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Gas-Phase Chemistry of Vanadium Oxide Cluster Cations 3. Reactions with CCl_4

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The reactions of selected vanadium oxide cluster cations with carbon tetrachloride were studied using a triple quadrupole mass spectrometer coupled with a laser vaporization source. The vanadium oxide species VO_2^+, $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{8-11}^+$, $V_5O_{11-13}^+$, $V_6O_{13-15}^+$, and $V_7O_{16-18}^+$ demonstrated several pathways for reaction with CCl_4. The chloride ion transfer reaction is the dominant reaction pathway for the smaller clusters that contain three or fewer vanadium atoms. For the larger clusters, the abstraction of two chlorine atoms with the transfer of oxygen to the neutral reactant molecule dominates their reactions with CCl_4, leading to the production of phosgene. This is consistent with the reactions that occur over the condensed-phase vanadium oxide catalyst for the degradation of carbon tetrachloride to phosgene and carbon dioxide. In addition, oxidation reactions are observed to occur more readily for clusters that contain vanadium atoms with oxidation states lower then +5.

Introduction

This study is a continuation in a series designed to elucidate the mechanisms by which vanadium oxide cluster cations react with halogen-containing molecules. Previous work was devoted to investigations on the reactions of C_2F_6 and CH_3-CF_3[1] and CH_2F_2[2] with selected vanadium oxide clusters, while the present study examines the aprotic compound carbon tetrachloride. An excellent review of the gas-phase reactions of metal-containing ions with organic halides has been presented by Eller and Schwarz.[3] Several gas-phase studies have been conducted for the reactions of CCl_4 with monomeric metal ions, showing that halide ion transfer generally occurs when the halide affinity of the metal cation is greater than that of the alkyl cation. Several of the monatomic metal ions, such as Ti^+, Au^+, Ga^+, and Al^+, undergo the chloride ion transfer reaction producing CCl_3^+ and the corresponding neutral metal chloride.[4−8] Also, the monatomic aluminum cation reacts rapidly with CCl_4 to produce the thermodynamically favored products CCl_3^+ and AlCl.[6−8] Specifically, it was shown that over the collision energy range of 1 to 6 eV, the only significant reaction of Al^+ with CCl_4 was chloride ion transfer. However, at the high end of this energy range, masses representing the products $AlCl_2^+$, $AlCl^+$, CCl_2^+, and CCl^+ were also observed with very low intensities.[8] In addition to the chloride ion transfer reaction, Ti^+ also forms the oxidative chloride transfer product $TiCl^+$, which reacts further with CCl_4 to abstract another chlorine atom forming $TiCl_2$ and CCl_3^+.[4] However, not all metal ions display the chloride ion transfer reaction. For example, oxidation processes dominate the chemistry of Mg^+ producing $MgCl_2$ and CCl_2^+,[7] while In^+ is inert toward reaction with carbon tetrachloride.[6]

Several studies of the condensed-phase reactions of CCl_4 with vanadium oxide catalysts have been reported. Morikawa and co-workers studied the decomposition of CCl_4 on a number of transition metal oxide surfaces,[9] including Nb_2O_5, Al_2O_3, V_2O_5, TiO_2, and ZrO_2. Carbon tetrachloride was shown to degrade to CO_2 and phosgene ($COCl_2$) at reaction temperatures ranging from 423 K to 623 K. At a reaction temperature of 453 K,[9] the TT phase of niobium oxide[10] was shown to be the most effective for degradation of CCl_4 into CO_2 without the production of phosgene. In contrast, the vanadium oxide catalyst was shown to give the highest percentage of conversion, with 32% and 68% selectivity for CO_2 and $COCl_2$, respectively, at a temperature of 623 K.

Based on studies made using a static reactor coupled with a quadrupole mass spectrometer, Mink et al. have proposed a reaction mechanism for the degradation of carbon tetrachloride on the surface of vanadium oxide.[11,12] They have suggested that once CCl_4 is adsorbed onto the surface, it dissociates, losing a chlorine atom to the metal site of a vanadyl group. The CCl_3 radical may then react with an adjacent vanadyl metal site to form phosgene. Thereafter, phosgene undergoes a similar process of chlorine abstraction with oxygen transfer to produce CO_2. The studies reported herein display a direct correlation between the condensed-phase reactions for the degradation of CCl_4 on the vanadium oxide surface and the vanadium oxide cluster ion reactions with carbon tetrachloride in the gas phase. The gas-phase results of the present study support the fact that similar mechanisms are operative. The selected vanadium oxide cluster ions are able to react with carbon tetrachloride to produce the chloride ion transfer product CCl_3^+, as seen for the gas-phase monatomic metal ion reactions with CCl_4. In addition, reaction channels leading to the formation of neutral phosgene and channels for oxidative chloride transfer are also observed.

Experimental Section

A triple-quadrupole mass spectrometer coupled with a laser vaporization source is used in the present study and has been described in detail previously.[13−15] Briefly, the metal oxide ions are formed by laser ablation of a vanadium rod. A 5−10% mixture of O_2 seeded in a helium carrier gas is injected into the metal plasma by a pulsed valve. Thereafter, the clusters undergo supersonic expansion as they enter the first differentially pumped chamber. The cluster ions then pass through a 3-mm-diameter skimmer and enter the main chamber, which houses the triple-quadrupole mass spectrometer. The cluster ions are focused by a set of electrostatic lenses as they enter the first

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quadrupole where a cluster of a particular mass is selected for study. The selected ions are focused by a second set of electrostatic lenses and enter the second quadrupole, which is operated in the radio-frequency (RF)-only mode. This quadrupole acts as the collision or reaction cell with reactant gases introduced at pressures ranging from 0.03 to 1.0 mTorr as monitored by a capacitance manometer. 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 selected and product ions, guided by a third set of lenses, enter the third quadrupole for mass analysis. The ions are detected by a channeltron electron multiplier, and a PC affixed with a multi-scalar card is employed to analyze the resulting signal.

