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# Gas-Phase Chemistry of Vanadium Oxide Cluster Cations. 1. Reactions with $C_2F_6$ and $CH_3CF_3$

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The reactivities of mass-selected vanadium oxide cluster cations with fluorocarbons were studied by using a triple-quadrupole mass spectrometer coupled with a laser vaporization source. The vanadium oxide species $V_2O_{4-7}^+$, $V_3O_{6-9}^+$, $V_4O_{8-11}^+$, $V_5O_{11-13}^+$, $V_6O_{13-16}^+$, and $V_7O_{16-18}^+$ displayed unique reactivities with $CH_3CF_3$ and $C_2F_6$. Among the reaction pathways observed were association, HF elimination, cracking of the carbon−carbon bond, and fluorine abstraction with oxygen transfer from the cluster to the neutral reactant molecule. Interestingly, the reactions differed for clusters within the same series and also from series to series. For example, the reaction of $V_2O_4^+$ with $CH_3CF_3$ produces the HF-elimination product $V_2O_4{\cdot}HF^+$. However, the cluster $V_2O_5^+$ reacts with $CH_3CF_3$ to produce the cracking product $V_2O_5{\cdot}CF_3^+$ but also reacts to abstract 2 fluorine atoms with transfer of an oxygen atom to the neutral reactant molecule. The reaction of these 2 clusters with $C_2F_6$ generates only association products.

## Introduction

Fluorocarbons have become important constituents in the chemical, pharmaceutical, and advanced materials industries.[1] Lubricants capable of withstanding high temperatures,[2] and many surfactants, are based on perfluoro acids and ethers, and numerous fluorine-containing molecules have been found to be biologically active, leading to efficient commercial products. For instance, certain perfluoro derivatives have shown the ability to dissolve both oxygen and carbon dioxide and have found use as blood substitutes that do not cause adverse biological effects.[3] Also, the advanced materials industry uses many different fluorine-containing monomers for the production of polymers. As the field of fluoro-organic chemistry continues to grow,[4] it is essential that we understand the basic chemical principles by which fluorocarbons interact with the catalytic surface so we can improve existing catalysts and develop new ones. The importance of this research has grown since it has become widely accepted that chlorine radicals play a major role in stratospheric ozone depletion.[5] Currently, intense efforts are underway for the search of new compounds to replace existing chlorofluorocarbons. As the search for effective alternatives to the existing compounds continues, industry has shifted its production of chlorofluorocarbons to hydrochlorofluorocarbons and hydrofluorocarbons.

Halocarbons have been studied extensively over the years to determine their properties in both gas and solution phases.[1,6−10] Gas-phase studies on the reaction of halogen-containing compounds with metals have primarily dealt with bare metal ions and ligated monomeric metal ions. A summary of these reactions can be found in an excellent review by Eller and Schwarz.[8] However, to the best of our knowledge, no studies on the reactivity of metal oxide cluster ions with fluorocarbons have been reported, except for the reactions of trifluoromethane ($CHF_3$) and 1,1-difluoroethane ($CH_3CHF_2$) with the molecular ion $PrO^+$ performed by Schwarz and co-workers.[11] Of these studies, only a few involve fluorine-containing compounds, including some of those discussed here. The gas-phase reactions of transition metal ions with sulfur hexafluoride performed by Jiao and Freiser[12] indicated that the reduced reactivity and absence of reactivity toward fluorine abstraction for the late-transition-metal ions was due to the lack of empty d-orbitals. They concluded that the empty d-orbitals, except for the $d_{z^2}$, have the proper symmetry to interact with the $e_g$ orbital of $SF_6$, thereby allowing the abstraction of fluorine to occur. They also showed that the reaction efficiencies were similar to those for the early transition metals investigated, except for the less active species $V^+$ and $Nb^+$. The group V transition metal ions have only one empty d-orbital and, therefore, the abstraction of fluorine from $SF_6$ was much less likely to occur due to the possibility that the nonreactive $d_{z^2}$ orbital was empty.

Several types of gas-phase reactions have been observed for hydrofluorocarbons. For example, the reaction of $Ti^+$ with $CH_3F$ studied by Ridge and co-workers[13] showed the abstraction of fluorine from methyl fluoride to form $TiF^+$. Hodges and Beauchamp[14] demonstrated that $Li^+$ was able to abstract HF from $C_2H_5F$ to form $LiHF^+$ but observed no single fluorine abstraction channel whereas the reaction of $Pr^+$ with trifluoromethane and 1,1-difluoroethane produced only fluorine abstraction channels, the reaction of $PrO^+$ did not activate $CHF_3$ but demonstrated an HF-elimination channel for reaction with $CHF_2CH_3$; the abstraction of fluorine alone was not observed.[11] Another interesting reaction is that of the ligated manganese anion $(OC)_3Mn^-$ with hexafluoroethane ($C_2F_6$) studied by Jones and McDonald.[15] This reaction yielded $Mn(C_2F_4)^-$ and, with the loss of two CO units from the cluster, $COF_2$.

Vanadium-containing compounds are important industrial catalysts for the oxidation and functionalization of hydrocarbons. It is therefore important to understand the mechanisms by which hydrocarbons react with the catalytic surface. Examining the reactions of these metal oxide cluster cations with various neutral reactant gases will contribute to an understanding of the principles by which catalytically important reactions such as oxygen transfer, dehydrogenation, dehydration, and cracking

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processes occur. In the present paper, we report the observed inert behavior of the selected vanadium oxide cluster cations with the perfluoroalkane $C_2F_6$. In addition, the activation of the strong C—F bond is achieved with the presence of hydrogen atoms on the adjacent carbon of the fluorocarbon, as seen for the reactions with $CH_3CF_3$.

