origin. Also transitions to the A_2 component of the Γ_4 state, the Γ_3 state, and the Γ_1 ground state are not observed.

Remaining to be explained is the nature of the 825–835-cm^{-1} interval. Since there are no tetrahedral $NiCl_4{}^{2-}$ (or $ZnCl_4{}^{2-}$) fundamentals at so high an energy, this interval must be due to a Et_4N^+ fundamental. Examination of the Raman and infrared spectra of the $(Et_4N)_2ZnCl_4$ compound shows a band at ~800 cm^{-1}. A vibration of this frequency can be assigned to the methyl–methylene–nitrogen, C–C–N, bending fundamental.[26] It would thus appear that this system of the tetrachloronickelate negative ion and tetraethylammonium cation is a unique example of an exciplex with a highly resolved emission spectrum.

Acknowledgment. We gratefully acknowledge the assistance of National Science Foundation Grant No. GP 16089 which financed this research.

Registry No. $(Et_4N)_2NiCl_4$, 5964-71-6; $(Et_4N)_2ZnCl_4$, 5964-74-9; Cs_3NiCl_5, 27976-95-0; Cs_3ZnCl_5, 20833-37-8.

References and Notes

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Thermochemistry of Vanadium Oxytrichloride and Vanadium Oxytrifluoride by Mass Spectrometry

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Received November 19, 1974

AIC40791S

Mass spectral and ionization efficiency data have been obtained for the positive and negative ions produced from $VOCl_3$ and VOF_3 by electron impact. From these data values have been calculated for several thermochemical parameters (eV): $IP_v(VOCl_3) = 11.90 \pm 0.05$, $IP_v(VOF_3) = 13.88 \pm 0.05$, $EA(VOCl_3) \geq 3.6$, $EA(VOF_3) = 3.1 \pm 0.3$, and $\Delta H_{f298}(VOF_3(g)) = -12.8 \pm 0.3$. Less precise values for these same parameters have been calculated for the observed positive and negative ion fragments and for the neutral fragments inferred to be produced in the mass spectrometer ion source. Bond energies (eV) are estimated to be $\bar{D}(V\text{–}O)_{VOCl_3} = 5.5$, $\bar{D}(V\text{–}Cl)_{VOCl_3} = 4.4$, $\bar{D}(V\text{–}O)_{VOF_3} = 5.9$, and $\bar{D}(V\text{–}F)_{VOF_3} = 5.8$. Bond energy values are also reported for the positive ion and neutral fragments.

Introduction

Several years ago there was considerable interest here in using volatile inorganic halides and oxyhalides as a means of introducing transition elements into a mass spectrometer for isotopic abundance studies.[1,2] These experiences provided some of the motivation for studies of the thermochemistry of these compounds. The paucity of mass spectral information about such compounds was also a factor. Baldock and Sites[3] briefly surveyed the mass spectra of $VOCl_3$ and VOF_3 in an investigation of possible feed materials for the electromagnetic separation of the vanadium isotopes. They made no detailed studies of the compounds. Svec[4] gave only preliminary results of studies of $VOCl_3$ and VOF_3 in a review of the mass spectrometry of volatile inorganic compounds. Ngai and Stafford[5] have reviewed the structure, thermochemistry, and mass spectra of various gaseous oxyhalides of transition elements and reported some data for $VOCl_3$ and VOF_3. In this report we present thermochemical information that can be obtained from a careful consideration of the ionization efficiency (IE) data generated when $VOCl_3$ and VOF_3 interact with energetic electrons. Singleton and Stafford[6] have reported correlations of mass spectra and ionization potentials which they observed in their studies of several oxyhalides of chromium, molybdenum, tungsten, rhenium, and osmium. Their work provides a test of some of the conclusions from the work now reported.

Experimental Section

The positive–negative ion mass spectrometer used in this research is a 6-in. 60°-sector instrument which has been described previously.[7] The instrument is operated with the ion source at ground potential and the two analyzer tubes at ±2200 V to extract and detect positive and negative ions simultaneously from a single electron beam.

All the mass spectral and IE data were accumulated using an ionizing current of 2 μA regulated at the anode. The mass spectral data were obtained with 70-V electrons and displayed on a strip chart recorder. The IE data were plotted by an X-Y recorder which is connected directly to the electron energy and ion current detectors.

The $VOCl_3$ and VOF_3 were prepared in the same manner as previously described for CrO_2Cl_2 and CrO_2F_2.[8] The vapors were admitted to the mass spectrometer at room temperature. The ion source temperature was estimated to be 65°.

Table I. Relative Positive Ion Abundances for $VOCl_3$ and VOF_3 (70 eV)

	X = Cl		X = F	
Ion	+	2+	+	2+
VOX_3	431		356	
VX_3	7	2	17	2
VOX_2	347	1	475	6
VX_2	31	<1	34	2
VOX	61	1	23	13
VX	39	9	21	5
VO	24	<1	10	2
V	43	4	27	6
Total	983	17	963	36

Table II. Relative Abundances of Negative Ions from $VOCl_3$ and VOF_3

	Relative abund at max	
Products	X = Cl	X = F
VOX_3^-	*a*	*a*
$VX_3^- + O$	800	940
$VOX_2^- + X$	1000	1000
$VX_2^- + O + X$	13	<<1
$VOX^- + X_2$	1	
$VOX^- + 2X$	35	2
$X_2^- + VOX$	17	
$X^- + VOX_2$	150	650
$X^- + VOX + X$	1500	80
$O^- + VX_3$	13	150
$O^- + VX_2 + X$	5	

[a] Parent negative ions are formed by means of ion-molecule reactions.

