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Matrix Isolation Investigation of the Photochemical Reaction of Methyl-Substituted Benzenes with $CrCl_2O_2$

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The matrix isolation technique, combined with infrared spectroscopy, has been used to characterize the products of the photochemical reactions of toluene, *m*-, *o*-, and *p*-xylene, mesitylene, and hexamethylbenzene with $CrCl_2O_2$. 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. The irradiation was shown to lead to oxygen atom transfer, forming complexes between methylcyclohexadienone derivatives and $CrCl_2O$. With the xylenes and mesitylene, di- and trimethylphenols, complexed to $CrCl_2O$, were also observed, respectively. This latter result arises from C−H bond activation and oxygen atom insertion into a C−H bond. The identification of the complexes was further supported by isotopic labeling (^{2}H) and by density functional calculations at the B3LYP/6-311G++(d,2p) level. Product distributions were rationalized by an analysis of the electron density distribution.

Introduction

The oxidation of organic substrates with metal oxo compounds, including $CrCl_2O_2$, 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(s) formed. These metal oxo compounds are able to transfer an 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] (hereafter PD) 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 a cyclic ketone, which then ring opens to a ketene. This lab has recently reported the photochemical product of the reaction of $CrCl_2O_2$ and benzene at 14 K in solid argon.[34] Spectroscopic evidence supported formation of 2,4-cyclohexadienone complexed to the $CrCl_2O$ species, through an oxygen atom transfer. The identification of the product was further supported by isotopic labeling and density functional calculations.

The present study examines the photochemical reactions of $CrCl_2O_2$ with toluene, *o*-, *m*-, and *p*-xylene, as well as mesitylene and hexamethylbenzene, to further explore the nature of the oxidation reaction. PD[35] have explored the reaction of O atoms, photochemically generated from O_3, with several of these organic species. However, the nature of the oxidation reaction of $CrCl_2O_2$ is quite different from that of an O atom and is important to our understanding of the role of high valent transition metal oxo compounds in these reactions.

Experimental Section

All of the experiments in this study were carried out on a conventional matrix isolation apparatus that has been described.[36] 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. Toluene (Fisher), toluene-d_8 (99%+ D, Acros), *m*-xylene (Acros), *m*-xylene-d_{10} (98% D, Cambridge Isotope Laboratories), *o*-xylene (Matheson, Coleman, and Bell), *o*-xylene-d_{10} (99%+ D, Acros), *p*-xylene (Fisher), *p*-xylene-d_{10} (99%+ D, Acros), and mesitylene (Baker) were introduced in a similar manner into a separate vacuum manifold and were purified by repeated freeze−pump−thaw cycles at 77 K. Hexamethylbenzene (Aldrich) is a solid at room temperature. A small sample was placed in a small stainless steel sidearm, connected to the deposition line by an Ultra Torr tee. The vapor pressure of the solid was entrained in flowing argon, carried to the cold window, and deposited. The vapor pressure and hence sample concentration could be controlled by placing a heating mantle around the sidearm and heating. Temperatures between room temperature and 56 °C were employed. Argon (Wright Brothers) was used as the matrix gas without further purification.

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Matrix samples were deposited in the twin jet mode. In the twin jet mode, 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 32−34 K to permit limited diffusion and then recooled to 14 K and additional spectra were 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 or with a 75 W Hg lamp with the Pyrex globe removed, after which additional spectra were recorded. The matrices were deposited at the rate of 2 mmol/h from each sample manifold onto the cold window. Final spectra were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer at 1 cm^{-1} resolution.

Theoretical calculations were carried out on likely intermediates in this study, using Gaussian 03 and 03W suites 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.

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,[38−45] 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.[23] Weak bands due to HCl impurity were noted in all of the $CrCl_2O_2$ blank experiments, as well as bands from the complexes of HCl with the methyl-substituted benzenes.[46]

$CrCl_2O_2$ + Toluene, Toluene-*d*$_8$. In an initial twin jet experiment, a sample of Ar/$CrCl_2O_2$ = 250 was co-deposited with a sample of Ar/toluene = 818. After 22 h of deposition, no new bands were detected. The matrix was irradiated for 2.0 h with the 75 W Hg lamp, which led to the observation of many new product bands, as listed in Table 1. The most intense bands were seen at 1662, 1641, 1566, 1541, 1456, 1397, 1348, 1266, 1137, 1017, 835, and 441 cm^{-1}. Most of the observed product bands were split into doublets or multiplets. Figure 1 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/toluene = 409 to Ar/toluene = 818. 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. The product bands were sharpest in the most dilute experiments and became much broader as the concentration of toluene increased, as was seen in the earlier study with benzene. This is consistent with the known aggregation of benzene and derivatives in argon matrices with increasing sample concentration.[47] The product bands grew in over 0.5 h period of irradiation and reached a maximum in 2.0 h of irradiation.

In addition, multiple twin jet experiments were conducted in which samples of Ar/$CrCl_2O_2$ were co-deposited with samples of Ar/toluene-*d*$_8$. After 22.0 h of deposition, the matrix was irradiated for 2.0 h with the 75 W lamp. This irradiation produced many new bands (see Table 1). Most of the observed product bands were split into doublets or multiplets.

