

Structure of the Photodissociation Products of CCl₄, CBr₄, and CI₄ in Solution Studied by DFT and ab Initio Calculations

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Various molecular species that can be populated during the photoreaction of carbon tetrahalides CX₄ (X = Cl, Br, I) in the gas phase and in solution have been studied by ab initio and density functional theory (DFT) calculations. Geometries, energies, and vibrational frequencies of CX₄, CX₃, CX₂, C₂X₆, C₂X₅, C₂X₄, X₂, and the isomer X₂CX–X were calculated and transition states connecting these species were characterized. Spin-orbit DFT (SODFT) computations were also performed to include the relativistic effects, which cannot be neglected for Br and I atoms. The calculated potential energy surfaces satisfactorily describe the reactions of the photoexcited CX₄ molecules. In the gas phase, the initial C–X bond rupture in CX₄ is followed by secondary C–X breakage in the CX₃ radical, leading to CX₂ and 2X, and the formation of C₂X₆ or C₂X₄ through bimolecular recombination of the CX₃ or CX₂ radicals is favored thermodynamically. In solution, by contrast, the X₂CX–X isomer is formed via X–X binding, and two CX₃ radicals recombine nongeminately to form C₂X₆, which then dissociates into C₂X₄ and X₂ through C₂X₅. The Raman intensities and the vibrational frequencies, as well as the absorption spectra and oscillator strengths of the Br₂CBr–Br isomer in the gas phase and in various solvents were computed and the calculated absorption and Raman spectra of the Br₂CBr–Br isomer in various solutions are in good agreement with the experimental data. The natural population analysis indicates that the Br₂CBr–Br isomer corresponds to the recently reported solvent-stabilized solvated ion pair (CBr₃^{+/}Br⁻)_{solv} in the highly polar alcohol solvent. The singlet–triplet energy separations of the CX₂ radicals in the gas phase and in solution were evaluated with high level computational methods, and the optimized geometric parameters are in good agreement with the experimental results. The geometric and energetic differences between the singlet and triplet states were explained by the electronic properties of the CX₂ radicals. C₂X₄, C₂X₅, and C₂X₆ (X = Br, I) in the gas phase and in solution were optimized at different computational levels, and the optimized geometric parameters of C₂I₄ are in very good agreement with the experimental data.

1. Introduction

Carbon tetrahalides, which validate the primary tenet of the natural tetravalence of carbon,¹ have been a subject of intense studies for decades.^{2–8} They have been found in the natural environment and are important sources of reactive halogens that have been linked to ozone depletion in both the troposphere and the stratosphere.^{9–12} Their photochemistry in the gas and condensed phases is important for describing reactions in natural environment and has become an area of active investigation.^{13–17} In early decades, the majority of research has been devoted almost exclusively to the photolysis and reactions of CCl₄. Studies using radiolysis of CCl₄ in methyl cyclohexane at low temperatures^{18–20} and two-photon excitation of liquid CCl₄ at 266 nm²¹ showed that the dissociation product of CCl₄ is a solvent-separated ion pair (CCl₃^{+/}Cl⁻)_{solv}. Photochemistry of

tetrabromomethane CBr₄ has been studied with increasing interest in recent years. However, experimental results show some discrepancies among each other. Picosecond time-resolved Raman spectroscopic study of CBr₄ in the liquid phase showed that the Br₂CBr–Br isomer with a lifetime of nanoseconds is formed after UV excitation.²² In a recent time-resolved absorption spectroscopic study, one photon excitation of CBr₄ at 266 nm in various solvents suggested formation of a solvent-stabilized solvated ion pair (CBr₃^{+/}Br⁻)_{solv}.²³ The ultrafast EXAFS study on CBr₄ in cyclohexane did not show any photodissociated intermediates.²⁴ Due to the disagreement of the experimental data, it is of great importance to describe the photodissociation process of CBr₄ in solution with high-level quantum chemical calculations.

The carbon tetraiodide CI₄ does not show high stability in solution and the photochemistry of CI₄ in liquid phase has not been reported. Gas-phase electron diffraction study revealed that the CI₄ molecule partially decomposes during heating and the free radicals CI₂, molecules I₂ and CI₄, and small amount of C₂I₄ coexist in the gas phase.²⁵ Electron diffraction on thermal decomposition of CBr₄ also showed that the major decomposi-

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tion products are CBr₂, with lesser amounts of C₂Br₆, CBr₃ radicals, and molecular bromine, Br₂.²⁶ As the major dissociation products in the gas phase, an important characteristic of the halocarbenes CX₂ is that they have two low-lying electronic states, a singlet and a triplet with markedly different geometries and chemical properties,⁸ which results in their high reactivity and importance in organic reactions.

Compared to the extensive experimental investigations, there are few theoretical studies on photodissociation reaction of carbon tetrahalides.^{25,27} Here, we present quantum chemical calculations to describe the whole photodissociation processes and putative photoproducts of dissociated carbon tetrahalides (CX₄, X = Cl, Br, I) in the gas phase and in solution to get a more detailed picture of the dissociation mechanism. The geometrical and electronic properties of the halocarbene radicals CX₂ and CX₃ are also evaluated with high level computations, and the results are compared with previous experimental and theoretical studies.

2. Computational Methods

Calculations were carried out by ab initio and density functional theory (DFT) methods using the Gaussian 03 code.²⁸ Geometries were fully optimized, and vibrational frequencies were calculated with analytical second-order derivatives. From these calculations, zero-point vibrational energies were derived and used to correct for zero-point energy (ZPE). The number of imaginary frequencies was used to characterize the nature of the structure. For the transition state, intrinsic reaction coordinate (IRC) calculations were performed to follow the reaction path. The structural parameters were also optimized with MP2 and the coupled cluster CCSD(T)²⁹ methods for comparison. The Becke three-parameter hybrid functional with the Lee–Yang–Parr correlation corrections (B3LYP) was used in the DFT calculation.^{30,31} The all-electron basis set 6-311+G(d) for C, Cl, and Br atoms,³² and the all-electron basis set 6-311G(d) with added d and f polarization functions and s and p diffuse functions for the I atom,^{33,34} which are referred to as 6-311+G(d), were used. Calculations with the 6-311+G(3df) basis set for the Br₂CBr–Br isomer and CX₂ (X = Cl, Br, I) radicals were also carried out to compare with available experimental data.

The solvent effects were calculated using self-consistent reaction field (SCRf) theory. The self-consistent isodensity polarized continuum model (SCIPCM),³⁵ which allows geometry optimization at the HF and DFT levels, was used to perform the solution calculation using an isodensity value of 0.0004 e/au³.

