Hydrogen Abstraction in the Neutral Molecular Cluster of Benzophenone and Hydrogen Donors Formed in a Supersonic Free Jet Expansion

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Photochemical reactions of benzophenone with hydrogen donors in neutral molecular clusters formed in a supersonic free jet expansion were studied. It was found that benzophenone undergoes photoreduction to form benzophenone ketyl radical in the benzophenone–1,4-cyclohexadiene mixed expansion. Good agreement between the action spectrum of the hydrogen abstraction reaction and the multiphoton ionization (MPI) spectrum of benzophenone–1,4-cyclohexadiene mixed clusters suggested that benzophenone ketyl radical is formed by an intracluster reaction after photoexcitation of benzophenone. This is the first observation of hydrogen abstraction in a neutral molecular cluster. However, no ketyl radical fluorescence is observed when ethanol, 2-propanol, or triethylamine is used as a hydrogen donor. The dependence of the cluster reactivity on the nature of the hydrogen donors is discussed.

Introduction

Recently, the energetics and dynamics of a wide range of solute-solvent clusters generated in a supersonic free jet expansion have been studied by laser spectroscopy.¹⁻³ Among the various properties of clusters, much attention has been paid to the reactions within microsolvent clusters.⁴⁻⁷ The investigation of intermolecular reactions in collision-free microsolvent clusters should ultimately lead us to an understanding of liquid-phase reactions at a molecular level without the complicating effects of solvent environment.

So far, most of these studies have centered on reactions in ionic clusters, except for studies of elementary proton transfer in neutral acid-base clusters pioneered by Leutwyler and co-workers.⁸ They demonstrated that excited-state proton transfer by α -naphthol occurs in microsolvated clusters (evidenced by the similarity of its fluorescence spectrum to that of naphtholate anion in solutions), and showed that the proton transfer depends mainly on the basicity and the number of solvent molecules. After this first observation by Leutwyler and co-workers, several other groups have studied proton-transfer reactions induced by electronic excitation of molecules whose ground and excited states have drastically different acidities.⁹⁻¹²

The reactivity of excited-state benzophenone is one of the most fundamental and important subjects in organic photochemistry.¹³⁻²³ Photoexcited benzophenone rapidly undergoes intersystem crossing and populates the lowest triplet state with a quantum yield of unity in the condensed phase. It is well-known that, due to the nature of the $n\pi^*$ electronic state, the lowest triplet benzophenone has a highly electrophilic carbonyl group, which may lead to charge transfer and/or hydrogen abstraction reactions. Hydrogen abstraction by the lowest triplet benzophenone from various hydrogen-donating compounds has been widely investigated in the condensed phase.

Although the mechanism for the photoreduction of benzophenone has been extensively studied, many questions remain unanswered. The role of surrounding solvent molecules in the reaction has not been adequately elucidated. It is not yet thoroughly understood whether a specific orientation between benzophenone and the hydrogen donor is necessary for the reaction to progress. If proton transfer following electron transfer between benzophenone and the hydrogen donor is the dominant process of the reaction, as in the case of benzophenone-amine systems, is a long-lived ion pair necessarily formed?

To solve these problems, we studied the photochemistry of benzophenone in the gas phase in which the contributions from surrounding solvent molecules are absent.²⁴ Whereas the photoreduction process of benzophenone in the condensed phase has been thoroughly studied, little has been reported on the gas-phase reaction of triplet benzophenone.²⁵

In a previous investigation,²⁴ we found that excited benzophenone is photoreduced to benzophenone ketyl radical (BPK) without contributions from surrounding solvent molecules by monitoring the fluorescence of BPK. The quenching rate constant measurements of triplet benzophenone show that, in addition to its role in the condensed phase, the charge-transfer interaction also plays an important role in the photoreduction process of benzophenone-amine systems in the gas phase.