## Experimental Section

The triple-quadrupole mass spectrometer coupled with a laser vaporization source (TQMS-LV) used in the present experiments has been described in detail previously.[16−18] Briefly, the second-harmonic output of a Nd:YAG laser is tightly focused onto the surface of a rotating and translating vanadium rod. Clusters of various sizes form as a mixture of $O_2$ seeded in helium (by ~10%) is injected over the ablating rod surface, during which time plasma reactions take place. Thereafter, the clusters undergo supersonic expansion as they exit the laser vaporization source. The cluster ions enter the main chamber through a 3-mm-diameter skimmer and are focused by a group of ion lenses. The ions then enter the first quadrupole, where an ion of a particular mass is selected for further examination. Guided by a second group of ion lenses, the selected cluster is injected into the second-quadrupole mass spectrometer operated in the radiofrequency (RF)-only mode, which serves as either a reaction or a collision cell. The pressure inside this quadrupole can be set between 0.03 and 1.0 mTorr as monitored by a capacitance manometer. 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 so that only thermal ions are introduced into the reaction region. As the product ions exit the collision cell, they are refocused by another set of ion lenses into the third quadrupole. Affixed with a dynode channeltron electron multiplier, this quadrupole acts as a mass filter, wherein the selected and product ions are detected.

## Results

These studies were conducted at or near thermal energies. That is, the ions experienced a ground potential as they entered the second quadrupole, which was operated in the RF-only mode with no dc potential applied to the rods, and the reactant gas was maintained at room temperature. Within the range of experimental conditions explored, the clusters $V_2O_7^+$, $V_3O_{6-9}^+$, $V_4O_{8-11}^+$, $V_5O_{11-13}^+$, $V_6O_{13-16}^+$, and $V_7O_{16-18}^+$ appear to be inert toward reaction with hexafluoroethane ($C_2F_6$). However, the smaller clusters, $V_2O_{4-6}^+$, demonstrate a minor channel for association, generating the products $V_2O_y{\cdot}C_2F_6^+$. The oxygen-rich clusters $V_2O_6^+$ and $V_2O_7^+$ display a channel for association upon loss of $O_2$ to form the products $V_2O_4{\cdot}C_2F_6^+$ and $V_2O_5{\cdot}C_2F_6^+$, respectively. The larger oxygen-rich clusters $V_3O_{8,9}^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15,16}^+$, and $V_7O_{18}^+$ simply lose $O_2$ upon collision with the neutral reactant $C_2F_6$. No association products were observed for any of the clusters containing more than 2 vanadium atoms. Minor peaks at lower masses corresponding to fragments of $C_2F_6$ were observed, but only the vanadium-containing products are discussed in this paper.

The cluster reactions with 1,1,1-trifluoroethane displayed several different pathways. Under single-collision conditions, all the clusters studied except $V_2O_7^+$ displayed a channel for the HF-elimination product $V_xO_y{\cdot}HF^+$. Under multiple-collision conditions, a second HF elimination occurred, forming $V_xO_y{\cdot}(HF)_2^+$ for the clusters $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_{8-10}^+$, $V_5O_{11}^+$, and $V_6O_{13}^+$. As an example, the spectrum of $V_2O_4^+$ with $CH_3CF_3$ at a reactant pressure of 0.25 mTorr is shown in Figure 1, which displays the HF-elimination products for multiple-collision conditions. Association of $CH_3CF_3$ to the surface of the clusters was not observed for any of the species studied, including the 2 series, which displayed association channels when reacted with $C_2F_6$.

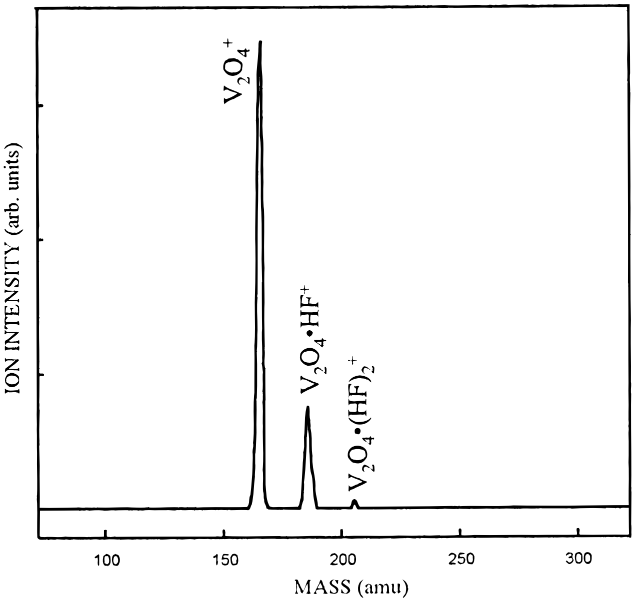


**Figure 1.** Spectrum for the reaction of $V_2O_4^+$ with $CH_3CF_3$ at 0.25 mTorr and near thermal conditions. This reaction displays an HF-elimination reaction to form the product $V_2O_4{\cdot}HF^+$. Abstraction of the additional HF to produce $V_2O_4{\cdot}(HF)_2^+$ under multiple collision conditions is also observed.