Time-dependent density functional theory (TD-DFT)³⁶ was used to calculate the vertical excitation energies and oscillator strengths. The TD-B3LYP method with 6-311+G(3df) basis set was used to calculate the absorption spectra of the Br₂CBr–Br isomer in the gas phase and in various solutions.

Since both Br and I atoms are heavy elements, the relativistic effects are not negligible. Therefore, we have considered the relativistic effects using relativistic effective core potential (RECP). Spin–orbit DFT (SODFT) computations were performed with NWChem program.³⁷ The B3LYP hybrid function with CRENBL RECP basis set for Br³⁸ and I atoms,³⁹ and all electron basis set 6-311+G(3df) for C atom were used for SODFT calculations. The valence electrons of Br and I atoms are described by modified basis sets, which are shown in Table 1S of the Supporting Information. Geometries were fully optimized including the SO effect, and vibrational frequencies were calculated.

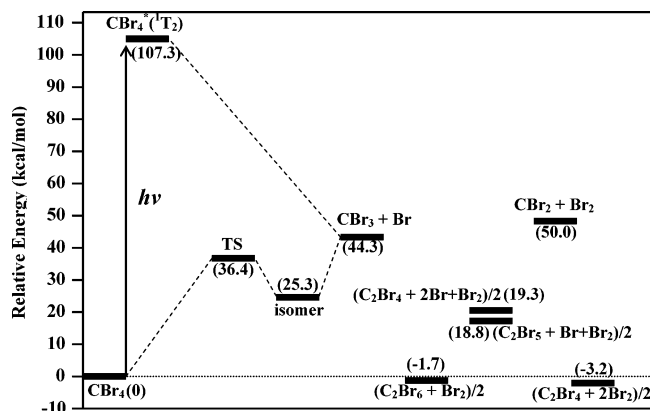


Figure 1. Potential energy levels relevant to photodissociation of CBr₄ in methanol, plotted using energies calculated at the B3LYP level with the 6-311+G(d) basis set for C and Br. The SCIPCM model is used to include the solvent effect. All energies were subjected to ZPE correction.

TABLE 1: Relative Energies (kcal/mol) of the Reaction Intermediates, Transition State, and Products in the Gas Phase and in Solution at B3LYP Level with Values in Parentheses Showing the Relative Energies from SODFT Calculations Including the Relativistic Effects^a

species	gas phase	in methanol		in cyclohexane
		6-311+G(d)	6-311+G(3df)	
CBr ₄	0 (0)	0	0	0
CBr ₃ + Br	44.6 (50.0)	44.3	45.6	44.5
CBr ₂ + Br ₂	50.8 (52.1)	50.0	49.4	50.5
CBr ₂ + 2Br	96.4	95.0	97.5	95.9
Br ₂ CBr–Br	32.2 (30.5)	25.3	25.9	30.1
(C ₂ Br ₆ + Br ₂)/2	-1.6	-1.7	-1.8	-1.6
(C ₂ Br ₅ + Br + Br ₂)/2	19.2	18.8	19.4	19.1
(C ₂ Br ₄ + 2Br + Br ₂)/2	19.9	19.3	20.1	19.7
(C ₂ Br ₄ + 2Br ₂)/2	-2.9 (-4.9)	-3.2	-4.0	-3.0
TS	44.6	36.4	36.7	41.6

^a All the values are corrected for the zero point energies. The relative energies of C₂Br₆ + Br₂, C₂Br₅ + Br + Br₂, and C₂Br₄ + 2Br₂ corresponding to CBr₄ are calculated with the following formulas: $E(\text{C}_2\text{Br}_6 + \text{Br}_2)/2 - E(\text{CBr}_4)$, $E(\text{C}_2\text{Br}_5 + \text{Br} + \text{Br}_2)/2 - E(\text{CBr}_4)$, and $E(\text{C}_2\text{Br}_4 + 2\text{Br}_2)/2 - E(\text{CBr}_4)$, respectively.

3. Results and Discussion

Most of the calculations were performed in a nonpolar solvent, cyclohexane with a dielectric constant ϵ of 2.023, and in a polar alcohol solvent, methanol with a dielectric constant ϵ of 32.63. Additional calculations in 2-propanol ($\epsilon = 20.18$), acetonitrile ($\epsilon = 36.64$), propylene carbonate ($\epsilon = 66.14$), and water ($\epsilon = 78.39$) for the Br₂CBr–Br isomer and in benzene ($\epsilon = 2.247$) and chloroform ($\epsilon = 4.9$) for Cl₄ decomposition were also performed. In section 3.1, the whole photodissociation potential energy surfaces and various dissociation channels of carbon tetrahalides in solution and in the gas phase are presented, and in section 3.2, the putative photoproducts and their properties are presented and discussed.

3.1. Dissociation Reaction Channels. The overall potential energy levels of various candidate species along the photoreaction pathways of CBr₄ in methanol are shown in Figure 1 and the relative energies of the reaction intermediates, transition states, and products as compared to the ground-state CBr₄ molecule in the gas phase and in solution are listed in Table 1. The corresponding potential energy levels and relative energies of various candidate species of Cl₄ decomposition are shown in Figure 1S and Table 2S of the Supporting Information. For a typical photodissociation at 266 nm in solution, the ground-state CBr₄ is pumped to an excited-state CBr₄* with an energy