Results and Discussion

Positive-Ion Spectra. The mononuclidic spectra for $VOCl_3$ and VOF_3 are presented in Table I. These spectra show that P^+ and $(P - X)^+$ are about equally abundant and account for more than 75% of the ions produced with 70-eV electrons. The other singly charged ions have approximately equal, low-abundance values. These observations indicate that strong ligand–metal bonds exist in all the ions, except for the X_2OV^+–X bond in P^+. This view is supported later in the discussion of bond dissociation energies.

Two dimeric ions, $V_2O_2Cl_4^+$ and $V_2O_2Cl_5^+$, were observed for the chloride, but only $V_2O_2F_5^+$ was observed for the fluoride. The abundances for all three ions exhibited a second-order pressure dependence. These ions are assumed to be produced in ion–molecule reactions between the parent gas and the abundant positive ions. This assumption is supported by IE experiments discussed later.

Negative-Ion Spectra. Negative ions may be produced by dissociative electron-capture processes at electron energies below 10–15 eV or by ion-pair processes for electrons of higher energy. Ion-pair production in VOX_3 is negligible, compared to secondary negative ion production, since pressure studies at 70 eV show that the negative ion abundances follow a second-order pressure dependence. The unique capabilities of the positive–negative ion mass spectrometer make it possible to display this dependence graphically by plotting directly on the X-Y recorder the negative ion vs. P^+ abundances as the pressure of VOX_3 is varied. The plots are clearly parabolas. The negative ions are presumably formed by dissociative capture of the low-energy, secondary electrons generated in the reactions forming positive ions. For this reason, only the relative, mononuclidic abundances at the electron-capture maxima are reported in Table II. The reaction products are listed since the IE data of some of the ions exhibit two maxima, clearly indicating two distinct ionization reactions. The energetics of the reactions were used to identify the neutral reaction products.

Other negative ions were observed but found to have second-order pressure dependences at the electron-capture maxima. They are P^-, VCl_4^-, and $VOCl_4^-$ for the oxychloride and P^-, VF_4^-, and $VO_2F_2^-$ for the oxyfluoride. These ions probably result from ion–molecule reactions between the parent gas and the abundant negative ions. This conclusion is supported by IE experiments discussed later.

Table III. Onset Potentials for Various Positive Ionization Reactions in VOX_3 (eV)

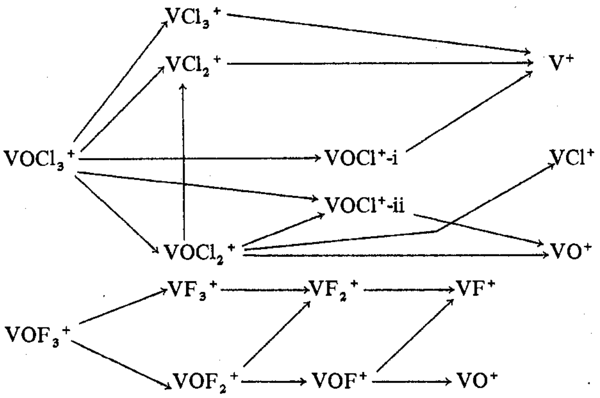
	Onset potentials	
Reaction products	X = Cl	X = F
$VOX_3^+ + e^-$	11.90 ± 0.05	13.88 ± 0.05
$VX_3^+ + O + e^-$	16.48 ± 0.28	16.76 ± 0.05
$VOX_2^+ + X + e^-$	13.25 ± 0.05	15.31 ± 0.06
$VX_2^+ + O + X + e^-$	18.98 ± 0.20	20.83 ± 0.19
$VOX^+ + X_2 + e^-$	14.05 ± 0.06	
$VOX^+ + 2X + e^-$	16.31 ± 0.05	19.92 ± 0.06
$VX^+ + O + 2X + e^-$	22.16 ± 0.07	25.75 ± 0.26
$VO^+ + 3X + e^-$	19.77 ± 0.09	24.41 ± 0.10
$V^+ + O + 3X + e^-$	26.83 ± 0.39	31.26 ± 0.19

Positive-Ion Ionization Efficiency Experiments. The IE data collected over the range of energies from onset to 75 eV showed no unusual behavior at higher energies. The onset potentials for the various reactions were determined by application of the extrapolated voltage-difference method[9] to the data obtained in the first 5-eV range of energies above the onset potential for each ion. Xenon IE data were used to calibrate the electron energy scale. The average onset potentials obtained from at least three determinations for each ion are listed in Table III. The uncertainty is the standard deviation of an individual determination. The electron volt (1 eV = 23.06 kcal/mol = 96.49 kJ/mol) is the choice of energy unit in this and the other tables because of its association with the mass spectrometric instrumentation.

