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Matrix isolation investigation of the photochemical reaction of activator-substituted benzenes with $CrCl_2O_2$

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Abstract

The matrix isolation technique, combined with infrared spectroscopy and theoretical calculations, has been used to characterize the products of the photochemical reactions of aniline, anisole, and *N*,*N*-dimethylaniline with $CrCl_2O_2$. While initial twin jet deposition of the reagents did not lead to product formation, new bands were noted following irradiation with light of $\lambda > 300$ nm. In the reactions of $CrCl_2O_2$ and aniline, irradiation led to HCl formation, very likely accompanied by $CrClO_2(H)NC_6H_5$ formation, and a mixture of isomers of $CrCl_2O$-aminocyclohexa-2,4-dienone via oxygen atom transfer. $CrCl_2O_2$ and aniline were also codeposited as cryogenic thin films, producing new bands. Irradiation of these films led to further growth of these bands. The same products were identified in the thin film studies as were observed in the argon matrix experiments. The irradiation of the matrices containing $CrCl_2O_2$ and anisole and *N*,*N*-dimethylaniline were shown to lead to oxygen atom transfer, forming complexes between the corresponding cyclic ketone derivatives and $CrCl_2O$. The identification of the complexes were supported by density functional calculations at the B3LYP/6-311G++(d,2p) level and isotopic labeling (in the case of aniline).

Keywords: Matrix isolation; Infrared spectroscopy; Theoretical calculations; Reaction intermediates

1. Introduction

The oxidation of organic substrates with metal oxo compounds, including $CrCl_2O_2$, is of continuing interest to a range of chemists. Of particular interest is the selectivity of the oxidation of organic compounds and the specificity of the product(s) formed. $CrCl_2O_2$ has been shown to be a versatile oxidant, but the mechanism is complex and not well understood, so its mechanism has been the object of many studies throughout the years [1–7]. While theses studies represent a significant advance in the in the overall understanding of these reactions, the work was limited to product studies and did not identify the initial intermediates in these reactions.

Aniline is a toxic chemical that is often present in dyes, rubber production, and agrochemical wastewater [8,9]. Aniline is considered to be a probable human carcinogen and a concentration as low as 600 μg/L in water sources is referred as having high probability of developing cancer upon water ingestion [10]. Catalytic wet air oxidation (CWAO) is one of the available treatment technologies, which consists in the total oxidation of the organic species present in the effluent to CO_2, N_2, and H_2O at moderate temperature and pressure. Transition metals have been packed in modified molecular sieves to be used as catalysts in the oxidation of various organic compounds [11–13]. Recently, chromium, vanadium, and copper have been tested using CWOA to break down aniline [11].

The matrix isolation technique was developed to facilitate the isolation and spectroscopic characterization of reactive intermediates [14–16] 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 $CrCl_2O_2$, $OVCl_3$, and OVF_3 with organic

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and inorganic substrates [17–31]. Recent studies in this laboratory [32–34] have examined the reactions of $CrCl_2O_2$ with benzene, methyl-substituted benzenes, and benzenes substituted with electron withdrawing groups. In the first system, light of $\lambda > 590$ nm led to reaction and oxygen atom transfer, forming a complex between 2,4-cyclohexadienone and $CrCl_2O$. In the second series of reactions, irradiation led to reaction and oxygen atom transfer, forming complexes between methylcyclohexadienone derivatives and $CrCl_2O$. With the xylene isomers and mesitylene, di- and trimethylphenols, complexed to $CrCl_2O$, were also observed, respectively. This was the first observation of C—H bond activation and oxygen atom insertion into a C—H bond from $CrCl_2O_2$. In the third series of reactions, irradiation led to reaction and oxygen atom transfer, forming complexes between the corresponding cyclic ketone derivatives and $CrCl_2O$. With benzonitrile, cyanophenol complexed to $CrCl_2O$ was also observed. The present study examines the photochemical reactions of $CrCl_2O_2$ with aniline, anisole, and *N*,*N*-dimethylaniline to further explore the nature of the oxidation reaction and the effects of electron-donating, i.e., activator, substituents on the product distribution.

2. Experimental

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described [35]. Chromyl chloride, $CrCl_2O_2$, (Acros), was introduced into the vacuum system as the vapor above the room temperature liquid, after purification by freeze-pump-thaw cycles at 77 K. Anisole (Acros) was introduced in a similar manner into a separate vacuum manifold and was purified by repeated freeze-pump-thaw cycles at 77 K. Aniline (Acros), aniline-d_7 (99% D, Acros), and *N*,*N*-dimethylaniline (Acros) were introduced into the vacuum system by placing 1 mL of the neat liquid in a small stainless steel sidearm connected to the deposition line through a needle valve to an UltraTorr tee. The needle valve was opened slightly, allowing a fraction of the vapor pressure of the samples at room temperature to be entrained in flowing argon, carried to the cold window, and deposited. Argon (Wright Brothers) was used as the matrix gas without further purification.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the two gas samples were deposited from separate nozzles onto the 14 K window, allowing for only a brief mixing time prior to matrix deposition. In addition, all of these matrices were subsequently 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 [36], in which the two deposition lines were joined with an UltraTorr tee at a distance from the cryogenic surface, and the flowing gas samples were permitted to mix and react during passage through the merged region. This region was varied, ranging from 32 to 100 cm in length and heated to temperatures as high as 100 °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.

Cryogenic thin films of $CrCl_2O_2$ + aniline and $CrCl_2O_2$ + aniline-d_7 were prepared by spraying the pure reagent gases onto the cold window without adding argon for approximately 6.5 h. Variation of the gas flow rates permitted differing mole ratios of reagents in the thin film. The thin films were warmed slowly to 160 K or higher with spectra recorded at several temperatures during the warm-up process, or irradiated for 0.5–5.0 h with the H_2O/Pyrex-filtered output of a 200 W medium-pressure Hg arc lamp, after which additional spectra were recorded. Final spectra were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using Gaussian 03W suite of programs [37]. Density functional calculations using the hybrid B3LYP functional were used to locate energy minima, determine structures, and calculate vibrational spectra. Final calculations with full geometry optimization employed the 6-311G++(d,2p) basis set, after initial calculations with smaller basis sets were run to approximately locate energy minima. Thermodynamic functions for the reactants and potential intermediates were also calculated at this level of theory.

3. Experimental results

Prior to any codeposition experiments, blank experiments were run on each of the reagents used in this study. Blank experiments were also run on $CrCl_2O_2$ and aniline independently as thin films at 14 K. In each case, the blanks were in good agreement with literature spectra [38–41], 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 the Ar/$CrCl_2O_2$ blank, where the growth of very weak bands due to photochemical reaction with impurity H_2O was seen [20]. Weak bands due to HCl impurity were noted at 2883 and 2863 cm^{-1} in all of the experiments involving $CrCl_2O_2$.