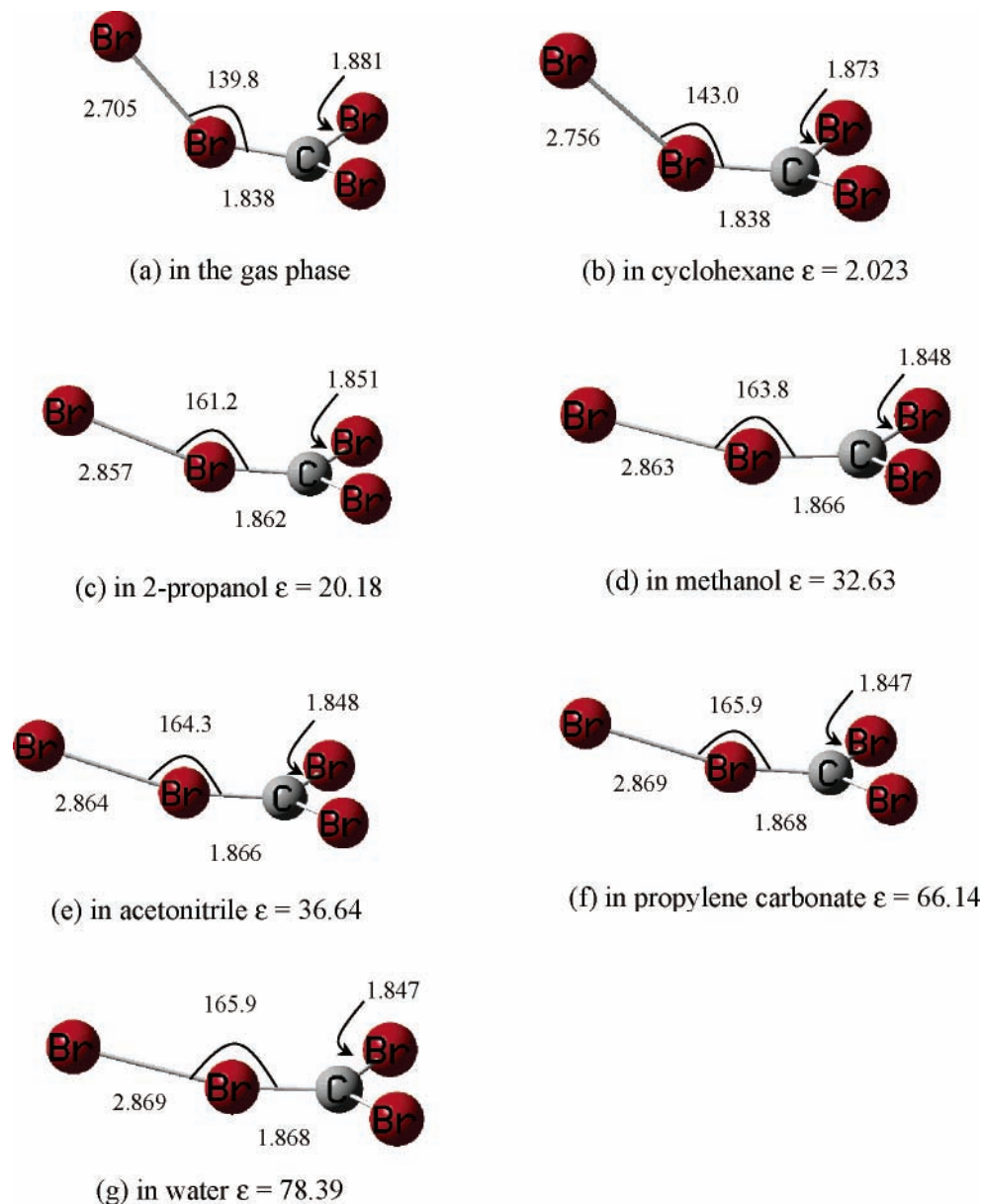


Figure 2. Geometries of the $\text{Br}_2\text{CBr}-\text{Br}$ isomer: (a) in the gas phase; (b) in cyclohexane; (c) in 2-propanol; (d) in methanol; (e) in acetonitrile; (f) in propylene carbonate; (g) in water. Calculations were performed at the B3LYP level; bond lengths are in angstroms, and angles in degrees.

of 107.3 kcal/mol (4.647 eV), which corresponds to the 12th (1T_2) excited-state according to the TDDFT calculation. The first step in dissociation is to form $\text{CBr}_3 + \text{Br}$. The direct formation of $\text{CBr}_2 + 2\text{Br}$ is excluded since the laser energy at 266 nm (4.647 eV) is not sufficient to break two C-Br bonds simultaneously, which has a bond energy of 56.3 kcal/mol (2.44 eV) or 61 kcal/mol (2.64 eV) from previous experimental data.⁴⁰ The calculated C-Br bond energy is 63.1 kcal/mol (2.74 eV) in the gas phase at the MP2/6-311+G(3df) level, which basically coincides with the experimental results. The $\text{CBr}_3 + \text{Br}$ radicals, generated from the decay of the excited molecule CBr_4^* , initially have an excess energy of 63.0 kcal/mol in methanol (62.8 kcal/mol in cyclohexane and 62.7 kcal/mol in the gas phase). The subsequent reactions have several pathways.

In the first case, the solvation cage may contain the liberated bromine atom within the interaction distance of the remaining bromines on CBr_3 and lead to the formation of a new species. As shown in Figure 1, the interaction of the free bromine atom with the CBr_3 radical can form a $\text{Br}_2\text{CBr}-\text{Br}$ isomer, which lies 19.0 kcal/mol lower than $\text{CBr}_3 + \text{Br}$ in methanol. The scan

along the Br-Br distance of the isomer shows that there is no energy barrier for the transition from $\text{CBr}_3 + \text{Br}$ to the $\text{Br}_2\text{CBr}-\text{Br}$ isomer. The scan calculation is shown in Figure 2S of the Supporting Information. Formation of isopoly(halomethane) has been observed in the transient resonance Raman spectroscopic study of ultraviolet photoexcitation of poly(halomethane)s (CH_2Br_2 , CHBr_3 , CFBr_3 , CBr_4 , CH_2I_2 , CHI_3 , and CH_2IBr) in solution.^{22,41} Photoexcitation of poly(halomethane)s in low-temperature matrix at 77 K also suggested isopoly(halomethane) as photoproducts.⁴²⁻⁴⁷

From our calculation, the most probable pathway following the formation of the $\text{Br}_2\text{CBr}-\text{Br}$ isomer is to relax back to the ground-state CBr_4 via a transition state. The transition state lies 11.0 kcal/mol higher than the isomer in methanol (11.5 kcal/mol in cyclohexane; 12.4 kcal/mol in the gas phase), as shown in Figure 1. Intrinsic reaction coordinate (IRC) calculations show that the transition state is a saddle point connecting the ground-state CBr_4 and the $\text{Br}_2\text{CBr}-\text{Br}$ isomer (Figure 3S in Supporting Information). The structure of the transition state in methanol is shown in Figure 4. The XYZ coordinates of the transition

