogous fluoride [6]. The discussion of technetium oxide fluoride chloride species which follows will further support the contention that $TcOCl_3$ is the parent molecule of the $TcOCl_3^+$ ion fragment, since only Tc^{V} was found in the analogous quaternary systems; given the greater oxidizing power of the fluorine component in the mixed halide molecules, it is chemically unlikely that $Tc^{VI}OCl_4(g)$ would result under conditions where only $Tc^{V}OF_xCl_{3-x}(g)$ were produced. The three technetium oxide chlorides, TcO_3Cl, $TcOCl_3$ and $TcOCl_4$, are all known [4]. Consistent with our conclusion that the oxide trichloride is the product here, the last of these is difficult to isolate and is of only limited stability [7].

In the high-temperature $Tc+ClF_3$ spectrum (Fig. 3, bottom) the ion $TcO_2Cl_2^+$ was also identified; no peak due to $TcO_2Cl_3^+$ could be detected to $<1\%$ of the intensity of this peak. This dioxide dichloride ion is especially significant because it must have derived from some previously unidentified technetium oxide chloride, either TcO_2Cl_2 or TcO_2Cl_3; it is not possible to positively exclude either of these potential neutral precursors from the observed spectra. For comparison, both ReO_2Cl_2 and ReO_2Cl_3 have been reported, although the former is apparently of only limited stability [8]. Thus, although it is clear that a new technetium oxide chloride has been produced, we are not able to definitively differentiate between the two possible neutral precursors based upon our results.

Among the more unique and unexpected ions identified in the high-temperature $Tc+ClF_3$ mass spectrum (Fig. 3, bottom) were those derived from quaternary technetium oxide fluoride chloride vapor species. In particular, both $TcOF_2Cl^+$ and $TcOFCl_2^+$ are evident at intensities comparable to those of the ternaries, $TcOF_3^+$ and $TcOCl_3^+$. No $TcOF_2Cl_2^+$ (223/225/227 amu) could be detected to $<1\%$ of the intensity of either $TcOF_2Cl^+$ or $TcOFCl_2^+$, or to $<0.5\%$ of the sum of these two ion intensities; because of the slightly greater background levels there, the other potential (Tc^{VI}) parent ions, $TcOF_3Cl^+$ (207/209 amu) and $TcOFCl_3^+$ (239/241/243/245 amu), can both be assigned a comparable limit of $<4\%$ of either observed ion, or $<2\%$ of their sum. Given the inability to detect any $TcOF_xCl_{4-x}^+$ ion to these rather low limits (compare with 12% $TcOF_4^+$ relative to $TcOF_3^+$), we conclude that the observed $TcOF_xCl_{3-x}^+$ ions derive from the two quaternary parent vapor species containing Tc^V, $TcOF_2Cl(g)$ and $TcOFCl_2(g)$. These compounds have not previously been reported and would seem to represent a new class of mixed technetium oxide halides.

Tungsten

In marked contrast to the technetium samples, the tungsten metal showed evidence of only very minor surface oxidation during storage, and it was necessary to introduce significant oxygen partial pressures into the reactive gas stream to promote the formation of oxygen-containing tungsten vapor species. Based upon the intense $WO_2F_2^+$ peak manifold, it is evident that WO_2F_2 is the dominant product of the reaction of tungsten with a 6:1 O_2/F_2 mixture. In contrast to WF_6, where the parent ion is present in only very small ($<1\%$) intensities, this tungsten(VI) oxide fluoride is seen to fragment relatively little under electron-impact ionization. In addition to the dominant $WO_2F_2^+$ manifold and those of the corresponding lighter ion fragments, there is also a much less intense WOF_3^+ peak manifold, which must derive from a more fluorine-rich oxide fluoride. Although no WOF_4^+ parent ion peaks could be definitively identified at higher masses, it is probable that $WOF_4(g)$ rather than $WOF_3(g)$ is indeed the precursor of the observed WOF_3^+ ion. It is instructive to refer back to the case of technetium where, for $TcOF_4(g)$, $I[TcOF_4^+]/I[TcOF_3^+]$ was about 12%; based upon the unavailability of a +7 oxidation state for tungsten, the relative intensity of WOF_4^+ from $WOF_4(g)$ is probably somewhat smaller, and the absence of any such parent peaks in the WOF_4 spectrum obtained here is consistent. In accord with this, Gotkis *et al.* [9] have determined the mass spectrum for WOF_4 and found that $I[WOF_4^+] \approx 0.01 \times I[WOF_3^+]$. Although WO_2F_2 was the primary gaseous constituent here, and has previously been identified as a vapor species [10], evidence for its possible existence as a solid compound is somewhat tenuous [11, 12]. In contrast, the minor vapor constituent WOF_4 is readily produced as a solid compound [12]. In accord with our assignment of WOF_4 as the neutral precursor for WOF_3^+, WOF_3 has not been reported as a stable compound [13].

