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Matrix Isolation Investigation of the Photochemical Reaction of Benzene with $CrCl_2O_2$ and $OVCl_3$

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The matrix isolation technique, combined with infrared spectroscopy, has been used to characterize the products of the photochemical reactions of benzene with $CrCl_2O_2$ and $OVCl_3$. While initial twin jet deposition of the reagents led to no visible changes in the recorded spectra, strong product bands were noted following irradiation with light of $\lambda > 300$ nm. Wavelength dependence studies determined that light of $\lambda < 590$ nm led to reaction and oxygen atom transfer, forming an η^1-complex between 2,4-cyclohexadienone and $CrCl_2O$. The identification of the complex was further supported by isotopic labeling (^{13}C and ^2H) and by density functional calculations at the B3LYP/6-311G++(d,2p) level. Merged-jet experiments in which thermal reactions are examined were also conducted, at temperatures as high as 150 °C. No products were observed.

Introduction

The oxidation of organic substrates with metal oxo compounds, including $CrCl_2O_2$ and $OVCl_3$, is of continuing interest to a range of chemists.[1,2] Of particular interest is the selectivity of the oxidation of organic compounds and the specificity of the product formed. These metal oxo compounds are able to transfer their oxygen atom to certain olefins and hydrocarbons.[3−12] Cook and Mayer observed a range of oxygenated products from the oxidation of aromatics such as ketones, aldehydes, chloro ketones, epoxides, and alcohols. They postulated a mechanism in which the $CrCl_2O_2$ oxidizes the cyclic compound by initial abstraction of a hydrogen atom. While these studies represent a significant advance in the overall understanding of these reactions, their work was limited to product studies and did not identify the initial intermediates in these reactions. Metal oxo compounds such as these have also been used as catalysts in organic or polymer synthesis and as models for the active sites in enzymes such as Cytochrome P-450.[13,14] Extensive theoretical calculations of the potential energy surfaces for the reactions of $CrCl_2O_2$ with small substrates have been conducted.[10,11,15−17] Finally, while much of the experimental work has been done in solution, a few studies have explored the reactions of $CrCl_2O_2$ in the gas phase.[3,4]

The matrix isolation technique was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates[18−20] and may provide access to the study of initial intermediates in the above reactions. Past studies in this laboratory have examined the matrix-isolated products of the thermal and photochemical reactions of $CrCl_2O_2$ and $OVCl_3$ with smaller organic and inorganic substrates.[12,21−32] Also, Parker and Davis[33] have studied the reaction of oxygen atoms (photochemically generated from ozone) and benzene using matrix isolation and have shown that an oxygen atom addition to benzene leads first to the formation of 2,4-cyclohexadienone, which then photolyzes to butadienylketene (hexa-1,3,5-triene-1-one). These results help guide the present study, which focused on the utilization of matrix isolation to identify intermediates in the reactions of $CrCl_2O_2$ and $OVCl_3$ with C_6H_6.

Experimental Section

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[34] 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. Benzene (Allied Chemicals), benzene-*d*$_6$ (99%+D, Acros), and benzene-$^{13}C_6$ (99%, Cambridge Isotope Laboratories) were introduced in a similar manner into a separate vacuum manifold and were purified by repeated freeze−pump−thaw cycles at 77 K. Argon and nitrogen (both Wright Brothers) were used as the matrix gases 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. 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, all of these matrices were irradiated for 0.5 h or more 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,[35] in which the two deposition lines were joined with an Ultra Torr 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 100 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. UV−visible spectra were recorded on a Varian Cary 4000 UV/visible spectrophotometer between 800 and 200 nm, using a 0.5 nm bandwidth.

Theoretical calculations were carried out on likely intermediates in this study, using the Gaussian 03W suite of programs.[36] Density functional calculations with the hybrid B3LYP functional were used to locate energy minima, determine structures,

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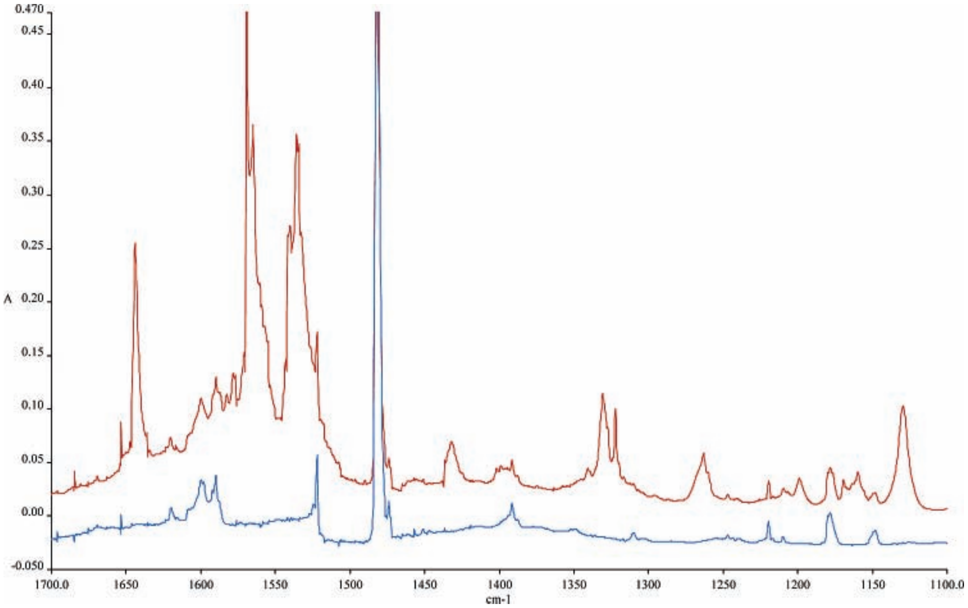

Figure 1. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/$CrCl_2O_2$ = 250 with a sample of Ar/C_6H_6 = 1000. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm.