3.1. $CrCl_2O_2$ + aniline

In an initial twin jet experiment, a sample of Ar/$CrCl_2O_2$ = 500 was codeposited with a sample of Ar/aniline. After 23.0 h of deposition, no new bands were detected. The matrix was irradiated for 6 h with the filtered ($\lambda > 300$ nm) output of a medium-pressure Hg arc lamp, which led to the observation of many new, product bands, as listed in Tables 1 and 2. The more intense product bands were seen at 2704, 2658, 1580, 1528, 1213, 1164, 1014, 673, and 443 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Fig. 1 shows a representa-

Table 1
Calculated (B3LYP/6-311G++(d,2p)) and observed frequencies[b] and isotropic shifts for $CrClO_2(H)NC_6H_5$ (structure 8e) via twin jet deposition

Normal isotope		^2H		Assignment
Calcd. freq.[a]	Exp. freq.	Calcd. shift	Exp. shift	
442	443	−5	−2	Cr—Cl st.
492		−76		
542	543	−19		Ring st.
605		−25		
644	639	−103		N—H wag
668	673	−161		C—H wag
701		−52		
754	768			C—H wag
	779			
809	816			C—H wag
861	858	−106		Ring st.
894		−259		
956	923	−179	−153	C—H wag
976	975	−166		C—H wag
981	991	−40	−38	Ring st.
1015		−183		
1036		−2		
1053	1014	1	0	Cr—O st.
1077	1096	−260		C—H rock; N—H rock
1149		−316		
1166	1164	−307		C—H rock; ring st.
1206	1214	−238	−238	C—H rock; N—H rock; ring st.
	1224			
1258	1257	−60	−56	C—H rock; N—H rock; ring st.
1317		−25		
1353		−291		
1458		−122	0	
1470	1489	−115	−135	C—H rock; ring st.
1563	1528	−42	2	N—H rock; ring st.
1578	1580	−38	−22	Ring st.
2658				HCl
2704			−771	HCl
3065		−803		
3078		−806		
3088		−804		
3099		−804		
3110		−806		
3423		−920		

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

tive region of this spectrum in the difference mode (after–before irradiation).

The above experiment was repeated numerous times using different absolute and relative concentrations of $CrCl_2O_2$ and aniline in argon. The same product bands were observed after irradiation throughout, with relative intensities that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments.

The reaction of this pair of reactants was studied in a number of merged jet experiments, using a 32 and 100 cm merged or reaction region, held at both room temperature and 100 °C. In all of these experiments, the parent bands were either reduced in intensity or absent (compared to the twin jet experiments run at the same sample concentrations), indicating that reaction was occurring. However, no new bands were observed in the spectrum, other than an increase of the intensity of the HCl bands at 2883 and 2863 cm^{-1}.

Table 2
Product band positions arising from the irradiation of matrices containing $CrCl_2O_2$ and aniline and the calculated[a] bands of a representative $CrCl_2O$-aminocyclohexa-2,4-dienone complex

$CrCl_2O_2$ + aniline (exp. freq.[b])	$CrCl_2O$-Aminocyclohexa-2,4-dienone (calcd. freq.)	Calcd. intensity (km/mol)	Assignment
443	407	191.3	Cr—Cl st.
	443	2.8	
	489	6.0	
	517	49.9	
	524	0.1	
543	560	22.9	Ring st.
639			
673			
	583	3.1	
	739	14.7	
768	767	60.9	C—H wag
779			
816	831	0.3	C—H wag
858	877	3.4	Ring st.
	895	5.6	
923	908	3.3	Ring st.
975	986	0.1	C—H wag
991	996	6.3	NH_2 rock; ring st.
1014	1071	78.8	Cr—O st.
1096	1080	113.5	C—H rock; NH_2 rock; ring st.
1164	1153	111.6	C—H rock
	1181	0.6	
1214			
1224			
	1250	6.9	
1257	1257	261.1	Ring st.
	1337	65.4	
	1373	27.8	
	1393	28.1	
	1409	94.5	
1489	1490	1125.6	C=C st.
1528	1548	78.9	
1575			
1580			
1585	1598	119.8	NH_2 scissor; ring st.
1595	1627	306.4	NH_2 scissor; ring st.
2658			HCl
2704			HCl
	2935	3.0	
	2962	0.2	
	3067	10.5	
	3084	10.4	
	3118	4.0	
	3496	159.9	
	3610	46.3	

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p).
[b] Frequencies in cm^{-1}.

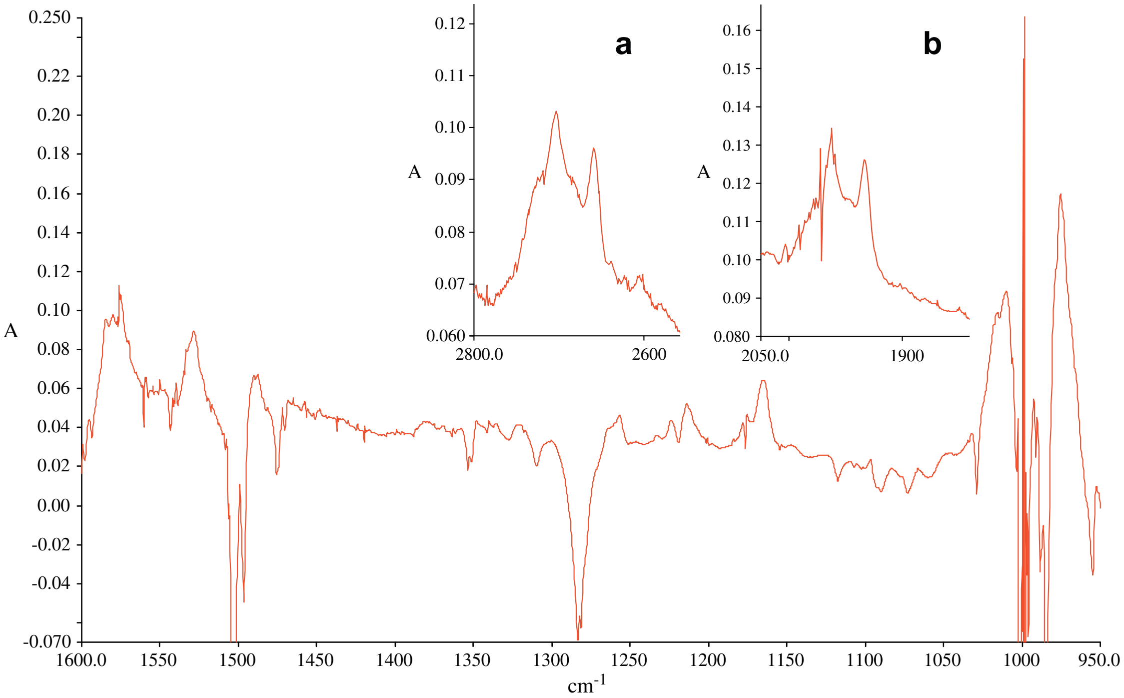

Fig. 1. Infrared difference spectrum before and after 6 h irradiation of a matrix formed by the twin jet deposition of a sample of $Ar/CrCl_2O_2 = 500$ with a sample of Ar/aniline. The upper regions are of the (a) H—Cl stretch and the (b) D—Cl stretch. The negative bands are due to loss of intensity in the parent absorptions after irradiation.

Cryogenic thin films of each pair of reagents were formed by the deposition of the pure vapor of each reagent onto the 14 K cold surface. Product bands were observed after deposition of the pure reagent gases onto the 14 K window as seen in Table 3. After 30 min of irradiation with the Hg arc lamp, these bands grew in intensity along with the appearance of three weak bands at 1546, 1188, and 1167 cm^{-1}. These product bands were similar to, but broader than, the product bands for the system in solid argon. Fig. 2 shows blank spectra of the two reagents each alone as a thin film, and Fig. 3 shows a representative region of the thin film of $CrCl_2O_2$ and aniline.

3.2. $CrCl_2O_2$ + aniline-d_7

Multiple twin jet experiments were conducted in which samples of $Ar/CrCl_2O_2$ were codeposited with samples of Ar/aniline-d_7. After 21.0 h of deposition, the matrix was irradiated for 6.0 h. This irradiation produced many weak new bands (see Table 1), with the more intense bands at 1933, 1558, 1544, 1529, 1393, 1201, 1009, 922, and 441 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Fig. 1 shows the D—Cl stretching region for this spectrum.