The vertical ionization potential (IP_v) of $VOCl_3$ is less than that of VOF_3 but much higher than that of V. Singleton and Stafford[6] suggested that the high IP value for a metal oxychloride occurs because the electron removed upon ionization is from a nonbonding molecular orbital of predominantly chlorine pπ character. For other metal oxyhalides, however, the electron is removed from a nonbonding molecular orbital of predominantly oxygen pπ character. Their reasoning is that values for the IP's of various oxychlorides cluster about 12 eV and are only slightly less than IP(Cl)[10] = 13.01 eV, while the IP's of various oxyfluorides cluster about 13 eV and are only slightly less than IP(O)[10] = 13.61 eV and much less than IP(F)[10] = 17.42 eV. Since IP($VOCl_3$) = 11.99 eV fits this generalization, it is reasonable to expect that the electron removed in the ionization of $VOCl_3$ is a nonbonding electron of chlorine pπ character. However, IP(VOF_3) = 13.88 eV does not fit the generalization so neatly as it is greater than IP(O) and falls nearly within the range of IP's observed for metal fluorides.[6] This is evidence that in VOF_3, the electron removed in ionization is a nonbonding electron of fluorine pπ character. Further evidence is the ion abundance ratio $(P - X)^+/(P - O)^+$ for the oxyhalides. In CrO_2Cl_2 and CrO_2F_2, where the IP's fit the generalization of Singleton and Stafford, this abundance ratio is 22 and 0.5, respectively.[8] The abundance ratios for $VOCl_3$ and VOF_3 are 50 and 28, respectively. This, along with the similarity of the mass spectra of $VOCl_3$ and VOF_3 compared to the dissimilarity of spectra of CrO_2Cl_2 and CrO_2F_2, indicates that VOF_3 does not fit the generalization. We conclude that the electron removed in the ionization of VOF_3 comes from a nonbonding orbital of fluorine character rather than of oxygen character.

The removal of a nonbonding electron of predominantly halogen character in the ionization of VOX_3 weakens the associated V–X bond in P^+. It is this weakened bond which results in the low values for the appearance potentials of the reactions producing $(P - X)^+$ and the high abundance of $(P - X)^+$.

Scheme I. Fragmentation Mechanisms for $VOCl_3$ and VOF_3 at Electron Energy 18 eV above the Ionization Potential



A definite second onset potential was observed for $VOCl^+$. The difference in the two onset values, 2.26 eV, was determined by a deconvolution technique[8] and agrees favorably with the dissociation energy of Cl_2, 2.52 eV.[11] We postulate that the disparity in these two values, 0.26 eV, is due to the difference in the equilibrium interchlorine distances in Cl_2 and $VOCl_3$, 1.99 and 3.50 Å, respectively.[12] Thus additional excitation energy in the form of bending vibrations is required to bring the Cl ligands into position to form the Cl–Cl bond for the Cl_2 formed in the lower energy process leading to the formation of $VOCl^+$.

Plots of the IE data for many of the low-abundance ions showed broadened onset regions. This resulted in larger values of uncertainty for the onset potentials. The low ion abundances made a more definitive study of the onset region difficult to undertake.

Plots of the IE data for the secondary ions $V_2O_2Cl_5^+$ and $V_2O_2F_5^+$ are the same as those for $VOCl_3^+$ and VOF_3^+, respectively. This indicates that only P^+ and P^0 are involved in the ion–molecule reactions generating $V_2O_2X_5^+$. In the case of $V_2O_2Cl_4^+$, a second break in the IE data indicates that both P^+ and $(P - Cl)^+$ are the reactant ions involved.

The fragmentation pathways postulated for the decompositions of the positive ions are shown in Scheme I. These pathways were determined from a deconvolution–convolution treatment[13] of the IE data obtained over the 18-eV range of electron energies immediately above the IP of the molecule. The symbols $VOCl^+$-i and $VOCl^+$-ii refer to the ion fragments produced in the lower and higher energy reactions, respectively. No significant number of V^+ ions from VOF_3 are observed in this energy range because of the high onset potential of the ionization reaction producing V^+.

Negative-Ion Ionization Efficiency Experiments. Plots of the negative-ion IE data yielded the usual bell-shaped resonance-capture curves. The linear, lower energy portion of each plot was extrapolated and the intercept with the energy axis taken as the onset potential. The electron energy calibrant was O^-/CO. The onset potentials, averaged from a least four determinations, are listed in Table IV. The uncertainty is the standard deviation of a single determination.

The only vanadium-containing, negative fragment ion to exhibit two discrete ionization reactions is $VOCl^-$. The difference between the two onset potentials, 2.20 eV, is in good agreement with the difference of the two onsets observed for $VOCl^+$, 2.26 eV. This value is less than the bond dissociation energy of Cl_2, and the same reasons as given above are cited.

The IE data for the secondary negative ions provide persuasive evidence for the identity of the reactant primary ions participating in the ion–molecule reactions involved. For example, a plot of the IE data for VCl_4^- is nearly identical with that for either Cl^- or VCl_3^- but is displaced from the IE plot for $VOCl_2^-$. Thus Cl^- and/or VCl_3^- participate in the ion–molecule reactions producing VCl_4^-, but $VOCl_2^-$ does not. The probable ion–molecule reactions involved in producing the negative secondary ions observed were decided in this manner and are listed in Table V.

