Gas-Phase Chemistry of Vanadium Oxide Cluster Cations. 2. Reactions with CH_2F_2

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Reactions comprised of oxygen transfer in conjunction with the abstraction of two fluorine atoms from difluoromethane are observed in the gas-phase chemistry of various selected vanadium oxide cluster ions. These studies were performed on a triple quadrupole mass spectrometer coupled with a laser vaporization source. Aside from the oxygen transfer reactions, channels for the loss of molecular oxygen and the association of CH_2F_2 to the clusters were also observed. For example, the cluster $V_3O_7^+$ reacted with CH_2F_2 to produce $V_3O_6F_2^+$ in addition to the association product $V_3O_7{\cdot}CH_2F_2^+$ with both channels occurring under single collision conditions and near thermal energies at ambient temperature. The vanadium oxide species $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{8-11}^+$, $V_5O_{11-13}^+$, $V_6O_{13-15}^+$, and $V_7O_{16-18}^+$ were individually selected and their reactivities compared by examining the relative product branching ratios. The reactivity of the $V_xO_y^+$ species with difluoromethane displayed a distinct dependence on the size of the clusters. The smaller clusters were most reactive while the larger clusters were observed to be inert toward reaction with difluoromethane with the exception of the oxygen-rich clusters, which simply lost molecular oxygen upon collision with the reactant gas.

Introduction

It is now widely accepted that chlorofluorocarbons contribute to the "greenhouse effect" and are also responsible for stratospheric ozone depletion via the formation of chlorine radicals.[1] For these reasons, intense efforts are being made in the search for new compounds to replace existing chlorofluorocarbons, which have been used extensively over the years. Until effective alternatives to replace organohalogen compounds become available, industry has shifted its production of chlorofluorocarbons to hydrochlorofluorocarbons and hydrofluorocarbons.[2] These compounds degrade at lower altitudes via reaction with hydroxyl radicals in the troposphere, thus, considerably reducing the potential for them to significantly contribute to ozone depletion. Fluorocarbons have become important constituents in the chemical, pharmaceutical, and advanced materials industries due to the low reactivity and high thermal stability of the carbon−fluorine bonds of the materials formed.[3] As the importance of these compounds is being realized, the field of fluoroorganic chemistry continues to grow,[4] becoming one of the most important areas in organic chemistry today.

Gas-phase studies concerning the interaction between metal-containing species and halogen-containing organic molecules have primarily dealt with bare metal ions and ligated monomeric metal ions. Eller and Schwarz[5] have presented an excellent review of these gas-phase reactions. Recent studies of vanadium oxide cluster cations with C_2F_6 and CH_3CF_3 have been reported by our group.[6] It was found that the vanadium oxide cluster cations studied were inert toward reaction with C_2F_6 except for the clusters $V_2O_{4-6}^+$ that displayed molecular addition products. However, the presence of hydrogen on the adjacent carbon allowed for HF elimination to occur for the reactions of the $V_xO_y^+$ clusters with CH_3CF_3. In addition, unique reactions were observed for the oxygen-rich species $V_xO_y(O_2)^+$ which displayed a channel for the abstraction of two fluorine atoms with the transfer of an oxygen atom to the neutral species accompanied by loss of O_2 from the cluster to form $V_xO_{y-1}F_2^+$. The present study concerns the reactions of difluoromethane (CH_2F_2) with the same selected vanadium oxide cations. Unlike the reactions with CH_3CF_3, dehydrohalogenation was not observed for CH_2F_2. The dominant channel for reaction was that of oxygen transfer in conjunction with the abstraction of two fluorine atoms from difluoromethane.

Experimental Section

The apparatus used for this work is a triple quadrupole mass spectrometer coupled with a laser vaporization source; the details of its operation have been described previously.[7−9] Briefly, a translating, rotating rod is ablated by the second harmonic of a 20 Hz Nd:YAG laser. A 5−10% mixture of O_2 seeded in a helium buffer gas is injected into the laser created metal plasma through a pulsed valve. As the plasma expands, multiple collisions occur between the walls of the source and between other atoms, leading to the formation and cooling of the clusters as they proceed through the nozzle. Thereafter, the clusters are further cooled as they undergo supersonic expansion upon exiting the laser vaporization source and entering the first differentially pumped chamber. The cluster ions enter the second chamber through a 3 mm skimmer, which houses the triple quadrupole mass spectrometer. A set of electrostatic lenses focuses the ion beam as they enter the first quadrupole where a cluster of a particular mass is selected. The selected ion is then focused by a second set of lenses into the second quadrupole. Operated in the RF-only mode, this quadrupole acts as a collision or reaction chamber with pressures ranging from 0.03 to 1.0 mTorr, as monitored by a capacitance manometer, and maintained at ambient temperature. To ensure that reactions take place at or near thermal energies, the translational energy is kept to a minimum by applying a ground potential to the entrance plate of the collision cell in order to introduce only thermal ions into the reaction region. The products are guided by a third set of lenses as they exit the second quadrupole for mass analysis. This is accomplished via a third quadrupole

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affixed with a dynode channeltron electron multiplier. The signal is then analyzed using a PC with a multiscalar card.

