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Matrix isolation study of intermediates in the reaction of $CrCl_2O_2$ with CH_3SH and $(CH_3)_2S$

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Abstract

Initial and secondary intermediates in the reaction of $CrCl_2O_2$ with CH_3SH and $(CH_3)_2S$ have been characterized by matrix isolation infrared spectroscopy and density functional calculations. Twin jet codeposition of these reagents led to a series of infrared absorptions that are assigned to the 1:1 molecular complexes $CH_3SH{\cdot}CrCl_2O_2$ and $(CH_3)_2S{\cdot}CrCl_2O_2$. The complexes were characterized by the shifts of Cr=O, Cr–Cl and S–H stretching modes. Irradiation of these matrices with light of $\lambda > 300$ nm led to complete destruction of the complexes, and for each system the growth of a number of new bands. For the $CH_3SH/CrCl_2O_2$ system, these are assigned to the $ClCr(O)_2SCH_3$ species, as well as to HCl arising from destruction of the complex. Identification of these species was supported by deuterium labeling as well as by density functional calculations. Good agreement was observed between the experimental and computed frequencies. For the $(CH_3)_2S/CrCl_2O_2$ system, photolysis product bands are tentatively assigned to CH_3Cl and $ClCr(O)_2SCH_3$.

Keywords: Matrix isolation infrared spectroscopy; Chromyl chloride; Irradiation

1. Introduction

$CrCl_2O_2$ is a strong oxidizing agent for a variety of organic compounds [1,2]. It is used as a catalyst for the polymerization of alkenes, the oxidation of hydrocarbons, in the Etard reaction to produce ketones and aldehydes and in the preparation of chromium coordination complexes [3]. In many industries, selective oxidation is important. Despite the importance of these oxidation processes, the mechanism is not well understood. This is because of the complexity of the reactions themselves and also because of the lack of a well-defined model.

The matrix isolation technique [4–6] 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 [7–11] 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, including NH_3 and CH_3OH. In addition, a matrix isolation study of the reaction of $OVCl_3$ with CH_3SH was recently published [12]. While $CrCl_2O_2$ is generally somewhat less reactive than $OVCl_3$, the origin of the differences between these two compounds is not clear. Consequently, a study was undertaken to identify and characterize initial and secondary intermediates in the reaction of $CrCl_2O_2$ with CH_3SH and $(CH_3)_2S$, and to compare this system to the previously studied systems. Density functional calculations were also carried out in support of the experimental observations.

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2. Experimental details

All the experiments in this study were carried out on conventional matrix isolation apparatus that has been described [13]. Chromyl chloride, $CrCl_2O_2$ (Aldrich), was introduced into the vacuum system as the vapor above the room temperature liquid, after purification by freeze–pump–thaw cycles at 77 K. CH_3SH (Matheson), CD_3SD (99% D, Isotec) and CH_3SD (99% D, CDN isotopes) were introduced from lecture bottles into a separate vacuum manifold and were purified by repeated freeze–pump–thaw cycles at 77 K. $(CH_3)_2S$ and $(CD_3)_2S$ (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. 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. A number of these matrices were subsequently warmed to 33–36 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 [14], 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 30 cm length was employed. This region could also be heated to as high as 300 °C to induce further reaction, prior to deposition. In both twin and merged jet, matrices were deposited at the rate of 2 mmol h^{-1} from each sample manifold onto the cold window. Final spectra were recorded on a Perkin–Elmer Spectrum 2000 or a Bruker 113 Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using the GAUSSIAN-94 suite of programs [15]. Density functional calculations using the hybrid B3LYP function were used to locate energy minima, determine structures and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-311G basis set, after initial calculations with smaller basis sets were run to approximately locate energy minima. Calculations were carried out on a Silicon Graphics Indigo 2 workstation.

3. Results

Prior to any codeposition 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 [16–21], and with blanks run previously in this laboratory. However, the spectra indicated that the purity of the CD_3SD sample was somewhat less than stated. Each blank experiment was then irradiated by the H_2O/Pyrex filtered output of a 200 W Hg arc lamp for 1.0 or more hours. No changes were observed in any of the blank spectra as a result of irradiation. Weak bands due to HCl impurity were noted in all of the $CrCl_2O_2$ blank experiments [22].