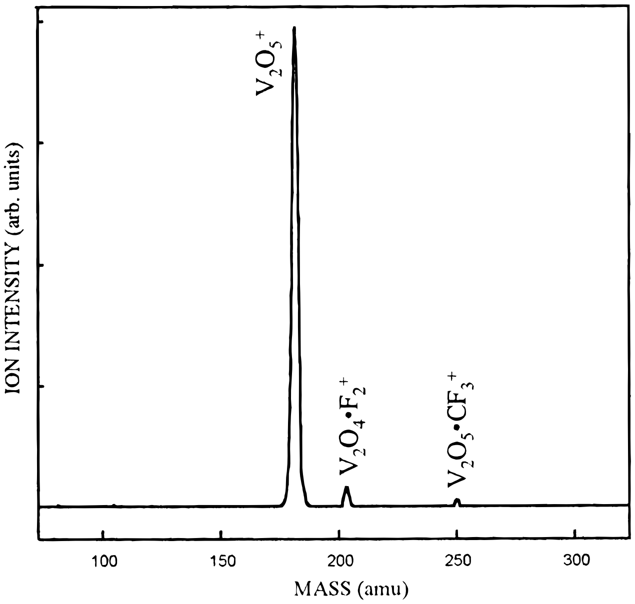


**Figure 2.** Spectrum for the reaction of $V_2O_5^+$ with $CH_3CF_3$ at 0.25 mTorr and near thermal conditions. The cluster $V_2O_5^+$ displays the abstraction of 2 fluorine atoms and transfer of a single oxygen atom to the neutral fluorocarbon and cracking of the carbon−carbon bond to produce $V_2O_5{\cdot}CF_3^+$.

The cluster $V_2O_5^+$ was the only cluster able to crack the carbon−carbon bond to form $V_2O_5{\cdot}CF_3^+$. This cluster also demonstrated a reaction channel for the abstraction of 2 fluorine atoms with transfer of an oxygen atom to the neutral reactant molecule, producing $V_2O_4{\cdot}F_2^+$; the spectrum for this reaction conducted at a pressure of 0.25 mTorr is shown in Figure 2. The oxygen-rich clusters $V_2O_{6,7}^+$, $V_3O_{8,9}^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15,16}^+$, and $V_7O_{18}^+$ displayed unique reactivities. Upon reaction with $CH_3CF_3$, the oxygen-rich species $V_xO_y(O_2)^+$

**TABLE 1: Reaction of Vanadium Oxide Cluster Cations $V_{2-7}O_y^+$ with $CH_3CF_3$ and $C_2F_6$ Near Thermal Energies and a Reactant Pressure of 0.25 MTorr**

| | reactant gas | |
|---|---|---|
| cluster $V_xO_y^+$ (*x*,*y*) | 1,1,1-trifluoroethane ($CH_3CF_3$) | hexafluoroethane ($C_2F_6$) |
| 2,4 | (2,4)·HF | (2,4)·$C_2F_6$ |
| | (2,4)·$H_2F_2$[a] | |
| 2,5 | (2,5)·HF | (2,5)·$C_2F_6$ |
| | (2,5)·$CF_3$ | |
| 2,6 | (2,4) | (2,4) |
| | (2,3)·$F_2$ | (2,4)·$C_2F_6$ |
| | (2,6)·HF | (2,6)·$C_2F_6$ |
| 2,7 | (2,5) | (2,5) |
| | (2,4)·$F_2$ | (2,5)·$C_2F_6$ |
| | (2,5)·$CF_3$ | |
| 3,6 | (3,6)·HF | no reaction |
| | (3,6)·$H_2F_2$[a] | |
| 3,7 | (3,7)·HF | no reaction |
| | (3,7)·$H_2F_2$[a] | |
| 3,8 | (3,6) | (3,6) |
| | (3,5)·$F_2$ | |
| | (3,8)·HF | |
| 3,9 | (3,7) | (3,7) |
| | (3,6)·$F_2$ | |
| | (3,9)·HF | |
| 4,8 | (4,8)·HF | no reaction |
| | (4,8)·$H_2F_2$[a] | |
| 4,9 | (4,9)·HF | no reaction |
| | (4,9)·$H_2F_2$[a] | |
| 4,10 | (4,8) | (4,8) |
| | (4,7)·$F_2$ | |
| | (4,10)·HF | |
| 4,11 | (4,9) | (4,9) |
| | (4,8)·$F_2$ | |
| | (4,11)·HF | |
| 5,11 | (5,11)·HF | no reaction |
| | (5,11)·$H_2F_2$[a] | |
| 5,12 | (5,12)·HF | no reaction |
| 5,13 | (5,11) | (5,11) |
| | (5,10)·$F_2$ | |
| | (5,13)·HF | |
| 6,13 | (6,13)·HF | no reaction |
| | (6,13)·$H_2F_2$[a] | |
| 6,14 | (6,14)·HF | no reaction |
| 6,15 | (6,13) | (6,13) |
| | (6,12)·$F_2$ | |
| | (6,15)·HF | |
| 6,16 | (6,14) | (6,14) |
| | (6,13)·$F_2$ | |
| | (6,16)·HF | |
| 7,16 | (7,16)·HF | no reaction |
| 7,17 | (7,17)·HF | no reaction |
| 7,18 | (7,16) | (7,16) |
| | (7,15)·$F_2$ | |
| | (7,18)·HF | |

[a] Denotes multi-collision conditions.

