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Matrix Isolation and Theoretical Study of the Reaction of Substituted Phosphines with $CrCl_2O_2$

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The reactions between CrO_2Cl_2 and a series of substituted phosphines have been investigated using matrix isolation infrared spectroscopy. For all of the phosphines except PF_3, twin jet co-deposition of the two reagents into argon matrices at 14 K initially led to the formation of weak bands due to the corresponding phosphine oxide. For all of the phosphines, subsequent irradiation with light of $\lambda > 300$ nm led to the growth of a number of intense new bands that have been assigned to the phosphine oxide complexed to $CrCl_2O$, following an oxygen atom transfer reaction. Gas-phase, merged jet reactions prior to matrix deposition led to a significant yield of the uncomplexed phosphine oxide. Theoretical calculations at the B3LYP/6-311++g(d,2p) level were carried out in support of the experimental work, to support product band assignments and clarify the nature of the molecular complexes.

Introduction

High-valent transition-metal oxo compounds, including $CrCl_2O_2$, are very strong oxidizing agents and are known to oxidize a wide range of organic substrates.[1,2] Of particular interest is the selectivity of the oxidation of organic compounds and the specificity of the product(s) formed, as these metal oxo compounds are able to transfer an oxygen atom to certain olefins and hydrocarbons.[3−12] In contrast, the reactions of $CrCl_2O_2$ with silanes, phosphines, and arsines are not well studied even though substituted phosphine oxides are analogs of nerve agents such as sarin.[13,14] Possible reactions include valence expansion and addition, and bond insertion (such as to form a silanol from the corresponding silane). Extensive theoretical calculations of the potential energy surfaces for the reactions of $CrCl_2O_2$ with small substrates have been conducted.[10,11,15−17] Finally, while much of the experimental work has been done in solution, only a few studies have explored the reactions of $CrCl_2O_2$ in the gas phase.

The matrix-isolation technique[16−18] was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates and may provide access to the study of initial intermediates in the above reactions. Recent matrix isolation studies from this laboratory have investigated the thermal and photochemical reactions of high-valent transition-metal compounds, including $CrCl_2O_2$, with a number of small organic and inorganic substrates. Three classes of reactions have been observed to date, the first of which is formation of an initial complex, followed by HCl elimination from the complex and addition of the organic (or inorganic) fragment to the metal center to retain a four-coordinate complex.[19,20] The second is oxygen atom transfer from the metal center to the substrate, leading to an oxidized substrate species, such as through the oxidation of a carbon−carbon multiple bond to a ketone or ketene (e.g., the oxidation of ethyne to ketene).[21−24] The third class is the insertion of an oxygen atom into a X−H bond (X= C, Si) to form an alcohol).[25] When the second or third reactions occurred as a result of irradiation after deposition, the two species (e.g., $CrCl_2O$ and oxidized substrate) then formed a relatively strongly bound complex. The aim of the present study was to investigate the reactions of CrO_2Cl_2 with a series of substituted phosphines to determine the mechanism(s) of reaction and whether phosphine oxides would formed in this manner. High-level theoretical calculations were employed to complement the experimental data.

Experimental Details

All of the experiments in this study were conducted on a conventional matrix isolation apparatus that has been described previously.[26] Chromyl chloride, CrO_2Cl_2 (Acros Organics), was introduced into the vacuum system as the vapor above the room-temperature liquid, after purification by freeze−pump−thaw cycles at 77 K. PF_3 (Ozark-Mahoning) was introduced into the vacuum manifold from a lecture bottle, while PCl_3, PBr_3, CH_3PCl_2, and $(CH_3)_2PCl$ (all Aldrich) were introduced into the vacuum manifold as the vapor above the room-temperature liquid and purified by repeated freeze−pump−thaw cycles at 77 K. Argon was used as the matrix gas 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 brief mixing time prior to matrix deposition. These matrices were then irradiated for 2 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 on a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer at 1 cm^{-1} resolution. In the merged-jet experiments the two deposition lines were joined with an Ultratorr tee approximately 90 cm from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region.[27] This region could be heated to temperatures as high as 200 °C.