In the present work, we have investigated the photochemical reactions in molecular clusters of benzophenone and hydrogen donors in a supersonic free jet expansion. We report the photoreduction to form BPK in the mixed expansion of benzophenone and 1,4-cyclohexadiene. The multiphoton ionization (MPI) spectrum of benzophenone-1,4-cyclohexadiene mixed clusters and the action spectrum of the hydrogen abstraction reaction are also presented. Good agreement between the action spectrum and the MPI spectrum of the mixed clusters suggested that BPK observed in this study was formed by the intracluster reaction after photoexcitation of benzophenone. We also discuss the reactivity of benzophenone-hydrogen donor clusters on the basis of the nature of the hydrogen donors.

Experimental Section

Benzophenone (Wako; GR grade) was purified by repeated recrystallization from ethanol. Triethylamine, 1,4-cyclohexadiene, ethanol, and 2-propanol were used as hydrogen donors without further purification. We confirmed that these compounds did not fluoresce following laser excitation (308 nm, 355–382 nm, and 465–575 nm).

Neutral benzophenone-hydrogen donor clusters were generated in a supersonic free jet expansion employing a magnetically-operated pulsed valve (General Valve Series 9) with a pulse width of 400-500 μ s. An electric heater was used to heat the valve and a reservoir of benzophenone to 415 K. Benzophenone at a vapor pressure between 1.0 and 5.0 Torr, corresponding to a temperature between 380 and 415 K, was seeded into the hydrogen donor/He gas mixture. The vapor pressure of the hydrogen donors ranged from 1.0 to 50.0 Torr, and the stagnation pressure ranged from 0.8 to 2.0 atm. The mixed gas was expanded into a vacuum chamber through either a conical nozzle (300- μ m diameter, 9-mm length) or a straight nozzle (500- μ m diameter, 5-mm length).

The $S_1 \leftarrow S_0$ excitation spectra of benzophenone and benzophenone-hydrogen donor clusters were recorded by one-color one-photon resonant three-photon ionization (1C3PI). A dye laser (Lumonics HyperDye-300) pumped by a XeCl laser (Lambda Physik EMG 52-MSC) was used as the ionization light source. The laser beam (355-382 nm) was focused with a lens of 50 cm focal length and intersected perpendicularly the free jet at X/D = 15. Ions generated by the MPI process were repelled by a positively charged plate electrode placed 2.5 cm from the focus of the laser beam and were detected with a channel electron multiplier (Murata Ceratron) positioned 4 cm from the ionization region. Both voltages on the electrode and the channeltron were adjusted for effective collection of ions. Signals from the chan-

neltron were amplified by a current amplifier (Keithlay 427).

The same chamber was used to measure the phosphorescence excitation spectrum of benzophenone and the fluorescence excitation and dispersed emission spectra of BPK. Benzophenone in the neutral clusters was excited by pulses from either a XeCl laser (Lambda Physik EMG 52-MSC) or a dye laser (Lumonics HyperDye-300) pumped by the XeCl laser at X/D = 15-25. The laser systems typically produced pulses of approximately 15-ns duration. BPK generated by the photoreduction of triplet benzophenone by hydrogen donors was subsequently excited with pulses from a dye laser (Molectron DL-14P) pumped by an N₂ laser (Molectron UV-22) at X/D = 18-30. The laser beams entered and exited through 10-cm-long baffle arms to reduce scattered light. The excitation and probe pulses were synchronized with a variable time delay from 100 ns to several microseconds. BPK fluorescence and benzophenone phosphorescence were detected by a photomultiplier (Hamamatsu R-928) connected to an amplifier (EG&G Model-115). The emission was passed through cut-off filters prior to detection for the fluorescence and phosphorescence excitation spectrum measurements. A monochromator (Nikon P-250) with a resolution of 2-5 nm was used to measure the dispersed emission spectrum.

The action spectrum of BPK formation was measured in the following way: Dye laser light between 355 and 382 nm was used to excite benzophenone in the neutral cluster. The excitation laser of benzophenone was scanned while fixing the dye laser at 530 nm to probe BPK. Excitation and probe lasers were synchronized with a constant time delay of about 1 μ s.

