Infrared Matrix Isolation and Theoretical Study of the Reactions of $MoCl_4O$ and $MoCl_2O_2$ with CH_3OH: Characterization of $Cl_3Mo(O)OCH_3$

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The matrix isolation technique has been employed to investigate the reactions of Cl_4MoO and $MoCl_2O_2$ with CH_3OH and C_2H_5OH. Using twin jet deposition, the initial intermediate in the mechanism was identified as a weakly bound molecular complex, characterized by perturbations to the Mo═O and O−H stretching modes. The complex between Cl_4MoO and CH_3OH was destroyed by near-UV irradiation, producing the novel $Cl_3Mo(O)OCH_3$ species and cage-paired HCl. The complex between CH_3OH and $MoCl_2O_2$ was not photosensitive. Merged jet deposition of CH_3OH and Cl_4MoO, with a 70 °C reaction zone, led to complete conversion to $Cl_3Mo(O)OCH_3$, the same product observed in after irradiation of the 1:1 complex. This species was identified by use of extensive isotopic labeling, by the observation of HCl (or DCl) as an additional reaction product, and by comparison to density functional calculations. Most of the fundamental vibrational modes of this species that lie above 400 cm^{-1} were observed, some with very high intensities. C_2H_5OH reacted in a very similar manner with Cl_4MoO, yielding $Cl_3Mo(O)OC_2H_5$ and HCl. In contrast, the merged jet co-deposition of CH_3OH with $MoCl_2O_2$ did not yield any reaction product.

Introduction

Oxidation−reduction reactions carry a great significance in chemistry, from synthetic organic chemistry to biological processes.[1,2] Westheimer was the first to investigate the mechanism of oxidation of alcohols in 1949, when he studied the reaction of chromyl chloride, $CrCl_2O_2$, with alcohols and the subsequent formation of aldehydes. High valent transition metal oxo compounds, including $CrCl_2O_2$, are very strong oxidizing agents, with a substantial degree of selectivity. Mechanistic details of the reactions, including experimental identification and characterization of reaction intermediates, are incomplete at best. In particular, little is known[3,4] about the mechanisms of reactions of the molybdenum analogue of chromyl chloride, $MoCl_2O_2$, and the related Mo(VI) compound $MoCl_4O$. On the other hand, several groups have carried out extensive theoretical calculations mapping the reaction surface and predicting a sequence of intermediates for these oxidation reactions.[5−9]

The matrix isolation technique[10−12] 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[13−17] 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 transition metal oxo compounds as strong oxidizing agents and the paucity of information concerning the reactions of $MoCl_2O_2$ and $MoCl_4O$, a matrix isolation study was undertaken to explore intermediates formed in the reactions of these compounds with CH_3OH as a prototype of the alcohol family. 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 a conventional matrix isolation apparatus that has been described.[18] Molybdenum oxytetrachloride, $MoCl_4O$, and molybdyl chloride, $MoCl_2O_2$ (both Aldrich), are solids at room temperature. For each, a small sample was placed in a small stainless steel sidearm, connected to the deposition line by an UltraTorr tee. The vapor pressure of the compound at the temperature of the sidearm was entrained in flowing argon, carried to the cold window, and deposited. The vaporization temperature could be adjusted by placing a heating mantle around the sidearm and heating. Temperatures between 55 and 65 °C were employed for $MoCl_2O_2$ samples, and temperatures between 70 and 75 °C were employed for $MoCl_4O$ samples. CH_3OH, CD_3OD (both Aldrich), $^{13}CH_3OH$, and $CH_3{}^{18}OH$ (both Cambridge Isotope Laboratory) were introduced into a separate vacuum manifold as the vapor above the room-temperature liquid after purification by repeated freeze−pump−thaw cycles at 77 K. Argon (Wright Brothers) 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 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,[19] in which the two deposition lines were joined with an UltraTorr tee at a distance from the cryogenic surface (beyond the stainless steel sidearm containing the solid Mo sample), and the flowing gas samples were permitted to mix and react during passage

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through the merged region. A mixing length of about 20 cm was employed. In both twin and merged jets, matrices were deposited at the rate of 2 mmol/hr from each sample manifold onto the cold window. Final spectra were recorded on a Mattson Cygnus Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using the Gaussian 98 suite of programs.[20] 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 3-21g and LANL2DZ basis sets, after initial calculations with the sto-3g basis set. Calculations were carried out on a on a 1.4 GHz Pentium IV personal computer.