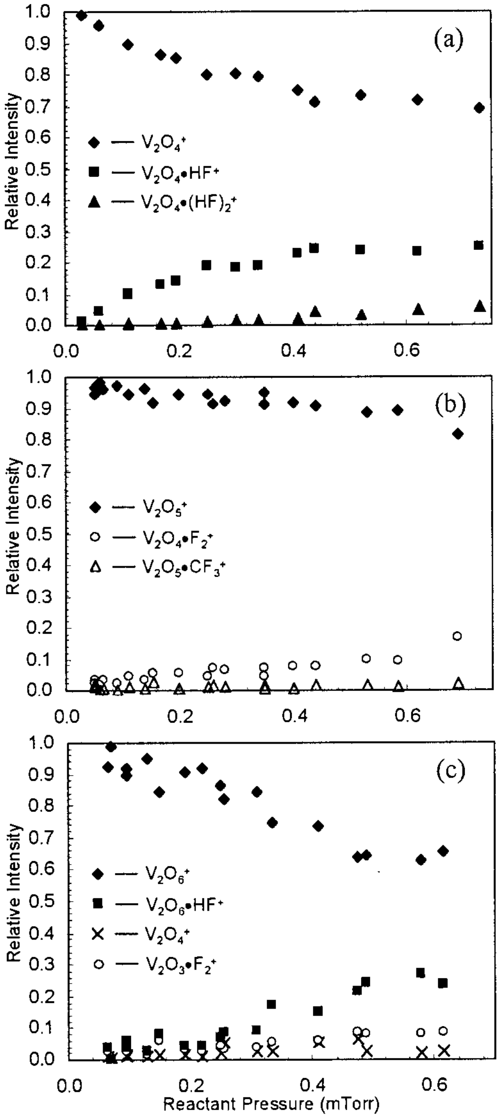
followed one of three pathways: abstraction of HF, loss of molecular oxygen to form $V_xO_y^+$, or abstraction of 2 fluorine atoms plus transfer of an oxygen atom to the neutral species with the subsequent loss of molecular oxygen to form $V_xO_{y-1}·F_2^+$. A summary of the reactions for the selected vanadium oxide clusters is displayed in Table 1. Peaks corresponding to fragments of $CH_3CF_3$ were observed but are not addressed in this paper.

## Discussion

The general inactivity of the vanadium oxide clusters ions toward reaction with the perfluorocarbon $C_2F_6$ may be attributed to the large C—F bond dissociation energy ($D°$ ($CF_3CF_2$—F) = 126.8 (1.8 kcal mol$^{-1}$),[19] in addition to the weak interactions between fluorocarbons and metals.[20-22] Gibson et al.[21] have shown that the vanadium complex V[2,4,6-$(CF_3)_3C_6H_2$]$_2$-Cl(THF) (THF = tetrahydrofuran) will produce a weak interaction between vanadium and fluorine. One of the fluorine atoms of a fluoromethyl group from each of the benzene rings forms weak CF···V interactions, which contribute to the pseudo-octahedral V($C_2OClF_2$) coordination sphere. In a related complex from this same study, a single, long-contact distance was observed between vanadium and fluorine atoms. Therefore, it is not clear whether the cleavage of the C—F bond of $C_2F_6$ by the vanadium oxide cluster cations is endothermic, because the bond dissociation energies of $V_xO_yF^+$ and $V_xO_yHF^+$ are unknown. The lifetime of the initially formed ion/molecule complex may be too short for reaction to occur, given such factors as the weakly polarizable nature of $C_2F_6$. However, this does not seem a likely scenario, because the two series displayed association products with no subsequent reaction with the molecule. Therefore, C—F bond activation may be both thermodynamically and kinetically disfavored for the reactions of $V_xO_y^+$ clusters with $C_2F_6$.

The vanadium oxide cluster cations are able to cleave the strong C—F bond ($D°$ ($CH_3CF_2$—F) = 124.8 ± 2 kcal mol$^{-1}$)[19] of $CH_3CF_3$. This reaction is attributed to the formation of an additional interaction between a hydrogen from the adjacent carbon of $CH_3CF_3$ and an oxygen atom on the cluster, which may result in lowering the energy of activation for this reaction. Therefore, the loss of HF from the neutral reactant occurs through a 1,2-elimination process. Studies by Schwarz and coworkers have shown that reaction of $PrO^+$ with trifluoromethane did not abstract HF, whereas reactions with 1,1-difluoroethane did demonstrate a channel for 1,2-HF elimination. However, the $Pr^+$ ion abstracted only fluorine atoms, and no HF abstraction was observed for either reactant species.[11] These reactions are consistent with those for difluoromethane with vanadium oxide cluster cations, which did not display a channel for HF elimination.[23] For these reactions, it seems appropriate to assume that the halogen atom bonds with the metal and the hydrogen bonds with the oxygen. For $PrO^+$, after the second abstraction, $H_2O$ was lost upon collision with another neutral reactant molecule.[11] However, for the vanadium oxide ions studied here, this may not be the case, because there were no peaks corresponding to the loss of $H_2O$ after the second HF abstraction at the pressures examined. The second HF abstraction may occur on a separate portion of the cluster or may simply form another —OH group on an adjacent oxygen atom instead of forming $H_2O$ as observed by Schwarz et al. This conjecture is also supported by studies conducted for the condensed phase of vanadium oxides. The adsorption of water onto the room-temperature $V_2O_5$ surface has been found to result in the dissociation of $H_2O$ to form an —OH group with the other hydrogen bonded to an adjacent vanadium.[24] From these temperature-programmed desorption studies, the authors postulated that desorption of water from the surface resulted in the recombination of adjacent V—H and V—OH surface species, but water was not from desorbed adjacent —OH groups.