3.1. $CrCl_2O_2 + CH_3SH$

In an initial experiment, a sample of $Ar/CH_3SH = 100$ was codeposited with a sample of $Ar/CrCl_2O_2 = 150$ in the twin jet mode. Initial concentrations of $Ar/CrCl_2O_2$ of 100:1, 250:1 and 100:1 were codeposited with Ar/CH_3SH concentrations of 100:1, 100:1 and 250:1. The resulting spectra showed intense bands due to the parent species along with new weaker bands at 434, 537, 748, 927, 945, 962, 1182, 1390 and 2514 cm^{-1}. Upon annealing the matrix to 34 K, the bands at 927, 945 and 962 cm^{-1} increased slightly. The rest of the bands remained unchanged. The annealed matrix was then irradiated for 1 h with a medium pressure Hg arc lamp and a H_2O/Pyrex filter. In the resulting spectra the bands at 927, 945 and 962 cm^{-1} disappeared while the band at 2514 cm^{-1} decreased slightly. The bands at 537, 748, 1182 and 1390 cm^{-1} remained unchanged. The band at 434 cm^{-1} was lost under new bands that grew in at 449, 438 and 436 cm^{-1} that were very intense. Other new bands grew at 415, 658, 668, 795, 939, 975, 1007, 1314, 1403, 1417, 2734 and 2752 cm^{-1}. Due to their different behavior with respect to annealing and