Results

The reactions of difluoromethane with the selected clusters $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{8-11}^+$, $V_5O_{11-13}^+$, $V_6O_{13-15}^+$, and $V_7O_{16-18}^+$ were studied, and product branching ratios were obtained for pertinent clusters. All reactions were studied under similar reaction conditions near thermal energies. Vanadium oxide cluster ions of the same series, that is each cluster in a series has the same number of vanadium atoms but differing numbers of oxygen atoms, displayed different reaction pathways with CH_2F_2. In addition, the degree of reactivity was observed to diminish significantly from the reactive smaller series to the observed inertness of the larger series.

Under single collisions conditions, the clusters $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_9^+$, and $V_5O_{12}^+$ all displayed a channel for the transfer of a single oxygen atom to the neutral reactant, along with the abstraction of two fluorine atoms to form the cation $V_xO_{y-1}F_2^+$. At higher pressures and hence under multiple reaction conditions, the clusters $V_2O_4^+$ and $V_3O_7^+$ were able to undergo a second oxygen transfer reaction, accompanied by dual fluorine abstraction forming the products $V_2O_2F_4^+$ and $V_3O_5F_4^+$, respectively. The clusters $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_{8,9}^+$, and $V_5O_{11,12}^+$ also displayed channels for the association of difluoromethane leading to the formation of $V_xO_y{\cdot}CH_2F_2^+$ under both single and multiple collision conditions. Representative spectra displaying the reaction of $V_3O_6^+$ and $V_3O_7^+$ at 0.30 mTorr, multiple collision conditions, are shown in Figure 1a,b, respectively. The cluster $V_2O_4^+$ also displayed a minor channel for the association of difluoromethane to the first reaction product, $V_2O_3F_2^+$, under multiple collision conditions to form $V_2O_3F_2{\cdot}CH_2F_2^+$. The reactions of the $V_xO_y^+$ clusters with difluoromethane display a dependence on the size of the cluster. The reactivity diminishes as the size of the clusters increases until the larger clusters, $V_6O_{13,14}^+$ and $V_7O_{16,17}^+$, which are observed to be inert toward reaction with difluoromethane. This dependence can be seen in the relative branching ratios for the reaction of $V_xO_y^+$ clusters with CH_2F_2, which are shown in Figures 2−5.

With the exception of $V_2O_5^+$, which lost only a single oxygen atom, all the other oxygen-rich clusters $V_2O_{5,6}^+$, $V_3O_8^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ displayed the loss of molecular oxygen to form the product $V_xO_{y-2}^+$ at both single and multiple collision conditions. The oxygen-rich clusters are considered to be the smaller, more stable parent clusters with molecular oxygen adsorbed to the surface of the cluster, which can be represented as $V_xO_y(O_2)_n^+$, where $V_xO_y^+$ is the parent cluster.[10] Similar results for the loss of O_2 from the oxygen-rich cluster ions have been observed for laser heating experiments performed on these species.[11] These findings provide further evidence for the oxygen-rich species containing weakly adsorbed oxygen molecules on the surface of the smaller clusters. Products representing the association of CH_2F_2 with the loss of O_2 were also observed for the clusters $V_2O_6^+$, $V_3O_8^+$, and $V_4O_{10,11}^+$ under both single and multiple collision conditions. By contrast, the larger oxygen-rich clusters $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ did not associate CH_2F_2 upon loss of O_2. The clusters $V_2O_{5,6}^+$, $V_3O_8^+$, and $V_5O_{13}^+$ also displayed a reaction pathway for the association of difluoromethane without the loss of O_2 for both single and multiple collision conditions. The smaller oxygen-rich clusters $V_2O_6^+$ and $V_3O_8^+$ also reacted to form the products observed for the parent clusters of these species, $V_2O_4^+$ and $V_3O_6^+$, respectively, accompanied by the loss of molecular oxygen under single collision conditions. For example, $V_3O_8^+$ reacts to form the products $V_3O_5F_2^+$ and $V_3O_6{\cdot}CH_2F_2^+$, in addition to the products already mentioned. Figure 1c displays the spectra for the reaction of $V_3O_8^+$ with 0.30 mTorr CH_2F_2 near thermal energies. The cluster $V_2O_5^+$ is unique in the fact that it is the only cluster able to lose a single oxygen atom. Channels for oxygen transfer with the abstraction of two fluorine atoms are also observed for $V_2O_5^+$ forming the products $V_2O_3F_2^+$ and $V_2O_4F_2^+$ under single collisions and near