Reaction of tungsten metal with either F_2 or ClF_3, even at relatively low temperatures, readily yielded WF_6. Upon reaction of tungsten with F_2 at 250 °C, an additional weak peak manifold was evident at higher masses and has been definitively assigned to WF_4Cl^+. From comparison with other halide and mixed halide mass spectra [14], we assign this ion to a WF_5Cl parent molecule. The oxidant in this case was nominally pure fluorine, and there should have been only a minimal supply of chlorine/chloride impurities as residues from previous experiments in the gas and/or solid phases; under such chlorine-efficient conditions the pentafluoride chloride molecule would indeed be the expected ternary halide product. It was not possible to definitively reproduce this result using conditions presumably even more thermodynamically conducive to mixed halide formation (e.g., using ClF_3 rather than F_2). Although the mechanism for the formation of this mixed halide in nominally pure fluorine (with chlorine available only as a minor impurity) is not clear, it is evident that such mixed tungsten halides are produced only under very limited conditions; given the apparent thermodynamic inconsistency regarding our inability to produce WF_5Cl under more thermodynamically favorable conditions, we might assume that the kinetics of its formation and/or decomposition was an important factor. Tungsten pentafluoride chloride has proved to be among the easiest mixed tungsten halides to produce in the condensed state; Peacock and co-workers have isolated it [15] as well as several other tungsten fluoride chlorides [16], but found its stability toward disproportionation to the binary hexahalides to deteriorate above −10 °C. It is consistent with their observations that we were able to achieve only a very low WF_5Cl partial pressure, and that only at a relatively low reaction temperature (250 °C), and have found it difficult to consistently generate this vapor species; it is, in fact, somewhat surprising that a mixed tungsten fluoride chloride vapor molecule was produced at all at a temperature so high in comparison to the reported disproportionation temperature.

In addition to WF_6, reaction of tungsten with ClF_3 (+oxygen impurity) at 680 °C generated other products. In particular, $WO_2F_2(g)$ ($WO_2F_2^+$) and $WO_2Cl_2(g)$ ($WO_2Cl_2^+$) were present at pressures comparable to that of $WF_6(g)$. In contrast to its oxide fluoride analog, the condensed compound WO_2Cl_2 is quite stable and has been prepared under rather mild conditions [17]. Although the mass spectrum for the reaction $W+ClF_3$ at 680 °C may have included a very weak peak manifold due to WF_4Cl^+, this assignment was inconclusive; there were no observed peaks from WCl_3^+, WCl_4^+, etc. which would have been indicative of a binary tungsten chloride [18].

Tantalum

The tantalum vapor species were not derived from interaction of a solid sample in the Knudsen cell with a gaseous oxidant, but rather from reaction of the tantalum heater coil with the reactive effusate; the sample temperature and atmosphere were therefore not as well-defined as in the other experiments. Tantalum pentafluoride was an ubiquitous product in the course of these studies, readily evident from its primary ion fragment TaF_4^+; as is also the case with other saturated binary fluorides (e.g. WF_6, as discussed above) there is very little contribution (<0.2% relative to $I[TaF_4^+]$) to the 70 eV electron-impact mass spectrum from the parent ion TaF_5^+. The two binary oxide halides containing Ta^V, $TaOF_3$ and $TaOCl_3$, were identified by their respective $TaOX_3^+$ parent ions. It is notable that despite the wide variety of conditions under which $TaOF_3$ was produced, sometimes in appreciable quantities, it was never possible to definitively identify TaO_2F. That TaO_2F

