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# Mass Spectrometric Study of the Vaporization of Tungsten Oxotribromide

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A Knudsen effusion mass spectrometric investigation indicates that in the temperature range, 410–690°K, solid $WOBr_3$ undergoes simultaneous evaporation and dissociation. Present results indicate that the system does not attain equilibrium in the Knudsen cell and the vaporizing species evaporation coefficients are $\leqslant 10^{-4}$. The decomposition leads to gaseous $WO_2Br_2$, in proportion comparable to $WOBr_3$ and minor amounts of $WOBr_4$, $WBr_5$, $WBr_4$, and $W_2Br_6$. These results are in discord with the proposed existence of $WOBr_4$ and $WO_2Br_2$ species reported from tensimetric work. Thus, a different decomposition scheme is suggested which involves the formation of $WBr_4$ and $WO_2Br_2$ and subsequent dissociation of $WBr_4$. The formation of gaseous $WOBr_4$ is related to certain gas-phase reactions. Thermal decomposition of solid $WBr_6$ at 360–395°K, also studied mass spectrometrically, is found to produce gaseous $WBr_5$ and $Br_2$.

## Introduction

Recent reviews of transition metal chemistry indicate the existence of halides and oxohalides in varied valence states of the refractory metals, molybdenum and tungsten.[1-3] Hexavalent compounds of these elements, *e.g.*, $MX_6$, $MO_2X_2$, and $MOX_4$, have been reasonably well characterized thermodynamically[1,2,4-6] and to a lesser degree structurally.[1-3] Lower valent oxohalides of the types $MOX_3$ and $MOX_2$, in particular the bromides, have been reported.[3,7-9] Solid-phase infrared spectra[10] of the $WOX_3$ (X = Cl and Br) compounds have been interpreted to indicate the existence of bridged oxygen bonding identical with that in $MoOBr_3$ which has been well characterized structurally.[9] There is, however, a complete lack of information on their thermochemical properties, mode of vaporization, gaseous molecular structure, etc. The present mass spectrometric investigation, was, thus, undertaken with a view to understand the vaporization behavior of $WOBr_3(s)$. Recent calorimetric and tensimetric work on $WOBr_3(s)$ by Oppermann and coworkers[11] fails to provide any insight into the vaporization mechanism. The present mass spectrometric results are discussed in comparison with these recent observations.[11]

## Experimental Section

The mass spectrometric technique has been described in detail earlier.[4] The present study utilized a tungsten Knudsen cell (0.064-cm orifice) with a modified heating system consisting of a seven-turn helical bifiral 0.05-cm Pt–13% Rh wire which fed through three alumina rods. The filament was heated by a 15-V, 10-A regulated ac supply and the cell temperature was measured with two Pt–Pt–10% Rh thermocouples. The ionizing electron energy was normally kept at 50 eV. Appearance potentials (AP) were evaluated by the vanishing current and/or extrapolated voltage difference method using internal Hg background and Kr for calibration.[12] AP curves were recorded automatically as described earlier[5] except that, now, continuously monitored voltage readings enabled periodic checks of the recorded values.

Tungsten powder from the GE Refractory Department and Reagent grade tungstic oxide and bromine from Fisher Scientific Co. were used to prepare $WOBr_3$ by the reported method.[8] Two independent analyses[13] of the selected dark, prismatic crystals dissolved in 2 *N* NaOH and $H_2O_2$ gave W:Br values of 1:2.95 and 1:3.02. However, X-ray diffraction powder patterns indicated the minor presence of $WO_2Br_2$.[14] This may be due to hydrolysis of $WOBr_4$ surface contamination, present in the preparation, even though the samples were handled in a drybox. Appropriate precautions were taken in transferring samples to the mass spectrometer although $WOBr_3$ solid is reported resistant to moisture.[8] Infrared spectra of $WOBr_3$ samples in Nujol mull taken with a Beckman IR-20 depicted a strong peak at 722 cm$^{-1}$, which has been reported as a characteristic bridged metal–oxygen stretching frequency in the solid phase.[7] Four separate series of experiments were performed: A and B with samples from one preparation and C and D from another.

