Matrix Isolation and Theoretical Study of the Photochemical Reaction of PH_3 with $OVCl_3$ and $CrCl_2O_2$

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The matrix isolation technique has been combined with theoretical calculations to identify and characterize the photoproducts in the reaction of PH_3 with $OVCl_3$ and $CrCl_2O_2$. In contrast to previous studies, HCl elimination from an initial complex is not observed. Instead, a number of product bands, some quite intense, were observed and have been assigned to phosphine oxide, H_3PO, through the direct O atom transfer from the transition metal oxo compound. This identification was supported by extensive isotopic labeling, and by comparison to theoretical calculations. H_3PO formed in this manner is cage-paired and interacts with the transition metal fragment (VCl_3 or Cl_2CrO), leading to a 113 cm^{-1} red-shift of the P=O stretching mode relative to isolated monomeric H_3PO.

Introduction

High-valent transition metal oxo compounds, including $OVCl_3$ and $CrCl_2O_2$, are very strong oxidizing agents and are known to oxidize a wide range of organic substrates. This oxidizing power has applications in catalysis as well as in organic synthesis.[1,2] While these compounds react, often vigorously, with a range of organic compounds and small second-row inorganic compounds (e.g., NH_3, H_2O), no mention is made in the literature of reaction with PH_3, and only a very few with substituted phosphines. For the most part, theoretical studies[3−7] of the reactivity of $OVCl_3$ and $CrCl_2O_2$ have also focused on second-row substrates, leaving a substantial gap in the understanding of the reactions of $OVCl_3$ and $CrCl_2O_2$.

The matrix isolation technique[8−10] 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[11−15] 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, as well as with NH_3 and H_2O. These studies have demonstrated that these reactions occur through the formation of an initial 1:1 complex, followed by thermal and/or photochemical elimination of HCl. While PH_3 is immediately below NH_3 in the periodic table, in many ways the chemistry of PH_3 is very different from that of NH_3. Consequently, to increase the understanding of reactions of third-row compounds with $OVCl_3$ and $CrCl_2O_2$, and specifically to compare directly the modes of interaction and reaction of PH_3 and NH_3 with $OVCl_3$ and $CrCl_2O_2$, a matrix isolation study was undertaken. Density functional calculations were also carried out in support of the experimental observations.

Experimental Details

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[16] Chromyl chloride, $CrCl_2O_2$ and $OVCl_3$ (both Aldrich), were introduced into the vacuum system as the vapor above the room-temperature liquid, after purification by freeze−pump−thaw cycles at 77 K. PH_3 (Matheson) and PD_3 (Aldrich, 98% D) were introduced into the vacuum manifold from lecture bottles, and were purified by repeated freeze−pump−thaw cycles at 77 K. Isotopically scrambled mixtures of PH_3, PH_2D, PHD_2, and PD_3 were synthesized through the reaction of Ca_2P_3 with mixtures of H_2O and D_2O, and purified by repeated freeze−pump−thaw cycles at 77 K. D/H ratios from 3/1 to 1/1 were prepared in this manner. Argon was used as the matrix gas in all experiments, and was 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. Several of these matrices were subsequently warmed to 33−35 K to permit limited diffusion and then recooled to 14 K, and additional spectra were 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.

A few 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/h from each sample manifold onto the cold window. Final spectra were recorded on either a Nicolet IR42 Fourier transform infrared spectrometer (early experiments) or a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer (later experiments) at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using the Gaussian 98W suite of programs.[18] Density functional calculations using the hybrid B3LYP functional were used to locate energy minima, determine structures, and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-311G+(d,2p) basis set,