Results

The reactions of carbon tetrachloride with the vanadium oxide cluster ions studied differ slightly between the stoichiometric clusters, VO_2^+, $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_{8,9}^+$, $V_5O_{11,12}^+$, $V_6O_{13,14}^+$, and $V_7O_{16,17}^+$, and the clusters that lose oxygen under collision induced dissociation (CID) reactions which we refer to as the oxygen-rich clusters $V_2O_{5,6}^+$, $V_3O_8^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$. In accordance with reaction 1, the chloride ion transfer reaction producing the product CCl_3^+ is observed for all the clusters, but is most prominent for the lower mass clusters with diminishing intensity as the cluster size increases.

$$V_xO_y^+ + CCl_4 \rightarrow V_xO_yCl + CCl_3^+ \qquad (1)$$

Representative spectra for the reactions of $V_2O_4^+$ and $V_7O_{17}^+$ with CCl_4 at 0.25 mTorr under near-thermal conditions are shown in Figures 1a and 1b, respectively. The term near-thermal energy indicates that the selected ions experience a ground potential as they enter the second quadrupole with the reactant gas maintained at room temperature. This quadrupole is operated in the RF-only mode with no external dc potential applied to the rods. The same experimental conditions were used for all the selected vanadium oxide cluster ions. However, the CCl_3^+ product has been omitted from the relative product branching ratios in Figures 2 through 7 for two reasons. First, the main focus of this paper is the formation of neutral phosgene and other vanadium-containing products. If the CCl_3^+ product were included in the product branching ratios for the smaller clusters, it would obscure the interpretation of the vanadium-containing products that are under investigation. Secondly, the effects of mass discrimination over a range covering the CCl_3^+ (118.4 amu) radical cation and the cluster $V_7O_{17}^+$ (628.6 amu) also warrant the exclusion of the CCl_3^+ product from the branching ratios. These points are discussed in further detail later in the paper. In addition, a low resolution was maintained for the third quadrupole during collection of the spectra for the relative product branching ratios to offset the effects of mass discrimination for the vanadium-containing species for any particular selected cluster.

With the exception of the cluster $V_4O_8^+$, the dominant reaction channel for the stoichiometric clusters, excluding the CCl_3^+ product, is the production of neutral phosgene ($COCl_2$) by reaction 2.

$$V_xO_y^+ + CCl_4 \rightarrow V_xO_{y-1}Cl_2^+ + COCl_2 \qquad (2)$$

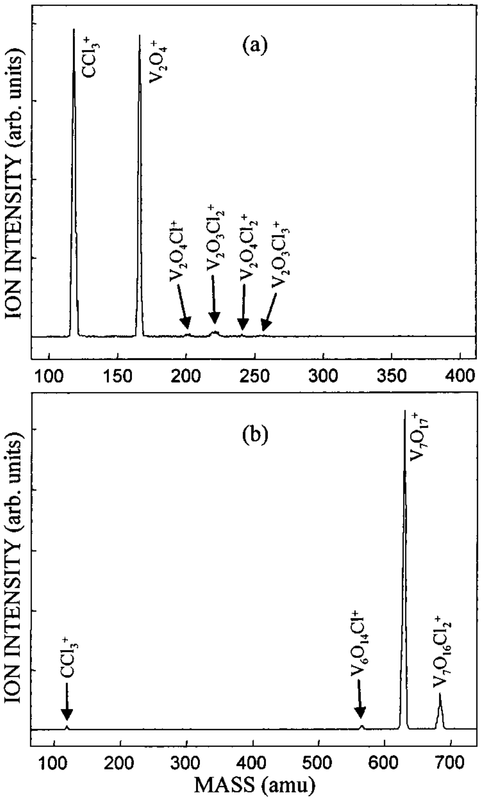


Figure 1. Spectra for the reaction of 0.25 mTorr of CCl_4 with the clusters (a) $V_2O_4^+$ in the range of 100−400 amu and (b) $V_7O_{17}^+$ in the range of 100−700 amu. The same experimental conditions were used for all the clusters with the exception of the entrance lenses for the third quadrupole, which were optimized for the mass range of the selected cluster under investigation.

On the other hand, $V_4O_8^+$ favors the oxidative halogen transfer reaction to form the product $V_4O_8Cl^+$, reaction 3.

$$V_xO_y^+ + CCl_4 \rightarrow V_xO_yCl^+ + CCl_3 \qquad (3)$$

The cluster $V_3O_6^+$ also displays this as a prominent channel, but with phosgene production still the dominant channel which is evident in the partial relative branching ratio shown in Figure 3a. The majority of the clusters display minor channels for this oxidative halogen transfer reaction, while $V_2O_4^+$, $V_3O_6^+$, and $V_4O_8^+$ are the only clusters to demonstrate a channel for the abstraction of two chlorine atoms under single-collision conditions as shown in reaction 4.

$$V_xO_y^+ + CCl_4 \rightarrow V_xO_yCl_2^+ + CCl_2 \qquad (4)$$

However, the products of reaction 4 represent less than 1% of the total reaction products and are not included in the respective product branching ratios for these clusters.