The signals were integrated with a gated integrator (Stanford SR-250) and then digitized by an analog/digital converter (Stanford SR-245). The output of the lasers was continuously monitored by a photodiode, and a personal computer was used to normalize the signals for laser intensity fluctuations.

Results and Discussion

MPI Spectra of Benzophenone and Benzophenone-Hydrogen Donor Complexes. The nature and dynamics of benzophenone's electronic excited state have drawn much attention because of their importance in photochemistry. The electronic absorption spectrum of benzophenone shows a weak, broad $n\pi^*$ transition centered at 350 nm even in the gas phase. Recently, Ito and co-workers²⁶ and Holtzclaw and Pratt²⁷ reported the excitation spectra of benzophenone with well-resolved vibrational structures under supersonic free jet conditions. Because of the low fluorescence quantum yield of excited benzophenone, these groups used sensitized phosphorescence excitation spectroscopy or, alternatively, an ellipsoidal reflector light collection system. These two groups measured the 0-0 band region of 382-370 nm and the vibronic bands involving the excited-state C=O stretching mode of ~ 1230 cm⁻¹ in the 364–355-nm region. Both spectral regions are characterized by long progressions of about 60 cm⁻¹, which are assigned to an excited-state totally-symmetric torsional mode of the phenyl rings.

Figure 1a shows a 1C3PI spectrum of benzophenone (1.0 Torr) seeded in 1.0 atm of He covering the $S_1 \leftarrow S_0$ origin region. The spectrum consists of several progressions with intervals of 60 cm⁻¹ starting from different origins and is in good agreement with the spectra reported by Ito and co-workers and Holtzclaw and Pratt.

Figure 1b shows a 1C3PI spectrum obtained from a benzophenone (1.0 Torr)-triethylamine (10.0 Torr) mixed expansion. The sharp peaks vanished completely, and only a broad and diffuse spectrum was observed. The observed spectrum is similar to the envelope of the 60-cm⁻¹ progressions of bare benzophenone in the corresponding region. Similar broadening of the MPI spectrum was observed when ethanol, 2-propanol, and 1,4-cyclohexadiene were used as hydrogen donors. The spectral shape did not change significantly when the pressure of the hydrogen donor was increased from 1.0 to 50.0 Torr.

The broadening of the spectrum in benzophenone-hydrogen donor mixed expansions probably arises from the generation of molecular clusters. The spectral congestion caused by low-frequency van der Waals (vdW) modes and isomer formation must



Figure 1. MPI spectra of (a) benzophenone (1.0 Torr) and (b) benzophenone (1.0 Torr)-triethylamine (10.0 Torr) mixed system seeded in 1.0 atm of He obtained by one-color one-photon resonant three-photon ionization. These spectra cover the $S_1 \leftarrow S_0$ origin region of benzophenone. The intensities of these spectra are not normalized with respect to the laser power spectrum (broken line).



Figure 2. Fluorescence excitation (Ex.) and dispersed emission (Em.) spectra obtained at 1.0 μ s after 308-nm excitation for the benzophenone (1.0 Torr) and 1,4-cyclohexadiene (50.0 Torr) mixed expansion. The XeCl and dye lasers were positioned at X/D = 15 and 20, respectively. The dispersed emission spectrum was obtained by 540-nm excitation. The spectral response of the fluorescence was not corrected.

produce such a broad spectral feature.

Mass-resolved spectroscopy should provide much information on the structure, energetics, and reactivity of molecular clusters. Mass analysis of the benzophenone-hydrogen donor clusters employing a vacuum-ultraviolet laser and a time of flight spectrometer is in progress to determine the association number of the solvent molecules.