The $WBr_6$ samples were kindly provided by Dr. L. J. Schupp of the GE Photo Lamp Department.

## Results

**Vaporization of Solid $WOBr_3$.** Mass spectra of the vapor species in the temperature range 410–690°K showed a great degree of complexity. Major ionic species at 50 eV observed in the lower temperature range, 410–480°K, were $WOBr_3^+$, $WO_2Br_2^+$, $WOBr_2^+$, $WBr_3^+$, and $WBr_4^+$ in a decreasing order of magnitude except during the initial runs in the experimental series C and D when $WO_2Br_2^+$ predominated. Above 480°K, additional ionic species observed were $WBr_5^+$, $W_2Br_6^+$, $W_2Br_5^+$, $W_2Br_4^+$, $W_2Br_3^+$, $W_2Br_2^+$, $W_2Br^+$, and $WOBr_4^+$ (see Table I). Lower mass fragments, *e.g.*, those containing less than two bromine atoms, $Br_2^+$ and $Br^+$, although observed are not considered because of their possible generation from many molecular precursors. The measured AP of $Br_2^+$, 11.5 eV, immediately suggested the absence of molecular bromine. Minor amounts of doubly charged ionic species were also detected. Unambiguous characterization of these ionic species was accomplished by the customary magnetic field mass calibration and comparison of the observed and calculated isotopic pattern. Shutter effects were also used to ensure that these species originated from the Knudsen cell.

Rather large $WO_2Br_2^+$ ion currents observed in the mass spectra (see Table I) even after extensive heating in the cell clearly establish $WO_2Br_2$ as a major decomposition product. Initial reduction and subsequent stabilization of $WO_2Br_2^+$ ion currents in series C and D and the X-ray diffraction patterns of these $WOBr_3$ samples indicated the presence of some

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**Table I.** Relative Ion Intensities of Gaseous Species over $WOBr_3(s)$ at 588°K

| Electron energies, eV | Rel intens | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $W_2Br_6^+$ | $W_2Br_5^+$ | $WBr_5^+$ | $WOBr_4^+$ | $WBr_4^+$ | $WOBr_3^+$ | $WBr_3^+$ | $WO_2Br_2^+$ | $WOBr_2^+$ | $WBr_2^+$ |
| 50 | 1.1 | 2.1 | 0.76 | 0.07 | 12.7 | 100 | 17.5 | 82.4 | 108 | 26.3 |
| 14 | 1.5 | 1.0 | 1.2 | | 13.3 | 100 | 4.7 | 44.1 | 25.4 | |
| 12 | 2.0 | | 1.8 | | 15.0 | 100 | 1.0 | 5.9 | 2.0 | |

**Table II.** Appearance Potentials (eV) and Assigned Molecular Precursors

| Ion | $WOBr_3(s)$ decompn | $WBr_6(s)$ decompn | Lit. results |
|---|---|---|---|
| $WX_5^+$ | 9.2 ± 0.3 ($WBr_5$) | 8.7 ± 0.5 ($WBr_5$) | 9.4 ± 0.5 ($WBr_5$)[a]<br>9.1 ($WCl_5$)[b]<br>10.9 ($WCl_6$)[c] |
| $WX_4^+$ | 8.6 ± 0.3 ($WBr_4$) | 9.2 ± 0.4 ($WBr_5$) | 9.8 ± 0.5 ($WBr_5$)[a]<br>8.0 ($WCl_4$)[b]<br>11.4 ($WCl_6$)[c] |
| $WX_3^+$ | 11.3 ± 0.4 ($WBr_4$) | 11.7 ± 0.5 ($WBr_5$) | 11.8 ($WCl_4$)[b]<br>15.4 ($WCl_6$)[c] |
| $WX_2^+$ | 15.2 ± 0.4 ($WBr_4$) | 15.5 ± 0.5 ($WBr_5$) | 19.4 ($WCl_6$)[c] |
| $W_2X_6^+$ | 9.3 ± 0.4 ($W_2Br_6$) | | 9.5 ($W_2Cl_6$)[b] |
| $W_2X_5^+$ | 11.5 ± 0.4 ($W_2Br_6$) | | 11.9 ($W_2Cl_6$)[b] |
| $WOX_3^+$ | 8.5 ± 0.4 ($WOBr_3$) | | 10.3 ± 0.2 ($WOBr_4$)[d]<br>10.5 ± 0.5 ($WOBr_4$)[a]<br>10.8 ± 0.5 ($WOCl_4$)[a] |
| $WOX_2^+$ | 11.5 ± 0.4 ($WOBr_3$) | | 14.4 ± 0.5 ($WOBr_4$)[d] |

