Matrix Isolation Study of the Thermal and Photochemical Reaction of $OVCl_3$ with NH_3: Spectroscopic and Theoretical Characterization of $Cl_2V(O)NH_2$

Bruce S. Ault*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnnati, Ohio 45221

Received: December 31, 2000; In Final Form: February 26, 2001

Initial and secondary intermediates in the reaction of $OVCl_3$ with NH_3 have been characterized by matrix isolation infrared spectroscopy and density functional calculations. Twin jet co-deposition of these two reagents led to a series of infrared absorptions that are assigned to the 1:1 molecular complex between these two species. Irradiation of these matrices with light of $\lambda > 300$ nm led to complete destruction of the complex, and the growth of a number of new bands. These are assigned to the $Cl_2V(O)NH_2$ species, as well as to HCl arising from destruction of the complex. Identification of these species was supported by extensive isotopic labeling (^{15}N and ^{2}H), as well as by B3LYP/6-311G+(2d,3p) density functional calculations. Good agreement was observed between the experimental and the computed frequencies. Similar experiments with $(CH_3)_3N$ led, at best, to a very small degree of complex formation.

Introduction

High valent transition metal oxo compounds, including $OVCl_3$ and $CrCl_2O_2$, have been used on many occasions as potent yet selective oxidizing agents in organic synthesis.[1,2] However, the high reactivity of these systems have prevented researchers in many cases from determing the mechanistic details of these oxidation reactions. In contrast, several detailed theoretical studies[3−7] have explored such systems and postulated the existence of multiple intermediates in model systems involving high valent transition metal oxo compounds. Although the reactions of $OVCl_3$ with a number of small molecules are known, the reaction of $OVCl_3$ with NH_3 had not been reported until very recently, when atmospheric pressure chemical vapor deposition[8] was carried out using a mixture of these two reagents, leading to formation of a vanadium oxychloride thin film. In this work, no consideration was given to the mechanism of reaction. In addition, the reaction of $OVCl_3$ with NH_3 has not been studied. The matrix isolation technique[9−11] was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates. This approach has been applied to the study of a wide range of species, including radicals, weakly bound molecular complexes, and molecular ions. Recent studies[12−15] from this laboratory have focused on the sequence of intermediates formed in the reactions of $OVCl_3$ and $CrCl_2O_2$ with small organic substrates, particularly those containing one or more heteroatoms. Given the high interest in these strong oxidizing agents and the utility of the $OVCl_3/NH_3$ reaction pair in chemical vapor deposition, a matrix isolation study was undertaken to explore intermediates formed in this reaction. Density functional calculations were also carried out in support of the experimental observations.

Experimental Section

All of the experiments in this study were carried out on conventional matrix isolation apparatus that has been described.[16] Oxyvanadium trichloride, $OVCl_3$ (Aldrich), was introduced into the vacuum system as the vapor above the room-temperature liquid, after purification by freeze−pump−thaw cycles at 77 K. NH_3 (Matheson), $^{15}NH_3$ (99% ^{15}N), ND_3 (99% D) (both Cambridge Isotope Laboratory) and $(CH_3)_3N$ (Aldrich) were introduced from lecture bottles into a separate vacuum manifold and were purified by repeated freeze−pump−thaw cycles at 77 K. Argon and nitrogen (Wright Brothers) were used as the matrix gas in different experiments, and were used without further purification.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K cold window, allowing for only a very brief mixing time prior to matrix deposition. A number of these matrices were subsequently warmed to 33−35 K to permit limited diffusion and then recooled to 14 K and additional spectra recorded. In addition, most of these matrices were irradiated for 1.0 or more hours with the H_2O/Pyrex filtered output of a 200 W medium-pressure Hg arc lamp, after which additional spectra were recorded.

Several experiments were conducted in the merged jet mode,[17] in which the two deposition lines were joined with an UltraTorr tee at a distance from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region. The length of this region was variable; typically, a 90 cm length was employed. In both twin and merged jet, matrices were deposited at the rate of 2 mmol/hr from each sample manifold onto the cold window. Final spectra were recorded on a Nicolet IR 42 Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using the Gaussian 94 suite of programs.[18] Density functional calculations using the Becke B3LYP functional were used to locate energy minima, determine structures and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-311G+(2d, 3p) basis set, after initial calculations with smaller basis sets were run to approximately locate energy minima. Calculations were carried out on a Silicon Graphics Indigo 2 workstation.