3.3. $CrCl_2O_2$ + anisole

In an initial twin jet experiment, a sample of $Ar/CrCl_2O_2 = 500$ was codeposited with a sample of Ar/anisole = 400. After 23.0 h of deposition, no new bands were detected. The matrix was irradiated for 24.5 h with the filtered ($\lambda > 300$ nm) output of a medium-pressure Hg arc lamp, which led to the observation of many weak new product bands, as listed in Table 4. The more intense bands were seen at 1568, 1548, 1431, 1279, 1241, 1204, 1017, 820, 708, and 440 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Fig. 4 shows a representative region of this spectrum.

Numerous additional twin jet experiments were conducted, at sample concentrations ranging from $Ar/CrCl_2O_2 = 250$ to $Ar/CrCl_2O_2 = 500$ and Ar/anisole = 300 to Ar/anisole = 400. The same product bands were observed after irradiation 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.

A series of merged jet experiments was conducted with samples of $Ar/CrCl_2O_2 = 500$ and Ar/anisole = 300. With the merged region held at room temperature, the resulting spectrum was identical to that observed in the twin jet experiments with no new product bands. In a subsequent experiment, with the merged region heated to 100 °C, no new product bands were observed.

3.4. $CrCl_2O_2$ + N,N-dimethylaniline

In an initial twin jet experiment, a sample of $Ar/CrCl_2O_2 = 500$ was codeposited with a sample of Ar/*N*,*N*-dimethylaniline. After 23.0 h of deposition, no new bands were detected. The matrix was irradiated for 25.0 h

Table 3
Product band positions arising from the irradiation of thin films of $CrCl_2O_2$ and aniline and the calculated[a] bands of $CrClO_2(H)NC_6H_5$ and a representative $CrCl_2O$-aminocyclohexa-2,4-dienone complex

$CrCl_2O_2$ + aniline (exp. freq.[b])	$CrClO_2(H)NC_6H_5$ (calcd. freq.)	Calcd. intensity (km/mol)	$CrCl_2O$-Aminocyclohexa-2,4-dienone (calcd. freq.)	Calcd. intensity (km/mol)
422	442	136.0	417	174.9
	492	17.2	483	32.2
	542	7.5	499	4.1
	605	0.1	506	11.3
637	644	22.8	518	9.3
	668	29.9	581	38.0
	701	19.7	626	17.6
788	754	59.1	717	2.7
	809	1.8	754	9.1
855	861	10.3	813	39.9
	894	2.0	877	2.5
	956	0.4	895	0.9
	976	0.3	922	4.5
	981	2.0	971	5.6
	1015	2.5	974	1.4
929	1036	144.5	1045	4.4
954	1053	171.3	1072	183.5
	1077	13.1	1160	58.2
	1149	0.1	1172	6.6
1167	1166	6.8	1247	157.9
1188	1206	14.8	1293	67.8
	1258	2.6	1332	2.0
	1317	1.5	1355	54.1
1378	1353	13.1	1385	9.9
1431	1458	11.8	1440	70.8
1469	1470	4.2	1513	1144.9
1493	1563	3.7	1529	42.7
1546	1578	14.8	1619	93.0
1572				
1673			1649	361.5
2610				
2658				
2704				HCl
	3065	3.2	2909	16.3
	3078	0.2	2937	2.2
	3088	10.2	3067	4.2
	3099	10.8	3087	5.5
	3110	2.5	3089	3.7
	3423	55.1	3497	168.7
			3612	53.9

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

[b] Frequencies in cm^{-1}.

with the filtered ($\lambda > 300$ nm) output of a medium-pressure Hg arc lamp, which led to the observation of many weak new product bands, as listed in Table 5. The more intense bands were seen at 1655, 1569, 1500, 1462, 1050, 1006, 974, 936, 775, and 450 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Fig. 5 shows a representative region of this spectrum.

The above experiment was repeated numerous times using different absolute and relative concentrations of $CrCl_2O_2$ and *N*,*N*-dimethylaniline in argon. The same product bands were observed after irradiation throughout, with relative intensities that appeared to be consistent. Band intensities were also consistent with the concentrations employed over all of the experiments.

A series of merged jet experiments was conducted with samples of $Ar/CrCl_2O_2 = 500$ and Ar/*N*,*N*-dimethylaniline. With the merged region held at room temperature, the resulting spectrum was identical to that observed in the twin jet experiments with no new product bands. In a subsequent experiment, with the merged region heated to 100 °C, again no new product bands were observed.

4. Results of calculations

The structures, energetics, and vibrational spectra of a number of possible products of the multiple systems were calculated using the B3LYP hybrid functional and basis sets as high as 6-311G++(d,2p). Since experimental evidence for oxygen atom transfer was observed (see below), calculations focused on possible products and isomers of oxygen atom transfer to form cyclic diene ketones, as determined from previous studies, complexed to the remaining

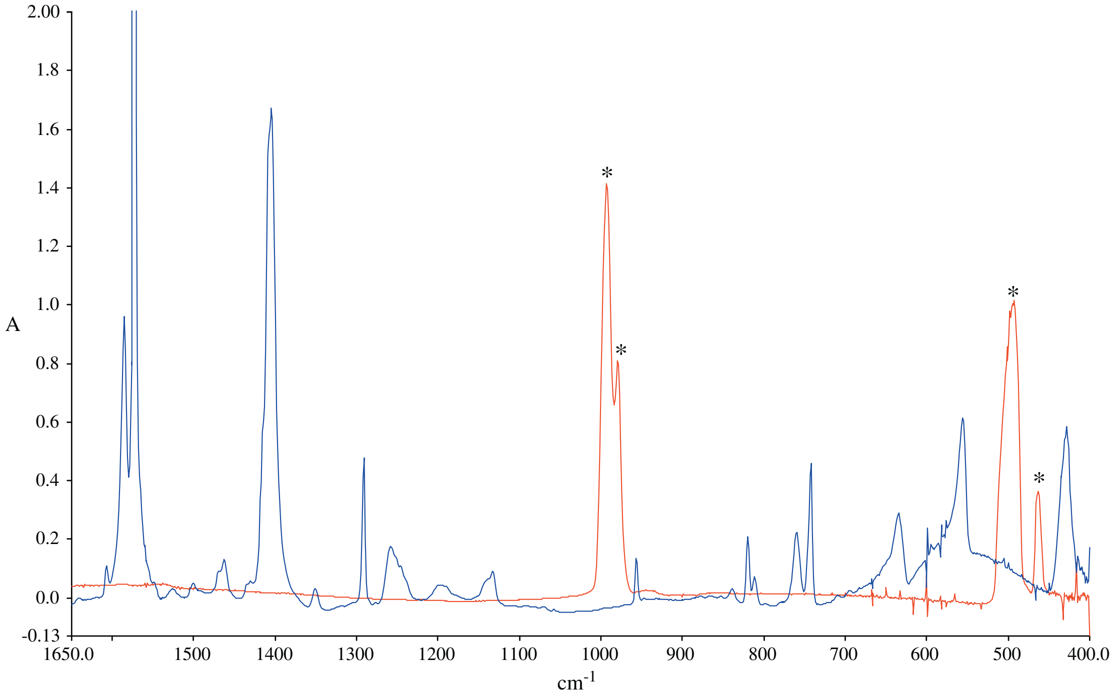

Fig. 2. Infrared spectra of thin films of each blank of $CrCl_2O_2$ and aniline-d_7. $CrCl_2O_2$ blank bands are marked with (∗).

