Matrix Isolation Studies of Photochemical and Thermal Reactions of 3- and 5-Membered Cyclic Hydrocarbons with CrCl$_2$O$_2$

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The matrix isolation technique has been combined with infrared spectroscopy and theoretical calculations to characterize the products of the photochemical and thermal reactions of cyclopentadiene, cyclopentene, cyclopentane, and cyclopropane with CrCl$_2$O$_2$. While initial twin jet deposition of the reagents led to no visible changes in the recorded spectra, product bands were observed following irradiation with light of $\lambda >$ 300 nm. The irradiation was shown to lead to oxygen atom transfer to the five-membered rings, forming complexes between cyclic alcohol derivatives and CrCl$_2$O. For the cyclopentadiene and cyclopentene systems, complexes between cyclic ketone derivatives and CrCl$_2$O were also observed. For cyclopropane, *a ring-opening oxidation reaction followed by fragmentation was observed for the first time*, forming the H$_2$C=O−CrCl$_2$O complex and C$_2$H$_4$. In the room temperature thermal (merged jet) reactions between CrCl$_2$O$_2$ and cyclopentadiene, cyclopent-3-enone was observed. At the higher temperatures, 150 and 200 °C, 1,3-cyclopentanedione was also observed as well. No product bands were detected in the merged jet experiments for the other three systems. These conclusions were supported by isotopic labeling (^{2}H) and by B3LYP/6-311G++(d,2p) density functional calculations.

Introduction

High-valent transition metal oxo compounds, including CrCl$_2$O$_2$, are very strong oxidizing agents and are known to oxidize a wide range of organic substrates. These metal oxo compounds are able to transfer an oxygen atom to certain olefins and hydrocarbons.[1–11] Most of these studies were limited to product studies, and there was no identification of the initial intermediates in these experiments. However, extensive theoretical calculations have explored such systems, and conclusions have been made as to the existence of multiple intermediates in model systems involving high-valent transition metal oxo compounds.[8,9,12–14]

The matrix isolation technique was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates[15–17] and may provide access to the study of initial intermediates in the above reactions. Past studies have used matrix isolation to study reactions of cyclopentadiene, cyclopentane, and cyclopropane. Margrave and co-workers codeposited iron atoms and cyclopentadiene in which cyclopentadienyliron hydride was produced.[18] Later, Samet and co-workers studied the hydrogen-bonded complexes of cyclopentadiene with strong bases (ammonia, trimethylamine, and dimethylether).[19] More recently, Miyazaki and Yamada studied the photochemistry of cyclopentadiene.[20] They observed that the super high-pressure Hg arc irradiation of cyclopentadiene led to bicyclo[2.1.0]-pent-2-ene, and at shorter wavelengths, with a low-pressure Hg arc lamp, further reactions of bicyclo[2.1.0]pent-2-ene were found to produce allylacetylene and vinylallene. Finally, Truscott and Ault studied 1:1 complexes of hydrohalides with cyclopropane.[21] They observed a slight shift of the hydrogen halide stretching frequency from the parent position indicating a weakly bound complex.

Past studies in this laboratory have examined the matrix-isolated products of the thermal and photochemical reactions of CrCl$_2$O$_2$, OVCl$_3$, and OVF$_3$ with organic and inorganic substrates.[10,22–34] Two recent studies in this laboratory[35,36] examined the reactions of CrCl$_2$O$_2$ with benzene and cyclic C$_6$ compounds with a lesser degree of unsaturation in the ring (cyclohexane and cyclohexene). In the first system, light of λ > 590 nm led to reaction and oxygen atom transfer, forming a complex between 2,4-cyclohexadienone and CrCl$_2$O. In the second series of reactions, irradiation led to reaction and oxygen atom transfer, forming complexes between cyclic alcohols and CrCl$_2$O. This was one of the first observations of C−H bond activation and oxygen atom insertion into a C−H bond from CrCl$_2$O$_2$. In addition, the reaction of cyclohexene with CrCl$_2$O$_2$ also led to the formation of cyclohexanone complexed to CrCl$_2$O. In other recent studies in this laboratory with CrCl$_2$O$_2$ and substituted benzenes, a similar product distribution was observed.[37–39] The present study examines the photochemical reactions of CrCl$_2$O$_2$ with cyclic C$_3$ and C$_5$ compounds to further explore the nature of the oxidation reaction and the effects of increasing ring strain on the product distribution.

Experimental Section

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[40] Chromyl chloride, CrCl$_2$O$_2$ (Acros), was introduced into the vacuum system as the vapor above the room temperature liquid, after purification by freeze−pump−thaw cycles at 77 K. Cyclopentadiene was prepared by cracking the dimer[41] (dicyclopentadiene, Aldrich, 95%). The resulting cyclopentadiene monomer, cyclopentene (Aldrich), cyclopentene-d_8 (98.7% D, CDN Isotopes), and cyclopentane (Aldrich) were introduced in a similar manner into a separate vacuum manifold and were purified by repeated freeze−pump−thaw cycles at 77 K. Cyclopropane (Aldrich) and cyclopropane-d_6 (99.1% D, CDN

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TABLE 1: Key Product Bands[a] Arising from the Irradiation of Matrices Containing CrCl$_2$O$_2$ and Cyclopentadiene Compared to the Calculated[b] Bands of CrCl$_2$O-cyclopent-2-enone, CrCl$_2$O-cyclopent-3-enone, and CrCl$_2$O-cyclopenta-1,3-dienol

CrCl$_2$O$_2$ + cyclopentadiene (exptl freq[c])	CrCl$_2$O-cyclopent-2-enone (calcd freq)	CrCl$_2$O-cyclopent-3-enone (calcd freq)	CrCl$_2$O-cyclopenta-1,3-dienol (calcd freq)	assignment
449	506	454	456	Cr–Cl st., CrCl$_2$O
1005	1130	1102	1103	Cr=O st., CrCl$_2$O
1564			1532	C=C st. (dienol)
1602	1628			C=O st. (2-enone)
1687		1671		C=O st. (3-enone)
3552			3577	O–H st. (dienol)

[a] For complete set of product bands, see Supporting Information Table S1. [b] Calculated at the B3LYP/6–311G++(d,2p) level of theory. [c] Band positions in cm^{-1}.

Isotopes) were introduced from lecture bottles into the vacuum system and were purified by freeze–pump–thaw cycles at 77 K. Argon (Wright Brothers) 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 window, allowing for only a 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, all of these matrices were irradiated for 1.0 h or more hours with the H$_2$O/Pyrex-filtered output of a 200-W medium-pressure Hg arc lamp, after which additional spectra were recorded.

Some of the experiments were conducted in the merged jet mode,[42] 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. This region was approximately 50 cm in length and could be heated to temperatures as high as 200 °C. 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 a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using Gaussian 03 and 03W suite of programs.[43] 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, after initial calculations with smaller basis sets were run to approximately locate energy minima. Thermodynamic functions for the reactants and potential intermediates were also calculated.

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[18,44–47] and with blanks run previously in this laboratory. Each blank experiment was then irradiated by the H$_2$O/Pyrex-filtered output of a 200-W Hg arc lamp for 1.0 h, and no changes were noted, other than in the Ar/CrCl$_2$O$_2$ blank, where the growth of very weak bands due to photochemical reaction with impurity H$_2$O was seen.[24] Weak bands due to HCl impurity were noted in all of the CrCl$_2$O$_2$ blank experiments.

CrCl$_2$O$_2$ + Cyclopentadiene. In an initial twin jet experiment, a sample of Ar/CrCl$_2$O$_2$ = 500 was codeposited with a sample of Ar/cyclopentadiene = 400. After 23.0 h of deposition, no new bands were detected. This sample was annealed to 32

K and another spectrum was recorded, and no new features were observed in the resulting spectrum. The matrix was then irradiated for 1.0 h with the filtered ($\lambda > 300$ nm) output of a medium-pressure Hg arc lamp. This produced many new product bands, as listed in Tables 1 and S1. The most intense bands were seen at 3552, 1687, 1602, 1352, 1005, 950, 919, 821, 783, 541, and 449 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure 1 shows representative regions of this spectrum.