TABLE 1: Calculated (B3LYP/6-311G++(d,2p)) and Observed Frequencies[b] and Isotopic Shifts for a Representative Methylcyclohexadienone−$CrCl_2O$ Complex from the Photochemical Reaction of $CrCl_2O_2$ with Toluene

normal isotope		^2H	
calcd. freq.[a]	exp. freq.	calcd. shift	exp. shift
413	441	1	−4
460		−69	
461	456	−22	−2
538		−20	
567		−24	
567		−12	
707		−3	
718	716	−54	−71
836	803	−99	
868	835	−100	
932		−117	
946		−176	
963			
975			
1039	1074	−177	
1058	1060	−244	−260
1074	1017	2	−4
1098	1137		
1157	1165	−324	−328
1161	1171	−256	−256
1249	1266		
1312	1325	−136	−126
1341	1348	−347	
1366	1341	−30	32
1383		−259	
1394	1397		
1435	1404	−402	
1452	1456	−412	−418
1527	1541	−12	−28
1562	1566	−12	−9
1633	1642	−46	−43
	1662		
2910		−790	
2917		−765	
2944		−828	
2992		−778	
3022		−782	
3064		−801	
3078		−808	
3097		−798	

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

$CrCl_2O_2$ + *m*-Xylene, *m*-Xylene-*d*$_{10}$. In an initial twin jet experiment, a sample of Ar/$CrCl_2O_2$ = 250 was co-deposited with a sample of Ar/*m*-xylene = 420. After 22 h of deposition, no new bands were detected. The matrix was 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 2. The matrix was annealed to notice if any changes in the spectrum would occur; however, there were no visible changes. Most of the observed product bands were split into doublets or multiplets. Figure 2 shows representative regions of this spectrum.

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/*m*-xylene = 420 to Ar/*m*-xylene = 780. The same products 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

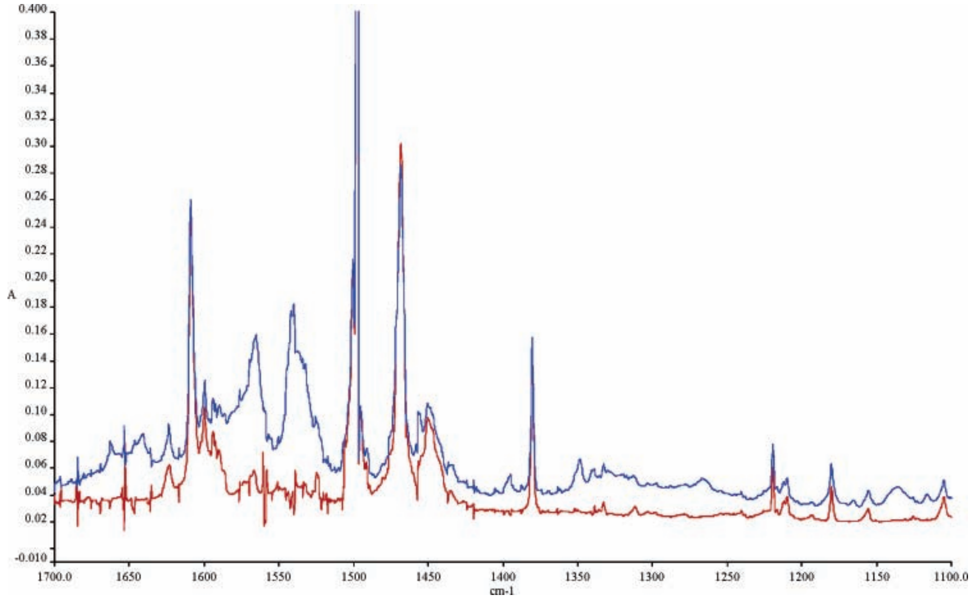

Figure 1. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/$CrCl_2O_2$ = 250 with a sample of Ar/toluene = 410. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm.

TABLE 2: Product Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Either *m*-, *o*-, or *p*-Xylene

$CrCl_2O_2$ + *m*-xylene (cm^{-1})	$CrCl_2O_2$ + *m*-xylene-d_{10} (cm^{-1})	$CrCl_2O_2$ + *o*-xylene (cm^{-1})	$CrCl_2O_2$ + *o*-xylene-d_{10} (cm^{-1})	$CrCl_2O_2$ + *p*-xylene (cm^{-1})	$CrCl_2O_2$ + *p*-xylene-d_{10} (cm^{-1})
	419		439	441	441
440	441	450	451		466
454	478	805		474	
740		848		757	
789	724	1012	1014	762	702
	791		787	815	
	796		817	830	
820		1070	823	846	
895			849	924	753
921		1102	802		810
	928		1106		841
931		1131	1146		845
1017	1015	1187	907	1015	1017
1070		1227	1210	1110	
1104	820	1260		1155	
1117		1279		1176	905
1178	831	1298	1291	1190	
1192		1331			1179
1214	1160	1342		1238	1210
1265	1176	1359	970	1267	1186
1324	1228	1391	1128	1310	1221
1348	1115		1296		1230
	1265		1305	1330	
	1299		1386	1354	1236
1391			1395		1318
1407	1366	1418		1384	1329
	1382	1526	1508	1396	1106
1430		1541	1554	1429	
1459		1563		1441	1032
1537	1520	1583	1598		1374
1567	1560	1646	1638	1534	1436
	1599	1659		1544	1518
1661	1633	3553	2622	1567	1560
3553	2622			1587	
				1649	1615
				3553	2622

intensities were also consistent with the concentrations employed over all of the experiments.

Multiple twin jet experiments were conducted in which samples of Ar/$CrCl_2O_2$ were co-deposited with samples of Ar/*m*-xylene-d_{10}. After 22.0 h of deposition, the matrix was irradiated for 1.0 h with the Hg arc lamp. This irradiation produced many new bands (see Table 2). Most of the observed product bands were split into doublets or multiplets.