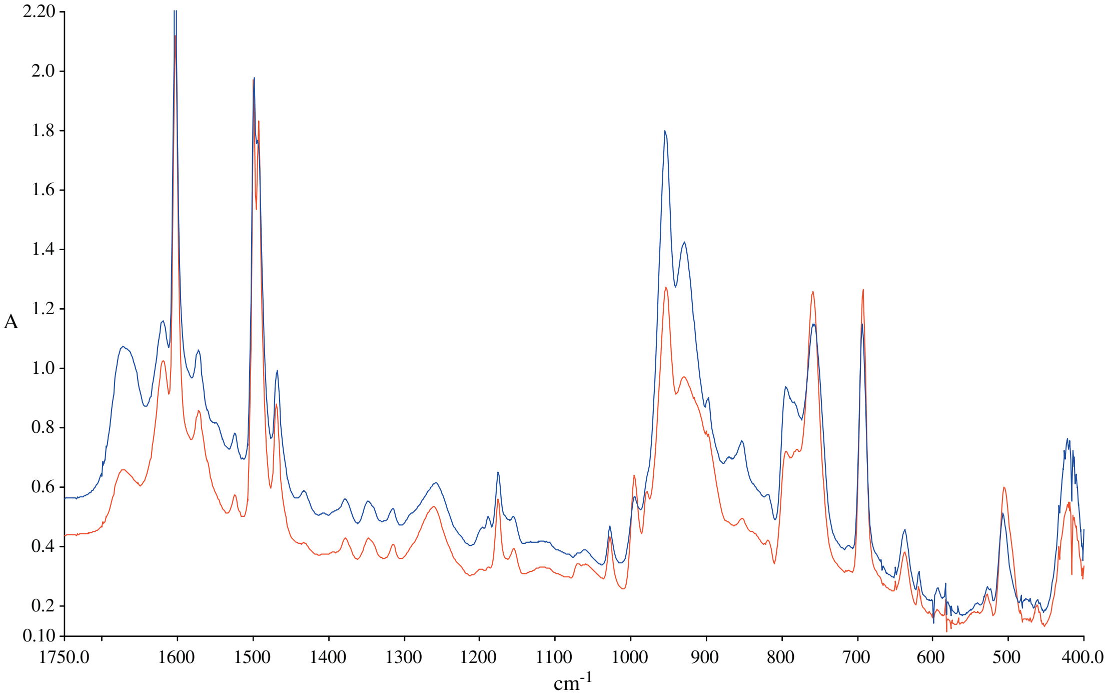

Fig. 3. Infrared spectra of a thin film by the twin jet deposition of $CrCl_2O_2$ with aniline. The lower trace is before irradiation, while the upper trace is after 30.0 min of irradiation with light of $\lambda > 300$ nm.

metal species, $CrCl_2O$ which is trapped within the same matrix cage. In addition, phenols formed through the insertion of an O atom into a C—H bond were considered, each complexed to $CrCl_2O$, plus the product of HCl elimination from the initial cage pair of $CrCl_2O_2$ + aniline. The possibility of ketene formation through ring opening was considered briefly. Similar to systems studied previous, this alternative is calculated to be much less favorably energetically, and the calculated spectra of the possible product ketenes do not correspond at all to the experimental spectra. Consequently, the structures and energetics of all of the possible ketene isomers were not calculated. Fig. 6 shows

Table 4
Product band positions arising from the irradiation of matrices containing $CrCl_2O_2$ and anisole and the calculated[a] bands of a representative $CrCl_2O$-methoxycyclohexa-2,4-dienone complex

$CrCl_2O_2$ + anisole (exp. freq.)[b]	$CrCl_2O$-Methoxycyclohexa-2,4-dienone (calcd. freq.)	Calcd. intensity (km/mol)	Assignment
440	415	181.8	Cr—Cl st.
454	434	3.1	Ring st.
	475	12.3	
	487	2.7	
	532	2.8	
	590	3.4	
	611	5.9	
708	741	37.8	Ring st.
750	761	14.6	C—H wag
845	780	17.7	Ring st.
820	814	38.7	C—H wag
901	894	1.4	C—H wag
	930	4.5	
	981	0.1	
	1011	59.4	
1032	1028	8.4	C—H rock; ring st.
1017	1074	155.2	Cr—O st.
	1136	5.5	
1148	1138	1.0	CH_3 twist
	1167	31.7	
	1168	0.5	
1204	1216	188.6	C—O st.; ring st.
1241	1245	29.5	C—H rock; ring st.
1279	1303	33.8	C—H rock; CH_2 wag; ring st.
	1328	9.4	
1354	1355	23.1	CH_2 scissor
1396	1410	58.7	C—H rock; ring st.; CH_3 wag
1417			
1431	1440	2.6	C—H rock; ring st.; CH_3 wag
1453	1452	11.3	CH_3 twist
1467	1463	19.8	CH_3 scissor
1548	1537	373.0	C=C st.; C=O st.
1568	1560	4.4	C=C st.; C=O st.
1587			
1641	1639	56.2	C=C st.
	2909	4.1	
	2916	0.1	
	2921	32.8	
	2978	27.8	
	3050	16.1	
	3085	1.9	
	3108	1	
	3109	4.9	

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p).
[b] Frequencies in cm^{-1}.

the energies of the calculated likely structures (products) relative to $CrCl_2O_2$ + aniline; the energies are also listed in Table 6. Fig. 7 shows the calculated structures of five possible representative complexes arising from the reaction of $CrCl_2O_2$ with aniline (a cyclohexadienone, a phenol, two ketenes, and HCl elimination). The Supporting Information shows graphic representations of all of these calculated structures (structures S1a-i and S2a-j) as well as tables listing the calculated energies relative to $CrCl_2O_2$ + the activator-substituted benzenes. All of the structures, except the HCl elimination product, correspond to a single oxygen transfer from the chromyl chloride to an activator-substituted benzene. All of the proposed complexes optimized to energy minima on their respective potential energy surfaces, with all positive vibrational frequencies.

5. Discussion

No distinct product bands were observed upon initial codeposition of any of the activator-substituted benzenes with $CrCl_2O_2$ into argon matrices. However, in each case subsequent irradiation of these matrices led to the formation of clear product bands. These results are quite similar to the previous systems studied in this laboratory [22,31–34]. For a photochemical reaction to occur, the reactants must be trapped in the same matrix cage. It is likely that there are cage pairs formed from the statistical distribution of components of the system during the matrix condensation process. 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 an activator-substituted benzene. This conclusion is reasonable because of the low concentrations employed in these studies, on the order of 1:1:1000, which makes dimer or aggregate formation unlikely, and the approximate 1:1 stoichiometry of the reactants. In addition, the relative intensities of the product bands remained constant as the concentration of the initial reagents was varied. This suggests that either a single reaction product arises from the initial 1:1 cage pair, or that more than one product is formed but the ratio of products is constant.

There are two probable modes of photochemical reaction between $CrCl_2O_2$ and an organic substrate: (1) HCl elimination from the initial cage pair and (2) oxygen atom transfer from $CrCl_2O_2$ to the organic substrate, yielding an oxidized product and $CrCl_2O$. In HCl elimination, the HCl that is produced is trapped within the matrix cage with the second photoproduct. The spectrum will be that of HCl molecule weakly hydrogen bonded to the second photoproduct, with bands appearing between 2650 and 2800 cm^{-1}, shifted from isolated monomeric HCl which absorbs at 2863 and 2888 cm^{-1} in solid argon [42,43]. Such absorptions were noted for the aniline system studied here, but not for the anisole and dimethylaniline systems. For the second possible mode of reaction, $CrCl_2O$ has been observed by several research groups [24,44,45], 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 $CrCl_2O$ to the oxidized product. In the present study, product bands were observed near 1014 and 440 cm^{-1} for all three systems studied here, and are very reasonably assigned to $CrCl_2O$.