The extent of reaction of the vanadium oxide cations with $CH_3CF_3$ differs greatly from cluster to cluster. The relative



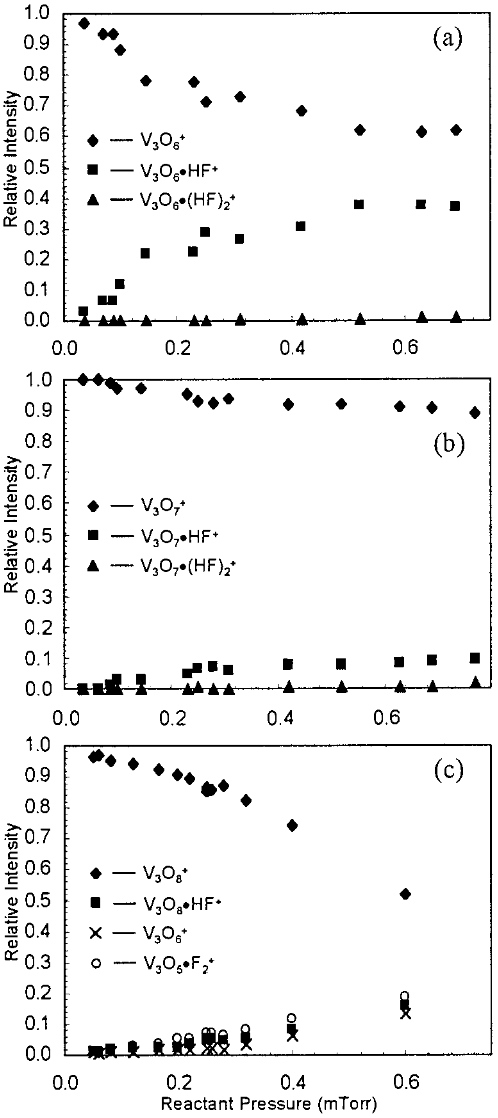


**Figure 3.** Plots of the relative product branching ratios of the vanadium-containing species for the reaction of $CH_3CF_3$ near thermal conditions with (a) $V_2O_4^+$, displaying the reaction products $V_2O_4$•$HF^+$ and $V_2O_4$•$(HF)_2^+$; (b) $V_2O_5^+$, which displays the reaction products $V_2O_4$•$F_2^+$ and $V_2O_5$•$CF_3^+$, and (c) $V_2O_6^+$, which shows the products $V_2O_4^+$, $V_2O_3$•$F_2^+$, and $V_2O_6$•$HF^+$ for this oxygen-rich species.

**Figure 4.** Plots of the relative product branching ratios of the vanadium-containing species for the reaction of $CH_3CF_3$ near thermal conditions with (a) $V_3O_6^+$, which displays the reaction products $V_3O_6$•$HF^+$ and $V_3O_6$•$(HF)_2^+$; (b) $V_3O_7^+$, displaying the reaction products $V_3O_7$•$HF^+$ and $V_3O_7$•$(HF)_2^+$; and (c) $V_3O_8^+$, displaying the observed products corresponding to $V_3O_6^+$, $V_3O_5$•$F_2^+$, and $V_3O_8$•$HF^+$.

branching ratios of the vanadium-containing products for the clusters $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{8,9}^+$, and $V_5O_{11,12}^+$ are shown in Figures 3 through 6, respectively. As evidenced by the data, and discussed in what follows, the abstraction of HF evidently depends on structural aspects of the cluster cation with little effect from such factors as the oxidation state or stoichiometry of the cluster. Nor did the size of the cluster cations affect the reactivities. Consider, for example, the clusters $V_3O_7^+$ and $V_5O_{12}^+$. From the structures deduced from collision-induced dissociation (CID) and other experiments performed previously on these cluster cations,[25] all of the vanadium atoms in these two clusters are expected to be in the +5 oxidation state. Nevertheless, the branching ratios for these two clusters, shown in Figures 4b and 6b, respectively, exhibit quite different reactivities for the abstraction of HF from $CH_3CF_3$. Consider next the cluster size, which often plays a major role in the reactivity of a cluster. For example, the reaction of 1,3-butadiene with the vanadium oxides $V_3O_7^+$, $V_5O_{12}^+$, and $V_7O_{17}^+$, all of which contain $V^{5+}$ exclusively, displays size dependence.[25] Upon reaction, $V_3O_7^+$ readily forms the dehydration product $V_3O_6$•$C_4H_4^+$, but only a weak dehydration product is observed for $V_5O_{12}^+$, and $V_7O_{17}^+$ is found to be inactive for this reaction pathway. For the reaction of the vanadium oxide cluster cations with $CH_3CF_3$, comparison of the branching ratios of the smaller clusters with those of the larger clusters does not indicate that size affects the reactivity of the clusters.

Based on the above findings and considerations, structure appears to be a key factor for the observed difference in reactivities of these clusters: The less-coordinated clusters seem able to abstract a second HF more efficiently than can the other clusters. This is most evident in the branching ratios for the clusters $V_4O_8^+$ and $V_4O_9^+$, shown in Figures 5a and 5b, respectively. Both of these clusters react readily with $CH_3CF_3$ to abstract HF, but the second HF abstraction by $V_4O_9^+$ is negligible, whereas $V_4O_8^+$ is the most-efficient cluster studied for eliminating the second HF. This may also indicate that the second HF abstraction occurs on a different vanadium atom. If the first abstraction put the vanadium atom involved in a state that favored abstraction of the second HF, then we would expect