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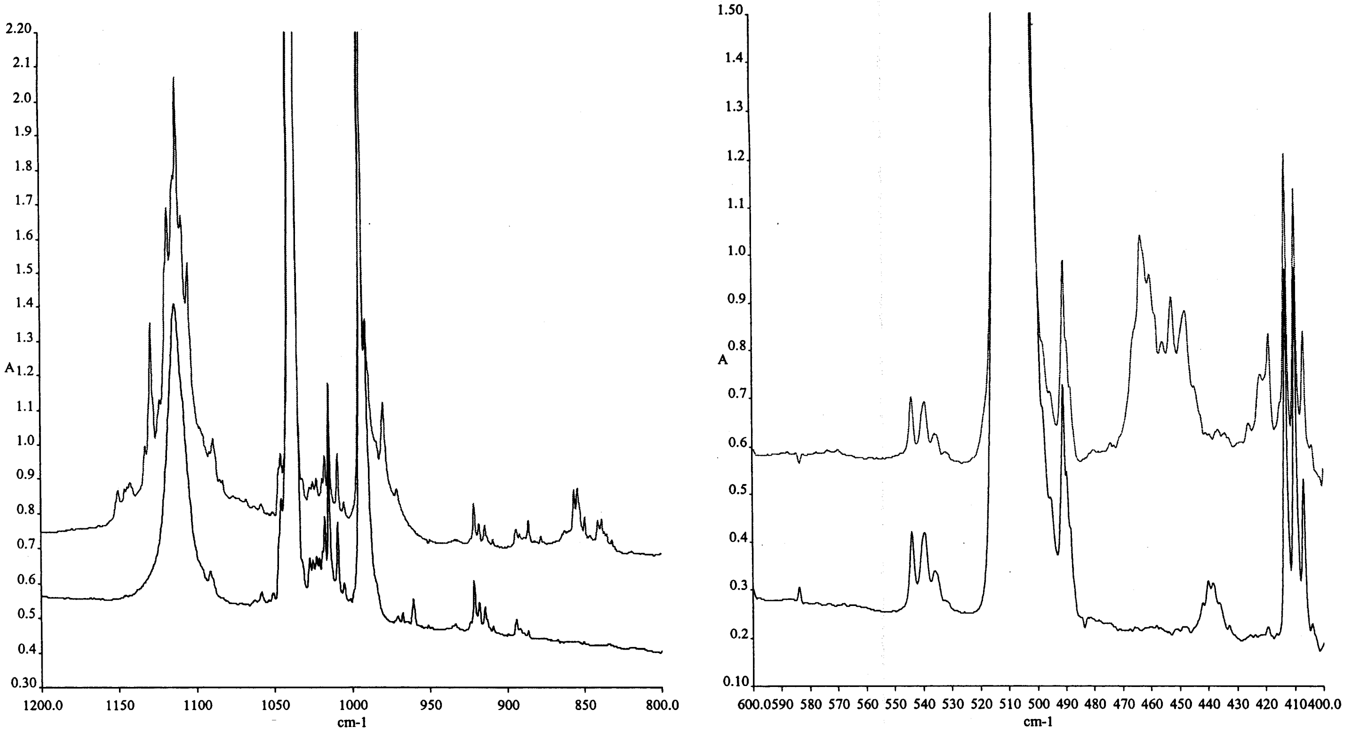

Figure 1. Infrared spectra, in the ranges 400−600 and 800−1200 cm^{-1}, of a matrix prepared by the twin-jet co-deposition of a sample of Ar/$OVCl_3$ = 250 with a sample of Ar/PH_3 = 250. The lower trace shows the spectrum of the matrix before irradiation, while the upper traces shows the spectrum after 1.5 h irradiation with light of $\lambda > 300$ nm.

after initial calculations with smaller basis sets were run to approximately locate energy minima.

Experimental Results

Prior to any co-deposition experiments, blank experiments were run on each of the reagents used in this study. In each case, the blanks were in good agreement with literature spectra[19−22] and with blanks run previously in this laboratory. Each blank experiment was then irradiated by the H_2O/Pyrex filtered output of a 200 W Hg arc lamp for 1.5 h. No changes were observed in any of the blank spectra as a result of irradiation. Very weak bands due to HCl impurity were noted in all of the $CrCl_2O_2$ and $OVCl_3$ blank experiments.[23]

PH_3 + $OVCl_3$. These two reagents were co-deposited in an initial twin jet experiment, with Ar/PH_3 = 250 and Ar/$OVCl_3$ = 500. No distinct new infrared absorptions were apparent upon initial matrix deposition, although two weak, broad features were seen near 442 and 950 cm^{-1}. When this matrix was annealed to 35 K and recooled, the resultant spectrum again showed no distinct new absorptions, although slight broadening of a number of the parent absorptions was noted. When this sample was then irradiated with the Pyrex/H_2O-filtered output of a medium-pressure Hg arc ($\lambda > 300$ nm), a number of new absorptions were apparent. The most intense of these was a multiplet with the most intense component at 1129 cm^{-1}, and an absorbance of approximately 0.3 OD. In addition, new bands were observed at 421, 457 (doublet), 835, 853 (multiplet), and 2438 cm^{-1}. At the same time, the weak, broad features near 442 and 950 cm^{-1} disappeared. Of particular note was the absence of any new absorptions between 2600 and 2900 cm^{-1}, despite a careful search.

