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

Kathryn A. Antle and Bruce S. Ault*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 45221

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The matrix-isolation technique has been combined with infrared spectroscopy to identify and characterize the products formed by irradiation of cage-paired $CrCl_2O_2$ and a series of chloroethenes, $C_2H_xCl_y$ ($x + y = 4$). For each system, oxygen-atom transfer occurred upon irradiation, yielding the corresponding acetyl chloride derivative and the Cl_2CrO species. The products were formed in the same matrix cage and strongly interacted to form a distinct molecular complex after formation. Three different modes of interaction were explored computationally: η^1 to the oxygen atom, η^2 to the C═O bond, and η^1 to the chlorine atom. In addition, a five-membered metallocycle and the chloroepoxide species were considered. No evidence was obtained for the chloroacetaldehyde derivative, indicating the occurrence of oxygen-atom attack at the more substituted carbon of the chloroethene. Evidence tentatively supporting the formation of the metallocycle was obtained as well. Theoretical calculations indicated that the acetyl chloride derivative was approximately 10 kcal/mol more stable than the corresponding chloroacetaldehyde species for each system at the B3LYP/6-311++g(d,2p) level of theory. The binding energy of each of the complexes was also found to be near 10 kcal/mol at this level of theory.

Introduction

There has been increased interest in recent years in developing a more complete understanding of the reaction of high-valent transition-metal oxo compounds,[1,2] including $CrCl_2O_2$ and $OVCl_3$. These compounds have been invoked as models for the active sites of a number of metalloenzymes as well as for heterogeneous catalysts. Matrix-isolation experiments[3−5] have provided the primary experimental approach, whereas extensive theoretical calculations of potential energy surfaces have been conducted.[6,7] This laboratory has studied the reaction of these transition-metal compounds and several related species with small organic and inorganic substrates containing a heteroatom.[8−13] These studies have permitted the identification of a sequence of intermediates in each system from which a reaction mechanism was (at least partially) deduced. Wistuba and Limberg have focused on the reaction of $CrCl_2O_2$ with alkenes and alkynes[14,15] and have reported several novel intermediates. Vinyl chloride, C_2H_3Cl, is an industrially important monomer,[16] leading to poly(vinyl chloride) (PVC) via transition-metal catalysis. The interaction and reaction of vinyl chloride with high-valent transition-metal oxo compounds may serve as a useful model for this catalysis. With this background and the continuing interest in these systems, a study employing matrix isolation was undertaken to trap, identify, and characterize intermediates in the thermal and photochemical reactions of chloroethenes with $CrCl_2O_2$ and $OVCl_3$. Extensive theoretical calculations in support of the experimental work were carried out as well.

Experimental Details

All of the experiments in this study were carried out on a conventional matrix-isolation apparatus that has been described.[17] Chromyl chloride, $CrCl_2O_2$, and oxyvanadium trichloride, $OVCl_3$, (both Aldrich), were introduced into the vacuum system as the vapor above the room-temperature liquid after purification by freeze−pump−thaw cycles at 77 K. Vinyl chloride, C_2H_3Cl, and vinyl chloride-d_3, C_2D_3Cl, (both Aldrich), were introduced from lecture bottles into a second vacuum manifold and were purified by freeze−pump−thaw cycles at 77 K. 1,1-Dichloroethene, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, C_2HCl_3, and C_2Cl_4 (all Aldrich) were introduced into the vacuum line 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 of the experiments and was used without further purification.

Matrix samples were deposited in both the twin-jet and merged-jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K cold window, allowing for only a very brief mixing time prior to matrix deposition. Several of these matrices were subsequently warmed to 33−35 K to permit limited diffusion and then recooled to 14 K, and additional spectra were recorded. In addition, most of these matrices were irradiated for 1 or more hours with the H_2O/Pyrex-filtered output of a 200-W medium-pressure Hg arc lamp, after which additional spectra were recorded.

A few experiments were conducted in the merged-jet mode[18] in which the two deposition lines were joined with an Ultratorr tee a cartain distance from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region. The length of this region was variable; typically, a 90-cm length was employed. In both the twin- and merged-jet modes, matrices were deposited at the rate of 2 mmol/h 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.

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* Corresponding author. E-mail: bruce.ault@uc.edu.