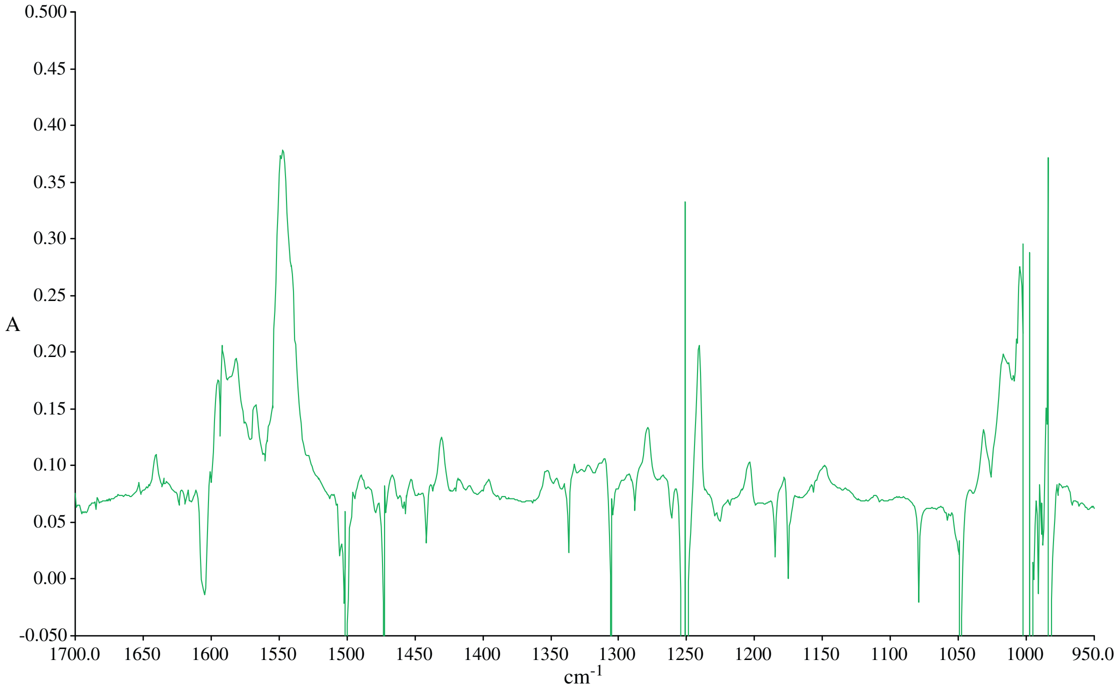

Fig. 4. Infrared difference spectrum before and after 25 h irradiation of a matrix formed by the twin jet deposition of a sample of $Ar/CrCl_2O_2 = 250$ with a sample of Ar/anisole = 400. The negative bands are due to loss of intensity in the parent absorptions after irradiation.

5.1. Aniline + $CrCl_2O_2$

After irradiation of matrices containing these two reactants, two new bands appeared at 2704 and 2658 cm^{-1}, indicative of HCl formation with hydrogen bonding to a second photoproduct. These new bands shifted to a broad band at 1933 cm^{-1} in experiments with aniline-d_7. This is precisely the isotopic dependence anticipated for HCl; the ν_H/ν_D ratio of 2704/1933 = 1.39 is almost identical to that observed for both gas phase [46] and matrix isolated [42,43] HCl, namely, 1.38. Given the isotopic behavior of these bands and the analogy to a number of well-established systems, the bands at 2704 and 2658 cm^{-1} are assigned to photoproduced HCl. Further, the HCl that is produced is trapped within the same matrix cage, and weakly hydrogen bonded to the species responsible for at least some of the photochemical bands. Based on previous studies [17,20,29], HCl would be formed from an amino hydrogen and a chlorine from $CrCl_2O_2$. Following these analogies, the HCl elimination product would be $CrClO_2(H)NC_6H_5$. This molecule should have a large number of vibrational modes and may well be responsible for a number of the product bands observed here. However, a second product (discussed in the following paragraph) is the $CrCl_2O$-aminocyclohexa-2,4-dienone complex (and isomers thereof). Structurally, these molecules are quite similar and will have many comparable vibrational modes, making assignment to one product versus the other nearly impossible. Table 1 compares the experimental bands for the $CrCl_2O_2$ + aniline system to those calculated for $CrClO_2(H)NC_6H_5$. As is apparent, there are numerous potential matches. Thus, based on these potential matches and the observation of hydrogen bonded HCl as a photoproduct, it is very likely that one of the products formed in the photochemical reactions of $CrCl_2O_2$ and aniline in argon matrices is the HCl elimination product, $CrClO_2(H)NC_6H_5$.

As noted above, the second mode of photochemical reaction of $CrCl_2O_2$ with an organic substrate is oxygen atom transfer from $CrCl_2O_2$ to the organic substrate, yielding an oxidized product and $CrCl_2O$. Since $CrCl_2O$ was clearly observed, this reaction pathway is also being followed. Based on calculated energetics and previous studies, the two classes of potential oxidation products are phenols (via insertion into a C—H bond) and cyclic dienones (via addition at one of the carbons). Each of these two classes has distinctive infrared signatures. Phenols are characterized by a distinct O—H stretch above 3400 cm^{-1}, and the cyclic dienones have strong absorptions from 1700 to 1500 cm^{-1} due to the C=O and C=C stretches (with the C=O group complexed to $CrCl_2O$ and shifted to lower energies relative to the isolated molecule). On this basis, phenols can be ruled out, as a band corresponding to the O—H stretch is completely absent. Rather, the spectral data strongly support formation of a cyclic dienone, consistent with the results from the previous studies of $CrCl_2O_2$ + benzene and benzene derivative reactions. There are five possible isomers for the cyclic dienone product, depending on the positions of the C=O and amino groups with respect to one another. Computationally, oxygen transfer reactions to form the separated isomer dienones and $CrCl_2O$ species were all calculated to be endothermic at the B3LYP/6-

Table 5
Product band positions arising from the irradiation of matrices containing $CrCl_2O_2$ and *N*,*N*-dimethylaniline and the calculated[a] bands of a representative $CrCl_2O$-(dimethylamino)cyclohexa-2,4-dienone complex

$CrCl_2O_2$ + *N*,*N*-dimethylaniline (exp. freq.)[b]	$CrCl_2O$-(Dimethylamino) cyclohexa-2,4-dienone(calcd. freq.)	Calcd. intensity (km/mol)	Assignment
450	415	179.8	Cr—Cl st.
	423	19.2	
477	498	2.4	Ring st.
	501	3.8	
	515	9.3	
	599	11.0	
	620	14.4	
696	693	19.5	Ring st.
775	779	18.0	Ring st.
816	788	1.4	C—H wag; CH_2 rock
834	828	21.4	C—H wag; CH_2 twist
	906	26.9	
	928	0.2	
936	932	1.9	Ring st.
974	985	0.9	C—H wag
	1007	18.7	
1050	1026	14.7	CH_3 wag
1006	1073	153.7	Cr—O st.
	1083	5.1	
1094	1094	42.6	Ring st.; CH_3 wag
	1142	1.5	
	1147	32.5	
1154	1164	1.7	CH_2 twist
	1184	19.2	
	1240	9.8	
	1275	13.4	
1293	1291	2.6	C—H rock; ring st.; CH_2 wag
	1316	16.9	
	1342	30.5	
1371			
	1404	0.1	
	1410	18.2	
1422	1428	0.3	CH_3 scissor
1436	1444	6.9	CH_3 scissor
	1456	28.3	
1462	1458	6.2	CH_3 scissor
	1474	7.0	
1500	1520	189.0	C=C st.; C=O st.
1569	1550	140.8	C=C st.; C=O st.
1655	1645	11.9	C=C st.
1710			
	2843	35.9	
	2848	115.6	
	2910	6.9	
	2918	0.1	
	2969	14.3	
	2971	47.3	
	3013	11.0	
	3015	28.4	
	3071	2.1	
	3090	1.4	
	3101	0.3	

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

[b] Frequencies in cm^{-1}.

