5984 J. Phys. Chem. A **2005,** *109,* 5984−5988

Photolysis of CBr_4 and Its Transient Solvent Stabilized $(CBr_3^+//Br^-)_{Solv}$ Ion Pair

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Received: January 12, 2005; In Final Form: April 15, 2005

In this paper we describe the mechanism of the photodissociation of CBr_4 in various solvents. We have monitored and identified the intermediate species and determined the growth and decay rates of the excited states and metastable species formed during the photodissociation process by means of ultrafast time-resolved spectroscopy. On the basis of the experimental data presented in this paper, the observed transient spectra and species have been assigned to the stabilized solvated ion pair $(CBr_3^+//Br^-)_{solv}$.

Introduction

The vast majority of research concerned with the photochemistry of alkyl halides has been devoted almost exclusively to the photolysis and reactions of CCl_4. However, the study of bromoalkanes has been increasing quite rapidly because it is now realized that they have as great a potential to dissociate ozone as alkyl chlorides.[1,2] Radiolysis experiments have shown that alkyl halides and especially alkyl bromides in solution have a high cross-section for electron capture, which induces further reactions that generate metastable species such as radicals and ions. High-energy electron[3,4] and two-photon excitation of CCl_4 reveal[5] that a broad band with a maximum at 480 nm is formed “immediately” after excitation. This band has been attributed to various species, including the CCl_4^+ cation[6] and a charge-transfer complex between CCl_4 and Cl.[7,8]

Radiolysis of CCl_4 in methyl cyclohexane (MCH) solution with 50-ns high-energy-electron pulses at low temperatures was found to generate a broad transient absorption band with a maximum at 470 nm that was assigned to the CCl_3^+ cation of the solvent-separated ion pair $(CCl_3^+//Cl^-)_{solv}$.[9−11]

Two 266-nm photon direct photoionization of liquid CCl_4 has been reported,[5] even though the ionization potential of liquid CCl_4 is 11.47 eV and the energy of a 266-nm photon is 4.66 eV. The transient absorption band formed by this nonlinear process was reported to have a maximum at ~490 nm and was assigned to the CCl_3^+ Cl^- solvated ion pair.[5] However, single-photon dissociation experiments in solution and formation of radical ion pairs have not been reported up to now for either CCl_4 or CBr_4 in solution.

Radiolysis experiments[11] have been performed in solutions of CCl_4 in various solvents. These experiments were aimed at understanding the effect that temperature, cationic scavengers, and electron scavengers have on the products of radiolysis and their influence on the reaction mechanism. Lately, CBr_4 photochemistry has been pursued with increasing interest because of the tendency of its photolysis products to react with chlorine in the stratosphere and promote chlorine radicals that contribute to maleficent atmospheric reactions.[12,13] CBr_4 photodissociation in the gas phase has been studied by excitation with 193-nm photons emitted by an ArF excimer laser[14] and in solution using high-energy electron radiolysis[15] and excimer laser photolysis.[16] The high-energy electrons used in the radiolysis experiments are sufficiently energetic to ionize both the solvent used and CBr_4. Subsequently, the solvent transfers its charge to CBr_4, generating the CBr_4^+ cation. The ground state of CBr_4^+ produced directly by the Franck−Condon ionization of CBr_4 is predicted by DFT calculations[17] to be unstable with regard to CBr_3^+ and Br. It has also been shown that assisted by Jahn−Teller distortion, CBr_4^+ is unstable and dissociates directly into products. Direct ionization of gas-phase CBr_4 to $CBr_3^+ + Br^-$ requires 10.27 eV,[17] or 9.85 eV calculated from CBr_4 fragmentation data.[18] Therefore, it is assumed that photolysis or radiolysis of CBr_4 with energies 10.27 eV and above will yield $CBr_3^+ + Br^-$. Using the 10.27 eV value for the photoionization of CBr_4 and 2.44 eV for the C−Br bond dissociation energy,[19] the CBr_3^+ ionization potential was estimated by DFT calculations to be 7.87 eV.[17]

In this paper we present data that show that a broad, structureless transient absorption band with a maximum at 470 nm is formed after one-photon, 266-nm excitation of CBr_4 in a 7.5×10^{-3} M CBr_4/cyclohexane solution. It will be shown that the data support the assignment of this band to a solvent-stabilized solvated ion pair $(CBr_3^+//Br^-)_{solv}$.