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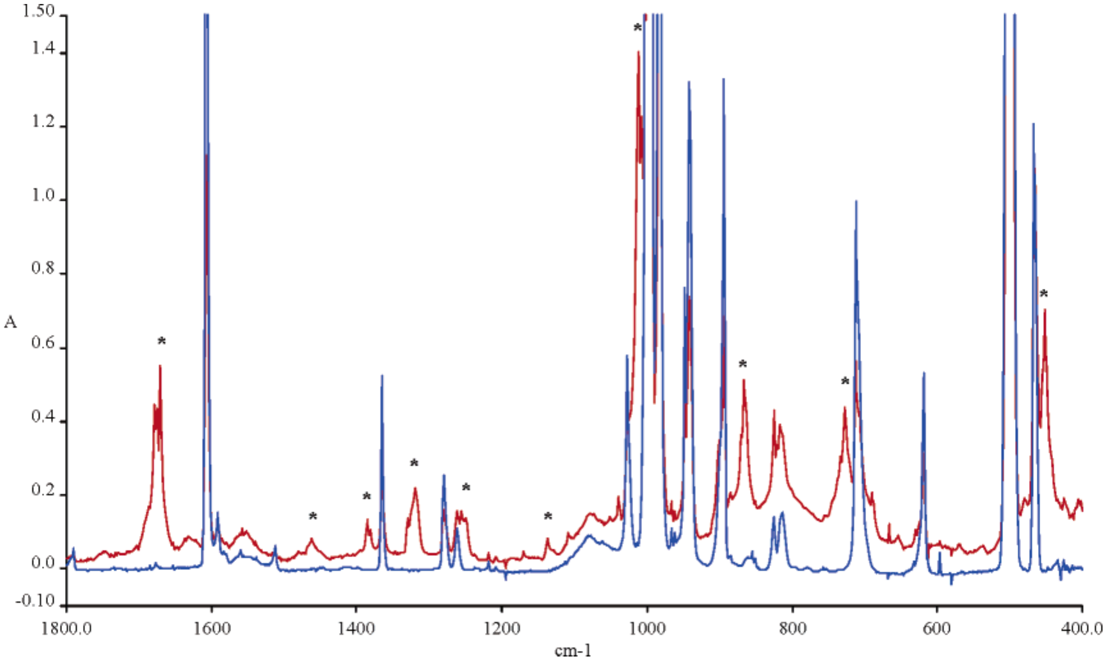

Figure 1. Infrared spectra of a matrix prepared by the twin-jet codeposition of a sample of Ar/C_2H_3Cl with a sample of Ar/$CrCl_2O_2$: lower trace (blue) is before irradiation; upper trace (red) is after irradiation. Bands marked with * are the most prominent photolysis product bands.

Theoretical calculations were carried out on likely intermediates in this study using the Gaussian 03W suite of programs.[19] Density functional calculations using the hybrid B3LYP functional were used to locate the energy minima, determine the structures, and calculate the 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 locate the energy minima approximately. Thermodynamic functions, including zero-point corrections, for reactants and potential intermediates were calculated as well.

Results

Prior to any codeposition experiments, blank experiments were run in which a single reagent diluted with argon was deposited. This was carried out for each of the reagents used in this study. In each case, the spectra of the blank was in good agreement with the literature spectra[20−27] and with the blanks run previously in this laboratory. Each blank experiment was then irradiated by the H_2O/Pyrex-filtered output of a 200-W Hg arc lamp for 1.5 h. No changes were observed in any of the blank spectra because of irradiation. Weak bands due to a HCl impurity were noted in all of the $CrCl_2O_2$ and $OVCl_3$ blank experiments.[28]

$CrCl_2O_2$ + C_2H_3Cl. A sample of Ar/$CrCl_2O_2$ = 400 was codeposited with a sample of Ar/C_2H_3Cl = 400 in an initial experiment using twin-jet deposition. After the initial deposition, no distinct new peaks were seen in the spectrum. This sample was then irradiated with the H_2O/Pyrex-filtered output of a medium-pressure Hg arc (e.g., $\lambda > 300$ nm) for 1.5 h. After irradiation, numerous new peaks were observed in the spectrum at 456, 691, 729, 825, 867, 1012, 1108, 1137, 1170, 1250, 1319, 1386, 1466, 1677, and 2925 cm^{-1}. The most intense of these was the band at 1677 cm^{-1}, which was approximately 0.25 absorbance units. However, no new bands were seen in the 2650−2850-cm^{-1} region because of irradiation. Figure 1 shows a representative spectrum of this system before and after irradiation.

This system was then studied in a series of six additional twin-jet experiments in a range of sample concentrations. Similar results were obtained in all of the experiments. The same set of bands was produced with relative intensities that remained constant from one experiment to the next. The absolute band intensities varied directly with the sample concentrations that were employed (e.g., when the concentration of one reagent was halved, the product-band intensities were reduced by a factor of approximately $^1/_2$. Many of these matrices were annealed to 30 K prior to irradiation; annealing generally led to somewhat increased product-band intensities. Finally, one experiment was run using merged-jet deposition and a typical set of sample concentrations. No product bands were observed in the merged-jet experiment.

