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A STUDY OF THE THERMAL DECOMPOSITION OF $Se_2O_2F_8$ AND $Te_2O_2F_8$, USING MOLECULAR BEAM TECHNIQUES

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ABSTRACT

The thermal decomposition of the vapor phases of the oxygen bridged dimers $Se_2O_2F_8$ and $Te_2O_2F_8$ has been studied by mass spectrometry, electric deflection and flight time analysis on a molecular beam generated directly from the decomposition products. $Se_2O_2F_8$ begins to decompose at ∿250°C; the principal products are SeF_4 and O_2, with $SeOF_2$ as a minor product. Decomposition is complete by ∿500°C. There is some decomposition to monomeric $SeOF_4$ between 200 and 350°C. $Te_2O_2F_8$ did not begin to decompose until a temperature of 400°C was reached. Again, the principal products observed were TeF_4, O_2, and $TeOF_2$ with no evidence for decomposition to the monomeric $TeOF_4$.

INTRODUCTION

Two new compounds, $Se_2O_2F_8$ and $Te_2O_2F_8$, have recently been synthesized [1,2] by the vacuum pyrolysis of the salts $Na^+SeOF_5^-$ and $Li^+TeOF_5^-$. The sodium pentafluoroorthoselenate salt yields monomeric $SeOF_4$ if the gas is collected below -100°C, otherwise the dimeric form will result. The lithium pentafluoro-orthotellurate decomposes to yield ∿60% dimeric $Te_2O_2F_8$ and the balance is an unspecified higher polymer, but no monomeric species. A double oxygen bridge is believed to hold the monomeric units together, [1,2,3] and the stability of these bridges is of interest, since it was commonly accepted that such bonding is weak.

A similar situation existed for the compound IO_2F_3, which was examined by a variety of techniques. Vapor density, [4] spectroscopic, [4] and molecular beam measurements including electric deflection and mass spectrometry [5] showed that IO_2F_3 was very likely a doubly oxygen bridged symmetric dimer in the vapor phase, which was stable up to temperatures of ca. 100°C. These findings were in contrast to other reports that the bonding in IO_2F_3 oligomers was weak, [6] and that the molecule exists as trimeric units. [7,8] Most recently [9] X-ray diffraction work has shown IO_2F_3 to be a centrosymmetric oxygen bridged dimer in the solid state.

IO_2F_3 and $TeOF_4$ are isoelectronic, and obviously have similar structures. Therefore, it seemed natural to extend the molecular beam/thermal decomposition studies to include $TeOF_4$ and $SeOF_4$ dimers. Two of the main objectives of this study were to see if monomeric $SeOF_4$ and $TeOF_4$ could be produced by thermal decomposition, (as could be done with IO_2F_3) and at what temperatures the dimeric compounds decomposed.

EXPERIMENTAL PROCEDURE

Synthesis

$Se_2O_2F_8$ was synthesized according to the procedures given in the literature, [1,2] viz by the vacuum pyrolysis of the salt $Na^+SeOF_5^-$. $Te_2O_2F_8$ was prepared by the sublimation of $B(OTeF_5)_3$ through a quartz tube heated to 600°C. The products were collected in a liquid nitrogen trap, and consisted of $Te_2O_2F_8$ (90%) with the balance consisting of $HOTeF_5$ and higher polymers of $TeOF_4$. Purification was achieved by trap to trap distillation washing with 30% sulfuric acid, and drying with P_2O_5. Subsequent distillation and fractional crystallization yields spectroscopically (^{19}F-NMR) pure $Te_2O_2F_8$ which melts at 28°C and boils at 77.5°C.

Molecular Beam Measurements

Flight time distribution measurements [10] can be performed on any ionic species that results from electron impact ionization of the molecules in the beam. These measurements are used to establish the molecular weight of the principal neutral species from which the ion is derived. A detailed explanation of how these measurements are made is given in reference 10, and in the following discussion section.

The molecular beam apparatus has been described in published reports, [5,10,11] however, the quadrupole mass filter employed as a detector in previous studies has been replaced with a magnetic sector mass spectrometer with a mass limit of 1200 AMU and a resolution of 1000. The principle of electric deflection for the detection of polar molecules in a molecular beam is also amply described in the literature. [10,12,13] The apparatus used in this study can detect dipole moments as small as 0.025D in symmetric top molecules.

Mass spectra were taken with a fixed emission of 300 μA and an electron energy of 70 eV. The ion optics of the source were maximized to the oxide fluoride monomer ions for scanning mass spectra, and the phase angle of the lock-in amplifier was set during the scan according to whether the low mass or the high mass region of the spectrum was being scanned. Spectra are reported as the intensity of any ionic species relative to the most intense. Selenium and tellurium each have many stable isotopes, hence the abundances reported in this study have been corrected for isotopic distributions (in the case of dimers) and overlap in the case of oxide fluoride vs binary fluoride ions.