Numerous additional experiments were conducted, using twin jet deposition to deposit the two reagents into solid argon matrices at different concentrations. The concentrations ranged from Ar/CrCl$_2$O$_2$ = 300 to Ar/CrCl$_2$O$_2$ = 600 and Ar/cyclopentadiene = 300 to Ar/cyclopentadiene = 500. The same products bands were observed throughout, with relative intensities (i.e., relative to all other bands in the set) that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments. The product bands that grew in during irradiation reached a maximum in 1.5 h of irradiation.

A series of merged jet experiments was conducted with samples of Ar/CrCl$_2$O$_2$ = 500 and Ar/cyclopentadiene = 500, using a 53 cm merged or reaction region. The temperature of the merged region was varied for the experiments: room temperature, 100, 150, and 200 °C. At the lower temperatures, many new bands were observed. The most intense product band was seen at 1759 cm^{-1}, while somewhat intense bands were seen at 2864, 1402, 1263, 1165, 1131, 1048, and 769 cm^{-1}. At the higher temperatures, additional new bands were seen while the bands observed in the previous experiments at the lower temperatures, were reduced. All of the merged jet product bands are listed in Table S2, while Table 2 lists key bands. Figure 2 shows a representative region of this spectrum with the merged region held at room temperature.

CrCl$_2$O$_2$ + Cyclopentene. In an initial twin jet experiment, a sample of Ar/CrCl$_2$O$_2$ = 400 was codeposited with a sample of Ar/cyclopentene = 400. After 23.0 h of deposition, no new bands were detected. This sample was annealed to 32 K, and another spectrum was recorded, and no new features were observed in the resulting spectrum. The matrix was then irradiated for 1.5 h with the filtered ($\lambda > 300$ nm) output of a medium-pressure Hg arc lamp. This produced many new product bands, as listed in Supporting Information Table S3. The more intense bands were seen at 3554, 1678, 1390, 1194, 1026, 1007, 916, 858, 825, 787, 778, and 447 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure 3 shows representative regions of this spectrum.

Numerous additional experiments were conducted, using twin jet deposition at concentrations ranging from Ar/CrCl$_2$O$_2$ = 400 to Ar/CrCl$_2$O$_2$ = 600 and Ar/cyclopentene = 300 to Ar/cyclopentene = 500. The same products bands were observed
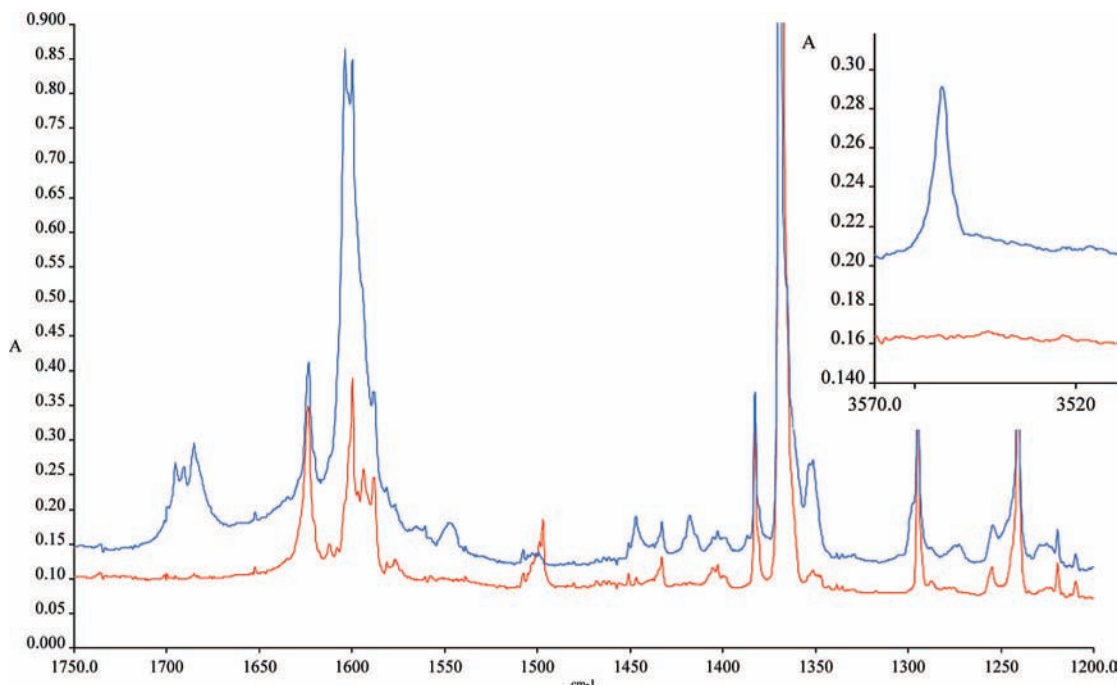
Figure 1. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/CrCl$_2$O$_2$ = 500 with a sample of Ar/cyclopentadiene = 400. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of λ > 300 nm. The upper spectra is of the O−H stretch region.

TABLE 2: Product Bands^a in the Merged Jet Codeposition of CrCl$_2$O$_2$ with Cyclopentadiene Assigned to Cyclopent-3-enone^b

product band position	cyclopent-3-enone (literature exptl freq^c)
627	623
769	766
772	772
954	957
1131	1135
1165	1167
1263	1266
1402	1410
1612	1617
1759	1765
1776	1774

^{a} Frequencies in cm^{-1}. ^{b} see Supporting Information Table S2 for complete set of product bands. ^{c} Vapor phase, see ref 49.

throughout, with relative intensities (i.e., relative to all other bands in the set) that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments. The product bands that grew in during irradiation reached a maximum in 1.5 h of irradiation.

A series of merged jet experiments was conducted with samples of Ar/CrCl$_2$O$_2$ = 500 and Ar/cyclopentene = 500. With the merged region held at room temperature, the resulting spectrum was identical to that observed in the twin jet experiments before irradiation, with no new product bands. In subsequent experiments, with the merged region heated to 100, 150, and 200 °C, no product bands were observed.

CrCl$_2$O$_2$ + Cyclopentene-d_8. Multiple twin jet experiments were conducted in which samples of Ar/CrCl$_2$O$_2$ were codeposited with samples of Ar/cyclopentene-d_8. After 22.0 h of deposition, the matrix was irradiated for 1.0 h. This irradiation produced many new bands, with the more intense bands at 2629, 1675, 1331, 1102, 1007, 978, 931, 822, 719, and 444 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure S1 shows representative regions of this spectrum.