Under multiple-collision conditions, the product ion $V_xO_{y-1}Cl_2^+$ from reaction (2) may undergo a second reaction to form the product $V_xO_{y-2}Cl_4^+$, which represents the production of a second neutral phosgene, reaction 5.

$$V_xO_{y-1}Cl_2^+ + CCl_4 \rightarrow V_xO_{y-2}Cl_4^+ + COCl_2 \qquad (5)$$

Alternatively, the product $V_xO_{y-1}Cl_2^+$ may abstract a single chlorine atom, producing $V_xO_{y-1}Cl_3^+$ as shown in reaction 6.

$$V_xO_{y-1}Cl_2^+ + CCl_4 \rightarrow V_xO_{y-1}Cl_3^+ + CCl_3 \qquad (6)$$

Minor fragmentation channels are also observed for the stoi-

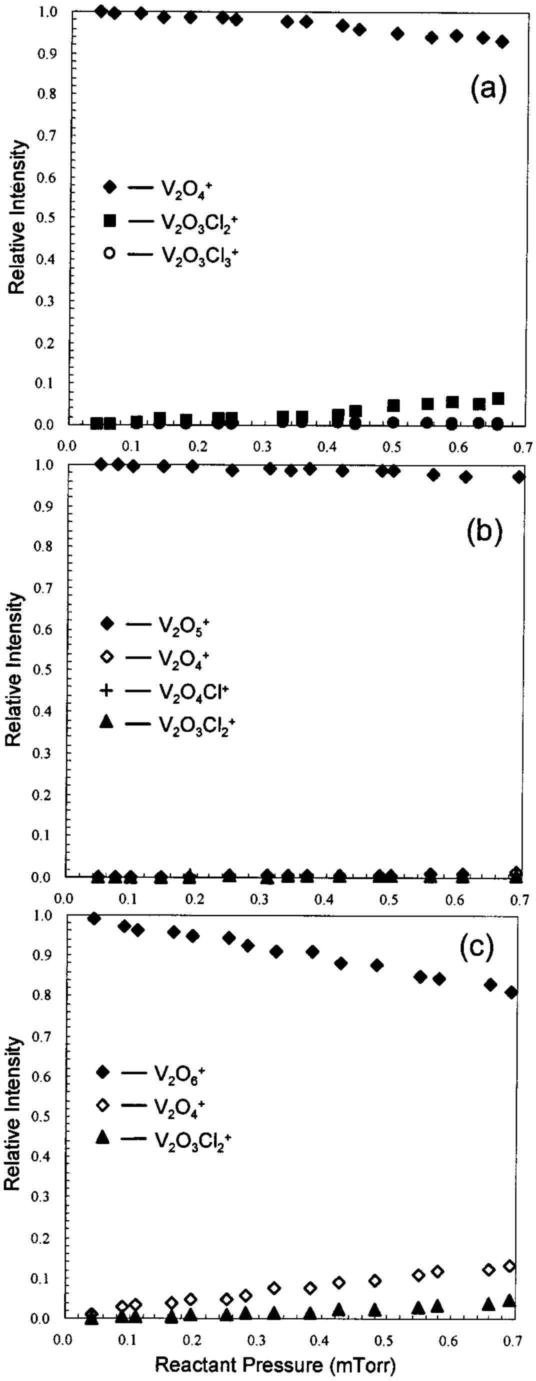


Figure 2. Plots for the partial relative product branching ratios of the vanadium-containing species for the reaction of CCl_4 with the clusters (a) $V_2O_4^+$, (b) $V_2O_5^+$, and (c) $V_2O_6^+$ under near-thermal conditions.