Theoretical calculations were carried out using the Gaussian 03 and 03W suites of programs.[28] Density functional calculations using the B3LYP functional were used to locate energy minima, determine structures, and calculate vibrational spectra of potential intermediate species. Final calculations with full geometry optimization employed the 6-311++G(d,2p) basis set,

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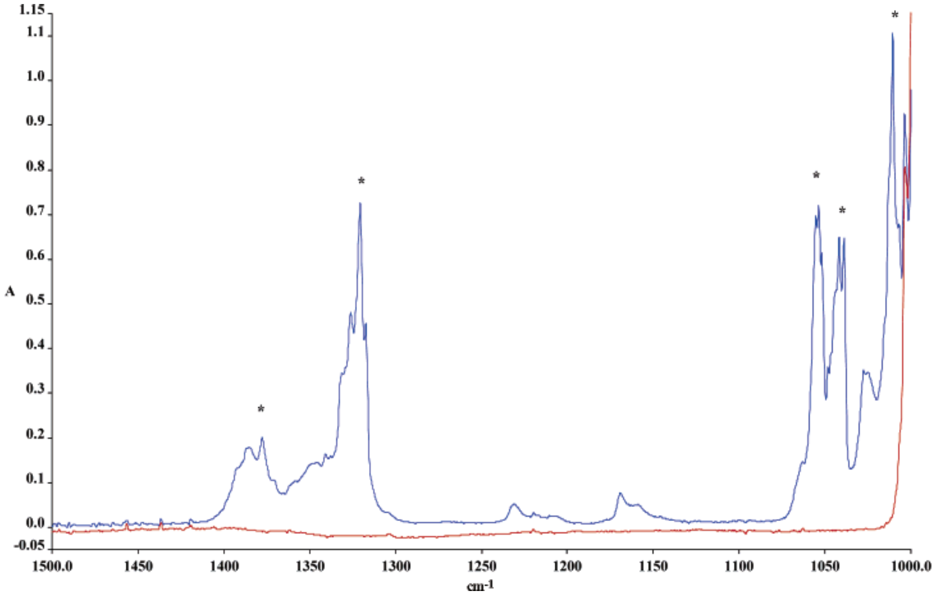

Figure 1. Infrared spectra before (lower) and after (upper) irradiation of argon matrices formed by the twin-jet deposition of samples of Ar/PF_3 and $Ar/CrCl_2O_2$. The band marked with an asterisk denotes the major product bands.

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

Results

Prior to any co-deposition experiments, blank experiments were conducted on each of the reagents used in this study. In each case the blanks were in good agreement with literature spectra[29−34] 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 2 h. No changes were observed in any of these spectra as a result of irradiation.

$CrCl_2O_2$ + PF_3. In an initial twin jet experiment, a sample of $Ar/CrCl_2O_2 = 250$ was co-deposited with a sample of $Ar/PF_3 = 500$. After 22 h of deposition, no new absorptions were noted in the spectrum. This matrix was then irradiated for 2 h with light of $\lambda > 300$ nm. Numerous new peaks were seen in the resulting spectrum, with the most intense features appearing at 449, 524, 1011, 1042, 1054, 1321 (multiplet), and 1378 cm^{-1}, as shown in Figure 1 and listed in Table 1.

This initial experiment was repeated several times, using a range of sample concentrations for each reagent, along with different irradiation times. Similar product bands were seen in all of these experiments, with product band intensities that varied directly with the concentration of the reagents. The product bands also maintained a relatively constant intensity ratio with respect to one another. One of these matrices was also annealed to 32 K, recooled, and a scan recorded (after initial deposition and before irradiation). No changes were observed as a result of annealing.

TABLE 1: Product Bands and Assignments after Irradiation of Argon Matrices Containing PF_3 and $CrCl_2O_2$

exptl[a]	calcd[b]	calcd[c]	lit[d]	assignment
449	436			$F_3PO{-}CrCl_2O$, Cr—Cl stretch
		441	473	F_3PO, δ (PF_3)
		454	485	F_3PO, δ (PF_3)
489	457			$F_3PO{-}CrCl_2O$, δ (PF_3)
524	515			$F_3PO{-}CrCl_2O$, δ (PF_3)
		815	873	F_3PO, P—F stretch
861	839			$F_3PO{-}CrCl_2O$, P—F stretch
		929	990	F_3PO, P—F stretch
990	968			$F_3PO{-}CrCl_2O$, P—F stretch
1046	990			$F_3PO{-}CrCl_2O$, P—F stretch h
1011	1135			$F_3PO{-}CrCl_2O$, Cr═O stretch
1321	1290			$F_3PO{-}CrCl_2O$, P═O stretch
		1388	1415	F_3PO, P═O stretch

[a] Twin-jet experiment. [b] Calculated for the $F_3PO{-}CrCl_2O$ complex, unscaled. [c] Calculated for F_3PO, unscaled. [d] From ref 38.