Results and Discussion

The experimental results on the photolysis of CBr_4 in solution presented in this paper were obtained at room temperature in various solvents. The solvents were selected to be either polar or nonpolar, act as cation or radical scavengers, and have ionization potentials higher than 10.27 eV and therefore could not be ionized by one- or even two-photon, 266-nm (4.66 eV) excitation. The ionization potentials (IPs)of the solvents used are listed in Table 1. All solvents were spectroscopic grade; CBr_4 (Aldrich, 99.99% pure) was used without further purification. The experimental system which has been described previously[20] consists of picosecond and femtosecond lasers, and a charge-coupled device, CCD, was used to detect the transient time-resolved spectra. The CBr_4 solution was excited either by a fourth harmonic, 266-nm pulse of a picosecond Nd/YAG laser or by the third harmonic, 267-nm pulse of a Ti/Sapphire femtosecond laser. The energy of these pulses is sufficient to induce photodissociation (266 nm = 4.66 eV, C−Br bond = 2.44 eV) but not CBr_4 ionization which requires 10.27 eV. The power of the laser pulses was sufficiently low to eliminate the possibility of two-photon transitions and allows only single-photon dissociation. The inset of Figure 1 shows that the

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10.1021/jp050221x CCC: $30.25

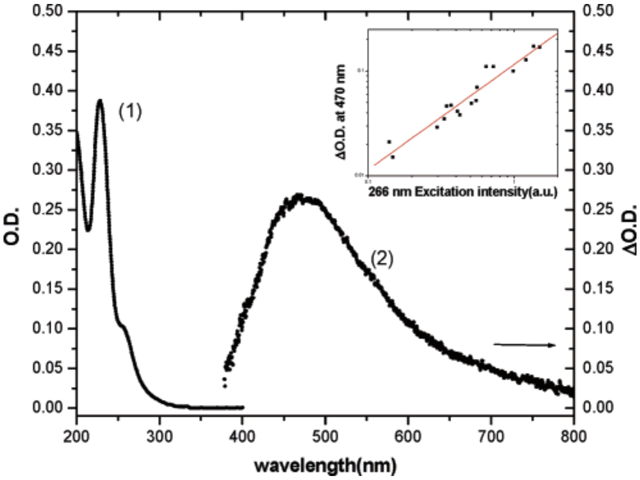

Figure 1. (1) Absorption spectrum of CBr_4 in cyclohexane. (2) Transient absorption spectra of CBr_4 in cyclohexane recorded 100 ps after excitation with a 266-nm pulse. Inset: Intensity dependence of (2) on 266-nm pulse intensity. Slope = 1.01.

TABLE 1: Properties and Kinetics of CBr_4 Transient in Various Solvents

	solvent properties		transient kinetics	
solvent	ϵ	IP (eV)	τ_{rise} (ps)	τ_{decay} (ns)
cyclohexane	2.02	9.88	58	1.5×10^3
dodecane	2.01	9.93	38	1.1×10^3
1-octanol	10.25		25	0.443
2-propanol	20.18	10.16	24	0.164
acetonitrile	36.64	12.22	56	3.5
propylene carbonate	66.14		58	5.4

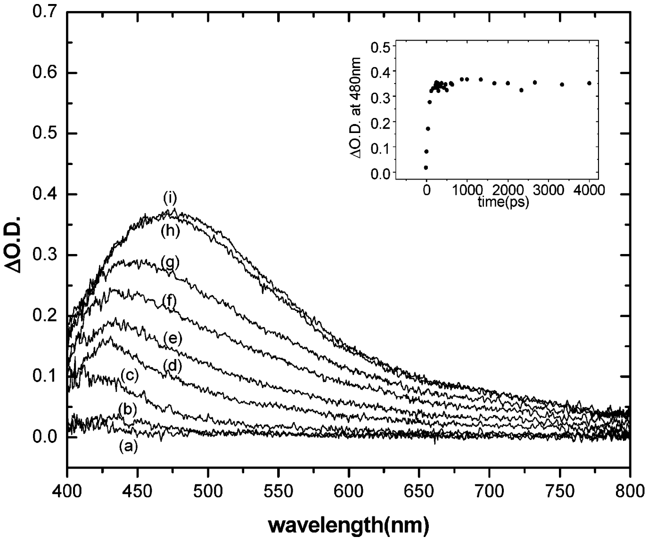

Figure 2. Transient absorption spectra of CBr_4 in cyclohexane at room temperature excited with a 266-nm laser pulse, recorded at (a) −13 ps, (b) 0 ps, (c)13 ps, (d) 27 ps, (e) 40 ps, (f) 53 ps, (g) 67 ps, (h) 133 ps, and (i) 200 ps after excitation (from bottom to top).