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.

Experimental Results

Prior to any co-deposition 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,[37−42] and with 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 1.0 h and no changes were noted, other than in Ar/$CrCl_2O_2$ and Ar/$OVCl_3$ blanks, where the growth of very weak bands due to photochemical reaction with impurity H_2O was seen.[23] Weak bands due to HCl impurity were noted in all of the $CrCl_2O_2$ blank experiments, as well as bands from the benzene−HCl complex.[43]

$CrCl_2O_2$ + Benzene. In an initial twin jet experiment, a sample of Ar/$CrCl_2O_2$ = 250 was co-deposited with a sample of Ar/benzene = 1000. After 22 h of deposition, no new bands were detected. This sample was annealed to 33 K and another spectrum was recorded, and again 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 process produced many new product bands which are listed in Table 1. The most intense bands were seen at 1643, 1567, 1535, 1431, 1330, 1322, 1263, 1130, 1016, 716, 538, and 438 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure 1 shows a representative region of this spectrum.

TABLE 1: Calculated (B3LYP/6-311G++(d,2p)) and Observed Frequencies[b] and Isotopic Shifts for the $CrCl_2O$−2,4-Cyclohexadienone Complex (Structure 5a)

normal isotope		^2H		^{13}C	
calcd freq[a]	exptl freq	calcd shift	exptl shift	calcd shift	exptl shift
	435				
413	438	0	2	0	−3
439	454	−63		−11	−12
481		−19		−8	
527	538	−99		−10	−16
549		−13		−14	
578		−21		−18	
711	716	−145	−153	−8	−7
	767				
771	785	−66	−62	−21	−16
805	804	−62	−35	−11	
904	904	−269		−20	−15
924	921	−27	−3	−30	−22
940	924			−26	−15
979	under parent	−176		−9	
981	under parent	−227		−21	
1002	1060			−10	45
1076	1016	1	1	0	−11
	1089				
1151	1130	−320	−301	−9	24
1161	1160	−270	−246	−5	1
1163	1198	−321	−361	−5	−16
1249	1263	−35	−63	−28	−24
1316	1322	−137	−186	−27	−21
1355	1330	−358		−8	−13
1373	1401			−16	−29
1415	1431	−101	81	−27	−28
1531	1535	−28	11	−54	−51
1559	1567	−11	−8	−40	−46
1634	1643	−46	−40	−56	−54
2919	2842	−793	−772	−6	−2
2933	2851	−767	−757	−10	0
3071	under parent	−806		−9	
3078	under parent	−807		−10	
3098	under parent	−799		−11	
3110	under parent	−805		−10	

[a] Frequencies scaled by a factor of 0.97. [b] Frequencies in cm^{-1}.

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/$CrCl_2O_2$ = 250 to Ar/$CrCl_2O_2$ = 500 and Ar/benzene = 430 to Ar/benzene = 1500. The same product 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 were the sharpest in the most dilute experiments and became much broader as the concentration of benzene increased. This is consistent with the known aggregation of benzene in argon matrices with increasing sample concentration.[38] The product bands grew in over a 0.5-h period of irradiation and reached a maximum in 3.0 h of

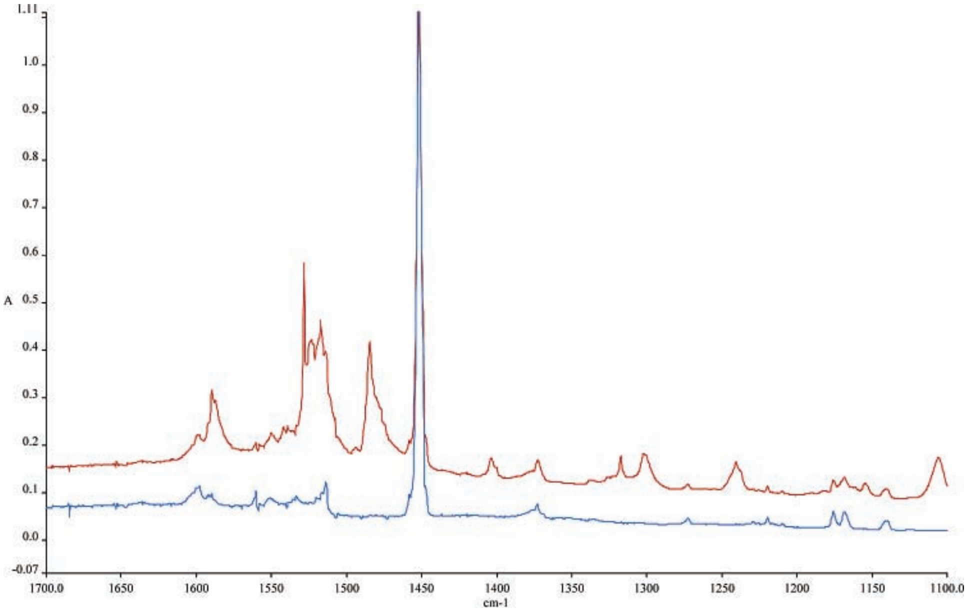

Figure 2. Infrared spectra of a matrix formed by the twin jet deposition of a sample of $Ar/CrCl_2O_2 = 250$ with a sample of $Ar/^{13}C_6H_6 = 450$. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm.