Six experiments were then run with samples of Ar/$CrCl_2O_2$ and Ar/C_2D_3Cl in the twin-jet mode. The results were, overall, very similar to those described above for normal isotopic vinyl chloride. Similar bands were seen, some of which shifted significantly as a result of deuteration, whereas some shifted by smaller amounts and a few did not shift. For example, the intense band at 1677 cm^{-1} shifted 15 cm^{-1} to 1662 cm^{-1}, whereas the band at 456 cm^{-1} did not shift. Again, the relative intensities of the product bands remained essentially constant with respect to one another in this series of experiments. Product bands for the normal isotopic species and the deuterated olefin are listed in Table 1.

$CrCl_2O_2$ + Dichloroethenes. In three separate but related sets of experiments, samples of Ar/$CrCl_2O_2$ were codeposited with samples of Ar/1,1-dichloroethylene, Ar/*cis*-1,2-dichloroethylene, and Ar/*trans*-1,2-dichloroethylene. In each set, no new bands were seen upon initial deposition or after sample annealing. However, in each case, after the matrix was irradiated with light of $\lambda > 300$ nm, distinct new product bands were observed. These are listed in Table 2 for all three olefins. The product bands with *cis*- and *trans*-1,2-dichloroethylene were quite similar in location and intensity, whereas the product bands with 1,1-dichloroethylene were clearly different. Several experiments were run in each set at different sample concentrations; the product bands for each pair of reactants maintained a constant intensity ratio with respect to one another throughout the set of experiments.

TABLE 1: Product-Band Positions and Assignments Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Vinyl Chloride

$CrCl_2O_2 + C_2H_3Cl$ (cm^{-1})	$CrCl_2O_2 + C_2D_3Cl$ (cm^{-1})	assignment
456	456	Cl_2CrO
691	601	η^1 complex
729		metallocycle
825	765	metallocycle
867	850	metallocycle
1012	1012	Cl_2CrO
1108	1094	η^1 complex
1137	1142	metallocycle
1170	1173	metallocycle
1250	1187	
1319	1050	metallocycle
1386	1287	η^1 complex
1466		η^1 complex
1677	1662	C═O st, η^1 complex
2925		η^1 complex

TABLE 2: Product-Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Dichloroethenes and C_2HCl_3[a]

$CrCl_2O_2$ + 1,1-$C_2H_2Cl_2$ (cm^{-1})	$CrCl_2O_2$ + *cis*-1,2-$C_2H_2Cl_2$ (cm^{-1})	$CrCl_2O_2$ + *trans*-1,2-$C_2H_2Cl_2$ (cm^{-1})	$CrCl_2O_2$ + C_2HCl_3 (cm^{-1})
	456	457	
710	743	743	569
722	795	794	644
899	880	880	677
			748
			867
	1013		1016
1101	1068	1063	1104
	1133	1135	1167
1237	1238		
1292	1326	1351	1325
1455		1368	
1682	1684	1685	1689

[a] Product bands are assigned to a mixture of η^1 and η^2 complexes of the appropriate acetyl chloride with Cl_2CrO.

$CrCl_2O_2 + C_2HCl_3$. Samples of $Ar/CrCl_2O_2$ were deposited in a series of twin-jet experiments with samples of Ar/C_2HCl_3, followed by irradiation. Essentially identical results were obtained in each experiment. Specifically, a few broad, weak, new features were seen upon initial codeposition. After matrix irradiation for 1.25 h with light of $\lambda > 300$ nm, numerous strong new product bands were observed, the most intense of which was located at 1689 cm^{-1}. All of the product bands are listed in Table 2. These bands are maintained at a constant intensity ratio with respect to one another throughout the several experiments conducted with this pair of reagents.

$CrCl_2O_2 + C_2Cl_4$. In several twin-jet experiments, samples of $Ar/CrCl_2O_2$ were deposited with samples of Ar/C_2HCl_3, followed by irradiation. In a manner similar to that for those systems described above, the same results were observed for each experiment. Sample concentrations in these experiments ranged from $Ar/CrCl_2O_2 = 150-500$ and $Ar/C_2Cl_4 = 300-750$. No distinct product bands were seen upon the initial depositions of these matrices. However, upon irradiation of these matrices with light of $\lambda > 300$ nm, a number of quite intense product bands were observed. The most intense was located at 1011 cm^{-1}, whereas bands at 932, 1694, and 892 cm^{-1} were also strong. Additional medium and weak bands were detected. All of the product bands are reported in Table 3 and shown in Figure 2. Analogous to the above systems, these bands maintained a constant intensity ratio with respect to one another throughout the several experiments conducted with this pair of reagents. Also, the absolute product-band intensities were increased or reduced linearly with a change in sample concentration (e.g., when $Ar/CrCl_2O_2$ was changed from 150 to 300, the product bands were reduced by a factor of 2 in intensity).