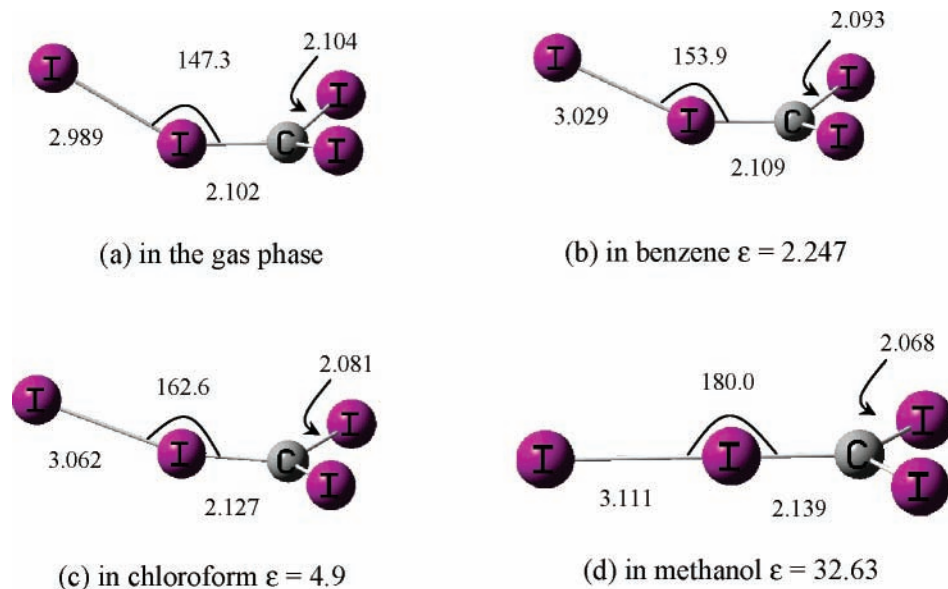


Figure 3. Geometries of the I₂CI-I isomer: (a) in the gas phase; (b) in benzene; (c) in chloroform; (d) in methanol, calculated at the B3LYP level. Bond lengths are in angstrom, and angles are in degrees. The solvent effect changes the I₂CI-I isomer from a bent structure to a linear one going from the gas phase to methanol.

states in CBr₄ and CI₄ decomposition for the gas phase and for various solvents are shown in Table 3S of the Supporting Information. The corresponding vibrational frequencies are provided in Table 4S of the Supporting Information.

Another possible reaction channel of the Br₂CBr-Br isomer is to form CBr₂ + Br₂ through the C-Br bond breakage, which needs 24.7 kcal/mol in methanol (20.4 kcal/mol in cyclohexane, 18.6 kcal/mol in the gas phase). Compared to the relaxation reaction through the transition state, this reaction is energetically less favorable. The CX₂ (X = Br, I) radicals were not observed in the photodissociation reaction of poly(halomethane)s in liquid^{22,41} and low-temperature matrix,⁴²⁻⁴⁷ indicating that the reaction to CBr₂ and Br₂ in liquid phase is not probable.

The CBr₃ and Br radicals can escape the solvation cage and interact with other partners to form C₂Br₆ and Br₂ through bimolecular recombination reactions. C₂Br₆ and Br₂ are 46.9 and 45.0 kcal/mol more stable than two free CBr₃ radicals or two free bromine atoms in methanol at B3LYP level, respectively. Energetically, C₂Br₆ or Br₂ can form directly without energy barriers as shown in Figure 1. In the gas-phase electron diffraction study on the pyrolysis of CBr₄, a well-defined peak at 4.6 Å was observed in the radial distribution function, and the data analysis indicated that the decomposition of CBr₄ resulted in about 15% conversion to C₂Br₆.²⁶ The dissociation reaction C₂Br₆ → C₂Br₄ + Br₂ is exothermic by 2.9 kcal/mol in methanol (2.7 kcal/mol in cyclohexane, 2.6 kcal/mol in the gas phase) according to our calculation. Therefore, the C₂Br₆ molecule can decompose into C₂Br₄ and bromine. The decomposition of C₂X₆ into C₂X₅ + X would be the first step involved in this process. C₂X₅ can further dissociate into C₂X₄ + X or a free X can abstract another X from C₂X₅ to form X₂ + C₂X₄. The remaining free X atoms will eventually recombine to form X₂. In summary, the final products are C₂X₄ + X₂. C₂X₄ has been expected to be present as the major decomposition product of CX₄, based on thermodynamics in a previous study.⁴⁸ An electron diffraction study on pyrolysis of CI₄ in the gas phase suggested that 3% of the total diffraction intensity was from the contribution of C₂I₄.²⁵ From our calculations, C₂Br₄ lies 106.3 kcal/mol lower in energy than two CBr₂ radicals in methanol (107.0 kcal/mol in cyclohexane, 107.4 kcal/mol in the gas phase), indicating that C₂Br₄ can be formed directly

from bimolecular combination of the CBr₂ radicals. However, since the formation of CBr₂ radicals in solution is unlikely from our calculation and previous experimental studies, C₂Br₄ in solution can be formed only through the exothermic dissociation reaction of C₂Br₆. Bimolecular combination of the CBr₂ radicals to C₂Br₄ most probably happens in the gas phase since the CX₂ (X = Br, I) radicals are the major dissociation products.^{25,26} Time-resolved X-ray diffraction studies on I₂⁴⁹ and Br₂⁵⁰ in solution showed that about 10% of free iodine or bromine atoms can escape the solvation cage to undergo the nongeminate recombination reaction, indicating that the formation of C₂Br₆ and C₂Br₄ is also probable in the photodissociation reaction of CBr₄ in solution.

Pyrolysis of tetrahalides CX₄ (X = Br, I) in the gas phase showed that the CX₂ radicals are the major products. CBr₂ and CI₂ accounted for 60%²⁶ and 20%²⁵ of the final products, respectively, which indicate that the secondary dissociation of the CBr₃ radical is an important reaction channel in the gas phase. From our calculation results shown in Table 1, the secondary dissociation of the CBr₃ radical to CBr₂ + Br needs an energy input of 50.7 kcal/mol in methanol (51.4 kcal/mol in cyclohexane, 51.8 kcal/mol in the gas phase). Compared to the formation of the Br₂CBr-Br isomer, which does not need any energy input, the large energy barrier makes the secondary dissociation of the CBr₃ radical less probable in solution. The absence of the CBr₂ radicals in previous photodissociation reactions in liquid^{22,41} or low-temperature matrix⁴²⁻⁴⁷ also confirms that the secondary dissociation of CBr₃ is not a major reaction pathway in solution even though it is so in the gas phase.

In conclusion, our calculation shows that the formation of the X₂CX-X isomer is energetically more favored than the secondary dissociation to CX₂ + 2X both in the gas phase and in solution. Previous experimental results show that the isomer is the major product in solution^{18-22,41} and in low-temperature matrix,⁴²⁻⁴⁷ while the CX₂ radicals are formed in the gas phase,^{25,26,51,52} indicating that the formation of isopoly(halomethane) is the reaction pathway in solution, whereas the secondary dissociation of the CX₃ (X = Br, I) radical is the main reaction channel in the gas phase. On the basis of our calculation and previous experimental results, the following