Table IV. Onset Potentials for Various Negative Ionization Reactions in VOX_3 (eV)

	Onset potential	
Reaction products	X = Cl	X = F
VOX_3^-		
$VX_3^- + O$	3.61 ± 0.05	4.72 ± 0.03
$VOX_2^- + X$	2.07 ± 0.08	4.02 ± 0.05
$VX_2^- + O + X$	8.48 ± 0.09	10.43 ± 0.10
$VOX^- + X_2$	3.85 ± 0.11	
$VOX^- + 2X$	6.05 ± 0.08	9.58 ± 0.07
$X_2^- + VOX$	3.49 ± 0.06	
$X^- + VOX_2$	1.62 ± 0.16	3.34 ± 0.13
$X^- + VOX + X$	3.81 ± 0.07	7.3 ± 0.5
$O^- + VX_3$	4.38 ± 0.09	4.89 ± 0.06
$O^- + VX_2 + X$	8.24 ± 0.15	

Table V. Negative Ion–Molecule Reactions Observed

$Cl^- + VOCl_3 \rightarrow VCl_4^- + O$
$VCl_3^- + VOCl_3 \rightarrow VCl_4^- + VOCl_2$
$Cl^- + VOCl_3 \rightarrow VOCl_4^-$
$VCl_3^- + VOCl_3 \rightarrow VOCl_4^- + VCl_2$
$VCl_3^- + VOCl_3 \rightarrow VOCl_3^- + VCl_3$
$VOCl_2^- + VOCl_3 \rightarrow VOCl_3^- + VOCl_2$
$Cl^- + VOCl_3 \rightarrow VOCl_3^- + Cl$
$VOF_2^- + VOF_3 \rightarrow VO_2F_2^- + VF_3$
$VF_3^- + VOF_3 \rightarrow VF_4^- + VOF_2$
$VOF_2^- + VOF_3 \rightarrow VOF_3^- + VOF_2$
$VF_3^- + VOF_3 \rightarrow VOF_3^- + VF_3$

Heats of Formation—Neutral Parent Molecules. The ionization reactions producing V^+ from $VOCl_3$ and VOF_3 are

$$VOCl_3 + e^- \rightarrow V^+ + O + 3Cl + 2e^- \ (\Delta H = 26.83 \pm 0.39 \text{ eV}) \quad (1)$$

and

$$VOF_3 + e^- \rightarrow V^+ + O + 3F + 2e^- \ (\Delta H = 31.26 \pm 0.19 \text{ eV}) \quad (2)$$

The heats of formation of gaseous $VOCl_3$ and VOF_3 can be calculated from these data, since the heats of formation of the various products are known. However, the calculation for $\Delta H_{f298}(VOCl_3(g))$ yields −8.47 eV, compared to a recently determined value[14] of −6.94 eV. This 1.53-eV difference is probably associated with kinetic energy and/or electronic excitations of the reaction products. The similar calculation for $\Delta H_{f298}(VOF_3(g))$ is expected to be in error for the same reasons. However, if it is assumed that such kinetic and/or electronic excitation energies have similar values for both reactions, the difference of these reactions

$$VOCl_3 + 3F \rightarrow VOF_3 + 3Cl \ (\Delta H = -4.43 \pm 0.43 \text{ eV}) \quad (3)$$

is subject to less error. Reaction 3 can also be obtained as the difference of the two reactions producing VO^+

$$VOCl_3 + e^- \rightarrow VO^+ + 3Cl + 2e^- \ (\Delta H = 19.77 \pm 0.09 \text{ eV}) \quad (4)$$

$$VOF_3 + e^- \rightarrow VO^+ + 3F + 2e^- \ (\Delta H = 24.41 \pm 0.10 \text{ eV}) \quad (5)$$

These give $\Delta H = -4.64 \pm 0.13$ eV for reaction 3. If these two values are weighted inversely according to their uncertainties, an average value of $\Delta H = -4.59 \pm 0.24$ eV is obtained. Using this value and the known heats of formation of $VOCl_3$, Cl, and F, the value calculated for $\Delta H_{f298}(VOF_3(g))$ is -12.8 ± 0.3 eV.

Heats of Formation—Positive Ions. When the heats of formation of the parent gas and neutral ligand fragments are known, the heats of formation of the various positive ion fragments can be calculated from the onset potentials of the reactions producing fragment ions. The results of these calculations for the positive ion fragments are listed in columns 2 and 5 of Table VI. The ancillary thermochemical values used in the calculations are listed in Table VII. The value

Table VI. Heats of Formation of Gaseous VO_mX_n Formed in the Mass Spectrometer (eV)

	ΔH_f					
	X = Cl			X = F		
Product	+ ions	Neutrals	− ions	+ ions	Neutrals	− ions
VOX_3	5.0	-6.9^g	<-10.6	1.0	−12.8	−15.9
VX_3	7.0	−3.7	−5.9	1.3	−9.1	−10.7
VOX_2	5.0	−3.0	−6.1	1.6	−6.9	−9.6
VX_2	8.2	-2.5^f	−3.8	4.6	-6.9^d	−7.3
VOX	6.8	−2.0	−3.4	5.4	−3.7	−4.9
VX	10.1	2.1^e		8.7	0.1^d	
VO	9.0	1.6^c		9.1	1.6^c	
V	12.1^b	5.3^a		12.1^b	5.3^a	

[a] Reference 17. [b] Reference 10. [c] Reference 19. [d] Reference 16. [e] Estimated, assuming $\Delta H(VCl \rightarrow V + Cl)/\Delta H(VCl_2 \rightarrow V + 2Cl) = \Delta H(VF \rightarrow V + F)/\Delta H(VF_2 \rightarrow V + 2F)$. [f] Reference 18. [g] Reference 14.

