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Matrix Isolation and Theoretical Study of the Reaction of Ethyne with $OVCl_3$ and $CrCl_2O_2$

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Infrared spectroscopy, coupled with matrix isolation and theoretical calculations, has been used to reexamine the photochemical reaction of C_2H_2 with $CrCl_2O_2$, as well as to extend the study to the reaction of C_2H_2 with $OVCl_3$. Two sets of product bands were observed, even at very high sample dilutions, and were assigned on the basis of density functional calculations to the η^1 end-on complex of ketene with Cl_2CrO and the η^2 (C═C) side-on complex, contrary to a previous report. Isomerization of the less stable η^1 complex to the more stable η^2 (C═C) complex was observed upon continued irradiation of the matrix with light of $\lambda > 300$ nm. A second possible η^2 complex (side-on to the C═O bond) was not observed, nor was evidence obtained for the five-membered metallocycle, which was calculated to be approximately as stable as the η^1 complex. The photochemical reaction of C_2H_2 with $OVCl_3$ followed a very similar course, although with lower overall yield.

Introduction

There has been increasing 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 $OVCl_3$. Matrix isolation experiments[3] have provided the primary experimental approach, while extensive theoretical calculations of potential energy surfaces have been conducted.[4,5] This laboratory has studied the reaction of these transition metal compounds, and several related species, with small organic and inorganic substrates containing a heteroatom.[6−10] 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 (hereafter WL) have focused on the reaction of $CrCl_2O_2$ with alkenes and alkynes[11,12] and have reported several novel intermediates. They studied the photochemical reaction of $CrCl_2O_2$ with C_2H_2 and reported several weak product bands.[11] They assigned several to ketene, C_2H_2O, complexed to Cl_2CrO, formed through oxygen atom transfer from $CrCl_2O_2$ to C_2H_2 within a matrix cage and subsequent complexation. In this study, they also reported two additional infrared absorptions, at 2132 and 2195 cm^{-1}, which they were not able to assign definitively. Unfortunately, they were only able to conduct their experiments at very high sample concentrations (e.g., $Ar/C_2H_2 = 20$) and consequently suggested that the additional bands were due to higher aggregates. However, no evidence was put forward to support this suggestion. Also, they only observed three of the nine possible fundamentals of ketene, and these were very weak.

With the ongoing interest in the reaction chemistry of high-valent transition metal oxo compounds in this laboratory, the $C_2H_2/CrCl_2O_2$ system was reinvestigated to clarify several unclear points. Much more dilute matrices were employed, along with higher level DFT calculations. This investigation was extended to the $C_2H_2/OVCl_3$ system as well.

Experimental Details

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[13] Chromyl chloride, $CrCl_2O_2$, and $OVCl_3$ (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. C_2H_2 (Wright Brothers) and C_2D_2 (99% D) (Cambridge Isotope Laboratory) were introduced into a separate vacuum manifold from lecture bottles and were purified by repeated freeze−pump−thaw cycles at 77 K. Argon (Wright Brothers) was used as the matrix gas in all experiments and was used without further purification.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K cold window, allowing for only a very brief mixing time prior to matrix deposition. A few of these matrices were subsequently warmed to 33−35 K to permit limited diffusion and then recooled to 14 K, and additional spectra recorded. In addition, most of these matrices were irradiated for 1.0 or more hours with the H_2O/Pyrex filtered output of a 200 W medium-pressure Hg arc lamp, after which additional spectra were recorded.

A few 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 90 cm length was employed. In both twin and merged jet, matrices were deposited at the rate of 2 mmol/hr 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 the Gaussian 03W suite of programs.[15] 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 reactants and potential intermediates were calculated as well.

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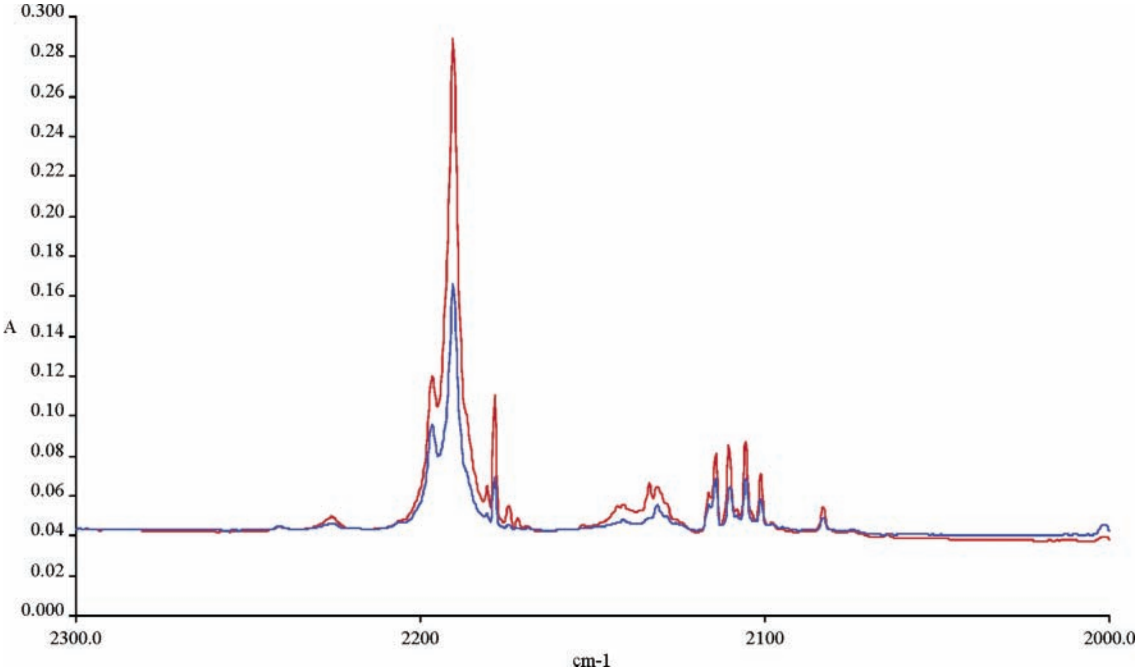