Experiments were also conducted in which the two reagents were deposited in the merged-jet mode at similar concentrations. When the merged region was kept at room temperature, no reaction products were observed. In two additional experiments, the merged or reaction region was heated, first to 120 °C and then to 170 °C. Final spectra in these experiments did not contain any new product bands.

$CrCl_2O_2$ + PCl_3, PBr_3. In an analogous manner, twin jet and merged jet experiments were conducted with $CrCl_2O_2$ and PCl_3. In each of the twin jet experiments, weak new absorptions were noted upon initial deposition (i.e., before irradiation), a doublet at 590 and 597 cm^{-1} and a multiplet near 1300 cm^{-1}, with the most distinct component at 1302 cm^{-1}. These initial product bands were unchanged by irradiation for 2 h with light of $\lambda > 300$ nm. However, many new product bands grew in upon irradiation, the most intense of which were located at 447, 629, 633, 1009, and 1215 cm^{-1}. All of the product bands are listed in Table 2 and shown in Figure 2. The results were consistent and reproducible in all of the twin jet experiments, with band intensities that varied directly with the sample concentrations.

TABLE 2: Product Bands and Assignments after Merged and Twin-Jet Deposition of PCl_3 and $CrCl_2O_2$ into Argon Matrices

exptl	calcd[a]	calcd[b]	lit[c]	assignment
447[d]	436			$Cl_3PO{-}CrCl_2O$
	490			$Cl_3PO{-}CrCl_2O$
546[e]		483	477	Cl_3PO
593[e]		551	586	Cl_3PO
629[d]		585		$Cl_3PO{-}CrCl_2O$
633[d]		589		$Cl_3PO{-}CrCl_2O$
1011[d]		1130		$Cl_3PO{-}CrCl_2O$
1215[d]		1193		$Cl_3PO{-}CrCl_2O$
1302[e]		1301	1313	Cl_3PO

[a] Calculated for the $Cl_3PO{-}CrCl_2O$ complex, unscaled. [b] Calculated for Cl_3PO, unscaled. [c] From ref 39. [d] Twin-jet experiment. [e] Merged jet.

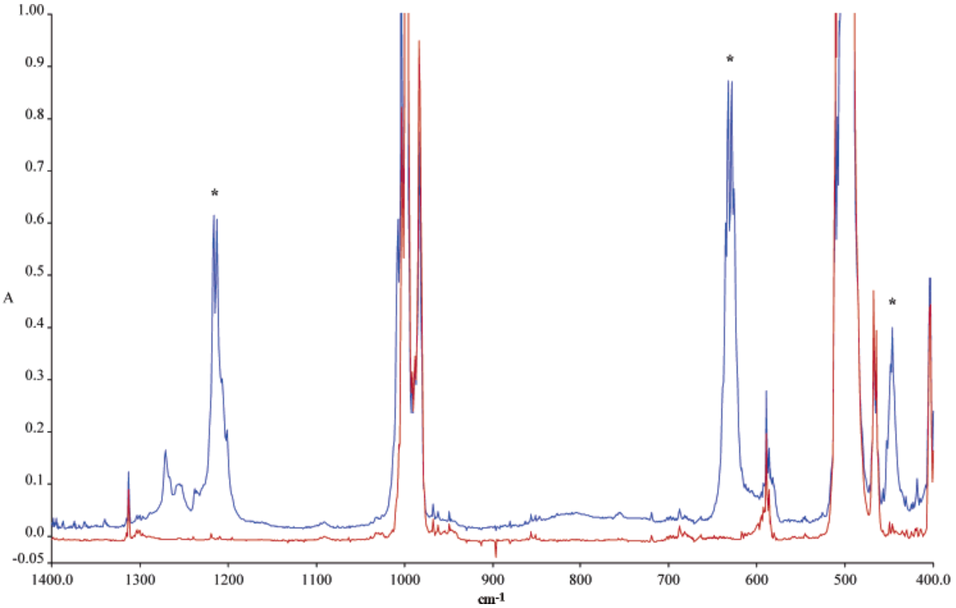

Figure 2. Infrared spectra before (lower) and after (upper) irradiation of argon matrices formed by the twin jet deposition of samples of Ar/PCl_3 and Ar/$CrCl_2O_2$. The band marked with an asterisk denotes the major product bands.