$CrCl_2O_2$ + *o*-Xylene, *o*-Xylene-d_{10}, *p*-Xylene, *p*-Xylene-d_{10}, and Mesitylene. A pattern of experiments very similar to the $CrCl_2O_2$ + *m*-xylene twin jet experiments described above were conducted for *o*-xylene, *p*-xylene, their perdeutero isoto-

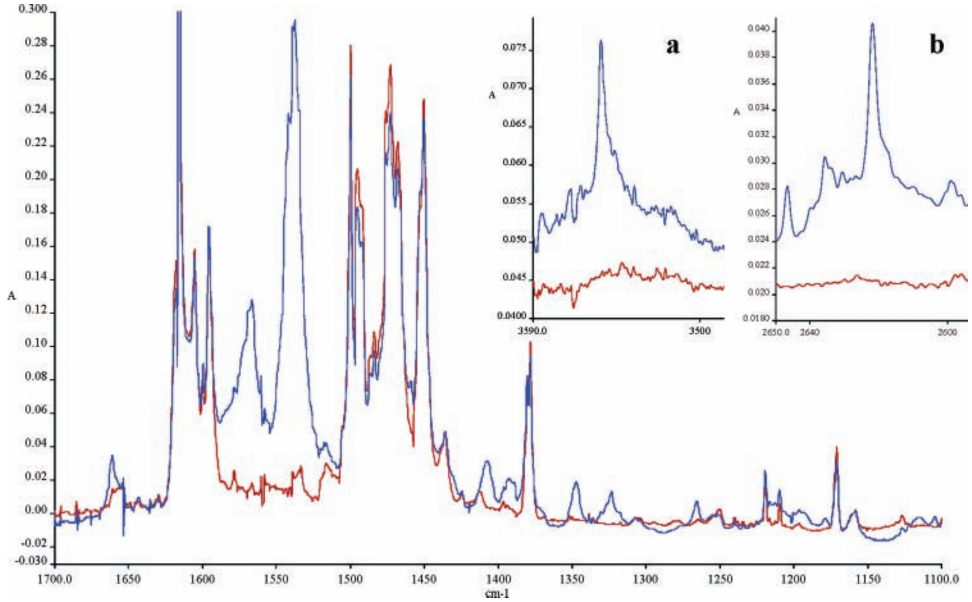

Figure 2. Infrared spectra of a matrix formed by the twin jet deposition of a sample of Ar/$CrCl_2O_2$ = 250 with a sample of Ar/*m*-xylene = 430. The red trace is before irradiation, while the blue trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm. The two upper spectra regions are of the (a) O−H stretch and the (b) O−D stretch.

pomers, and mesitylene (1,3,5-trimethylbenzene). Matrices were deposited over a range of sample concentrations, irradiated for 1.0 h, and some matrices were then annealed. A number of products bands were observed in each of these experiments, some of which had substantial intensity. All of the product bands from all of these pairs of reagents are listed in Tables 2 and 3. Product band intensities for a given pair of reagents maintained constant relative intensities in the different experiments that were conducted and had absolute intensities that varied directly with the concentrations of the reagents.

$CrCl_2O_2$ + Hexamethylbenzene (HMB). In an initial twin jet experiment, a sample of Ar/$CrCl_2O_2$ = 250 was co-deposited with a sample of Ar + HMB. 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 4 h with the filtered ($\lambda > 300$ nm) output of a medium pressure Hg arc lamp. Only three weak product bands were observed, at 3438, 3426, and 746 cm^{-1}, arising from the photochemical reaction of $CrCl_2O_2$ with impurity H_2O.[23] This experiment was repeated two more times with a more concentrated sample of Ar + HMB, while the Ar/$CrCl_2O_2$ concentration was held constant. The samples were each irradiated for 1 h. Again, no product bands were observed in each of the trials.

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). Because 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 the previous study, complexed to the remaining metal fragment, $CrCl_2O$, which is trapped within the same matrix cage. In addition, phenols formed through the insertion of an O atom into a C−H bond and ketenes formed through a ring-opening reaction were considered, each complexed to $CrCl_2O$. Two modes of coordination, end on, η^1, and side on, η^2, to the C═O bond were calculated. Figure 3 shows the energies of the 21 calculated likely structures (products) relative to $CrCl_2O_2$ + toluene; the energies are also listed in the Supporting Information. Figure 4 shows the calculated structures of three representative complexes arising from the reaction of $CrCl_2O_2$ with toluene (a cyclohexadienone, a phenol, and a ketene). The Supporting Information shows graphics representations of all of these calculated structures (structures **S1a**−**S1h**, **S2a**−**S2c**, **S3a**−**S3j**) as well as tables listing the calculated energies relative to $CrCl_2O_2$ + the methyl-substituted benzenes. All of the structures correspond to a single oxygen transfer from the chromyl chloride to a methyl-substituted benzene. All of the proposed complexes optimized to energy minima on their respective potential energy surfaces, with all positive vibrational frequencies. For the $CrCl_2O$−cyclic diene ketone complexes produced from toluene and *m*-, *o*-, *p*-xylene as well as the $CrCl_2O$−phenols produced from *m*-, *o*-, *p*-xylene, and mesitylene, vibrational frequencies were also calculated for the completely deuterated isotopomers. Representative calculated frequencies are given in Tables 1−3.