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 5.

$WO_2Br_2$ impurity. In an attempt to purify, the D series sample was subjected to a 24-hr thermal treatment in a sealed, evacuated tube in a 525/300°K temperature gradient. This treatment did not eliminate all the $WO_2Br_2$ impurity even though its reported vapor pressure at 520°K is $7 \times 10^{-2}$ Torr.[6,15] In the C series, the ratio $I_{WO_2Br_2^+}/I_{WOBr_3^+}$, at 486°K, decreased from 450 to 2 after the initial three runs at 420-545°K. X-Ray diffraction powder patterns of this $WOBr_3$ sample showed complete absence of $WO_2Br_2$. The D series time dependence was identical with that of the C series.

Besides $WO_2Br_2$, the presence of $W_2Br_6$ and $WOBr_4$ gaseous species is obvious from the mass spectra in Table I. The mass spectrum of the $W_2Br_6$ molecule comprising six $W_2Br_n^+$ ($n$ = 1-6) ion peaks with their respective intensities 9.6, 13.5, 19.4, 15.1, 100, and 49.7 is in good agreement with that reported recently.[16] The AP's of $W_2Br_x^+$ species compare well with those reported for $W_2Cl_x^+$ [17] and clearly establish the presence of only one $W_2Br_x$ species, *i.e.*, $W_2Br_6$. $W_3Br_x^+$ species are not detected in the present investigation which suggests the absence of $W_3Br_9$ molecules unlike the W-Cl system.[17] Singelton and Stafford[16] in their $WOBr_4$ study, observed only $W_2Br_6$ species and could not establish $W_3Br_x^+$ ions. $WOBr_4^+$ ion currents were generally observed above 510°K. *In situ* 2-hr sample bake-outs at ~400°K prior to each run should eliminate any $WOBr_4$ impurity due to its high vapor pressure;[6,15] otherwise its presence would be easily detected well below 510°K. Assignment of other observed ionic species was accomplished with the aid of the appearance potentials (AP) and ion intensities measured on all these samples at different times and temperatures. The evaluated AP's are listed in Table II along with their standard deviations. Some recently reported AP's for $WOBr_4$,[5] $WBr_5$,[16] $WCl_5$,[17] $WCl_6$,[18] and $W_2Cl_6$[17] species are also compared.

The AP data clearly indicate $WOBr_3$ and $WBr_5$ as additional gaseous species. The measured AP's of $WOBr_3^+$ and $WOBr_2^+$ were temperature independent and much lower than those reported from $WOBr_4$[5] and thus are assigned to the $WOBr_3$ molecule. Possible existence of $WOBr_2$ species is also ruled out on this basis and the relative ion current changes with electron energies (Table I). The $WOBr_3^+$ ionization efficiency curve failed to show any discontinuity due to $WOBr_4$ contribution because of $WOBr_3$ vapor-phase predominance.