absorbance of this transient depends linearly on excitation intensity, which indicates strongly that the photolysis was performed by a single-photon process. Excitation of a 7.5 × 10^{-3} M CBr_4/cyclohexane solution with a 20-ps, 266-nm pulse is expected to photodissociate CBr_4 to $CBr_3 + Br$. The concerted dissociations to $CBr_2 + Br + Br$ or to $CBr_2 + Br_2$ are not considered as equally probable and, as stated previously the photon did not contain the energy necessary to ionize CBr_4 to CBr_4^+ or CBr_3^+ cations. After excitation, a broad structureless transient absorption band with a maximum at 480 nm was observed. The spectrum of this transient recorded 100 ps after excitation of CBr_4 in cyclohexane is shown in Figure 1. The spectrum consists of a broad structureless band with a bandwidth of ~170 nm and a wavelength maximum located at 470 nm. The characteristics of this band are strikingly similar to the transient band observed in the "two-photon" photoionization of CCl_4.[5]

The formation of the CBr_4 photolysis intermediates was monitored by means of transient time-resolved spectroscopy, and their spectra, displayed in Figure 2, are in the form of change in optical density, ΔA vs λ at various times after excitation. This figure shows that at $t = 0$ ps a new absorption band is formed with a maximum $\Delta A = 0.03$ at ~425 nm. At $t = 13$ ps the band increases in intensity, and its maximum shifts to longer wavelengths. At $t = 100$ ps it consists of a broad, structureless band extending from 400 to 600 nm with a bandwidth, FWHM, of 125 nm, while its intensity has reached a value of $\Delta A = 0.37$ and its maximum has shifted to 480 nm. The spectra shown in Figure 2 maintain the same shape and wavelength maximum from about 100 ps after excitation to about 1 μs, suggesting that the intermediate species assigned to this band is rather stable. Possible assignments for this absorption band include the CBr_3 radical, which is expected to be an initial product of the CBr_4 dissociation. However this assignment may be excluded, because CBr_3 has been reported not to have absorption in the visible region of the spectrum.[21] During the early times after excitation, <10 ps, a transient absorption appears with a maximum in the 425-nm region, which is probably due to $S_1 \rightarrow S_n$ excited-state absorption. The short decay lifetime of this band and its shift to the 480-nm band at the same rate as the formation of the 480-nm transient suggests that it may be its precursor. Because the ionization potential of CBr_4 is much higher than the 4.66 eV energy of the exciting 266-nm photon, assignment of the 480-nm band to direct ionization to CBr_4^+ (10.2 eV)[17] or directly from CBr_4 to CBr_3^+ (9.85 eV) may also be eliminated. Figure 2 also shows that the intensity of the 480-nm transient remains constant for several hundred nanoseconds and then, as listed in Table 1, decays with a microsecond lifetime. From the time-resolved spectra presented in Figure 2, we estimated the rate of formation of the 480-nm intermediate to be 1.7×10^{10} s^{-1}. The rationale for such a fast formation rate is discussed when we propose assignment of this band.

Similar experiments were performed in a solution of 7.5 × 10^{-3} M CBr_4 in dodecane. The transient spectra recorded at various times after 266-nm excitation and shown in Figure 3also consist of a broad, structureless absorption band with a maximum intensity at 480 nm and formed with a rate of 2.6×10^{10} s^{-1} and a decay lifetime of about 1 μs (see Figure 3 inset). To establish the nature of the 480-nm transient, we photodissociated CBr_4 in several additional solvents that are known to be ion or radical scavengers but that vary in polarity. The dielectric constants of the solvents used are listed in Table 1. Ethanol and other alcohols are known to be cation scavengers that operate by proton transfer.[22] We excited CBr_4 in 7.5 × 10^{-3} M ethanol and 2-propanol solutions and recorded their transient spectra. For 2-propanol, we observed initially a transient absorption band with a maximum at ~440 nm and ΔA of 0.045. The absorption maximum shifts with time to longer wavelengths, achieving a maximum absorption intensity of 0.165 ΔA at 540 nm, 60 ps after excitation. The data depicted in Figure 4 show that in 2-propanol the decay rate of the transient increases from 10^6 to 2.3×10^9 s^{-1}, which is the result of the high reactivity of the alcohol with the transient species.