Emission Spectra of BPK in a Supersonic Free Jet Expansion. It is widely well established that BPK is generated by the photoreduction of benzophenone by hydrogen-donating solvents. In the condensed phase, BPK has an absorption band in the visible region with a maximum at around 545 nm and a shoulder at 500–520 nm. Fluorescence of BPK characterized by a maximum at 575 nm is readily observable after excitation into the D_1 state.^{28–32}

We tried to detect hydrogen abstraction by benzophenone in a supersonic free jet expansion by monitoring the fluorescence of BPK. Figure 2 shows the fluorescence excitation (Ex.) and dispersed emission (Em.) spectra obtained in the mixed expansion of benzophenone (1.0 Torr)-1,4-cyclohexadiene (50.0 Torr) seeded in 1.0 atm of He. These spectra were measured at 1.0 μ s after 308-nm excitation. The dye laser was tuned to 540 nm to measure



Figure 3. (a) Dispersed emission spectrum for the benzophenone (1.0 Torr) and 1,4-cyclohexadiene (50.0 Torr) mixed expansion obtained by one-color excitation at 308 nm. (b) Laser power dependence of BPK fluorescence intensity by 308-nm excitation.

the dispersed emission spectrum. The spectra were very similar to those of BPK in the condensed phase. The good agreement of the spectral data indicated that the luminescent chemical species generated in the mixed expansion was BPK. Contrary to the case of 1,4-cyclohexadiene, no ketyl radical formation was observed when 2-propanol, ethanol, or triethylamine was used as the hydrogen donor.

The fluorescence decay matched the time profile of the dye laser pulse. Considering the time resolution of about 15 ns of the system used in this study, the fluorescence lifetime of BPK was estimated to be less than 10 ns. The emission of BPK in the 550–650-nm region attributed to doublet-doublet transition was reported to have a fluorescence lifetime of approximately 2–5 ns in solution at room temperature^{29,33,34} and ~20 ns in a low-temperature matrix.³⁰ Therefore, fluorescence lifetime measured in a supersonic jet agrees well with that in the condensed phase.

Two mechanisms for BPK generation can be proposed from the above results: (i) collision-induced reaction and (ii) intracluster reaction in a benzophenone-1,4-cyclohexadiene neutral cluster.

To reveal which mechanism is correct, a dispersed emission spectrum for the mixed expansion was measured for the one-color 308-nm excitation (Figure 3a). The spectrum is similar to that obtained for the 540-nm excitation shown in Figure 2. The laser power dependence of the fluorescence intensity was also examined: The log-log plot (Figure 3b) of the fluorescence intensity versus the XeCl laser intensity has a slope of 1.9 ± 0.1 , indicating that the fluorescence was generated by a two-photon excitation process. This fact implies that BPK generated by the 308-nm excitation absorbed an additional photon within the time width of the laser pulse. Therefore, in contrast to the gas-phase reaction initiated by collisions,²⁴ the reaction in a supersonic free jet expansion must occur at a very fast rate. This indicates that the BPK observed in this study was generated by the intracluster reaction in the benzophenone-1,4-cyclohexadiene neutral clusters.

If bare BPK absorbs and emits light under collision-free conditions, the spectral shape should depend on the excitation wavelength. However, the shapes of the emission spectra obtained with 540- and 308-nm excitation (Figures 2 and 3a, respectively) are in good agreement with each other as well as with the emission spectra of BPK in the liquid phase. The shape of the emission spectrum in a supersonic jet did not alter by changing the distance between the orifice and excitation laser beam up to $X/D \approx 30$, where collisional relaxation of hot BPK radicals does not play an important role. These facts suggest the existence of a heat bath of hot BPK radicals and that the generated BPK is still surrounded by solvent molecules. Therefore, intracluster energy redistribution and evaporation of solvent molecules from the clusters must cool the excited radical to lower vibrational levels of the first excited doublet state.