This experiment was repeated more than 20 times, using a wide range of sample concentrations (from 1000/1 to 100/1) for each reagent, along with several different irradiation times, from 10 min to 3 h. All of these experiments resulted in essentially identical spectra; the multiplet patterns varied slightly, as did bandwidths, but the number of new bands, their locations and their relative intensities remained constant throughout all of these experiments. In the most productive experiments, the multiplet near 1129 cm^{-1} had an intensity as high as 1.0 OD. In each experiment, a careful search was conducted between 2600 and 2900 cm^{-1}. The only features that were ever observed in this region after irradiation were very weak bands at 2750 and 2768 cm^{-1}, due to the photoreaction[15] of $OVCl_3$ with traces of H_2O impurity. The intensity of these bands (always very weak when detected at all) were proportional to the level of H_2O impurity in the matrix, and not proportional to the PH_3 concentration. Figure 1 shows the spectra obtained from a representative twin jet experiment.

The reaction of this pair of reagents was also explored in several merged-jet experiments, using a range of sample concentrations. With the merged region or reaction zone held at room temperature, the resulting spectrum was identical to that observed in the twin-jet experiments (i.e., no products, other than the weak, broad features near 442 and 950 cm^{-1}). In subsequent experiments in which the merged region was heated stepwise to as high as 200 °C, identical results were obtained. Irradiation of these matrices thereafter resulted in the growth of the same set of product bands described above, with the same relative intensities.

$OVCl_3$ + PD_3, PH_xD_y, $x + y = 3$. Since merged-jet and twin-jet deposition gave rise to identical results, the remaining experiments for this pair of reagents were conducted in the twin-jet mode. When a sample of Ar/PD_3 = 250 was co-deposited with a sample of Ar/$OVCl_3$ = 500, the only new feature was a weak, broad band near 442 cm^{-1}. When this matrix was then irradiated with light of $\lambda > 300$ nm, the weak feature at 442 cm^{-1} was destroyed, and a set of new absorptions grew in. The most intense of these was a multiplet with the most intense component at 1101 cm^{-1}, and with an intensity of approximately