Results

Prior to any co-deposition experiments, blank experiments were run on each of the reagents used in this study. For the methanol blanks, spectra were in good agreement with literature spectra[21] and with blanks run previously in this laboratory. The actual $^{13}C/^{12}C$ ratio in the $^{13}CH_3OH$ blank and the $^{18}O/^{16}O$ ratio in the $CH_3{}^{18}OH$ blank, as determined by relative parent band intensities, were both approximately 5/1. In the CD_3OD experiments, the D/H ratio was approximately 4/1 for the $-OD(H)$ group, and much higher for the $-CD_3$ group. Blank spectra of $MoCl_2O_2$ were in good agreement with literature spectra.[22] On the other hand, blank spectra[23] of $MoCl_4O$ initially showed considerable $MoCl_2O_2$ impurity. However, after 1−2 h of deposition, the growth of $MoCl_2O_2$ decreased greatly and bands due to $MoCl_4O$ grew in. HCl was a minor impurity in all of these experiments.[24]

$MoCl_2O_2 + CH_3OH$. Because $MoCl_2O_2$ is always present as an impurity in samples of $MoCl_4O$, initial experiments explored the reactivity of $MoCl_2O_2$ with CH_3OH in both twin jet and merged jet deposition experiments. In several twin jet experiments, four very weak product bands (O.D. < 0.02) were observed, at 422, 1008, 1090, and 3571 cm^{-1}. No other bands were seen in any of these experiments. Two of these experiments were subsequently irradiated for between 1.0 and 2.0 h, the first with light of $\lambda > 300$ nm and the second with light of $\lambda > 220$ nm. In both of these experiments, no changes were detected as a result of irradiation. Merged jet experiments with these two reagents (and $MoCl_2O_2 + CD_3OD$) led to similar results as the twin jet experiments. Intense bands due to unreacted parent were observed, as well as the above-mentioned weak product bands. Some additional HCl (or DCl) was detected, along with the complexes[25,26] of HCl with impurity H_2O and N_2 and with CH_3OH/CD_3OD, but the extent of the reaction was still very small. The results were essentially identical in further experiments in which the merged region or reaction zone was heated to as high as 120 °C.

$MoCl_4O + CH_3OH$. These two reagents were co-deposited in a large number of experiments, both twin jet and merged jet. In an initial twin jet experiment, with $Ar/CH_3OH = 500$ and $MoCl_4O$ sublimed at 70 °C, two weak product bands near 1090 and 3595 cm^{-1} were observed. When this sample was subsequently irradiated with light of $\lambda > 300$ nm, a series of weak-to-medium intensity new bands grew in, at 579, 588, 1136, 1154, 1441, 2760, 2785, and 2982 cm^{-1}, as listed in Table 1, with some loss of intensity for the 3595 cm^{-1} band; see Figure 1. The experiment was repeated several times, using somewhat different concentrations of the two reagents, and very similar results were obtained. When these matrices were irradiated with light of $\lambda > 220$ nm, no further changes were observed.

TABLE 1: Product Bands[a] and Assignments from the Twin and Merged Jet Co-deposition of $MoCl_4O$ and CH_3OH into Argon Matrices

twin jet			
before hν	after *hν*	merged jet	assignment
3595			O−H stretch, 1:1 complex
	2982	2976	C−H stretch, $Cl_3Mo(O)OCH_3$
			C−H stretch, $Cl_3Mo(O)OCH_3$
	2863, 2888	2863, 2888	$HCl{\bullet}N_2$, HCl
	2760, 2785		$HCl{\bullet}Cl_3Mo(O)OCH_3$
	1441	1441	CH_3 bend, $Cl_3Mo(O)OCH_3$
			CH_3 bend, $Cl_3Mo(O)OCH_3$
			CH_3 bend, $Cl_3Mo(O)OCH_3$
	1154	1156	CH_3 rock, $Cl_3Mo(O)OCH_3$
	1136	1136	CH_3 rock, $Cl_3Mo(O)OCH_3$
1090	1090	1090	from impurity $MoCl_2O_2$
		1067	M=O str., $Cl_3Mo(O)OCH_3$
		1060	C−O stretch, $Cl_3Mo(O)OCH_3$
		608, 616	Mo−O str., $Cl_3Mo(O)OCH_3$
	579, 588	579, 588	Mo−O str. $Cl_3Mo(O)OCH_3$[b]

[a] Band positions in cm^{-1}. [b] Cage-paired with HCl.

The reaction of this pair of reagents was also studied in a series of merged jet experiments, with the merged region held at approximately 70 °C (to avoid condensation of the sublimed $MoCl_4O$ in the deposition line). These experiments were very productive, with a series of medium-to-intense product bands observed in each experiment. This series contained all of the bands observed in the twin jet experiments *after irradiation*, in addition to a number of additional product bands, as shown in Figure 2. In addition, there was a distinct reduction in the intensity of the parent bands, indicating that reaction was occurring in the merged region. Table 1 lists all of the product bands observed in the set of merged jet experiments that were run with these reactants. In as much as significant product was observed as a result of merged jet deposition, these matrices were not irradiated.