311G++(d,2p) level of theory (see Fig. 6). However, when complexation energy of the dienone to the $CrCl_2O$ species was included, the ΔE_0^o's to form the products from $CrCl_2O_2$ and aniline were calculated to be exothermic, except for the $CrCl_2O$-6-aminocyclohexa-2,4-dienone complex, where ΔE_0^o was calculated to be +9.1 kcal/mol. As discussed above, definitive assignment of product bands (other than the C=O stretch of the cyclic carbonyl) versus the HCl elimination product is very difficult. Table 2 compares the experimental bands for the $CrCl_2O_2$ + aniline system to those calculated for one isomer of $CrCl_2O$-aminocyclohexa-2,4-dienone. Again, there are numerous potential matches, but no definitive assignments can be made since there are potential matches to the HCl elimination product as well. Thus, the products formed in the photochemical reaction of $CrCl_2O_2$ with aniline in solid argon matrices are identified as a mixture of isomers of $CrCl_2O$-aminocyclohexa-2,4-dienone complexes and very likely the HCl elimination product, $CrClO_2(H)NC_6H_5$.

Cryogenic thin film experiments were conducted to further study the reaction between $CrCl_2O_2$ + aniline. A band at 2610 cm^{-1} was observed, which increased in intensity after irradiation, and assigned to HCl hydrogen bonded to the species responsible for some of the photochemical bands. This is assignment is further supported by the shift of the DCl band to 1969 cm^{-1} upon using a deuterated sample of aniline. Thus, it is likely that $CrClO_2(H)NC_6H_5$ is formed in these thin film experiments. Additionally, there is evidence of carbonyl formation with a strong band at 1673 cm^{-1} indicating that one or more isomers of $CrCl_2O$-aminocyclohexa-2,4-dienone are formed. Given the increased breadth of the product bands in the thin film experiments, individual band assignment cannot be made to either product, except for the identification of HCl as a product, and the presence of a C=O group from $CrCl_2O$-aminocyclohexa-2,4-dienone. Table 3 compares the observed product bands to those calculated for both the HCl elimination product and the dienone product. Finally, it should be noted that the Cr=O and Cr—Cl stretches shifted more in the cryogenic thin films than in the argon matrices, consistent with the more strongly interacting environment in the thin film.

The thin films were gradually heated and spectra were recorded in 10 K intervals up to 160 K. The first noticeable change in the spectrum occurred at 40 K, and the same results were observed during the warming of the films as after the irradiation of the films. Slight growth of the bands continued until about 90 K, after which the films started to degrade. From the cryogenic thin film studies, the key conclusion is the products formed between $CrCl_2O_2$ and aniline are identified as a mixture of isomers of $CrCl_2O$-aminocyclohexa-2,4-dienone and very likely $CrClO_2(H)NC_6H_5$.

5.2. Anisole + $CrCl_2O_2$

A significant number of product bands were observed in the photochemical reaction of $CrCl_2O_2$ with anisole,

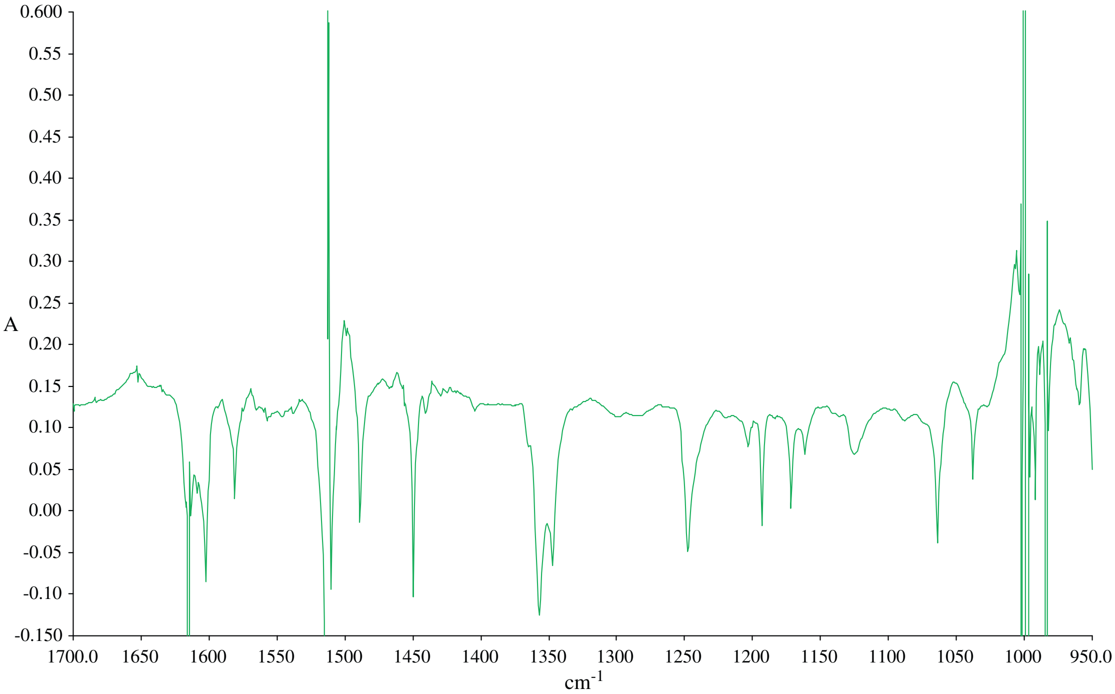

Fig. 5. Infrared difference spectrum before and after 25 h irradiation of a matrix formed by the twin jet deposition of a sample of Ar/$CrCl_2O_2$ = 250 with a sample of Ar/*N*,*N*-dimethylaniline. The negative bands are due to loss of intensity in the parent absorptions after irradiation.