Figure 1. Infrared spectra obtained after irradiation of matrices formed by the codeposition of samples of Ar/C_2H_2 = 2000 + Ar/$CrCl_2O_2$ = 1000 (upper trace) and Ar/C_2H_2 = 3000 + Ar/$CrCl_2O_2$ = 500 (lower trace).

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[16−18] and with blanks run previously in this laboratory. C_2H_2 is known to dimerize readily in matrices,[16] as a function of the matrix window temperature. Comparison to the literature indicated that, at the concentrations employed here, a high percentage of the ethyne was isolated as the monomeric species, and only a low level of dimer was seen. 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 as a result of irradiation. Weak bands due to HCl impurity were noted in all of the $CrCl_2O_2$ and $OVCl_3$ blank experiments.[19]

$CrCl_2O_2$ + C_2H_2: An initial twin jet experiment was conducted with Ar/C_2H_2 = 250 and Ar/$CrCl_2O_2$ = 175, in an attempt to reproduce the results of WL. No distinct new bands were observed upon initial deposition. After 1.5 h of irradiation with light of $\lambda > 300$ nm, many new bands were observed in the resulting spectrum. The bands seen previously by WL were present, although the 2195 cm^{-1} band (a sharp central feature with two associated satellites or shoulders, forming a multiplet) was substantially more intense than the 2105 cm^{-1} band (a multiplet of sharp features centered near 2105 cm^{-1}) assigned by WL to complexed ketene.[11] In addition, a weak band near 2136 cm^{-1} reported by WL was also seen as well as a number of additional new bands not reported by WL. It should be noted that the concentrations employed here were substantially more *dilute* than that employed by WL. Even so, a much richer spectrum was obtained.

In order to understand these differences, and to explore whether aggregation was responsible for the 2195 cm^{-1} absorption, as suggested by WL, a series of similar experiments was undertaken in which the sample concentrations were decreased steadily. In each experiment in the series, the same set of product bands was observed, *and with the same relative intensities.* The most dilute experiment in the series used a sample of Ar/C_2H_2 = 3000, a factor of 150 more dilute than WL. The Ar/$CrCl_2O_2$ ratio in that experiment was 1000 (WL did not quote an Ar/$CrCl_2O_2$ ratio, but it is inferred to be quite high also). Moreover, the change in absolute intensity of a given product band with a change in sample concentration was approximately linear, that is, when the C_2H_2 concentration was halved, the band intensities were approximately halved. Thus, concentration is *not* the determining factor in the production of the species responsible for the 2195 cm^{-1} band relative to that responsible for the 2105 cm^{-1} band. Figure 1 shows the 2000−2300 cm^{-1} spectral region for two different matrix samples, at two different sample concentrations, after identical irradiation times, demonstrating that a reduction in sample concentration reduces the 2105 and the 2195 cm^{-1} bands equally. This result is supported by an experiment in which a sample of Ar/C_2H_2 = 1000 was codeposited with a sample of Ar/$CrCl_2O_2$ = 667 and then irradiated. Both the 2105 and 2195 cm^{-1} bands were present, with similar intensities. This matrix was then annealed to 31 K, recooled, and scanned. While both peaks sharpened slightly, the intensity ratio of the two peaks remained constant after annealing.

Noting that WL irradiated their matrices for 15 min while longer times were generally employed here, additional twin jet experiments were conducted to test the importance of the irradiation time on product yield. A "standard" matrix was deposited, with Ar/C_2H_2 = 2000 and Ar/$CrCl_2O_2$ = 1000. This matrix was then irradiated for 30 s only, and a spectrum recorded. This spectrum showed that the 2105 cm^{-1} band was relatively more intense than the 2195 cm^{-1}band, although both were present, as shown in the lower trace of Figure 2. This matrix was irradiated for another 30 s, and then for 1−2 min lengths, up to 10 min total. Scans were taken between each irradiation time. After the 10 min mark (total time), slightly longer times were used, and then finally a full hour of irradiation at the end. Several interesting observations arose from this series. First, the 2105 cm^{-1} band grew in over the first 10 min, reached a maximum, and then decreased with further irradiation, although it was never completely destroyed (when a similar