10.1021/jp004606l CCC: $20.00

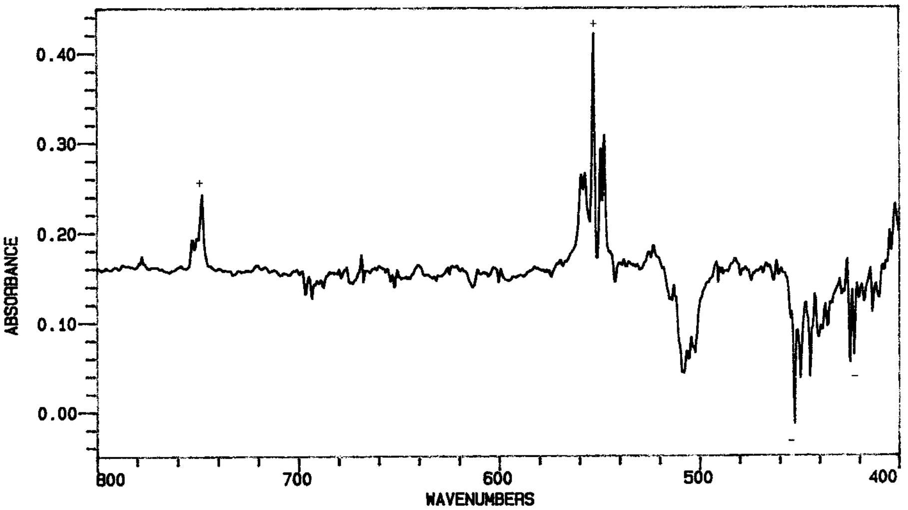

Figure 1. Difference spectrum arising from the spectra taken before and after irradiation of an argon matrix containing the 1:1 complex between $OVCl_3$ and NH_3, in the 400−800 cm^{-1} region. Bands or multiplets marked with a "+" are assigned to $Cl_2V(O)NH_2$; bands or multiplets marked with a "−" are assigned to the 1:1 complex $Cl_3VO{:}NH_3$.

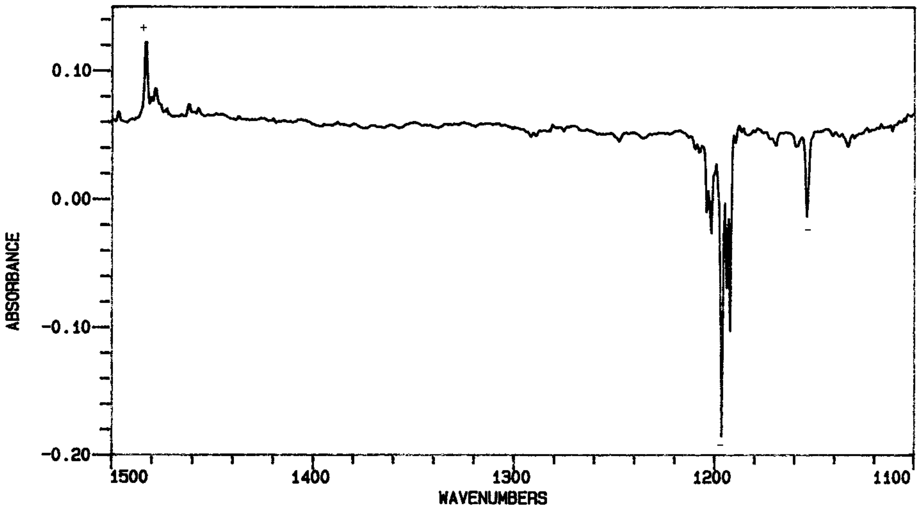

Figure 2. Difference spectrum arising from the spectra taken before and after irradiation of an argon matrix containing the 1:1 complex between $OVCl_3$ and $^{15}NH_3$, in the 1100−1500 cm^{-1} region. Bands or multiplets marked with a "+" are assigned to $Cl_2V(O)^{15}NH_2$; bands or multiplets marked with a "−" are assigned to the 1:1 complex $Cl_3VO{:}^{15}NH_3$.

Experimental Results

Prior to any co-deposition experiments, blank experiments were run on each of the reagents used in this study, in both argon and nitrogen matrices (with the exception of ND_3, which was studied only in nitrogen matrices). In each case, the blanks were in good agreement with literature spectra,[19−23] and with blanks run previously in this laboratory. The actual $^{15}N/^{14}N$ ratio in the $^{15}NH_3$ blank, as determined by relative parent band intensities, was approximately 8/1, whereas in the ND_3 experiments, the D/H ratio was approximately 7/1, after extensive conditioning. Each blank experiment was then irradiated by the H_2O/Pyrex filtered output of a 200 W Hg arc lamp for 1.0 h. No changes were observed in any of the blank spectra as a result of irradiation. Weak bands due to HCl impurity were noted in all of the $OVCl_3$ blank experiments.[24]

$OVCl_3$ + NH_3. These two reagents were deposited in an initial twin jet experiment, with $Ar/OVCl_3 = 500$ and $Ar/NH_3 = 250$. A number of new infrared absorptions were noted after deposition, at 424, 451, 692, 1159, 1202, 1600, 3291, and 3398 cm^{-1}, in addition to strong bands due to the parent species. The band at 1202 cm^{-1} was the most intense and was split into a tightly spaced multiplet centered at 1202 cm^{-1}. The band at 1600 cm^{-1} appeared as a shoulder on the parent NH_3 band in this region. These bands will hereafter be referred to as set A. After spectra were recorded, this sample was irradiated for 1.0 h with the H_2O/Pyrex filtered output of a 200 W Hg arc (i.e., $\lambda > 300$ nm). When an additional spectrum was recorded after irradiation, all of the above bands were completely destroyed by irradiation. In their place, new bands were observed at 552, 748, 1047, 1473, 1496, 2750, 2770, 3330, and 3442 cm^{-1}. As will be shown below, the bands at 2750 and 2770 cm^{-1} showed different behavior as a function of concentration and isotopic substitution than the rest of the listed bands, and will hereafter be referred to as set C. The remainder of these bands (552, 748, 1047, 1473, 1496, 3330, and 3442 cm^{-1}) will be referred to as set B.