CrCl$_2$O$_2$ + Cyclopentane. In an initial twin jet experiment, a sample of Ar/CrCl$_2$O$_2$ = 500 was codeposited with a sample of Ar/cyclopentane = 500. After 23.0 h of deposition, no new bands were detected. The matrix was then irradiated for 1.0 h with the filtered (λ > 300 nm) output of a medium-pressure Hg arc lamp. This produced many new product bands, as listed in Table S4. The more intense bands were seen at 3573, 1439, 1338, 1189, 1171, 1050, 1006, 946, 933, 723, and 447 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure 4 shows representative regions of this spectrum.
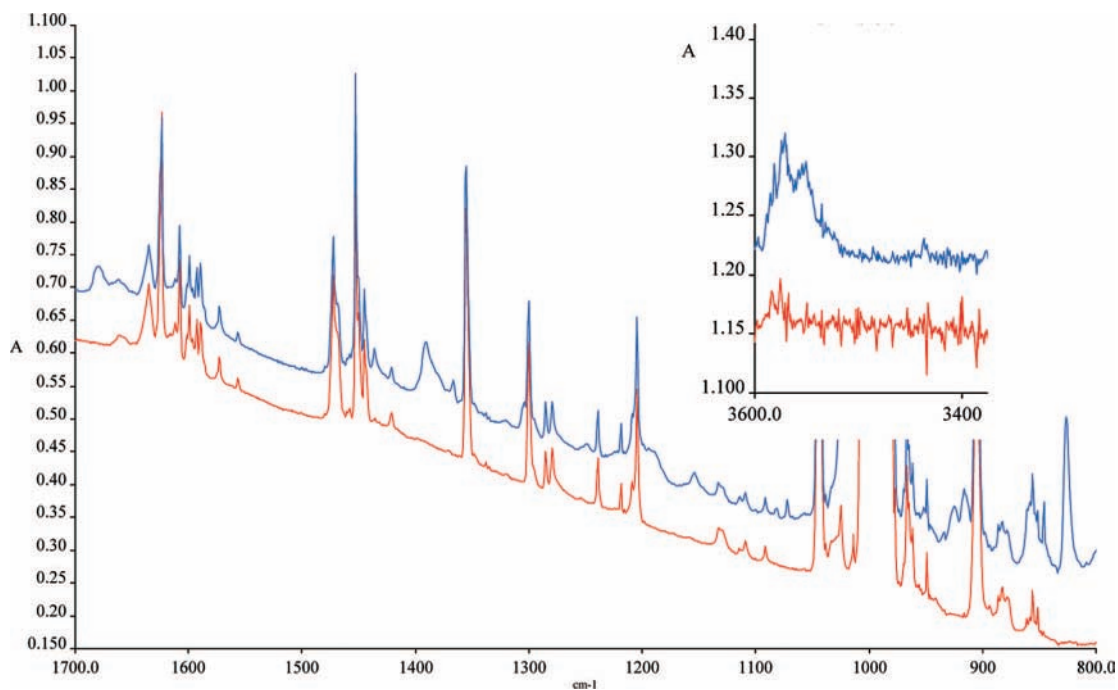
Numerous additional twin jet experiments were conducted at concentrations ranging from Ar/CrCl$_2$O$_2$ = 400 to Ar/CrCl$_2$O$_2$ = 900 and Ar/cyclopentane = 300 to Ar/cyclopentane = 900. The same products bands were observed throughout, with relative intensities (i.e., relative to all other bands in the set) that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments. The product bands that grew in during irradiation reached a maximum in 1.0 h of irradiation.

A series of merged jet experiments was conducted with samples of Ar/CrCl$_2$O$_2$ = 500 and Ar/cyclopentane = 500. With the merged region held at room temperature, the resulting spectrum was identical to that observed in the twin jet experiments with no new product bands. In subsequent experiments, with the merged region heated to 100 and 150 °C, again no new product bands were observed.

CrCl$_2$O$_2$ + Cyclopropane. In an initial twin jet experiment, a sample of Ar/CrCl$_2$O$_2$ = 500 was codeposited with a sample of Ar/cyclopropane = 450. After 23.0 h of deposition, no new bands were detected. The matrix was then irradiated for 1.0 h with the filtered (λ > 300 nm) output of a medium-pressure Hg arc lamp. This produced new product bands at 1673, 1490, 1480, 1440, 1249, 1009, 967, 948, and 459 cm^{-1} and are listed in Table 3. Most of the observed product bands were split into doublets or multiplets. Figure 5 shows representative regions of this spectrum.

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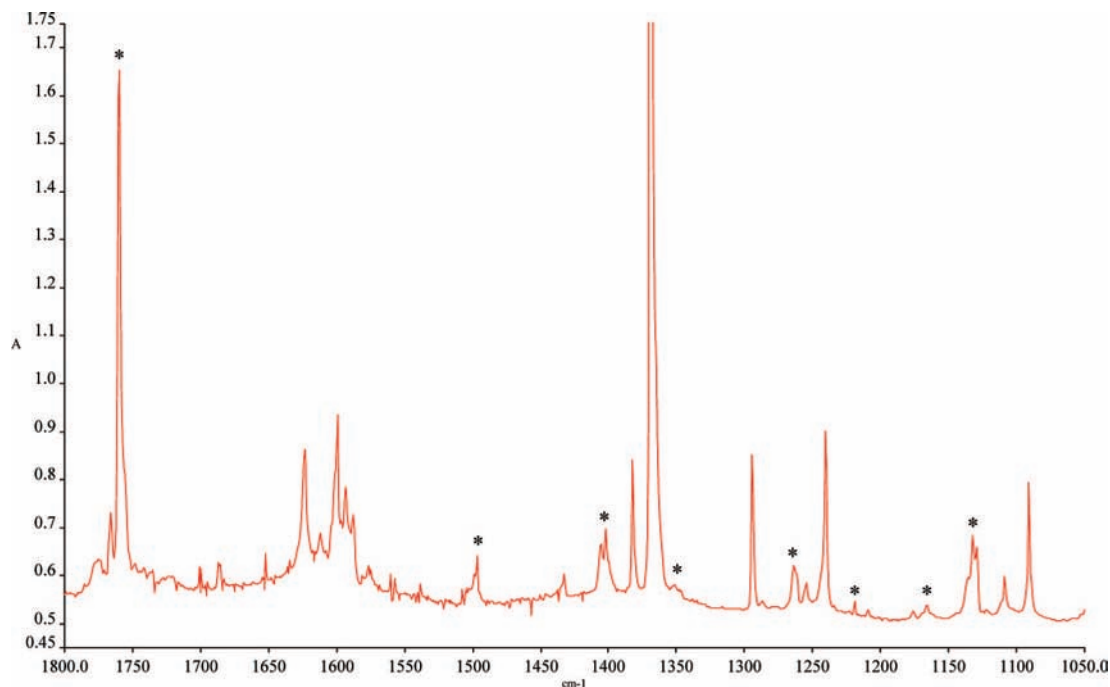
Figure 2. Infrared spectrum of a matrix formed by the merged jet deposition of a sample of Ar/CrCl$_2$O$_2$ = 500 with a sample of Ar/cyclopentadiene = 450. Bands marked with an asterisk are due to the resulting products. The merged region was held at room temperature.
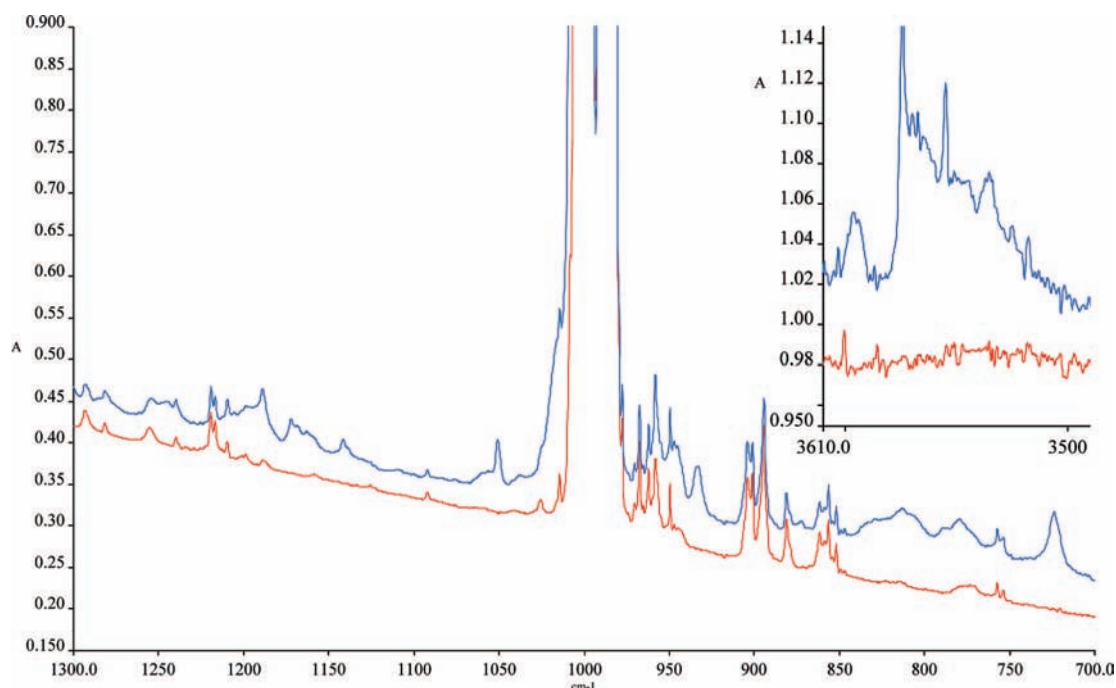

Figure 3. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/CrCl$_2$O$_2$ = 400 with a sample of Ar/cyclopentene = 400. The lower trace is before irradiation, while the upper trace is after 1.5 h of irradiation with light of λ > 300 nm. The upper spectra is of the O−H stretch region.