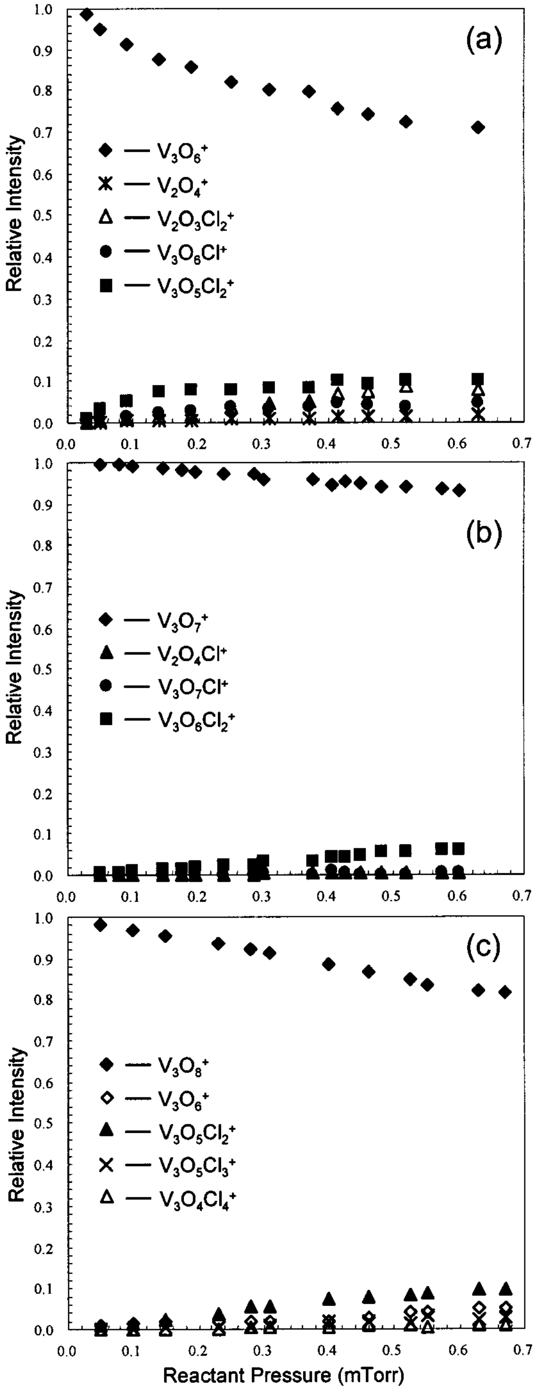


Figure 3. Plots for the partial relative product branching ratios of the vanadium-containing species for the clusters (a) $V_3O_6^+$, (b) $V_3O_7^+$, and (c) $V_3O_8^+$ with carbon tetrachloride under near-thermal conditions.

chiometric clusters, but not for the oxygen-rich clusters. For example, the cluster $V_7O_{17}^+$ reacts with CCl_4 to form the products that have already been mentioned, in addition to the fragmentation species $V_6O_{14}Cl^+$, which can be seen in Figure 1b.

The oxygen-rich clusters $V_2O_{5,6}^+$, $V_3O_8^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ differ slightly in their reactions with carbon tetrachloride. With the exception of $V_2O_5^+$, these clusters react to lose molecular oxygen under single-collision conditions near thermal energies. In addition, similar products are formed as were observed for the stoichiometric clusters with the loss of molecular oxygen. The cluster $V_2O_5^+$ reacted differently than the other oxygen-rich clusters, losing only a single oxygen and forming the same product ions as were observed for the cluster $V_2O_4^+$. The reactions of the vanadium oxide cluster cations with carbon tetrachloride have been summarized in Table 1. This table does not include the product ion CCl_3^+, which was observed for all the clusters studied. In addition, the reaction of VO_2^+ with CCl_4^+ produced only CCl_3^+ and has been excluded from Table 1 as well.

Discussion

A chloride transfer channel producing CCl_3^+ was observed for all the vanadium oxide cluster cations studied. However, the extent to which this reaction occurs is dependent on the size of the cluster. As the cluster size increases, the prominence of this channel decreases, with a notable decline starting with

TABLE 1: Reaction of Vanadium Oxide Cluster Cations $V_{2-7}O_y^+$ with CCl_4 at Near-Thermal Energies and a Reactant Pressure of 0.25 mTorr

selected cluster $V_xO_y^+$ (x,y)	product ions for reactant gas[a]: carbon tetrachloride (CCl_4)	selected cluster $V_xO_y^+$ (x,y)	product ions for reactant gas[a]: carbon tetrachloride (CCl_4)
2,4	V_2O_4Cl $V_2O_3Cl_2$ $V_2O_4Cl_2{}^c$ $V_2O_3Cl_3{}^b$	5,11	V_4O_9 $V_4O_8Cl^c$ $V_4O_9Cl^c$ $V_4O_8Cl_2$ $V_5O_{11}Cl$ $V_5O_{10}Cl_2$ $V_5O_{10}Cl_3{}^{b,c}$ $V_5O_9Cl_4{}^{b,c}$
2,5	V_2O_4 V_2O_4Cl $V_2O_3Cl_2$	5,12	V_4O_9Cl $V_5O_{12}Cl^c$ $V_5O_{11}Cl_2$
2,6	V_2O_4 $V_2O_3Cl_2$ $V_2O_3Cl_3{}^{b,c}$	5,13	V_5O_{11} $V_5O_{10}Cl_2$ $V_5O_9Cl_4{}^b$
3,6	V_2O_4 $V_2O_3Cl^c$ $V_2O_4Cl^c$ $V_2O_3Cl_2$ $V_2O_4Cl_2{}^c$ V_3O_6Cl $V_3O_5Cl_2$ $V_3O_6Cl_2{}^c$ $V_3O_5Cl_3{}^{b,c}$	6,13	$V_5O_{11}{}^c$ $V_5O_{11}Cl^c$ $V_5O_{10}Cl_2$ $V_6O_{13}Cl$ $V_6O_{12}Cl_2$ $V_6O_{12}Cl_3{}^b$ $V_6O_{11}Cl_4{}^b$
3,7	V_2O_4Cl V_3O_7Cl $V_3O_6Cl_2$	6,14	V_5O_{12} $V_5O_{11}Cl^c$ $V_5O_{11}Cl_2{}^c$ $V_6O_{14}Cl$ $V_6O_{13}Cl_2$ $V_6O_{13}Cl_3{}^{b,c}$ $V_6O_{12}Cl_4{}^{b,c}$
3,8	V_3O_6 $V_3O_5Cl_2$ $V_3O_5Cl_3{}^b$ $V_3O_4Cl_4$	6,15	V_6O_{13} $V_6O_{12}Cl_2$ $V_6O_{11}Cl_4{}^b$
4,8	V_3O_6 $V_3O_6Cl^c$ $V_3O_5Cl_2$ V_4O_8Cl $V_4O_7Cl_2$ $V_4O_8Cl_2{}^c$ $V_4O_7Cl_3{}^b$	7,16	V_6O_{14} $V_6O_{13}Cl^c$ $V_6O_{14}Cl^c$ $V_6O_{13}Cl_2$ $V_7O_{16}Cl^c$ $V_7O_{15}Cl_2$ $V_7O_{15}Cl_3{}^{b,c}$ $V_7O_{14}Cl_4{}^b$
4,9	V_3O_7 V_3O_6Cl V_4O_9Cl $V_4O_8Cl_2$	7,17	$V_6O_{14}Cl$ $V_7O_{16}Cl_2$
4,10	V_4O_8 $V_4O_7Cl_2$ $V_4O_7Cl_3{}^b$	7,18	V_7O_{16} $V_7O_{15}Cl_2$
4,11	V_4O_9 $V_4O_8Cl_2$ $V_4O_7Cl_4{}^b$		