A number of additional studies were conducted with this pair of reactants at different concentrations in an argon matrix. Concentrations ranged from 1000/1 to 250/1. In all of these experiments, the same set A bands were observed upon deposition, in the same ratio of relative intensities. All of these experiments were subsequently irradiated under the same

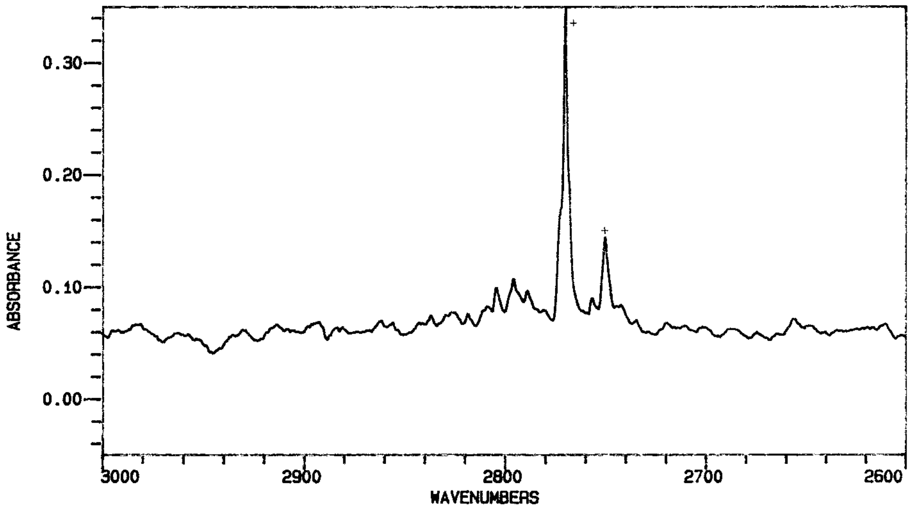

Figure 3. Difference spectrum arising from the spectra taken before and after irradiation of an argon matrix containing the 1:1 complex between $OVCl_3$ and $^{15}NH_3$, in the 2700−3100 cm^{-1} region. Bands or multiplets marked with a "+" are assigned to HCl hydrogen bonded to $Cl_2V(O)^{15}NH_2$ arising from irradiation of the 1:1 complex $Cl_3VO{:}^{15}NH_3$.

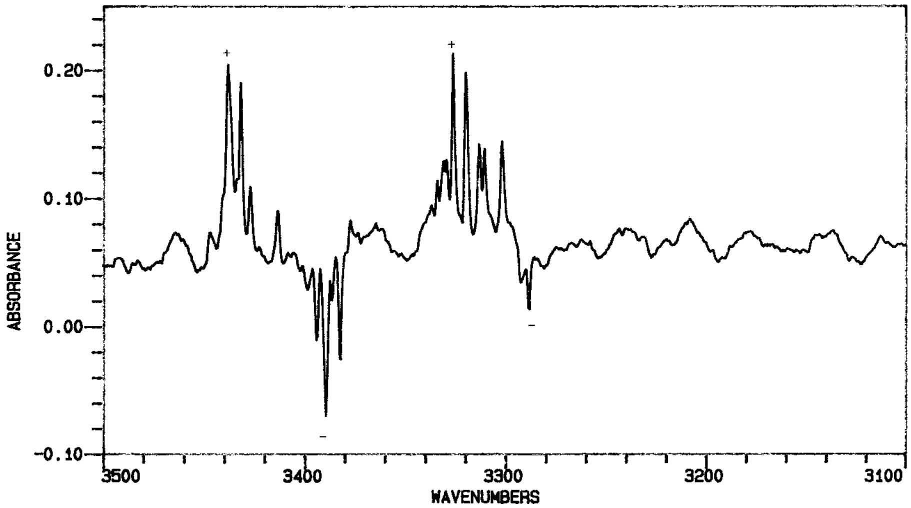

Figure 4. Difference spectrum arising from the spectra taken before and after irradiation of an argon matrix containing the 1:1 complex between $OVCl_3$ and $^{15}NH_3$, in the 3100−3500 cm^{-1} region. Bands or multiplets marked with a "+" are assigned to $Cl_2V(O)^{15}NH_2$; bands or multiplets marked with a "−" are assigned to the 1:1 complex $Cl_3VO{:}^{15}NH_3$.

conditions as the initial experiment, above. All of the set A bands were destroyed in each experiment, and the sets B and C bands grew in. The bands within set B maintained a constant intensity ratio with respect to one another throughout these experiments. The overall yield of set A bands and then sets B and C was noted to vary directly with the concentration of the reagents (i.e., increasing concentration of one or both reagents led to increasing band intensities for set A and then sets B and C after irradiation).