Numerous additional experiments were conducted, using twin jets to deposit the two reagents into solid argon matrices at different concentrations. The concentrations ranged from Ar/CrCl$_2$O$_2$ = 400 to Ar/CrCl$_2$O$_2$ = 900 and Ar/cyclopropane = 350 to Ar/cyclopropane = 900. The same products bands were observed throughout, with relative intensities (i.e., relative to all other bands in the set) that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments. The product bands that grew in during irradiation reached a maximum in 1.5 h of irradiation.

A series of merged jet experiments was conducted with samples of Ar/CrCl$_2$O$_2$ = 500 and Ar/cyclopropane = 450. With the merged region held at room temperature, no product bands were observed. In subsequent experiments, with the merged region heated to 100, 150, and 200 °C, no product bands were noted.

CrCl$_2$O$_2$ + Cyclopropane-d_6. Multiple twin jet experiments were conducted in which samples of Ar/CrCl$_2$O$_2$ were codeposited with samples of Ar/cyclopropane-d_6. After 23.0 h of deposition, the matrix was irradiated for 1.0 h. This irradiation

Figure 4. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/CrCl$_2$O$_2$ = 400 with a sample of Ar/cyclopentane = 400. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm. The upper spectra is of the O−H stretch region.

TABLE 3: Observed[a] and Calculated[b] Frequencies Isotopic Shifts for the CrCl$_2$O−Formaldehyde Complex[c]

band position		deuterium shift		
exptl	calcd	exptl	calcd	assignment
459	447	−3	−2	Cr−Cl stretch, CrCl$_2$O
1009	1120	0	2	Cr=O stretch, CrCl$_2$O
1249	1248	−281	−261	CH$_2$ rock, CH$_2$O
1490	1500	−402	−402	CH$_2$ bend, CH$_2$O
1673	1676	−47	−42	C=O stretch, CH$_2$O

[a] Band positions in cm^{-1}. [b] Calculated at the (B3LYP/6-311G++(d,2p)) level. [c] Bands of C$_2$H$_4$ observed at 948, 967, 1440, and 1480 cm^{-1}.

produced many new bands, at 2184, 2138, 1633, 1626, 1088, 1075, 1071, 1009, 968, 957, 734, and 456 cm^{-1}. Most of the observed product bands were split into doublets or multiplets.

Results of Calculations

The structures, energetics, and vibrational spectra of a number of possible products of the four systems were calculated using the B3LYP hybrid functional and basis sets as high as 6-311G++(d,2p). Since experimental evidence for oxygen atom transfer was observed (see below), calculations focused on the possible products of oxygen atom transfer, complexed to the remaining metal fragment, CrCl$_2$O, as well as the products of HCl elimination from the initial cage pair. These include cyclic ketones through O atom addition and cyclic alcohols through O atom insertion. All the proposed complexes optimized to an energy minima on their respective potential energy surfaces, with all positive vibrational frequencies. Figure 6 shows the energies of the calculated likely structures (products) relative to CrCl$_2$O$_2$ + cyclopentadiene; the energies are also listed in Table 4. Figure S2 of Supporting Information shows a representation of these calculated structures (structures **S2a−l**). Tables S5−S7, in the Supporting Information, list the energies of the calculated likely structures (products) relative to CrCl$_2$O$_2$

+ cyclopentene, CrCl$_2$O$_2$ + cyclopentane, and CrCl$_2$O$_2$ + cyclopropane, respectively. The Supporting Information also shows graphic representations of all of these calculated structures (structures **S3a−g**, **S4a−c**, and **S5a−g**) as well as a figure showing the calculated energies relative to CrCl$_2$O$_2$ + cyclopentene.

Discussion

For the four systems studied here, no distinct product bands were observed upon initial twin jet deposition. Subsequent irradiation with light of $\lambda > 300$ nm led to the formation of strong product bands. These results are similar to recent systems studied in this laboratory.[35–39] Since most molecules do not diffuse within the argon lattice at 14 K, a photochemical reaction can only occur after twin jet deposition between reactants trapped within the same matrix cage. Cage pairs are formed from the statistical distribution of components of the system during the matrix condensation process. At the low concentrations employed in these studies, on the order of 1:1:1000, it is very probable that the stoichiometry of the cage pairs is 1:1, i.e., one molecule of CrCl$_2$O$_2$ and one substrate molecule (e.g., cyclopentadiene). In addition, the relative intensities of the product bands remained constant as the concentration of the initial reagents was varied, indicating that either one product is formed, or if more than one is formed the products are always formed in the same relative amounts.

Two different modes of photochemical reaction of CrCl$_2$O$_2$ with small molecules have been observed in recent matrix studies. The first involves HCl elimination from the initial cage pair and addition of the organic or inorganic fragment to the chromium center (e.g., CrCl$_2$O$_2$ + NH$_3$ → ClCr(O)$_2$NH$_2$ + HCl). These two species could then form a weakly hydrogen-bonded complex within the matrix.[10,23,24,31,33] The second involves oxygen atom transfer from CrCl$_2$O$_2$ to the reaction partner, followed by complexation between the oxidized product and the CrCl$_2$O species.[27,28] In twin jet experiments with all four systems, the HCl elimination product can readily be
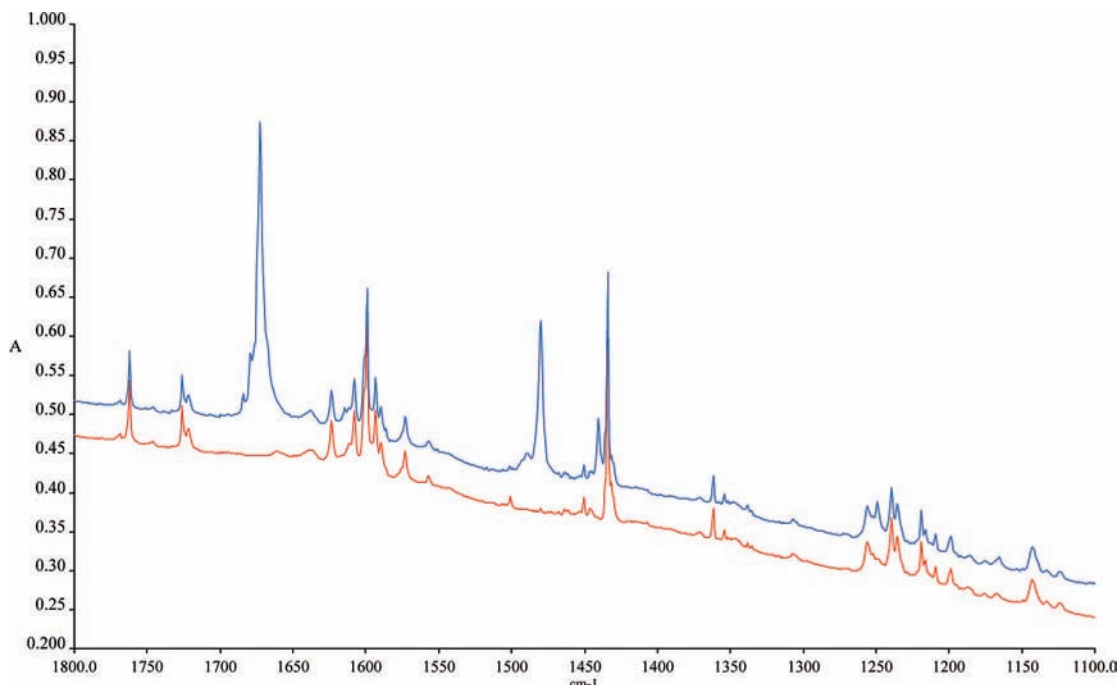
Figure 5. Infrared spectra of a matrix formed by the twin jet deposition of a sample of $Ar/CrCl_2O_2 = 500$ with a sample of $Ar/cyclopropane = 450$. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm.
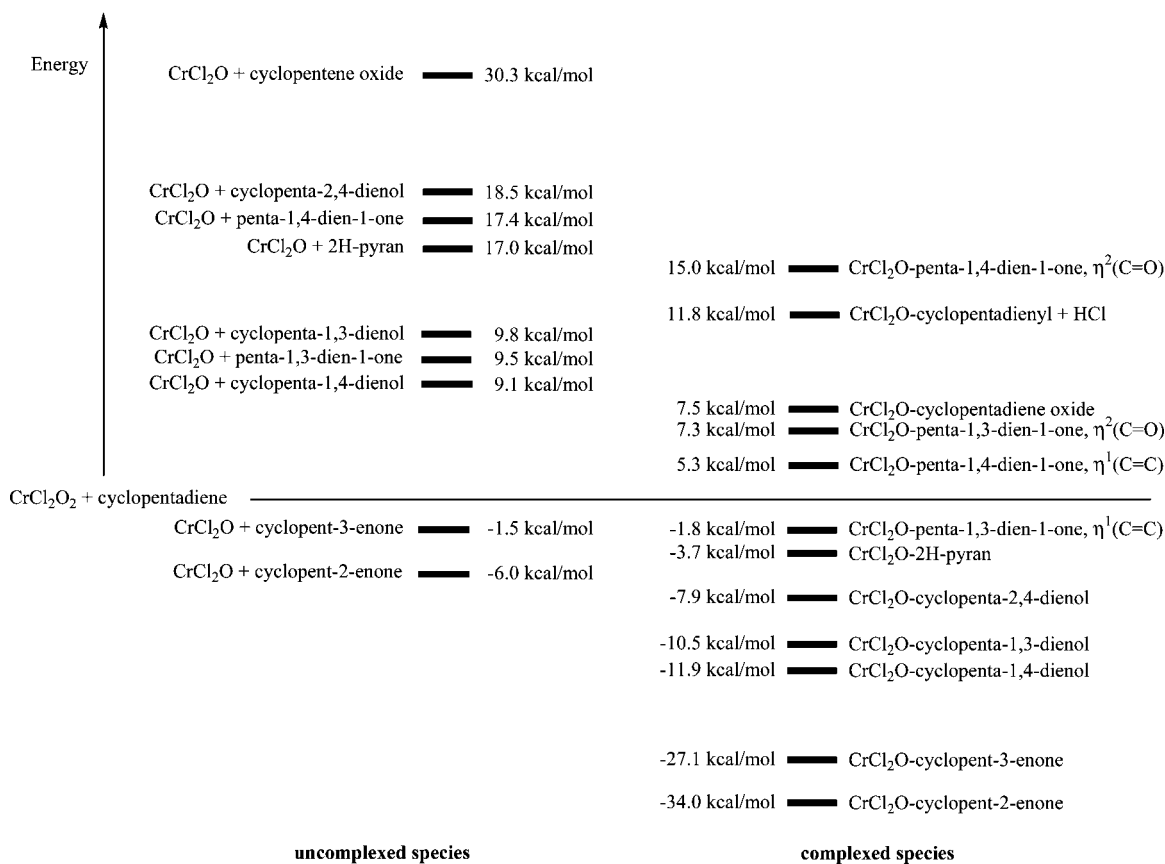
Figure 6. Relative energies of the uncomplexed and complexed products as compared to $CrCl_2O_2$ and cyclopentadiene.