[a] All the clusters formed the CCl_3^+ product and are not shown in the table. In addition, the cluster VO_2^+ reacted with carbon tetrachloride to form CCl_3^+ exclusively and has not been included in the table. [b] These reaction channels are observed under multiple collision conditions at near-thermal energies. [c] These species represent less than 3% of the total products and are not displayed in the relative product branching ratios so that the more dominant species can be viewed more clearly.

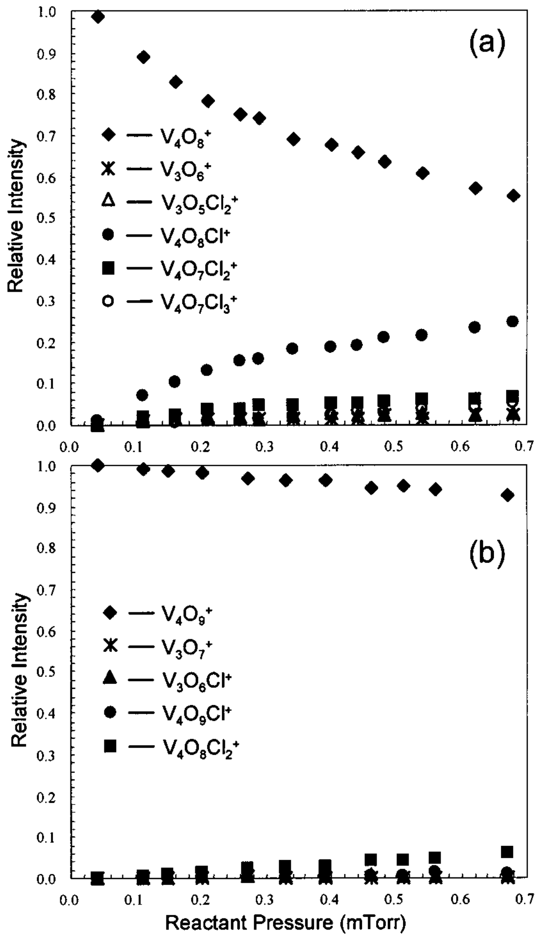


Figure 4. Plots for the partial relative product branching ratios of the vanadium-containing species for the reactions of (a) $V_4O_8^+$ and (b) $V_4O_9^+$ with CCl_4 under near-thermal conditions.

the cluster series $V_4O_y^+$, and then continues to gradually decline as the cluster size further increases. The gradual decline in the intensity of the CCl_3^+ species could be attributed to both the effects of mass discrimination and the change in reaction products being formed. At the series $V_5O_y^+$, the prominent reaction pathway becomes the production of neutral phosgene. This can be seen in the partial relative branching ratios in Figures 2 through 7, as the larger clusters appear to become more reactive, which is due to the exclusion of the CCl_3^+ species from the branching ratios. The spectrum for the reaction of $V_2O_4^+$ with 0.25 mTorr of CCl_4 is shown in Figure 1a and, for comparison, the spectrum of $V_7O_{17}^+$ under the same experimental conditions is shown in Figure 1b.

The change in the dominant reaction pathway from the CCl_3^+ product to the production of neutral phosgene with increasing size is interesting. We propose that this change may occur for a couple of reasons. First, although the chloride affinities for these clusters are unknown, it is reasonable to assume that they may change with cluster size. Secondly, the transfer of Cl^- to the cluster may occur at the charge center as was proposed for the reactions of the vanadium oxide cluster ions with CH_2F_2.[2] It was proposed that the structures of the clusters change as their size increases.[16] The structure of the smaller clusters allows easy access to all the vanadium atoms, but with the larger clusters, beginning with the cluster series containing four vanadium atoms, ring structures and branching of the clusters becomes possible. This can be seen in Figure 8, which shows possible structures for $V_3O_7^+$ and $V_4O_9^+$. For the larger clusters, the vanadium sites become more highly coordinated, which may make the charge center less accessible. Another possibility is that the increased number of vanadium atoms acts to delocalize the charge. With the electrostatic effects due to the charge lessened, the chloride affinities of the clusters may change, making the chloride transfer reaction less favorable.