NH_3 is known to undergo hindered rotation in solid argon,[20] leading to a complex spectrum in the regions of the NH_3 fundamentals. This rotation is quenched in N_2 matrices,[21] leading to a simpler spectrum. Consequently, several twin jet experiments employing samples of $N_2/OVCl_3$ and N_2/NH_3 were carried out. The results were very similar to those reported above in solid argon. An initial set of bands was observed upon deposition, at 429, 451, 722, 1195, 1230, 1601, 3299, and 3401 cm^{-1}. Again, the feature near 1230 cm^{-1} was the most intense, and was split into a doublet, whereas the feature at 1601 cm^{-1} was a shoulder on the intense parent band near 1610 cm^{-1}. Each of these product bands is a direct analogue of the argon matrix bands described above. Hg arc irradiation ($\lambda > 300$ nm) of this matrix led to a complete destruction of these bands, and the growth of new bands at 443, 591, 754, 1047, 1484, 2762, 3317, and 3434 cm^{-1}. The band at 2762 cm^{-1} was quite broad, and analogous to the set C bands in argon; the remaining bands are direct analogues of the set B bands observed in the argon matrix experiments.

Additional experiments were conducted in N_2 matrices, at different sample concentrations. The same set A bands were observed upon initial deposition in each experiment and destroyed by irradiation, whereas the sets B and C bands grew in upon irradiation. The set A bands maintained a constant intensity ratio with respect to one another in all experiments, whereas the set B bands did likewise after irradiation.

Two merged jet experiments were also carried out with these two reagents and argon as the matrix gas. The merged region was 90 cm in length, and the region was held at room temperature. At the conclusion of the first experiment, no product bands were observed. In addition, no parent bands of NH_3 were seen, and the bands of parent $OVCl_3$ were relatively weak (certainly much weaker than in the blank spectra). In the second experiment, identical conditions were employed. However, in this experiment, a spectrum was recorded after 10 h.

TABLE 1: Band Positions and Assignments for the 1:1 Complex $OVCl_3$:NH_3 in Solid Argon[b]

$OVCl_3$:$^{14}NH_3$ (cm^{-1})	parent (cm^{-1})	$OVCl_3$:$^{15}NH_3$ (cm^{-1})	$OVCl_3$:$^{14}ND_3$ (cm^{-1})	assignment
424	411	424	427[a]	VCl_3 sym st
451	505	451	448[a]	VCl_3 antisym st
692		690		NH_3 rock
1159	974	1154		NH_3 sym def[c]
1202	974	1196	949[a]	NH_3 sym def[c]
1600	1618	1590	1177[a]	NH_3 antisym def
3291	3330	3288	2394[a]	NH_3 sym st
3398	3440	3393	2536[a]	NH_3 antisym st

[a] Nitrogen matrix positions. [b] Bands were also observed at 995 and 1480 cm^{-1}, and are assigned to the partially deuterated species $OVCl_3$:NHD_2. [c] see text for assignment details.

This spectrum was very similar to that in the first experiment, with no product bands, no NH_3 parent bands, and weak $OVCl_3$ parent bands. The flow of Ar/$OVCl_3$ was then stopped, while the flow of Ar/NH_3 was allowed to continue for an additional 10 h. The spectrum recorded at the conclusion of this second 10-hour segment showed strong bands due to parent NH_3.

Isotopic Studies. Several twin jet experiments were conducted employing samples of Ar/$OVCl_3$ and Ar/$^{15}NH_3$. As noted above, bands due to residual $^{14}NH_3$ were present as well, although much weaker than the $^{15}NH_3$ bands. Upon initial deposition, bands analogous to the set A bands described above were seen at 424, 451, 690, 1154, 1196, 1590, 3288, and 3393 cm^{-1}, as well as weak ^{14}N product bands at 692, 1159, 1202, 1600, 3291, and 3398 cm^{-1}. The relative intensities were in the same ratio as in the $^{14}NH_3$ experiments described above. Irradiation of these matrices led to complete destruction of these product bands, and the growth of new bands corresponding to the sets B and C bands described above. Set B ^{15}N bands were located at 549, 733, 1046, 1482, 3326, and 3437 cm^{-1}, whereas the set C bands were unshifted at 2750 and 2770 cm^{-1}. Similar results were obtained in N_2 matrices, with set A bands observed upon initial deposition and destroyed upon irradiation, and sets B and C observed upon irradiation of the matrix. ^{14}N, ^{15}N doublets were observed for many of these bands, just as in solid argon.

Several twin jet experiments were conducted with deuterated ammonia as well. Given the increased potential for overlapping bands due to the presence of NHD_2 and NH_2D as well as NH_3 and ND_3, experiments were only conducted in N_2 matrices where the overall spectrum is simpler due to lack of rotation. Initial deposition of a sample of Ar/$OVCl_3$ = 250 with a sample of Ar/ND_3 = 250 led to a number of new product bands as listed in Table 1. Bands due to parent NH_3 were quite weak, and the product bands observed above for the NH_3/$OVCl_3$ reaction pair (e.g., 1225, 1234 cm^{-1}) were not observed. Irradiation of this matrix led to complete destruction of the initial product bands, and the growth of bands at 497, 701, 1047, 1127, 2001, 2431, 2509, 2566, and 3403 cm^{-1}. The band at 497 cm^{-1} appeared as a shoulder on the intense parent band of $OVCl_3$ at 505 cm^{-1}; the band at 2001 cm^{-1} was quite broad, analogous to the 2762 cm^{-1} band in the NH_3 experiments. Overall, the deuteration experiments yielded similar results, with set A bands observed upon initial twin jet deposition and destroyed by irradiation, and sets B and C bands formed upon irradiation.