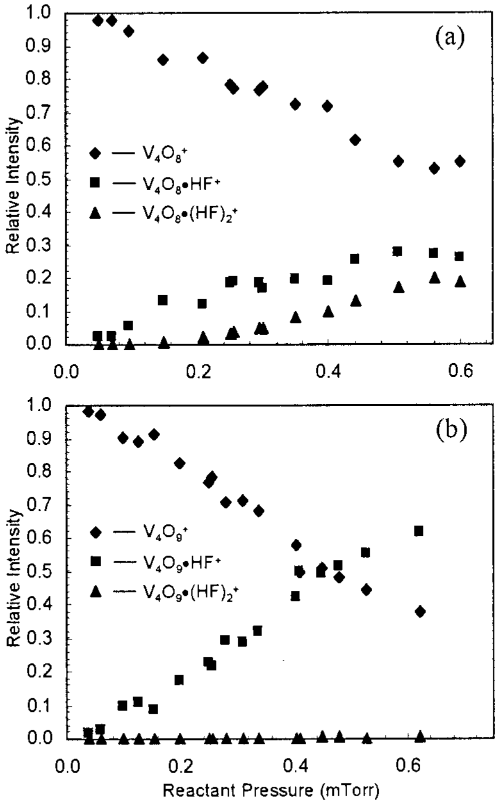


**Figure 5.** Plots of the relative product branching ratios of the vanadium-containing species for the reaction of $CH_3CF_3$ near thermal conditions with (a) $V_4O_8^+$, which displays the reaction products $V_4O_8$·$HF^+$ and $V_4O_8$·$(HF)_2^+$; and (b) $V_4O_9^+$, showing the reaction products $V_4O_9$·$HF^+$ and $V_4O_9$·$(HF)_2^+$.

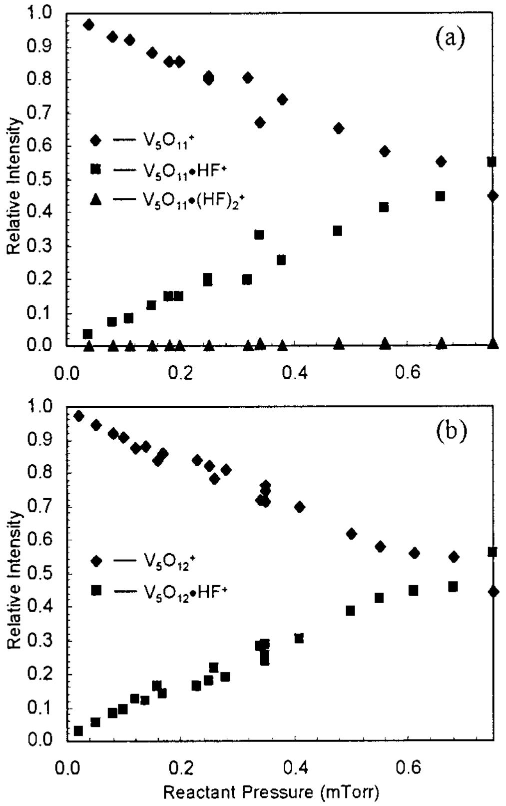


**Figure 6.** Plots of the relative product branching ratios of the vanadium-containing species for the reaction of $CH_3CF_3$ near thermal conditions with (a) $V_5O_{11}^+$, displaying the reaction products corresponding to $V_5O_{11}$·$HF^+$ and $V_5O_{11}$·$(HF)_2^+$, and (b) $V_5O_{12}^+$, which displays the observed reaction product $V_5O_{12}$·$HF^+$.

the other clusters to display a dominant channel for the second abstraction as well. From the predicted structures,[25] $V_4O_8^+$ has the least-coordinated vanadium atoms of the clusters investigated and, therefore, has more exposed vanadium atoms.

Previous studies[25] of vanadium oxide cluster cations demonstrated that the oxygen-rich clusters $V_2O_{5-6}^+$, $V_3O_{8-9}^+$, $V_4O_{10}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ were able to lose $O_2$ at thermal energies except $V_2O_5^+$. The loss of $O_2$ occurred both for CID reactions with krypton and xenon at single-collision conditions near thermal energies, and during reactions near thermal energies with neutral hydrocarbon species, which were also attributed to a CID process. From these studies we determined that molecular oxygen was weakly adsorbed to the smaller, more-stable clusters of the series. For example, the adsorption of $O_2$ onto the parent cluster $V_2O_4^+$ produces $V_2O_4(O_2)^+$, otherwise referred to as $V_2O_6^+$.

The observed reaction behavior of $CH_3CF_3$ indicates that adsorption of $O_2$ onto the parent ion $V_xO_y^+$ to form the oxygen-rich clusters $V_xO_y(O_2)^+$ alters the properties of these clusters and therefore affects their reactivities in comparison with those of the parent ions. Upon reaction with $CH_3CF_3$, the oxygen-rich species are able to follow three different pathways under single-collision conditions. The first channel is the HF-elimination reaction, producing $V_xO_y(O_2)$·$HF^+$, as previously observed for the other clusters. The second channel is loss of $O_2$, which is believed to be simply a CID reaction with no chemical interaction between the neutral reactant species and the selected vanadium oxide cation. (This is the same mechanism used to explain the loss of $O_2$ in the reaction of $C_2F_6$ with the selected oxygen-rich clusters.) However, a third possible channel corresponds to the abstraction of 2 fluorine atoms with the transfer of an oxygen atom to the neutral reactant molecule, followed by or combined with the loss of $O_2$ from the cluster. These are not conclusive results, because the observed peak may correspond to the loss of $O_2$ and abstraction from $CH_3CF_3$ of $H_3F$, that is, the HF-elimination product and the additional abstraction of 2 hydrogen atoms. However, reaction of several of the vanadium oxide cluster cations (including stoichiometric clusters such as $V_3O_6^+$) with difluoromethane demonstrate the same channel for dual fluorine abstraction with oxygen atom transfer and no formation of HF-elimination product.[23] Therefore, we postulate that the adsorbed oxygen molecule on the parent cluster affects the structure and electronic properties and, accordingly, the reactivity of the parent cluster ion.