TABLE 2: Comparison of Calculated Vibrational Frequencies (cm⁻¹) and Raman Intensities (in Parentheses) of the Br₂CBr–Br Isomer in Various Solvents at B3LYP/6-311+G(3df) Level to Previous Transient Raman Spectroscopic Experimental Data (Refs 22 and 55), Where the SCIPCM Model Was Used to Include the Solvent Effect^a

		calculation in cyclohexane	experiment in cyclohexane	calculation in water	calculation in acetonitrile	experiment in acetonitrile and trace of water
C–Br str	A'	818.4 (58)	828	797.0 (8)	795.6 (10)	828
Br–C–Br wag	A''	761.8 (6)		775.2 (130)	777.2 (110)	
Br ₂ –C–Br wag	A'	343.9 (2)		411.1 (172)	408.4 (156)	
Br ₂ –C–Br sym Str.	A'	283.0 (7)		278.5 (334)	278.7 (289)	280
Br ₂ –C–Br bend	A''	181.5 (2)		185.2 (5)	185.0 (5)	
BrCBr bend + Br–Br str	A'	174.6 (14)	179	170.0 (34)	170.0 (23)	
Br–Br str. + BrCBr bend	A'	147.4 (24)	155	107.5 (13)	108.7 (23)	
torsion	A''	49.6 (5)		47.7 (14)	47.6 (15)	
Br ₂ CBr–Br bend	A'	35.6 (10)		18.7 (28)	19.9 (23)	

^a The Raman intensities in solution were calculated with the PCM model, based on the geometries optimized with the SCIPCM model. The SCIPCM model is not available for the Raman intensity calculation in solution.

early time delays. The CX₃ and X radicals are probably able to dimerize to form C₂X₆ and X₂, respectively, and then C₂X₆ will decompose into C₂X₄ and X₂ at late time delays. So the final products, based on thermodynamics, would be the CX₄, C₂X₄, and X₂ molecules. Compared to the DFT results, the SODFT computations give slightly different energies as shown in Table 1, but the dissociation PES does not change.

3.2. Putative Photoproducts. The X₂CX–X Isomer. Figure 2 shows the structures of the Br₂CBr–Br isomer in the gas phase and in various solvents. The XYZ coordinates of the Br₂CBr–Br isomer for the gas phase and for various solvents are shown in Table 5S of the Supporting Information and the calculated vibrational frequencies are listed in Table 6S. The structure of the Br₂CBr–Br isomer changes dramatically from the gas phase to solution, as shown in Figure 2. The Br–Br distance of the isomer elongates from 2.705 to 2.756 Å in going from the gas phase to cyclohexane with a dielectric constant of 2.023 and keeps increasing to 2.869 Å in water with a dielectric constant of 78.39. The Br–Br–C angle also increases from 139.8 to 165.9° in going from the gas phase to water, as shown in Figure 2. The Br–Br distance elongation and the Br–Br–C angle increase indicate that the solvent effect weakens the Br–Br interaction in the Br₂CBr–Br isomer. Figure 3 shows the structures of the I₂CI–I isomers in the gas phase and in various solvent. The solvent has the same effects on the I₂CI–I isomer as described above, that is the polar alcohol solvent with stronger interaction with the solute molecule weakens the I–I interaction in the I₂CI–I isomer. An important difference from the Br₂CBr–Br isomer is that the I₂CI–I isomer changes from a bending structure with C_s symmetry in the gas phase and in most of nonpolar solvents to a planar structure with C_{2v} symmetry in methanol. Since the Cl₄ molecule is not stable in solution, there are no experimental reports about the photodissociation reaction of Cl₄ in liquid phase. Our calculation shown in Figure 1S indicates that the I₂CI–I isomer would also be the major photodissociation products of Cl₄ in solution at early time delays. The XYZ coordinates of the I₂CI–I isomer in the gas phase and in various solvents are provided in Table 7S, and the calculated vibrational frequencies and IR intensities in the gas phase and in various solvents are shown in Table 8S of the Supporting Information. The structure of the Br₂CBr–Br isomer changes slightly when the relativistic effects are considered. The Br–Br bond length changes from 2.71 Å of the DFT calculation to 2.68 Å of the spin–orbital calculation, and the BrBrC angle changes from 140.0 to 142.1 degree. The XYZ coordinates of the X₂CX–X (X = Br, I) isomer in the gas phase from SODFT calculation are included in Table 5S and Table 7S of the Supporting Information, respectively.

Although the Br₂CBr–Br isomer is the major product in the UV photolysis of CBr₄ in solution^{22,53} and in a low-temperature matrix,⁴² no direct information about geometrical parameters of the isomer has been obtained from the laser spectroscopic studies. To compare with the available experimental data, the Raman intensities and the vibrational frequencies, as well as the absorption spectra and oscillator strengths of the Br₂CBr–Br isomer in the gas phase and in various solvents were computed. Table 2 shows the comparison of calculated vibrational frequencies of the Br₂CBr–Br isomer in cyclohexane, acetonitrile, and water to those previously reported from transient resonance Raman spectroscopic experiments.^{22,55} The calculated frequencies and Raman intensities in cyclohexane are in good agreement with the observed results. The calculation results shows that the C–Br stretching fundamental band is at 818.4 cm⁻¹, and the Br–C–Br bend and Br–Br stretching bands with less stronger Raman intensities are at 174.6 and 147.4 cm⁻¹. In comparison with the observed frequencies at 828, 179, and 155 cm⁻¹, an averaged empirical frequency scaling of 0.971 is needed between theory and experiment. Our calculation shows that the maximum Raman intensity of the Br₂CBr–Br isomer changes from the C–Br stretching mode at 818.4 cm⁻¹ in cyclohexane to the Br–Br–C–Br symmetric stretching mode at 278.5 and 278.7 cm⁻¹ in water and acetonitrile. The calculated results accord with the experimental data, where the ν₃ Br–Br–C–Br symmetric stretching mode is more clearly observed in acetonitrile than in cyclohexane.⁵⁵ According to the computed Raman intensity in acetonitrile, the Br–C–Br wag band around 400 cm⁻¹ should be observed in the acetonitrile experiment, but no experimental data about this vibrational mode has been reported in a previous study.⁵⁵

In a recent photolysis study of CBr₄, the absorption spectra of an intermediate in various solvents were reported, and a solvent-stabilized solvated ion pair (CBr₃⁺//Br⁻)_{solv} was suggested to form.²³ Table 3 shows the calculated absorption and oscillator strengths of the Br₂CBr–Br isomer in the gas phase and in various solvent with the TD-DFT method and the comparison with the experimental data for the proposed ion pair. The computed absorption peaks in cyclohexane and dodecane are located at 482 and 480 nm respectively, which are almost identical to the observed absorption at 480 nm. The calculated absorption peak at 650 nm in the polar alcohol solvent acetonitrile is also in good agreement with the observed absorption at 635 nm. To explain the origin of this excellent agreement between the observed absorption peaks for the proposed ion pair and the calculated ones for the Br₂CBr–Br isomer, we carried out natural population analysis (NPA) of the Br₂CBr–Br isomer in the gas phase and in various solutions