eliminated by careful examination of the HCl stretching region. No new bands were detected in this region in any experiment, other than a very weak HCl absorption known to arise from the photochemical reaction of $CrCl_2O_2$ with impurity H_2O. Further, the vibrational spectra calculated for HCl elimination products were not consistent with the experimental spectra. Thus, it is reasonable to conclude that the HCl elimination

reaction channel does not occur photochemically for any of these systems. However, in the cyclopentadiene system there is evidence of HCl elimination in the merged jet experiments (see below).

The second reaction pathway involves O atom transfer to the substrate and leads to the formation of $CrCl_2O$, complexed to an oxidized product. $CrCl_2O$ has been observed by several

TABLE 4: Calculated (B3LYP/6-311G++(d,2p)) Relative Energies[a] of Possible Products (Uncomplexed and Complexed) from the $CrCl_2O_2$ and Cyclopentadiene Reaction

uncomplexed products	relative energies (kcal/mol)	complexed products	relative energies (kcal/mol)
$CrCl_2O$ + cyclopentadiene oxide	30.3	$CrCl_2O$-penta-1,4-dien-1-one, η^2 (CO)	15.0
$CrCl_2O$ + cyclopenta-2,4-dienol	18.5	$CrClO_2$-cyclopentadienyl + HCl	11.8
$CrCl_2O$ + penta-1,4-dien-1-one	14.4	$CrCl_2O$-cyclopentadiene oxide	7.5
$CrCl_2O$ + 2H-pyran	17.0	$CrCl_2O$-penta-1,3-dien-1-one, η^2 (CO)	7.3
$CrCl_2O$ + cyclopenta-1,3-dienol	9.8	$CrCl_2O$-penta-1,4-dien-1-one, η^1 (end on)	5.3
$CrCl_2O$ + penta-1,3-dien-1-one	9.5	$CrCl_2O$-penta-1,3-dien-1-one, η^1 (end on)	−1.8
$CrCl_2O$ + cyclopenta-1,4-dienol	9.1	$CrCl_2O$-2H-pyran	−3.7
$CrCl_2O$ + cyclopent-3-enone	−1.5	$CrCl_2O$-cyclopenta-2,4-dienol	−7.9
$CrCl_2O$ + cyclopent-2-enone	−6.0	$CrCl_2O$-cyclopenta-1,3-dienol	−10.5
		$CrCl_2O$-cyclopenta-1,4-dienol	−11.9
		$CrCl_2O$-cyclopent-3-enone	−27.1
		$CrCl_2O$-cyclopent-2-enone	−34.0

[a] Energies relative to the reactants, $CrCl_2O_2$ + cyclopentadiene.

research groups[5,28,48] and has characteristic absorptions near 1014 and 450 cm^{-1}. The exact positions of the absorptions vary slightly from system to system, due to complexation to the oxidized product. In the present study, product bands were observed near 1014 and 450 cm^{-1} for every system and are very reasonably assigned to $CrCl_2O$. Moreover, these two bands did not shift in experiments with deuterated isotopomers, indicating that the species responsible for these two bands very likely does not contain H (or D). Thus, the spectral evidence strongly supports formation of $CrCl_2O$ through oxygen atom transfer from $CrCl_2O_2$ to all three of the 5-membered rings and the 3-membered ring in a reaction analogous to the previously studied $CrCl_2O_2$/benzene system.

$CrCl_2O_2$ + Cyclopentadiene. A significant number of product bands were observed in the photochemical reaction of $CrCl_2O_2$ with cyclopentadiene, as listed in Tables 1 and S1. $CrCl_2O$ was observed with absorptions at 1005 and 449 cm^{-1}. The two double bonds in the ring increase the number of possible oxidation products. All of the species considered as candidates for the experimental spectrum are listed in Table 4. The $CrCl_2O$–cyclopentadiene oxide complex was computed to be one of the highest energy complexes under consideration, as shown in Figure 6 and Table 4. A number of the more intense bands in the calculated spectrum did not match well to the observed spectra. For example, a band with intensity of 216 km/mol was calculated to come at 1095 cm^{-1}. No product bands were observed near this position. Thus, the $CrCl_2O$–cyclopentadiene oxide complex can be ruled out as an observed product in this study.

Two ketene isomers, formed through a ring-opening reaction, were considered as possible products. Ketenes are generally characterized by an intense absorption near 2100 cm^{-1}, although this is likely to shift to lower energy upon complexation. In this study, the uncomplexed ketenes, penta-1,3-dien-1-one and penta-1,4-dien-1-one, had calculated C=O=O absorptions of 2134 and 2138 cm^{-1}, respectively. Upon complexation with $CrCl_2O$, the absorption was calculated to shift to 2093 cm^{-1} for the η^1 and 1778 cm^{-1} for the η^2 (C=O) penta-1,3-dien-1-one complexes and 2105 cm^{-1} for the η^1 and 1855 cm^{-1} for the η^2 (C=O) penta-1,4-dien-1-one complexes. The calculated infrared spectra for all four structures were compared to the experimental spectrum and the match was quite poor; thus these structures can be ruled out.