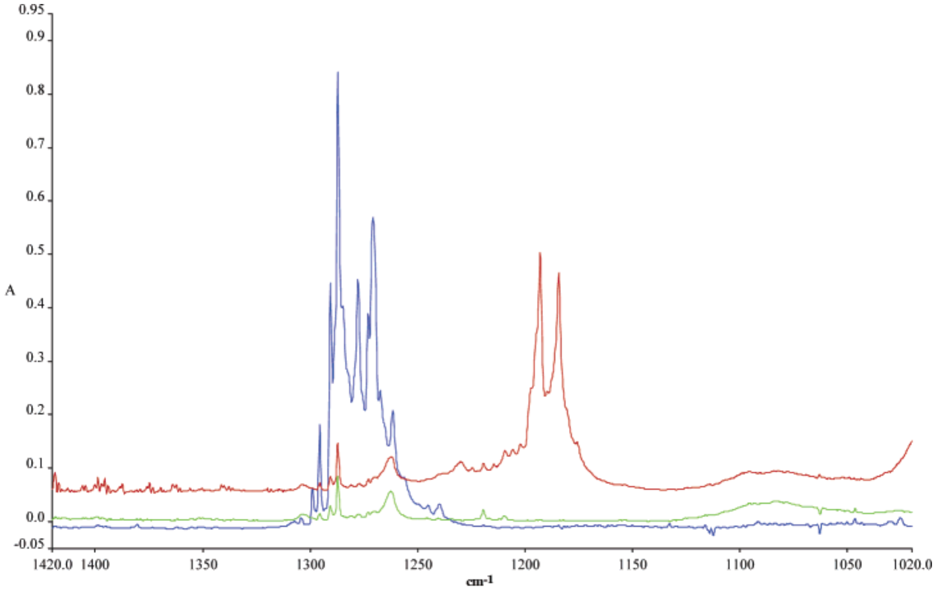

Figure 3. Infrared spectra before (middle) and after (top) irradiation of argon matrices formed by the twin jet deposition of samples of Ar/PBr_3 and Ar/$CrCl_2O_2$, compared to a similar matrix prepared by merged jet deposition (bottom).

Several merged jet experiments were conducted at different concentrations as well, with the merged region held at room temperature. In each experiment, distinct product bands were observed, at 546 (m), 590 (s), 597 (s), and 1302 (s) cm^{-1}, along with a significant reduction in the intensities of the parent bands. The relative intensities of the product bands remained constant throughout the merged jet experiments. It is noteworthy that the more intense bands in these experiments matched exactly the weak product bands observed in the twin-jet experiments before irradiation. Since extensive reaction occurred with the reaction zone at room temperature, experiments with added heat were not carried out.

The reaction of $CrCl_2O_2$ and PBr_3 was also explored using twin and merged jet deposition. In the twin jet experiments, a weak band was noted at 1279 cm^{-1} upon initial deposition. This band was not affected by subsequent irradiation. However, strong new product bands were observed upon irradiation, at 440, 520, 526, 1008, 1185, and 1193 cm^{-1}. These results were reproduced in several experiments at different sample concentrations. In several merged jet experiments, different product bands were observed along with a reduction in the intensities of the parent bands. The most intense were at 490 (doublet) and 1279 cm^{-1}, this latter band matching the weak product band observed before irradiation in the twin-jet experiments. Additionally, a weaker product band was observed at 558 cm^{-1}. Figure 3 shows merged and twin-jet spectra in the P═O stretching region, while product band positions are listed in Table 3.

$CrCl_2O_2$ + CH_3PCl_2, $(CH_3)_2PCl$. Samples of Ar/$CrCl_2O_2$ were co-deposited with samples of Ar/CH_3PCl_2 in several twin-jet experiments. Weak product bands were observed at 547 and 1306 cm^{-1} upon initial matrix deposition. After irradiation of the matrix, these two bands were unchanged. However, distinct new product bands were noted, at 441, 595, 777, 897, 901, 1008, 1180, and 1200 cm^{-1}. Several of these were moderately intense. The product bands in these twin jet experiments were reproduc-