irradiation. In one experiment, after deposition the matrix was annealed, irradiated, and then annealed again to see if any of the product bands would become sharper. However, none of the bands did so. In another experiment a wavelength study was conducted, using a selection of colored filters, to determine the wavelength at which the onset of product formation occurred. A small amount of product could be detected at $\lambda = 590$ nm, while more rapid product formation was noted at $\lambda < 590$ nm.

A series of merged jet experiments was conducted with samples of $Ar/CrCl_2O_2 = 250$ and $Ar/C_6H_6 = 1000$. With the merged region held at room temperature, the resulting spectrum was identical with that observed in the twin jet experiments with no new product bands. In a subsequent experiment, with the merged region heated to 150 °C, identical results were obtained. In all of the merged jet experiments, the bands due to the benzene–HCl complex did grow in more than those in the twin jet experiments. Irradiation of one of the matrices ($\lambda > 220$ nm) resulted in the same set of product bands described above, with the same relative intensities.

An additional experiment was conducted in which N_2 was used as the matrix gas in an attempt to reduce the extent of the site splitting in the spectra. A sample of $N_2/CrCl_2O_2$ was co-deposited with a sample of N_2/benzene for approximately 22 h and was then irradiated for 1 h. While the same product bands appeared after irradiation, the extent of site splitting was not reduced and the product bands were generally broader than those in argon.

$CrCl_2O_2$ + Benzene-*d*$_6$. Multiple twin jet experiments were conducted in which samples of $Ar/CrCl_2O_2$ were co-deposited with samples of Ar/C_6D_6. After 22.0 h of deposition, the matrix was irradiated for 1.0 h. This irradiation produced many new bands (see Table 1), with the most intense bands at 1603, 1559, 1546, 1512, 1360, 1136, 1016, 837, 563, and 440 cm^{-1}. When more dilute samples were used, additional bands were seen at 2630, 2622, 2618, 2105, 2100, 1200, 1036, 1017, 803, and 723 cm^{-1}. Most of the observed product bands were split into doublets or multiplets.

$CrCl_2O_2$ + Benzene-$^{13}C_6$. Two twin jet experiments were undertaken in which samples of $Ar/CrCl_2O_2$ were co-deposited with samples of Ar/benzene-$^{13}C_6$. After 22.0 h of deposition, the two bands of the benzene–HCl complex were observed, as well as bands at 2159, 2154, and 1937 cm^{-1}. The matrix was then irradiated for 1.0 h, and many new product bands were seen as listed in Table 1. The most intense bands were located at 1589, 1521, 1484, 1403, 1372, 1317, 1301, 1239, 1105, 1010, 709, 522, and 442 cm^{-1}. With a change in the concentration of the reagents, additional product bands were noticed, most being very weak. Again, most of the observed product bands were split into doublets or multiplets. Figure 2 shows a representative region of this spectrum.

$OVCl_3$ + C_6H_6. $OVCl_3$ was used as an alternative oxygen source for the reaction between the two reagents in several experiments. In an initial twin jet experiment, a sample of $Ar/OVCl_3 = 250$ was co-deposited with a sample of $Ar/ C_6H_6 = 1000$. After 22 h of deposition, no new product bands were detected. The matrix was then irradiated for 1 h, a spectrum was recorded, and then the matrix was irradiated for an additional 2 h with the filtered ($\lambda > 300$ nm) output of a medium pressure Hg arc lamp. Only three weak product bands were observed, at 790, 795, and 3599 cm^{-1}, arising from the photochemical reaction of $OVCl_3$ with impurity H_2O.[23] This experiment was repeated with a more concentrated sample of $Ar/C_6H_6 = 450$, while the $Ar/OVCl_3$ concentration was held constant. The sample was irradiated for 1 h, and then for an additional 3 h. Again, no product bands were observed.

Visible/UV Studies. In two experiments, samples of $Ar/CrCl_2O_2$ were deposited with samples of Ar/C_6H_6 with use of twin jet deposition. After the initial deposition of the reagents, bands of both parent species were present, but no new bands were observed. These matrices were then irradiated; in the resulting spectrum the parent absorptions of C_6H_6 and $CrCl_2O_2$ were reduced in intensity but not destroyed. No new bands were observed.