The molecular oxygen may act to withdraw electron density from the cluster; that is, the oxygen atoms of the parent cluster ion would have a larger partial negative charge and the vanadium atoms a larger partial positive charge, thus slightly changing their electronegativities. The unique electronic properties of these clusters may allow a carbon−oxygen bond to begin to form in conjunction with the 2 fluorine atoms bonding to a vanadium atom in an exothermic process, producing the energy needed to expel molecular oxygen from the cluster. Because no $O_2$ loss was observed when HF was abstracted from $CH_3CF_3$ for these same oxygen-rich clusters, we think the $O_2$ is lost after or during the initial reaction steps. A potential driving force for the reaction of $V_xO_y(O_2)^+$ with $CH_3CF_3$ to form acetyl fluoride, $CH_3COF$, can be related to the thermodynamics for this reaction. Approximate values for the bond dissociation energies are as follows: 1 V−O bond ($D°$ (V−O) = 149[26] or 131[27] kcal $mol^{-1}$) and 2 C−F ($D°$ ($CH_3CF_2$−F) = 125 kcal $mol^{-1}$)[19] bonds are broken. This is offset by the formation of 2 V−F ($D°$ (V−F) = ~141 kcal $mol^{-1}$)[28] bonds and a C═O double bond ($D°$ (C═O) = ~178 kcal mol$^{-1}$)[29] to form $CH_3COF$ and $V_xO_{y-1}(O_2)^+$. Therefore, the reaction is thought to be exothermic with the excess energy causing the ejection of the loosely bound $O_2$ molecule. However, this pathway was not observed for $C_2F_6$ and therefore we postulate that the initial oxygen−hydrogen bond may act to influence the reaction complex and allow the reaction to occur more readily. We suggest that the activation energy barrier for this reaction is lowered by the presence of the additional $O_2$; however, the exact mechanism of this reaction is unknown and may involve different isomers of the oxygen-rich species. Another possibility is that the initial attachment of $CH_3CF_3$ may occur on different metal centers of the cluster cation, leading to different reaction pathways.

The unique ability of the oxygen-rich cluster $V_2O_5^+$ to abstract 2 fluorine atoms with oxygen transfer to the neutral species and also crack the carbon−carbon bond of $CH_3CF_3$ ($D°$ ($CH_3CF_3$) = 101.2 ± 1.1 kcal mol$^{-1}$),[30] may be attributed to the manner in which the oxygen atoms are bound to this cluster and to the possible formation of a hydrogen bond (which was not available for the $C_2F_6$ reaction). The CID results for the other oxygen-rich clusters demonstrated the loss of molecular oxygen near thermal energies. None of the clusters studied lost only 1 oxygen atom except $V_2O_5^+$, which was able to lose both a single oxygen atom at ~1 eV, and a molecular oxygen at ~2 eV center-of-mass reference frame of energy, the single oxygen loss being the dominant dissociation channel.[25] The reason for this exception is accounted for by the less-stable oxidation states of the vanadium atoms for the product $V_2O_3^+$ formed by the loss of $O_2$ during the CID process. For molecular oxygen to be lost, both oxygen atoms are assumed to come from the same vanadium atom; therefore, loss of $O_2$ would leave one of the vanadium atoms in the 2+ oxidation state. The cluster would then have to rearrange to have the vanadium atoms in the 4+ and 3+ oxidation states. In addition, the intensity of $V_2O_3^+$ in the mass distribution is minuscule in comparison with the other clusters formed in the laser vaporization source; this also indicates its instability compared with the other clusters formed.[25]

These assumptions are made because the vanadium oxide cluster cations are thought to have considerable ionic character. For the oxygen-rich clusters, if all the oxygen atoms were directly bonded to the metal centers, the vanadium atoms would have oxidation states >5+, the highest stable oxidation state for vanadium. For example, the vanadium atoms in the cluster $V_2O_6^+$ would have oxidation states of 6+ and 7+ if all the oxygen atoms were considered to be in the 2− oxidation state and each was individually bonded to the metal centers as bridge or end sites. However, this does not appear to be the case for the oxygen-rich clusters, as the facile loss of $O_2$ was observed under thermal, single-collision CID conditions except for $V_2O_5^+$, which did not show loss of $O_2$ under these same conditions. For these reasons, we believe that $V_2O_5^+$ reacted with $CH_3CF_3$ in a similar fashion as the other oxygen-rich clusters, but the excess energy produced by the formation of $V_2O_4{\cdot}F_2^+$ and acetyl fluoride was not enough to expel oxygen from the cluster. Furthermore, the product ion $V_2O_4{\cdot}F_2^+$ would not be considered a highly stable species because of the high oxidation states of the vanadium atoms. This may also help to explain why cracking the carbon−carbon bond is observed for this cluster and not the others.