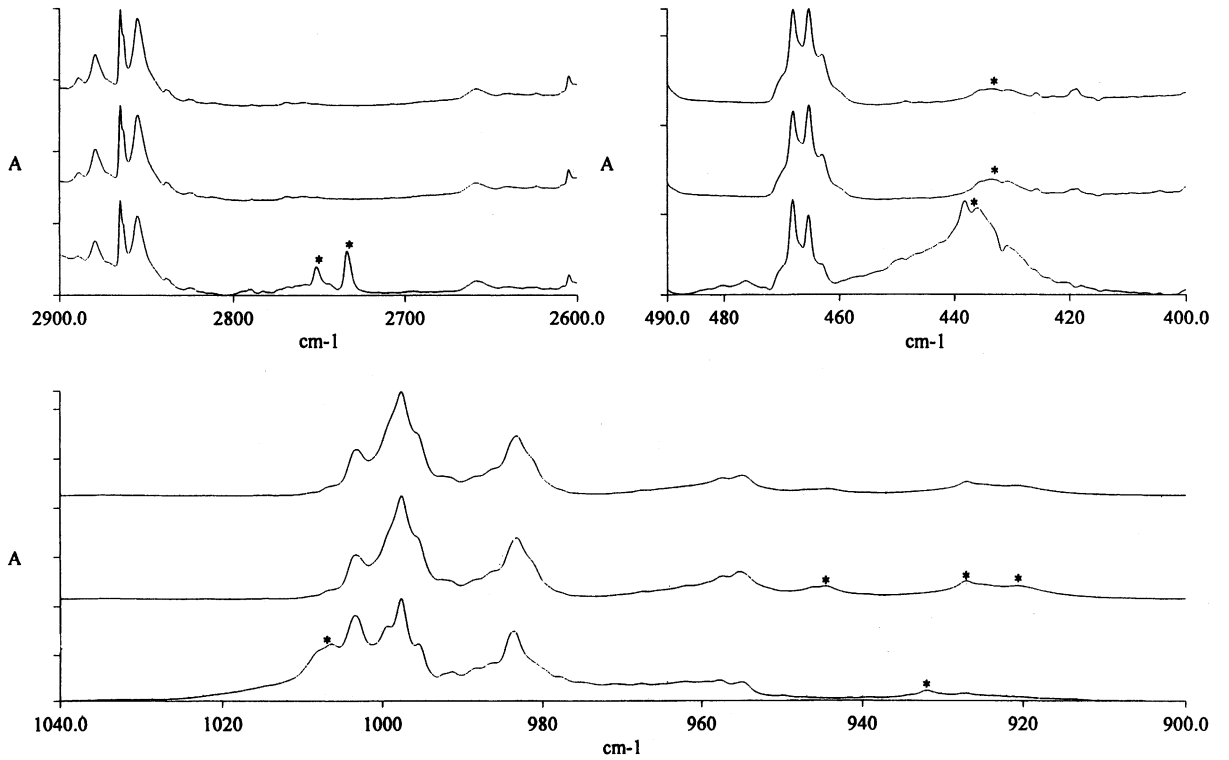

Fig. 1. Infrared spectra of the matrix formed by the twin jet codeposition of a sample of Ar/CH_3SH with a sample of $Ar/CrCl_2O_2$. The top trace shows the spectrum of the matrix upon initial deposition, the middle trace after annealing, and the bottom trace after irradiation with $\lambda >$ 300 nm. Bands marked with an asterisk are due to product species.

irradiation, the bands at 434, 927, 945 and 962 cm^{-1} will be referred to as set A. The bands at 438, 658, 668, 932, 975, 1007, 1311, 1403 and 1417 cm^{-1} that formed upon irradiation will be referred to as group B and the bands at 2752 and 2734 cm^{-1} as group C. The bands at 537, 748, 1182 and 1390 cm^{-1} appear to be independent of CH_3SH and are therefore thought to be due to an impurity. These bands will therefore not be discussed further. Fig. 1 shows spectra for this pair of reagents, after initial deposition, annealing and irradiation.

A number of additional twin jet experiments were carried out with these two reagents, at several different concentration combinations. The results described previously were reproducible in all of these experiments, with the same bands appearing. Within each set, the bands maintained a constant intensity ratio with respect to one another in all of these experiments. In an additional experiment, irradiation times were varied at 15 min intervals from 15 min to 2 h. After 1 h, the spectra no longer changed. In another experiment, irradiation was done prior to annealing with the irradiated spectrum essentially the same as all the other irradiated spectra. Annealing after irradiation had no effect on this spectrum.

Samples of $Ar/CrCl_2O_2$ and Ar/CH_3SH were codeposited in a set of merged jet experiments, employing the same concentration combinations as was used in the twin jet experiments. The initial product bands that were present in the twin jet experiments were also present in the merged jet but were slightly more pronounced. There were no additional new bands present. The reaction zone of the merged system was then heated in several of these experiments, to 100, 200 and 250 °C. Again, there were no new bands, beyond those seen in the twin jet experiments. Annealing had no effect on the merged jet experiments, while irradiation of the matrices produced the same bands as in the twin jet experiments.