A single, sharp band was observed at 3552 cm^{-1} as shown in Figure 1 and listed in Table 1. This clearly can be assigned to an O−H stretch and indicates the formation of cyclopentadienol. There are three possible isomers, differentiated by location of the OH group on the ring relative to the two

carbon−carbon double bonds. Each of these would be complexed to $CrCl_2O$ through an oxygen atom. All three complexes were calculated at the B3LYP/6-311G++(d,2p) level and were found to be of comparable stability, as shown in Table 4. All three complexes were calculated to have an intense O−H stretch between 3570 and 3630 cm^{-1} (initial calculated values scaled by a factor of 0.97). Together, these observations provide strong support for the formation of a $CrCl_2O$−cyclopentadienol complex, through the insertion of an oxygen atom from $CrCl_2O_2$ into a C−H bond of cyclopentadiene. The single, relatively sharp, band observed in the experimental spectrum indicates that only one isomer is being formed. While the $CrCl_2O$-cyclopenta-1,3-dienol complex is the isomer with a calculated O−H stretch (3570 cm^{-1}) closest to the observed O−H stretch at 3552 cm^{-1}, inherent uncertainties in these calculations preclude definitive distinction between the three isomeric complexes.

Another possible product is the $CrCl_2O$-cyclopentenone complex, arising from the oxidation of one of the carbon−carbon double bonds to a ketone. Computationally, the $CrCl_2O$−cyclopentenone complexes were found to be the most stable of all of the complexes. Furthermore, a cyclic ketone complex has been observed in the previous oxidation reactions of $CrCl_2O_2$ with 6-membered rings. Two $CrCl_2O$−cyclopentenone complex isomers are possible in the present study, $CrCl_2O$−cyclopent-2-enone and $CrCl_2O$−cyclopent-3-enone; these were calculated to have strong C=O absorptions at 1628 and 1671 cm^{-1}, respectively. Experimentally, a strong band was observed at 1602 cm^{-1} and a weaker multiplet was observed at 1687 cm^{-1}. This agreement strongly supports the formation of both $CrCl_2O$−cyclopentenone isomeric complexes in these experiments.

The final isomer of C_5H_6O under consideration was 2H-pyran, a cyclic ether formed by oxygen atom insertion into a C−C bond and ring expansion and then complexed to $CrCl_2O$. The possibility that this species also formed cannot be eliminated, since most of the calculated band positions for this complex and the cyclic alcohol complex were relatively close together. Further, the reaction to form this complex is energetically favorable. However, there is no definitive evidence supporting the formation of this isomer, while there is such evidence for the cyclic ketones and alcohols.

Merged jet experiments were also carried out, to provide the reagents with more time to react before deposition onto the cold window. Since the experiments produced more bands than could be assigned to one product, it indicates that a mixture of products is forming. The major product at the lower temperatures (room temperature and 100 °C) can be identified by comparison to the literature gas phase spectrum of cyclopent-3-enone.[49] A

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number of the more intense bands, including the very intense 1759 cm^{-1} band, matched very well the gas phase spectrum of this species given anticipated gas-to-matrix shifts and are so assigned as shown in Table 2. The identity of the absorber(s) responsible for the remaining quite weak bands could not be readily determined. At higher merged jet temperatures (150 and 200 °C), the bands due to cyclopent-3-enone were observed with reduced intensity. In addition, a number of bands appeared at these higher temperatures. These can be assigned, on the basis of comparison to calculated values, to the doubly oxidized parent, 1,3-cyclopentanedione. Whether both O atoms arise from a single CrCl$_2$O$_2$ molecule, or from reaction of cyclopent-3-enone with a second molecule of CrCl$_2$O$_2$ cannot be distinguished under the experimental conditions employed here. The products observed in these experiments represent one of the few examples of a thermal gas phase reaction of CrCl$_2$O$_2$ in which O atoms are transferred to an organic substrate. It should be noted that other products of this reaction are CrCl$_2$O and perhaps CrCl$_2$, formed by direct O atom transfer(s) from CrCl$_2$O$_2$ to cyclopentadiene. These would not be volatile species, and would very probably condense on the walls of the deposition line prior to reaching the cold window.

CrCl$_2$O$_2$ + Cyclopentene. Cyclopentene oxide was computed to be the highest energy isomer of C$_5$H$_8$O under consideration, as shown in Table S5 of Supporting Information. Also, all attempts to optimize the structure of CrCl$_2$O– cyclopentene oxide complex from different starting structures led to dissociation into parent CrCl$_2$O$_2$ and cyclopentene. Thus, the CrCl$_2$O–cyclopentene oxide complex can be ruled out as a product in this study.

A strong product band was observed at 3568 cm^{-1} as shown in Figure 3, with a clear deuterium counterpart at 2629 cm^{-1}. This clearly may be assigned to an O–H stretch, indicating the formation of an isomer of cyclopentenol. There are three possible isomers, differentiated by location of the OH group on the ring relative to the carbon–carbon double bond. Each of these would be complexed to CrCl$_2$O through the O atom. All three complexes were calculated at the B3LYP/6-311G++(d,2p) level and were found to be of comparable stability, as shown in Table S5 of Supporting Information. Not surprisingly, all three were calculated to have an intense O–H stretch between 3590 and 3630 cm^{-1}. Together, these observations provide strong support for the formation of the CrCl$_2$O–cyclopentenol complex, through insertion of an oxygen atom from CrCl$_2$O$_2$ into a C–H bond of cyclopentene. At the same time, the calculated and experimental spectra do not permit the determination of which isomer (1-, 2-, or 3-cyclopentenol) was formed. In fact, given the breadth and band shape of the 3568 cm^{-1} absorption, more than one of these isomers may have been formed.

A second possible product is the CrCl$_2$O–cyclopentanone complex, arising from the oxidation of the carbon–carbon double bond to a ketone. Computationally, CrCl$_2$O-cyclopentanone was found to be the most stable out of all of the complexes by 17 kcal/mol. Cyclic ketone complexes were observed in many of the recent studies with CrCl$_2$O$_2$ and cyclic organic substrates. In the present study, the CrCl$_2$O–cyclopentanone complex was calculated to have a C=O stretch at 1662 cm^{-1} with a deuterium shift of −7 cm^{-1}. In the present study, a weak-medium band was observed at 1678 cm^{-1} which shifted −3 cm^{-1} upon deuteration. The cyclopentenol products (above) are also calculated to absorb in this region (the C=C stretch). However, this mode was calculated to have a −35 cm^{-1} shift, much larger than the observed shift. The position and

deuterium shift together support assignment to the CrCl$_2$O– cyclopentanone complex in these experiments. The relative amounts of the alcohol and ketone that formed are hard to estimate directly from band intensities. Nonetheless, it is not surprising that the bands of the alcohol were more intense since alcohol formation can occur at any of the 5 ring carbons while ketone formation can only occur at the carbon–carbon double bond. Kinetic barriers may also affect the relative amounts of the two products.

CrCl$_2$O$_2$ + Cyclopentane. Similar to the two previous systems, a strong product band was observed at 3573 cm^{-1} as shown in Figure 4. The upper region is characteristic of an O–H stretch, particularly one in which the oxygen atom is coordinated to the CrCl$_2$O species. This is strong support for the formation of cyclopentanol, through insertion of an oxygen atom from CrCl$_2$O$_2$ into a C–H bond of cyclopentane. There are several possible isomers of this complex, given the nonplanar structure of cyclopentane and cyclopentanol. However, these are very close in energy to one another and are very difficult to distinguish spectroscopically. Given the band shape and the several maxima within this band shape (see inset to Figure 4), it is probable that several different isomers form in this reaction. Many products bands were observed in addition to the 3573, 1006, and 447 cm^{-1} absorptions. When the intrinsic uncertainty associated with a given vibrational band is taken into account (standard deviation of approximately 3% for B3LYP/6-311G++(d,2p)), most of the remaining product bands can be assigned to the CrCl$_2$O–cyclopentanol complex as done in Table S4 of Supporting Information.