$OVCl_3$ + $(CH_3)_3N$. A sample of Ar/$OVCl_3$ = 250 was co-deposited with a sample of Ar/$(CH_3)_3N$ = 250 in a single twin jet experiment. After 20 h of deposition, no distinct new bands indicative of product formation were observed, while parent bands of $OVCl_3$ and $(CH_3)_3N$ were quite intense. One or more very weak bands were possibly seen between 420 and 470 cm^{-1}, but were so weak that further exploration was not carried out.

Discussion

Numerous product bands and several product species were isolated in the reaction of $OVCl_3$ with NH_3 under a range of reaction conditions. As noted above, many of the product bands can be grouped into sets, based on the conditions under which they appeared, and the fact that bands within a given set maintained a constant intensity ratio with respect to other bands in that set. It is also apparent that the different product species are formed in sequence, as reaction conditions are altered and additional energy deposited into the system. The identity of the species responsible for each set of product bands will be discussed, followed by the results of ab initio calculations and an overview of the mechanism of reaction.

Product Identification

The bands in set A were formed under the conditions of shortest reaction time and lowest reaction temperature, namely in the twin jet deposition experiments where mixing of the two reactants occurs on the surface of the condensing matrix. This indicates the species A is the initial intermediate in the reaction between $OVCl_3$ and NH_3. It is also noteworthy that each of these bands (except for the band near 690 cm^{-1}) was observed relatively near a parent mode of either $OVCl_3$ or NH_3. For example, the 424 and 451 cm^{-1} bands are shifted from the parent VCl_3 stretching modes at 505 and 410 cm^{-1}, whereas the 3291 and 3398 cm^{-1} bands lie near the NH_3 stretching modes of ammonia. Further, the isotopic dependence of each of the set A bands mirrored closely the isotopic dependence of the nearby parent mode. These observations are indicative of the formation of a molecular complex between the two reacting species, where each subunit is perturbed in the complex, yet maintains its molecular identity.[25] On this basis, the bands in set A are assigned to a molecular complex between $OVCl_3$ and NH_3 and its isotopomers in argon and nitrogen matrices.

The stoichiometry of the complex is not as readily determined. However, the observation of only a single product after co-deposition over a wide range of concentrations suggest that the stoichiometry is 1:1. Certainly, it would be difficult to envision formation of higher complexes (e.g., 2:1 or 1:2) without also forming the 1:1 complex. The observation of a single product argues against this and for the formation of the 1:1 complex. Consequently, the set A bands described above are assigned to the 1:1 molecular complex between $OVCl_3$ and NH_3. *This species represents the initial intermediate in the reaction between these two compounds*.

The 1:1 molecular complex is clearly very sensitive to ultraviolet irradiation, as bands due to this complex were complete destroyed by 1 h of irradiation with light of $\lambda > 300$ nm. Similar results were observed for the $OVCl_3 \cdot S(H)CH_3$ complex[15] and the $CrCl_2O_2 \cdot O(H)CH_3$ complex.[12] In each of these cases, it was shown conclusively that complex destruction occurred through HCl elimination, after absorption of a photon. The HCl produced in these systems, however, was trapped within the matrix cage with the second photoproduct ($Cl_2V(O)SCH_3$ and $ClCr(O)_2OCH_3$, respectively). The HCl spectrum, then, was that of weakly hydrogen bonded HCl, with bands appearing near 2750 cm^{-1}. Similar absorptions were seen in the present experiments, at 2750 and 2770 cm^{-1} in argon matrices, and at 2762 cm^{-1} in N_2 matrices (the latter band being quite broad). These bands did not shift upon ^{15}N substitution, but did shift in solid N_2 to 2001 cm^{-1} upon deuteration. This is precisely the isotopic dependence anticipated for HCl. In addition, the ν_H/ν_D ratio of 2762/2001 = 1.38 is identical to that observed[26-28] for both gas phase and matrix isolated HCl, namely 1.38. Given the isotopic behavior of the set C bands and the analogy to several well-established systems, the set C bands are assigned to photoproduced HCl, arising from the decomposition of the initial 1:1 molecular complex. Further, the HCl that is produced is trapped within the same matrix cage, and weakly hydrogen bonded to the species responsible for the set B bands. As discussed below, species B contains a chloro, an oxo and an amide ligand, all of which are potential hydrogen bond acceptors. It is difficult to anticipate where the trapped HCl may interact, and indeed, a bifurcated or bridged structure might occur. The density functional calculations (see below) suggest that the nitrogen atom carries the greatest negative charge (−0.51 units), followed by the oxygen atom (−0.25 units) and then the chlorine atom (−0.10 units). This suggests that the hydrogen bonding may take place at the amide group, but the evidence is limited.