Table VII. Ancillary Thermochemical Values Used in Calculations

Reaction[a]	ΔH, eV	Ref
$O_2 \rightarrow 2O$	5.16	11
$F_2 \rightarrow 2F$	1.64	11
$Cl_2 \rightarrow 2Cl$	2.52	11
$O^- \rightarrow O + e^-$	1.48	15
$F^- \rightarrow F + e^-$	3.45	15
$Cl^- \rightarrow Cl + e^-$	3.61	15
$V \rightarrow V^+ + e^-$	6.74	10
$VF_2 \rightarrow VF_2^+ + e^-$	11.5	16
$V(s) \rightarrow V(g)$	5.34	17
$VCl_3(s) \rightarrow VCl_3(g)$	2.06	18
$VO \rightarrow V + O$	6.34	19
$VF \rightarrow V + F$	6.1	16
$VCl_2 \rightarrow V + 2Cl$	10.4	18
$V(s) + {}^1/_2O_2(g) + {}^3/_2Cl_2(g) \rightarrow VOCl_3(g)$	−6.94	14
$V(s) + {}^3/_2Cl_2(g) \rightarrow VCl_3(s)$	−6.0	20

[a] Reactants and products gaseous unless otherwise noted.

Table VIII. Ionization Potentials and Electron Affinities for Gaseous VO_mX_n Species (eV)

	X = Cl		X = F	
Neutral species	IP	EA	IP	EA
VOX_3	11.9	>3.6	13.9	3.1
VX_3	10.6	2.2	10.4	1.6
VOX_2	8.0	3.2	8.5	2.8
VX_2	10.7	1.2	11.5^a	0.4
VOX	8.9	1.4	9.2	1.2
VX	8.1		8.6	
VO	7.5		7.5	
V	6.7^b		6.7^b	

[a] Reference 16. [b] Reference 10.

for V^+ was calculated as the sum of $\Delta H_{subl}(V)$ and IP(V(g)). In the case of $VOCl^+$ the appearance potential of the $VOCl^+$-ii reaction was used in the calculations.

Heats of Formation—Neutral Fragments. Calculations similar to those above were used to evaluate the heats of formation of the neutral fragments VX_3, VOX_2, and VOX from the onset potentials of the ionization reactions producing the neutral fragments and negative ligand ions. These values are listed in columns 3 and 6 of Table VI. The remaining values in the "neutrals" columns are literature values or estimated, as noted.

Heats of Formation—Negative Ions. The heats of formation of VX_3^-, VOX_2^-, and VOX^- were calculated as above from the onset potentials of the pertinent negative ionization reactions. The values calculated are listed in columns 4 and 7 of Table VI. The values for VOX_3^- were deduced from electron affinity calculations since VOX_3^- species were not observed as primary ions. The values for VX_2^- were corrected on the basis of the calculations described later in the section on electron affinities.

The values listed in Table VI are internally consistent. For instance, the average difference in the heats of formation of the corresponding halogen-containing positive ions (column 2 minus column 5) is 1.6 eV ± 0.2 eV/halogen atom. Similarly, the average difference for neutrals (column 3 minus column 6) is 2.0 ± 0.2 eV/halogen atom and for negative ions (column 4 minus column 7) is 1.7 ± 0.2 eV/halogen atom.

In most cases the information in Table VI is not available from other sources and comparisons cannot be made. However, for VCl_3, calculations involving the heats of formation[20] and sublimation[18] of $VCl_3(s)$ yield $\Delta H_{f298}(VCl_3(g)) = -3.9$ eV. This compares favorably with the value −3.7 eV given in the table.

On the basis of the internal consistencies, comparisons, and reasonableness of the values, the accuracy of the data in Table VI is estimated to be ±0.5 eV.

Ionization Potentials. The IP's of the parent gases were discussed above. The IP's of the neutral fragments, listed in Table VIII, were calculated from the difference in the heats of formation of the neutral fragment and the corresponding positive ion fragment. The accuracies of these values are estimated to be ±0.1 eV or less for the parent gases and ±0.5 eV for the neutral fragments.

The IP's of the fluorine-containing fragments are higher than those of the corresponding chlorine-containing fragments, except for VX_3. The slightly lower IP for VF_3 compared with VCl_3 is particularly striking in view of the difference of the IP's observed for VOX_3.

Literature values which can be compared to these data are $IP(VF_3) = 10.8 \pm 0.3$ eV[16] and IP(VO) = 8 ± 1 eV,[19] which are considered to be in good agreement with the values reported here.

Electron Affinities. When the electron affinity (EA) of a species has a positive value, an experimental electron bombardment value must be determined indirectly. Three indirect methods were used to calculate the EA's listed in Table VII: observation of ion–molecule reactions, observation of complementary negative ions, and calculation of differences in heats of formation.