Results of Calculations

The structures, energetics, and vibrational spectra of a number of possible products of the two systems were calculated with the B3LYP hybrid functional and basis sets as high as 6-311G++(d,2p). Figure 3 shows the energies of the seven calculated likely structures (products) relative to $CrCl_2O_2$ + benzene; the energies are also listed in Table 2. Figure 4 shows

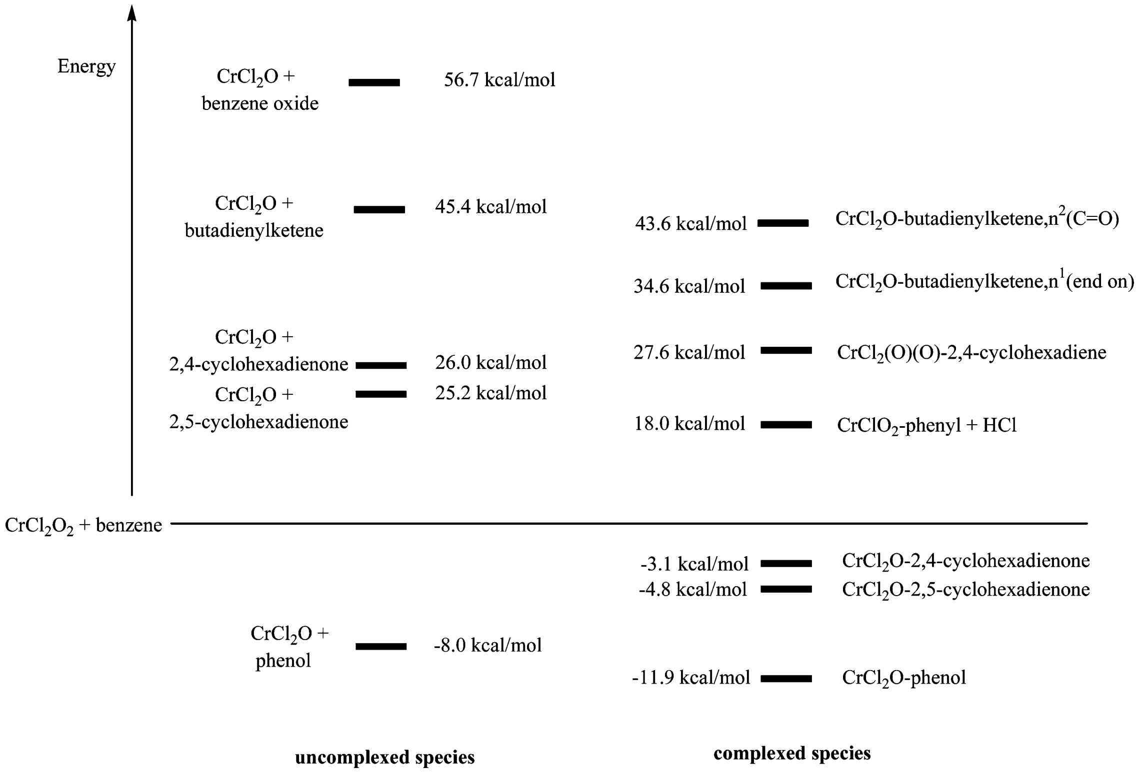

Figure 3. Relative energies of the uncomplexed and complexed products as compared to $CrCl_2O_2$ and benzene.

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

uncomplexed products	rel energies, kcal/mol	complexed products	rel energies, kcal/mol
$CrCl_2O$ + benzene oxide	56.7	$CrCl_2O$−butadienylketene, η^2 (C=O)	43.6
$CrCl_2O$ + butadienylketene	45.4	$CrCl_2O$−butadienylketene, η^1 (end on)	34.6
$CrCl_2O$ + 2,4-cyclohexadienone	26.0	$CrCl_2(O)(O)$−2,4-cyclohexadiene	27.6
$CrCl_2O$ + 2,5-cyclohexadienone	25.2	$CrClO_2$−phenyl + HCl	18.0
$CrCl_2O$ + phenol	−8.0	$CrCl_2O$−2,4-cyclohexadienone	−3.1
		$CrCl_2O$−2,5-cyclohexadienone	−4.8
		$CrCl_2O$−phenol	−11.9

[a] Energies relative to the reactants, $CrCl_2O_2$ + C_6H_6.

a representation of these calculated structures (structures **4a**−**g**). 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 (Cl_2CrO or Cl_3V), plus the product of HCl elimination from the initial cage pair (**4g**). Specifically, the following complexes were optimized: $CrCl_2O$−phenol, $CrCl_2O$−benzene oxide, $CrCl_2O$−butadienylketene (in all three modes of coordination, end on, η^1, and side on, η^2, to either the C=O or the C=C bond), $CrCl_2(O)(O)$−2,4-cyclohexadiene, $CrCl_2O$−2,4-cyclohexadienone, and $CrCl_2O$−2,5-cyclohexadienone (both the η^1 and η^2 (C=O) modes of coordination). All of these structures except the diene complex correspond to a single oxygen transfer from the chromyl chloride to the benzene while the diene complex corresponds to a double oxygen transfer. For all the butadienylketene and 2,4-cyclohexadienone complexes, the vanadium analogues were calculated as well. All of the proposed complexes optimized to energy minima on their respective potential energy surfaces, with all positive vibrational frequencies. For the $CrCl_2O$−2,4-cyclohexadienone complex **4a**, vibrational frequencies were calculated for the completely deuterated and carbon-13 isotopomers for comparison to experimental spectra and are listed in Table 1, while Table 3 lists all calculated infrared absorptions with intensities greater than 6 km/mol for structures **4b**−**g**.