Discussion

No distinct product bands were observed upon initial co-deposition of the methyl-substituted benzenes and their isotopomers with $CrCl_2O_2$ into argon matrices. However, subsequent irradiation of these matrices led to the formation of strong product bands. This is identical to the most recent system studied in this lab,[34] $CrCl_2O_2$ + benzene, as well as past systems,[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. It is likely that there are cage pairs formed from the statistical distribution of components of the system during the matrix condensation process. All of the product bands for a given system maintained a constant intensity ratio with respect to one another in the several different experiments at different concentrations that were run with each pair of reactants. This is suggestive of the formation of either a single product, or two or more products formed in each experiment in the same relative amounts within experimental error. Whether the former or the latter is correct, the product(s) still must arise from one molecule of each reactant. This is a

TABLE 3: Product Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Mesitylene and the Calculated[a] Bands of $CrCl_2O$−2,4,6-Trimethylcyclohexa-2,4-dienone and $CrCl_2O$−2,4,6-Trimethylphenol

$CrCl_2O_2$ + mesitylene (exp. freq.[b])	$CrCl_2O$− 2,4,6-trimethylcyclohexa-2,4-dienone (calcd. freq.)	calcd. intensity (km/mol)	$CrCl_2O$− 2,4,6-trimethylphenol (calcd. freq.)	calcd. intensity (km/mol)
440	404	163.5	422	149.3
	424	2.7	473	16.3
454	455	6.0	491	2.8
474	499	12.6	506	0.2
	531	2.1	511	11.8
	548	2.9	559	0.8
	641	2.4	566	0.6
	726	4.8	583	8.2
750	786	6.6	717	3.0
830	829	16.8	745	20.1
	884	4.8	847	17.6
	906	19.6	878	0.0
923	915	2.0	920	4.0
944	961	4.4	945	1.7
	974	8.6	1001	8.3
	1005	13.0	1004	0.3
	1017	5.2	1026	2.4
1029	1038	0.7	1028	7.1
1048	1041	3.1	1030	5.6
1094	1073	9.2	1031	0.3
1012	1092	233.0	1093	209.7
1153	1113	0.1	1106	67.1
1195	1175	4.6	1173	42.1
1216	1219	6.1	1204	115.0
1266	1244	8.5	1248	10.8
1292	1312	6.1	1288	7.2
1347	1330	10.6	1296	7.7
	1369	2.8	1376	1.2
1384	1374	32.5	1382	1.7
1389	1380	7.8	1385	0.0
1397	1384	18.8	1400	0.7
	1436	9.9	1418	3.2
1434	1443	6.8	1445	9.2
	1450	2.4	1451	7.4
	1455	13.6	1454	0.5
	1458	2.2	1454	8.0
1459	1462	13.0	1464	24.2
1540	1538	293.9	1476	51.2
1580	1570	39.8	1588	14.3
1660	1650	13.4	1595	3.7
	2930	28.5	2930	16.3
	2936	1.7	2934	23.6
	2943	11.8	2946	12.4
	2950	25.8	2983	5.7
	2974	12.8	2984	15.7
	2990	6.0	2994	7.1
	3015	11.4	3009	12.9
	3017	10.0	3019	14.5
	3020	11.4	3022	10.7
	3041	0.2	3063	12.8
	3047	11.4	3065	7.8
3553	3062	6.9	3572	119.0

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

situation similar to that seen in a recent study with the reaction of $CrCl_2O_2$ + chloroethenes.[48]

One potential mode of photochemical reaction involves oxygen atom transfer from $CrCl_2O_2$ to the organic substrate, yielding an oxidized product and $CrCl_2O$. Cl_2CrO has been observed by several research groups[7,27,49] 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 near 1014 and 440 cm^{-1} for every system and are very reasonably assigned to Cl_2CrO. Further, these bands did not shift measurably with D isotopic substitution, further supporting this assignment. Thus, the spectral evidence strongly supports formation of Cl_2CrO and oxygen atom transfer to the substituted benzenes in a reaction analogous to the $CrCl_2O_2/C_6H_6$ system.

Toluene. Based on calculated energetics and previous studies, the three classes of potential oxidation products are cyclic dienones and phenols that form while keeping the ring intact, and ketenes that form through a ring-opening reaction; representative structures of these three classes each complexed to $CrCl_2O$ are shown in Figure 4. Each class of products has very distinctive infrared signatures. Phenols are all characterized by an distinct O−H stretch above 3000 cm^{-1}, ketenes by an intense