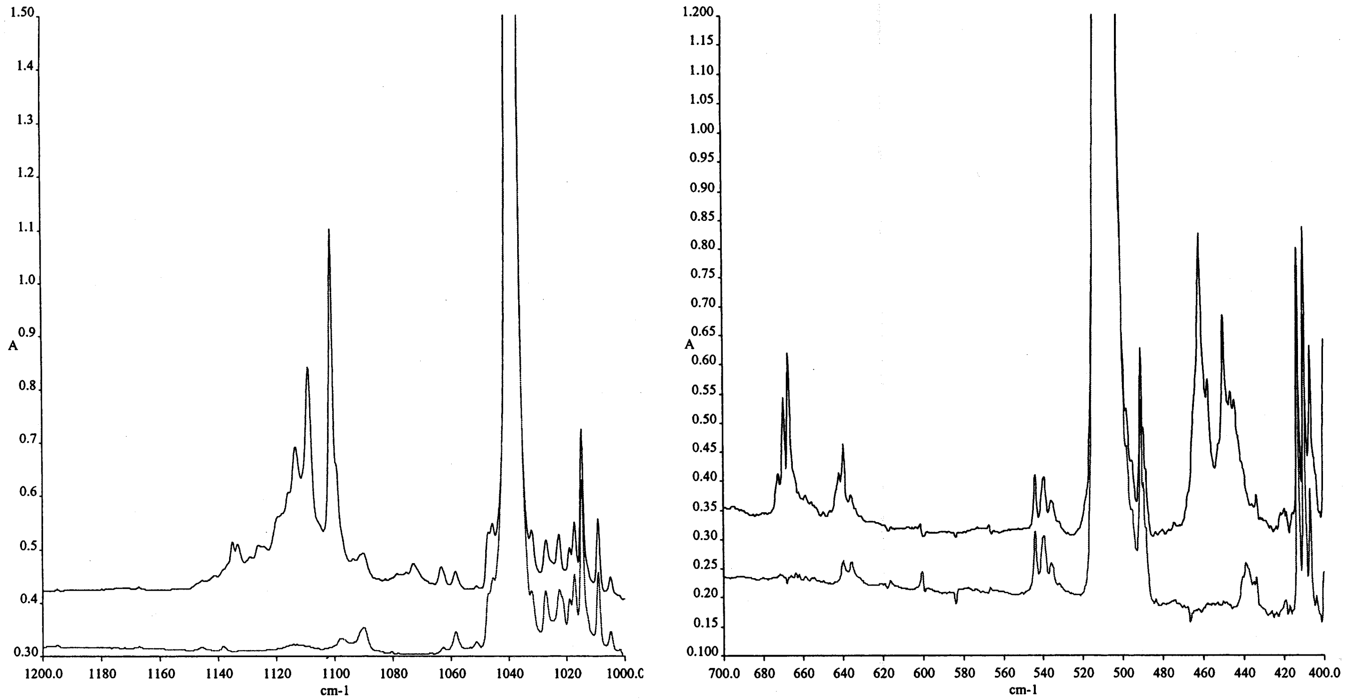

Figure 2. Infrared spectra, in the ranges 400−700 and 1000−1200 cm^{-1}, of a matrix prepared by the twin-jet co-deposition of a sample of Ar/OVCl$_3$ = 250 with a sample of Ar/PD$_3$ = 250. The lower trace shows the spectrum of the matrix before irradiation, while the upper traces show the spectrum after 1.5 h irradiation with light of λ > 300 nm.

0.30 OD. Additional bands were observed at 457 (doublet), 640, 668 (multiplet), and 1757 cm^{-1}. A careful search was conducted in the region 1900−2200 cm^{-1}, and no new bands were seen in this region. This experiment was repeated approximately 10 times, using a range of sample concentrations from 1000/1 to 100/1. In every experiment, the results were essentially identical, with the one weak feature before irradiation, the destruction of this feature after irradiation, and the growth of the above set of product bands. These bands maintained a constant intensity ratio with respect to one another throughout these experiments. Figure 2 shows the spectra obtained from a representative experiment with this pair of reagents.

Samples of Ar/OVCl$_3$ were co-deposited with isotopically scrambled samples of Ar/PH$_x$D$_y$, $x + y = 3$ in several experiments. After initial deposition, only the single weak feature near 442 cm^{-1} was observed. When this matrix was subsequently irradiated with light of λ > 300 nm, product bands were again observed, although with overall reduced intensity, since the total intensity is spread over a number of different isotopic combinations. In the lower energy region, the product bands at 640 and 668 cm^{-1} observed in the OVCl$_3$ + PD$_3$ experiments were again observed, as well as the bands at 835 and 853 cm^{-1} observed in the OVCl$_3$ + PH$_3$ experiments (above). In addition, new bands were seen at 706 and 814 cm^{-1}, with somewhat greater intensity. In the 1100 cm^{-1} region, overlapping multiplets between approximately 1090 and 1140 cm^{-1} were observed. Some components of the multiplet match those in the earlier OVCl$_3$ + PH$_3$ and OVCl$_3$ + PD$_3$ experiments, while some appeared new. The region was sufficiently congested that definitive conclusions were not clear. This experiment was repeated twice and quite similar results were obtained. Table 1 summarizes band positions seen after irradiation of matrices containing OVCl$_3$ and PH$_3$ (and its isotopomers).

CrCl$_2$O$_2$ + PH$_3$. This pair of reagents was co-deposited in a series of experiments similar to those described above for the OVCl$_3$ + PH$_3$ system. Both twin-jet and merged-jet modes were employed, and led to identical results. Specifically, no distinct bands were seen after initial deposition, at any set of reagent concentrations. After these matrices were irradiated with light of λ > 300 nm, a set of new bands grew in, at 416, 442, 835, 854, 1126, and 2441 cm^{-1}. These are very close to, but not identical to, the bands produced above for the OVCl$_3$ + PH$_3$ system. Moreover, the relative intensities were very similar, with the multiplet near 1126 cm^{-1} being the most intense. Again, a careful search was done in the region 2600−2900 cm^{-1}, and no new product bands were observed. This set of bands was seen in all of the experiments, twin-jet and merged-jet, and with a constant intensity ratio.