$MoCl_4O + {}^{13}CH_3OH, CH_3{}^{18}OH, CD_3OD$. Because the merged jet experiments were much more productive in leading to reaction between $MoCl_4O$ and CH_3OH, all of the experiments employing isotopically labeled methanol were carried out in the merged jet deposition mode. Typically, two to three merged jet experiments using different concentrations were run for each isotopomer of methanol (except with $CH_3{}^{18}OH$, where a single merged jet experiment was run due to the very small amount of $CH_3{}^{18}OH$ available). In all of these experiments, medium-to-intense product bands were observed. These were not identical in position to those observed in the CH_3OH experiments. Rather, they occurred in the same general region but typically shifted somewhat to lower energy. Product bands were reproducible from experiment to experiment with a given pair of reagents. Of particular note was the production of a set of bands at 2043, 2060, 2077, and 2095 cm^{-1} in the $MoCl_4O + CD_3OD$ experiments. Table 2 lists all of the product bands observed in these experiments with isotopically labeled CH_3OH, whereas Figure 3 shows the 500−700 cm^{-1} region for all four isotopomers.

$MoCl_4O + C_2H_5OH$. For comparison, an experiment was run in which $MoCl_4O$ was co-deposited with C_2H_5OH in a merged jet experiment. A number of product bands were observed in this experiment, several of which were quite intense. In addition, a number were noted quite close to product bands reported above for the reaction of $MoCl_4O$ with CH_3OH. Furthermore, bands due to HCl at 2888 and 2863 cm^{-1} were quite clear,[24] as well as the known complexes[25,26] of HCl with H_2O and with C_2H_5OH. The product bands observed in this experiment are listed in Table 3.

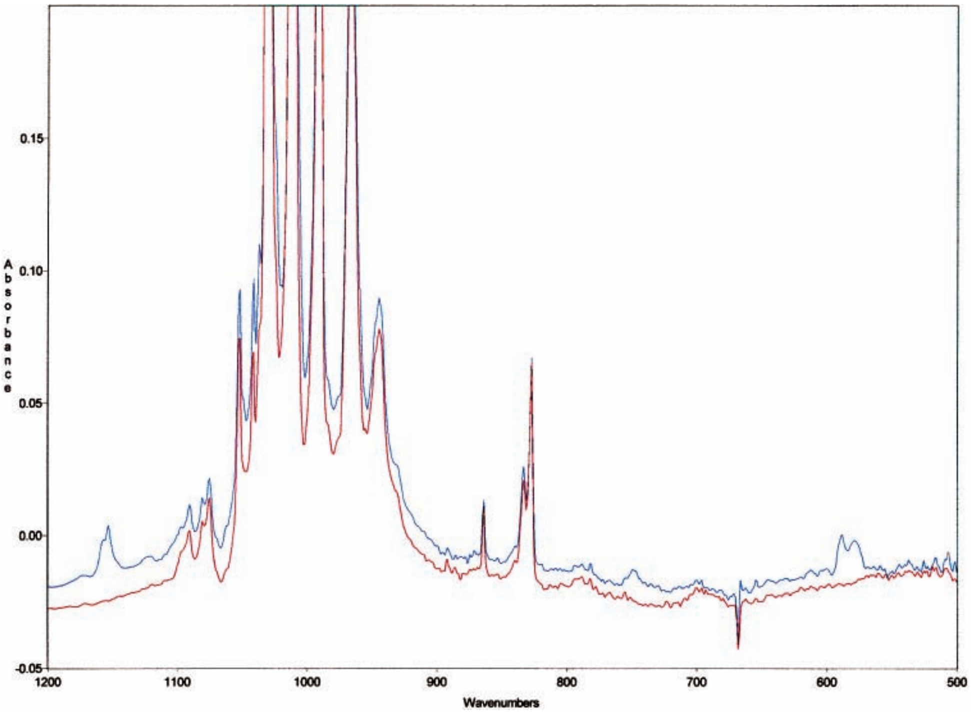

Figure 1. Infrared spectrum between 500 and 1200 cm^{-1} of a matrix formed by the twin jet deposition of Ar/Cl_4MoO and Ar/CH_3OH, after 1.0 h of irradiation with light of $\lambda > 300$ nm (blue trace) compared to a spectrum of the same matrix before irradiation (red trace).