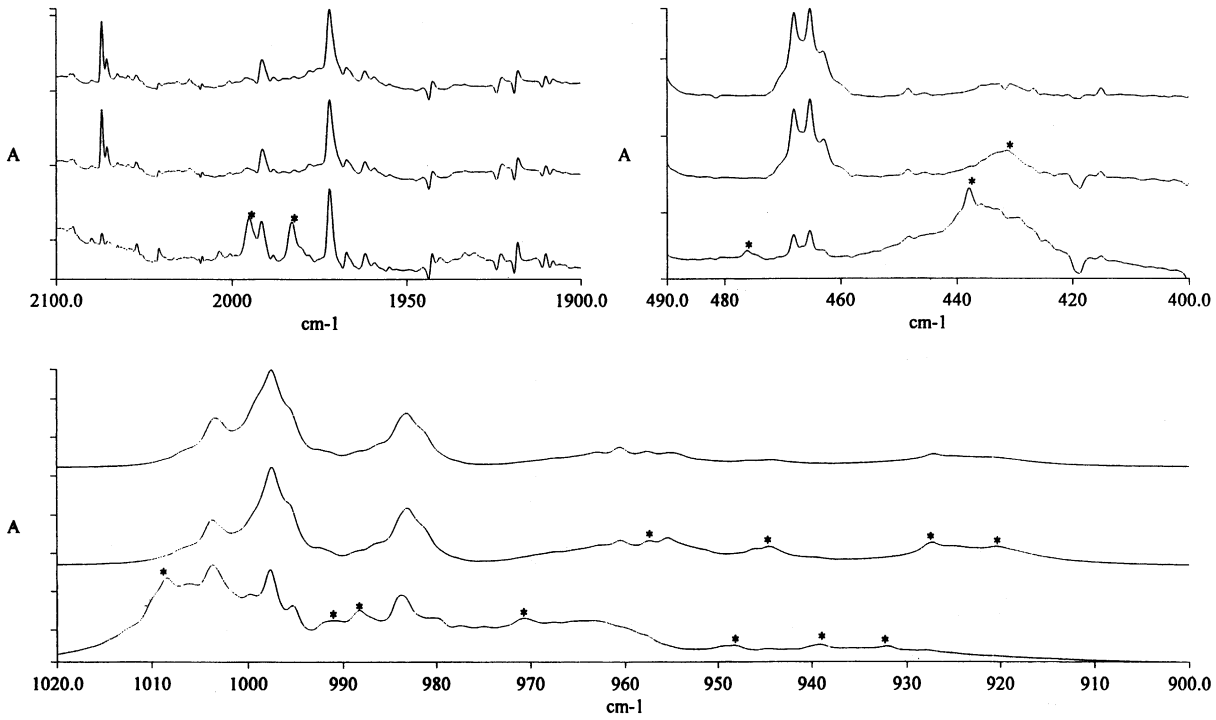

Fig. 2. Infrared spectra of the matrix formed by the twin jet codeposition of a sample of Ar/CH_3SD with a sample of $Ar/CrCl_2O_2$. The top trace shows the spectrum of the matrix upon initial deposition, the middle trace after annealing, and the bottom trace after irradiation with $\lambda >$ 300 nm. Bands marked with an asterisk are due to product species. Note particularly the bands near 1983 and 1995 cm^{-1} due to photo-produced DCl.

3.2. $CrCl_2O_2 + CD_3SD$

Samples of Ar/CD_3SD were codeposited with samples of $Ar/CrCl_2O_2$ in a series of twin jet experiments, using concentrations comparable to those used in the abovementioned experiments with CH_3SH. New product bands formed upon initial deposition were seen at 407, 424, 435, 518, 775, 804, 920, 927, 940, 946, 960, 990, 2508 and 2539 cm^{-1}; some of these bands appeared as doublets or multiplets. Annealing the matrix to 36 K had no discernable effect on the spectra. Irradiation of the matrix created bands at 437, 457, 977, 1008, 2424, 2442, 2563, 2574, 2685, 2726 and 2734 cm^{-1}; again, several of these appeared as doublets or multiplets. At the same time the initial product bands at 920, 927, 940, 946 and 960 cm^{-1} were essentially destroyed. The bands at 424 and 435 cm^{-1} were completely obliterated by new, intense product bands in the same region so it was difficult to determine their fate. The bands designated by group A are 424, 435, 920, 927, 940, 946 and 960 cm^{-1} since these bands were destroyed by irradiation. group B bands are 437, 457, 980 and 1008 cm^{-1}, as these bands all grew uniformly upon irradiation. New bands that also appeared upon irradiation but had no counterpart in the undeuterated methanethiol reactions were located at 2424, 2441, 2444, 2563, 2574 and 2685 cm^{-1} and are referred to as group D. These bands are in the range of the methanethiol dimer and larger aggregates and are so assigned. The bands at 2726 and 2734 cm^{-1} are most likely due to HCl formed from isotopically impure methanethiol-d_4.