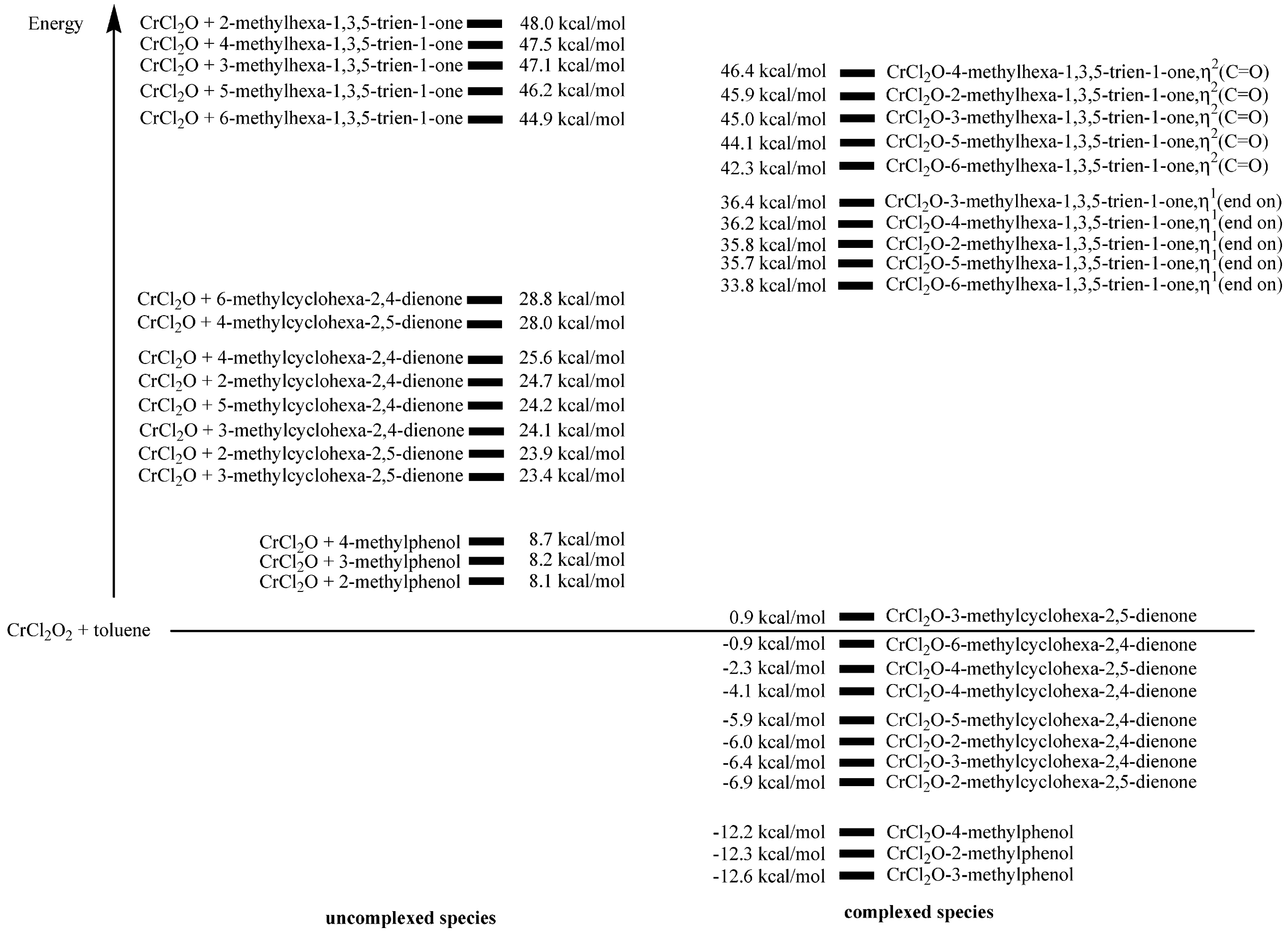

Figure 3. Relative energies of the uncomplexed and complexed products as compared to $CrCl_2O_2$ and toluene.

absorption between 1900 and 2000 cm^{-1} (near 2100 cm^{-1} for the free ketene, and shifted somewhat to lower energy by complexation to $CrCl_2O$), while the cyclic dienones have strong absorptions from 1500 to 1700 cm^{-1} due to the C═O stretch and the C═C stretches. On this basis, both phenols and ketenes can be ruled out, as these characteristic bands were completely absent. Rather, the spectral data strongly support formation of a cyclic dienone, consistent with the results from the previous study of the $CrCl_2O_2$ + benzene reaction. There are eight possible isomers for the cyclic dienone product, depending on the positions of the C═O and methyl groups with respect to each other and to the two carbon−carbon double bonds. Computationally, oxygen transfer reactions to form the separated isomeric dienones and $CrCl_2O$ species were all calculated to be endothermic at the B3LYP/6-311++g(d,2p) level of theory (see Figure 3). However, when complexation energy of the dienone to the $CrCl_2O$ species was included, the $\Delta E_{298}°$'s to form the products from $CrCl_2O_2$ and toluene were calculated to be exothermic, except for the complex of 3-methylcyclohexa-2,5-dienone with $CrCl_2O$ where $\Delta E_{298}°$ was calculated to be +0.9 kcal/mol. All eight isomers were calculated to lie within 8 kcal/mol of one another.

Three isomers require a 1,4 hydrogen shift (to form the 2,5 dienones), while five isomers require a 1,2 hydrogen shift (to form the 2,4 dienones). The latter shift appears more feasible from a kinetic point of view, although thermodynamically $CrCl_2O$-2-methylcyclohexa-2,5-dienone is calculated to be among the more stable isomers. The primary means, then, to distinguish between the isomers is the infrared spectra of the product(s), both normal isotope and perdeuterated. The spectra clearly show bands in the expected spectral regions, for example, two bands near 1650 cm^{-1} for C═C stretching modes and near 1550 cm^{-1} for coordinated C═O stretching modes, in agreement with the calculations. The presence of two bands in the C═O stretching region suggests that more than a single isomer is formed in these reactions. Further, all of the remaining product bands and their deuterium counterparts cannot be accounted for by any one isomer. Rather, the spectra suggest formation of more than one isomeric form of the methylcyclohexadienone. It is tempting to try to assign each of the product bands to a specific isomer on the basis of the calculated band positions for each of the isomers. However, given the intrinsic approximations in the calculation of vibrational frequencies in B3LYP and all theoretical models at present, it is more appropriate to identify the absorbing species responsible for the number of product bands observed after irradiation of matrices concerning $CrCl_2O_2$ and $CH_3C_6H_5$ as an isomeric mixture of methylcycohexadienones, each complexed to $CrCl_2O$, without uniquely assigning each product band to a specific isomer. This product identification is useful in understanding the mechanism of oxidation of toluene, and it stands in contrast to the results of Parker and Davis who observed ring opening and ketene formation in photochemical matrix reactions of O atoms with toluene. As will be discussed below, this identification also differs somewhat from those products identified in the reaction of $CrCl_2O_2$ with the more heavily methyl-substituted benzene derivatives.