Inlet pressures were measured with a capacitance manometer with ±0.01 torr reproducibility, and exit temperatures were measured with an iron-constantan thermocouple. Preconditioning of the inlet pipe was done by heating the exit segment to 350°C while flowing molecular fluorine through it for several hours. Thermal decompositions were done with stepwise ascending and descending temperatures, as well as random temperature excursions. The orifice sizes used in these experiments were 0.013 cm dia for the $Te_2O_2F_8$ and 0.020 cm for the $Se_2O_2F_8$. Inlet pressures were maintained at 1.2 torr and 0.65 torr, respectively, resulting in a molecular beam which has component velocity distributions typified by low Mach numbers (Mach 1 to Mach 2). The samples were subjected to several freeze-pump-thaw outgassing cycles prior to beginning the experiment.

RESULTS AND DISCUSSION

$Te_2O_2F_8$

Mass spectra were recorded for $Te_2O_2F_8$ at exit temperatures of 29, 100, 200, 300, 375, 400, 425 and 450°C, with the sample being at -10°C and the inlet pressure at 1.2 torr. The mass spectra show very intense dimer ions corresponding to $Te_2OF_7^+$, $Te_2O_2F_7^+$ and the parent ion, $Te_2O_2F_8^+$. These ions constitute between 43 and 19 percent of the total ion intensity between the temperatures of 29°C and 400°C. Table I shows the spectra recorded at 29, 350, 400 and 450°C. Very little change occurred in the spectra up to 400°C, except for an intensification of the TeF_5^+ ion. Above 400°C, thermal decomposition becomes significant, in fact by 425°C all evidence of dimer ions is gone, and by 450°C the mass spectrum shows ions which are consistent with the complete thermal decomposition to the products TeF_4, $TeOF_2$ and O_2 (see Table I). It is risky to conclude that decomposition does not take place until 400°C on the basis of mass spectra alone, but the focussing measurements and flight time measurements also corroborate this.

TABLE I

Mass Spectra of $Te_2O_2F_8$ at Various Exit Temperatures, Normalized to 100 for the Largest Peak.

ION	29°C	350°C	400°C	450°C
O_2	-	3	6	15
Te^+	8.7	12	14	14
TeO^+	7.7	-	-	-
TeF^+	9.6	15	24	12
$TeOF^+$	19	19	11	-
TeF_2^+	21	25	25	23
$TeOF_2^+$	11	17	14	11
TeF_3^+	96	100	100	100
$TeOF_3^+$	78	68	37	-
TeF_4^+	-	-	12	-
$TeOF_4^+$	7.7	15	-	-
TeF_5^+	6.7	28	62	-
$Te_2OF_7^+$	29	58	30	-
$Te_2O_2F_7^+$	100	81	27	-
$Te_2O_2F_8^+$	71	59	16	-

\- below the detection limit.

Electric deflection measurements on the neutrals in the molecular beam observed on various ions at temperatures where decomposition might have occurred are summarized in Table II. The same amount of defocussing was observed on $Te_2O_2F_8^+$, $TeOF_4^+$ and $TeOF_3^+$ at ambient temperature, which is expected if both of the fragment ions result from electron impact cracking of the symmetric neutral species $Te_2O_2F_8$. Focussing measurements were made on those fragment ions which were most likely to result from monomeric species at elevated temperatures, e.g.

$$TeOF_4 + e^- \rightarrow TeOF_3^+ + F + 2e \qquad [1]$$

Table II shows that polarity was not observed on any species until 400°C was reached. $TeOF_2^+$ focussed strongly at 400°C while TeF_2^+ and TeF_3^+ focussed weakly, and $TeOF_3^+$ did not focus. Examination of the mass spectra (Table I) in conjunction with these results leads to the conclusion that four distinct compounds comprise the molecular beam at 400°C, viz O_2, $Te_2O_2F_8$, $TeOF_2$ and TeF_4. Dimer ions are clearly still present (at 19% of the total ion current) and electron impact produces the $TeOF_3^+$ fragment, which does not focus. Strong focussing on the $TeOF_2^+$ ion rules out the possibility that it is derived from the $TeOF_3^+$ ion or the dimeric ions. This species is undoubtedly a parent ion of $TeOF_2$ which is expected to exhibit strong focussing. TeF_3^+ and TeF_2^+ exhibit the same amount of weak focussing, and hence TeF_2^+ cannot be uniquely related to $TeOF_2$ through electron impact cracking. The dominant ion in the spectrum is TeF_3^+, which is undoubtedly a result of electron impact cracking on TeF_4. The focussing behavior remains essentially unchanged at temperatures above 400°C, and the mass spectra show that the dimer ions and the $TeOF_3^+$ ion disappear. TeF_4 monomers are known to have an asymmetric structure [14] similar to that of SeF_4 [15] and should therefore focus.