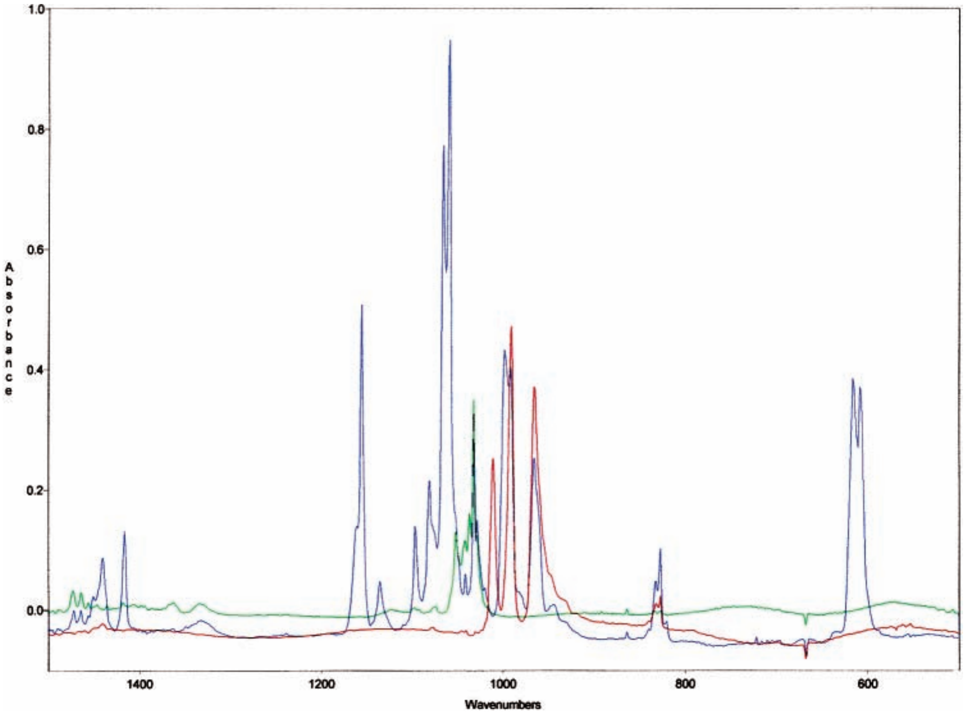

Figure 2. Infrared spectrum (blue) of a matrix formed by the merged jet co-deposition of Ar/Cl_4MoO and Ar/CH_3OH, compared to blank spectra of Ar/CH_3OH (green) and Ar/Cl_4MoO (red) alone in argon.

Theoretical Calculations

Theoretical calculations were carried out for the likely products in the reaction of Cl_4MoO with CH_3OH and C_2H_5-OH, namely, $Cl_3Mo(O)OCH_3$ and $Cl_3Mo(O)C_2H_5$, using density functional theory with the B3LYP functional. These species were considered most likely, based on previous studies of analogous reactions, and the experimental data obtained here (see below). Given molybdenum's position in the periodic table, a limited number of basis sets were available, including STO-3G, 3-21g, and LANL2DZ. All three were used, for both the above compounds and parent Cl_4MoO. Although the results were similar throughout, 3-21g did slightly better in reproducing the infrared spectrum of parent Cl_4MoO, and was the basis set of choice for all of the isotopic studies.

$Cl_3Mo(O)OCH_3$ and $Cl_3Mo(O)C_2H_5$ both optimized to stable minima, with the geometric parameters listed in Table 4. Both optimized structures were approximately square pyramidal about the Mo center, with the oxo oxygen in the apical position, and the three chlorines and the alkoxy oxygen forming the base of the square pyramid, as shown in Figure 4. All of the geometric

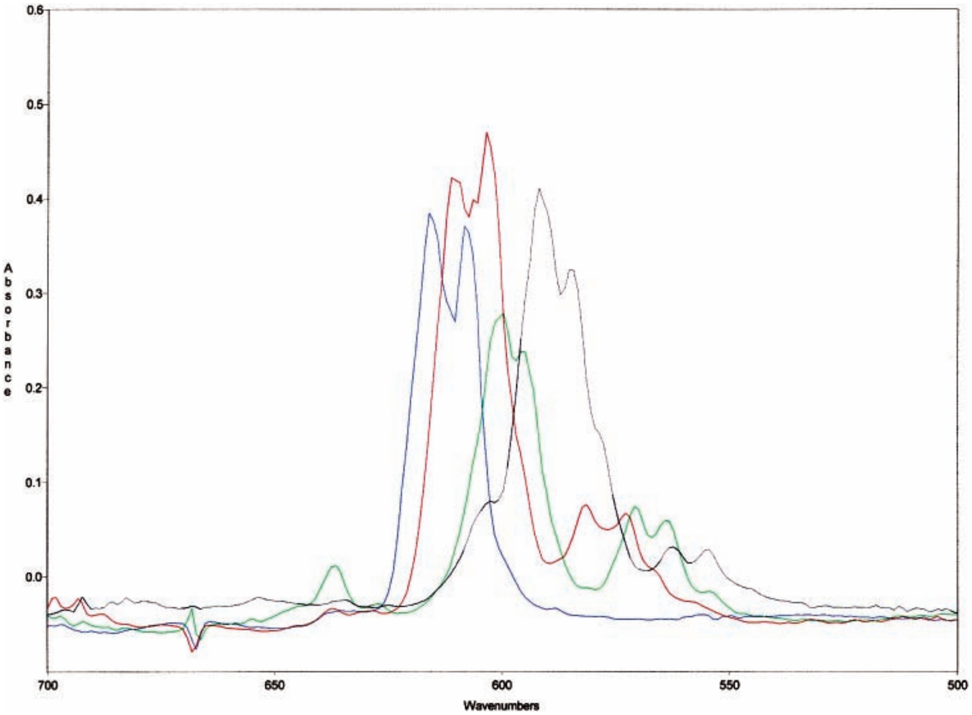

Figure 3. Infrared spectra between 500 and 700 cm^{-1} of matrices formed by the merged jet co-deposition of samples of Ar/Cl$_4$MoO with Ar/CH$_3$OH, (blue), Ar/^{13}CH$_3$OH (red) Ar/CH$_3$^{18}OH (green) and Ar/CD$_3$OD (black).