TABLE 3: Calculated Absorption (nm) and Oscillator Strengths (in Parentheses) of the Br₂CBr–Br Isomer at Different Excited States in the Gas Phase and in Various Solution at the TD-B3LYP/6-311+G(3df) Level, and Comparison with the Experimental Data^a

excited states	Br ₂ CBr–Br isomer					
	gas phase	in cyclohexane	in dodecane	In 2-propanol	in acetonitrile	in propylene carbonate
2	883 (0)	897 (0)	895 (0)	985 (0)	997 (0)	1000 (0)
3	799 (0)	823 (0)	821 (0)	936 (0)	955 (0)	962 (0)
4	719 (0.0002)	751 (0.0001)	749 (0.0001)	893 (0)	914 (0)	922 (0)
5	651 (0.0004)	685 (0.0002)	684 (0.0002)	824 (0)	845 (0.0001)	853 (0.0001)
6	459 (0.1843)	482 (0.1951)	480 (0.1963)	622 (0.1211)	650 (0.1051)	663 (0.0988)
7	417 (0)	406 (0)	406 (0)	429 (0)	434 (0)	436 (0)
8	374 (0)	388 (0)	387 (0)	340 (0.0001)	404 (0)	406 (0)
9	360 (0.0646)	365 (0.0001)	365 (0.0001)	382 (0)	381 (0)	381 (0)
10	357 (0)	354 (0)	354 (0.0524)	368 (0)	373 (0)	375 (0)
11	354 (0.0001)	354 (0.0516)	354 (0)	361 (0)	364 (0)	366 (0)
12	349 (0)	346 (0)	346 (0)	358 (0)	360 (0)	360 (0)
13	342 (0)	342 (0)	342 (0)	352 (0)	354 (0)	355 (0)
14	324 (0)	333 (0)	333 (0)	348 (0.0001)	349 (0.0001)	350 (0.0001)
15	315 (0)	326 (0)	326 (0)	347 (0.010)	347 (0.0070)	347 (0.0059)
16	310 (0.2370)	310 (0.2274)	310 (0.2274)	336 (0)	339 (0)	340 (0)
		Experimental Data (Ref 23)				
		480	480	540	635	635

^a Some of the calculated excitation energies have negative values at the first excited state, so the absorption spectra were shown from nstates = 2.

TABLE 4: Computed Natural Population Analysis (NPA) of the Br₂CBr–Br Isomer in the Gas Phase and in Various Solutions at the B3LYP/6-311+G(3df) Level, Where the SCIPCM Model Is Used to Include the Solvent Effects

atoms	Br ₂ CBr–Br isomer						
	gas phase	in cyclohexane	in dodecane	in 2-propanol	in acetonitrile	in propylene carbonate	in water
Br	0.243 85	0.273 95	0.273 48	0.355 06	0.364 59	0.369 21	0.370 10
Br	0.243 85	0.273 95	0.273 48	0.355 06	0.364 59	0.369 21	0.370 10
C	−0.58708	−0.56717	−0.56793	−0.50387	−0.49618	−0.49293	−0.49240
Br	0.521 72	0.514 68	0.515 86	0.455 34	0.445 69	0.442 35	0.441 63
Br	−0.42233	−0.49541	−0.49490	−0.66160	−0.67870	−0.68784	−0.68943

as shown in Table 4. The NPA shows that the Br₂CBr group of the Br₂CBr–Br isomer has a positive charge of 0.422 while the attached Br atom has a negative charge of −0.422, in the gas phase. This charge separation increases to ±0.495 in cyclohexane and keeps increasing in the highly polar alcohol solvent as shown in Table 4. In water ($\epsilon = 78.39$), the Br₂CBr group has a positive charge of 0.689, and the attached Br atom has a negative charge of −0.689. So, the Br₂CBr–Br isomer can be approximated as a solvated ion pair (Br₂CBr⁺–Br[−]), especially in high polar alcohol solvent. On the basis of this, we suggest that the proposed solvent-stabilized solvated ion pair (CBr₃^{+/Br})_{solv} in a recent study²³ is actually the Br₂CBr–Br isomer in our study.

The CX₂ and CX₃ Radicals. CX₂ are the major dissociation products in the gas phase. The electronic structure of the substituted carbenes is an interesting subject and has been intensively studied.^{2,56} They have two low-lying orbitals, one with a₁ and one with b₁ symmetry. Depending on the arrangement of the electrons on these two orbitals, CX₂ have two electronic states, an ¹A₁ singlet (a₁)² or a ³B₁ triplet (a₁)(b₁) with markedly different geometries and chemical properties. The relative energies of these two states are important characteristics. Because of the large disagreement between computations and experiments about the singlet–triplet energy separation,^{57,58} it is important to evaluate the ground state and singlet–triplet energy separation of CX₂ with high level computation methods both in the gas phase and in solution.

Table 5 shows the relative energies of the singlet and triplet states of CX₂ (X = Cl, Br, I) in the gas phase and in solution, and Table 6 shows the comparison of the ground-state geometrical parameters of CX₂ at various computational levels with the experimental data. The CX₂ has the ¹A₁ singlet as the ground

TABLE 5: Relative Energies ΔE_{S-T} (kcal/mol) of the Singlet and Triplet States of CX₂ (X = Cl, Br, I) in the Gas Phase at Various Computational Levels and in Solution, Where the All-Electron Basis Sets 6-311+G(3df) for C and Br Atoms, and 6-311+G(d) for I Atom Were Used and the SCIPCM Model Was Used for Solution Calculations

	B3LYP				
	gas phase	in cyclohexane	in methanol	MP2	CCSD(T)
CCl ₂	17.4	17.6	18.0	18.1	19.4
CBr ₂	14.3	14.4	14.7	14.1	15.3
CI ₂	7.0	7.2	7.4	7.1 ^a	7.5 ^a

^a All the values are corrected for the zero point energies, except for CI₂ at MP2 and CCSD(T) levels.

state at all computational levels in the gas phase and in solution. The relative energy ΔE_{S-T} becomes smaller going from Cl to I with decreasing ligand electronegativity as shown in Table 5. The ΔE_{S-T} is 18.1 kcal/mol for CCl₂, and drops to 14.1 and 7.1 kcal/mol for CBr₂ and CI₂ at the MP2 level. Because of the computational complexity, few calculations has been done on CI₂.^{6,25} The ΔE_{S-T} for CI₂ is 7.5 kcal/mol at CCSD(T) level, which is lower than previous coupled cluster results of about 9 kcal/mol.^{6,25} As shown in our previous study,⁵⁴ the all-electron basis set 6-311+G(d) for iodine atom gives much better results than the Stuttgart ECP basis sets. The calculated C₂I₄ geometrical parameters in the present study are also much better than previous results with the ECP basis sets for I atom,^{6,25} as is shown in the next section. Therefore, the ΔE_{S-T} of 7.512 kcal/mol for CI₂ at CCSD(T) level with the all-electron basis set 6-311+G(d) for I atom would be more precise than previous results.^{6,25} The optimized geometrical parameters in Table 6 are in good agreement with the experimental values, except for