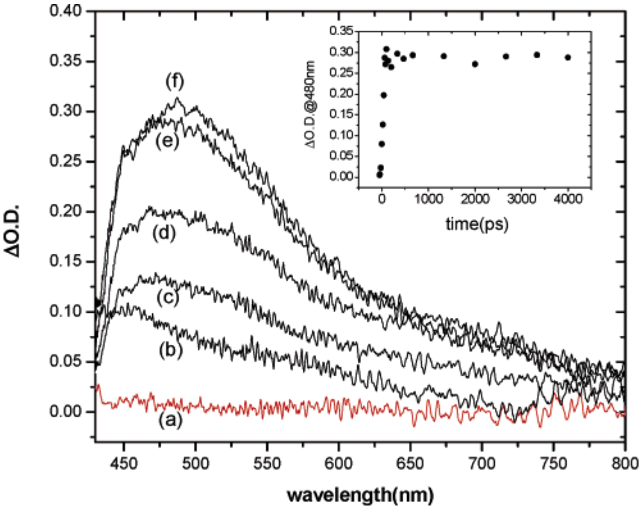

Figure 3. Transient absorption spectra of CBr_4 in dodecane excited with a 266-nm pulse, recorded at (a) −40 ps, (b) 0 ps, (c) 20 ps, (d) 40 ps, (e) 60 ps, and (f) 100 ps after excitation. Inset: Formation kinetics.

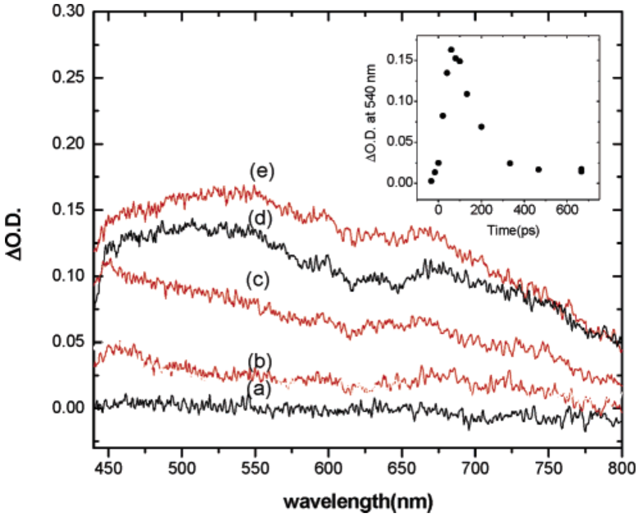

Figure 4. Transient absorption spectra of CBr_4 in 2-propanol at room temperature excited with a 266-nm laser pulse, recorded at (a) −33 ps, (b) 0 ps, (c) 20 ps, (d) 40 ps, and (e) 60 ps after excitation (from bottom to top).

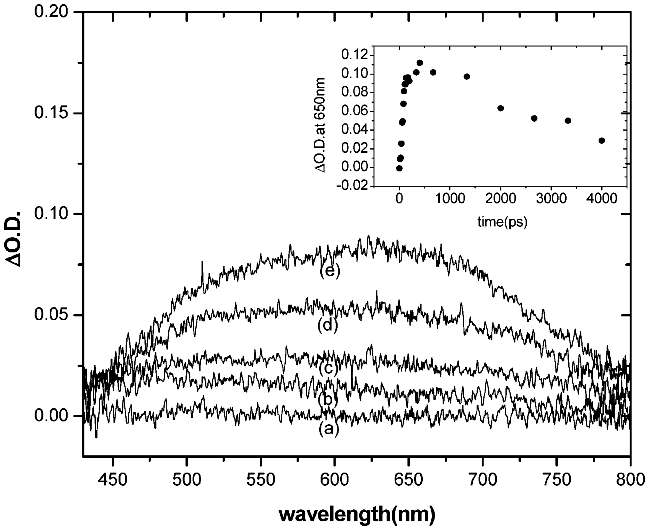

Figure 5. Transient absorption spectra of CBr_4 in acetonitrile excited with a 266-nm laser pulse, recorded at (a) −13 ps, (b) 0 ps, (c) 40 ps, (d) 67 ps, and (e) 100 ps after excitation. Inset: Formation and decay kinetics.