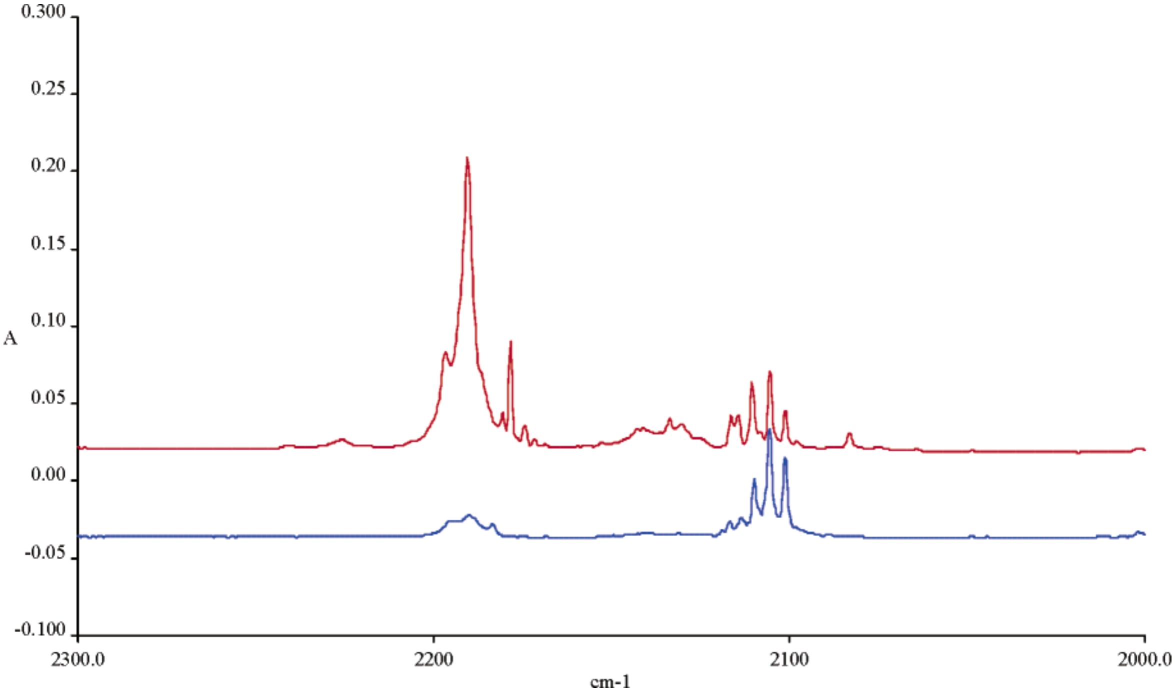

Figure 2. Infrared spectra of a matrix formed by the codeposition of a sample of $Ar/C_2H_2 = 2000$ with a sample of $Ar/CrCl_2O_2 = 1000$, after a 30 s irradiation (lower trace) and a 2 h irradiation (upper trace).

matrix was irradiated for a very long time, 12 h, the 2105 cm^{-1} band was reduced to about 0.01 absorbance unit but was still perceptible above the baseline). The upper trace of Figure 2 shows a spectrum of this matrix after a 2.0 h irradiation. Several other bands in the spectrum followed this pattern as well (collectively, set A). Second, the 2195 cm^{-1} band was present very weakly in the initial 30 s irradiation and grew with longer irradiation times. It continued to grow up to $1-1^1/_2$ hr, and then it leveled off but did not decline. Several bands elsewhere in the spectrum followed this pattern as well (collectively set B).

WL used an irradiation wavelength of 411 nm, while a broad band source with $\lambda > 300$ nm was used in the present experiments. To test the role of wavelength, several matrices were deposited and then irradiated with different cutoff filters. When a filter was used which allowed only light of $\lambda > 600$ nm to pass, no product bands were seen in the resulting spectrum. When a filter was used which allowed only light of $\lambda > 580$ nm to pass, a slight hint of the bands at 2100 and 2195 cm^{-1} was seen. However, they were too weak to measure their intensities accurately. When light of $\lambda > 560$ nm was used, all of the bands in the spectrum seen in the earlier experiments were observed to grow in, and with the same relative intensities (for a fixed length of irradiation time).

Samples of $Ar/C_2H_2 = 1000$ and $Ar/CrCl_2O_2 = 500$ were also codeposited in an initial merged jet experiment, using a 45 cm merged or reaction region held at room temperature. The spectrum of the resulting matrix was identical to that obtained by twin jet deposition and essentially identical to the superimposed blank spectra of the two reagents.

$CrCl_2O_2 + C_2D_2$: To support the experiments described above, a similar set of experiments was undertaken using samples of Ar/C_2D_2, over a range of sample concentrations. Overall, very similar results were obtained. The bands reported by WL for the reaction of C_2D_2 were seen, but again their unassigned minor product at 2177 cm^{-1} is now the dominant product band, and the band they assigned to the end-on coordinated ketene-d_2 at 2073 cm^{-1} is a minor product. In addition, a band of medium intensity was observed at 2255 cm^{-1} along with a number of weak, new product bands seen in the present experiments that were not reported by WL. This experiment was repeated several times at steadily decreasing sample concentrations. Again, the relative intensities of the product bands did not change as a function of parent concentration, while the absolute intensities varied approximately linearly with parent concentration.