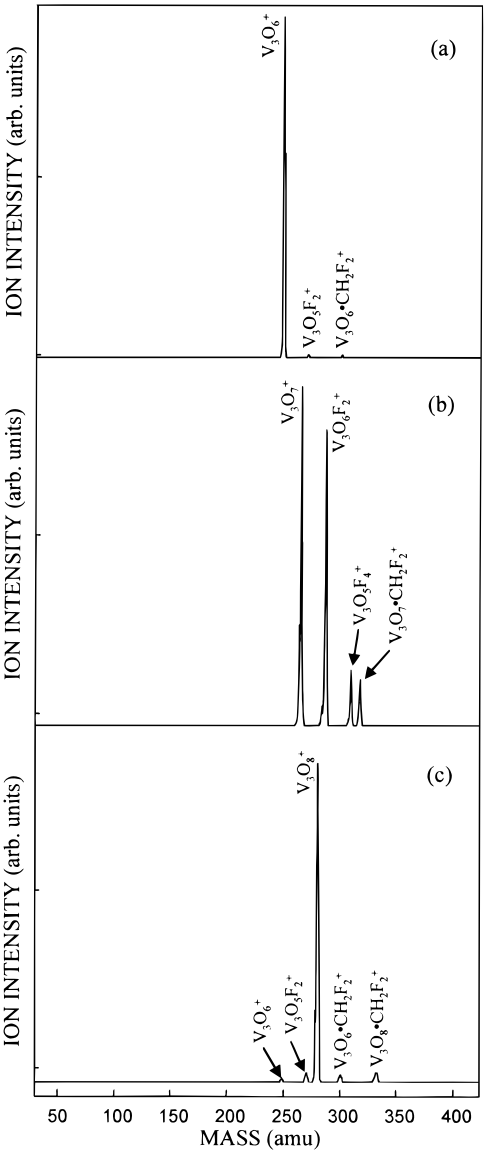

Figure 1. Spectra for the reaction of CH_2F_2 with the clusters $V_3O_{6-8}^+$ near thermal conditions at a reactant pressure of 0.30 mTorr. (a) The spectrum for $V_3O_6^+$ displays a channel corresponding to the transfer of a single oxygen atom and uptake of two fluorine atoms, along with one leading to an association product. (b) The reaction of $V_3O_7^+$ displays the loss of a single oxygen and uptake of two fluorine atoms, which occurs under single-collision conditions. Under multiple collision conditions, as shown here, the reaction of this first product with a second CH_2F_2 results in the abstraction of two more fluorine atoms and transfer of another oxygen atom to the neutral reactant molecule. A less intense peak corresponding to the association of difluoromethane is observed as well. (c) Spectra for the reaction of the oxygen-rich cluster $V_3O_8^+$ with difluoromethane shows several reaction pathways. The association of CH_2F_2, the loss of molecular oxygen, association accompanied by the loss of O_2, and a product representing the oxygen transfer with fluorine abstraction channel with the loss of O_2 are all observed.

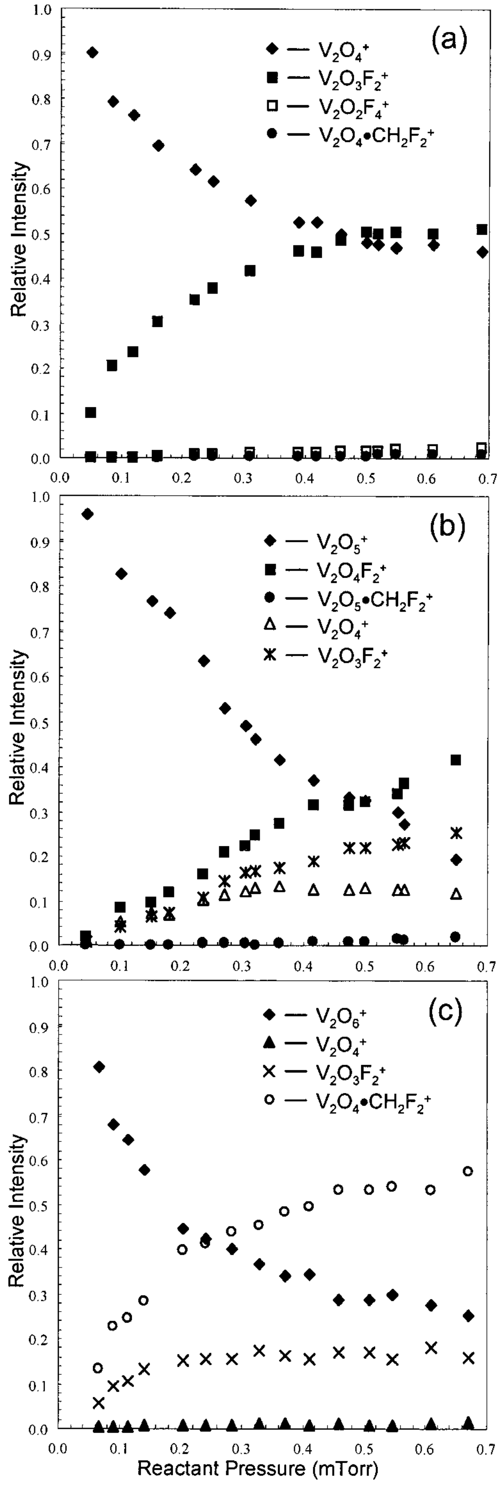

Figure 2. Plots for the relative product branching ratios for the reaction of (a) $V_2O_4^+$, (b) $V_2O_5^+$, and (c) $V_2O_6^+$ with CH_2F_2 near thermal conditions.