An illustration of the first is the estimation of EA(P). In the case of VOF_3, the IE data for VOF_3^- indicate that VOF_2^- and VF_3^- charge exchange with the parent gas to form VOF_3^-, while F^- *does not.* Therefore $EA(VOF_3)$ is greater than $EA(VOF_2)$ or $EA(VF_3)$ but less than EA(F). In the case of $VOCl_3$, the IE data indicate that $VOCl_3^-$ results from charge exchange of $VOCl_2^-$, VCl_3^-, and Cl^- with parent molecules. Therefore $EA(VOCl_3)$ is greater than $EA(VOCl_2)$, $EA(VCl_3)$, or EA(Cl). Thus we find $EA(VOF_3) = 3.1 \pm 0.4$ eV and $EA(VOCl_3) \geq 3.6$ eV.

The method of complementary ions is illustrated in the case of VCl_2 by the negative ionization reactions

$$VOCl_3 + e^- \rightarrow VCl_2^- + O + Cl \ (\Delta H = 8.48 \pm 0.09 \text{ eV}) \qquad (6)$$

$$VOCl_3 + e^- \rightarrow VCl_2 + O^- + Cl \ (\Delta H = 8.24 \pm 0.15 \text{ eV}) \qquad (7)$$

The difference of these reactions

$$VCl_2 + O^- \rightarrow VCl_2^- + O \ (\Delta H = 0.24 \pm 0.18 \text{ eV}) \qquad (8)$$

is also the difference of the two reactions defining EA(O) and $EA(VCl_2)$. Thus $EA(VCl_2)$ can be calculated

$$O^- \rightarrow O + e^- \ (\Delta H = 1.48 \text{ eV}) \qquad (9)$$

and

$$VCl_2^- \rightarrow VCl_2 + e^- \ (\Delta H = 1.48 - 0.24 = 1.24 \pm 0.18 \text{ eV}) \qquad (10)$$

This calculation assumes that the kinetic and/or electronic excitation energies of the products of reactions 6 and 7 are the same, but not necessarily negligible. This method was also used to calculate the EA's for VX_3, VOX_2, and VOX.

The final method of calculating EA's is demonstrated by

Table IX. Energy Required to Produce Ionic and Neutral Vanadium-Containing Species from Parent Molecules (eV)

	ΔH		
Reaction	+ ions	Neutrals	− ions
$VOCl_3 \rightarrow VOCl_3$	11.9	0.0	<−3.6
$\rightarrow VCl_3 + O$	16.5	5.9	3.6
$\rightarrow VOCl_2 + Cl$	13.2	5.2	2.1
$\rightarrow VCl_2 + O + Cl$	19.0	8.2	7.0
$\rightarrow VOCl + 2Cl$	16.3	7.4	6.0
$\rightarrow VCl + O + 2Cl$	22.2	14.1	
$\rightarrow VO + 3Cl$	19.8	12.3	
$\rightarrow V + O + 3Cl$	25.4	18.6	
$VOF_3 \rightarrow VOF_3$	13.9	0.0	−3.1
$\rightarrow VF_3 + O$	16.8	6.4	4.7
$\rightarrow VOF_2 + F$	15.3	6.8	4.0
$\rightarrow VF_2 + O + F$	20.8	9.3	9.0
$\rightarrow VOF + 2F$	19.9	10.8	9.6
$\rightarrow VF + O + 2F$	25.8	17.2	
$\rightarrow VO + 3F$	24.4	16.9	
$\rightarrow V + O + 3F$	30.0	23.2	

the case used for VX_2. The heat of formation of VCl_2 is reported[18] to be −2.6 eV, while that of VCl_2^- is calculated to be −2.3 eV from the onset potential of the reaction by which the negative ion is produced. The difference of these heats of formation gives EA(VCl_2) = −0.3 eV. This value disagrees with the value of 1.2 eV calculated above for reaction 10. The disagreement of 1.5 eV is explained on the basis that the onset potentials of the reactions producing VCl_2^- and O^- (reactions 6 and 7) include kinetic and/or electronic excitation energies of the reaction products. Thus the value for $\Delta H_f(VCl_2^-)$ listed in Table VI has been corrected to obtain 1.2 eV as the difference in the heats of formation of VCl_2 and VCl_2^-. It has been further assumed that this same correction is applicable to the calculation of the heat of formation of VF_2^-. The difference between the reported $\Delta H(VF_2^-)$ value of $\Delta H_f(VF_2)$ and the corrected value for $\Delta H_f(VF_2)$ gives the value of 0.4 eV for EA(VF_2) which is listed in Table VIII.

Bond Dissociation Energies. The fragmentation reactions of interest and the energies required to produce them are tabulated in Table IX in a form convenient for calculating bond dissociation energies. Bond dissociation energies can be calculated by taking appropriate differences in the listed reactions and energy values. For example, the energy required to break the oxygen bond in $VOCl_3^+$ is the difference between the energy values for the first two positive-ion reactions of the chloride set: 16.5 − 11.9 = 4.6 eV. The results of such calculations for the bond dissociation energies in the ionic and neutral fragments are given in Table X. In particular, note the low value for $D(X_2OV^+{-}X)$ compared to the other dissociation energy values for the positive ions. This explains the dominance of VOX_3^+ and VOX_2^+ in the mass spectra listed in Table I.