TABLE II
Focussing Summary for $Te_2O_2F_8$

Exit Temperature, °C ION	25	200	300	350	375	400	425	450
TeF_2^+				0		6	7	5
$TeOF_2^+$				0	0	88	100	97
TeF_3^+		0	0	0	0	5	5	5
$TeOF_3^+$	d 12	0	0	0	0	0	-	-
$TeOF_4^+$	d 13					-	-	-
$Te_2O_2F_8^+$	d 12							

d - defocussing
- - signal too weak for focussing measurement

Flight time measurements of the neutral components of the molecular beams were made on several ions at exit temperatures of 25, 200, 300, 400 and 450°C. These measurements are used to deduce the molecular weight of the neutral species that is transported to the ion source, and thereby circumvent the problem of electron impact cracking of large neutral molecules into lower molecular weight fragment ions. The details of the method used are given in reference 10, but the essence of the technique is this: The leading edge of the current pulses observed for any ion in the modulated mass spectrum is a convolution of the chopper opening function and the flight time distribution of the neutral species. The flight time distribution is determined by the temperature, molecular weight and Mach number that characterizes the flow velocity of the gas stream through the orifice. An approximation to the flight time distribution can be obtained by differentiating the leading edge of the current pulse; this provides a Mach number and molecular weight to be used in a Fourier Transform convolution of the theoretical flight time distribution [16] with the chopper opening function. The result of the convolution should agree with the experimental data. Experience has shown that the molecular weight is the principal determinant for obtaining agreement between theory and experiment.

The current pulses for the ions $TeOF_3^+$ and $Te_2O_2F_8^+$, were virtually coincident at an exit temperature of 25°C. Convolutions based upon dimer molecular weight and Mach number 2 gave satisfactory agreement with the experimental data. Attempts to convolute with a monomeric molecular weight were also made, and agreement between theory and experiment could not be obtained.

The time-dependent ion current for TeF_3^+ and $TeOF_3^+$ at an exit temperature of 300°C was also measured. The convolution for a dimeric molecular weight and Mach #1.75 fit the experimental data extremely well. A gradual lowering of the Mach number occurs as the exit temperature is increased due to a reduction in the number density at the exit orifice, i.e. a small pressure gradient develops in the molecular beam source. The flight time measurements obtained when the exit temperature was raised to 450°C were taken on TeF_3^+, the strongest ion in the mass spectrum. Convolution using monomeric molecular weight with Mach numbers 1.25 and 1.5 bracket the experimental data. Decomposition to the monomer results in further reduction of the Mach number, as a result of the mean free path being increased by a smaller collision cross-section.

When taken together, these results establish rather firmly that the $Te_2O_2F_8$ dimer is quite stable, at least to temperatures of 375°C, and it decomposes at higher temperatures. The mass spectra show that the preferred decomposition path is

$$Te_2O_2F_8 \rightarrow 2TeF_4 + O_2 \qquad [2]$$

with a possible secondary path

$$Te_2O_2F_8 \rightarrow TeOF_2 + TeF_4 + O + F_2 \qquad [3]$$

However, the $TeOF_2$ observed may also result from bimolecular reactions in the heated exit tube, since this is not a collision-free zone. No evidence for molecular fluorine could be found.

The only apparent anomoly in the data occurs in the mass spectra. The TeF_5^+ ion becomes more intense as the temperature is raised, indicating a possible thermal decomposition to TeF_6. However, TeF_5^+ is present at all temperatures below 400°C and disappears above 400°C. It might also arise from a TeF_6 impurity in the sample itself but this would not increase as exit temperature is increased. Either decomposition to TeF_6 or a TeF_6 impurity can also be ruled out by the lack of a TeF_4^+ ion to accompany the TeF_5^+ ion at all temperatures. A TeF_4^+ ion was observed only at 400° and 425°C where the highest absolute signal levels for TeF_3^+ were observed.

The TeF_5^+ ion most likely results from a unimolecular rearrangement of the $Te_2O_2F_8^+$ ion which becomes more probable as the temperature increased, and disappears when there is no more dimer to ionize.

$Se_2O_2F_8$

Mass spectra representative of the thermal decomposition paths at exit temperatures of 25, 250, 370 and 500°C are given in Table III for the sample vaporizing at ambient temperature and the inlet pressure held at 0.6 torr. In addition to the spectra given in Table III, mass spectra were also recorded at 100, 150, 200, 300 and 350°C.