$OVCl_3 + C_2H_2$: The reaction of this pair of reagents was studied in a number of experiments, as an alternative oxygen atom source, with the goal of better understanding the overall reaction mechanism. In an initial experiment, a sample of $Ar/OVCl_3 = 300$ was codeposited with a sample of $Ar/C_2H_2 = 500$ in the twin jet mode. After deposition, no new product bands were observed. When this sample was then irradiated for 2 h with light of $\lambda > 300$ nm, several new bands were seen in the spectrum. The most intense was located at 2190 cm^{-1}, while a very weak band was seen near 2100 cm^{-1}, as shown in Figure 3. In addition, a moderately intense band was seen at 769 cm^{-1}, along with quite weak features at 471, 595, 1068, and 1219 cm^{-1}. These all lie relatively near bands observed for set B, above.

This experiment was repeated with a more dilute sample of Ar/C_2H_2 (1000/1), while the $Ar/OVCl_3$ concentration was held constant. After 1 h of irradiation, quite weak bands were seen at 769 and 2190 cm^{-1}. When the sample was irradiated for an additional 2 h, these bands grew significantly in intensity, and a very weak feature was seen near 2100 cm^{-1}. No other product bands were detected in this experiment.

Samples of $Ar/C_2H_2 = 1000$ and $Ar/OVCl_3 = 300$ were also codeposited in a merged jet experiment, using a 45 cm merged or reaction region held at room temperature. The spectrum of the resulting matrix was identical to that obtained by twin jet deposition and essentially identical to the superimposed blank spectra of the two reagents.

Results of Theoretical Calculations

WL reported ketene complexed to Cl_2CrO as the primary (and only identifiable) photoproduct in the $C_2H_2/CrCl_2O_2$ system.

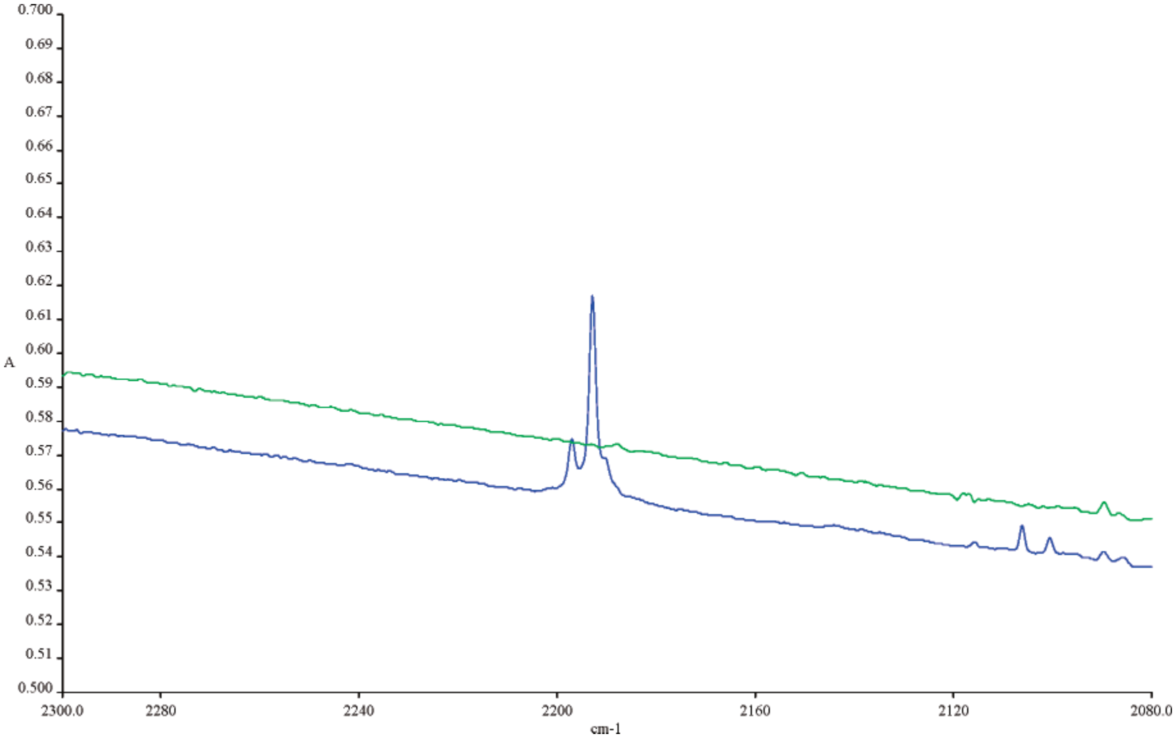

Figure 3. Infrared spectra of a matrix formed by the codeposition of a sample of Ar/C_2H_2 = 500 with a sample of Ar/$OVCl_3$ = 300. Upper trace is before irradiation, while the lower trace is after a 3.0 h irradiation with light of $\lambda > 300$ nm.