Comparison of the corresponding chloride and fluoride data in Table X shows that, on the average, the corresponding oxygen-bond dissociation energies in the positive and neutral species are 0.3 ± 0.6 eV *less* for the fluorides than for the chlorides. At the same time the halogen dissociation energies are 1.3 ± 0.5 eV *greater* for the fluorides than for the chlorides. This is evidence that the addition of a stronger bonding ligand may reduce the dissociation energy of the other ligands present.

Table X. Bond Dissociation Energies in VO_mX_n (eV)

	X = Cl			X = F		
	+ ions	Neutrals	− ions	+ ions	Neutrals	− ions
$X_3V{-}O$	4.6	5.9	>7.2	2.9	6.4	7.8
$X_2V{-}O$	5.8	3.0	4.8	5.5	2.5	4.9
$XV{-}O$	5.9	6.7		5.9	6.4	
$V{-}O$	5.6	6.3		5.6	6.3	
$X_2OV{-}X$	1.3	5.2	>5.7	1.4	6.8	7.1
$X_2V{-}X$	2.5	2.3	3.3	4.0	2.9	4.2
$XOV{-}X$	3.1	2.2	3.9	4.6	4.0	5.6
$XV{-}X$	3.2	5.9		5.0	7.9	
$OV{-}X$	3.5	4.9		4.5	6.1	
$V{-}X$	3.2	4.5		4.2	6.0	

Table XI. Estimates of Bond Energies in VO_mX_n Positive and Neutral Fragments (eV)

	X = Cl			X = F		
Atomization reaction	ΔH	ΔH per O	ΔH per Cl	ΔH	ΔH per O	ΔH per F
$VOX_3^+ \rightarrow V^+ + O + 3X$	13.5	5.5	2.7	16.1	5.0	3.7
$VX_3^+ \rightarrow V^+ + 3X$	8.9		3.0	13.2		4.4
$VOX_2^+ \rightarrow V^+ + O + 2X$	12.2	5.8	3.2	14.7	5.7	4.5
$VX_2^+ \rightarrow V^+ + 2X$	6.4		3.2	9.2		4.6
$VOX^+ \rightarrow V^+ + O + X$	9.1	5.8	3.3	10.1	5.8	4.3
$VX^+ \rightarrow V^+ + X$	3.2		3.2	4.2		4.2
$VO^+ \rightarrow V^+ + O$	5.6	5.6		5.6	5.6	
Average		5.7 ± 0.1	3.1 ± 0.2		5.5 ± 0.4	4.3 ± 0.3
$VOX_3 \rightarrow V + O + 3X$	18.6	5.5	4.4	23.2	5.9	5.8
$VX_3 \rightarrow V + 3X$	12.7		4.2	16.8		5.6
$VOX_2 \rightarrow V + O + 2X$	13.4	5.3	4.0	16.4	5.1	5.7
$VX_2 \rightarrow V + 2X$	10.4		5.2	13.7		6.8
$VOX \rightarrow V + O + X$	11.2	6.5	4.7	12.4	6.4	6.0
$VX \rightarrow V + X$	4.6		4.5	6.0		6.0
$VO \rightarrow V + O$	6.4	6.4		6.3	6.3	
Average		5.9 ± 0.6	4.5 ± 0.4		5.9 ± 0.6	6.0 ± 0.4

Bond Energies. Since there are insufficient negative-ion data, bond energies were calculated only for the various positive and neutral fragments. The case for $VOCl_3^+$ serves as an example of the manner in which these calculations were made. The four different stepwise paths by which the ligands could be removed were considered equally probable. The dissociation energy for each stepwise loss was taken from Table X. The value for the vanadium–oxygen dissociation in each path was weighted equally and averaged to obtain 5.5 eV. The remaining energy of atomization, 8.0 eV, was considered to be equally divided among the three chlorine bonds. Thus the values obtained for the V–O and V–Cl bond energies in $VOCl_3^+$ are 5.5 and 2.7 eV, respectively. Similar calculations were made for the other positive and neutral fragments VO_mX_n. The results are presented in Table XI. Examination of these results shows that the V–O bond energy is affected only slightly by the number or choice of halogens or the presence of the positive charge. The bond energy of V–X decreases appreciably when the fragment is positively charged. The bond energy of V–F is greater than that of V–Cl and both values follow the trend of the data reported by Ngai and Stafford.[5]

Summary

Mass spectra, ionization potentials, and appearance potentials have been obtained for the positive and negative ions produced by electron bombardment of $VOCl_3$ and VOF_3. The use of these data to obtain ionization potentials, electron affinities, heats of formation, and dissociation energies for neutral and ionic fragments has been demonstrated.

Registry No. $VOCl_3$, 7727-18-6; VOF_3, 13709-31-4.