Comparison of the AP's of $WBr_x^+$ with those obtained from $WBr_5$[16] and also with those of $WCl_x^+$ reported by Rinke and Schafer[17] points out the possible existence of both $WBr_5$ and $WBr_4$. The measured AP($WBr_4^+$) although somewhat lower than AP($WBr_4^+/WBr_5$), is comparable within experimental error. In principle, the difference between the AP($WBr_4^+/WBr_4$) and AP($WBr_4^+/WBr_5$) should be approximately equal to $D°(WBr_4\text{-}Br)$ which, on the basis of available thermochemical data[19] on $WBr_6$ and $WBr_5$, is ~37 kcal or 1.6 eV, while the observed difference is 0.6 or 1.2 eV if the recently reported AP($WBr_5^+$)[17] is used. The smaller observed difference may arise due to a minor contribution from an ion-pair formation of $WBr_4^+$ from $WBr_5$. Such ion-pair formations have been proposed in electron impact studies of $TiCl_4$ and $CCl_4$[20] although a later work questions this.[21]

The AP's of $WBr_3^+$ and $WBr_2^+$, in the presence of $WBr_4$, would also be expected to be lower than those from $WBr_5$. However, as is evident from Table II, the differences in the AP's are well within the experimental uncertainty. The ionization efficiency curves for $WBr_4^+$, $WBr_3^+$, and $WBr_2^+$ did not show any noticeable discontinuities that would arise from the presence of both $WBr_5$ and $WBr_4$ species. This is due to the overwhelming fragmentation of $WBr_5$ to produce the lower ions and to the relatively small proportion of $WBr_4$ present in the vapor phase.

Mass spectra of the vapor phase at 50-eV electron energies (Table I) can also be analyzed to establish the presence of $WBr_4$. The known contribution due to $WBr_5$ and $WOBr_4$ on deduction from the mass spectra leave $WBr_4^+$ ion currents

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which are believed to be due to $WBr_4$ molecules. Fragmentation contributions from $W_2Br_6$ molecules are considered negligible. Vapor-phase mass spectra at 14- and 12-eV electron energies are also compared in Table I with the 50-eV mass spectra. The constancy of the ratio $I_{WBr_5^+}/I_{WBr_4^+}$ indicates that AP($WBr_4^+/WBr_5$) is not much different from the AP($WBr_4^+/WBr_4$). Thus, the $WBr_5$ as well as $WBr_4$ contributions to the $WBr_4^+$ ion currents do not change significantly as the electron energy approaches the AP value. Significant decreases in the $WBr_3^+$ and $WBr_2^+$ ion currents indicate $WBr_5$ as their primary molecular precursor and also rule out the existence of $WBr_3$, the monomer of $W_2Br_6$, in the vapor phase. This is analogous to the W-Cl system where monomeric $WCl_3$ was not detected also.[17]

The presence of six species in different proportions with their overlapping fragmentation contributions made even a semiquantitative analysis of the mass spectral data rather difficult. Low electron energy mass spectra could not be used because of unusually low molecular ion intensities. Thus, for the calculation of total ion intensities, the procedure adopted here involved successive deduction of molecular contributions using known mass spectra. This method suffers from obvious errors due to the use of inaccurate mass spectra and low molecular ion peaks.

Since mass spectra of $WOBr_3$ and $WBr_4$ are unknown, these were indirectly evaluated or estimated. Relative ion current data only at temperatures above 640°K were used since the absence of $WOBr_4$ in these cases was believed certain and the $WBr_4$ proportion was comparatively high. The evaluated ratio 85:100 for $WOBr_3^+$:$WOBr_2^+$ appears reasonable in view of the corresponding value of 60:100 obtained for the $MoOBr_3$ fragmentation in a preliminary study of the W-Mo-O-Br system at 930-1100°K.[22] The total ion current values for $WOBr_3^+$ were estimated to be 2.3 times the $I_{WOBr_3^+}$ in comparison with the $WO_2Br_2$ fragmentation. The evaluated ion current ratio $WBr_4^+$:$WBr_3^+$:$WBr_2^+$ = 45:100:35 for the $WBr_4$ fragmentation is comparable to the corresponding ratio 35:100:– reported for $WCl_4$[17] and 60:100:30 for the $MoBr_4$ fragmentation measured in the W-Mo-O-Br investigation.[22] These fragmentation patterns also compare well with the reported mass spectra for some metal tetrahalides, *e.g.*, $TiCl_4$.[21] The total ion current values for $WBr_4^+$ were evaluated as $3.5I_{WBr_4^+}$ in view of the estimated fragmentation pattern. Fragmentation contributions to $WBr_x^+$ from $W_2Br_6$ were assumed negligible, due to relatively minor amounts of $W_2Br_6$ in the vapor phase. At lower temperatures, *i.e.*, 410-480°K, where no $WBr_5^+$ could be detected, $WBr_4^+$ ion currents were assumed to be all due to $WBr_5$ species. Present data suggest that $WBr_4$ is present only at temperatures above 480°K.