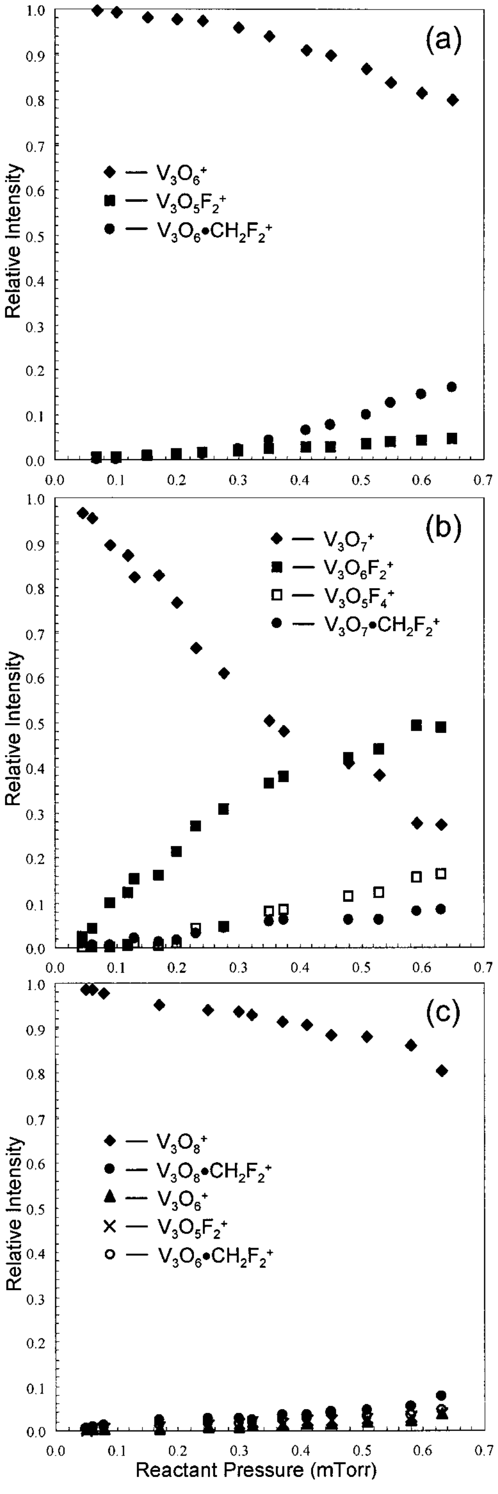

Figure 3. Plots for the relative product branching ratios for the reaction of difluoromethane with the clusters (a) $V_3O_6^+$, (b) $V_3O_7^+$, and (c) $V_3O_8^+$ near thermal conditions.

thermal energies. A complete summary of the reaction products for all the selected cluster ions is shown in Table 1.

Discussion

Vanadium oxide based catalysts in the bulk phase are used extensively for the conversion of SO_2 to SO_3, as well as the heterogeneous oxidation of aromatic and C_4H_n hydrocarbons.[12,13] As for gas-phase reactions, the ability of the vanadium oxide cluster cations to transfer oxygen to the neutral reactant gases has been demonstrated for both carbon tetrachloride[14] and 1,3-butadiene.[10] The reactions of the stoichiometric vanadium oxide cations with CH_3CF_3 displayed a dominant channel for the process of dehydrohalogenation.[6] This reaction is attributed to the formation of an additional interaction between an oxygen atom from the cluster and a hydrogen atom from the adjacent carbon of the C−F bond to be cleaved. The initially weak hydrogen bond may form a strong covalent O−H bond in concert with the breaking of the C−F bond, releasing the neutral $H_2C{=}CF_2$. Therefore, the loss of HF from the neutral reactant

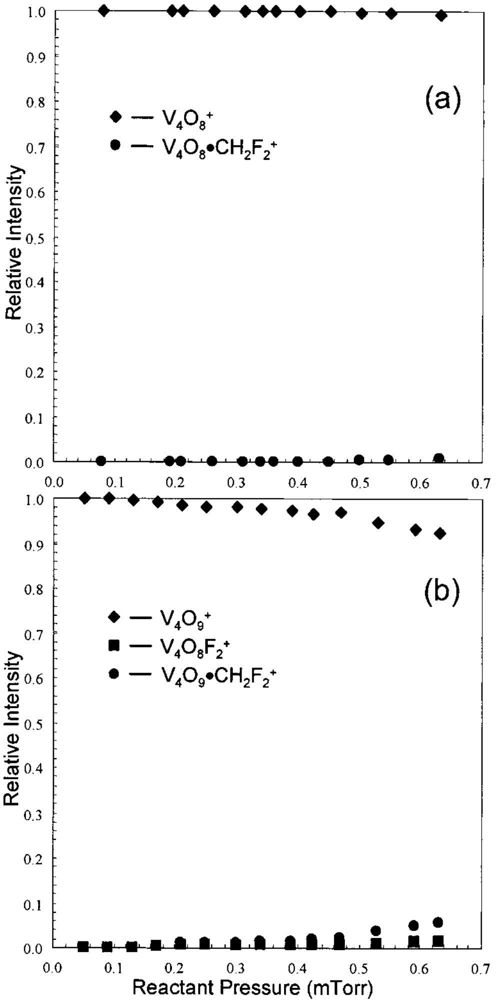

Figure 4. Plots of the relative product branching ratios for the reaction of (a) $V_4O_8^+$ and (b) $V_4O_9^+$ with CH_2F_2 near thermal conditions.