A series of merged jet experiments were also conducted with samples of Ar/CD_3SD and $Ar/CrCl_2O_2$. As in the experiments with the normal isotope of methanethiol, no new bands were present in the merged jet experiments (that were not present in the twin jet experiments). Heating the reaction line and annealing again had no effect on the bands

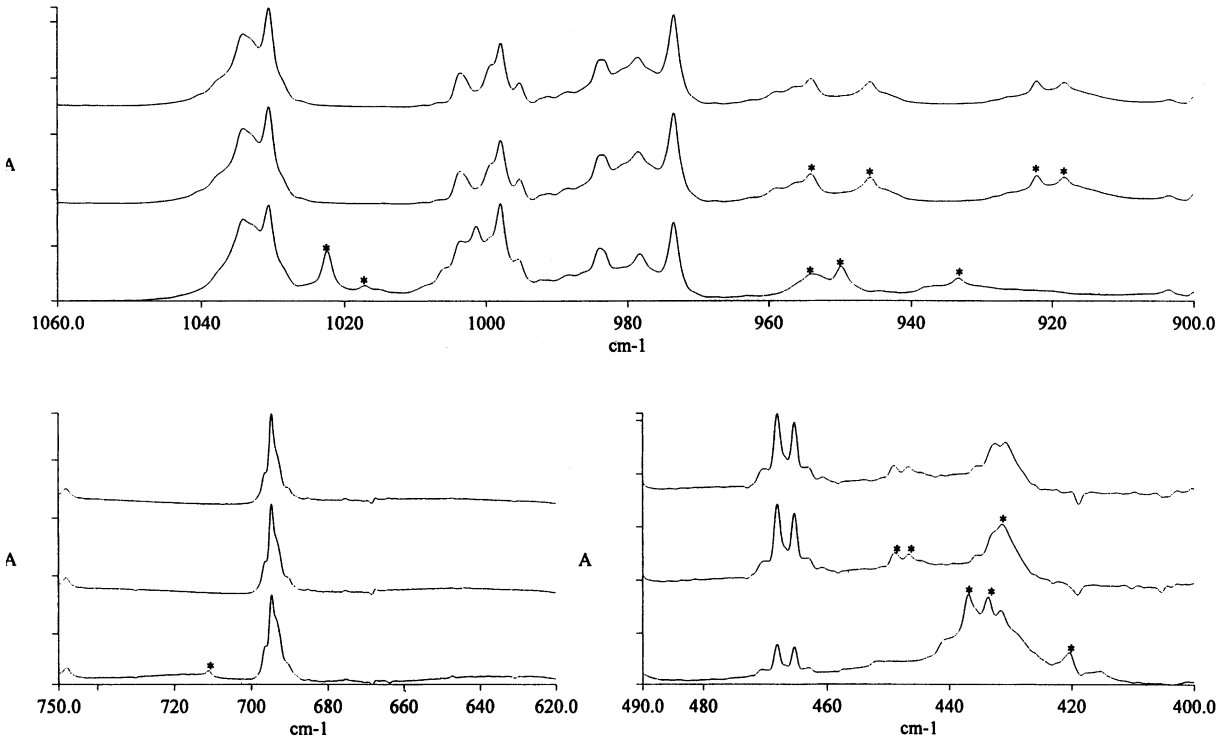

Fig. 3. Infrared spectra of the matrix formed by the twin jet codeposition of a sample of Ar/$(CH_3)_2S$ with a sample of Ar/$CrCl_2O_2$. The top trace shows the spectrum of the matrix upon initial deposition, the middle trace after annealing, and the bottom trace after irradiation with $\lambda >$ 300 nm. Bands marked with an asterisk are due to product species.

produced. Irradiation of the matrix produced the same product bands as in the twin jet mode.

3.3. $CrCl_2O_2 + CH_3SD$

Samples of Ar/CH_3SD were also codeposited with samples of Ar/$CrCl_2O_2$ in a series of twin jet experiments. Product bands appearing upon initial deposition were located at 431, 800, 807, 920, 927, 957, 1392, 1417, 2071, 2074, 2510 and 2558 cm^{-1}. Annealing the matrix to 36 K again showed no discernable effect on the spectrum. Irradiation of the matrix for 1 h created new bands at 438, 476, 755, 932, 939, 948, 971, 980, 988, 991, 1008, 1405, 1983 and 1995 cm^{-1}. All of the product bands that appeared upon initial deposition were essentially gone. The bands at 431, 800, 807, 920, 927 and 957 cm^{-1} again will be referred to as set A. The bands at 438, 476, 755, 932, 939, 948, 971, 980, 988, 991, 1008 and 1405 cm^{-1} will be referred to as set B and the bands at 1983 and 1995 cm^{-1} as set C. Fig. 2 shows spectra for this pair of reagents, after initial deposition, annealing and irradiation.