The second channel observed for the reaction of $V_2O_5^+$ with trifluoroethane is the cracking of the carbon−carbon bond, which again may be explained by the unique bonding of the oxygen to the vanadium atoms within this cluster. Instead of following the above pathway to completion, we postulate that, as an oxygen forms a bond with the carbon atom of the methyl fluoride group of $CH_3CF_3$ (an integral step for the formation of the $V_2O_4{\cdot}F_2^+$ and acetyl fluoride), the reaction follows a different channel, breaking the carbon−carbon bond and releasing the methyl radical. From an electrostatic view, this would be a favorable pathway because the cluster would then have all the metal atoms in a 5+ oxidation state, and all the oxygen atoms would be forming complete bonds. Prior to reaction, the oxidation states of the vanadium atoms would be 5+ and 6+ if all the oxygen atoms were completely bonded to the cluster. That is, a V═O double bond would have to be broken to form the V−O−$CF_3$ bond and thus transform the unstable 6+ oxidation state into the most-stable 5+ oxidation state. The proposed mechanisms are fully consistent with the experimental observations. In addition, experimental and theoretical studies are in progress to gain further insight into the structures and electronic configurations of the vanadium oxide cluster ions.

## Conclusions

Direct interactions between vanadium and fluorine alone are not enough to overcome the bonding energy of the C−F bond. However, the energy of interaction of a hydrogen atom on an adjacent carbon of the neutral species with an oxygen atom on the cluster is enough to lower the activation barrier for the cleavage of the C−F bond. The extent to which these clusters are able to abstract HF from the neutral reactant gas appears to be independent of such factors as oxidation state or size and may depend more on the structure and coordination of the clusters. The highly reactive nature of the $V_2O_5^+$ cluster is presumed to be associated with the unstable nature of the bonded oxygen, which is unique to this cluster among the species studied. The ability of the oxygen-rich clusters to abstract 2 fluorine atoms and transfer an oxygen to the neutral reactant with the subsequent loss of molecular oxygen may be due to the interaction of $O_2$ with the cluster. This interaction may act to withdraw electron density from the vanadium atom with the adsorbed $O_2$ and also alter the electronic properties of neighboring atoms, therefore allowing a stronger initial interaction with the fluorine.

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## References and Notes

(1) Rozen, S. In *The Chemistry of Functional Groups*, Suppl. D2; Patai, S.; Rapoport, Z., Eds.; John Wiley: New York, 1995; Chapter 12.

(2) Snyder, C. E.; Gschwender, L. J.; Tamborski, C. *Lubr. Eng.* **1981**, *37*, 344. (b) Caporiccio, G.; Corti, C.; Soldini, S.; Carniselli, G. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 515. (c) Caporiccio, G.; Corti, C.; Soldini, *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 520.

(3) Yamanouchi, K.; Heldebrant, C. *Chemtech*, **1992**, 359.

(4) Seebach, D. *Angew. Chem., Int. Ed. Engl.*, **1990**, *29*, 1320.

(5) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810. (b) Manzer, L. E.; Rao, V. N. M. *Adv. Catal.* **1993**, *39*, 329.

(6) Smart, B. E. In *The Chemistry of Functional Groups*, Suppl. D.; Patai, S.; Rapoport, Z., Eds.; John Wiley: New York, 1983; Chapter 14.

(7) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363.

(8) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(9) Saunders: G. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2615.

(10) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425.

(11) Heinemann, C.; Goldberg, N.; Tornieporth-Oetting, I. C.; Klapötke, T. M.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 213.

(12) Jiao, C. Q.; Freiser, B. S. *J. Am. Chem. Soc.* **1993**, *115*, 6268.

(13) Kinser, R.; Allison, J.; Dietz, T. G.; deAngelis, M.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 2706.

(14) Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825.

(15) Jones, M. T.; McDonald, R. N. *Organometallics* **1988**, *7*, 1221.

(16) Kerns, K. P.; Guo, B. C.; Deng, H. T.; Castleman, A. W., Jr. *J. Chem. Phys.* **1994**, *101*, 8529.

(17) Deng, H. T.; Kerns, K. P.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 13386.

(18) Kerns, K. P.; Guo, B. C.; Deng, H. T.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 16817.

(19) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(20) Weydert, M.; Anderson, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 8837.

(21) Gibson, V. C.; Redshaw, C.; Sequeira, L. J.; Dillon, K. B.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1996**, 2151.

(22) Dillon, K. B.; Gibson, V. C.; Howard, J. A. K.; Redshaw, C.; Sequeira, L.; Yao, J. W. *J. Organometallic Chem.* **1997**, *528*, 179.

(23) Bell, R. C.; Zemski, K. A.; Castleman, A. W., Jr. *J. Phys. Chem. A*, submitted for publication.

(24) Moshfegh, A. Z.; Ignatiev, A. *Surf. Sci. Lett.* **1992**, *275*, L650.

(25) Bell, R. C.; Zemski, K. A.; Kerns, K. P.; Deng, H. T.; Castleman, A. W., Jr. *J. Phys. Chem. A* **1998**, *102*, 1733.

(26) Berkowitz, J.; Chupka, W. A.; Inghram, M. G. *J. Chem. Phys.* **1957**, *27*, 87. (b) Balducci, G.; Gigli, G.; Guido, M. *J. Chem. Phys*. **1983**, *79*, 5616. (c) Pedley, J. B.; Marshall, E. M. *J. Phys. Chem. Ref. Data* **1983**, *12*, 967.

(27) Kappes, M. M.; Staley, R. H. *J. Phys. Chem.* **1981**, *85*, 942. (b) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.

(28) Kondratiev, V. N. In *Bond Dissociation Energies, Ionization Potentials and Electron Affinities*; Mauka Publishing House: Moscow, 1974. *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991; **9**-107.

(29) Wade, L. G., Jr. *Organic Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; Chapter 11.

(30) Rodgers, A. S.; Ford, W. G. F. *Int. J. Chem. Kinet.* **1973**, *5*, 965.