Mass discrimination makes it difficult to accurately compare

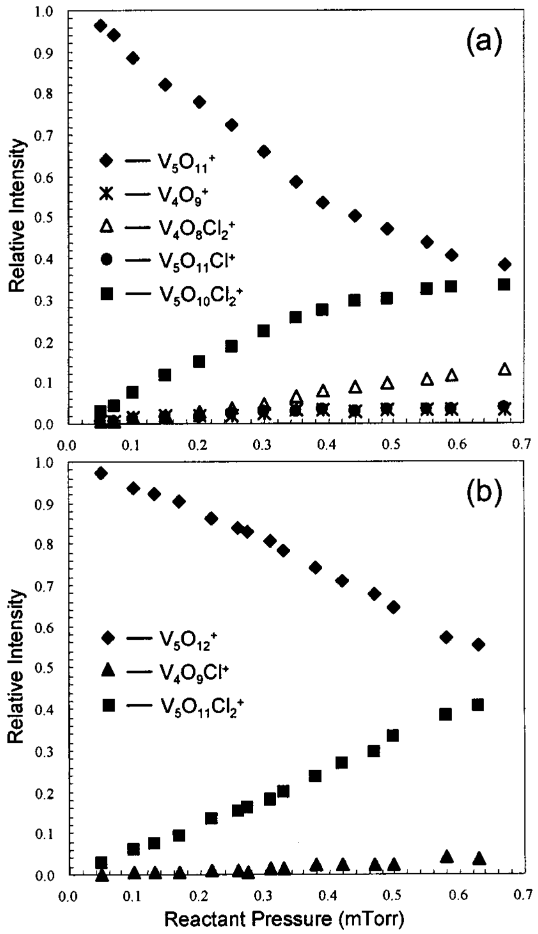


Figure 5. Plots for the partial relative product branching ratios of the vanadium-containing species for the reaction of carbon tetrachloride with the clusters (a) $V_5O_{11}^+$ and (b) $V_5O_{12}^+$ under near-thermal conditions.

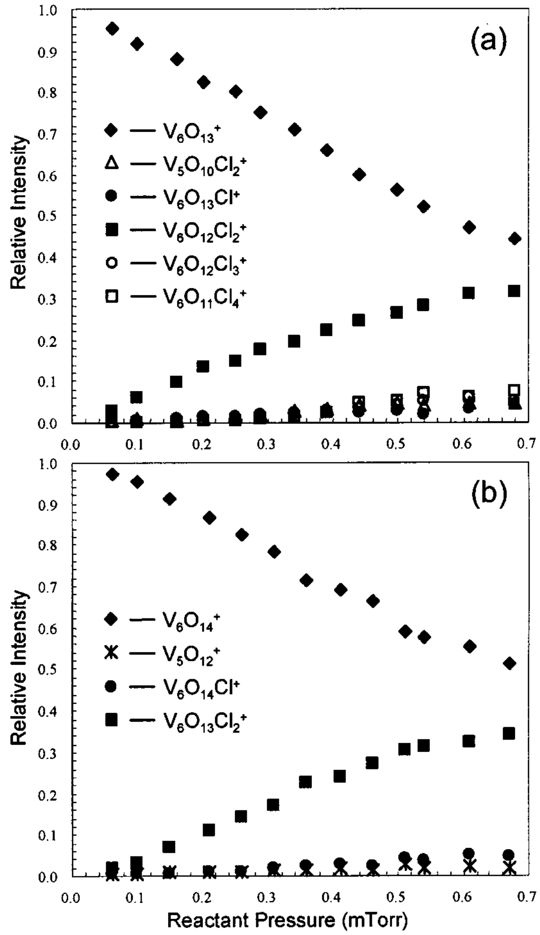


Figure 6. Plots for the partial relative product branching ratios of the vanadium-containing species for the reactions of (a) $V_6O_{13}^+$ and (b) $V_6O_{14}^+$ with carbon tetrachloride under near-thermal conditions.

the production of CCl_3^+ for the reactions of the smaller clusters with those of the larger ones. However, this paper focuses on the vanadium-containing species and, in particular, the production of phosgene ($COCl_2$) for comparison with the condensed-phase reactions. The formation of CCl_3^+ is strictly a gas-phase, ion−molecule reaction, which is not observed in the condensed-phase chemistry for the degradation of CCl_4 on the vanadium oxide surface. For these reasons, the branching ratios shown in Figures 2 through 7 are partial branching ratios including only the vanadium-containing species. These branching ratios do not account for the CCl_3^+ product so that other reaction pathways can be examined more thoroughly and are not obscured because of the intensity of this species.

The studies performed by Mink and co-workers determined that carbon dioxide is the primary product for the degradation of CCl_4 on the vanadium oxide catalyst.[11,12] After a short period of time, the production of phosgene begins and passes over an inflection point in the kinetic curve. At a later time, volatile $VOCl_3$ begins to form and soon approaches a quasi-steady-state value for its formation. They proposed a mechanism in which CCl_4 formed phosgene and carbon dioxide in a two-step process involving two vanadium centers in the condensed phase.[12] The first step of this mechanism involves the adsorption and dissociation of carbon tetrachloride at a vanadyl site, forming a dative vanadium−chlorine bond with the CCl_3 radical adsorbed onto a second vanadyl site. The second step involves the abstraction of a second chlorine atom from the CCl_3 radical, with the transfer of a surface oxygen atom forming adsorbed phosgene which, in turn, can also desorb. Once the vanadium−oxygen bond is broken to form phosgene, the dative vanadium−chlorine bond becomes a real bond. Therefore, the formation of products results in the substitution of surface oxygen by chlorine. The phosgene may then undergo the same process to form CO_2.