Discussion

No distinct product bands were observed upon initial codeposition of benzene and its isotopomers with $CrCl_2O_2$ into argon matrices. However, subsequent irradiation of these matrices led to the formation of strong product bands. This is very similar to other systems studied in this lab,[25] including the reactions of $CrCl_2O_2$ + PH_3 and $OVCl_3$ + PH_3. For a photochemical reaction to occur, the reactants must be trapped in the same matrix cage. The visible/UV spectroscopic experiment indicated that the interaction between the two reaction partners in the matrix cage must be small, as no perturbations to the electronic structure were apparent in the visible or UV regions upon initial matrix deposition. Nonetheless, it is likely that there are cage pairs formed from the statistical distribution of components of the system during the matrix condensation process. Further, it is very probable that the stoichiometry of the cage pairs is 1:1, i.e., one molecule of $CrCl_2O_2$ and one molecule of benzene. This conclusion is reasonable because (1) the concentrations of the reactants were quite low throughout, so that dimers are statistically unlikely, and (2) the relative

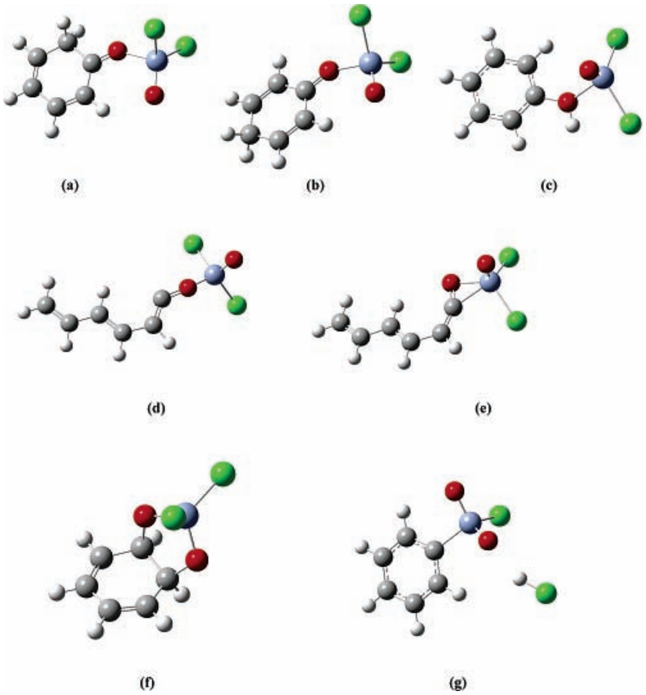

Figure 4. Calculated structures of the complexes of the photochemical reaction of $CrCl_2O_2$ and benzene: (a) $CrCl_2O_2$−2,4-cyclohexadienone, (b) $CrCl_2O_2$−2,5-cyclohexadienone, (c) $CrCl_2O_2$−phenol, (d) $CrCl_2O_2$−butadienylketene, η^1 (end on), (e) $CrCl_2O_2$−butadienylketene, η^2 (C=O), (f) $CrCl_2(O)(O)$−2,4-cyclohexadiene, and (g) $CrClO_2$−phenyl + HCl.

TABLE 3: Calculated[a] Bands ($I > 6$ km/mol) of Structures 4b−g

$CrCl_2O$−2,5-cyclohexa-dienone (cm^{-1})	$CrCl_2(O)$-(O)−2,4-cyclohexadiene (cm^{-1})	$CrCl_2O$−ketene η^1 (end on) (cm^{-1})	$CrCl_2O$−ketene η^2 (C=O) (cm^{-1})	$CrCl_2O$−phenol (cm^{-1})	$CrCl_2O$−phenyl (cm^{-1})
383	427	415	416	424	480
414	432	421	427	475	648
486	472	673	494	487	669
557	482	698	525	529	721
800	492	849	759	570	977
809	565	919	905	679	1000
865	661	948	910	745	1036
905	691	965	938	797	1051
970	712	1009	1005	1014	1054
1074	759	1102	1091	1069	1071
1169	781	1301	1099	1098	1171
1273	787	1370	1252	1153	1306
1371	865	1593	1275	1173	1414
1399	956	2075	1299	1188	1544
1550	968	3039	1569	1328	3098
1583	984	3049	1609	1457	
1643	1297	3066	1737	1477	
3070	2916	3127	3030	1584	
	2951		3041	1602	
	3088		3050	3090	
	3094		3125	3577	

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p).

intensities of the product bands remained constant as the concentration of the initial reagents was varied. This implies a single reaction product, arising from an initial 1:1 cage pair.

Two different modes of photochemical reaction of $CrCl_2O_2$ with small molecules have been observed in recent matrix studies. The first involves HCl elimination from the initial cage pair, with (in this case) formation of $ClCr(O)_2C_6H_5$ ($CrClO_2$−phenyl), **4g**. These two would then form a weakly hydrogen bonded complex within the matrix.[12,22,23,30,32] The second involves oxygen atom transfer from $CrCl_2O_2$ to the reaction partner, followed by complexation between the oxidized product and the Cl_2CrO fragment.[26,27] The first possibility can be 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. This band did not shift when C_6D_6 was employed, demonstrating that the hydrogen arises from H_2O and not C_6D_6. No new HCl stretching modes were observed. Further, $ClCr(O)_2C_6H_5$ would not be expected to exhibit the spectrum that was observed experimentally. Thus, it is reasonable to conclude that HCl elimination and C_6H_5 addition to the chromium center does not occur.