TABLE 3: Product-Band Positions and Assignments Arising from the Irradiation of Matrices Containing $CrCl_2O_2/C_2Cl_4$ Mixtures

$CrCl_2O_2 + C_2Cl_4$ (cm^{-1})	assignment
462	Cr−Cl antisym. stretch, Cl_2CrO
607	C−Cl stretch, η^1 complex
631	C−Cl stretch, η^2 complex
742	C−Cl stretch, tetrachlorometallocycle
785	C−Cl stretch, η^1 complex
879	C−C stretch, tetrachlorometallocycle
892	C−C stretch, chlorine-bound complex?
923	C−C stretch, tetrachlorometallocycle
1011	Cr═O stretch, Cl_2CrO
1077	C−C stretch, η^1 complex
1285	C═O stretch, η^2 complex
1694	C═O stretch, η^1 complex
1808	C═O stretch, chlorine-bound complex

$OVCl_3 + C_2H_3Cl$. Several analogous experiments involving codeposition and subsequent irradiation of samples of $Ar/OVCl_3$ with samples of Ar/C_2H_3Cl were carried out as well. No new products were observed in any of these experiments.

Results of Calculations

The photochemical reaction of $CrCl_2O_2$ with $C_2H_xCl_y$ could, in principle, lead to a wide range of reaction products. Observation of the Cl_2CrO fragment (discussion below) as one product strongly suggests that oxidation of the alkenes is occurring. For all of the unsymmetrical alkenes (for example, vinyl chloride), oxidation may occur at either end of the molecule, leading to either an acetyl chloride or a chloroacetaldehyde. Alternatively, addition across the double bond could occur, leading to either a five-membered metallocycle or chloroepoxide formation. It is also possible that more than one product forms in these reactions. These alternatives are complicated further by the fact that Cl_2CrO is also formed within the same matrix cage and will interact with the oxidation product. Several different structures for these complexes could be envisioned, including η^1 (end-on coordination of the Cr center to the lone-pair electrons on the oxygen atom of the oxidized alkene), η^2 (side-on coordination to the π electrons of the C═O bond), or η^1 coordination to one of the chlorine atoms on the oxidized alkene. (See Figure 3 for a depiction of these coordination modes.)

Although a number of the chloroacetaldehydes and acetyl chlorides have been observed previously, none of the complexes with Cl_2CrO that were described above are known. Consequently, theoretical calculations were carried out on all of the possible combinations of photoproducts and coordination structures to determine (1) which structures corresponded to local energy minima, (2) if multiple structures were found, which structures were lowest in energy for a given pair of reactants, and (3) theoretical vibrational spectra for each complex, whether they were the lowest-energy structure or not. All of the calculations were finalized at the B3LYP/6-311++(d,2p) level of theory. The detailed results are extensive; from them, the following generalities could be reached. First, multiple structures correspond to the energy minima for these complexes. Second, for all systems, the acetyl chloride derivative complexes were more stable than the analogous chloroacetaldehyde complexes (by around 10 kcal/mol at this level of theory). Third, the η^1