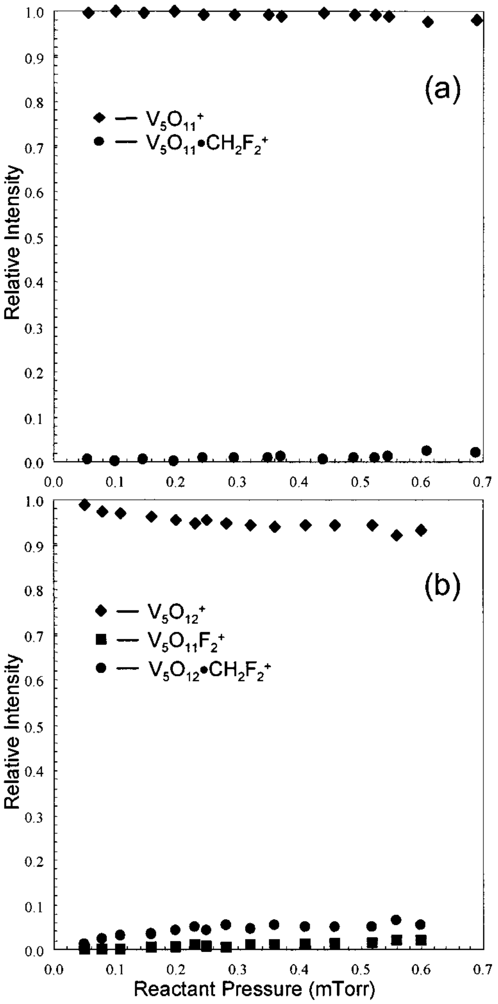

Figure 5. Plots for the relative product branching ratios for the near thermal reactions of difluoromethane with the clusters (a) $V_5O_{11}^+$ and (b) $V_5O_{12}^+$.

occurs through a 1,2-elimination process. It was postulated that the initial interaction between hydrogen and oxygen acts to lower the energy of activation for the cleavage of the C−F bond. From a thermodynamic point of view, the strength of the C−F bond ($D°(CH_3CF_2{-}F) = 124.8 \pm 2$ kcal mol^{-1})[15] in CH_3CF_3 is not substantially different than that of difluoromethane ($D°(F{-}CH_2F) = 122 \pm 1$ kcal mol^{-1})[16] suggesting the mechanisms of these reactions are different with the HF elimination channel having a lower reaction barrier than that for oxygen-transfer with dual fluorine abstraction.

In similar studies performed by Schwarz and co-workers, it was shown that PrO^+ did not activate trifluoromethane, while reactions with 1,1-difluoroethane demonstrated a channel for dehydrohalogenation.[17] This reaction presumably occurs through a 1,2 elimination of HF, since PrO^+ does not activate the 1,1 elimination of HF from trifluoromethane. Reaction of these species with Pr^+ demonstrated fluorine abstraction channels with no HF abstraction observed.[17] Similar to the case of PrO^+ with trifluoromethane, the reactions of the $V_xO_y^+$ clusters with CH_2F_2 did not demonstrate a reaction channel for the dehydrohalogenation process. Instead, the vanadium oxide cation transferred an oxygen atom to the neutral species with the abstraction of two fluorine atoms onto the cluster forming formaldehyde (H_2CO). It is possible that molecular hydrogen and carbon monoxide is formed during the reaction. However, reactions of the vanadium oxide cluster cations with CCl_4 demonstrate the same reaction channel for oxygen transfer with dual chlorine abstraction[14] and is believed to follow the same mechanism for the degradation of carbon tetrachloride on the bulk vanadium oxide surface to form phosgene and carbon dioxide.[18]

The reactions of the $V_xO_y^+$ clusters with difluoromethane display a strong dependence on the size of the cluster with the smaller clusters being more reactive than the larger ones. There are several possible factors such as internal cluster temperature, ionization potentials, charge densities, and oxidation states of the vanadium sites that warrant consideration in accounting for the observed variation in reactivity with respect to cluster size. First, the smaller clusters might be considered as being more energetic than the larger clusters. Factors that potentially could influence the energy of the clusters are the lens and quadrupole potentials, fluence of the ablation laser, or inefficient cooling during cluster formation and supersonic expansion. However, the bias of the first quadrupole and the lens voltages are changed by no more then a few volts during the course of these experiments over the range of cluster sizes investigated. Moreover, the clusters are generated at a ground potential with the entrance lens to the second quadrupole at ground potential, and no other potentials are added to the RF-only quadrupole during the course of these experiments.