The gas-phase reactions of CCl_4 with the vanadium oxide cluster ions support the mechanism proposed by Mink and co-workers. The cluster VO_2^+ does not form phosgene. This could be taken to imply that the reaction does occur at two vanadium sites. However, this is not conclusive, as the formation of CCl_3^+ may dominate the ion−molecule reaction and inhibit the production of other products. Accepting the two-vanadium-site mechanism, the first chlorine abstraction may be more favorable at vanadium sites with lower than +5 oxidation states. The clusters $V_3O_7^+$, $V_5O_{12}^+$, and $V_7O_{17}^+$ contain vanadium atoms exclusively in the +5 oxidation state. The ability of these clusters to abstract a single chlorine atom from CCl_4 is minor, while facile abstraction of a single chlorine atom occurs for clusters with vanadium in lower oxidation states. For example, the dominant channel for the reaction of $V_4O_8^+$ with carbon tetrachloride is that of oxidative chlorine abstraction. Of all the clusters studied, $V_4O_8^+$ has the lowest overall oxidation states for its vanadium atoms. The smaller clusters with the same 1:2 metal-to-oxygen ratio have a slightly higher oxidation state per vanadium atom because of the positive charge on the clusters. The cluster $V_3O_6^+$, which has the second-lowest average oxidation state of the clusters studied, demonstrates a substantial chlorine abstraction channel. However, phosgene production is

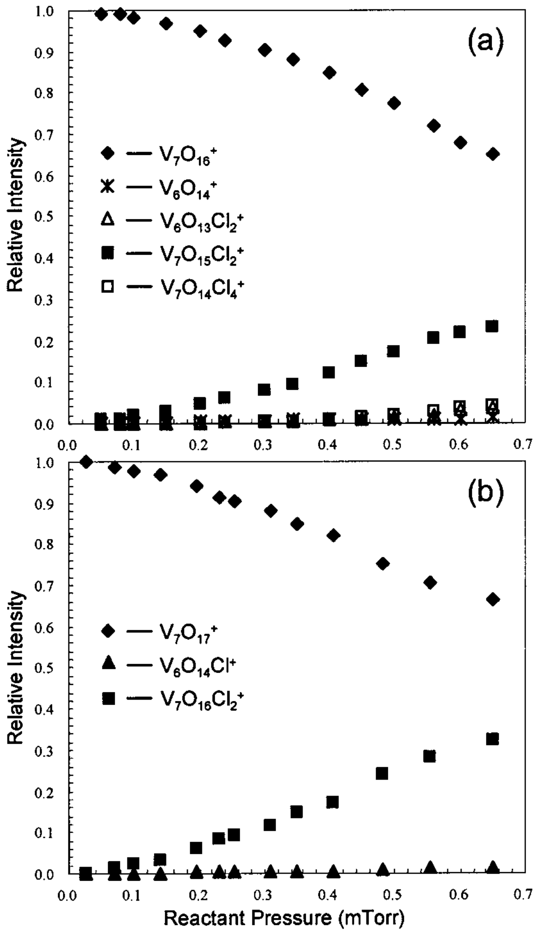
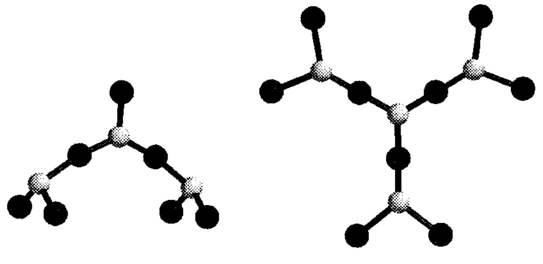


Figure 7. Plots for the partial relative product branching ratios of the vanadium-containing species for the reaction of CCl_4 with the clusters (a) $V_7O_{16}^+$ and (b) $V_7O_{17}^+$ under near-thermal conditions.



(a) (b)

Figure 8. Figures for the possible structures of the clusters (a) $V_3O_7^+$ and (b) $V_4O_9^+$.

still the prominent reaction pathway for this cluster. For all the other stoichiometric clusters, the dominant vanadium-containing channel is that of phosgene production. For these reasons we believe that the abstraction of chlorine occurs most readily on vanadium atoms with a lower oxidation state, and oxygen transfer occurs most readily on vanadyl groups in the +5 oxidation state.

The vanadium oxide catalyst is observed to lose surface vanadium through the production of solid $VOCl_2$ and volatile $VOCl_3$,[9,12] which occurs when bridging vanadium−oxygen bonds are broken. Mink and co-workers suggested that the abstraction of the first chlorine resulted in the formation of a dative chlorine−vanadium bond and would form a real bond upon cleavage of any neighboring vanadium−oxygen bond.[12] Therefore, the source of the oxygen to form $COCl_2$ and CO_2 can come from either terminal or bridging oxygen atoms. The observed fragmentation of the gas-phase vanadium oxide clusters is consistent with this view. However, only minor fragmentation was observed for those clusters with vanadium exclusively in the +5 oxidation state, indicating that the favored path for oxygen transfer occurs at the terminal oxygen of V^{+5} sites. The clusters with vanadium in lower oxidation states are observed to fragment more readily. In addition, product ions containing carbon were not detected, which is consistent with the condensed-phase studies that showed that carbon-containing species did not remain on the vanadium oxide surface.[9]

Considering these observations and those previously discussed, it is evident that clusters with lower oxidation state vanadium atoms display dominant oxidative chlorine transfer channels, while clusters with vanadium exclusively in the +5 oxidation state predominantly form phosgene. This would indicate that the loss of surface vanadium in the condensed-phase reactions may occur as follows. At the beginning of the reaction in the static reactor,[11,12] the degradation of CCl_4 proceeds to completion, forming, predominantly, CO_2. However, as the surface of the catalyst becomes covered with chlorine, the production of phosgene becomes more prominent. This may occur because of the lack of oxygen bound to vanadyl sites with vanadium in the +5 oxidation state. With the lack of oxygen, the CCl_3 radical more readily attacks bridging oxygen, which allows the formation of the species $VOCl_3$ and $VOCl_2$. The release of these species exposes fresh vanadium sites and the formation of CO_2 and $COCl_2$ continues.