TABLE 2: Band Positions and Assignments for the Reaction Product of MoCl$_4$O with Isotopomers of CH$_3$OH in Argon Matrices

CH$_3$OH	^{13}CH$_3$OH	CH$_3$^{18}OH	CD$_3$OD	assignment
2976 cm^{-1}	2965	2975	2155	C−H stretch, Cl$_3$Mo(O)OCH$_3$
2922	2916	2922	2108	C−H stretch, Cl$_3$Mo(O)OCH$_3$
1441	1437	1441	1150	CH$_3$ bend, Cl$_3$Mo(O)OCH$_3$
1417	1413	1415	1100	CH$_3$ bend, Cl$_3$Mo(O)OCH$_3$
1350	1344	1350		CH$_3$ bend, Cl$_3$Mo(O)OCH$_3$
1156	1148	1152	895	CH$_3$ rock, Cl$_3$Mo(O)OCH$_3$
1136	1127	1132	868	CH$_3$ rock, Cl$_3$Mo(O)OCH$_3$
1067	1056	1064	1059	M=O str., Cl$_3$Mo(O)OCH$_3$
1060	1050	1036	1059	C−O stretch, Cl$_3$Mo(O)OCH$_3$
608, 616	604, 611	596, 601	585, 593	Mo−O str., Cl$_3$Mo(O)OCH$_3$
579, 588	574, 583	564, 571	563, 555	Mo−O str., Cl$_3$Mo(O)OCH$_3$[a]

[a] Cage-paired with HCl.

TABLE 3: Tentative Product Bands and Assignments from the Twin and Merged Jet Co-deposition of MoCl$_4$O and C$_2$H$_5$OH into Argon Matrices

band position	calculated position	assignment
3015 cm^{-1}	3086	C−H stretch
2993	3072	C−H stretch
2736, 2744		HCl stretch in complex
1349	1379	CH$_2$ bend
1285	1312	CH$_3$ rock
1119	1123	CH$_3$ rock
1063, 1076	1044	Mo=O stretch
977	1020	C−O stretch
936	949	C−C stretch
911		combination/overtone
781	831	CH$_2$ twist
650	612	Mo−O stretch

parameters were quite reasonable, by comparison to the calculated and experimental[27] structures of the parent compound Cl$_4$MoO (see also Table 4). Infrared spectra were calculated for both species, resulting in all positive frequencies, confirming that minima had been located. Calculations for the ^{13}C, ^{18}O, and CD$_3$ derivatives of Cl$_3$Mo(O)OCH$_3$ were carried out as well, and predicted shifts were determined. These are presented in Table 5.

TABLE 4: Calculated Geometric Parameters for Cl$_3$Mo(O)OCH$_3$ and Cl$_3$Mo(O)OC$_2$H$_5$ at the B3LYP/3-21g Level

parameter	Cl$_3$Mo(O)OCH$_3$	Cl$_3$Mo(O)OC$_2$H$_5$	Cl$_4$MoO (calc.)	Cl$_4$MoO (expt.)[a]
R(Mo=O)	1.70 Å	1.70 Å	1.69 Å	1.69 Å
R(Mo−O)	1.85	1.85		
R(Mo−Cl)	2.38[b]	2.38[b]	2.36	2.32
R(C−O)	1.45	1.46		
R(C−C)		1.53		
R(C−H)	1.09	1.09		
α(Mo−O−C)	143°	145°		
α(Cl−Mo−Cl)[c]	85[d]	85[d]	85°	88°
α(Cl−Mo=O)	105[e]	105[e]	103	101
α(H−C−H)	111	109		

[a] From ref 27. [b] Average value; range = 2.37−2.41 Å. [c] Adjacent chlorines. [d] Average value, range = 83−87°. [e] Average value; range = 100−108°.

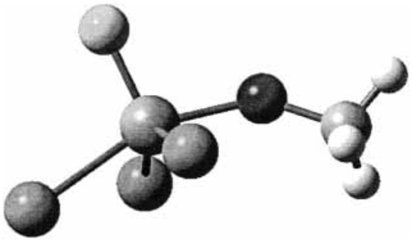

Figure 4. Molecular representation of Cl$_3$Mo(O)OCH$_3$ obtained by geometry optimization at the B3LYP/3-21g level of theory.