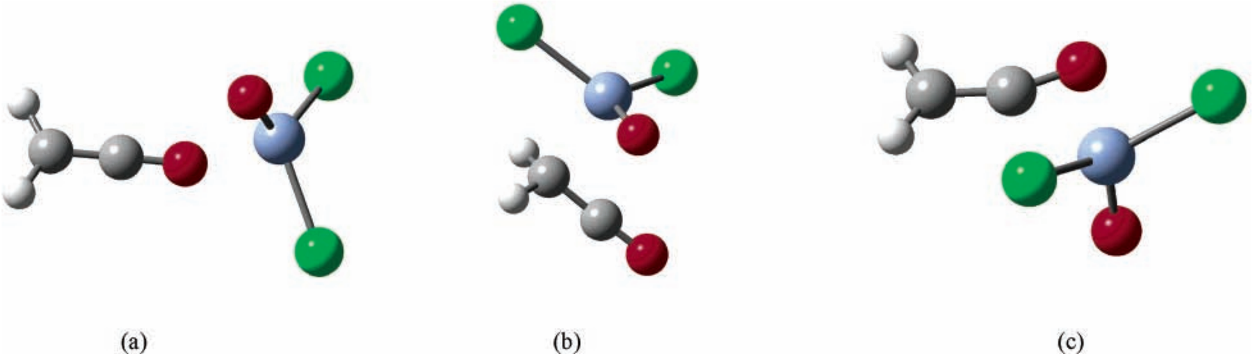

Figure 4. Calculated structures of three complexes of ketene with Cl_2CrO: (a) η^1 (end-on), (b) η^2 (C=C), and (c) η^2 (C=O).

They considered the alternative product, oxirene (a cyclic three-membered ring) complexed to Cl_2CrO, but saw no spectral evidence for this species. For $C_2H_2O-Cl_2CrO$, they considered three modes of coordination, end-on (η^1) and side-on (η^2) to either the C=O or the C=C bond. They calculated the structure and infrared spectra of these complexes at the B3LYP/LANL2Z level of theory but did not actually report calculated spectra for the η^2 complexes. In the present study, these calculations were extended to a higher level of theory, B3LYP/6-311++g(d,2p), to more accurately predict spectra and to assess the relative energetics of the different complexes. Also considered were (1) ethynol, HC≡COH, (2) a five-membered metallocycle formed by addition of C_2H_2 to the O=Cr=O moiety, and (3) the double oxygen transfer product HOC≡COH.

All three complexes of ketene with Cl_2CrO optimized to stable minima, with all positive vibrational frequencies. Figure 4 depicts the calculated structure of all three complexes. The calculated spectra for all three are compared in Table 1, including calculated deuterium shifts, along with the calculated spectrum of ketene at the same level of theory and the relative energies of these species. Also included in Table 1 is the calculated spectrum of the potential metallocycle product. The η^2 (C=C) complex was calculated to be lower in energy than the (η^1) complex by 9.2 kcal/mol, while the η^2 (C=O) complex was calculated to be higher in energy than the η^2 (C=C) complex by 18.5 kcal/mol. The five-membered metallocycle was nearly identical in energy to the (η^1) complex and 9.47 kcal/mol above the η^2 (C=C) complex. The gas phase energetics of oxygen atom transfer from $CrCl_2O_2$ to ethyne to form ketene and Cl_2CrO were also calculated; $\Delta E°_{298}$ was computed to be -20.9 kcal/mol. In addition, the η^2 (C=C) complex was calculated to be lower in energy than the separated C_2H_2O and Cl_2CrO species by 18.1 kcal/mol. Finally, calculations were carried out from several different starting geometries on the 1:1 complex of oxirene with Cl_2CrO as a possible product in this system. The complex spontaneously decomposed into $C_2H_2 + CrCl_2O_2$, indicating that this complex is not stable and isolable. This is also consistent with the fact that the reaction $C_2H_2 + CrCl_2O_2 \rightarrow$ oxirene + Cl_2CrO was calculated to be substantially endothermic.

Similar calculations were carried out for the reaction of $OVCl_3$ with C_2H_2, leading to ketene complexed to VCl_3. All three complex structures (η^1 (end-on)), η^2 (C=C), and η^2 (C=O)) optimized to stable minima; calculated infrared spectra and

TABLE 1: Comparison of Calculated Infrared Spectra for Complexes of Ketene with Cl_2CrO[a,c]