The computed total ion intensity values for the D series, depicted in Figure 1, reflect the vapor-phase composition. The observed time dependence of ion intensities in the C and D series (Figure 1) is interesting. The relative time unit is approximately 3 hr of heating the sample in the Knudsen cell at 550-610°K. The vapor composition does not change significantly within this temperature range and stabilizes after about 12 hr. Data from other series are also in qualitative agreement with those in Figure 1. No attempt has been made to smooth the curves, because of large uncertainties, especially, in the $WBr_4^+$, $WBr_5^+$, and $WOBr_4^+$ ion currents.

Vaporization rates at 640-680°K were relatively high and the sample was rapidly depleted of the gaseous species. The residue from the Knudsen cell produced a poor X-ray diffraction pattern indicative of its amorphous nature. The X-ray pattern did not correspond to the reported patterns of $WOBr_2$(s),[8] $WBr_2$(s),[23] $WBr_4$(s),[23] or any of the known tungsten oxides. Thus, the present results do not appear to support the formation of $WOBr_2$ residue proposed by Oppermann and coworkers.[11]

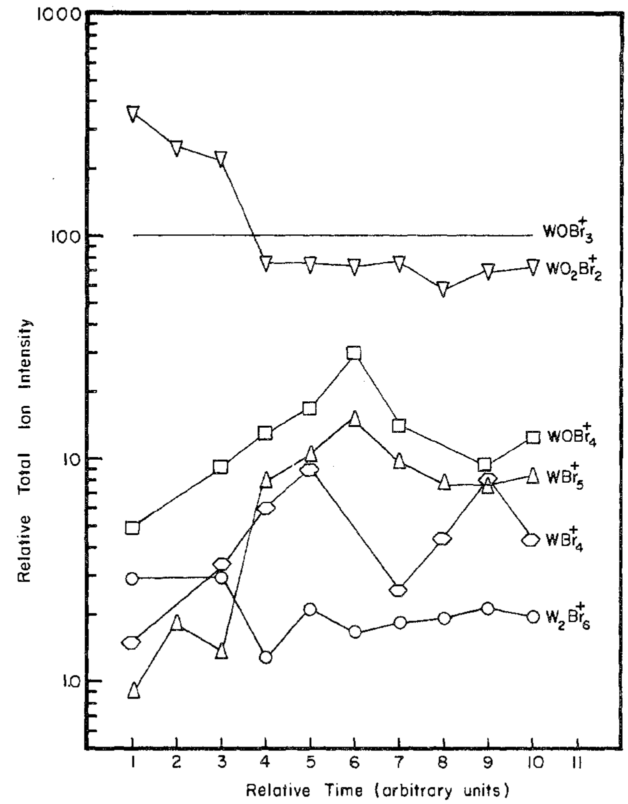

**Figure 1.** Time dependence of the relative total ion intensities of the vapor species over solid $WOBr_3$. The relative time unit is approximately 3 hr of *in situ* sample heating at 550-610°K.