was not detected as a vapor molecule is consistent with studies of the behavior of solid tantalum oxide fluoride upon heating: decomposition to oxygen-rich solid phases occurs, with release of gaseous TaF_5 and $TaOF_3$ [19]. Whereas solid $TaOF_3$ is rather easily produced [20], Morozov and Karlova [21] were able to obtain $TaOCl_3$(s) only with more difficulty and found that it decomposes at 327 °C. In addition, these authors [21] confirmed the findings of others that sublimation of solid tantalum oxide chlorides does not result in the production of TaO_xCl_y vapor species. Our demonstration of the importance of $TaOCl_3$ as a major product of the oxidation of tantalum under these conditions is an example of the potential novelty of high-temperature gas-phase chemistry.

The most interesting tantalum-containing ions identified were TaF_3Cl^+, $TaF_2Cl_2^+$ and $TaFCl_3^+$. In contrast to the situation with WF_4Cl^+, these mixed tantalum halide ions gave rather intense peaks, especially at relatively low temperatures (~300 °C heater). These ions are attributed to the saturated Ta^V halides for which it would not expected to be possible to detect the parent ion. Although the compositions of these three ternary ions require simultaneous contributions from at least one fluorine-rich ($F/Ta \geq 3$), and one chlorine-rich ($Cl/Ta \geq 3$) neutral precursor, the absence of the parent ions makes it difficult to infer the molecular composition of the vapor. However, consideration of the variation of the relative intensities of the ion-fragment peaks as a function of experimental conditions, such as temperature, helps to deconvolute their origins. For example, the following ion-peak intensity ratios were measured upon increasing the cell temperature from 200 °C to 550 °C (estimated increase in tantalum heater temperature from ~300 °C to ~750 °C): $TaCl_4^+$/0.060; $TaFCl_3^+$/0.22; $TaCl_3^+$/0.33; $TaF_2Cl_2^+$/0.55; $TaFCl_2^+$/0.60; TaF_3Cl^+/0.70. Clearly, the average chlorine content of the tantalum halide vapor decreases with increasing temperature; accordingly, the TaF_5-derived peaks (especially TaF_4^+) concurrently intensify over this temperature range. The differing rates of depletion of the $TaCl_4^+$, $TaFCl_3^+$ and $TaCl_3^+$ peaks with increasing temperature suggest, for example, that $TaCl_5$, $TaFCl_4$ and TaF_2Cl_3 are all contributing to the spectra. Consideration of the variations of all of the peaks with increasing temperature would suggest that several fluorine-rich and chlorine-rich TaF_xCl_{5-x} vapor species were produced in appreciable quantities. The reproducible synthesis of several mixed tantalum pentahalides, even at temperatures exceeding 600 °C, is in marked contrast to the very limited stabilities of the tungsten fluoride chlorides. A variety of TaF_xCl_{5-x} from $x=1$ to $x=4$ have been isolated as condensed phases [22], and the mass spectrum of $TaFCl_4$ has been reported [14].

Summary

Several halide and oxide halide vapor species have resulted from the high-temperature oxidation of technetium, tungsten and tantalum. It has been demonstrated that TcF_5(g) is stable under ~0.1 Torr F_2(g) to ~550 °C.

The three technetium oxide fluorides, TcO_3F, TcO_2F_3 and $TcOF_4$, have been reported in condensed phases and have now been observed here as molecular vapor species. In addition to the known oxide chlorides TcO_3Cl and $TcOCl_3$, we have now identified the mixed oxide fluoride chloride molecules $TcOF_2Cl$ and $TcOFCl_2$. The ion $TcO_2Cl_2^+$ has provided evidence for a new binary oxide chloride, which is either TcO_2Cl_2 or TcO_2Cl_3. The existence of several tungsten and tantalum halide, oxide halide and, most interesting, mixed fluoride chloride vapor species has also been established.

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