Species B is clearly identified with the species resulting from an HCl elimination process from the molecular complex. In the two previous studies cited above ($OVCl_3 + CH_3SH$ and $CrCl_2O_2 + CH_3OH$) as well as in the $OVCl_3 + CH_3OH$ system,[14] only one HCl elimination product was possible. This was the product arising from the elimination of one HCl unit from the complex, yielding $Cl_2V(O)SCH_3$, $ClCR(O)_2OCH_3$, and $Cl_2V(O)OCH_3$ respectively. However, in the present case, the possibility of the elimination of one, two, or even three HCl units from the molecular complex is present, to yield $Cl_2V(O)NH_2$, ClV(O)NH, and OVN, respectively. The bands due to species B maintained a constant intensity ratio in all of the experiments, including different irradiation times, and different sample concentrations. This indicates that only one product (other than HCl) is formed upon irradiation. Then, OVN can be ruled out on the basis that several of the set B product bands shifted upon deuteration, yet OVN has no hydrogen atoms. Thus, OVN cannot be responsible for the set B bands. The second species, ClV(O)NH would have one N−H stretching band (and it's deuterium counterpart would have one N−D stretching band). However, two strong bands were observed in the N−H stretching region, arguing against assignment to this species. Further, three bands were observed in the N−D stretching region; assignment to ClV(O)ND is not consistent with this observation. However, the first species $Cl_2V(O)NH_2$ is consistent with all of these observations. In the N−D stretching region, two N−D stretches are anticipated for $Cl_2V(O)ND_2$. In addition, the mixed species [$Cl_2V(O)NHD$] should be formed at the level of isotopic enrichment employed here, which would contribute a third band in the N−D stretching region. This mixed species would also lead to one new band in the N−H stretching region in the deuterated experiment, and one was observed, at 3403 cm^{-1}.

To further distinguished between these two possibilities ($Cl_2V(O)NH_2$ versus ClV(O)NH), theoretical calculations were undertaken as described below. The calculated spectra of these two species were compared to the experimental spectrum; as shown below, the fit to the computed spectrum of $Cl_2V(O)NH_2$ is much better. Therefore, the bands in set B, as listed in Table 2, are assigned to the single HCl elimination product from the 1:1 molecular complex, namely $Cl_2V(O)NH_2$. *This marks the first observation of this intermediate in the $OVCl_3/NH_3$ reaction system.*

TABLE 2: Band Positions and Assignments[a] for Argon Matrix Isolated $Cl_2V(o)NH_2$

$Cl_2V(O)^{14}NH_2$ (cm^{-1})	$Cl_2V(O)^{15}NH_2$ (cm^{-1})	$Cl_2V(O)^{14}ND_2$ (cm^{-1})	assignment
552	549	497[b]	torsion
748	733	701[b]	V−N stretch
1047	1047	1047[b]	V═O stretch
1488	1482	1127[b]	NH_2 bend
3330	3326	2431[b]	NH_2 sym stretch
3442	3437	2566[b]	NH_2 antisym stretch

[a] Bands were also observed at 2509 and 3403 cm^{-1} and are assigned to the N−D and N−H stretches of the partially deuterated species $Cl_2V(O)NHD$. [b] Nitrogen matrix positions.

Band Assignments

Band assignments for the 7 of the 8 observed bands of this complex are straightforward, based on their proximity to parent modes. These assignments are collected in Table 1, for the complexes of $OVCl_3$ with NH_3, $^{15}NH_3$, and ND_3. Of note is ν_2, the symmetric deformation or "umbrella" mode of NH_3. This mode has been shown many times[25,26] to be extremely sensitive to complexation and to shift to higher energy upon complex formation. In hydrogen bonding interactions, this mode has been observed to shift 25−100 cm^{-1} to higher energy, whereas in a Lewis acid−base complex, shifts of up to 400 cm^{-1} to higher energy have been observed; shifts of 200 cm^{-1} are typical. In solid argon, both the band at 1159 and the multiplet at 1202 cm^{-1} might be so assigned. Both show the exactly correct ^{15}N shift (4 cm^{-1}), and both shift strongly with deuteration. In as much as no other NH_3 modes are expected in this spectral region, and no Fermi resonance interactions involving ν_2 appear feasible, they are both assigned to the perturbed ν_2 mode in the 1:1 complex. The difference between the two may lie either in two slightly different conformations of the complex, leading to different band positions, or to two quite different matrix sites. Because a similar pair of bands was observed in N_2 matrices, site splitting seems less likely. Although this splitting appears large, the great sensitivity of ν_2 to complexation suggests that slightly different conformers might shown this magnitude of splitting.

In addition, one new band (the 8th band) was formed as a result of complexation, at 692 cm^{-1}. This band does not have its origins in a parent mode of either of the subunits in the complex. Rather, studies[25] have shown that complexed NH_3 undergoes a rocking motion when complexed; this motion has been observed[29] near 700 cm^{-1} for moderately strongly bound complexes of NH_3. This (and 5 lower frequency modes) arise from the loss of 3 translational and 3 rotational degrees of freedom upon complex formation. The others, including the V−N stretching mode, are expected to lie below the 400 cm^{-1} cutoff of the infrared spectrometer.