The second reaction pathway involving O atom transfer to the substrate leads to the formation of Cl_2CrO complexed to oxidized product. Cl_2CrO has been observed by several research groups,[7,27,44] and has characteristic absorptions near 1014 and 450 cm^{-1}. The exact position of these absorptions varied slightly from system to system, due to complexation of Cl_2CrO to the oxidized product. In the present study, product bands were observed at 1014 and near 440 cm^{-1}, and are very reasonably assigned to Cl_2CrO. Further, these bands did not shift measurably with ^{13}C and D isotopic substitution, further supporting this assignment. Thus, the spectral evidence supports formation of Cl_2CrO, and oxygen atom transfer to C_6H_6. This conclusion also rules out the formation of the metallocycle $CrCl_2(O)(O)$−2,4-cyclohexadiene, **4f**, formed by the addition of both oxygens of Cl_2CrO_2 to two adjacent carbons in the ring, while retaining both Cr−O linkages (Figure 4f), as this cyclic structure would not be consistent with the formation of Cl_2CrO. In addition, while this structure was calculated to be a local energy minimum, this species was much higher in energy than several other possible structures, as shown in Figure 3. Further, the calculated spectrum for this product matched very poorly the experimentally observed spectrum.

Two modes of oxygen atom transfer have been observed in similar reaction systems, oxygen atom insertion to (in this case) a C−H bond to form phenol, C_6H_5OH, or addition to one of the C=C double bonds in the ring. This latter mode could lead to any one or several different structures including benzene oxide (epoxide formation), 2,4-cyclohexadienone (ketone formation with a hydrogen shift, keeping the six-membered ring intact), 2,5-cyclohexadienone (an isomer of the 2,4-compound), and butadienylketene (ketene formation accompanied by ring opening). Each of these five structures could then be complexed to the Cl_2CrO species by either η^1 or (in some cases) η^2 coordination, increasing the number of possibilities. Comparison of the theoretical spectra of each possible product to that observed experimentally combined with the isotopic labeling results is essential to reach a conclusion as to the structure that is formed.

Phenol is the best known and is calculated to be the most stable isomer of C_6H_6O. The known experimental spectrum of the pure material[45] and the theoretically calculated spectrum show a strong O−H stretch absorption at 3729 cm^{-1}. This band is calculated to shift slightly to 3577 cm^{-1} as a result of complexation to Cl_2CrO still with high intensity. However, no product bands were observed in this spectral region in any experiments. Along with this, the product bands that were observed do not match well those calculated for the C_6H_5OH−Cl_2CrO complex, **4c**, see Table 3. Thus, phenol can be eliminated as a possible product in the present photochemical reaction.

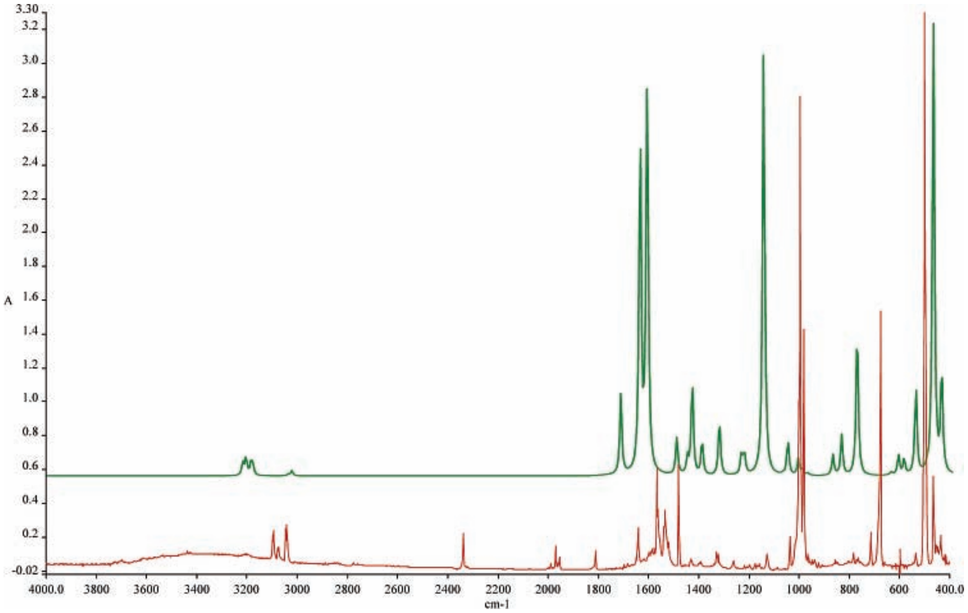

Figure 5. Bottom: Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/$CrCl_2O_2$ = 250 with a sample of Ar/C_6H_6 = 1000. Top: Calculated (unscaled) infrared spectrum of the 2.4-cyclohexadienone complex at the B3LYP/6-311G++(d,2p) level of theory.

Benzene oxide was calculated to be a high-energy isomer of C_6H_6O, as shown in Figure 3 and Table 2. More importantly, the calculated spectrum of the uncomplexed molecule has only a few very weak absorptions in the 1400−1700 cm^{-1} region, unlike in the experimental spectra where the absorptions in this region were very intense. Further, calculations have shown that the $CrCl_2O$−benzene oxide complex is unstable with respect to dissociation. All attempts to optimize the structure of this complex from different starting structures led to dissociation into parent $CrCl_2O_2$ and benzene. Thus, the $CrCl_2O$−benzene oxide complex can be ruled out as the observed product in this study.