***m*-Xylene.** A significant number of product bands were observed in the photochemical reaction of $CrCl_2O_2$ with *m*-xylene, as listed in Table 2. Because $CrCl_2O$ was again observed, oxidized products including dimethylphenol, dimethylcyclohexadienone, and dimethylketenes must be considered.

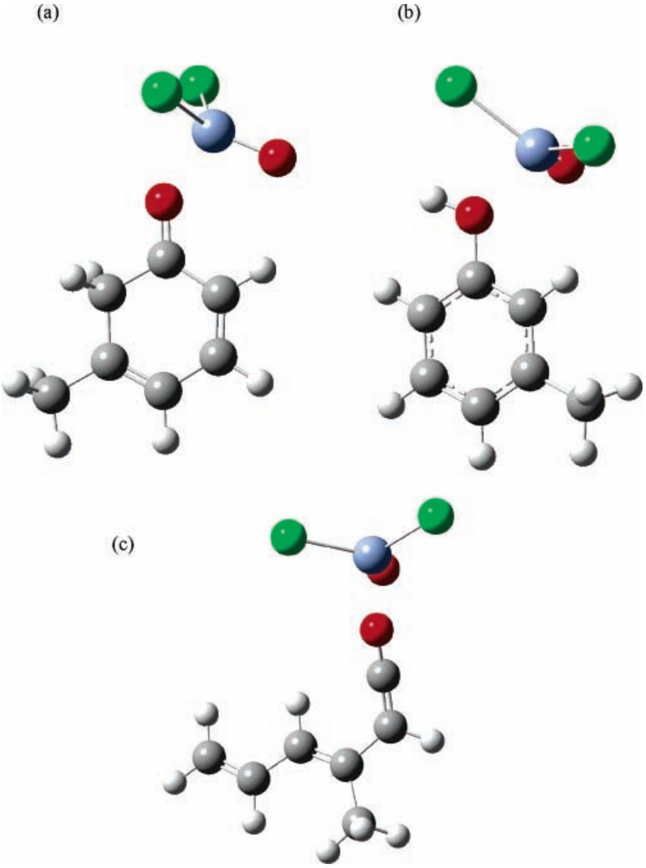

Figure 4. Representative structures of the complexes of $CrCl_2O$ with (a) a methylcyclohexadienone, (b) a phenol, and (c) a methyl ketene (one isomer of each shown).

Many of the product bands are quite similar in location and intensity to those observed above in the reaction with toluene. For example, moderately intense bands were seen near 1550 and 1650 cm^{-1}, while no bands were observed near 2000 cm^{-1}, in the ketene stretching region. However, one significant difference was the observation of a strong, sharp product band at 3553 cm^{-1}, with a clear deuterium counterpart at 2622 cm^{-1} as shown in Figure 2. This upper region is characteristic of an O−H stretch, particularly one in which the oxygen atom is coordinated to the $CrCl_2O$ species. Moreover, the H/D ratio of 1.355 is just that expected for a somewhat anharmonic O−H oscillator. There are six possible isomers of dimethylphenol, each complexed to $CrCl_2O$ through the O atom. All six complexes were calculated at the B3LYP/6-311++g(d,2p) level and were found to be similar in energy to one another, and lower in energy than the possible ketene or dimethylcyclohexadienone products. In addition, all six were calculated to have a strong O−H stretch between 3550 and 3600 cm^{-1}. This is strong support for the formation of dimethylphenol, through insertion of an oxygen atom from $CrCl_2O_2$ into a C−H bond of *m*-xylene. While several reaction pathways have been observed for the photochemical reactions of $CrCl_2O_2$ with organic and inorganic substrates, this is the first observed of C−H bond activation and oxygen atom insertion into a C−H bond from $CrCl_2O_2$.

It is clear from the observed product bands that isomers of dimethylcyclohexadienone are also formed in these matrices. There are seven possible isomers, and as above it is not possible to definitively identify a single isomer as the product. Rather it appears that a mixture of two or more isomers are formed, each complexed to $CrCl_2O$. All seven were found computationally to be stable, although not quite as stable as dimethylphenol, and have quite similar vibrational spectra. As such, unique assignment of each product band to a specific isomer of dimethylcyclohexadienone−$CrCl_2O$ is not possible. The key conclusion is that the products formed in the photochemical reaction of $CrCl_2O_2$ with *m*-xylene in solid argon matrices are identified as a mixture of isomers of $CrCl_2O$−dimethylcyclohexadienone and $CrCl_2O$−dimethylphenol.