TABLE 3: Product Bands and Assignments after Merged and Twin-Jet Deposition of PBr_3 and $CrCl_2O_2$ into Argon Matrices

exptl	calcd[a]	calcd[b]	lit[c]	assignment
	410			$Br_3PO{-}CrCl_2O$, P−Br stretch
440[d]	443			$Br_3PO{-}CrCl_2O$, Cr−Cl stretch
490[e]		463	488	Br_3PO, P−Br stretch
520[d]	484			$Br_3PO{-}CrCl_2O$, P−Br stretch
526[d]	495			$Br_3PO{-}CrCl_2O$, P−Br stretch
1008[d]	1127			$Br_3PO{-}CrCl_2O$, Cr=O stretch
1189[d]	1156			$Br_3PO{-}CrCl_2O$, P=O stretch
1279[e]		1277	1261	Br_3PO, P=O stretch

[a] Calculated for the $Br_3PO{-}CrCl_2O$ complex, unscaled. [b] Calculated for Br_3PO, unscaled. [c] From ref 40. [d] Twin-jet experiment. [e] Merged jet.

TABLE 4: Product Bands and Assignments after Merged and Twin-Jet Deposition of CH_3PCl_2 and $CrCl_2O_2$ into Argon Matrices

exptl	calcd[a]	calcd[b]	lit[c]	assignment
441[d]	431			$CH_3Cl_2PO{-}Cl_2CrO$, Cr−Cl stretch
		462	497	CH_3Cl_2PO
	515			$CH_3Cl_2PO{-}Cl_2CrO$
547[e]		512	552	CH_3Cl_2PO
595[d]	554			$CH_3Cl_2PO{-}Cl_2CrO$
756[e]		738	756	CH_3Cl_2PO
777[d]	753			$CH_3Cl_2PO{-}Cl_2CrO$
888[e]		925	893	CH_3Cl_2PO
893[e]		928	898	CH_3Cl_2PO
897[d]	941			$CH_3Cl_2PO{-}Cl_2CrO$
901[d]	951			$CH_3Cl_2PO{-}Cl_2CrO$
1008[d]	1126			$CH_3Cl_2PO{-}Cl_2CrO$
1190[d]	1181			$CH_3Cl_2PO{-}Cl_2CrO$, P=O st.
1285[e]		1281	1302	CH_3Cl_2PO, P=O stretch
	1358			$CH_3Cl_2PO{-}Cl_2CrO$, δ CH_3

[a] Calculated for the $CH_3Cl_2PO{-}Cl_2CrO$ complex, unscaled. [b] Calculated for CH_3Cl_2PO, unscaled. [c] From ref 34. [d] Twin-jet experiment. [e] Merged jet

ible and had relative intensities that were constant in all of the several experiments. Merged-jet experiments with a room-temperature reaction zone and this pair of reagents led to rather different product bands. Quite intense bands were observed at 547 and 1306 cm^{-1} along with somewhat less intense bands at 756, 888, and 893 cm^{-1}. Product band positions for both twin and merged jet experiments are listed in Table 4.

A similar set of experiments was conducted with $CrCl_2O_2$ and $(CH_3)_2PCl$ as reactants. In the twin-jet experiments, weak product bands at 432, 540, 720, 863, 920, 1007, 1156, 1260, and 1309 cm^{-1} were observed upon initial deposition. In contrast to the above systems, the majority of these bands grew strongly upon irradiation, while the bands at 863, 1260, and 1309 cm^{-1} were unaffected by irradiation. These results were reproducible in several experiments. To test whether the initial weak product bands were forming as a result of light from either the infrared source of the instrument or room lights, a dark experiment was conducted in which the sample was exposed to radiation only during the time in which the spectrum was recorded. Identical results were observed in this experiment.

Merged jet experiments were also conducted, leading to an extended multiplet of product bands between 1260 and 1309 cm^{-1}, along with bands at 695 and 863 cm^{-1}. The 1260-cm^{-1} band was the most intense component of this multiplet. These results were reproduced in several experiments, including one in which the length of the merged region was reduced to 15 cm to shorten the time available for reaction. In all of the merged jet experiments, the bands of parent $(CH_3)_2PCl$ were completely absent. Product band positions for both twin and merged jet experiments are listed in Table 5.