TABLE 6: Comparison of the Geometrical Parameters of CX₂ (X = Cl, Br, I) at Various Computational Levels with the Experimental Data. The-all Electron Basis Sets 6-311+G(3df) for C and Br Atoms, and 6-311+G(d) for I Atom Were Used^a

	B3LYP		MP2		CCSD(T)		experiment	
	r(C-X)	∠(X-C-X)	r(C-X)	∠(X-C-X)	R(C-X)	∠(X-C-X)	r(C-X)	∠(X-C-X)
CCl ₂	1.722 (1.673)	109.9 (128.9)	1.699 (1.665)	109.9 (127.8)	1.718 (1.675)	109.6 (128.1)	1.7157(20)	109.2(2) ⁵¹
CBr ₂	1.899 (1.840)	110.7 (130.1)	1.868 (1.823)	110.5 (129.3)	1.891 (1.834)	110.4 (129.7)	1.74(3)	114.1 ²⁶
CI ₂	2.116 (2.038)	113.2 (133.8)	2.070 (2.014)	112.8 (132.9)	2.098 (2.024)	112.8 (134.2)	2.085(13)	112.3 ^{25 b}

^a Bond lengths in Å and angles in degree. Values in parentheses are the geometrical parameters of triplet state. ^b The geometrical parameters of CI₂ from ref 25 are not direct experimental measurements but were assumed from computation.

CBr₂, for which the experimental data might be in error as mentioned in a previous study.²⁵ Compared to the experimental results in Table 6, the CCSD(T) method reproduces the experimental value most precisely. Another noticeable geometric characteristic for the CX₂ (X = Cl, Br, I) radicals is that a quite large difference of the X-C-X angle between singlet and triplet is observed in Table 6.

The trend of relative energy ΔE_{S-T} from Cl to I with decreasing ligand electronegativity has been explained in terms of molecular orbitals of CX₂ (X = F, Cl, Br, I) at singlet state in previous study,²⁵ and our calculations on the HOMO and LUMO of CX₂ at the MP2/6-311+G(3df) level produce similar results as shown in Figure 4S of the Supporting Information. The calculated s orbital coefficients of the C atom at HOMO (a₁) are as follows: (-0.05025, -0.08616, 0.25703, 0.38216, 0.04477) for CCl₂, (-0.04398, -0.07553, 0.22829, 0.33638, 0.25444) for CBr₂, and (0.03583, 0.06157, -0.18775, -0.27617, -0.04505) for CI₂ respectively, indicating that contribution from s orbital of the C atom decreases with decreased electronegativity of the ligands. The natural bond orbital (NBO) analysis shows that the ratios of the s character of the bonding orbital are 18.68%, 16.49%, and 16.29% for CCl₂, CBr₂, and CI₂ respectively, which also indicates that the ratio of s character of the bonding orbital decrease with decreased electronegativity of the ligands. Consequently, the energies of the HOMO (a₁) orbital increase from CCl₂ to CI₂. The calculated energies of the HOMO (a₁) orbital are -0.39795, -0.38054, and -0.34941 au for CCl₂, CBr₂ and CI₂, respectively. The LUMO (b₁) orbital has a strong antibonding characteristic consisting of a p_π orbital between the C atom and the ligands. As the electronegativity of the ligand decreases, the p contribution from the C atom decreases. Our calculated molecular orbital coefficients of the p orbital of the C atom at LUMO (b₁) are as follows: (0.20047, 0.33717, 0.45142, 0.57436) for CCl₂, (0.19791, 0.33359, 0.45187, 0.52439) for CBr₂ and (0.18848, 0.30756, 0.47719, 0.53311) for CI₂, respectively. The energy of the LUMO (b₁) orbital decreases as the p contribution of the C atom drops. The calculated energies of the LUMO (b₁) orbitals are 0.2782, 0.01376, and -0.34941 au for CCl₂, CBr₂, and CI₂. Therefore, the energies of HOMO (a₁) and LUMO (b₁) orbitals become closer as the electronegativity of the ligands decrease. Consequently, the relative energies ΔE_{S-T} of CX₂ decrease from Cl to I with decreased electronegativity.

The CX₃ radical is the major products in the first step of the dissociation reaction of CX₄ (X = Cl, Br, I). The ground-state CX₃ (²A₁) has a pyramid structure in the gas phase and in solution. As an example, the geometry of CBr₃ is shown in Figure 4. The XYZ coordinates of CX₃ in the gas phase and in solution are shown in Table 9S of the Supporting Information, and the calculated vibrational frequencies in Table 10S. The SODFT calculation produces the same geometrical parameters for the CBr₂ and CBr₃ radicals in the gas phase, and the XYZ

TABLE 7: Geometric Parameters of C₂Br₄, C₂Br₆, C₂I₄, and C₂I₆ Computed at the MP2 Level and Comparison with the Experimental Results of C₂I₄, Where the All-Electron Basis Sets 6-311+G(d) for C and Br Atoms and 6-311+G(d) for I Atom Were Used^a

geometric parameters	computed				exptl data ⁵⁹ of C ₂ I ₄
	C ₂ Br ₆	C ₂ Br ₄	C ₂ I ₆	C ₂ I ₄	
r(C-C)	1.572	1.358	1.557	1.363	1.363(15)
r(C-X)	1.952	1.881	2.177	2.091	2.106(5)
∠(X-C-C)	110.5	122.4	111.4	122.9	122.9(5)

^a Bond lengths in Å and angles in degree. The C-C, C-I bond lengths and I-C-C bond angle of C₂I₄ were calculated to be 1.347 Å, 2.084 Å and 123.3° with the ECP basis set for I atom from a previous study.²⁵

coordinates of the CBr₃ radical from SODFT calculation are included in Table 9S.