***o*-Xylene, *p*-Xylene, and Mesitylene.** The product bands for the photochemical reactions of $CrCl_2O_2$ with *o*-xylene, *p*-xylene, and mesitylene followed closely the results described above for *m*-xylene. A distinct, sharp band was observed in the 3550 cm^{-1} region, in some cases split into a doublet, as well as moderately strong bands in the 1500−1700 cm^{-1} region, and numerous weaker bands below 1500 cm^{-1}. In all of these systems, no bands were seen near 1900−2100 cm^{-1} where ketenes are known to absorb. Thus, the same general conclusions can be reached as for *m*-xylene. For *o*- and *p*-xylene, the band in the 3550 cm^{-1} region is assigned to one or more isomers of dimethylphenol. The remainders of the bands are best assigned to a mixture of isomers of the appropriate dimethylcyclohexadienone, while no ketenes were observed. For mesitylene, as a result of its higher symmetry, only a single isomer of trimethylphenol is likely, and only a single isomer of trimethylcyclohexadienone. The product bands for the $CrCl_2O_2$ + mesitylene system are assigned to a mixture of these two products. Theoretical calculations are consistent with these conclusions, finding stable minima for all isomers, with exothermic $\Delta E_{298}°$'s and vibrational frequencies that agreed well with the observed frequencies.

Hexamethylbenzene. The photochemical reaction of $CrCl_2O_2$ with hexamethylbenzene was explored in a manner similar to the above systems. Here, however, product formation can only occur by a methyl group shift or insertion into a carbon−carbon bond. Calculations indicated that hexamethylcyclohexadienone that would form by a 1,2 methyl group shift is thermodynamically feasible. However, this does not consider the kinetic barriers to such a shift in a rigid argon matrix. Consistent with this, no products were observed upon irradiation of these matrices.

Further Considerations. The mechanism of the photochemical reaction leading to the observed products is of interest as well. Recent visible/UV spectroscopic studies[50,51] 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 previous $Ar/CrCl_2O_2$ + Ar/C_6H_6 study[34] 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 C_6H_6 and in the present study, suggesting that there is some electronic interaction between the cage-paired partners. However, 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 that was not detected, or simply two species held in close proximity by the rigid argon matrix structure. The observation that $CrCl_2O_2$ alone in solid argon is not photochemically active (i.e., to form $CrCl_2O$ + O) strongly suggests that a cage reactant pair is required. This is also in agreement with the fact that the energy of a photon in the 500 nm region, where onset of photochemical reaction has been observed to occur, is significantly less than the Cr=O bond strength in $CrCl_2O_2$.

Two additional interesting questions arise from the results obtained here. The first arises from a comparison of the results of Parker and Davis (PD) to those obtained here. PD observed ring opening and methylketene formation after the reaction of O atoms (generated from the irradiation of O_3) with toluene and the xylenes. This was in agreement with their study of the reaction of O atoms with benzene. This is in contrast to the present study, above, where no evidence was seen for ketene formation. Instead, only methylcyclohexadienones and methylphenols were observed. This result was independent of the length of irradiation, whereas PD observed methylcyclohexadienones first and then methylketene formation. A clear difference in the two studies is the source of O atoms, O_3 in the PD study and $CrCl_2O_2$ in the present study. The remaining precursor fragment (O_2 or $CrCl_2O$) remains trapped in the same matrix cage with the oxidized product. As calculations demonstrate, the $CrCl_2O$ complexes strongly ($\geq$10 kcal/mol), while O_2 does not. This complexation may stabilize the methylcyclohexadienones and prevent their conversion to the ring-opened methylketenes. However, calculations also demonstrate clearly that the methylketenes are much higher energy species, with the methylcyclohexadienones and methylphenols being similar in energy and significantly more stable ($\sim$40 kcal/mol) than the methylketenes. Thus, the methylketenes represent metastable species on the global potential energy surface and are formed as a result of excess energy put into the system during the irradiation process. However, once formed, there are likely to be large steric effects and kinetic barriers to the ring-closing reaction to reform the methylcyclohexadienones in the matrix environment.

The second question arises from the observation of both methylcyclohexadienones and methylphenols for the xylenes and mesitylene, while only methylcyclohexadienones were observed with benzene and toluene. The answer may lie with the changing electron density distribution in the organic substrate as a result of increasing methyl substitution. Methyl groups are known to be electron donors, increasing the electron density on the ring. This is supported by a population analysis of the ring carbons and attached hydrogens using theoretical calculations. Because the electron density is not a quantum mechanical observable, any scheme for calculating the electron density is necessarily arbitrary. Nonetheless, using Mulliken population analysis to model the partial atomic charges, the partial negative charge on the carbons bearing the hydrogen atoms on the ring increases from -0.3 au for benzene to approximately -1.7 au for mesitylene. For the xylenes, not all ring positions are equivalent, so only average values can be used. These are intermediate, in the range of -0.7 to 0.8 au. At the same time, the charge on the ring hydrogens stays nearly constant, between $+0.1$ and $+0.2$ au. Thus, the polarity of the C$-$H bonds on the ring increases significantly with increasing methyl group substitution, which may help facilitate O atom insertion into the C$-$H bond. Further studies are underway to explore the effects of electron-withdrawing and electron-donating substituents on the product distribution.

Conclusions

Irradiation of matrices containing $CrCl_2O_2$ and toluene, *m*-, *o*-, and *p*-xylene, and mesitylene led to transfer of an oxygen atom to form the methylcyclohexadienone complexed to remaining $CrCl_2O$ species. With the xylenes and mesitylene, methylphenols were also produced through insertion into a C$-$H bond. These conclusions were supported by isotopic labeling (^{2}H) and by B3LYP/6-311G++(d,2p) density functional calculations. In contrast, irradiation of mixtures of $CrCl_2O_2$ and hexamethylbenzene did not yield any products. The product distributions were rationalized by analysis of the atomic populations on the ring atoms as a function of methyl substitution.