TABLE 1: Band Positions and Assignments for Bands Formed by Irradiation of Argon Matrices Containing PH$_3$ and Its Isotopomers, and OVCl$_3$

PH$_3$ + OVCl$_3$	PD$_3$ + OVCl$_3$	PH$_x$D$_y$ + OVCl$_3$	PH$_3$O[d]	assignment
421 cm^{-1}				VCl$_3$ sym. st.
457	457	457		VCl$_3$ antisym. st.
835	640	640, 835		H−P−O bend[c]
		706, 814		H−P−O bend, H$_x$D$_y$PO
853	668	853, 668	853	H−P−O bend
1129[a]	1101[a]	1101, 1129[b]	1240	P=O stretch
2438	1757		2372	PH$_3$ antisym. st.

[a] Multiplet. [b] Overlapping multiplets. [c] The H−P−O bend is doubly degenerate for the isolated molecule and split when complexed to VCl$_3$, see text. [d] Ref 27.

CrCl$_2$O$_2$ + PD$_3$, PH$_x$D$_y$, $x + y = 3$. The co-deposition of samples of Ar/CrCl$_2$O$_2$ and Ar/PD$_3$ led to very similar results, with isotopic shifting of some of the product bands. Again, no new bands were evident after initial deposition, while irradiation produced a set of new bands, at 414, 442, 650, 669, 1100, and 1758 cm^{-1}. Several of these were split into multiplets, as above. The 1100 cm^{-1} multiplet was the most intense of the group, with intensities approaching 0.7 OD. in the most productive experiments. No product bands were observed in the region 1900−2200 cm^{-1}. These bands also maintained a constant

TABLE 2: Band Positions and Assignments for Bands Formed by Irradiation of Argon Matrices Containing PH_3 and Its Isotopomers, and $CrCl_2O_2$

PH_3 + $CrCl_2O_2$	PD_3 + $CrCl_2O_2$	PH_xD_y + $CrCl_2O_2$	PH_3O[d]	assignment
416 cm^{-1}	414			Cl_2CrO sym. st.
442	442			Cl_2CrO antisym. st.
835	650	640, 835		H−P−O bend[c]
		706, 813		H−P−O bend, H_xD_yPO
854	669	853, 668	853	H−P−O bend
1126[a]	1100[a]	1101, 1129[b]	1240	P=O stretch
2441	1758		2372	PH_3 antisym. st.

[a] Multiplet. [b] Overlapping multiplets. [c] H−P−O bend is doubly degenerate for the isolated molecule and split when complexed to Cl_2CrO, see text. [d] Ref 27.

TABLE 3: Calculated[a] Band Positions[b] for Potential Product Species in the Photochemical Reaction of $OVCl_3$ and PH_3

$Cl_2V(O)$-PH_2	(I)[c]	$Cl_2V(O)$-PD_2	Cl_3V-$(OH)PH_2$	(I)[c]	$Cl_2V(O)$-PHCl	(I)[c]	$Cl_2V(O)$-PDCl
429 cm^{-1}	(52)	*d*	424	(265)	426	(83)	*d*
436	(39)	*d*	452	(87)	464	(33)	434
522	(102)	519	584	(11)	482	(56)	476
578	(3)	455	664	(180)	532	(84)	523
1085	(20)	780	680	(6)	834	(15)	605
1114	(149)	1114	778	(121)	1109	(158)	1109
2371	(15)	1700	1131	(19)	2366	(17)	1700
2390	(16)	1719	2417	(14)			
			2430	(18)			
			3760	(214)			

[a] Calculated at B3LYP/6-311G+(d,2p) level of theory; listed frequencies are unscaled. [b] Band positions in cm^{-1}, only bands above 400 cm^{-1} are listed. [c] Intensity, in km/mol. [d] Below 400 cm^{-1}.

intensity ratio with respect to one another over the series of experiments that were conducted with this pair of reagents.

Samples of Ar/$CrCl_2O_2$ were co-deposited with isotopically scrambled samples of Ar/PH_xD_y, $x + y = 3$ in several experiments. Again, no distinct new bands were observed after initial deposition. When this matrix was subsequently irradiated with light of $\lambda > 300$ nm, product bands were again observed, although with overall reduced intensity, as with $OVCl_3$. In the lower energy region, the bands at 640 and 668 cm^{-1} seen in the $CrCl_2O_2 + PD_3$ experiments were observed weakly, along with the bands at 835 and 854 cm^{-1} seen in the $CrCl_2O_2 + PH_3$ experiments. In addition, new features were seen at 706 and 813 cm^{-1}. These results were reproduced in a second experiment at different concentrations. Table 2 summarizes band positions seen after irradiation of matrices containing $CrCl_2O_2$ and PH_3 (and its isotopomers).