C₂X₆ and C₂X₄. C₂Br₆ and C₂Br₄ are 47.0 and 106.3 kcal/mol more stable than two CBr₃ or CBr₂ radicals in methanol at B3LYP/6-311+G(d) level. Both CBr₃ and CBr₂ may dimerize. As discussed in section 3.1, C₂Br₆ probably forms through bimolecular recombination of two CB₃ radicals and dissociate to C₂Br₄ and Br₂ as the final products in solution. Formation of CBr₂ radicals is excluded from our calculation and previous experimental studies,^{22,42-47} so the direct formation of C₂Br₄ through CBr₂ dimerization is not relevant in solution. The bimolecular recombination of CX₂ to C₂X₄ probably happens in the gas phase as suggested by the electron diffraction of pyrolysis of Cl₄.²⁵ The structures of C₂Br₆ and C₂Br₄ in methanol are shown in Figure 4. The calculated XYZ coordinates of C₂X₆ and C₂X₄ (X = Br, I) in the gas phase and in various solutions at B3LYP level are shown in Table 11S and Table 13S of the Supporting Information, and the vibrational frequencies are shown in Table 12S and Table 14S, respectively.

Since the experimental data about C₂Br₆ from gas-phase electron diffraction study might be in error,²⁶ and the C₂I₆ did not form in thermal dissociation of Cl₄,²⁵ the experimental data are available only for C₂I₄ in the gas phase.⁵⁹ Table 7 shows the geometric parameters of C₂Br₄, C₂Br₆, C₂I₄, and C₂I₆ at the MP2 level, and the comparison with the experimental data of C₂I₄. The computed C-C and C-I bond lengths of 1.363 and 2.091 Å and I-C-C bond angle of 122.9° for C₂I₄ are in very good agreement with the measured C-C and C-I bond lengths of 1.363 and 2.106 Å and the I-C-C bond angle of 122.9°.⁵⁹ Compared to the previous MP2 results with ECP basis set for I atom,²⁵ the present study with the all-electron basis set 6-311+G(d) for I atom gives better results. C₂X₆ have two possible structures; the staggered and eclipsed conformer. The energies of the eclipsed conformers are 23.3 and 28.8 kcal/mol higher than those of the staggered conformers for C₂Br₆ and C₂I₆ respectively at the MP2 level. The XYZ coordinates of the eclipsed conformers of C₂X₆ (X = Br, I) at the MP2 level are shown in the Supporting Information Table 15S.

C_2X_5 . Our calculation shows that C_2Br_6 dissociates through an intermediate molecule C_2Br_5 . Two conformers, the anti and bridged structures of the C_2X_5 ($X = Br, I$) molecule were calculated. The anti conformer of C_2Br_5 is the ground-state structure in the gas phase and in solution, while the bridged conformer has imaginary frequencies, indicating that it is a saddle point in the potential energy surface. The structure of C_2Br_5 in methanol is shown in Figure 4. C_2I_5 also has the anti conformer as the ground state, while the bridged structure has an imaginary frequency, in the gas phase. The calculated XYZ coordinates of C_2X_5 ($X = Br, I$) in the gas phase and in various solutions at B3LYP level are shown in Table 16S of the Supporting Information, and the vibrational frequencies are shown in Table 17S.

4. Conclusion

The photodissociation of CX_4 ($X = Br, I$) in the gas phase and in various solutions was investigated with ab initio and DFT methods. The relativistic effects were evaluated with Spin-Orbit DFT (SODFT) computations. According to our calculation, the excited CX_4^* dissociates in a multistep process: in the gas phase, initial C–X bond rupture is followed by secondary cleavage of the C–X bond in the CX_3 radical. In solution, the X–X binding reaction to form the X_2CX-X ($X = Br, I$) isomer becomes the most important pathway and formation of C_2X_6 through nongeminate recombination of the CX_3 radicals followed by the dissociation to C_2X_4 and X_2 is a parallel reaction channel. The calculated absorption and Raman spectra of the $Br_2CBr-Br$ isomer in various solutions are in good agreement with the experimental data. The natural population analysis indicates that the $Br_2CBr-Br$ isomer corresponds to the recently reported solvent-stabilized solvated ion pair $(CBr_3^+/Br^-)_{solv}$ in the highly polar alcohol solvent. The CX_2 ($X = Cl, Br, I$) radicals have the 1A_1 singlet as the ground state in the gas phase and in solution at various computational levels. The optimized geometric parameters of C_2I_4 are in good agreement with the experimental results.

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Supporting Information Available: Tables showing the valence basis sets of Br and I atoms, which were used in the SODFT calculations, relative energies of the reaction intermediates, transition state, and products of Cl_4 decomposition in the gas phase, in methanol, benzene, and chloroform at the B3LYP level, optimized structural parameters and the XYZ coordinates of the transition states connecting X_2CX-X isomer and CX_4 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, calculated vibrational frequencies and IR intensities of the transition states (TS) connecting X_2CX-X isomer and CX_4 ($X = Br, I$) in the gas phase and in various solvents, optimized XYZ coordinates of the $Br_2CBr-Br$ isomer in the gas phase and in various solvents at the B3LYP level, calculated vibrational frequencies, IR intensities of the $Br_2CBr-Br$ isomer in the gas phase and in various solvents at B3LYP level, optimized XYZ coordinates of the I_2CI-I isomer in the gas phase and in various solvents at the B3LYP level, calculated vibrational frequencies and IR intensities of the I_2CI-I isomer in the gas phase and in various solvents at the B3LYP level, optimized XYZ coordinates of the CX_3 ($X = Cl, Br, I$) radicals in the gas phase and in various solvents at the B3LYP level,

calculated vibrational frequencies and IR intensities of the CX_3 ($X = Cl, Br, I$) radicals in the gas phase and in various solvents at the B3LYP level, optimized XYZ coordinates of C_2X_6 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, calculated vibrational frequencies, IR intensities of C_2X_6 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, optimized XYZ coordinates of C_2X_4 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, calculated vibrational frequencies and IR intensities of C_2X_4 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, optimized XYZ coordinates of the eclipsed C_2X_6 ($X = Br, I$) conformers in the gas phase at the MP2 level, and optimized XYZ coordinates of C_2X_5 ($X = Br, I$) with the anti conformer in the gas phase and in various solvents at the B3LYP level, and calculated vibrational frequencies and IR intensities of C_2X_5 ($X = Br, I$) in the gas phase and in various solvents at the B3LYP level, and figures showing the potential energy levels of the photodissociation of Cl_4 in methanol, plotted using energies calculated at the B3LYP level, 6-311+G(d) basis set for C and 6-311+G(d) basis set for I, optimized PES along the Br–Br distance of the $Br_2CBr-Br$ isomer, which indicates that no energy barrier exists between $CBr_3 + Br$ and the $Br_2CBr-Br$ isomer, IRC calculation of the transition state connecting CBr_4 and the $Br_2CBr-Br$ isomer in the gas phase, indicating that the transition state is a saddle point connecting CBr_4 and the $Br_2CBr-Br$ isomer and HOMO and LUMO depictions of singlet (1A_1) and triplet (3B_1) CX_2 ($X = Br, I$) at the MP2 level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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