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Supporting Information Available: Figures of the structures of the considered products between $CrCl_2O_2$ and toluene, tables listing the calculated energies relative to $CrCl_2O_2$ + the methyl-substituted benzenes, and a representative spectrum of the photochemical products of the reaction of $CrCl_2O_2$ with mesitylene in an argon matrix. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 4543.

(2) Yajima, A.; Matsuzaki, R.; Saeki, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1098.

(3) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1855.

(4) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7139.

(5) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441.

(6) Limberg, C.; Koppe, R.; Schnockel, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 496.

(7) Limberg, C.; Koeppe, R. *Inorg. Chem.* **1999**, *38*, 2106.

(8) Torrent, M.; Deng, L.; Duran, M.; Sola, M.; Ziegler, T. *Can. J. Chem.* **1999**, *77*, 1476.

(9) Torrent, M.; Deng, L.; Ziegler, T. *Inorg. Chem.* **1998**, *37*, 1307.

(10) Ziegler, T.; Li, J. *Organometallics* **1995**, *14*, 214.

(11) Deng, L.; Ziegler, T. *Organometallics* **1997**, *16*, 716.

(12) Ault, B. S. *J. Am. Chem. Soc.* **1998**, *120*, 6105.

(13) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992.

(14) Ortiz de Montellano, P. R.; Ed. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Plenum: New York, 1985.

(15) Deng, L.; Ziegler, T. *Organometallics* **1996**, *15*, 3011.

(16) Rappe, A. K.; Goddard, W. A., III *Nature* **1980**, *285*, 311.

(17) Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.

(18) Cradock, S.; Hinchcliffe, A. J. *Matrix Isolation*; Cambridge University Press: Cambridge, 1975.

(19) Hallam, H. E. *Vibrational Spectroscopy of Trapped Species*; John Wiley: New York, 1973.

(20) Andrews, L.; Moskovits, M.; Eds. *Chemistry and Physics of Matrix-Isolated Species*; Elsevier Science Publishers: Amsterdam, 1989.

(21) Anderson, S. R.; Ault, B. S. *J. Mol. Struct.* **2002**, *609*, 149.

(22) Anderson, S. R.; Ault, B. S. *J. Phys. Chem. A* **2002**, *106*, 1419.

(23) Subel, B. L.; Kayser, D. A.; Ault, B. S. *J. Phys. Chem. A* **2002**, *106*, 4998.

(24) Antle, K. A.; Ault, B. S. *J. Mol. Struct.* **2003**, *655*, 331.

(25) Kayser, D. A.; Ault, B. S. *J. Phys. Chem. A* **2003**, *107*, 6500.

(26) Griner, G. M.; Kayser, D. A.; Ault, B. S. *Chem. Phys.* **2004**, *300*, 63.

(27) Ault, B. S. *J. Phys. Chem. A* **2004**, *108*, 5537.

(28) Ault, B. S. *Spectrochim. Acta, Part A* **2003**, *59A*, 1989.

(29) Kayser, D. A.; Ault, B. S. *Chem. Phys.* **2003**, *290*, 211.

(30) Ault, B. S. *J. Phys. Chem. A* **2001**, *105*, 4758.

(31) Ault, B. S. *J. Phys. Chem. A* **2000**, *104*, 11796.

(32) Ault, B. S. *J. Phys. Chem. A* **1999**, *103*, 11474.

(33) Parker, J. K.; Davis, S. R. *J. Am. Chem. Soc.* **1999**, *121*, 4271.

(34) Hoops, M. D.; Ault, B. S. *J. Phys. Chem. A* **2005**, *109*, 4497.

(35) Parker, J. K.; Davis, S. R. *J. Phys. Chem. A* **2000**, *104*, 4108.

(36) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

(37) Frisch, M. J.; Trucks, G. W.; Schlegal, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.;

Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(38) Wilmshurst, J. K.; Bernstein, H. J. *Can. J. Chem.* **1957**, *35*, 911.

(39) La Lau, C.; Snyder, R. G. *Spectrochim. Acta, Part A* **1971**, *27*, 2073.

(40) Keefe, C. D.; Pearson, J. K.; MacDonald, A. *J. Mol. Struct.* **2003**, *655*, 69.

(41) Green, J. H. S. *Spectrochim. Acta, Part A* **1970**, *26*, 1913.

(42) Green, J. H. S. *Spectrochim. Acta, Part A* **1970**, *26*, 1503.

(43) Green, J. H. S. *Spectrochim. Acta, Part A* **1970**, *26*, 1523.

(44) Draeger, J. A. *Spectrochim. Acta, Part A* **1985**, *41A*, 607.

(45) Cesaro, S. N.; Martini, B.; Bencivenni, L.; Spoliti, M.; Maltese, M. *Spectrochim. Acta, Part A* **1980**, *36A*, 165.

(46) Barnes, A. J. *J. Mol. Struct.* **1983**, *100*, 259.

(47) Brown, K. G.; Person, W. B. *Spectrochim. Acta, Part A* **1978**, *34A*, 117.

(48) Antle, K. A.; Ault, B. S. *J. Phys. Chem. A* **2005**, *109*, 947.

(49) Wistuba, T.; Limberg, C. *Eur. J. Inorg. Chem.* **1999**, 1335.

(50) Goldberg, N.; Ault, B. S. *Chem. Phys. Lett.* **2005**, *401*, 89.

(51) Goldberg, N.; Ault, B. S. *J. Mol. Struct.* **2005**, *759*, 84.