Results of Calculations

As will be discussed below, there are a number of possible products for these two systems, including such species as $Cl_2V(O)PH_2$, $Cl_3V(OH)PH_2$, and $Cl_2V(O)PHCl$, corresponding to HCl elimination, hydrogen shift, and H_2 elimination products. Also possible are species such as H_3PO and H_2POH, which have been characterized in low-temperature matrices. For the first three species there are chromium analogues as well (potentially arising from the reaction of $CrCl_2O_2$ with PH_3). For all of the novel metal-containing species, DFT calculations were undertaken using the B3LYP hybrid functional and basis sets as high as 6-311G+(d,2p). All of these compounds optimized to energy minima on their respective potential energy surfaces, with all positive vibrational frequencies, as listed in Table 3. Vibrational frequencies were also calculated for the normal isotope, the completely deuterated isotopomer, and the mixed H/D isotopomer, for comparison to experimental spectra. Finally, since the spectra of H_2DPO and HD_2PO are not completely known experimentally, they were calculated as well.

Discussion

Co-deposition of PH_3 and its isotopomers with either $OVCl_3$ or $CrCl_2O_2$ into argon matrices did not lead initially to any distinct product bands. Two weak, broad features were seen in the $OVCl_3$ experiments, while nothing was apparent in the $CrCl_2O_2$ experiments. However, irradiation of these matrices, with or without annealing, led to growth of very distinct product bands. In fact, the bands in the $CrCl_2O_2 + PH_3$ experiments were very similar in position and intensity to the bands produced in the $OVCl_3 + PH_3$ experiments, suggesting that the products in these two systems are quite similar, if not identical. These photoproduct bands required the presence of both PH_3 and $OVCl_3$ (or $CrCl_2O_2$). Since the matrix is rigid at the time of irradiation, this result strongly suggests that the PH_3 and $OVCl_3$ molecules are trapped within the same matrix cage or site. Moreover, the product bands persisted in very low concentration experiments, such as when Ar/PH_3 = 1000 and Ar/$OVCl_3$ = 1000. At these dilutions, the likelihood of trapping two of one kind of molecule and one of the other in the same cage is very small, while the likelihood of trapping one molecule of PH_3 with one molecule of $OVCl_3$ is relatively much more probable. While it is possible to have some sites with 1:1 stoichiometry and some sites with 1:2 stoichiometry, this is likely to lead to two different photoproducts. However, the fact that all of the bands due to the photoproduct(s) maintained a constant intensity ratio with respect to one another over a range of different sample concentrations suggests that this is not occurring. Rather, it is very likely that the stoichiometry within the matrix cage or site leading to photochemical reaction is 1:1, i.e., one molecule of PH_3 and one molecule of $OVCl_3$ (or $CrCl_2O_2$). Whether this might be described as a very weak molecular complex or simply a cage pair is unclear, although it is likely that there is some weak, perhaps nonspecific, interaction between the two species.

This result is overall similar to that seen in studies[11−15] of the reactions of $OVCl_3$ and $CrCl_2O_2$ with second row (stronger) Lewis bases, including NH_3 and CH_3OH. In those cases, the initial species was a well-defined 1:1 complex, which was then photochemically converted to product. In each of the previous systems studied, the same reaction mechanism was observed, namely HCl elimination from the complex and formation of a novel transition metal species (e.g., $OVCl_3 + NH_3 + h\nu \rightarrow Cl_2V(O)NH_2 + HCl$). In these cases, the HCl was trapped in the same matrix site with the transition metal species, and weakly hydrogen-bonded. Thus, bands due to HCl were observed in the range 2740−2810 cm^{-1}, depending on the product rather than at 2863 and 2888 cm^{-1}, the location of isolated monomeric HCl in solid argon.[24]

In the present study, a careful search was made between 2600 and 2900 cm^{-1} for HCl and between 1900 and 2200 cm^{-1} for DCl in the PD_3 experiments. No evidence at all was seen to indicate photoproduction of HCl. Moreover, the HCl elimination products in these systems would be $Cl_2V(O)PH_2$ and $ClCr(O)_2PH_2$. The infrared spectra calculated theoretically for these two species were very substantially different from the experimentally observed spectra. This is consistent with the lack of observation of HCl, and demonstrates that *$Cl_2V(O)PH_2$ is not the photoproduct is this system.*