Assignment of the observed fundamentals of $Cl_2V(O)NH_2$ are made in concert with the theoretical calculations that will be described below. A torsional mode is calculated to lie, with substantial intensity, between 500 and 600 cm^{-1}, with a 3 cm^{-1} ^{15}N shift and a larger deuterium shift. The product band at 552 cm^{-1} in argon and 591 cm^{-1} in nitrogen meets these criteria and is so assigned. The band at 748 cm^{-1} in argon (752 cm^{-1} in nitrogen) lies very near a band computed at 763 cm^{-1} which corresponds to the V−N stretching mode. This mode is calculated to have a 13 cm^{-1} red shift with ^{15}N substitution and a 50 cm^{-1} red shift with deuterium substitution; experimental shifts of 15 and 50 cm^{-1}, respectively, were observed. This level of agreement is found throughout between the

TABLE 3: Key Computed Structure Parameters

parameter	$Cl_2V(O)NH_2$	$ClV(O)NH$
V−Cl	2.18 Å	2.21 Å
V=0	1.56 Å	1.58 Å
V−N	1.81 Å	1.66 Å
N−H	1.01 Å	1.02 Å
α (Cl−V−O)	110.9°	120.0°
α (Cl−V−Cl)	110.7°	
α (H−N−H)	112.7°	
spin multiplicity	1	

computed spectrum of $Cl_2V(O)NH_2$ and the experimental spectrum. The detailed assignments are collected in Table 2.

Theoretical Calculations

To assist in the assignment of the set B bands to $Cl_2V(O)NH_2$ versus ClV(O)NH, density functional calculations were undertaken, using the B3LYP functional and the 6-311G+(d, 2p) basis set. These calculations converged to stable structures for both species, indicating that these species are minima on their respective potential energy surfaces. Key structural parameters for both species are given in Table 3 whereas a comparison of the computed spectrum and isotopic shifts for each species is made in Table 4. Direct comparison between experiment and theory comes from the infrared spectrum. Of course, with fewer atoms, the computed spectrum of ClV(O)NH only has five bands above 500 cm^{-1}. One of these is computed to lie in the mid-900 cm^{-1} region with high intensity and a large (23 cm^{-1}) ^{15}N shift. *No product bands were seen in this region*. In addition, the computed spectrum does not contain any bands near 1500 cm^{-1}, whereas a band was observed experimentally near 1490 cm^{-1}. Of course, the computed spectrum only contains one N−H stretching mode, whereas two distinct bands were seen in that region. In the 700 cm^{-1} region, the computed spectrum of ClV(O)NH contains a band at 722 cm^{-1}, somewhat low of the band observed experimentally at 752 cm^{-1}. More important, the computed ^{15}N shift is 4 cm^{-1}, whereas the experimental shift was 15 cm^{-1}. The deuterium shift for this mode of ClV(O)NH was computed to be −165 cm^{-1}, whereas the experimental shift was only −53 cm^{-1}. Overall, the computed spectrum of ClV(O)NH is not in good agreement with the experimental spectrum. On the other hand, the computed spectrum of $Cl_2V(O)NH_2$ is in excellent overall agreement with experiment. The computed spectra of both species are listed in Table 4, along with comparison to the experimentally observed bands. Thus, assignment of the set B bands to $Cl_2V(O)NH_2$ is supported, and band assignments as indicated in Table 2 are made.

Further Considerations

Several matrix isolation studies[12−15] of the reaction mechanism of $OVCl_3$ and $CrCl_2O_2$ with small molecules all suggest that the first step in the reaction is the formation of a molecular complex, for those small molecules containing a heteroatom (N, O, P, S). This agrees with theoretical calculations as well.[3,4] The second step in each system studied has been HCl elimination. In several cases, this was observed to occur thermally, in a merged jet system, whereas in other cases (including the present study), the reaction was photochemically induced. For those systems that were photochemically driven to eliminate HCl, two different circumstances were noted in the merged jet experiment. In the first, typified by the $OVCl_3/CH_3SH$ system, no reaction was observed during the merged jet experiments. This suggests that the initial molecular complex is sufficiently weakly bound that the complex is largely dissociated in the gas phase at room temperature, so that subsequent HCl elimination cannot occur. Here, the cryogenic temperature of the matrix is required to produce significant amounts of the complex, and then photochemical excitation is needed.

In the second circumstance, including the present $OVCl_3/NH_3$ study, complete reaction appears to occur in the merged jet region, with no intermediates or products reaching the cold window. In the present study, it was clear that both reagents were present in the merged region because when the $OVCl_3$ stream was turned off, bands due to NH_3 grew in the matrix spectrum thereafter. It is likely that the complex forms in the gas phase, and although it is relatively strongly bound, the barrier to HCl elimination and then to further reaction is very low. Thus, the first and second intermediates are formed and destroyed in the merged region, and only nonvolatile stable products are produced. In these cases, it is difficult to prove that the same sequence of intermediates (i.e., mechanism) occurs in the thermal reaction and the photochemical reaction. However, in at least one case,[12] it has been shown clearly that the thermal and photochemical reactions follow the same pathway. Although not proven, it is likely here as well.