Considering the laser fluence in cluster production, there may exist the possibility of inefficient cooling of the clusters due to the high laser fluence required to ablate the metal rod. But, if this were true, it would be thought that the power of the ablation

TABLE 1: Reaction of Vanadium Oxide Cluster Cations $V_{2-7}O_y^+$ with CH_2F_2 near Thermal Energies and a Reactant Pressure of 0.25 mTorr

selected cluster $V_xO_y^+$: x, y	product ions for reactant gas difluoromethane (CH_2F_2)	selected cluster $V_xO_y^+$: x, y	product ions for reactant gas difluoromethane (CH_2F_2)
2,4	$V_2O_3F_2$	4,9	$V_4O_8F_2$
	$V_2O_2F_4$ a		$V_4O_9{\cdot}CH_2F_2$
	$V_2O_4{\cdot}CH_2F_2$	4,10	V_4O_8
	$V_2O_3F_2{\cdot}CH_2F_2$[a,b]		$V_4O_8{\cdot}CH_2F_2$
2,5	V_2O_4		
	$V_2O_3F_2$	4,11	V_4O_9
	$V_2O_4F_2$		$V_4O_9{\cdot}CH_2F_2$
	$V_2O_5{\cdot}CH_2F_2$		
2,6	V_2O_4	5,11	$V_5O_{11}{\cdot}CH_2F_2$
	$V_2O_3F_2$		
	$V_2O_4{\cdot}CH_2F_2$	5,12	$V_5O_{11}F_2$
	$V_2O_3F_2{\cdot}CH_2F_2$[a,b]		$V_5O_{12}{\cdot}CH_2F_2$
	$V_2O_6{\cdot}CH_2F_2$ [b]	5,13	V_5O_{11}
			$V_5O_{13}{\cdot}CH_2F_2$
3,6	$V_3O_5F_2$		
	$V_3O_6{\cdot}CH_2F_2$	6,13	no reacn
3,7	$V_3O_6F_2$		
	$V_3O_5F_4$[a]	6,14	no reacn
	$V_3O_7{\cdot}CH_2F_2$		
		6,15	V_6O_{13}
3,8	V_3O_6		
	$V_3O_5F_2$		
	$V_3O_6{\cdot}CH_2F_2$	7,16	no reacn
	$V_3O_8{\cdot}CH_2F_2$	7,17	no reacn
4,8	$V_4O_8{\cdot}CH_2F_2$	7,18	V_7O_{16}

[a] These reaction channels are observed under multiple collision conditions near thermal energies. [b] These reaction pathways represent less than 1% of the total reaction products and are not displayed in their respective relative product branching ratios.

laser would influence the reactivity of these clusters. However, upon the changing of the laser power in the usable range for cluster formation of 10−75 mJ/pulse (up to the highest output of our system), the relative branching ratios were not affected for the clusters $V_2O_4^+$ and $V_3O_7^+$. A plot for the relative branching ratio of $V_2O_4^+$ and the dominant product $V_2O_3F_2^+$ at 0.09 mTorr versus laser power is shown in Figure 6. Clearly the range of laser powers with which these clusters are generated does not affect the reactivity of the clusters. However, this does not exclusively rule out the possibility that the fluence of the laser might give rise to limited affects on the reactivity. A related possibility is that the smaller clusters are not as efficiently cooled during the formation process. Although direct measurements of the internal energy are not conducted, several observations imply that this factor does not significantly influence the course of the reactions studied. Under similar experimental conditions, such as laser fluence, backing pressure, and reactant concentration, clusters with sizes throughout the range studied have been observed to exit the source with attached N_2 and CH_4.[9] The presence of these weakly bound ligands is evidence that the cluster temperatures are quite low.

The differences in the structure, charge densities, and ionization potentials may also influence the reactivity of the $V_xO_y^+$ clusters. That is, the charge may be more localized on a particular vanadium atom for the smaller clusters but may be delocalized onto several vanadium atoms for the larger clusters leading to species of mixed valence. With the charge concentrated in one particular area of the cluster, the reactivity may be enhanced due to the mechanism for the reaction of CH_2F_2 with the vanadium oxide cluster ions. It is proposed that this reaction is initiated by the formation of an ionic bond between the fluorine atoms and a metal center. Pauling has suggested resonance structures with double bond and nonbond character to account for the bond shortenings of the fluoromethanes.[19] These resonance structures are shown in Figure 7. This valance bond description is supported by ab initio calculations (4-31G).[20,21] Here it is proposed that, with difluoromethane in the type-B structure, the fluorine begins to form an ionic bond with the more electropositive vanadium center. This would invoke the carbon of the difluoromethane molecule to become more susceptible to attacking the oxygen of the cluster, with subsequent abstraction of the second fluorine atom. The initial formation of the fluorine−vanadium bond would weaken the oxygen−vanadium bond, allowing the oxygen transfer process to occur.