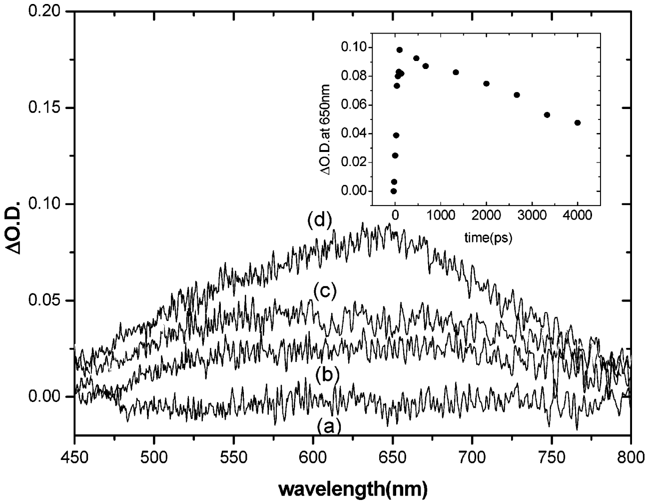

Figure 6. Transient absorption spectra of CBr_4 in propylene carbonate at room temperature excited with a 266-nm laser pulse, recorded at (a) −33 ps, (b) 0 ps, (c) 20 ps, and (d) 80 ps after excitation Inset: Formation and decay kinetics.

Highly polar solvents such as acetonitrile and propylene carbonate (see Table 1) are known to interact with almost any ion that might have been formed by ionization or charge transfer to generate fast-decaying intermediate species. Under the same 266-nm excitation conditions as with cyclohexane and alcohol, a 7.5×10^{-3} M CBr_4/acetonitrile solution and then a 7.5×10^{-3} M CBr_4/propylene carbonate solution produced the time-resolved transient spectra shown in Figures 5 and 6. They consist of a single rather weak, but very broad, absorption band with a maximum at 635 nm that is formed with a rate of 1.8×10^{10} s^{-1} and decays with a lifetime of 3.5 ns. The formation rates of these intermediate species are essentially the same as the ones observed for the nonpolar hydrocarbons used as solvents; however, the decay lifetimes are orders of magnitude faster. In addition, the absorption bands of the polar solvent transient species were found to shift toward longer wavelengths that resulted in very broad structureless bands, extending from ∼450 to ∼800 nm with intensity maxima located in the 635-nm region. Our data suggest that polar solvents generate intermediate species whose maximum absorption wavelength red-shifts almost linearly with the value of the solvent dielectric constant, Figure 7. Polar solvents also induce shorter decay lifetimes and lower transient stability than those measured for nonpolar solvents. These results strongly suggest that the 480-nm intermediate is a cation.

We must therefore account for the formation of a cation, because direct formation of ions is not feasible when one considers the energies of the exciting photon, 4.66 eV, and the 10.2 eV ionization potential of CBr_4. Similarly, there is not sufficient excess excitation energy to ionize the CBr_3 radical to CBr_3^+, which has an ionization potential between 7.5 eV[18] and 7.87 eV.[17] In addition, the excitation energy used in our experiments is also inadequate to excite or generate ions of the solvent, which if formed could generate bromoalkane ions by charge transfer. Rise and decay lifetimes of the CBr_4 photolysis transients in the various solvents used are also shown in Table 1. Cyclohexane and dodecane are both nonpolar solvents with ionization potential values about equal to those of CBr_4 in solution, while ethanol, acetonitrile, and propylene carbonate are polar molecules with ionization potentials slightly higher.