	η^1 (end-on)	$\Delta\nu$(D)	η^2(C=O)	$\Delta\nu$(D)	η^2(C=C)	$\Delta\nu$(D)	ketene (calc)	ketene (expt)[b]	Cl_2CrO (calc)	metallocycle
	434 (3)	−38	433 (15)		421 (28)		445 (3)	438		485 (179)
	438 (191)	−1	451 (134)	−6	428 (123)	−4			522 (135)	507 (3)
	536 (5)	−13	563 (6)	−39	583 (21)	−116	551 (42)	528		585 (24)
			573 (75)	−26	590 (21)	−41	594 (89)	588		636 (25)
	704 (91)	−146	735 (69)	−156	849 (142)	−179				770 (38)
	957 (5)	−128	964 (119)	−158	1060 (6)	−177	988 (6)	977		860 (36)
	1175 (16)	−251	1089 (56)	−165	1072 (2)	−151	1170 (6)	1118		870 (0)
	1128 (192)	0	1141 (157)	−1	1125 (190)	−1			1138 (211)	1082 (19)
	1404 (7)	−141	1410 (14)	−227	1384 (22)	−236	1407 (18)	1388		1163 (24)
	2192 (584)	−33	1926 (263)	−21	2254 (674)	−27	2221 (694)	2152		1376 (1)
	3155 (55)	−833	3142 (17)	−846	3096 (31)	−825	3174 (29)	3071		1533 (109)
	3245 (24)	−828	3261 (5)	−834	3174 (22)	−816	3267 (9)	3166		3218 (1)
										3241 (9)
E_{rel}	+9.2		+18.5		0.0					+9.47 kcal/mol

[a] Calculated values are unscaled frequencies, B3LYP/6-311++g(d,2p); only those above 400 cm^{-1} are listed. [b] From refs 21 and 22. [c] Numbers given parenthetically are calculated intensities, in km/mol.

TABLE 2: Comparison of Calculated Infrared Spectra for Complexes of Ketene with Cl_3V[a,c]

	η^1 (end-on)	η^2(C=O)	η^2(C=C)	ketene (calc)	ketene (expt)[b]	Cl_3V (calc)
	432 (133)[c]	435 (15)	416 (19)	445 (3)	438	506 (152)
	487 (150)	510 (134)	453 (78)			506 (152)
	502 (29)	521 (6)	503 (64)	551 (42)	528	
		610 (75)	533 (83)	594 (89)	588	
	724 (91)	634 (87)				
		823 (119)	812 (101)			
	943 (3)	991 (26)		988 (6)	977	
	1156 (16)	1076 (56)	1069 (18)	1170 (6)	1118	
	1416 (12)	1423 (14)	1373 (20)	1407 (18)	1388	
	2160 (213)	1750 (263)	2213 (698)	2221 (694)	2152	
	3136 (14)	3139 (17)	3097 (31)	3174 (29)	3071	
	3222 (12)	3248 (5)	3178 (17)	3267 (9)	3166	
E_{rel}	+9.38	+0.31	0.0 kcal/mol			

[a] Calculated values are unscaled frequencies, B3LYP/6-311++g(d,2p); only those above 400 cm^{-1} are listed. [b] From refs 21 and 22. [c] Numbers given parenthetically are calculated intensities, in km/mol.

relative energies are listed in Table 2. Again, the η^2 (C=C) complex was calculated to be lowest in energy, 9.38 kcal/mol lower in energy than the η^1 complex, while the η^2 (C=O) complex was close in energy to the η^2 (C=C) complex. A five-membered ring metallocycle is not possible for this system and hence could not be calculated. Calculations were also carried out on the complex between oxirene and VCl_3, and this complex also decomposed spontaneously.

Discussion

Similar results where obtained in experiments employing $C_2H_2 + OVCl_3$ compared to experiments with $C_2H_2 + CrCl_2O_2$, although the overall yield was higher in this second system. Since WL studied only the $C_2H_2 + CrCl_2O_2$ system, the discussion here will focus on this system, and then the conclusions will be extended to the $C_2H_2 + OVCl_3$ system.

No distinct new bands were detected upon twin jet deposition of samples of Ar/C_2H_2 with $Ar/CrCl_2O_2$, in agreement with WL. Irradiation of these matrices with broad band visible/near-UV light ($\lambda > 300$ nm) led to most of the same product bands seen by WL, along with numerous less intense bands not reported by WL. Both studies observed bands near 450 and 1014 cm^{-1} which are readily assigned to the Cl_2CrO fragment, based on comparisons to the literature.[12] The 1014 cm^{-1} was a shoulder on the high-energy side of the parent Cr=O absorption near 1005 cm^{-1} but was nonetheless observable. It is noteworthy that the absolute intensities of the bands common to both studies were greater in the present study, and the relative intensities were generally different. Most importantly, very different concentration regimes were examined in these two studies. WL used concentrations of Ar/C_2H_2 between 20/1 and 50/1, while concentrations as low as $Ar/C_2H_2 = 3000/1$ were used here. Similarly low concentrations of $Ar/CrCl_2O_2$ were employed here, while WL did not report $Ar/CrCl_2O_2$ values.