Multiple possible products might be envisioned for this reaction, three of which involve formation of a V−P bond. These are $Cl_3V(OH)PH_2$ through hydrogen transfer to the oxo group, $Cl_2V(O)PHCl + H_2$ through H_2 elimination, and Cl_3VPH through H_2O elimination. All three are novel species, for which experimental data are not available (other than the production of H_2O in the last case). Bands due to H_2O did not grow upon irradiation,[25,26] indicating that Cl_3VPH can be eliminated as a possible photoproduct. Likewise, $Cl_3V(OH)PH_2$ and $Cl_2V(O)PHCl$ can be eliminated as possible products since the calculated spectra for each were not consistent with the observed spectrum. The same arguments hold for the analogous chromium species $Cl_2V(O)(OH)PH_2$, $ClCr(O)_2PHCl$, and $Cl_2Cr(O)PH$, and these species can be eliminated.

Direct reaction of $OCVl_3$ and PH_3 to form $H_3PO + VCl_3$, $H_2POH + VCl_3$, or $HPO + H_2 + VCl_3$ remain as possibilities. The last option can be eliminated, on the basis of the observation of intermediate species in the scrambled Ar/PH_xD_y, $x + y = 3$ experiments which requires the presence of at least two hydrogens in the product. Also, HPO has been observed in matrices on two occasions,[27,28] and the spectra recorded do not match the spectra observed here. Andrews[27] has observed both H_3PO and H_2POH in argon matrices, although not cage paired with VCl_3 (or Cl_2CrO) as must occur in the current experiments. This cage pairing or complexation should lead to perturbations to one or more modes of the species, but there should be some general correspondence between Andrews's spectra and those recorded here. In fact, the spectra recorded here for both $OVCl_3 + PH_3$ and $CrCl_2O_2 + PH_3$ are quite similar to that obtained by Andrews for H_3PO. In contrast, there is a very poor match between the present spectra and those reported by Andrews for H_2POH, thus eliminating H_2POH as the photoproduct.

The spectra obtained here match very well the reported spectrum of H_3PO, with the exception of the P═O stretch. This mode was observed by Andrews at 1242 cm^{-1}, slightly more than 100 cm^{-1} higher than the 1129 cm^{-1} band observed here. However, the deuterium shift, approximately 28 cm^{-1} here, is close to Andrews shift of 23 cm^{-1} and the 39 cm^{-1} calculated shift. The remaining fundamentals match very well. In addition, in the lower energy region, two bands were observed in the mixed H/D isotopic experiments, at 708 and 814 cm^{-1} for $OVCl3 + PH_xD_y$ and similarly at 706 and 813 cm^{-1} for $CrCl_2O_2 + PH_xD_y$. These two species must correspond to the two mixed isotopic species HD_2PO and H_2DPO, verifying the presence of 3 hydrogen atoms in the photoproduct. Thus, agreement between the present work and Andrews study is excellent, except for the P═O stretching mode.

VCl_3 (or Cl_2CrO), the second product of this reaction, is known to be a strong Lewis acid,[29−31] forming complexes with a number of electron donors, including $(CH_3)_3N$ and $(CH_3)_3P$. While little is known about the coordination chemistry of H_3PO, $(CH_3)_3PO$ is a strong Lewis base, and coordinates through the oxygen atom to Lewis acids.[32−34] In doing so, red-shifts between 70 and 110 cm^{-1} have been reported in complexes to transition metal centers.[32−34] This provides a rationale for the 100+ cm^{-1} shift observed here, and the very slight differences in the spectra for the $OVCl_3 + PH_3$ and $CrCl_2O_2 + PH_3$ systems, since VCl_3 is the Lewis acid partner in the former case, and Cl_2CrO in the latter case. This also accounts for the differences between 400 and 500 cm^{-1}, where the V−Cl and Cr−Cl stretching modes occur. Finally, Limberg[35] has reported oxygen atom transfer from $CrCl_2O_2$ to olefins in argon matrices as a result of irradiation, leading to epoxides interacting with Cl_2CrO. His observations support oxygen atom transfer and then complexation in the present study. All of these arguments strongly support identification of H_3PO as the photoproduct in both the $OVCl_3 + PH_3$ and $CrCl_2O_2 + PH_3$ systems, complexed to or interacting with the transition metal-containing product (VCl_3 or Cl_2CrO) in the matrix cage.