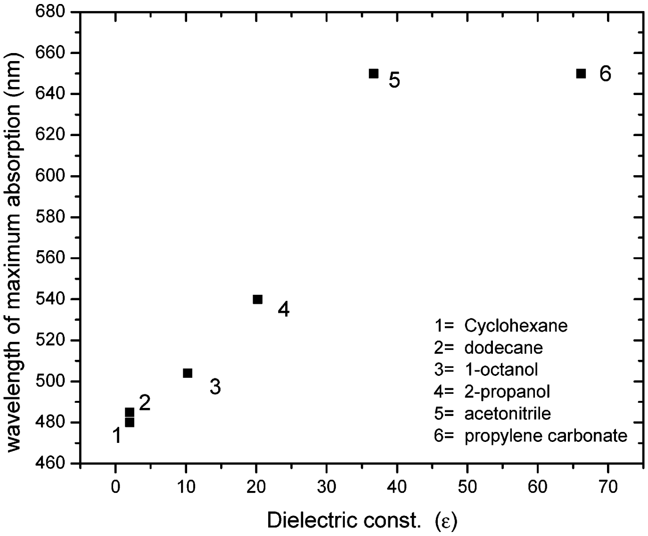

Figure 7. Maximum absorption wavelength of the CBr_4 photolysis intermediates as a function of solvent dielectric constant.

Time-resolved transient absorption data show that a transient species is formed immediately upon excitation; therefore diffusion-controlled reactions, which occur orders of magnitude slower, may be safely eliminated. The transient absorption spectra in all solvents are composed of a broad structureless band; however, the shape and location of the absorption band maximum was found to depend on the solvent, as is its rate of formation and especially the decay lifetime. The CBr_4 transient spectra in acetonitrile and propylene carbonate solutions are shown in Figures 5 and 6, respectively, and their kinetics are depicted in the insets in the form ΔA vs time (ps). Close examination of the 480-nm transient absorption bands in various solvents, shown in Figures 2−6, reveals that the absorption maximum shifts to the red with increasing dielectric constant, Figure 7. In addition this transient absorption in polar solvents becomes very broad, void of structure, and rather symmetric. As the polarity of the solvent increases, the 450-nm maximum that appears during the first 10 ps after excitation disappears, as shown in Figures 5 and 6 for acetonitrile and the very polar propylene carbonate solutions, respectively. The 2-propanol and ethanol transient spectra appear to form band maxima at about 675 nm, several picoseconds after excitation, confirming that a cation-scavenging process takes place between the solvent and CBr_4 photolysis products. The above data suggest that the 480-nm spectrum is due to a cation, which in cyclohexane solution and other nonpolar solvents decays with a lifetime of 2 μs. The long lifetime of this transient tends to eliminate the assignment of this absorption band to excited states absorption, and its assignment to the CBr_3 radical is excluded because it absorbs in the UV region.[21] The reaction of this 480-nm intermediate with polar solvents, its lifetime, wavelength, and shape of its spectrum suggest that the 480-nm band belongs to a transient cation.

Direct ionization of CX_4 leads to CX_4^+ (where X = halogen), which is known to be unstable and to dissociate immediately to $CX_3^+ + X$.[23−25] The thermodynamic instability of CBr_4^+ and the fragmentation of the parent ion to form CBr_3^+ is predicted also by DFT and is supported by the absence of CBr_4^+ in mass spectroscopic data of CBr_4. DFT Gaussian calculations[17,26,27] have shown that the CBr_3^+ cation is stable in the gas phase, and its detailed structure has been determined.[25,26] On the basis of experimental data, we propose that a 266-nm one-photon dissociation process of CBr_4 in solution forms CBr_3^+ cations by either of the following two processes.

1. Even though direct ionization of CBr_4 in the gas phase with one 26-nm photon is not energetically feasible, the solvated excited state of CBr_4 may dissociate to $CBr_3^+ + Br^-$. Both of these ions are stable, and the solvation energy could be large enough to dissociate the excited species to the two ions. The fact that the formation rate of the 480-nm species is 1.7×10^{10} s^{-1} argues against this mechanism.

2. The excited CBr_4 dissociates to CBr_3 and Br.[15,28] However, the ground-state gas-phase CBr_3 radical absorbs in the 270-nm region, and therefore it is not expected to absorb in solution in the 480-nm region. In addition, it is thought to be very short-lived; therefore, it is excluded from being the species responsible for the long-lived 480-nm spectrum. The electron affinity of Br is −3.36 eV and its electronegativity is 2.96 eV; CBr_3, which has been studied by IR in inert matrixes,[29] has an electron affinity value of +0.57 eV and electronegativity value of 3.74 eV and is known to be a highly polarizable species. The 0.57-eV spin unrestricted electron affinity of CBr_3 suggests that this radical may easily be induced by electrostatic forces in solution to transfer an electron to bromine and generate an ion pair.