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Acid Properties of the Oxytetrafluorides of Molybdenum, Tungsten, and Uranium toward Some Inorganic Fluoride Ion Donors

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Received March 13, 1974

AIC40173B

The behavior of $MoOF_4$, WOF_4, and UOF_4 has been studied in the presence of ion donors of various strength: FNO, $ClOF_3$, ClF_3, ClF_5, and HF. For both $MoOF_4$ and WOF_4 in HF solutions, evidence for a partial ionization into $Mo_2O_2F_9^-$ and $W_2O_2F_9^-$ has been shown. From the equilibrium constant values, WOF_4 is found to be a stronger Lewis acid than $MoOF_4$, whereas no direct comparison with the strength of UOF_4 is possible because of its quasiinsolubility in HF. Lewis acid properties of the oxytetrafluorides studied are also demonstrated by the ionic structures found for the adducts with the strong bases FNO and $ClOF_3$. The new adducts $NOMo_2O_2F_9$, $NOW_2O_2F_9$, $ClOF_2Mo_2O_2F_9$, $ClOF_2MoOF_5$, $(NO)_2MoOF_6$, and $(NO)_2WOF_6$ were prepared. Their vibrational spectra and, for some of them, X-ray powder diffraction patterns are given. The unit cell parameters of the adducts $NOMoOF_5$, $NOWOF_5$, and $(NO)_2WOF_6$ have been determined. A study of the HF solutions of the nitrosyl salts has been made by Raman and ^{19}F NMR spectroscopy. This, together with data on propylene carbonate solutions of the same adducts, allowed the identification of the species in the oxytetrafluoride–FNO–HF system. Depending on the F^- concentration the anions $M_2O_2F_9^-$, MOF_5^-, and MOF_6^{2-} (M = Mo or W) are formed, which are in equilibrium with the solvent. The mechanisms of these equilibria are proposed. The results obtained with the F^- donor fluorinating agents indicate that ionic intermediary steps occur in the fluorination process of the oxytetrafluorides to the corresponding hexafluorides.

Introduction

Ionic complexes containing oxypentafluoromolybdate(VI) or oxypentafluorotungstate(VI) anions have already been reported through reactions between organic bases,[1-3] N_2O_4,[4] or alkali fluorides in the presence of moisture or SO_2[5,6] and the corresponding hexafluorides.

Reaction between NF_3 and WO_3[7] is reported to give $NOWOF_5$ while reaction between KF, WO_3, and SeF_4 gives $KWOF_5$.[8] $NaWOF_5$ has been obtained from reaction between tungsten hexacarbonyl and moist sodium iodide in the presence of IF_5.[6] Reactions between $MoOF_4$ or WOF_4 and organic bases[9-11] give solutions from which structural information on the present species has been obtained by NMR spectroscopy. As no systematic study regarding the behavior of the oxytetrafluorides of molybdenum, tungsten, and uranium toward inorganic fluoride donors has yet been reported, it was interesting to try to rationalize their fluoride acceptor ability. The use of fluoride donors of various strength should allow knowledge of the fluorination step expected to take place with some of them.

Experimental Section

Materials and Apparatus. Nonvolatile solid samples were transferred in a dry glove box and volatile materials were manipulated in a vacuum line. This line is made, for its most part, of Monel metal tubing equipped with valves purchased from F.W. Co. and with differential gauges from "Etudes et Constructions Aéronautiques". To allow observation, part of the apparatus is equipped with Kel-F tubes and Kel-F valves purchased from Viennot Co. Before working, the vacuum line was passivated with ClF_3 and the compound to be handled. The starting materials MoF_6, WF_6, UF_6, HF, F_2, ClF_3, and ClF_5, were purchased from "Societé des Usines Chimiques de Pierrelatte". NO was obtained from "Air Liquide" and HNO_3 from "Prolabo". UOF_4 was prepared by hydrolysis of UF_6 in HF according to the process described by Wilson.[12] $MoOF_4$ and WOF_4 were prepared by reaction of fluorine with the corresponding trioxides at 300°. FNO was obtained by reaction between F_2 and NO at −196° and $ClOF_3$ was prepared by the process of Pilipovich et al.[13]

Prior to use, the volatile fluorides were purified by fractional condensation, and all compounds were checked for purity by Raman and infrared spectroscopy, powder X-ray diffraction patterns, and microsublimation, whenever the physical state of the sample allowed these methods to be used. Propylene carbonate and acetonitrile used as solvents were purchased in their purest grade from Koch-Light Laboratories and Prolabo, respectively. Prior to use they were stored over 5-A molecular sieves from Union Carbide International Co.

Spectra. Infrared spectra were recorded with a Beckman Model IR 9. Spectra of gases were recorded using a 10 cm long Monel-body gas cell equipped with AgCl windows sealed with Teflon gaskets. Powders were pressed between two thin plates of AgCl.

Raman spectra were recorded with a Coderg Model T 800 using as exciting light the 514.5-nm line of a Model 165 Spectra Physics laser. The samples were handled in 4-mm o.d. Kel-F or FEP Teflon tubing (from Viennot and Penntube Plastics, respectively), attached to a Kel-F valve. X-Ray diffraction powder patterns were taken using a 114-mm diameter Philips camera with copper Kα radiation (0.15418 nm). The samples were loaded in the dry nitrogen atmosphere of the glove box into quartz capillaries (~0.5 mm).

^{19}F NMR spectra were recorded at 56.4 MHz using a Varian NV 14 spectrometer equipped with a variable-temperature probe. As external reference $CFCl_3$ was used and the spectrometer was locked on this resonance. Double-resonance experiments were carried out by irradiating the fluorine atoms of the HF or ClF_3 solvent with increasing field intensity while the fluorine signal due to the dissolved species was being observed. These experiments readily show up even slow chemical exchanges.[14]