As with the two previous methanethiols, merged jet experiments produced no new bands. Annealing the matrix again had no effect on the spectra, while irradiation produced the same bands as in the twin jet experiments.

3.4. $CrCl_2O_2 + (CH_3)_2S$

Initial twin jet experiments involving chromyl chloride and dimethylsulfide (DMS) were carried out at the same concentrations as those used in the chromyl chloride/methanethiol reactions. The resulting spectra again showed intense bands due to the parent species along with new weak bands at 432, 448, 918, 922, 946, 953 and 2268 cm^{-1}. Annealing the matrix to 36 K had no effect on the band intensities nor were any new bands formed. Irradiation for 1 h

with the Hg arc lamp produced new bands at 436, 441, 452, 711, 933, 950, 1001, 1017 and 1022 cm^{-1}. The band at 432 cm^{-1} appeared to grow significantly but this was more likely due to the nearby intense band at 436 cm^{-1} that grew in. The bands at 918, 922, 946 and 953 cm^{-1} decreased tremendously while the band at 2268 cm^{-1} exhibited no change. Again, due to the different behavior, the bands at 432, 448, 918, 922, 946 and 953 cm^{-1} will be referred to as group E, the bands at 436, 441, 452, 711, 933, 950, 1001, 1017 and 1022 cm^{-1} will be referred to as group F and the band at 2268 cm^{-1} as group G. Irradiation times were again varied in 15 min intervals. After 1 h, no further changes took place. Fig. 3 shows spectra for this pair of reagents, after initial deposition, annealing and irradiation.

Samples of $Ar/(CH_3)_2S$ and $Ar/CrCl_2O_2$ were allowed to mix prior to deposition in a merged jet system, using a 30 cm reaction zone. The resultant spectra were essentially identical to those obtained in the twin jet mode. Again, the reaction zone was heated to 100, 200 and 250 °C in subsequent experiments but no new bands occurred. Annealing had no effect on the results, while irradiation of the matrix produced the same results as the twin jet experiments after irradiation.

3.5. $CrCl_2O_2 + (CD_3)_2S$

Samples of $Ar/(CD_3)_2S$ were substituted for DMS in a series of experiments with $CrCl_2O_2$. Product bands upon initial deposition were located at 435, 440, 757, 920, 946, 954, 1021 and 2265 cm^{-1}. No changes were detected upon annealing the matrix to 36 K. Irradiation with the H_2O/Pyrex filtered output of a medium pressure Hg arc led to the formation of new bands at 410, 417, 432, 446, 688, 832, 930, 962, 967, 972, 988, 995, 1002, 1027 and 1048 cm^{-1}. The initial product bands at 435, 1021 and 2265 cm^{-1} appeared to increase with irradiation while the bands at 757, 920, 946 and 954 cm^{-1} decreased or disappeared with irradiation. Again due to the different behavior of these bands with respect to irradiation, they can be grouped as follows: group E consists of 435, 440, 757, 920, 946, 954 and 1021 cm^{-1}; group F consists of 410, 417, 432, 446, 688, 832, 930, 962, 967, 972, 988, 995, 1002, 1027 and 1048 cm^{-1} and group G consist of 2265 cm^{-1}.

These two reactants were also studied in several merged jet experiments, with a 30 cm reaction zone. The resultant spectra were essentially identical as in the twin jet mode. Again, the reaction zone was heated to 100, 200 and 250 °C in subsequent experiments but no new bands were observed. Annealing had no effect on the spectrum, while irradiation of the matrices led to spectra that were identical to those obtained in the twin jet experiments after irradiation.

4. Discussion

Twin jet and merged jet deposition led to identical results for each of the systems studied here. In each case, several product species are formed, based on the band groupings and their behavior with respect to irradiation. For the $CH_3SH/CrCl_2O_2$ system, the bands formed upon initial deposition were identified as group A, while the bands of group B were formed upon irradiation, as the bands of group A were destroyed. This strongly suggests sequential product formation. It should also be noted that within a given group, all of the bands maintained a constant intensity ratio with respect to one another, strongly supporting the idea that all of the bands within that group are due to a single absorber.