Therefore, while CBr_3 and Br still reside in their formation cage, electron transfer from CBr_3 to Br is promoted that results in the formation of the ion pair, CBr_3^+ Br^-. In the free form the ion pair may be unstable or recombine; however, in solution a dipole is induced in the nonpolar cylohexane by the charge field of the ion pair, and the solvent dipoles align around the ion pair, providing the energy needed for the stabilization of the now-solvated ion pair. To separate and prevent recombination of the charged ions, solvent molecule(s) are imbedded between the anion and cation, thus stabilizing further the now-solvent-separated solvated ion pair, $(CBr_3^+//Br^-)_{solv}$. Because the induced interactions are related to the distance by $1/R$, the electrostatic interaction, the formation of the ion pair is only feasible while CBr_3 and Br are still in the solvent cage. Therefore, owing to their close proximity in the cage, the relatively fast formation of the ion pair is expected. At slower rates of formation the radicals may diffuse out of the cage, making charge transfer from one radical to the other very inefficient if not impossible. If the two ions CBr_3^+ and Br^- are not separated by one or more solvent molecules, they will recombine with rate orders of magnitude faster than the measured microsecond decay lifetime of the 480-nm transient absorption band.

Even though we represent the 480-nm species as a complete cation and anion with +1 and −1 charges, respectively, there is a possibility that they exist in a $(CBr_3^{\delta+}// Br^{\delta-})_{solv}$ type of dipole form and achieve complete charge as soon as they escape from their cage. Energetics also support the formation of the $(CBr_3^+//Br^-)_{solv}$ solvent-separated ion pair: the dissociation of CBr_4 to CBr_3 and Br requires 2.44 eV,[18] and the ionization potential of CBr_3 is 7.5 eV.[18] The electron affinity of Br is 3.36 eV; therefore, the in-cage charge-transfer reaction $CBr_3 \cdot Br \rightarrow CBr_3^+ Br^-$ requires 4.14 eV, while the complete reaction $CBr_4 \rightarrow CBr_3^+ + Br^-$ is endothermic by 6.58 eV. The electrostatic solvation ion-pair energy is ∼−280 kJ/mol, as calculated by Gremlitch at al.[29] for the electrostatic solvation energy of $(CCl_3^+//Cl^-)_{solv}$ or −2.90 eV/mol, which reduces the energy required to form the solvated ion pair to 3.68 eV. The energy of the exciting 266-nm photon is 4.66 eV; therefore, there is sufficient energy to form the $(CBr_3^+//Br^-)_{solv}$ ion pair with a single 266-nm photon. The argument on energetics requires that the excess energy of the exciting photon above the CBr bond energy (excess energy = 4.66 eV − 2.44 eV) remain as electronic energy in the radical pair, which is the available energy for the process leading to the solvent-separated ion pair. It is conceivable that the short-lived transient observed at 425 nm is an electronically excited CBr_3 radical. As noted before, ground-state CBr_3 has no absorption in the visible. The structure of the CBr_3^+ radical ion formed during the bromomethane photolysis in solution is not known. There have been, however, a limited number of theoretical calculations of the CBr_3 and CBr_3^+ structures in the gas phase.[16,25−27]

The experimental data presented in this paper strongly uphold our assignment of the 480-nm transient absorption band to the solvated ion complex $(CBr_3^+//Br^-)_{sol}$ formed after the 266-nm excitation of CBr_4 in solution. In addition, the CBr_3 neutral radical does not absorb in the 480- nm region, and there has been no evidence that the contact ion pair $CCl_3^+{\cdot}Cl^-$ is stable[29] and no reason to expect that the $CBr_3^+{\cdot}Br^-$ ion pair is stable. We also showed that cation scavengers affect strongly the spectra and kinetics of the 480-nm intermediate species. Data on the radiolysis of chloroalkanes agree with our experimental data and our assignment of the 480-nm photolysis intermediate to the solvent-stabilized $(CBr_3^+//Br^-)_{solv}$ ion pair. On the basis of experimental IR CBr_3 data a pyramidal structure has been proposed for this radical. We are performing time-resolved X-ray absorption experiments, which should reveal the structure of the CBr_4 photolysis transients in cyclohexane and determine the structure of the solvated CBr_3^+ cation and its distance from the Br^- ion.

Acknowledgment. We thank Professor Ivan Tomov for critical comments and suggestions. This research was supported in part by AFOSR under Grant F49620-03-1-0087.

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