Discussion

Product Identification. Initial experiments involving co-deposition of MoCl$_2$O$_2$ with CH$_3$OH using both twin jet and merged jet deposition led to very little reaction. Four very weak bands were observed, in the Mo−Cl, Mo=O, C−O, and O−H stretching regions. These bands were not photosensitive and were not enhanced by merged jet deposition, including with pyrolysis. Although it is difficult to definitively identify the absorbing species, it is very likely to be a small amount of

TABLE 5: Calculated and Experimental Band Positions for Cl3Mo(O)OCH3 at the B3LYP/3-21G Level of Theory

Cl3Mo(O)OCH3		Cl3Mo(O)O13CH3			Cl3Mo(O)18OCH3			Cl3Mo(O)OCD3			
calc.	expt.	calc.	calc.. shift	expt. shift	calc.	calc. shift	expt. shift	calc.	calc. shift	expt. shift	assignment
591	612	583	−8	−4	579	−12	−13	564	−27	−23	Mo−O str.
1039	1060	1028	−11	−10	1007	−32	−24	1041	2	−1	C−O str.
1049	1067	1046	−3	−11	1046	−3	−3	1051	2	−3	Mo═O str.
1126	1136	1118	−8	−9	1121	−5	−4	876	−250	−268	CH3 rock
1151	1156	1143	−8	−8	1143	−8	−6	880	−269	−261	CH3 rock
1466	1350	1462	−4	−6	1462	−4	−1	1101	−365		CH3 bend
1528	1417	1526	−2	−4	1528	0	−2	1106	−422	−313	CH3 bend
1537	1441	1535	−2	−4	1537	0	0	1119	−418	−287	CH3 bend
3024		3021	−3		3024	0		2164	−860		CH3 str.
3103	2922	3093	−10	−6	3103	0	0	2297	−806	−814	CH3 str.
3158	2976	3146	−12	−12	3158	0	−1	2342	−816	−821	CH3 str.

molecular complex. This has been seen previously after the twin jet co-deposition of $OVCl_3$ and $CrCl_2O_2$ with CH_3OH, as well as a range of Lewis bases.[13−17] However, the lack of both thermal reactivity (in the merged jet experiments) and photochemical reactivity (in the twin jet experiments) prevented the formation of additional, secondary intermediates for this pair of reagents. On the other hand, these results demonstrate that the presence of impurity $MoCl_2O_2$ in samples of Cl_4MoO will not contribute to the spectrum, and will not interfere with the spectrum of reaction products for this latter system.

Two weak new bands were observed upon twin jet deposition of Cl_4MoO and CH_3OH into argon matrices, at 1090 and 3595 cm^{-1}. The latter was subsequently destroyed by irradiation with light of $\lambda > 300$ nm, whereas the former persisted upon irradiation. This indicates that the 1090 cm^{-1} band is likely due to reaction of CH_3OH with impurity $MoCl_2O_2$, whereas the 3595 cm^{-1} band must be due to the reaction of CH_3OH with Cl_4MoO. This band appears in the O−H stretching region, at somewhat lower energy than the O−H stretch of parent CH_3OH at 3667 cm^{-1}. This strongly suggests a perturbed O−H stretching mode, presumably perturbed by a molecule of Cl_4MoO (i.e., the formation of a weak molecular complex). In addition, a 72 cm^{-1} red shift is characteristic of the formation of a weak hydrogen bond.[13,28] Thus, it is likely that the twin jet co-deposition of Cl_4MoO with CH_3OH initially leads to formation of a weakly hydrogen bonded complex between the two reactants. Given the low sample concentrations, it is likely that this is a 1:1 complex. The result is entirely consistent with earlier twin jet studies of the reactions of $OVCl_3$ and $CrCl_2O_2$ with CH_3OH, where an initial 1:1 complex was detected. The low intensity of this one product band suggests that the intensity of other bands of the complex will be quite low and only slightly shifted from the corresponding parent vibrations. As such, they were not detected in these experiments.

It is noteworthy that when the band at 3595 cm^{-1} was destroyed by irradiation, a set of weak-to-medium bands appeared in the subsequent spectrum. This, too parallels earlier studies on related systems. Of particular note is the pair of bands at 2760 and 2785 cm^{-1}, in the HCl stretching region. These band positions are very near bands observed in the earlier studies[13−17] with $OVCl_3$ and $CrCl_2O_2$ and assigned to HCl that is produced during the photodecomposition of the 1:1 complex. Although matrix isolated HCl (and the $HCl{\cdot}N_2$ complex) is known[24] to absorb at 2863 and 2888 cm^{-1}, the HCl in the present experiments was produced in the same matrix cage as the remaining photoproduct(s). As such, the two species weakly interact, and the H−Cl stretch is shifted to lower energy. Thus, the bands produced at 2760 and 2785 cm^{-1} upon irradiation of the initial complex are assigned to HCl, cage paired with one or more additional photoproducts.