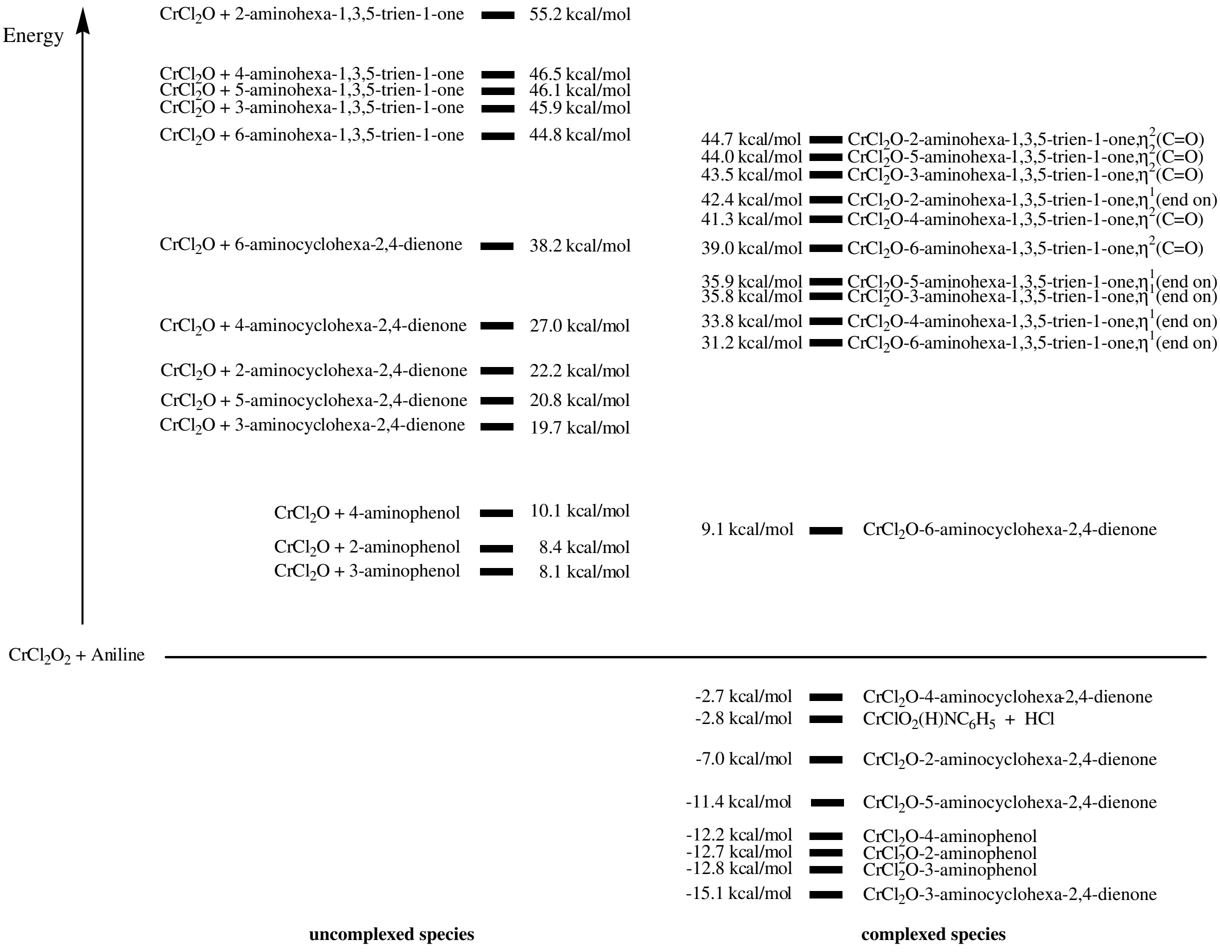

Fig. 6. Relative energies of the uncomplexed and complexed products as compared to $CrCl_2O_2$ and aniline.

Table 6
Calculated (B3LYP/6-311G++(d,2p)) relative energies[a] of possible products (uncomplexed and complexed) from the $CrCl_2O_2$ and aniline reaction

Uncomplexed products	Rel. energies	Complexed products	Rel. energies
$CrCl_2O$ + 2-Aminohexa-1,3,5-trien-1-one	55.2 kcal/mol	$CrCl_2O$-2-Aminohexa-1,3,5-trien-1-one, η^2 (C=O)	44.7 kcal/mol
$CrCl_2O$ + 4-Aminohexa-1,3,5-trien-1-one	46.5	$CrCl_2O$-5-Aminohexa-1,3,5-trien-1-one, η^2 (C=O)	44.0
$CrCl_2O$ + 5-Aminohexa-1,3,5-trien-1-one	46.1	$CrCl_2O$-3-Aminohexa-1,3,5-trien-1-one, η^2 (C=O)	43.5
$CrCl_2O$ + 3-Aminohexa-1,3,5-trien-1-one	45.9	$CrCl_2O$-2-Aminohexa-1,3,5-trien-1-one, η^1 (end on)	42.4
$CrCl_2O$ + 6-Aminohexa-1,3,5-trien-1-one	44.8	$CrCl_2O$-4-Aminohexa-1,3,5-trien-1-one, η^2 (C=O)	41.3
		$CrCl_2O$-6-Aminohexa-1,3,5-trien-1-one, η^2 (C=O)	39.0
		$CrCl_2O$-5-Aminohexa-1,3,5-trien-1-one, η^1 (end on)	35.9
		$CrCl_2O$-3-Aminohexa-1,3,5-trien-1-one, η^1 (end on)	35.8
		$CrCl_2O$-4-Aminohexa-1,3,5-trien-1-one, η^1 (end on)	33.8
		$CrCl_2O$-6-Aminohexa-1,3,5-trien-1-one, η^1 (end on)	31.2
$CrCl_2O$ + 6-Aminocyclohexa-2,4-dienone	38.2	$CrCl_2O$-6-Aminocyclohexa-2,4-dienone	9.1
$CrCl_2O$ + 4-Aminocyclohexa-2,4-dienone	27.0	$CrCl_2O$-4-Aminocyclohexa-2,4-dienone	−2.7
$CrCl_2O$ + 2-Aminocyclohexa-2,4-dienone	22.2	$CrCl_2O$-2-Aminocyclohexa-2,4-dienone	−7.0
$CrCl_2O$ + 5-Aminocyclohexa-2,4-dienone	20.8	$CrCl_2O$-5-Aminocyclohexa-2,4-dienone	−11.4
$CrCl_2O$ + 3-Aminocyclohexa-2,4-dienone	19.7	$CrCl_2O$-3-Aminocyclohexa-2,4-dienone	−15.1
		$CrClO_2(H)NC_6H_5$ + HCl	−2.8
$CrCl_2O$ + 4-Aminophenol	10.1	$CrCl_2O$-4-Aminophenol	−12.2
$CrCl_2O$ + 2-Aminophenol	8.4	$CrCl_2O$-2-Aminophenol	−12.7
$CrCl_2O$ + 3-Aminophenol	8.1	$CrCl_2O$-3-Aminophenol	−12.8

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

as listed in Table 3. $CrCl_2O$ was again observed, with absorptions at 1017 and 440 cm^{-1}, so oxidized products including methoxycyclohexadienone and methoxyphenol must be considered. The methoxyphenol complexes can be ruled out, as the characteristic O—H stretch was absent from the spectra. The spectral data strongly supports the formation of an isomeric mixture of methoxycyclohexadienones formed in the argon matrices. There are five possible isomers of this species, and it is not possible to identify a single isomer as the product. Rather it appears that a mixture of two or more isomers are formed, each complexed to $CrCl_2O$. The reactions to form 3 of the 5 complexes from $CrCl_2O_2$ + anisole were found computationally to have ΔE_0^{o} values <0 so that multiple isomers are possible. These 3 are calculated to have quite similar vibrational spectra. As such, unique assignment of each product band to a specific isomer of $CrCl_2O$-methoxycyclohexa-2,4-dienone is not possible. The key conclusion is that the product formed in the photochemical reaction of $CrCl_2O_2$ with anisole in solid argon matrices is identified as a mixture of isomers of $CrCl_2O$-methoxycyclohexa-2,4-dienone.

5.3. *N,N-Dimethylaniline + $CrCl_2O_2$*

The product bands for the photochemical reaction of $CrCl_2O_2$ with *N,N*-dimethylaniline followed closely to the results described above for anisole. Moderately strong bands were observed in the 1700–1500 cm^{-1} region, and numerous weaker bands below 1500 cm^{-1}. The product bands are assigned to a mixture of isomers of $CrCl_2O$-dimethylaminocyclohexadienones, while no dimethylaminophenols were observed. Theoretical calculations are consistent with these conclusions, finding stable minima for all of the five isomers and vibrational frequencies that agreed well with the observed frequencies.

Merged jet experiments were also carried out for the reactions between $CrCl_2O_2$ and anisole and $CrCl_2O_2$ and *N,N*-dimethylaniline, to provide the reagents with more time to react before deposition onto the cold window. In these experiments, no reaction products were detected, with heating of the reaction zone to as high as 100 °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 [17,20,29] and oxygen atom transfer [23] from the transition metal compound. Of all of the possible products from the two systems, the calculations demonstrate that the potential reactions are endothermic and are not likely to occur thermally in the temperature range that was used.

It is noteworthy that HCl elimination was observed only in the aniline experiments. Previous studies [17,20,29] have observed the HCl elimination reaction only from reaction pairs when the substrate has an acidic hydrogen, such as an amine. Aniline has a pK_a of 4.63, which makes it a weak acid. Dimethylaniline and anisole have only hydrogens bound to carbon which are not sufficiently acidic to undergo HCl elimination.