CrCl$_2$O$_2$ + Cyclopropane. A number of product bands were observed in the photochemical reaction of CrCl$_2$O$_2$ with cyclopropane, as listed in Table 3. CrCl$_2$O was observed with absorptions at 1009 and 459 cm^{-1}. All of the species that are likely candidates to contribute to the experimental spectrum are listed in Table S7. After irradiation, there was no indication of any new bands above 3000 cm^{-1}. This strongly suggests that species containing an O–H bond are not formed. Also, there is no deuterium counterpart O–D stretch in the cyclopropane-d_6 experiments. Consequently, two complexes can be quickly removed from consideration: CrCl$_2$O–2-propenol (open-chain alcohol) and CrCl$_2$O–cyclopropanol (ring alcohol).

Insertion of an O atom into a C–C bond can lead to either oxetane, retaining a 4-membered ring structure, or methoxy-ethene from a ring-opening reaction. The reactions to form the CrCl$_2$O–oxetane and CrCl$_2$O–methoxyethene complexes were both calculated to be exothermic, but many of the predicted bands for both complexes were absent in the spectrum. Thus, these species can be ruled out as well.

An intense band is observed at 1673 cm^{-1}, in the region characteristic of a C=O stretch of a carbonyl species. Two likely oxidation products are acetone and propanal each complexed to CrCl$_2$O, formed through ring-opening reactions. As shown in Table S7 of Supporting Information, the most energetically favored product is the CrCl$_2$O–acetone complex. It should be noted that acetone and propanal complexes have similar calculated C=O stretches (1692 and 1700 cm^{-1}) and deuterium shifts to the C=O stretch (−14 and −17 cm^{-1}, respectively). While the experimental band for the normal isotope (1673 cm^{-1}) fits reasonably well, the experimental deuterium shift is much larger (−47 cm^{-1}) than calculated for either complex. Further, the absence of key predicted bands makes assignment to either complex assignment unlikely. For example, three moderately intense bands are predicted for the CrCl$_2$O–acetone complex in the region between 1420 and 1350 cm^{-1}, while no bands

were observed in this region of the spectrum. Thus, these two complexes are eliminated from consideration.

An additional, novel possibility is oxygen atom transfer to cyclopropane followed by ring opening and then fragmentation, to form the $H_2CO-CrCl_2O$ complex and ethene. For this channel, the fit of the computed spectrum to the experimental spectrum is excellent. As shown in Table 3, all of the computed bands of the $H_2CO-CrCl_2O$ complex were observed with appropriate intensities within a few wavenumbers. For example, the $C=O$ stretch was calculated to come at 1676 cm^{-1} with a deuterium shift of -42 cm^{-1}, in very good agreement with the experimental values of 1673 cm^{-1} and deuterium shift of -47 cm^{-1}. Also, the second most intense band of H_2CO comes at 1499 cm^{-1}. This is shifted to 1490 cm^{-1} in the complex. The experimental deuterium shift, -402 cm^{-1}, is identical to that calculated for the $H_2CO-CrCl_2O$ complex, as shown in Table 3. In addition, product bands at 1440 and 948 cm^{-1} match very well-known absorptions of ethene[50] as do the counterpart bands in the deuterated experiments. Bands were also seen at 1480 and 967 cm^{-1}, likely arising from ethene molecules interacting with an electron-rich environment (i.e., the $H_2CO-CrCl_2O$ complex), causing a shift to higher energy. Thus, the $CrCl_2O$-formaldehyde complex is identified, along with cage paired ethene, as products in the photochemical reaction of $CrCl_2O_2$ with cyclopropane in argon matrices, marking the first observation of a ring-opening product in a photochemical reaction of $CrCl_2O_2$.

Merged jet experiments were also carried out on the cyclopentene, cyclopentane, and cyclopropane systems. In all three systems, no reaction products were detected, with heating of the reaction zone to as high as 150 °C. Calculations demonstrate that the reactions to form the most favorable products in the cyclopentene and cyclopropane systems (cyclopentanone and acetone, respectively) are both exothermic. The fact that these reactions did not occur in the merged jet experiments suggests that the activation barriers to these reactions are sufficiently high to prevent reaction, i.e., that the reaction is kinetically limited. In contrast, the reaction to form the most stable product (cyclopentanol) in the cyclopentane system is endothermic by 11 kcal/mol and is not likely to occur thermally at 150 °C.

Further Considerations

The mechanism of the photochemical reaction leading to the observed products is of interest as well. Recent visible/UV spectroscopic studies from this laboratory[51,52] have shown that a number of σ and π electron donors form 1:1 molecular complexes with $OVCl_3$ and $CrCl_2O_2$, with charge transfer transitions in the visible region. Excitation into these charge transfer transitions has then been shown to lead to photochemical reaction for a number of systems. Thus, the photochemical mechanism arises from excitation of cage-paired partners, whether these form a weakly bound molecular complex, which was not detected, or simply two species held in close proximity by the rigid argon matrix structure. The observation that $CrCl_2O_2$ alone in solid argon is not photochemically active (i.e., to form $CrCl_2O + O$) strongly suggests that a cage reactant pair is required. This is also in agreement with the fact that the energy of a photon in the 500-nm region, where onset of photochemical reaction has been observed to occur, is significantly less than the $Cr=O$ bond strength in $CrCl_2O_2$.

As noted above, the photochemical reaction of $CrCl_2O_2$ with cyclopropane gave rise, for the first time, to a ring-opened product. For all of the *saturated* cycloalkanes studied, the lowest energy product retaining the ring structure is the cyclic alcohol

while the lowest energy "ring-opened" product is a ketone. In each case, the ring-opened ketone was the overall lowest energy product. However, this product was not observed for cyclohexane and cyclopentane, while ring opening did occur for cyclopropane. The reason may be that as the ring size decreases, *the difference in energy between the ring-opened product (ketone) and the cyclic product (alcohol) was computed to increase substantially,* from -10 kcal/mol for $C_6H_{12}O$ to -31 kcal/mol C_3H_6O. This energy difference apparently was sufficient to drive the cyclopropane reaction to the ring-opened product, and the exothermicity led to further fragmentation of the ring-opened ketone into the $H_2CO-CrCl_2O$ complex + C_2H_4.

For *unsaturated* hydrocarbon rings, reaction with $CrCl_2O_2$ can lead to both O atom insertions into a $C-H$ bond and O atom addition to a $C=C$ can occur, leading to a cyclic alcohol or a cyclic ketone. In most cases, the ketone was calculated to be lower in energy, the exception being benzene where phenol was the lowest energy product. For many of these systems, both the cyclic ketone and alcohol were observed, despite significant energy differences between the two products. Since these reactions are all photochemically activated by visible and UV radiation, sufficient energy is available to access either channel (as well as additional, less energetically favorable channels). The distribution of products in these cases probably reflects the different cage pairing geometries that are formed upon initial matrix deposition prior to irradiation. If an oxygen of $CrCl_2O_2$ is aligned near a $C=C$, then excitation is likely to lead to the cyclic ketone. If the oxygen is not aligned near a $C=C$, it must be directed toward a $C-H$ bond, and excitation is likely to lead to the cyclic alcohol. While calculating initial cage pair geometries explicitly including nearest neighbor argon atoms is beyond the scope of this study, it would be an interesting study for those groups who are equipped to carry out large scale calculations, whether density functional theory or Monte Carlo.

As a final note, the role of the $CrCl_2O$ species in these complexes is of interest. The complexation energies of $CrCl_2O$ to the oxidized product were computed to be large, ranging from -15 to -40 kcal/mol over the wide range of complexes that have been studied. To some degree, these complexes may be viewed as molecular species in their own right. The $Cr\cdots O$ distances in these complexes were typically calculated to be between 1.95 and 2.00 Å, not unlike a typical $Cr-O$ single bond distance. At the same time, the $C=O$ bond lengths of the ketone products are not significantly elongated (~0.02 Å) compared to the uncomplexed products. Thus, these photooxidation experiments provide a novel route a to series of interesting new molecules, in addition to shedding some light on the mechanisms of photochemical oxidation reactions of $CrCl_2O_2$.