Action Spectrum of BPK Formation. Jet-cooled benzophenone emitted long-lived phosphorescence by 382-370-nm excitation. By monitoring the phosphorescence intensity of benzophenone at X/D = 15, we obtained the $S_1 \leftarrow S_0$ excitation spectra of benzo-



Figure 4. Phosphorescence excitation spectra of (a) benzophenone and (b) benzophenone-1,4-cyclohexadiene mixed system seeded in 1.0 atm of He obtained by monitoring the phosphorescence intensity at X/D = 15.



Figure 5. (a) Action spectrum of BPK formation. The excitation laser of benzophenone was scanned while fixing the probe laser at 530 nm. Excitation and probe lasers were synchronized with a constant time delay $(\sim 1 \ \mu s)$. The experimental conditions employed to obtain the spectra shown in Figure 4 were retained during this experiment. (b) MPI spectrum of benzophenone-1,4-cyclohexadiene mixed clusters obtained by one-color one-photon resonant three-photon ionization.

phenone (Figure 4a) and benzophenone-1,4-cyclohexadiene (Figure 4b) mixed system seeded in 1.0 atm of He. Good agreement of the excitation spectrum of benzophenone with the 1C3PI spectrum (Figure 1a) suggests that a collision-free environment was successfully achieved under our experimental conditions. As shown in Figure 4b, phosphorescence was effectively quenched in the benzophenone-1,4-cyclohexadiene mixed cluster. From the ratio of intensities of the 60-cm⁻¹ torsional mode in Figure 4, we estimated that the proportion of bare benzophenone that did not form a cluster in the mixed expansion was very low. Similar phosphorescence quenching was observed in the benzophenone-triethylamine mixed expansion. However, the phosphorescence intensity did not decrease when ethanol or 2-propanol was used as a hydrogen donor.

To confirm that BPK observed in the supersonic free jet expansion was generated by the intracluster reaction, we took an action spectrum of BPK formation (Figure 5a) under the experimental conditions employed to obtain the spectra shown in Figure 4. The excitation dye laser of benzophenone was scanned while fixing the other dye laser at 530 nm to probe BPK. Excitation and probe lasers were synchronized with a constant time delay (~1 μ s). A linear relation was observed between the fluorescence intensity and probe laser power. As seen in the figure, hydrogen abstraction occurred even when the excitation laser wavelength was close to the origin region of the $S_1 \leftarrow S_0$ transition of benzophenone. Figure 5b shows the MPI spectrum of benzophenone-1,4-cyclohexadiene mixed clusters. Good agreement of these spectra strongly suggests that BPK observed in this study is formed by the intracluster hydrogen abstraction reaction following photoexcitation of benzophenone.

Reactivity of Benzophenone-Hydrogen Donor Clusters. As mentioned above, different hydrogen donors showed different reactivity in photoexcited benzophenone-hydrogen donor clusters. 1,4-Cyclohexadiene and triethylamine both quenched the benzophenone phosphorescence, but ethanol and 2-propanol did not. Moreover, fluorescence due to the formation of BPK was observed only in the benzophenone-1,4-cyclohexadiene mixed clusters and not when ethanol, 2-propanol, or triethylamine was used as the hydrogen donor. In this section, we will discuss the difference in the reactivity of hydrogen donors in the clusters.

In our previous investigation,²⁴ we measured the quenching rate constants of triplet benzophenone by several kinds of hydrogen donors in the gas phase. The results suggested that the rate constants in the gas phase show a trend similar to those in the liquid phase. The quenching rate constants for amines are 30-500 times larger than that for 2-propanol in the gas phase, which is comparable to a relative reactivity of $1.5 \times 10^2 - 10^3$ in the liquid phase. The quenching rate constant of 1,4-cyclohexadiene is also 50 times larger than that of 2-propanol in the gas phase.

There are two plausible reasons why BPK fluorescence was not observed in the benzophenone-alcohol clusters: The first is the inefficiency of reaction by alcohols based on their small quenching rate constants in the gas and liquid phases. The second is the rigid orientation within the clusters; the hydrogen-bonded structure of the benzophenone-alcohol mixed cluster may not be amenable to hydrogen abstraction because cleavage of the O-H bond in alcohols does not occur in the reaction. When the reaction proceeds in the mixed cluster, an α -hydrogen should be transferred.