Upon initial deposition of samples of Ar/CH_3SH and $Ar/CrCl_2O_2$, group A bands were formed. Since in twin jet deposition the reactants mix only very briefly on the surface of the matrix, group A may be identified with the initial intermediate in this system. The yield in the twin jet was very low but increased slightly with annealing. Merged jet yield was slightly more intense but product formation was still very low. Since this product forms upon initial deposition in the twin jet mode, the barrier to formation must be very low. Based on previous studies [7–9] of the reaction of $CrCl_2O_2$ with CH_3OH, $(CH_3)_2O$ and NH_3, as well as ab initio calculations, the species responsible for the group A bands is identified as the molecular complex between the two reactants, $CrCl_2O_2{\cdot}HSCH_3$. Characteristically, complexes form with essentially no activation barrier, and the formation of a complex is indicated by the small shifts of the vibrational modes of the two subunits. Based on the relatively low sample concentrations used and analogy to previous studies, the stoichiometry of the complex is

Table 1
Band positions (cm^{-1}), assignments and comparison to theoretical calculations for $ClCr(O)_2SCH_3$

Band (expt.)	Band (calc.)[a]	D-shift (expt.)[b]	D-shift (calc.)	Assignment
438	454	− 1	− 2	S–Cr–Cl asym. st.
448	469	+ 9	0	S–Cr–Cl sym. st.
658, 668	620	–		S–C stretch
932	988	–		$–CH_3$ rock
939	1000	–		$–CH_3$ rock
975	1072	+ 2	+ 1	O=Cr=O sym. st.
1007	1107	+ 1	+ 1	O=Cr=O asym. st.
1311	1393	–		$–CH_3$ sym. bend
1403	1487	–		$–CH_3$ asym. bend
1417	1502	–		$–CH_3$ asym. bend

[a] Unscaled frequency, from B3LYP/6-311G calculation.
[b] Limited results were obtained with CD_3SD; calculated shifts are only reported for those bands that were observed experimentally in the CD_3SD experiments.

very likely 1:1. For the $CrCl_2O_2{\cdot}HSCH_3$ complex, the S–H stretch shifted from 2604 cm^{-1} in the parent to 2514 cm^{-1} in the complex, while the Cr–Cl stretches near 500 cm^{-1} shifted to 434 cm^{-1} and the Cr=O stretches between 981 and 1003 cm^{-1} shifted to 920 and 960 cm^{-1}. The relatively large red shift of the S–H stretching mode suggested that the structure of the complex involves hydrogen bonding formation [23], from the S–H group to either the oxo or chloride groups on $CrCl_2O_2$. A red shift of the stretching modes of the Lewis acid ($CrCl_2O_2$) suggests some transfer of electron density to the acid, and a slight reduction in the stretching force constants.

The initial group A product bands were destroyed by irradiation with the Hg arc lamp, leading to the appearance of the bands in groups B and C. In previous studies [7,8] of the photochemical reaction of $CrCl_2O_2$ with CH_3OH and NH_3, and $OVCl_3$ with CH_3OH, NH_3 and CH_3SH, in each case the initial complex was destroyed by irradiation and HCl elimination. However, the HCl that is formed is trapped within the same matrix cage as the second photoproduct, and interacts weakly with that species. Consequently, the absorption band(s) of the photo-produced HCl do not occur where isolated HCl has been observed previously [24,25], but is shifted to lower energy. For each of the previous systems, HCl complexed to the photoproduct was observed between 2700 and 2800 cm^{-1}, near the group C bands in the current study. Moreover, when CH_3SD was employed, the bands in the present study shifted to 1983 and 1995 cm^{-1}. This is precisely the shift anticipated for HCl, and the shift observed previously [24,25]. Based on the earlier studies, and this deuterium shift, the bands in group C are assigned to HCl (DCl) arising through photoelimination from the initial molecular complex.