Further investigations of the $WOBr_3$(s) decomposition were separately conducted in sealed and evacuated reaction tubes. The sample was subjected to different heat treatments with the other end of the reaction tube at ambient temperature. Heating of the $WOBr_3$ sample at ~470°K up to 20 hr did not produce any noticeable sublimate. However, a brownish black sublimate was observed after 40 hr of additional heating at 550°K. Further heating at 650°K for 35 hr darkened the earlier sublimate and produced a fluffy grayish black residue. The X-ray diffraction pattern indicated that the sublimate was predominantly $WO_2Br_2$ with some $WOBr_3$, while the residue gave a poor pattern identical with those obtained with Knudsen cell residue from the mass spectrometric study. Another sample heated at 720°K gave identical results. The possible existence of minor amounts of $WOBr_4$ and other species in the sublimate cannot be discounted since these, on hydrolysis in the capillary, could give rise to $WO_2Br_2$. In contrast, Oppermann, *et al.*, have found only $WOBr_4$ in such sublimates.[11]

**Decomposition of $WBr_6$(s).** The investigation of solid $WBr_6$ decomposition, in the temperature range 360-395°K, was conducted in the same tungsten Knudsen cell used for the $WOBr_3$ study. In spite of handling precautions, the $WBr_6$ sample, due to its extreme susceptibility to moisture attack,

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(22) S. K. Gupta, unpublished work.

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hydrolyzed slightly to produce $WOBr_4$, $WO_2Br_2$, and HBr.[24] The observed $WBr_6$ decomposition threshold temperature of ~360°K prevented *in situ* sublimation of the $WOBr_4$ impurity.

The mass spectrum observed at 384°K is compared with those of other pentahalides in Table III. The $WBr_5$ fragmentation pattern also listed was obtained by subtraction of the appropriate contributions due to $WOBr_4$ and $WO_2Br_2$, the hydrolysis products. The shutter profiles indicated that a major proportion of the observed $WO_2Br_2$ came from the radiation shields. Ion intensities of $WBr_4^+$, $WBr_3^+$, and $WBr_2^+$ relative to that of $WBr_5^+$ were independent of the sample temperature; thus $WBr_5$ is believed to be the only binary species. The $WBr_5$ mass spectrum compares well with the reported patterns of $WCl_5$ [17,25] and $MoCl_5$.[18] The appearance potentials, listed in Table II, are in fair agreement with those reported by Singelton and Stafford.[16] The ion current ratio for $Br_2^+$:$WBr_4^+$ varied from 1.5 to 2.5 in the temperature range 372–394°K. The measured $AP(Br_2^+) = 10.6$ eV, compared to the reported electron impact value of 10.7 eV,[26] further confirms the existence of molecular bromine as one of the decomposition products. These results clearly point out that $WBr_6$ solid dissociation begins at fairly low temperatures and, thus, appropriate purification procedures should be adopted in $WBr_6$ preparations.

## Discussion

**$WOBr_3$(s) Decomposition Reactions.** Our results are in good agreement with the conclusions of Schafer and Rinke[27] regarding the vapor-phase species over solid $WOBr_3$ at 410–690°K. Oppermann and coworkers, however, have suggested the presence of only $WO_2Br_2$ on the basis of their tensimetric investigation.[11] Their proposed mechanism involves a primary reaction

$$2WOBr_3(s) = WOBr_2(s) + WOBr_4(g) \quad (1)$$

and a secondary reaction

$$2WOBr_2(s) = WBr_2(s) + WO_2Br_2(g) \quad (2)$$

which becomes significant above 670°K. The complexity of the system is evident by the fact that their static tensimetric experiments required several days to attain chemical equilibrium. Nevertheless, they applied their proposed reaction mechanism to the nonequilibrium dynamic investigation which employs a sample heating rate of 1°/min. In view of the slow kinetics of the $WOBr_3$(s) evaporation reactions, observed by Oppermann, *et al.*,[11] the present Knudsen effusion (orifice = 0.064 cm; orifice:cell surface ratio = $10^{-4}$) study may also be nonequilibrium, and evaporation coefficients of the vapor species for solid $WOBr_3$ may be $\leq 10^{-4}$. Evaporation coefficients considerably less than unity have been reported for vaporization phenomena involving dissociation, rearrangements, association, etc.[28] However, the particular mode of vaporization of a substance would rarely change drastically from somewhat of a nonequilibrium (*e.g.*, Knudsen effusion) to a complete equilibrium (*e.g.*, static tensimetric) evaporation.