It has long been established that the reaction rates of triplet benzophenone with various amines are close to the diffusioncontrolled rate and the yields of the reaction are very high in the condensed phase.^{13,14,16,17,19} Cohen and co-workers^{16,17} proposed the following reaction mechanism to explain the effective photoreduction of triplet benzophenone by amines to yield BPK: First, an electron is transferred from the amine to the triplet state of benzophenone, forming a charge-transfer or ion pair complex. This complex is then quenched either by proton transfer generating BPK and an amine radical or by back electron transfer following spin inversion resulting in the ground-state benzophenone and amine. In this generally accepted mechanism, the charge-transfer interaction plays an important role, and the mechanism is represented as follows (scheme 1):



The quenching rate constant measurements in our previous investigation have suggested that, in addition to its role in the condensed phase, the charge-transfer interaction also plays an important role in the photoreduction process of benzophenoneamine systems in the gas phase.²⁴

Recently, Miyasaka et al.³⁵ have studied the photoreduction of excited benzophenone with several kinds of amine by means of picosecond-femtosecond laser photolysis and time-resolved transient absorption spectroscopy. According to their results for the benzophenone-dimethylaniline (DMA) system, the charge recombination rate of the ion pair produced by the excitation of the charge-transfer complex formed in the ground state is much greater than that of the ion pair formed by the electron transfer during the encounter between excited benzophenone and DMA in solution. From the experimental results, they concluded that the benzophenone-DMA ion pair formed by the excitation of the ground-state complex has a rather rigid structure and cannot reorient to take a structure suitable for proton transfer before recombination, whereas the ion pair formed by the encounter of excited benzophenone and DMA has a rather loose structure and a lifetime long enough to form a geometry suitable for proton transfer. Though it is somewhat difficult to compare directly the structure and dynamics of ground-state complexes formed in a supersonic free jet expansion to the liquid phase, we can expect that the quenching mechanism of triplet benzophenone in the liquid phase is applicable for the mixed clusters.

Very recently Kajii et al.³⁶ observed the hydrogen-bonded 1:1 complex formation of BPK and triethylamine in nonpolar solvents by means of transient absorption spectroscopy. They found that the equilibrium constants for complex formation are $99 \pm 6 \text{ M}^{-1}$ in cyclohexane and $37 \pm 4 \text{ M}^{-1}$ in benzene, and that BPK in the complex is nonfluorescent whereas bare BPK has a relatively high fluorescence quantum yield under the same experimental conditions. According to their results, if BPK is formed in the benzophenone-triethylamine mixed clusters, it easily forms a complex with the amine and excited BPK is quenched in the complex.

The effective quenching of triplet benzophenone by 1,4cyclohexadiene in the gas and liquid phases may be explained in terms of the fairly low bond energy of the C-H bond which is cleaved in the reaction. In addition, it should be noted that 1,4-cyclohexadiene has four equivalent hydrogen atoms. This fact probably makes it easy for the molecules in the mixed clusters to take an orientation suitable for hydrogen abstraction.

Conclusion

The study of chemical reactions in solute-solvent clusters enables us to obtain information on the mechanisms of liquid-phase reactions at a molecular level. In this investigation, the photochemical reactions in the molecular clusters of benzophenone and hydrogen donors formed in a supersonic free jet expansion were studied.

We found that benzophenone underwent photoreduction to form BPK in the mixed expansion of benzophenone and 1,4-cyclohexadiene by monitoring fluorescence of the radical. We have confirmed from the following observations that BPK was formed by the intracluster reaction after photoexcitation of benzophenone: (i) BPK was generated within the time width of the 308-nm laser pulse. (ii) The action spectrum of BPK formation was in good agreement with the MPI spectrum of benzophenone-1,4-cyclohexadiene mixed cluster in the $S_1 \leftarrow S_0$ origin region of benzophenone. This study is the first observation of hydrogen abstraction in a neutral molecular cluster.