TABLE 5: Product Bands and Assignments after Merged and Twin-Jet Deposition of $(CH_3)PCl$ and $CrCl_2O_2$ into Argon Matrices

exptl	calcd[a]	calcd[b]	lit[c]	assignment
432[d]	433			$(CH_3)_2ClPO{-}Cl_2CrO$, Cr−Cl stretch
540[d]	511			$(CH_3)_2ClPO{-}Cl_2CrO$, P−Cl stretch
695[e]		671	696	$(CH_3)_2ClPO$, P−C stretch
720[d]	691			$(CH_3)_2ClPO{-}Cl_2CrO$, P−Cl stretch
863[e]		886	868	$(CH_3)_2ClPO$, CH_3 rock
920[d]	897			$(CH_3)_2ClPO{-}Cl_2CrO$, CH_3 rock
1007[d]	1126			$(CH_3)_2ClPO{-}Cl_2CrO$, Cr=O stretch
1156[d]	1153			$(CH_3)_2ClPO{-}Cl_2CrO$, P=O stretch
1249[e]		1249	1271	$(CH_3)_2ClPO$, P=O stretch

[a] Calculated for the $(CH_3)_2ClPO{-}Cl_2CrO$ complex, observed bands only, unscaled. [b] Calculated for $(CH_3)_2ClPO$, observed bands only, unscaled. [c] From ref 34. [d] Twin-jet experiment. [e] Merged jet.

Results of Calculations. The evidence presented below strongly supports oxygen atom transfer from $CrCl_2O_2$ to each of the substituted phosphines. On the basis of prior experience and the literature, the most likely products are the corresponding phosphine oxide, $CrCl_2O$, and the complex between the two, $X_3PO{:}CrCl_2O$. Consequently, theoretical calculations focused on locating energy minima for each of these species. Density functional theory calculations were undertaken using the B3LYP hybrid functional and basis sets as high as 6-311++G(d,2p). All of these species optimized to energy minima on the potential energy surface, with all real frequencies. The complexes were all complexed via η^1 coordination, with the $CrCl_2O$ species interacting with a lone pair on the oxygen atom. Thermodynamic quantities were also determined for all of the species, the zero-point-corrected $\Delta E°$ for the oxygen transfer and complexation reactions. A representative calculated structure is shown in Figure 4, the unscaled vibrational frequencies listed in Tables 1−5, and the $\Delta E°$ values in Table 6.

Discussion

The growth of new bands, in some systems following thermal reaction and in other systems following irradiation, indicates the formation of products for all of the systems studied here. Each system will be discussed and products assigned, based on the type and extent of reaction that was observed.

For the reaction pair $CrCl_2O_2$ and PF_3, product bands were *not* observed upon initial twin-jet co-deposition but strong new bands were observed after irradiation of these matrices with light

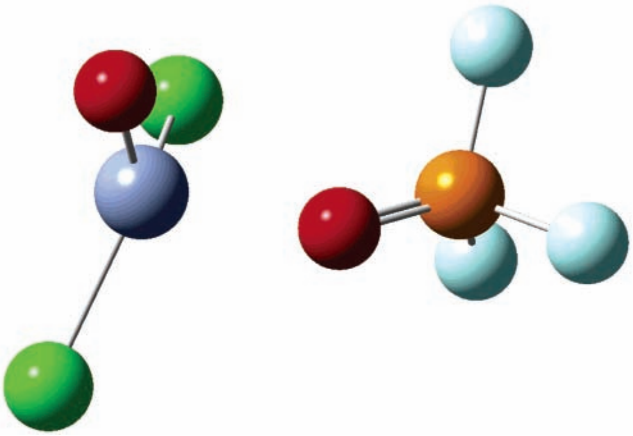

Figure 4. Representation of the $Cl_2CrO - OPF_3$ complex, calculated at the B3LYP/6-311++g(d,2p) level.

TABLE 6: Reaction Energetics[a] for the Reactions of $CrCl_2O_2$ with Substituted Phosphines

phosphine	$\Delta E°$ (free)[b] (kcal/mol)	$\Delta G_{298}°$ (free)[b] (kcal/mol)	$\Delta E°$ (complexed)[c] (kcal/mol)
PF_3	−3.1	−3.7	−17.7
PCl_3	+ 1.7	+ 0.6	−16.5
PBr_3	−36.6	−37.3	−55.6
CH_3PCl_2	−6.1	−6.6	−24.4
$(CH_3)_2PCl$	−10.6	−11.3	−39.6

[a] Calculated at the B3LYP/6-311++g(d,2p) level. [b] For the reaction $CrCl_2O_2 + PX_3 \rightarrow Cl_2CrO + X_3PO$. [c] For the reaction $CrCl_2O_2 + PX_3 \rightarrow X_3PO{-}Cl_2CrO$.