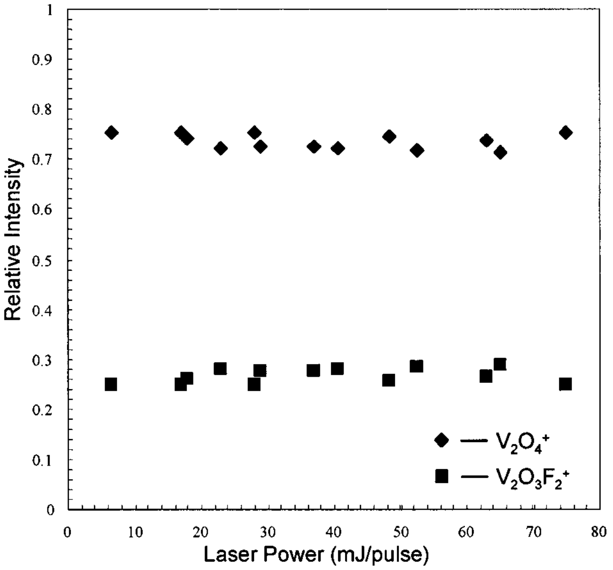

Figure 6. Partial relative product branching ratio for the cluster $V_2O_4^+$ and the product $V_2O_3F_2^+$ at a reactant pressure of 0.09 mTorr versus laser power displaying the independence of the reactivity of the cluster on the power of the ablation laser.

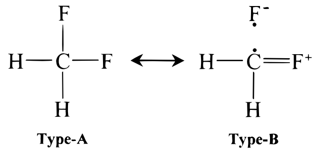

Figure 7. Resonance structures for difluoromethane showing the π-type donation of a lone pair of electrons from fluorine to a C−F σ-bond.

Therefore, the size-dependent nature of these reactions may depend on the structure of the clusters and the resulting differences in charge densities of the vanadium sites. The charge could be dispersed over the entire cluster or may be more localized at a particular metal site. If the charge is delocalized, the smaller clusters must concentrate the charge onto fewer vanadium atoms, which is a possible reason for the enhanced reactivity of the $V_2O_y^+$ series and a contributing factor to the size-dependent nature of these reactions. However, if the charge is localized, the charge center of the larger clusters may not be as accessible to the neutral reactant molecule due to branching of the cluster. That is, the charge center of the larger clusters might be located in the center with the other vanadium atoms surrounding it via bridging oxygen atoms. Therefore, this higher degree of coordination may act to block the reactive site of the cluster from the neutral reactant. In terms of the Langevin reaction cross section consideration, it is unlikely that the incoming molecule experiences any differences until it has formed the ion−molecule complex.

In addition, the ionization potentials (IP) of the clusters may also play a role in the observed differences in reactivity of the $V_xO_y^+$ species. The ionization threshold energies for bare vanadium clusters decrease with increasing cluster size. The smallest vanadium clusters have the highest photoionization threshold of 6.74, 6.10, 5.49, 5.63, and 5.47 eV for V_2-V_5, respectively, which continue in this same downward trend beginning to level off ~5 eV at V_{11}.[22] The vanadium oxide clusters may display a similar trend in the ionization potentials, which may influence their reactions in a size-dependent manner. As the number of vanadium atoms in the cluster increases, the IP would be expected to drop. However, the presence of oxygen is expected to increase the ionization potentials of the clusters. Using collision-induced dissociation (CID) results,[10] relative IP's were determined by examining the CID products to determine which fragment retained the charge.[23] It is considered that the fragment that retains the charge has a lower IP than the neutral fragment, assuming that the neutral fragment is intact. These results indicate that there is a trend toward higher IP's for clusters with increased oxygen-to-metal ratios. The larger clusters have a higher oxygen-to-metal ratio[10] and therefore should possess higher IP's. This same trend was observed for the IP's of niobium oxide cluster ions determined from similar CID studies.[24]

Many bare metal clusters have been found to display a dependence on reactivity with cluster size that is partially related to the difference in IP's. The reactions of both bare niobium[25-27] and vanadium[28] clusters to partially or completely dehydrogenate benzene display an anticorelation between cluster IP and benzene conversion probability and a correlation between the rate of activated D_2 chemisorption and the benzene conversion probability.[26,28] That is, an increase in the conversion probability of benzene is observed as the IP's of the clusters decreased. To consider the trend between the ionization potentials of the $V_xO_y^+$ clusters and the reactivity with CH_2F_2, we limit such influences as oxidation states of the vanadium atoms within the clusters by focusing on the clusters that contain V^{5+} exclusively, i.e., $V_3O_7^+$, $V_5O_{12}^+$, and $V_7O_{17}^+$. The reactivity of these clusters decreased until the observed inertness of the cluster $V_7O_{17}^+$ toward reaction with C_4H_8 and C_4H_6[10,23] under the same experimental conditions employed in this study. This same trend was observed for the reactions of difluoromethane, which suggests that the IP could be a contributing factor to the reactivity of these clusters.