TABLE III

Mass Spectra of $Se_2O_2F_8$ at Various Exit Temperatures, Normalized to 100 for the Largest Peak.

ION	25°C	250°C	370°C	500°C
O_2^+	-	-	43	NS
Se^+	1.6	5.5	21	12
SeO^+	2.1	4.7	8.5	5
SeF^+	2.3	9.1	25	15
$SeOF^+$	6.9	9.3	54	33
SeF_2^+	4.6	7.9	39	45
$SeOF_2^+$	6.1	20	44	29
SeF_3^+	14	52	100	100
$SeOF_3^+$	100	100	70	8
$SeOF_4^+$	12	14	7	-
$Se_2O_2F_7^+$	0.8	-	-	-

NS - not scanned.

— - below detection limits.

The differences between the room temperature mass spectra of $Se_2O_2F_8$ and $Te_2O_2F_8$ are most pronounced in the abundance of the dimer ions and in the trifluoride ion. Flight time measurements at exit temperatures up to 200°C show excellent conformity to a predominance of dimeric neutral species. Therefore the low abundance of dimer ions in the $Se_2O_2F_8$ mass spectra is due to the instability of the dimeric ion, which is analogous to the $I_2O_4F_6$ situation. [5] It is worthwhile to emphasize the fact that a low abundance of dimer ions does not reflect a low abundance of the corresponding neutral species.

Thermal decomposition of the $SeOF_4$ dimer begins at ca 200°C as detected by focussing on the $SeOF_4^+$ and $SeOF_3^+$ ions (Table IV). Defocussing was observed on all measurements made at temperatures below 200°C, which corroborates well with flight time measurements indicating insignificant decomposition to monomeric species of any type. Decomposition progressed between 200 and 375°C, but it was by no means complete. The mass spectrum at 370°C shows a significant $SeOF_3^+$ ion, but this ion focussed only 3-5%, not 50-100% as would be expected if it were derived entirely from monomeric $SeOF_4$. Flight time measurements made in the temperature interval $200 < T \leq 375°C$ also showed clearly that the monomeric ions were derived from a mixture of monomeric and dimeric neutrals.

The decomposition path of $Se_2O_2F_8$ is similar to that of the $TeOF_4$ dimers, however, a comparison of the mass spectra (at temperatures where decomposition is appreciable) shows that the oxide fluoride ions are more abundant for the selenium compound. The dominant path is still the formation of the tetrafluoride and oxygen, but the mass spectra at 500°C still show appreciable abundances of $SeOF_2^+$ and $SeOF^+$. These ions are undoubtedly derived from $SeOF_2$ but there is also a small $SeOF_3^+$, which may be a cracking product of $SeOF_4$ monomers. Flight time measurements at 500°C yielded excellent fits for monomeric molecular weight neutrals.

TABLE IV

Focussing Summary for $Se_2O_2F_8$

Exit Temperature, °C								
ION	25	100	150	200	250	300	350	490
$SeOF_4^+$				0.3	-	-	-	-
$SeOF_3^+$	d8	d9	d9	3	4	5	3	-
SeF_3^+					10		16	13
$SeOF_2^+$					11		44	
$SeOF^+$							61	107

d - defocussing

\- - signal too weak for focussing measurement

SUMMARY

The results of this study reinforce the general similarities between the chemistry of selenium and tellurium. [17] Both oxygen bridged dimeric units $Se_2O_2F_8$ and $Te_2O_2F_8$ decompose primarily into the tetrafluoride and oxygen, with the secondary path leading to the oxide difluoride. $SeOF_2$ is known to be a pyramidal molecule with C_{2v} symmetry and a dipole moment of 3.18 D. [18] A near-symmetric top molecule with such a large dipole moment is expected to focus strongly, as observed. It is very likely that $TeOF_2$ has a similar structure.

The fact that $Te_2O_2F_8$ and $I_2O_4F_6$ are isoelectronic seems to have little influence on their respective thermal decomposition products. The double oxygen bridge in $Te_2O_2F_8$ is so strong that it cannot be broken without raising the internal energy of the molecule to the point where the monomeric unit is unstable. In contrast, the $I_2O_4F_6$ dimer decomposes into monomeric units at relatively low temperatures. [5] $Se_2O_2F_8$ behaves more like $Te_2O_2F_8$ than it does like $I_2O_4F_6$, although some monomeric

$SeOF_4$ can be formed, and there is a greater tendency f oxygen to remain bonded to the selenium atom when thermally decomposing. It is of interest to note that SeO_2F_2 (which is a known compound) is not a decomposition product.

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Note added in proof - plots showing the fit of theoretical flight times vs. the experimental data can be obtained from the author (M. J. Vasile).

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