Butadienylketene, a ketene formed through a ring-opening reaction, must be considered as well. In the experiments of Parker and Davis, ^{3}P oxygen atom addition to benzene was reported to lead to the formation of 2,4-cyclohexadienone, which was photolytically converted to butadienylketene. Ketenes are generally characterized by an intense absorption near 2100 cm^{-1}, although this is likely to shift to lower energy upon complexation. Parker and Davis observed the absorption of the ketene near 2125 cm^{-1}, while in the present study this band was calculated at 2128 cm^{-1}. The calculations found stable minima for the η^1 complex, **4d**, and the η^2 (C=O) complex, **4e**, while the η^2 (C=C) complex would not optimize. Upon complexation with $CrCl_2O$ the absorption was calculated to shift to 2075 cm^{-1} for η^1 and 1737 cm^{-1} for the η^2 (C=O) complex (listed in Table 3). These calculated infrared spectra for both structures were compared to the experimental spectrum, and the match was quite poor, thus these structures can be ruled out. This is consistent with the relatively high energies of the two complexes, 34.8 and 43.0 kcal/mol higher in energy respectively than the two reactants. While this energy is in principle available from the absorbed photon, stabilization of these complexes is less likely.

The final two likely structures are the 2,4- and 2,5-cyclohexadienone complexes of Cl_2CrO. Formation of the 2,4 isomer arises from migration of the hydrogen at the carbon atom that is being oxidized (the ketone) to an adjacent carbon atom, while formation of the 2,5 isomer requires migration of this hydrogen across the ring to the opposite carbon atom (in the 4 position). This latter migration appears to be less likely. The 2,4 isomer was reported by Parker and Davis in their matrix study of the irradiation of ozone in the presence of benzene. They also reported that 2,4-cyclohexadienone was photochemically unstable and ultimately converted to butadienylketene. The 2,4- and 2,5-cyclohexadienone complexes of Cl_2CrO were calculated to be very close in energy to one another. While the η^1 and η^2 (C=O) complexes are possible, in both cases the η^2 (C=O) complexes spontaneously rearranged into the analogous η^1 complexes, indicating that the η^1 complexes are lower in energy and there is no energy barrier separating the two complexes. Overall, while the oxygen transfer reaction to form the separated 2,4- (and 2,5-) cyclohexadienone and Cl_2CrO species was calculated to be endothermic, ΔE°_{298} to form the complex was found to be slightly exothermic (−3.1 kcal/mol for the 2,4 isomer), as a result of the energy of complexation of −29.1 k cal/mol. Computationally, 2,4-cyclohexadienone was found to be substantially more stable than butadienylketene, as shown in Table 2 and Figure 3.

Comparison of the calculated spectra for the 2,4- and 2,5-cyclohexadienone complexes, **4a** and **4b**, of Cl_2CrO with the experimental spectrum shows that the 2,4-isomer complex is a very good match, while the 2,5-isomer complex is a lesser match. Figure 5 compares a twin jet experimental spectrum after irradiation to an *unscaled* calculated spectrum. This is supported by the isotopic shift data as well. For example, a C=C stretch of the 2,4-isomer complex was calculated at 1634 cm^{-1} with a calculated deuterium shift of −46 cm^{-1} and a calculated ^{13}C shift of −56 cm^{-1}. The corresponding experimental band occurred at 1643 cm^{-1}, with an observed deuterium shift of −40 cm^{-1} and a ^{13}C shift of −54 cm^{-1}. In a similar vein, an out-of-plane hydrogen bending mode was calculated at 711 cm^{-1}, with isotopic shifts of −145 and −8 cm^{-1} for ^{2}H and ^{13}C, respectively. The corresponding experimental band was observed at 716 cm^{-1}, with isotopic shifts of −153 and −7 cm^{-1}, respectively. With some allowance for anharmonicity in the hydrogenic stretching vibrations, the agreement between the calculated spectrum of the 2,4-cyclohexadienone complex with Cl_2CrO was excellent throughout, as can be seen in Table 1 and Figure 5. *Thus, the product formed in the photochemical reaction of Cl_2CrO_2 with C_6H_6 in argon matrices is identified as the 2,4-cyclohexadienone−Cl_2CrO complex.*

TABLE 4: Calculated[a] Bands of 2,4-Cyclohexadienone and $CrCl_2O-$2,4-Cyclohexadienone

2,4-cyclohexadienone (cm^{-1})	calcd intensity (km/mol)	$CrCl_2O-$2,4-cyclohexadienone (cm^{-1})	calcd intensity (km/mol)
431	0.1	412	184.5
443	8.4	439	0.6
480	12.7	481	35.7
522	9.1	527	6.3
563	1.2	549	8.2
702	63.6	578	1.2
723	8.7	711	62.6
787	4.9	771	16.5
913	1.1	805	8.4
918	5.2	904	0.9
927	2.6	924	2.5
969	14.1	940	6.8
973	1.0	979	0.5
992	0.2	981	13.5
1127	16.2	1002	0.4
1158	5.4	1076	174.4
1160	4.4	1151	8.8
1211	19.5	1161	1.9
1297	8.8	1163	6.3
1359	16.7	1249	23.1
1368	18.8	1316	14.4
1403	6.4	1355	38.6
1555	33.0	1373	6.8
1636	22.4	1415	15.4
1675	328.2	1531	168.7
2922	1.5	1559	142.8
2938	0.9	1634	32.8
3056	2.1	2919	2.1
3061	11.1	2933	0.6
3086	16.9	3071	3.8
3093	4.9	3078	4.9
		3098	7.1
		3110	5.3

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p).