Merged jet deposition led to a very substantial reduction in parent bands intensities for CH_3OH and Cl_4MoO, and the growth of a number of quite intense new bands. The more intense of these new bands matched exactly the set of bands produced by irradiation of the 1:1 complex in the twin jet experiments. However, in the merged jet experiments, the HCl that is produced is gas phase and, hence, can be isolated in different matrix sites than the other product(s). Indeed, substantial growth in the bands at 2863 and 2888 cm^{-1} for free HCl was noted, although the bands at 2760 and 2785 cm^{-1} weakly persisted. This suggests that a small amount of the HCl is trapped in the same cage as the additional product(s), whereas the majority of the HCl is trapped as the isolated monomer. The assignment of these bands to complexed and free HCl in argon matrices is further supported by the observation of bands of DCl near 2100 cm^{-1} when CD_3OD was employed and the lack of any shift when $^{13}CH_3OH$ and $CH_3{}^{18}OH$ were employed.

The identity of the species responsible for the remaining product absorptions is of particular importance, as this represents the second intermediate(s) in both the thermal and photochemical reaction mechanisms. Several pieces of data point toward the production of a single absorber. First, the intensity ratio of the product bands remained constant over a number of experiments and was also constant between the twin jet and merged jet experiments. Second, as will be shown below, all of the absorptions fit very well the calculated spectrum of a single absorber, namely, $Cl_3Mo(O)OCH_3$. Third, analogous thermal and photochemical studies of the reaction of CH_3OH with $OVCl_3$ and $CrCl_2O_2$ produced only a single product in addition to HCl. Therefore, the species responsible for the product absorptions after irradiation in the twin jet experiments and, after deposition in the merged jet experiments, is identified as the HCl elimination product from the initial 1:1 complex, $Cl_3Mo(O)OCH_3$. As noted above, this species was calculated to be a stable minimum on the potential energy surface and, thus, a likely product in this reaction.

Another potential product in the reaction of CH_3OH with Cl_4MoO reaction is $Cl_4Mo(OH)OCH_3$, arising from the transfer of the hydroxyl hydrogen to the oxo group on the Mo center.[5−7] However, this species should have a strong band in the O−H stretching region and none was observed. Also, production of this species cannot account for the observation of substantial HCl, after irradiation in the twin jet experiment and after deposition in the merged jet experiments. Finally, a hydrogen transfer product was not observed in analogous experiments with $OVCl_3$ and with $CrCl_2O_2$. This, too, supports assignment of the product bands observed here to $Cl_3Mo(O)OCH_3$.

Merged jet experiments employing C_2H_5OH and Cl_4MoO led to quite similar results, including the production of a significant amount of monomeric, isolated HCl. This argues strongly that a similar mechanism is occurring and that the product is $Cl_3Mo(O)OC_2H_5$. As noted above, this species was also calculated to be a minimum on the potential energy surface. Furthermore, the most intense product bands for this species were located rather close to those assigned to $Cl_3Mo(O)OCH_3$, which is anticipated, because the substitution of an ethyl group for a methyl group should not have a major impact on the spectrum of the $Cl_3Mo(O)O-$ fragment in the product. Finally, as noted in Table 3, calculations at the B3LYP/3-21g level predict an infrared spectrum for this product that is in good agreement with the observed spectrum. Therefore, the product bands observed in the merged jet experiments employing C_2H_5OH and Cl_4MoO are assigned to $Cl_3Mo(O)OC_2H_5$.

Band Assignments. Assignment of product bands to specific vibrations in the $Cl_3Mo(O)OCH_3$ molecule can be made on the basis of the location of the bands, by the isotopic dependences of the bands, and by comparison to the theoretical calculations. Table 5 lists the calculated band positions for $Cl_3Mo(O)OCH_3$, as well as the calculated ^{13}C, ^{18}O, and D isotopic shifts. Also listed are the experimental band positions for this species and all of the observed isotopic shifts. *The calculated bands are unscaled*. Thus, the agreement for the lower energy bands (below 1200 cm^{-1}) is excellent, whereas the higher frequencies bands ($-CH_3$ bend and stretching modes) are systematically high. B3LYP calculations[29] are typically 3−4% high, largely because of anharmonicity in the vibrations of hydrogen and other light atoms. Thus, with this proviso, the fit of the calculated bands to the experimental bands, and the isotopic band shifts, is excellent. In addition to providing strong support for the identification of $Cl_3Mo(O)OCH_3$, this agreement provides a consistent set of well-supported band assignments.