Conclusions

Irradiation of matrices containing $CrCl_2O_2$ and cyclopentadiene, cyclopentene, and cyclopentane led to a transfer of an oxygen atom and insertion into a $C-H$ bond to form the corresponding alcohol, complexed to the $CrCl_2O$ species. With cyclopentadiene and cyclopentene, cyclic ketones were also produced through the oxidation of a carbon−carbon double bond. In contrast, photochemical reaction of $CrCl_2O_2$ with the more highly ring-strained cyclopropane led to a ring-opening reaction followed by fragmentation, forming the $H_2CO-CrCl_2O$ complex and cage-paired C_2H_4. In the merged jet experiments of $CrCl_2O_2$ and cyclopentadiene, cyclopent-3-enone was observed with the merged region held near room temperature.

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Above 150 °C, 1,3-cyclopentanedione was also observed. No product bands were detected in the merged jet experiments of the other three systems studied here. These conclusions were supported by isotopic labeling (^{2}H) and by B3LYP/6-311G++(d,2p) density functional calculations.

Supporting Information Available: Complete sets of observed and calculated product bands for the cyclopentadiene, cyclopentene and cyclopentane reactions with $CrCl_2O_2$ are given. Figures of the structures of the considered products between $CrCl_2O_2$ + cyclopentadiene are shown. For the $CrCl_2O_2$ + cyclopentene system, figures of the considered products, a figure of the calculated energies relative to the two reagents, a table showing the calculated energies, and a representative spectrum of the photochemical products of the reaction of $CrCl_2O_2$ with cyclopentene-d_8 in an argon matrix are presented. For the $CrCl_2O_2$ + cyclopentane system, a figure of the considered products and a table of the calculated energies relative to the two reagents is shown. For the $CrCl_2O_2$ + cyclopropane system, a figure showing each of the possible products considered here and a table of the calculated energies of these products relative to the two reagents is also shown. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1855.
(2) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7139.
(3) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441.
(4) Limberg, C.; Koppe, R.; Schnockel, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 496.
(5) Limberg, C.; Koeppe, R. *Inorg. Chem.* **1999**, *38*, 2106.
(6) Torrent, M.; Deng, L.; Duran, M.; Sola, M.; Ziegler, T. *Can. J. Chem.* **1999**, *77*, 1476.
(7) Torrent, M.; Deng, L.; Ziegler, T. *Inorg. Chem.* **1998**, *37*, 1307.
(8) Ziegler, T.; Li, J. *Organometallics* **1995**, *14*, 214.
(9) Deng, L.; Ziegler, T. *Organometallics* **1997**, *16*, 716.
(10) Ault, B. S. *J. Am. Chem. Soc.* **1998**, *120*, 6105.
(11) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.
(12) Deng, L.; Ziegler, T. *Organometallics* **1996**, *15*, 3011.
(13) Rappe, A. K.; Goddard, W. A., III *Nature* **1980**, *285*, 311.
(14) Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.
(15) Cradock, S.; Hinchcliffe, A. J. *Matrix Isolation*; Cambridge University Press: Cambridge, 1975.
(16) Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; John Wiley: New York, 1973.
(17) *Chemistry and Physics of Matrix-Isolated Species*; Andrews, L., Moskovits, M. , Eds.; Elsevier Science Publishers: Amsterdam, 1989.
(18) Ball, D. W.; Kafafi, Z. H.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **1985**, *24*, 3708.
(19) Hilfiker, M. A.; Mysak, E. R.; Samet, C.; Maynard, A. *J. Phys. Chem. A* **2001**, *105*, 3087.
(20) Miyazaki, J.; Yamada, Y. *J. Mol. Struct.* **2004**, *692*, 145.
(21) Truscott, C. E.; Ault, B. S. *J. Mol. Struct.* **1987**, *157*, 61.
(22) Anderson, S. R.; Ault, B. S. *J. Mol. Struct.* **2002**, *609*, 149.
(23) Anderson, S. R.; Ault, B. S. *J. Phys. Chem. A* **2002**, *106*, 1419.
(24) Subel, B. L.; Kayser, D. A.; Ault, B. S. *J. Phys. Chem. A* **2002**, *106*, 4998.
(25) Antle, K. A.; Ault, B. S. *J. Mol. Struct.* **2003**, *655*, 331.
(26) Kayser, D. A.; Ault, B. S. *J. Phys. Chem. A* **2003**, *107*, 6500.
(27) Griner, G. M.; Kayser, D. A.; Ault, B. S. *Chem. Phys.* **2004**, *300*, 63.
(28) Ault, B. S. *J. Phys. Chem. A* **2004**, *108*, 5537.
(29) Ault, B. S. *Spectrochim. Acta, Part A* **2003**, *59A*, 1989.
(30) Kayser, D. A.; Ault, B. S. *Chem. Phys.* **2003**, *290*, 211.
(31) Ault, B. S. *J. Phys. Chem. A* **2001**, *105*, 4758.
(32) Ault, B. S. *J. Phys. Chem. A* **2000**, *104*, 11796.
(33) Ault, B. S. *J. Phys. Chem. A* **1999**, *103*, 11474.
(34) Hoops, M. D.; Ault, B. S. *J. Mol. Struct.* **2002**, *616*, 91.
(35) Hoops, M. D.; Ault, B. S. *J. Phys. Chem. A* **2005**, *109*, 4497.
(36) Hoops, M. D.; Ault, B. S. *J. Mol. Struct.* **2007**, *826*, 36.
(37) Hoops, M. D.; Ault, B. S. *J. Phys. Chem. A* **2006**, *110*, 892.
(38) Hoops, M. D.; Ault, B. S. *Chem. Phys.* **2007**, *334*, 18.
(39) Hoops, M. D.; Ault, B. S. *J. Mol. Struct.,* accepted.
(40) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.
(41) Williamson, K. L. *Macroscale and Microscale Organic Experiments*; D.C. Heath and Co.: Lexington, 1989.
(42) Carpenter, J. D.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 3502.
(43) Frisch, M. J.; Trucks, G. W.; Schlegal, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N. ; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J. ; Cammi, R. ; Pomelli, C. ; Ochterski, J. W. ; Ayala, P. Y.; Morokuma, K. ; Voth, G. A. ; Salvador, P. ; Dannenberg, J. J. ; Zakrzewski, V. G. ; Dapprich, S. ; Daniels, A. D. ; Strain, M. C. ; Farkas, O. ; Malick, D. K. ; Rabuck, A. D. ; Raghavachari, K. ; Foresman, J. B. ; Ortiz, J. V. ; Cui, Q. ; Baboul, A. G. ; Clifford, S. ; Cioslowski, J. ; Stefanov, B. B. ; Liu, G. ; Liashenko, A. ; Piskorz, P. ; Komaromi, I. ; Martin, R. L. ; Fox, D. J. ; Keith, T. ; Al-Laham, M. A. ; Peng, C. Y. ; Nanayakkara, A. ; Challacombe, M. ; Gill, P. M. W. ; Johnson, B. ; Chen, W. ; Wong, M. W. ; Gonzalez, C. ; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
(44) Varetti, E. L.; Mueller, A. *Spectrochim. Acta, Part A* **1978**, *34A*, 895.
(45) Villarreal, J. R.; Laane, J.; Bush, S. F.; Harris, W. C. *Spectrochim. Acta, Part A* **1979**, *35A*, 331.
(46) Schettino, V.; Marzocchi, M. P.; Califano, S. *J. Chem. Phys.* **1969**, *51*, 5264.
(47) Duncan, J. L.; Burns, G. R. *J. Mol. Spectrosc.* **1969**, *30*, 253.
(48) Wistuba, T.; Limberg, C. *Eur. J. Inorg. Chem.* **1999**, 1335.
(49) Lewis, J. D.; Laane, J. *Spectrochim. Acta, Part A* **1975**, *31A*, 755.
(50) Barnes, A. J.; Howells, J. D. R. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 532.
(51) Goldberg, N.; Ault, B., S. *Chem. Phys. Lett.* **2005**, *401*, 89.
(52) Goldberg, N.; Ault, B. S. *J. Mol. Struct.* **2005**, *749*, 84.