**Table III.** Mass Spectra of Gaseous Species over $WBr_6$(s) at 384°K

| | Rel intens | | | | |
|---|---|---|---|---|---|
| | $WBr_6$ decompn | | $WCl_5$ | $WCl_5$ | $MoCl_5$ |
| Ion | *a* | *b* | *c* | *d* | *e* |
| $MX_5^+$ | 9.72 | 9.85 | 13 | 9 | 4.3 |
| $MX_4^+$ | 100 | 100 | 100 | 100 | 100 |
| $MX_3^+$ | 42.0 | 35.4 | 27 | 25 | 62.8 |
| $MX_2^+$ | 42.1 | 27.8 | | 20 | 35.7 |
| $MX^+$ | 30.5 | 20.3 | | 12 | 37.3 |
| $M^+$ | 18.2 | 12.2 | | 9 | 50.8 |
| $X_2^+$ | 87.8 | 80.9 | | | |
| $X^+$ | 22.0 | 6.0 | | | |
| $MOX_3^+$ | 107 | | | | |
| $MO_2X_2^+$ | 5.2 | | | | |

[a] Mass spectra as measured at 50 eV. [b] $WBr_5$ mass spectrum except $Br_2^+$ and $Br^+$ values. [c] Reference 17. [d] Reference 25. [e] Reference 18.

The characterization procedure adopted in the tensimetric studies is acceptable for simple systems but can be misleading in complex cases. For instance, the tensimetric *P vs. T* curve, assigned to $WOBr_4$, could arise from a mixture of higher and lower vapor pressure components, *e.g.*, $WO_2Br_2$, $WBr_5$, and $WOBr_3$. $WOBr_3$, clearly shown in the present work to be the most predominant vapor species, is not even considered while another important decomposition species, $WO_2Br_2$, is postulated as significant only above 670°K. The major species suggested by these workers, $WOBr_4$, according to this study, is only of minor importance. The proposed decomposition reaction 1 is also not supported by analyses of the condensed phase, assumed to be $WOBr_2$ only on the basis of the *P vs. T* curves.[11]

Present results suggest the following reactions for $WOBr_3$(s) vaporization in the temperature range 400–700°K

$$WOBr_3(s) = WOBr_3(g) \quad (3)$$

$$2WOBr_3(s) = WBr_4(g \text{ or } s) + WO_2Br_2(g) \quad (4)$$

$$2WBr_4(g \text{ or } s) = WBr_5(g) + {}^1/_2W_2Br_6(g) \quad (5)$$

$$WOBr_3(g) + WBr_5(g) = WOBr_4(g) + WBr_4(g) \quad (6)$$

The evaporation and dissociation reactions 3 and 4 are believed to be of primary importance. Since $WBr_5$ and $W_2Br_6$ are detected only above 480°K, reaction 5 assumes prominence at these temperatures. The total ion current data, plotted in Figure 1, support reaction 6 as the most likely source of $WOBr_4$ in the vapor phase. Further evidence is found, for example, in high-temperature (>640°K) runs, wherein $WOBr_4$ was reduced beyond detection as the $WBr_4$ level appreciated dramatically.

The production of an additional condensed phase as suggested by reaction 4 or other possible reactions could not be ascertained. Solid $WCl_4$ and $WCl_3$ have been reported to vaporize as $WCl_5$, $WCl_4$, and polymeric $(WCl_3)_n$ ($n = 2, 3$) in the temperature range 570–620°K.[17] Analogous reactions for solid $WBr_4$ would explain the observation of $WBr_5$, $WBr_4$, and $W_2Br_6$ among the gaseous species. Analysis of the $WOBr_3$ residue gave a W:Br molar ratio 1:2.1 in one case and 1:3.6 in another; the latter may be due to the presence of some $WBr_4$ in the residue which was removed at a somewhat earlier stage of the decomposition study.

**Registry No.** $WOBr_3$, 20213-56-3; $WBr_6$, 13701-86-5.

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