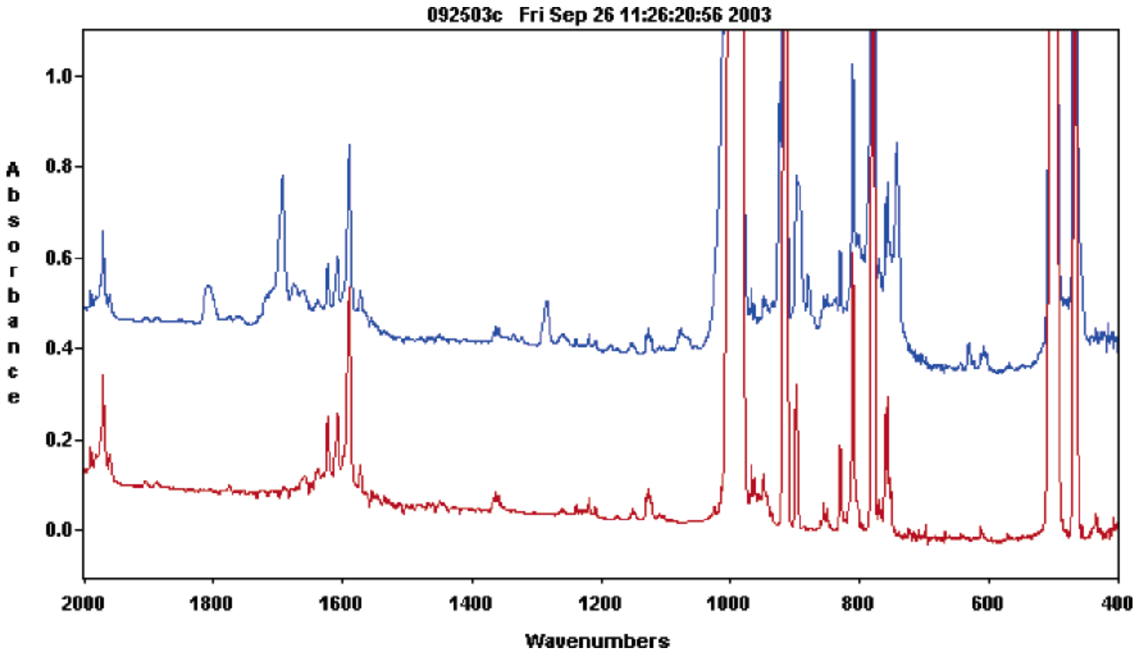

Figure 2. Infrared spectra of a matrix prepared by the twin-jet codeposition of a sample of Ar/C_2Cl_4 with a sample of Ar/$CrCl_2O_2$: lower trace (red) is before irradiation; upper trace (blue) is after irradiation.

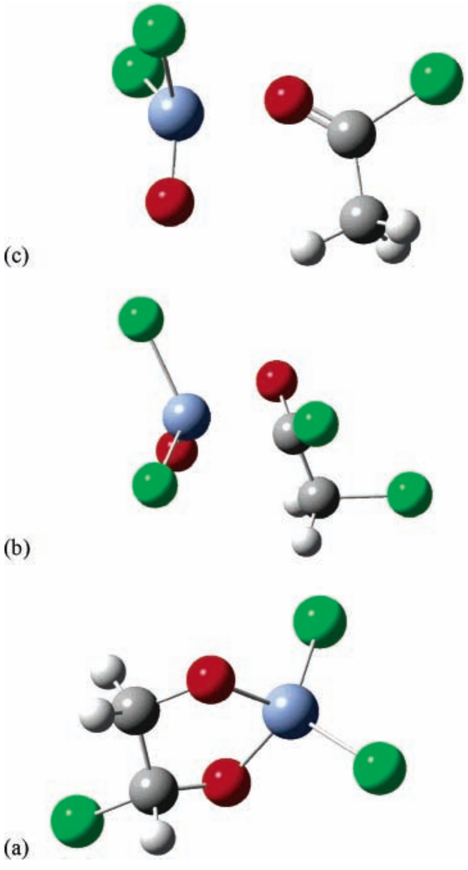

Figure 3. Representations of three calculated structures: (a) the five-membered metallocycle formed by addition across the C═C of vinyl chloride; (b) the η^2 complex of Cl_2CrO with $CH_2ClC(Cl)O$; (c) the η^1 complex of Cl_2CrO with $CH_3C(Cl)O$.

oxygen complexes were more stable than the η^2 complexes, which were, in turn, more stable than the η^1 chlorine-bound complexes. The η^1 complexes were consistently more stable than the η^2 complexes by around 10 kcal/mol. Fourth, the reaction to form the "free" or uncomplexed products was energetically favorable for the acetyl chloride derivatives by around −10 kcal/mol at the B3LYP/6-311++g(d,2p) level, whereas the reaction to form the uncomplexed chloroacetaldehyde derivative was nearly thermoneutral. Fifth, the energy of complexation (e.g., the $\Delta E°$ for the reaction $CH_3C(Cl)O + Cl_2CrO \rightarrow \eta^1$ complex) was exothermic by 8−12 kcal/mol. All of the positive frequencies for the calculated vibrational spectra demonstrated that these structures all are local energy minima. Also, the five-membered metallocycle formed by addition across the carbon−carbon double bond was found to represent a local energy minimum, although it is higher in energy than the η^1 complexes. In a similar manner, stable complexes of the possible chloroepoxide complexes with Cl_2CrO were calculated to be local energy minima, although they are also substantially higher in energy than the η^1 and η^2 complexes. Tables 4 and 5 list the relative energies of all of these species.