Finally, it is noteworthy that the twin jet co-deposition of $Ar/(CH_3)_3N$ with $Ar/OVCl_3$ led to essentially no product bands. Certainly, $(CH_3)_3N$ is known[30] to be more basic than NH_3, so that complexation is anticipated. However, $(CH_3)_3N$ is much bulkier than NH_3, and the region around the vanadium center

TABLE 4: Comparison of Computed and Experimental Band Positions and Shifts for $Cl_2V(O)NH_2$ and CLV(O)NH

			band position			^{15}N		$-ND_2$	
molecule	mode	*I*	unscaled	scaled (.97)	expt	comp shift	expt shift	comp shift	expt shift*
$Cl_2V(O)NH_2$	VCl_2 sym. st.	32	424	411		−1		−12	
	NH_2 twist	55	427	414		0		−90	
	torsion	52	479	465		−3		−98	
	VCl_2 asym. st	203	529	513	552	−1	−3	−25	−94
	NH_2 rock	6	635	616		−4		−126	
	V-N st.	94	763	740	748	−13	−15	−50	−53
	V═O st.	167	1121	1087	1047	0	−1	−2	0
	NH_2 bend	45	1523	1477	1488	−6	−6	−359	−357
	NH_2 sym. st	115	3513	3408	3330	−5	−4	−947	−886
	NH_2 asym. st.	55	3630	3521	3442	−11	−5	−922	−868
ClV(O)NH	V-Cl stretch	77	445	432		−1		−41	
	V═N-H bend	76	623	604		−5		−86	
	V═N-H bend	116	722	700		−4		−165	
	V═N stretch	133	968	939		−23		−16	
	V═O stretch	216	1083	1051		0		0	
	N-H stretch	74	3491	3396		−8		−933	

may be too sterically congested to permit formation of detectable amounts of the molecular complex.

Acknowledgment. The National Science Foundation is gratefully acknowledged for support of this research, through Grant No. CHE 9877076.

References and Notes

(1) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc*. **1992**, *114*, 4543.

(2) Yajima, A.; Matsuzaki, R.; Saeki, Y. *Bull Chem. Soc. Jap*. **1978**, *51*, 1098.

(3) Deng, L.; Ziegler, T. *Organometallics* **1996**, *15*, 3011.

(4) Deng, L.; Ziegler, T. *Organometallics* **1997**, *16*, 716.

(5) Ziegler, T.; Li, J. *Organometallics* **1995**, *14*, 214.

(6) Rappe, A. K.; Goddard, W. A., III *Nature* **1980**, *285*, 311.

(7) Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc*. **1982**, *104*, 3287.

(8) Elwin, G. S.; Parkin, I. P. *Chem. Vap. Deposition* **2000**, *6*, 59.

(9) Craddock, S.; Hinchliffe, A. *Matrix Isolation*; Cambridge University Press: Cambridge, 1975.

(10) Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; John Wiley: New York, 1973.

(11) Andrews, L.; Moskovitz, M., Eds. *Chemistry and Physics of Matrix Isolated Species*; Elsevier Science Publishers: Amsterdam, 1989.

(12) Ault, B. S. *J. Am. Chem. Soc*. **1998**, *120*, 6105.

(13) Infrared Matrix Isolation Study of the Reaction of $CrCl_2O_2$ with $(CH_3)_2O$ and $(CH_3)_2CO$, *J. Mol. Struc*. **2000**, *526*, 227.

(14) Ault, B. S. *J. Phys. Chem. A* **1999**, *103*, 11 474.

(15) Ault, B. S. *J. Phys. Chem. A* **2000**, *104*, 11 796.

(16) Ault, B. S. *J. Am. Chem. Soc*. **1978**, *100*, 2426.

(17) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3502.

(18) Gaussian 94, Revision E.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, M.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(19) Filgueira, R. R.; Fournier, L. L.; Varetti, E. L. *Spectrochim. Acta* **1982**, *38A*, 965.

(20) Abouaf-Marguin, L.; Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1977**, *67*, 34.

(21) Nelander, B. *Chem. Phys.* **1984**, *87*, 283.

(22) Goldfarb, T. D.; Khare, B. N. *J. Chem. Phys*. **1967**, *46*, 3379.

(23) Purnell, C. J.; Barnes, A. J.; Suzuki, S.; Ball, D. F.; Orville-Thomas, W. J. *Chem. Phys*. **1976**, *12*, 77.

(24) *Matrix Isolation Study of the Interaction of HCl with* $CrCl_2O_2$ *and* $OVCl_3$, *J. Mol. Struct.* **2000**, *526*, 97.

(25) Ault, B. S. *Rev. Chem. Intermed.* **1988**, *9*, 233.

(26) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997.

(27) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. *Trans. Faraday Soc*. **1969**, *65*, 3150.

(28) Maillard, D.; Schriver, A.; Perchard, J. P. *J. Chem. Phys*. **1979**, *71*, 505.

(29) *Matrix Isolation Studies of Lewis Acid/Base Interactions: Infrared Spectra of the 1:1 Adduct* $SiF_4 \cdot NH_3$; *Inorg. Chem*. **1981**, *20*, 2817.

(30) Henderson, W. G.; Taagepera, M.; Holtz, D.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc*. **1972**, *94*, 4728.