Infrared band assignments for the complex are relatively straightforward, particularly with the aid of calculated and experimental isotopic shifts, and are given in Table 1. Relatively few modes are strongly affected by the complexation of the Cl_2CrO subunit. As expected, the C=O stretch is one of these, shifting nearly 120 cm^{-1} to lower energy in the complex relative to the free molecule, to 1559 cm^{-1}. This large shift is consistent with the strong (−29.1 kcal/mol) interaction between the subunits and the C=O bond as the site of coordination. Table 4 compares the more intense ($I > 6.0$ km/mol) calculated bands of the 2,4-cyclohexadienone$-Cl_2CrO$ complex to those calculated for 2,4-cyclohexadienone.

Merged jet experiments were also carried out to provide the reagents with more time to react before deposition onto the cold window. Even so, no reaction products were detected in the merged jet experiments, with heating of the reaction zone to as high as 150 °C. Past studies in this lab have shown that ample collisions occur in the merged jet region for reaction to occur. Reactions studied in this manner include HCl elimination[12,32] and oxygen atom transfer[26] from the transition metal compound. While, as outlined above, a number of products are possible in this system, the calculations demonstrate that most of the potential reactions are strongly endothermic and are not likely to occur thermally in the temperature range that was used. Two reactions were calculated to be exothermic, the reaction to form the 2,4-cyclohexadienone$-Cl_2CrO$ complex, which was just slightly exothermic, and the reaction to form phenol (free or complexed). These two reactions did not occur in the merged jet experiments, suggesting that the activation barriers to these reactions are sufficiently high to prevent reaction from occurring. In contrast, in the twin jet experiments the absorbed photon has an energy ≥50 kcal/mol (taking the onset wavelength to be about 580 nm), clearly sufficient energy for the cage-paired reactants to form the 2,4-cyclohexadienone$-Cl_2CrO$ complex but *not* the $C_6H_5OH-Cl_2CrO$ complex.

A recent visible/UV spectroscopic study[46] 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 photochemical reaction. Visible/UV spectra recorded in the present study did not show any new electronic absorptions which is consistent with the lack of observation of a molecular complex in the infrared *upon initial matrix deposition*. This is also consistent with one room temperature study of the visible/UV spectra of $CrCl_2O_2/C_6H_6$ mixtures in CCl_4, where only very weak interactions were observed.[46] Nonetheless, photochemical reaction was observed, suggesting some electronic interaction between the cage-paired partners. However, this electronic interaction is sufficiently weak to escape spectroscopic detection. The photochemical product, the 2,4-cyclohexadienone$-Cl_2CrO$ complex, should have electronic transitions as well. However, none were observed. The dienone would be expected to absorb near or below 250 nm. This region is superimposed on a strong scattering background (2−3 OD) from the matrix itself, and has remaining absorption from parent C_6H_6, which is present in excess. These factors combine to prevent observation of the anticipated absorption.

While C_6H_6 reacted photochemically with $CrCl_2O_2$ to form the 2,4-cyclohexadienone$-Cl_2CrO$ complex, no infrared product bands were formed as a result of the irradiation of the $OVCl_3$ and C_6H_6 in an argon matrix. Calculations carried out on the η^1 coordination mode of the VCl_3-2,4-cyclohexadienone complex provide an explanation. The energy of oxygen atom transfer from $OVCl_3$ to benzene to form separated 2,4-cyclohexadienone and VCl_3 was computed to be 61.4 kcal/mol. The complexation energy was calculated to be −27.2 kcal/mol, for a net endothermicity for the formation of the VCl_3-2,4-cyclohexadienone complex of 34.2 kcal/mol. While a visible photon contains more energy than this, any additional activation barrier to the rearrangement process (such as for the required hydrogen shift) will keep the reaction from occurring.

One question that remains arises from a comparison of the present work that the earlier work of Parker and Davis. They reported that continued irradiation of 2,4-cyclohexadienone converted this species into butadienylketene. In an attempt to repeat this, irradiation times of up to 5 h were used. No decrease in the intensity of the bands of the 2,4-cyclohexadienone$-Cl_2CrO$ complex was observed and no new bands appeared. The difference in these two results may lie in the stabilization provided by the complexation of the 2,4-cyclohexadienone to Cl_2CrO. In the Parker and Davis study, the 2,4-cyclohexadienone was formed uncomplexed or at most very weakly interacting with O_2. It should also be noted that the calculations demonstrate that 2,4-cyclohexadienone is substantially more stable than butadienylketene, so that formation of butadienylketene in their study is a metastable process. However, once the ring has opened (to form butadienylketene) relaxation back to the more stable 2,4-cyclohexadienone is probably sterically not feasible.

Conclusions

Irradiation of matrices containing $CrCl_2O_2$ and C_6H_6 led to transfer of an oxygen atom and formation of the $CrCl_2O-$2,4-

cyclohexadienone complex. This conclusion was supported by isotopic labeling (^{13}C and ^{2}H) and by B3LYP/6-311G++(d,2p) density functional calculations. The most stable C_6H_6O isomer, phenol, was not observed in these experiments, presumably as a consequence of a high activation barrier. Also, the $OVCl_3 + C_6H_6$ system yielded no photochemical products, in agreement with theoretical predictions.

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