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$\pi^* \leftarrow$ n Transitions of Monohalo-Substituted Phenyl Radicals in Solid Argon at 12 K

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Monosubstituted halocyclohexadienyl radical isomers are produced and trapped in solid argon from the reaction of hydrogen atoms with monosubstituted halobenzene molecules. These radicals are converted into the corresponding structural isomers of monohalophenyl radicals upon photolysis with a filtered mercury arc lamp. The absorptions of fluorophenyl radicals at 279.0, 284.6, and 288.0 nm, chlorophenyl radicals at 274.2, 286.4, and 294.2 nm, and bromophenyl radicals at 278.0, 285.0, and 295.0 nm are assigned to the π^* (2²B₁) \leftarrow n (1²A₁) transitions of ortho-, para-, and meta-substituted phenyl radicals, respectively.

Introduction

Spectroscopic information on the phenyl radical, one of the most important hydrocarbon radicals, is rare. The reason for this is the high reactivity of phenyl radical with itself and the parent molecule from which it is produced. Phenyl radical has been generated in sufficient concentration for recording its infrared absorption spectrum by the photodissociation of benzyl peroxide in solid argon.¹ The most complete work on the visible absorption spectroscopy of phenyl and halophenyl radicals was that of Porter, in which it was produced by the gas-phase flash photolysis of halobenzene molecules.² In the ultraviolet region, a transient absorption band near 260 nm was found for phenyl, formed by the pulse radiolysis of iodobenzene solution, and was correlated with the UV absorption of benzene near 260 nm.³ Direct observation of another transition at 245 nm was reported from the flash photolysis of a series of halobenzenes in the gas phase.⁴ In solid argon, a radical with an absorption peak at 288 nm was produced from the photolysis of the cyclohexadienyl radical and was attributed to the phenyl radical.⁵ This transition was correlated with the absorption band of the phenyl radical in solution at 260 nm.⁵ Photoconversion of ipso-fluorocyclohexadienyl radical to HF and the phenyl radical has been investigated by Jacox.⁶ In the present study, we have investigated the formation and the photoconversion of halocyclohexadienyl radicals to halophenyl radicals, assigned the electronic energy levels responsible for the ultraviolet absorption of the halophenyl radicals, and explicitly

distinguished between o-, p-, and m-halophenyl isomers. From the photolysis behavior of these species, the assignments of the o-, p-, and m-halocyclohexadienyl radical isomer absorption spectra follow.

Experimental Section

The matrix isolation apparatus consisted of a closed cycle helium refrigerator (Air Products, Inc., Models 1R02A and DE202) with a nickel-plated copper window mount attached to the cold head. A sapphire disk, having a thickness of 1 mm and a diameter of 25 mm, was mounted onto the sample holder using an indium gasket to maintain good thermal contact. The temperature of the copper sample holder was typically maintained near 12 K monitored by a digital temperature controller (Air Products, Model 3700). The cold head was enclosed in a stainless steel vacuum shroud (Air Products APD, Model 202) which had four ports surrounding the sapphire window. In our system, one of the ports was devoted to the inlet lines. Three optical quality quartz windows, each with a thickness of 5 mm and a diameter of 45 mm, were affixed to the other three ports for spectroscopic studies and access for photolysis radiation.

Absorption spectra were recorded with an IBM UV-vis absorption spectrophotometer (Model 9420) interfaced to an IBM PC/XT computer. All of the spectra were recorded with a spectral bandwidth of 0.5 nm and data points spaced 0.2 nm apart.

A high-pressure mercury arc lamp (1000 W) with a water filter and two Pyrex filters with cut-off wavelengths at 316 nm (316-1000 nm) and 336 nm (336-1000 nm) were used for photolysis studies.

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