Finally, the oxidation states of the vanadium sites in conjunction with the charge densities and IP's of the cluster apparently influence the reactivity of the $V_xO_y^+$ clusters. That is, the oxygen transfer with dual fluorine abstraction is observed to occur most readily for clusters with vanadium atoms in higher oxidation states. If charge density and cluster IP were the only determining factors, then clusters within the same series but with differing numbers of oxygen atoms should display a greater reactivity for the less oxygenated species. However, this is not the case. For example, in a comparison of the $V_3O_y^+$ series, the cluster $V_3O_6^+$ would be expected to display a greater reactivity toward this reaction channel. However, by examination of the branching ratios in Figure 3, the cluster $V_3O_7^+$ is much more reactive and is even able to transfer a second oxygen and abstract two more fluorine atoms onto the cluster under multiple collision conditions. This same trend is seen for the $V_4O_y^+$ and $V_5O_y^+$ series as well. This indicates that the oxidation states of the metal sites also play an important role for these reactions.

Previous studies performed on vanadium oxide cluster cations showed that the oxygen-rich clusters, $V_2O_{5,6}^+$, $V_3O_{8,9}^+$, $V_4O_{10}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$, displayed a prominent reaction channel involving the loss of O_2 upon collision with the neutral reactant species.[6,10,14] The loss of O_2 occurred for both collision-induced dissociation (CID) reactions and during reactions with neutral hydrocarbon species, which was also attributed to a CID process.[10] Both processes occurred under single-collision conditions near thermal energies. It is postulated that molecular oxygen is weakly adsorbed onto the smaller, more stable clusters of the series. For example, the cluster $V_2O_6^+$ is thought to be $V_2O_4^+$ with molecular oxygen adsorbed to the surface forming $V_2O_4(O_2)^+$. The only cluster for which there is an apparent exception is that of $V_2O_5^+$. This cluster was able to lose both a single oxygen atom at ~1 eV and molecular oxygen at ~2 eV center-of-mass frame of reference with the single oxygen loss being the dominant dissociation channel.[10] In addition, it is postulated that the adsorbed oxygen alters both the geometric and electronic structure of the parent cluster.[6]

In a similar fashion, the present study reveals that the oxygen-rich clusters $V_2O_6^+$, $V_3O_8^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ all lose O_2 under single-collision conditions near thermal energies upon interaction with difluoromethane, which is attributed to a CID process. However, in contrast to the case with CH_3CF_3, the cluster $V_2O_5^+$ does not lose O_2 during reaction with CH_2F_2 but instead loses only a single oxygen atom. Association of CH_2F_2 without the loss of molecular oxygen was observed for most of the oxygen-rich cluster ions. The only exceptions are the clusters $V_4O_{10,11}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$. The same type of association channels were observed for the oxygen-rich clusters when reacted with *n*-butane, 1-butene, and 1,3-butadiene.[10] It was also observed for the reaction of C_2F_6 with $V_2O_{4-6}^+$ but for no other clusters, and no association was observed for any of the clusters with CH_3CF_3.[6]

The oxygen-rich cluster ions displayed some of the same reaction products observed for their respective parent cluster ions. For example, the cluster $V_2O_6^+$ reacts with difluoromethane to produce the products observed for the parent cluster $V_2O_4^+$, forming the species $V_2O_3F_2^+$ and $V_2O_4{\cdot}CH_2F_2^+$ in addition to the O_2 loss and association products already mentioned. However, the product that is attributed to the association of difluoromethane with O_2 loss corresponds to the same mass-to-charge ratio as HF abstraction without loss of molecular oxygen, but this seems an unlikely pathway for the reaction to follow. Under multiple collision conditions, the product $V_2O_3F_2^+$ associates CH_2F_2 to form $V_2O_3F_2{\cdot}CH_2F_2^+$. The same association product is observed for reaction of $V_2O_4^+$ with difluoromethane under multiple collision conditions. The pathway for oxygen transfer accompanied by dual fluorine abstraction with the loss of molecular oxygen was the same reaction mechanism observed for the reactions of the oxygen-rich clusters with CH_3CF_3.[6]

Conclusions

The reactions of the vanadium oxide clusters ions with difluoromethane demonstrate a dominant reaction pathway for the transfer of oxygen to the neutral species and abstraction of two fluorine atoms onto the selected cluster. This reaction displays a strong dependence on the size of the cluster that is not observed for reactions with the similar fluorocarbon CH_3CF_3.[6] This is likely an indication for the difference in mechanisms by which these reactions take place. The reactivities of these clusters with CH_2F_2 appear to be influenced by such factors as charge density, ionization potentials, and oxidation states of the vanadium atoms. It is postulated that the reaction occurs due to the ability of the π-type donation of a lone pair of electrons from a fluorine atom to an acceptor C−F σ-bond. In the type-B resonance structure suggested by the findings, the ability of the vanadium−fluorine bond to form is enhanced. This may set in motion the transfer of oxygen to the neutral species, with the subsequent abstraction of an additional fluorine atom onto the cluster.

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