Central to the analysis are the two bands (or multiplets) noted in both studies, near 2105 and 2195 cm^{-1} (WL also reported a weak band at 2132 cm^{-1}; this feature was seen only very weakly in several but not all of the present experiments, and little can be concluded about the origin of this band). In the present study, the 2105 and 2195 cm^{-1} features were always present in the nearly the same intensity ratio after prolonged irradiation, *independent of the sample concentrations employed.* This fact, combined with the very low concentrations employed (as dilute as 3000/1 + 1000/1), argues strongly that the 2195 cm^{-1} feature is not due to the reaction of one $CrCl_2O_2$ molecule with two molecules of C_2H_2, that is, a result of aggregation as suggested by WL. This is further supported by the fact that the same intensity ratio was observed when the $CrCl_2O_2/C_2H_2$ ratio was as high as 5/1. Finally, the intensities of both the 2105 and the 2195 cm^{-1} features varied linearly with the sample concentrations (i.e., when the C_2H_2 concentration was halved, the final intensities of both bands were approximately halved). This behavior is also inconsistent with aggregation. Thus, it is clear that the assignment of the 2195 cm^{-1} proposed by WL is not correct, while the assignment of the 2105 cm^{-1} band (to the η^1 end-on complex) may still be correct.

In experiments in which the matrix sample was exposed to multiple short irradiation times, the 2105 cm^{-1} feature was observed to grow in quickly (quite apparent after 30 s of irradiation), reach an intensity maximum after about 10 min of irradiation, and then decrease with further irradiation (up to 2 h), at which point only minor changes occurred. In contrast, the 2195 cm^{-1} band initially grew more slowly (it was much weaker than the 2105 cm^{-1} band after 30 s of irradiation as seen in the lower trace of Figure 2), and then it grew to a maximum over the next 2 h. After about 15 min the 2195 cm^{-1} band was comparable to the 2105 cm^{-1} band in intensity, and by the end of the prolonged irradiation the 2195 cm^{-1} band was approximately 4 times as intense at the 2105 cm^{-1} band. These results require (1) that the 2105 and 2195 cm^{-1} bands are due to different chemical species (species A for the 2105 cm^{-1} band and species B for the 2195 cm^{-1} band) and (2) that both species arise from one C_2H_2 molecule and one $CrCl_2O_2$ molecule. Further, the results strongly suggest that species B is formed from species A under continued irradiation. This is also apparent from the wavelength-dependent studies, where the same growth behavior as a function of irradiation time was observed *independent of the wavelength of light used* (for $\lambda < 580$ nm; for longer wavelength, no significant product formation was observed).

While a number of possible products might be considered for species A and B (as WL indicated), most can be eliminated. While oxirene is a higher energy isomer of C_2H_2O, calculations demonstrated that the oxirene−Cl_2CrO complex is unstable with respect to dissociation to $C_2H_2 + CrCl_2O_2$. Further, the spectrum calculated for oxirene[20] shows no bands in the 1800−2400 cm^{-1} region. The observed spectrum is not consistent at all with ethynol,[21] HC≡COH, another high-energy isomer of C_2H_2O. The five-membered metallocycle formed by addition of C_2H_2 across the two oxo groups of $CrCl_2O_2$ was calculated to be a stable species, with an absolute energy comparable to several of the ketene−Cl_2CrO isomers. However, this metallocycle was not calculated to have any infrared absorptions in the 1600−2600 cm^{-1} region and hence cannot be assigned as either species A or B. On the other hand, ketene ($H_2C{=}C{=}O$) absorbs strongly in the 2100−2200 cm^{-1} region (2156 cm^{-1} for the gas phase species and 2142 cm^{-1} isolated in an argon matrix[21,22]), and ketene is the lowest energy isomer of C_2H_2O. Finally, the deuterium shifts observed for both species A and species B were nearly identical to the deuterium shift of gas phase and matrix isolated ketene, suggesting products very closely related to ketene.

As noted above and by WL, if ketene is produced in these experiments by O atom transfer from $CrCl_2O_2$ to C_2H_2, then the resulting ketene is cage-paired with the Cl_2CrO fragment that must also be produced and in fact was observed. There are several different possible modes of complexation, as described above. End-on (η^1) complexation is expected to reduce the C=O stretching frequency somewhat (as shown in Table 1); calculations suggest a shift of 29 cm^{-1} to lower energy. η^2 (C=O) complexation is expected to strongly reduce the C=O stretching frequency; calculations indicate a shift of 266 cm^{-1} to lower energy. In contrast, calculations predict that η^2 (C=C) complexation should increase the C=O stretching frequency relative to free ketene, specifically 62 cm^{-1} to higher energy. With the use of these calculated shifts and the experimental argon matrix band position for free ketene,[21,22] the η^1 complex is predicted to be observed at 2113 cm^{-1} and the η^2 (C=C) complex at 2204 cm^{-1}. These are very close to the experimental bands of species A (2105 cm^{-1}) and species B (2195 cm^{-1}) [note: all calculated vibrational frequencies are unscaled] and suggest assignment to species A and B. Further, as shown in Table 1, the most stable of the three complexes between ketene and Cl_2CrO is the η^2 (C=C) complex, by about 9 kcal/mol. Thus, if there is a mechanism for the conversion of one complex to another, then the η^2 (C=C) complex should be the final stable product of the system. This, too, is consistent with experimental observation, where the 2195 cm^{-1} band continues to grow on irradiation for up to 2 h, while the 2105 cm^{-1} band reaches a maximum and then decreases upon prolonged irradiation. Therefore, the 2105 cm^{-1} band is assigned as the η^1 complex, in agreement with WL, while the 2195 cm^{-1} is assigned to the η^2 (C=C) complex and not to an aggregate species.