Discussion

No distinct new bands were detected upon twin-jet deposition of samples of Ar/$C_2H_xCl_y$ ($x + y = 4$) with Ar/$CrCl_2O_2$. In some experiments, weak, broad features were observed, but these were not well defined or readily assignable to a distinct chemical species. Upon irradiation of these matrices with light of $\lambda >$ 300 nm, numerous product bands were seen for each of the chloroalkene/$CrCl_2O_2$ systems. Although the entire set of bands varied from one chloroethene to the next, several common features and patterns were observable, which guide product identification.

First, the intensities of the product bands in each system varied linearly with the sample concentrations employed because the concentrations of each reagent were varied systematically. This linear dependence strongly suggests that the reaction product is formed from one molecule of $CrCl_2O_2$ and one molecule of chloroethene. This is supported by the absolute concentrations because the same product bands persisted at dilutions as high as 1000/1. Under these conditions, product formation involving more than one molecule of either reactant is quite unlikely. Thus, it appears that the product bands arise from the irradiation of one molecule of $CrCl_2O_2$ with one molecule of chloroethene.

TABLE 4: Computed Relative Energies of Possible Products in the Photooxidation of C_2H_3Cl and C_2HCl_3 by $CrCl_2O_2$[a]

$C_2H_3Cl + CrCl_2O_2 + h\nu$		$C_2HCl_3 + CrCl_2O_2 + h\nu$	
species	E^0_{rel}, kcal/mol	species	E^0_{rel}, kcal/mol
$CH_3C(Cl)O{\cdot}Cl_2CrO$, η^1	0	$CHCl_2C(Cl)O{\cdot}Cl_2CrO$, η^1	0
$CH_3C(Cl)O{\cdot}Cl_2CrO$, η^2	[b]	$CCl_2C(H)O{\cdot}Cl_2CrO$, η^1	+10.3
$CH_2ClC(H)O{\cdot}Cl_2CrO$, η^1 (O)	+11.9	$CHCl_2C(Cl)O{\cdot}Cl_2CrO$, η^2	+12.1
$CH_2ClC(H)O{\cdot}Cl_2CrO$, η^2	+22.5	metallocycle	+12.9
metallocycle	+22.9	$CCl_2C(H)O{\cdot}Cl_2CrO$, η^2	+10.3
$CH_2ClC(H)O{\cdot}Cl_2CrO$, η^1 (Cl)	+24.0	trichloroepoxide$\cdot Cl_2CrO$	+32.5
chloroepoxide$\cdot Cl_2CrO$	+38.1		

[a] Computed at the B3LYP/6-311++g(d,2p) level of theory. [b] Structure converted without a barrier to the corresponding η^1 structure.

TABLE 5: Computed Relative Energies of Possible Products in the Photooxidation of $C_2H_2Cl_2$ and C_2Cl_4 by $CrCl_2O_2$[a]

$C_2H_2Cl_2 + CrCl_2O_2 + h\nu$		$C_2Cl_4 + CrCl_2O_2 + h\nu$	
species	E^0_{rel}, kcal/mol	species	E^0_{rel}, kcal/mol
$CH_2ClC(Cl)O{\cdot}Cl_2CrO$, η^1	0	$CCl_3C(Cl)O{\cdot}Cl_2CrO$, η^1	0
$CHCl_2C(H)O{\cdot}Cl_2CrO$, η^1	+8.6	tetrachlorometallocycle	+8.6
$CH_2ClC(Cl)O{\cdot}Cl_2CrO$, η^2	+12.7	$CCl_3C(Cl)O{\cdot}Cl_2CrO$, η^2	+14.6
trans-1,2-metallocycle	+15.4	tetrachloroepoxide$\cdot Cl_2CrO$	[b]
cis-1,2-metallocycle	+18.0		
1,1-metallocycle	+18.1		
$CHCl_2C(H)O{\cdot}Cl_2CrO$, η^2	+19.0		
cis-dichloroepoxide$\cdot Cl_2CrO$	+33.3		
trans-dichloroepoxide$\cdot Cl_2CrO$	+34.3		
1,1-dichloroepoxide$\cdot Cl_2CrO$	+37.9		

[a] Computed at the B3LYP/6-311++g(d,2p) level of theory. [b] Dissociated spontaneously to $C_2Cl_4 + CrCl_2O_2$.