Overall, the match between calculated and experimental band positions is excellent and will not be discussed at length here. However, one band bears special note. In the twin jet experiments, a doublet was produced by irradiation at 579, 588 cm^{-1}. In the merged jet experiments, this doublet was present, but weak, although a strong doublet at 608, 616 cm^{-1} was observed at slightly higher energy. Both lie near the calculated band position, 591 cm^{-1}, for the Mo−O stretch of the methoxy group. Further, both show appropriate ^{13}C, ^{18}O, and ^2H shifts for this vibration, in comparison to calculation, as shown in Table 5 and Figure 3. Because in the twin jet experiment, $Cl_3Mo(O)OCH_3$ is produced cage-paired with HCl, and the 579, 588 cm^{-1} doublet is assigned to the Mo−O stretch of the species weakly interacting with HCl. In the merged jet experiments, most of the HCl was present as the isolated monomer, although a small fraction was present complexed to $Cl_3Mo(O)OCH_3$. Thus, the 608, 611 cm^{-1} doublet is assigned to isolated, monomeric $Cl_3Mo(O)OCH_3$. The fact that the Mo−O stretch is the only vibrational mode of the product affected by complexation with HCl suggests that the site of interaction of the HCl with $Cl_3Mo(O)OCH_3$ is at the oxygen of the methoxy group.

Conclusions

Merged jet co-deposition of samples of Ar/CH_3OH with Ar/Cl_4MoO led to the formation of the reaction intermediate $Cl_3Mo(O)OCH_3$, as well as HCl. This species was identified by its vibrational spectrum, including extensive isotopic labeling, and by comparison to high level density functional calculations. Twin jet deposition of this pair of reagents led to the formation of a small amount of the 1:1 molecular complex, which was in turn converted to $Cl_3Mo(O)OCH_3$ and HCl by near-UV irradiation. A similar reaction was observed for C_2H_5OH with Cl_4MoO, whereas no reaction was observed for CH_3OH with $MoCl_2O_2$. These results indicate that the reaction of CH_3OH with Cl_4MoO follows the same pattern observed for the reactions of CH_3OH with $OVCl_3$ and $CrCl_2O_2$, namely, complex formation followed by HCl elimination and formation of the methoxy derivative. Both Cl_4MoO and $OVCl_3$ reacted essentially quantitatively in the merged jet experiments, whereas $CrCl_2O_2$ reacted only to a small extent. The reasons for these differences in reactivity are not clear and will be explored further in the future. Finally, no evidence was obtained in this study, or the previous studies, for a hydrogen shift reaction to the oxo group on the transition metal center.

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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. Jpn*. **1978**, *51*, 1098.
(3) Kaneshiro, H.; Hayano, S.; Masuda, T. *Macromol. Chem. Phys*. **1999**, *200*, 113.
(4) Koplich, A. J.; Jenkins, S. M. *PCT Int, Appl.* 1999.
(5) Deng, L.; Ziegler, T. *Organometallics* **1996**, *15*, 3011.
(6) Deng, L.; Ziegler, T. *Organometallics* **1997**, *16*, 716.
(7) Ziegler, T.; Li, J. *Organometallics* **1995**, *14*, 214.
(8) Rappe, A. K.; Goddard, W. A., III, *Nature*, **1980**, *285*, 311.
(9) Rappe, A. K.; Goddard, W. A., III, *J. Am. Chem. Soc*. **1982**, *104*, 3287.
(10) Craddock, S.; Hinchliffe, A. *Matrix Isolation*; Cambridge University Press: Cambridge, 1975.
(11) Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; John Wiley: New York, 1973.
(12) Andrews, L., Moskovitz, M., Eds.; *Chemistry and Physics of Matrix Isolated Species;* Elsevier Science Publishers: Amsterdam, 1989.
(13) Ault, B. S. *J. Am. Chem. Soc*. **1998**, *120*, 6105.
(14) Ault, B. S., *J. Mol. Struct*. 2000, **526**, 227.
(15) Ault, B. S. *J. Phys. Chem. A* **1999**, *103*, 11474.
(16) Ault, B. S. *J. Phys. Chem. A* **2001**, *105*, 4758.
(17) Anderson, S. R.; Ault, B. S. *J. Phys. Chem. A* **2002**, *106*, 1419.
(18) Ault, B. S. *J. Am. Chem. Soc*. **1978**, *100*, 2426.
(19) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem*. **1991**, *95*, 3502.
(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(21) Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc*. **1970**, *66*, 1920, 1932.
(22) Beattie, I. R.; Livingston, K. M. S.; Reynolds, D. J.; Ozin, G. A. *J. Chem. Soc. A* **1970**, 1210.
(23) Levason, W.; Narayanaswamy, R.; Ogden, J. S.; Rest, A. J.; Turff, J. W. *J. Chem. Soc., Dalton Trans*. **1981**, 2501
(24) Maillard, D.; Schriver, A.; Perchard, J. P.; Giradet, C. *J. Chem. Phys*. **1979**, *71*, 505.
(25) Barnes, A. J. *J. Mol. Struc*. **1980**, *60*, 343.
(26) Luck, W. A. P.; Schrems, O. *Chem. Phys. Lett*. **1980**, *76*, 75.
(27) Taylor, J. C.; Waugh, B. A. *J. Chem. Soc., Dalton Trans*. **1980**, 2006.
(28) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, CA, 1960.
(29) Bytheway, I.; Wong, M. W. *Chem. Phys. Lett*. **1998**, *282*, 219.