Several additional weaker product bands followed the temporal irradiation behavior of the 2105 cm^{-1} band, including the 1134 cm^{-1} band reported by WL. While weak, they match up reasonably well with the more intense bands calculated for the η^1 complex, although these bands are calculated to be much weaker than the 2105 cm^{-1} band. Other bands followed the temporal behavior of the 2195 cm^{-1} band and lie reasonably close to calculated bands for the η^2 (C=C) complex. As such, these weak bands are assigned to the respective complexes. The only questionable band is one observed at 774 cm^{-1} (reported at 773 cm^{-1} by WL). They assigned this to the η^1 complex. However, this band clearly shows the same temporal behavior at the η^2 (C=C) complex, with an intensity of 0.006 absorbance units after 30 s of irradiation, and increasing monotonically to 0.090 units after prolonged irradiation. The η^2 (C=C) complex is calculated to have a band of moderate intensity (second highest in the ketene subunit) at 849 cm^{-1}. With scaling appropriate for this level of theory, this could reasonably account for a band at 774 cm^{-1}. Given its clear temporal behavior, assignment to the η^2 (C=C) complex is appropriate.

The experiments employing $CrCl_2O_2$ and C_2D_2 support these conclusions as well. The observed deuterium shifts (−18 and −32 cm^{-1}) of the η^1 and η^2 (C=C) complexes were quite close to those calculated and listed in Table 1 (−33 and −27 cm^{-1}). Further, the calculations predict that one of the C−D stretching modes for the η^2 (C=C) complex should have moderately high intensity, as a consequence of mixing with the C=O stretching mode, and should occur approximately 50 cm^{-1} to higher energy. The product band observed at 2255 cm^{-1} in the C_2D_2 experiments is an excellent candidate for this mode.

Analysis of the $OVCl_3 + C_2H_2$ results follows a similar pattern. The most intense product band was observed at 2190 cm^{-1}, with a very weak feature near 2100 cm^{-1}. This is very reminiscent of the 2105 and 2195 cm^{-1} bands above, although the overall product yield was lower than with $CrCl_2O_2$. The η^1 complex is calculated to have its strongest band at 2160 cm^{-1}, 61 cm^{-1} to lower energy of the band calculated for free ketene. The η^2 (C=C) complex is calculated to absorb at 2213 cm^{-1}. The η^2 (C=O) complex is again calculated to have its most intense band at lower energy (1750 cm^{-1} in this case). Thus, assignment of the more intense 2190 cm^{-1} band to the η^2 (C=C) complex is made, with the quite weak band near 2100 cm^{-1} assigned to the η^1 complex. The remaining weak bands, at 471, 595, 1068, and 1219 cm^{-1}, are also assigned to the η^2 (C=C) complex, with the except of the 471 cm^{-1} band which is assigned to the VCl_3 fragment. These results are again consistent with the calculated relative energies of the three isomers of the 1:1 complex of ketene with VCl_3. The η^2 (C=C) complex was calculated to be the most stable complex, with the η^1 complex calculated to be 9.38 kcal/mol higher in energy.

Further Considerations

It is noteworthy that the reaction of C_2H_2 with $CrCl_2O_2$ did not occur in the gas phase in merged jet experiments, even when the reaction zone was heated to as high as 150 °C. $\Delta G°_{298}$ for the oxygen transfer reaction was calculated to be −23.9 kcal/mol, yet the reaction did not take place. This indicates that the system is kinetically limited, and there must be a significant activation barrier for the reaction. On the other hand, as noted above, within the matrix the η^1 complex converted to the η^2 (C=C) complex under conditions of continued irradiation, although this rearrangement did not occur by simple matrix annealing. Continued irradiation very likely excites the Cl_2CrO chromophore and leads to rearrangement to the more stable η^2 (C=C) complex. The rate of this process is probably dictated by the cage of argon atoms surrounding the 1:1 complex. While the 2105 cm^{-1} band reached a maximum in 10 min and decreased thereafter, only after very long irradiation times (>11 h) was this band essentially completely destroyed.

Two earlier studies[23,24] involving oxygen atom transfer from $CrCl_2O_2$ or $OVCl_3$ to a substrate demonstrated significant differences between $CrCl_2O_2$ and $OVCl_3$. Specifically, oxygen atom transfer occurred from $CrCl_2O_2$ to DMSO and to PH_3, while the analogous reactions of $OVCl_3$ did not occur. Here, the differences are not so great. The overall yield of ketene, as judged by band intensities, was less for the $OVCl_3$ system. However, several of the remaining features (e.g., time dependence of irradiation) were quite similar. The calculated energetics are quite different; as noted above the O atom transfer reaction from $CrCl_2O_2$ to C_2H_2 is approximately 23 kcal/mol exothermic, while the analogous reaction for $OVCl_3$ is 12 kcal/mol endothermic. Only the complexation energy of ketene and the VCl_3 fragment (−13.2 kcal/mol) makes the overall matrix reaction exothermic in this case.

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