Second, two product bands near 455 and 1012 cm^{-1} were common to all of these experiments. This latter band appeared as a shoulder on the nearby parent-$CrCl_2O_2$ band in some experiments and was clearly resolved and intense in other experiments. (At lower parent-$CrCl_2O_2$ concentrations, at which the parent bands were sharper, this band was more readily resolved.) These two bands have been seen previously by several researchers in the field[13-15] and assigned to the Cl_2CrO fragment. This assignment is supported by the fact that these two bands did not shift when C_2D_3Cl was substituted for C_2H_3Cl in several experiments. Thus, Cl_2CrO is a product common to all of these systems. This is consistent with the observation that no product bands were detected between 2650 and 2850 cm^{-1}. The lack of a product band in this region demonstrates that an HCl elimination reaction is not occurring in these systems but rather oxygen-atom transfer is occurring, yielding the Cl_2CrO species.

Third, all of the product bands for a given system maintained a constant intensity ratio with respect to one another in several different experiments that were run with each pair of reactants. This is suggestive of the formation of a single reaction product. Alternatively, two (or more) products could be formed, always in the *same* relative amounts within experimental error. Whether the former or latter is correct, the product(s) still must arise from one molecule of each reactant.

The observation of the Cl_2CrO species as a photoproduct in each reacting system indicates that oxygen-atom transfer and oxidation of the alkene must be occurring. This is consistent with previous studies of the reaction of ethene and ethyne with chromyl chloride, where O-atom transfer occurred (to form acetaldehyde and ketene, respectively, complexed to the Cl_2CrO fragment). Both of those systems employed a symmetric precursor, leading to only one possible product (although with potentially more than one coordination mode for the Cl_2CrO fragment). Using the vinyl chloride/$CrCl_2O_2$ system in the present study as a prototype, there are five possible closed-shell isomers of the resulting C_2H_3ClO product arising from O-atom transfer to vinyl chloride. These are (1) chloroacetaldehyde, (2) acetyl chloride, (3) chloroethene oxide, (4) chlorovinyl alcohol, and (5) a five-membered metallocycle formed by the cycloaddition of the carbon−carbon double bond across the O−Cr−O segment of $CrCl_2O_2$. Although the first three are known chemical species,[29-31] their complexes with Cl_2CrO (such as those that must occur in the matrix environment) are not known. Thus, product identification from among this set must come from a combination of theoretical calculations and analogy to the solution and/or crystalline-phase infrared spectra.

The chlorovinyl alcohol isomer can be readily eliminated from consideration by observing that no product bands were seen above 3000 cm^{-1}, a region where the O−H stretch is expected to absorb strongly. Even if the O−H bond was involved in hydrogen bonding and shifted, the band should be above 3000 cm^{-1} and intensified. Because no such band was seen, chlorovinyl alcohol is ruled out.

A spectral feature that is similar in all of the different systems studied is a very strong band in the 1675−1700-cm^{-1} region. For example, in the $CrCl_2O_2/C_2H_3Cl$ system, this band was observed at 1677 cm^{-1}, whereas in the $CrCl_2O_2/C_2HCl_3$ system it was observed at 1689 cm^{-1}. This spectral region is characteristic of the C═O stretch of a carbonyl-containing species, and the intensity is appropriate as well. The 15-cm^{-1} shift of this band upon deuteration in the C_2D_3Cl experiments is also characteristic of carbonyl stretching modes and matches well with the calculated deuterium shifts of acetyl chloride and chloroacetaldehyde complexed with Cl_2CrO (−6 to −11 cm^{-1}). Consequently, the strong band in the 1675−1700-cm^{-1} region is assigned to a carbonyl-containing species formed through the photooxidation of each chloroethene derivative. Moreover, only *one* such band was seen in this region, except for in the C_2Cl_4 system where a second, weaker band was seen at 1808 cm^{-1} at the upper end of the "normal" carbonyl region. Thus, although there are two possible isomers that might form in each system (the acetyl chloride derivative and the chloroacetaldehyde derivative), only one appears to form. (The second band in the C_2Cl_4 system will be accounted for separately; see below.)

As shown in Tables 4 and 5, the calculated energetics (at the B3LYP/6-311++g(d,2p) level) for all of these reactions favors the formation of the acetyl chloride derivative over the chloroacetaldehyde derivative, in each case by approximately 10 kcal/mol. The formation of the acetyl chloride derivative for vinyl chloride arises from the attack of the oxygen atom at the more highly substituted and positively polarized carbon followed by a hydrogen shift to the second carbon to form the methyl group of the acetyl chloride. This follows the general concept of Markinikov reactions[32] for hydrogen halide attack at a carbon–carbon double bond, and although there is no formal rule for oxidations like this one, the model appears to be reasonable. Finally, the scaled fit, using the ratio of the calculated and experimental frequencies of the uncomplexed product and comparing it to the calculated complexed product to predict the experimental position of the complexed product, is better in every case for the acetyl chloride derivative. Taken together, these argue *strongly* for the assignment of the photoproduct band between 1650 and 1700 cm^{-1} to the acetyl chloride derivative in each system complexed to Cl_2CrO.