The observation that the bands in groups B and C grow in under the same conditions while the group A bands were destroyed suggests that the bands in group B may be assigned to the HCl elimination product from the complex, namely $ClCr(O)_2SCH_3$. This is consistent with all of the previous studies on similar systems, including the $OVCl_3/CH_3SH$ system. To further support this identification, density functional calculations were carried out on this intermediate species. These calculations converged to an energy minimum, demonstrating that $ClCr(O)_2SCH_3$ should be a stable species. Further, the calculations yielded a theoretical infrared spectrum, for comparison to experiment. As shown in Table 1, the agreement between experiment and theory is quite reasonable, particularly recognizing that calculations at the B3LYP/6-311G level of theory are typically 3–4% high. Consequently, the set B bands in the $CH_3SH/CrCl_2O_2$ experiments are assigned to the novel $ClCr(O)_2SCH_3$ intermediate.

Further photolysis of the matrix, and the heating of the reaction line in the merged jet experiments, did not lead to any new species. This indicates that the $ClCr(O)_2SCH_3$ species is relatively stable to photochemical decomposition. This is in contrast to several

of the previously studied systems, where further thermal reaction and decomposition was seen.

The sequence of product formation in the $(CH_3)_2S/CrCl_2O_2$ system was quite similar to that described earlier for the $CH_3SH/CrCl_2O_2$ system. Initial weak product bands were formed upon twin jet deposition (group E). These were destroyed by Hg arc irradiation as group F bands grew in. This observation, combined with the argument presented above concerning the formation of molecular complexes, strongly suggests that the group E bands are due to the formation of the isolated 1:1 complex, $CrCl_2O_2{\cdot}S(CH_3)_2$. This complex is characterized by the following shifts of the vibrational modes of the two subunits: the Cr–Cl stretching bands around 500 cm^{-1} shifted to 434 cm^{-1}; the Cr=O stretches between 981 and 1003 cm^{-1} shifted to 919 and 954 cm^{-1}; and the CH_3 rocking band at 1030 cm^{-1} shifted to 1021 cm^{-1}. In contrast to the complex of $CrCl_2O_2$ with CH_3SH, $(CH_3)_2S$ does not have a hydrogen available for hydrogen bonding, and the interaction is probably a classical coordination compound, with the donation of a pair of electrons from the sulfur to the Cr center.

The group E product bands were destroyed by irradiation with a Hg arc lamp, bringing about the appearance of the bands in group F. Group F grows as group E decreases which suggests that it is formed from the initial product. While HCl elimination is less likely in this case (and no bands due to HCl formation were observed), a hint as to the product comes from the band at 711 cm^{-1} in the $(CH_3)_2S/CrCl_2O_2$ system and the band at 688 cm^{-1} in the $(CD_3)_2S/CrCl_2O_2$ system. These bands fall very near the most intense band of CH_3Cl and CD_3Cl, namely the C–Cl stretch [26]. Unfortunately, the product yield was low and the regions where other bands of CH_3Cl might be observed were obscured by parent band absorptions. Nonetheless, these bands indicate the formation of $CH_3Cl(CD_3Cl)$, which would be a potential and reasonable elimination product from the initial complex. The second photoproduct would be $ClCr(O)_2SCH_3$, the same intermediate observed for the $CH_3SH/CrCl_2O_2$ system. Indeed, the remainder of the set F bands was close to the set B bands, above. However, the product band intensities and product yields were quite low, less than that in the $CH_3SH/CrCl_2O_2$ experiments. Thus, the identification of $ClCr(O)_2SCH_3$ as the second photoproduct in this system must be regarded as tentative.

Finally, the one band in group G at 2268 cm^{-1} can be assigned to the hydrogen bonded complex of HCl with $(CH_3)_2S$, $ClH\cdots S(CH_3)_2$. This complex has been described previously [27], the group G band matches very well. Since HCl is a minor impurity in all experiments containing $CrCl_2O_2$, the presence of this complex is very reasonable. An analogous band, at 2514 cm^{-1}, was observed in the $CH_3SH/CrCl_2O_2$ system, and is likewise assigned.

Acknowledgements

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