The degradation of CCl_4 in the condensed phase occurs only when the V_2O_5 catalyst[11] is maintained at 373 K or above, while the observed cluster reactions occur at approximately 300 K. The production of excited clusters is one possibility, but is unlikely. Studies have shown that monatomic ions produced with a pulsed laser vaporization source can be kinetically excited with a spread of transnational energies up to several electron-volts.[17] However, the cluster VO_2^+ reacted to form only CCl_3^+. If this cluster were in an excited state, one would expect the appearance of several reaction products as was observed for the reaction of excited Al^+ with carbon tetrachloride[8] mentioned previously. Another remote possibility is involvement of the clustering process itself, whereby larger clusters become thermally excited as the cluster size increases through growth via condensation. If this were to occur for the clusters created by the laser ablation process, it is thought that the fluence of the laser would also influence the reactivity of the metal oxide clusters. However, studies performed on the reactions of vanadium oxide cluster cations with CH_2F_2 did not display a dependence on laser fluence. This may indicate that the clusters are not in excited states due to the laser ablation process[2] and that the clusters are sufficiently cooled through supersonic expansion after the clusters have been formed. For these reasons, it is believed that the clusters are not excited, as were the monatomic ions.[17] An alternate possibility is that the charge on the cluster and the high polarizability of CCl_4 plays a role in the observed difference in reactivity between the condensed- and gas-phase reactions. The most probable reason is that the chloride affinity of the cation is greater than that of condensed-phase vanadium oxide. The greater chloride affinity would act to lower the barrier of activation for the initial C−Cl bond cleavage, thus lowering the temperature needed for the reaction to occur.

The oxygen-rich clusters $V_2O_6^+$, $V_3O_8^+$, $V_4O_{10,11}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ differ slightly in their reactions with carbon tetrachloride, but form similar product ions as those observed for the stoichiometric clusters. The oxygen-rich clusters are proposed to be the more stable stoichiometric clusters, but with molecular oxygen adsorbed to their surface.[16] For example, molecular oxygen is adsorbed onto the cluster $V_2O_4^+$, forming $V_2O_4(O_2)^+$ or, alternatively, $V_2O_6^+$. Therefore, $V_2O_4^+$ is considered the *parent* cluster of $V_2O_6^+$. The reactions of carbon tetrachloride are similar to those observed for the *parent* clusters with the loss of O_2 in addition to the other products formed. For example, the cluster $V_2O_4^+$ reacted with CCl_4, producing $V_2O_4Cl^+$, $V_2O_3Cl_2^+$, and $V_2O_4Cl_2^+$ under single-collision conditions and $V_2O_3Cl_3^+$ under multiple-collision conditions. The reaction of $V_2O_6^+$ (or, alternatively, $V_xO_y(O_2)^+$) with CCl_4 produces neutral phosgene as did the *parent* cluster $V_2O_4^+$ (or $V_xO_y^+$), but also loses O_2 as shown in reaction 8.

$$V_xO_y(O_2)^+ + CCl_4 \rightarrow V_xO_{y-1}Cl_2^+ + COCl_2 + O_2 \quad (8)$$

Other products formed by the reaction of $V_2O_6^+$ with CCl_4 are $V_2O_3Cl_2^+$ under single-collision conditions and $V_2O_3Cl_3^+$ under multiple-collision conditions. Presumably, the same reaction mechanisms occur for the oxygen-rich clusters as for the stoichiometric clusters, but with the additional loss of O_2. The loss of molecular oxygen may take place during the course of the reaction or may be expelled as a result of the energy created by the formation of the other products. In addition, the oxygen-rich clusters react with CCl_4 to lose molecular oxygen. This is believed to be a collision-induced dissociation channel forming the more stable *parent* clusters. The loss of O_2 from vanadium oxide cluster ions has been observed previously for the oxygen-rich clusters.[1,2,16]

Conclusions

The ion−molecule reactions of the selected vanadium oxide cluster cations establish that there is a dependence on the size of the cluster for the products formed during the reaction with carbon tetrachloride. The smaller clusters reacted with CCl_4 to produce the chloride transfer product CCl_3^+ as the dominant reaction pathway. But as the size of the cluster increases, beginning with the series $V_4O_y^+$, the production of neutral phosgene begins to dominate the reaction. The reaction products observed for the larger clusters support the mechanisms proposed for the condensed phase degradation of CCl_4 on the vanadium oxide catalyst. These studies may lead to a better understanding of the relationships between the condensed- and gas-phase chemistries. However, a more thorough knowledge of these clusters is necessary to quantify the results to either support or negate the proposals that have been set forward. New studies are currently underway to determine the cluster structures and the kinetics of these reactions to further our understanding of these systems.

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