As noted above, there are at least three possible structures for the resulting cage pair or complex with Cl_2CrO, with the η^1 complex being calculated as the lowest in energy by about 10 kcal/mol. However, more product bands are observed than can be readily accounted for by the η^1 complex alone. It is possible that the spectrum arising from the irradiation of $CrCl_2O_2$/chloroethene samples in solid argon may be the superposition of the η^1 and η^2 complexes or the η^1 complex and the metallocycle. Using the vinyl chloride system as a prototype, the product bands were most effectively accounted for by a superposition of the spectra of the η^1 complex and the metallocycle, as shown in Table 1. The relative amounts of the products formed are probably a function of the relative orientations of the two precursor molecules in the matrix cage prior to irradiation. Finally, it should be noted that the C═O stretch of the chlorine-bound complex was calculated to be blue-shifted by more than 120 cm^{-1}. An additional weak, strongly blue-shifted band was only seen in the C═O stretching region of one system. This was for the reaction of $CrCl_2O_2$ with C_2Cl_4, in which coordination to the chlorine appears most readily accessible. Thus, for this system, a second structure of the oxidation product with Cl_2CrO may be formed as well.

Band assignments are clear for the C═O stretch of the acetyl chloride derivative in each case, as well as for the two detectable modes of Cl_2CrO discussed above. Detailed assignment of the remaining bands is somewhat difficult because the calculated band positions for the η^1 complex and the metallocycle are relatively close to one another and the calculated intensities are not large. With the help of deuterium isotopes, a nearly complete set of assignments can be made for the reaction products of vinyl chloride with $CrCl_2O_2$, as listed in Table 1. For the di-, tri-, and tetrachloroethene reactions with $CrCl_2O_2$, specific band assignments are more difficult and are best identified as arising from a mixture of the η^1 complex of the respective acetyl chloride derivatives with Cl_2CrO, the respective five-membered metallocycle, and in some cases the η^2 complex.

There are several additional interesting points to note. First, the formation of acetyl chloride by oxygen addition to chloroethene requires a hydrogen-atom shift in most of the systems, for which there is ample precedent in organic chemistry. In the perchloro case, $C_2Cl_4 + CrCl_2O_2$, a chlorine-atom shift is required for the observed $CCl_3C(Cl)O$ complex with Cl_2CrO. There is less precedent for such a shift. However, the matrix cage may facilitate the transfer by preventing the separation of the fragment species during the rearrangement process. Second, essentially identical products were formed in the reactions of $CrCl_2O_2$ with *cis*- and *trans*-1,2-chloroethene. As the hydrogen shift occurs, relaxation into the lowest-energy conformer is apparently able to take place. Third, although the oxidation process to form the acetyl chloride derivative complexed to Cl_2CrO was calculated to be exothermic in all cases, the thermal reaction was not observed in the merged-jet experiments. This suggests that there is a substantial activation barrier to the oxidation/rearrangement process. Rather, these systems require photochemical excitation to facilitate reaction. A very recent visible/UV spectroscopic study[33] has shown that a number of σ and π electron donors form 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 a photochemical reaction. Finally, it should be noted that these complexes are relatively strongly bound, with interaction energies in the range of 8–12 kcal/mol, and hence must be viewed as distinct new chemical species. This is consistent with the computational identification of two to three distinct energy minima corresponding to different complexation arrangements.

Conclusions

Irradiation of matrices containing chloro-substituted ethenes and $CrCl_2O_2$ has been shown to lead to oxygen-atom transfer and the formation of a relatively strongly bound molecular complex. In each case, the preferred oxidation product is the acetyl chloride derivative, formed through oxygen-atom attack at the more highly substituted carbon, followed by a hydrogen- or chlorine-atom shift. Theoretical calculations at the B3LYP/6-311++g(d,2p) level supported this conclusion, with the acetyl chloride derivative being more stable than the chloroacetaldehyde derivative by approximately 10 kcal/mol in each case. Possible modes of coordination of the Cl_2CrO fragment to the oxidation product included η^1 end-on to the oxygen atom and η^2 side-on to the carbonyl bond as well as bound through the chlorine atom. Calculations demonstrated that the η^1 complex was more stable than the η^2 complex by about 10 kcal/mol in every case. The infrared spectra are best assigned as a superposition of the η^1, the appropriate five-membered metallocycle, and, in some cases, the η^2 complex.

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