With this identification, band assignments to the observed bands here are straightforward, based on comparison to Andrews's earlier study.[27] These are compiled in Tables 1 and 2. One point to note is that in the present study, two bands were observed near 850 cm^{-1} (835 and 854 cm^{-1}), while Andrews observed only one, at 853 cm^{-1}. A similar result was seen in the PD_3 experiments, with two bands at 640 and 668 cm^{-1}, while Andrews observed only one, at 656 cm^{-1}. These bands are assigned to the H−P−O bending mode, which is largely hydrogenic in character. For free H_3PO, this mode is doubly degenerate. However, when H_3PO interacts with a Lewis acid, particularly in a matrix cage, this mode is very likely to split into two components, as observed here. This point is supported by the fact that in complexes of $(CH_3)_3PO$ with transition metal centers, the P−O−M bond angle is typically around 140°, so that the C_3 symmetry axis is lost, and doubly degenerate modes split into two components.[33,34]

The net reaction, $H_3P + Cl_3VO \rightarrow H_3PO{\bullet}VCl_3$, corresponds to the direct transfer of an oxygen atom from one reaction to the other, i.e., direct oxidation. In all of the reactions of Cl_3VO and $CrCl_2O_2$ with small organic and inorganic substrates studied in matrices to date,[11−15] this mechanism of reaction has *not* been observed. [in one system currently under investigation, oxygen atom transfer has been observed, both photochemically in matrices and thermally in the gas phase]. Rather the primary mechanism of reaction has been HCl elimination from the initial complex, and addition of the second fragment to the metal center. Theoretical calculations[3−5] have suggested the alternative possibility of H atom transfer to the oxo group, with addition of the remaining fragment to the metal center. Neither of these mechanisms were observed here. It is likely in the current system that the hydrogens in PH_3 are not sufficient active to lead to HCl elimination, further demonstrating the differences in reactivity between NH_3 and PH_3. *Thus, this study represents the first direct O atom transfer reaction involving Cl_3VO in cryogenic matrices.*

It is important to note that during merged jet deposition, where the reactants have longer times to mix and potentially react thermally in the gas phase, the reaction to form $H_3PO + VCl_3$ did not occur. This may be due to kinetics, with the reactant molecules having insufficient thermal energy at 298 K to overcome the activation barrier to the oxygen transfer reaction. Alternatively, the lack of reaction may be due to thermodynamic considerations, if the net reaction is endothermic. The observation that the oxygen atom transfer reaction occurs photochemically within a matrix cage indicates that the energy of the absorbed photon is sufficient to overcome any activation barrier that may be present. The enthalpy of interaction between H_3PO and VCl_3, combined with stabilization by the matrix environment, is then sufficient to overcome the endothermicity, if any, of the overall reaction. The result here demonstrates the unique ability of the matrix cage effect to permit synthesis of novel species (a complex in this case) which cannot be formed by conventional methods.

The primary indicator of complex formation between the two species in the matrix cage was the strong (100+ cm^{-1}) red-shift of the P═O stretching mode relative to isolated H_3PO. While a significant shift, this magnitude is not unusual for matrix-isolated complexes, or for transition metal complexes in general. As noted above, complexes of the related species $(CH_3)_3PO$ with transition metal centers show a red-shift between 70 and 110 cm^{-1}. In matrices, shifts of up to 400 cm^{-1} have been observed for particularly sensitive modes of subunits in molecular complexes (e.g., the symmetric deformation mode ν_2 of NH_3).[36] A more direct comparison might be to the approximately 50 cm^{-1} red-shift of the C═O stretch[37] of $(CH_3)_2CO$ complexed to $OVCl_3$. Since the magnitude of the shift of a particular mode in a series of complexes generally increases with the strength of interaction in the complex, the 100+ cm^{-1} shift observed here is indicative of a strong interaction between the subunits in the matrix-isolated complex. To the degree that the P═O stretch in H_3PO can be approximated as a P═O diatomic oscillator, the 100+ cm^{-1} red-shift observed here corresponds to a roughly 18% reduction in the stretching force constant. Clearly, this represents a substantial perturbation to the H_3PO subunit in the complex.

Conclusions

The photochemical reaction between the transition metal oxo compounds $OVCl_3$ and $CrCl_2O_2$ and PH_3 leads to oxygen atom transfer, and formation of phosphine oxide, H_3PO in argon matrices. This species is cage-paired and strongly interacts with the transition metal fragment (VCl_3 or Cl_2CrO). This reaction mechanism differs from the previously studied systems from this la1995, *14*, 214.

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