of $\lambda > 300$ nm. Merged-jet deposition did not yield any thermal reaction product. Identification of the photochemical product comes from location of the product bands combined with theoretical calculations. Two of the product bands for this system were observed at 449 and 1011 cm^{-1}, very near known bands of Cl_2CrO. This species has been observed by several research groups,[25,35−37] and has characteristic absorptions near 1014 and 450 cm^{-1}, with the exact position of these absorptions varying slightly from system to system, due to complexation of Cl_2CrO to the oxidized product. The two product bands observed here (and their counterparts in the photochemical reactions described below for the other systems in this study) are very reasonably assigned to Cl_2CrO. *This assignment indicates that oxygen atom transfer has occurred.*

On the basis of the known chemistry of PF_3, addition of an oxygen atom might well lead to valence expansion, forming triflurophosphine oxide, F_3PO. However, since this product would be formed in the same matrix cage with Cl_2CrO, interaction will occur leading to complex formation. Thus, the observed product in this case is likely to be F_3PO:$ClCr_2O$. To examine this possibility, theoretical calculations were carried out for both “free” PF_3O and the F_3PO:$ClCr_2O$ molecular complex. The complex was found to be bound by 18 kcal/mol relative to the separated species, indicating a significant interaction between the species. As shown in Table 1, the P═O stretch of the complex was calculated to come at 1290 cm^{-1}, close to the observed band at 1321 cm^{-1}. Further the shift of this mode upon complexation was calculated to be −98 cm^{-1}, very close to the shift of −94 cm^{-1} (gas phase[38] for PF_3O minus argon matrix for the complex). Similar shifts were observed upon complexation for the P−F stretching modes (+61 cm^{-1} calculated vs +56 cm^{-1} experimental). All of the observed product bands can be assigned in a similar manner, supporting assignment of the product bands observed here to the F_3PO:$ClCr_2O$ molecular complex.

The systems $PCl_3 + CrCl_2O_2$, $PBr_3 + CrCl_2O_2$, and $CH_3PCl_2 + CrCl_2O_2$ had similar reaction characteristics to one another, and different from those described above for PF_3. For these 3 systems, merged-jet co-deposition led to thermal reaction products. Also, weak product bands were observed upon initial twin jet deposition before irradiation and matched the bands seen in the merged jet experiments. These bands did not grow upon irradiation of the resulting matrix, while strong new product bands grew in. The products in the merged-jet experiments, typified by the bands at 490 and 1279 cm^{-1} in the $PBr_3 + CrCl_2O_2$ system all were quite close to the known bands of the corresponding phosphine oxide. For example, Br_3PO absorbs at 483 and 1287 cm^{-1} in an argon matrix.[39] Given the experimental differences, the agreement for all of these systems is excellent, and the products of the merged-jet co-deposition for each system are identified as the substituted phosphine oxide[34,40] formed through gas-phase oxygen atom transfer from $CrCl_2O_2$ to the phosphine. Oxygen atom transfer in merged jet deposition has been observed previously for the $CrCl_2O_2 + (CH_3)_2SO$ and H_2S systems.[24,41] These results are also consistent with the calculated $\Delta E_0°$ and $\Delta G_{298}°$ values shown in Table 6, where these values ranged from essentially thermoneutral for the PCl_3 reaction to −37 kcal/mol for the PBr_3 reaction. The observation of the uncomplexed phosphine oxide upon initial deposition in the twin-jet experiments demonstrates that the oxygen transfer reaction is very rapid and occurs with a low activation barrier. The second product of the thermal oxygen transfer reaction is $CrCl_2O$. Consistent with previous merged-jet studies, this species was not observed. This is very likely due to the low volatility of $CrCl_2O$, leading to condensation on the walls of the deposition line tubing.