6. Further considerations

As seen in the previous studies of $CrCl_2O_2$ + benzenes with electron withdrawing groups, a decrease in the yield of the photochemical products was observed, compared to the benzene and methyl-substituted benzenes studies, as measured by band intensities (computed band intensities for the complexes in this and previous studies are similar, suggesting that it is yield rather than absorption coefficient

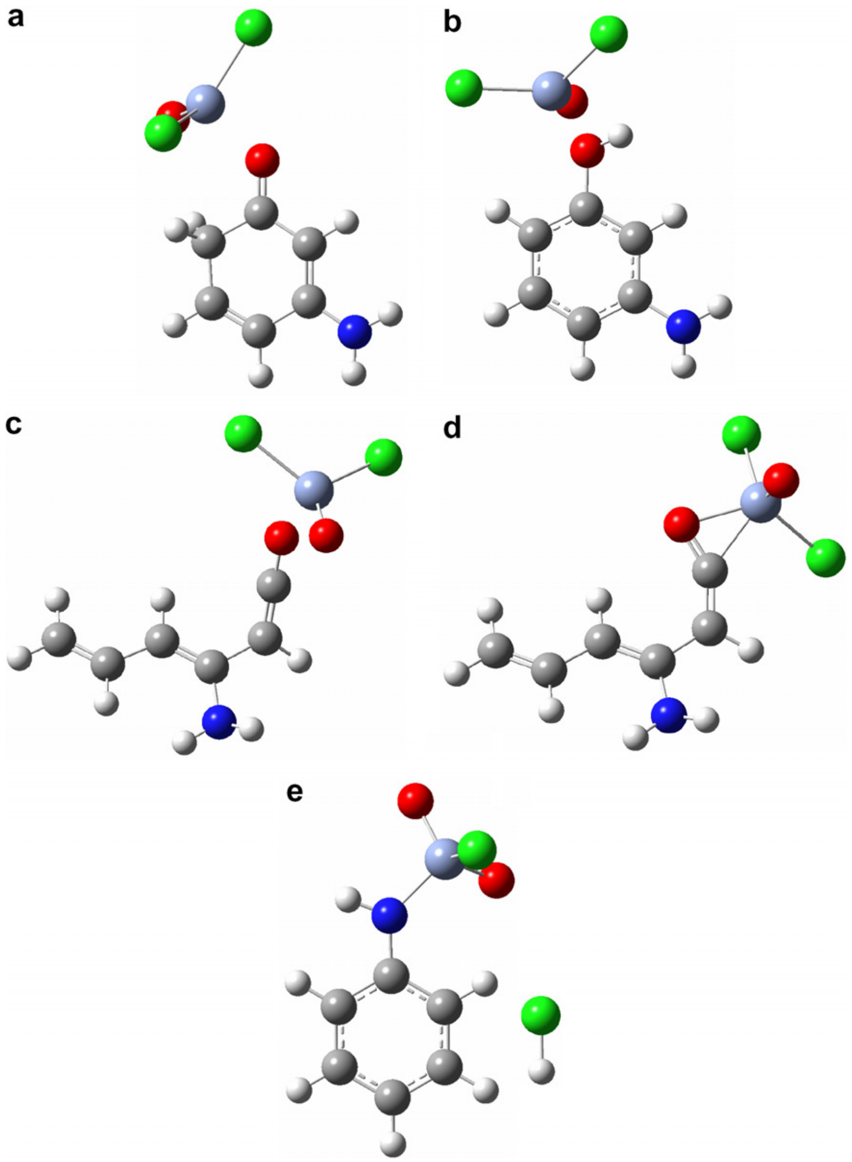

Fig. 7. Representative structures of the complexes of $CrCl_2O$ with (a) an aminocyclohexadienone, (b) an aminophenol, (c) an aminohexa-1,3,5-trien-1-one, η^1 (end on), and (d) an aminohexa-1,3,5-trien-1-one, η^2 (C=O). Also, the HCl elimination product, (e) $CrClO_2(H)NC_6H_5$.

that leads to the low band intensities). In the present study, the greatest yield of photochemical product was seen in the reaction of $CrCl_2O_2$ with anisole while the yield was much lower with aniline and *N*,*N*-dimethylaniline. This may be a consequence of either kinetic or thermodynamic factors. Kinetics may be involved either through the number of initial cage pairs that form, or through the rate of conversion of cage pairs to product. While the low vapor pressure and method of deposition of *N*,*N*-dimethylaniline does not permit a direct measurement of sample concentration, a comparison of band intensities for analogous modes of known systems (e.g. benzene) indicates that the concentrations of *N*,*N*-dimethylaniline are similar to others employed in these studies. Thus, the low intensities are not a result of low reactant concentration and number of cage pairs. The product bands for anisole and *N*,*N*-dimethylaniline continued to grow in with the longer irradiation times demonstrating that the yields in these photochemical reactions are likely kinetically controlled. However, the product bands for aniline reached maximum intensity after 6 h of irradiation.

From a thermodynamic perspective, it is possible to get an approximation of the extent of the reaction by estimating the equilibrium constant at 14 K. K can be calculated from the free energy differences calculated by Gaussian. However, the uncertainties in the calculated values of $\Delta G°$ at this level of theory suggest that only a qualitative argument can be made. All of the $CrCl_2O$-aminocyclohexa-2,4-dienone complexes isomers, except $CrCl_2O$-6-aminocyclohexa-2,4-dienone, had favorable equilibrium constants (negative ΔG). Thus, qualitatively it appears that the product yield for the reaction between $CrCl_2O_2$ and aniline is thermodynamically controlled. However, this does not suggest that the reaction is in dynamic equilibrium at 14 K. Rather, the initially photochemically excited cage pair can either lose excess energy and reform the initial cage pair, or can proceed to form the oxidized product complex. This apportioning between cage pair and product during the energy loss process appears to qualitatively follow the calculated thermodynamics for each system.

The mechanism of the photochemical reaction leading to the observed products is of interest as well. Recent visible/UV spectroscopic studies [47,48] have shown that a number of σ and π electron donors form 1:1 molecular complexes with $OVCl_3$ and $CrCl_2O_2$, with charge transfer transitions in the visible region. Excitation into these charge transfer transitions has then been shown to lead to photochemical reaction for a number of systems. However, visible/UV spectra recorded in the earlier $Ar/CrCl_2O_2 + Ar/C_6H_6$ study [32] did not show any distinct new electronic absorptions. This was consistent with the lack of observation of a distinct molecular complex in the infrared upon initial matrix deposition. Nonetheless, photochemical reaction was observed both in the benzene and in the present study, suggesting that there is some electronic interaction between the cage-paired partners. Apparently, this electronic interaction is sufficiently weak to escape spectroscopic detection. Nonetheless, the photochemical mechanism very likely arises from excitation of cage-paired partners, whether these form a weakly bound molecular complex which was not detected, or simply two species held in close proximity by the rigid argon matrix structure. The observation that $CrCl_2O_2$ alone in solid argon is not photochemically active (i.e., to form $CrCl_2O + O$) strongly suggests that a cage reactant pair is required. This is also consistent with the fact that the energy of a photon in the 500 nm region, where onset of photochemical reaction has been observed to occur, is significantly less than the Cr=O bond strength in $CrCl_2O_2$.

7. Conclusions

Irradiation of the argon matrices and cryogenic thin films of $CrCl_2O_2$ + aniline led to HCl elimination and very likely $CrClO_2(H)NC_6H_5$, as well as a mixture of isomers of $CrCl_2O$-aminocyclohexa-2,4-dienone. Irradiation of the matrices containing $CrCl_2O_2$ and anisole and *N*,*N*-dimethylaniline led to transfer of an oxygen atom to form the corresponding cyclic ketone complexed to the remaining $CrCl_2O$ species. These conclusions were supported by isotopic labeling (aniline) and B3LYP/6-311G++(d,2p) density functional calculations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.12.023.

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