After irradiation in the twin jet experiments, a different set of intense product bands was observed for each system, typified by the bands at 447, 629, 633, 1011, and 1215 cm^{-1} for the $CrCl_2O_2 + PCl_3$ system. The bands at 447 and 1011 cm^{-1}, as with the PF_3 system above, are assigned to Cl_2CrO and demonstrate that oxygen atom transfer has occurred photochemically in the argon matrix. The 629- and 633-cm^{-1} bands are assigned to P−Cl stretching modes, shifted from 593 cm^{-1} for uncomplexed Cl_3PO in the merged jet experiment due to complexation with the Cl_2CrO species. The shift from “free” to “complexed” Cl_3PO was calculated to be +34 and +38 cm^{-1}, compared to the +36 and +40 cm^{-1} shifts that were observed. In the uncomplexed phosphine oxide, the P−Cl mode is doubly degenerate and splits in the complex due to the lower symmetry of the complex. Likewise, the complexation shift of the P═O stretch was calculated to be −108 cm^{-1}, while a shift of −87 cm^{-1} was observed. These large shifts suggest a strong interaction in the complex. This is supported by the calculated complexation energies, which ranged from −15 to −19 kcal/mol for these three complexes. All of these points support assignment of the product bands produced upon irradiation after twin jet deposition to the respective phosphine oxide complexed to Cl_2CrO.

The results for the final system, $(CH_3)_2PCl + CrCl_2O_2$, were in several ways similar, but they differed in one major respect from the above systems. Merged jet co-deposition led to product formation, with bands observed at 695, 863, and 1285 cm^{-1}. These bands were also seen weakly upon initial twin-jet deposition, did not grow upon irradiation, and are readily assigned based on the literature and on theoretical calculations to the phosphine oxide $(CH_3)_2ClPO$ (literature bands at 696, 868, and 1271 cm^{-1} in the gas phase).[34] The difference for this system is that a number of additional weak product bands were formed upon initial twin-jet deposition. All of these bands grew more than a factor of 10 upon irradiation with light of $\lambda > 300$ nm. Among these were bands at 432 and 1007 cm^{-1}, which can be assigned to Cl_2CrO. This suggests oxygen atom transfer and complexation of $(CH_3)_2ClPO$ to Cl_2CrO. This is supported by the agreement of the observed bands with those calculated for the complex (e.g., P═O stretch calculated at 1153 cm^{-1} and observed at 1156 cm^{-1}) and calculated shifts relative to uncomplexed $(CH_3)_2ClPO$ (for the P═O stretch, calculated shift of −96 cm^{-1} vs the observed shift of −129 cm^{-1}). Thus, the product bands that were observed upon initial deposition and grew upon irradiation are assigned to the $(CH_3)_2MeClPO$:Cl_2CrO complex. *The observation of this complex prior to irradiation has not been seen previously and indicates that oxygen atom transfer and complex formation occurs within the cryogenic matrix cage* (reaction before cage formation would likely lead to the uncomplexed products). This requires a very low activation barrier, as well as the proper orientation of the two molecules within the matrix cage.

Nature of the Complex. As noted above, theoretical calculations indicated that all of the phosphine oxide complexes with Cl_2CrO were strongly bound, with $\Delta E°$ values for the complexation reaction ranging from −14 to −18 kcal/mol. The site of coordination was between the chromium atom and the oxygen atom of the phosphine oxide, specifically interacting with one of the oxygen lone pairs. The P═O—Cr angle was calculated to range from 136° for the $F_3PO—Cl_2CrO$ complex to 150° for the $CH_3Cl_2PO—Cl_2CrO$ complex. For each complex, the P═O bond was lengthened approximately 0.03 Å relative to the free phosphine oxide. The dihedral angle in the Cl_2CrO species (a measure of the degree of deviation from planarity) ranged from 146 to 150°, indicating substantial flattening out of the species compared to 120° for this angle in the pseudotetrahedral parent $CrCl_2O_2$ [free or uncomplexed Cl_2CrO is calculated to be planar (dihedral angle of 180°)]. At the same time, the X—P═O angle in the complexes ranged from 111 to 114°, slightly less than the range of 114−117° for the corresponding parent compounds. All of these observations demonstrate that these molecular complexes are distinct, interesting chemical species, and suggests that the chemistry of the X_3PO subunit in the complex is likely to differ from that of the free X_3PO species.

Conclusions

Merged-jet reactions of a series of substituted phosphines with $CrCl_2O_2$ led to gas-phase oxygen atom transfer and formation of the corresponding phosphine oxide, for all of the phosphines except PF_3. While this last reaction is calculated to be exothermic, the activation barrier must be too high for reaction to occur at temperatures up to 170 °C. Twin-jet deposition of the same reagents led to the formation of small amount of the phosphine oxide on initial deposition (except, again, for PF_3). Subsequent irradiation left the phosphine oxide unchanged, and produced the phosphine oxide:Cl_2CrO complex in substantial yield.

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