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Density Functional Theory Investigation of the Reaction of the Chlorine Atom−Carbon Disulfide Molecular Complex with Dimethylbutane: Implications for Tertiary Selectivity in Alkane Photochlorination Reactions

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We report a density functional theory (DFT) investigation of the chemical reactivity of the S═C═S⋯Cl complex toward 2,3-dimethylbutane (DMB) and compare it to the related reaction of a Cl atom with DMB. The DFT calculations predict that the reaction of a Cl atom with DMB will have little tertiary selectivity toward chlorination consistent with experimental results for photochlorination of alkanes in inert solvents. However, the DFT calculations indicate that the reaction of the S═C═S⋯Cl complex with DMB is different with the primary H abstraction reaction being noticeably more difficult than the tertiary H abstraction reaction. This indicates there will be significant tertiary selectivity for the reaction of the S═C═S⋯Cl complex with DMB and this is consistent with experimental results for chlorination of DMB in CS_2 solvent. We examine the reaction mechanism and properties of the S═C═S⋯Cl complex and explore potential implications for tertiary selectivity for other related photochlorination reactions.

Introduction

Alkane photochlorination reactions exhibit a substantially enhanced selectivity for tertiary versus primary chlorination when carried out in a number of aromatic solvents or carbon disulfide solvent.[1−19] 2,3-Dimethylbutane (DMB) has typically been used as a substrate to study and measure this interesting chemical selectivity, S^m, for photochlorination reactions (where S^m = [2-chloro-2,3-dimethylbutane]/[1-chloro-2,3-dimethylbutane] = [2-ClDMB]/[1-ClDMB]). An equilibrium between free Cl atoms and those bound to a solvent complex (either arene/Cl π complex or a CS_2/Cl complex or a pyridine/Cl σ complex) where the complexes have a greater reactivity toward tertiary over primary sites in the alkane substrate has been used to help explain the observed increased tertiary selectivity in the photochlorination reactions.[1−19] However, the reaction mechanism and properties of the solvent/Cl complexes responsible for the enhanced tertiary selectivity are still not well understood.

Pulsed radiolysis and laser flash photolysis techniques have also been used to study the benzene/Cl complex[5,7,16−18,20] and the related pyridine/Cl[11] and dimethyl sulfoxide/Cl (DMSO/Cl) complexes.[21−25] The CS_2/Cl complex has been examined using similar methods, and its electronic absorption, kinetics of formation, and chemical reactivity toward DMB were compared to those of the benzene/Cl and pyridine/Cl complexes.[26] The CS_2/Cl complex has a strong electronic absorption band (with a maximum around ∼370 nm and a shoulder ∼490 nm).[26] A reversible adduct complex has been observed in the gas-phase reaction of the chlorine atom with CS_2,[27−29] and several theoretical studies were performed to consider possible structures of the CS_2/Cl complex or adduct species. The theoretical studies found possible structures with either the chlorine atom attached to the carbon atom of CS_2 or the chlorine atom attached to the S atom of CS_2.[30,31] We recently reported a solution phase transient resonance Raman investigation[32] performed to directly probe the structure and bonding of the CS_2/Cl complex associated with the ∼370 nm transient absorption band observed in solution phase photochlorination reactions.[26] Comparison of the resonance Raman experimental vibrational frequencies to those estimated from density functional theory (DFT) calculations for the likely CS_2/Cl complex structures showed that the CS_2/Cl complex has a structure with the chlorine atom attached to the S atom of CS_2 (e.g., an S═C═S⋯Cl complex). This S═C═S⋯Cl complex is responsible for the increased tertiary selectivity observed for photochlorination reactions done in the presence of CS_2 solvent.

In this paper, we use density functional theory and ab initio methods to investigate the chemical reactivity of the S═C═S⋯Cl complex toward DMB and compare it to the corresponding reaction of a Cl atom with DMB. We find that the reaction of the Cl atom is exothermic for both primary and tertiary abstraction of DMB with very similar barriers for the last rate-determining step. This predicts little tertiary selectivity for the Cl atom reaction with DMB and is consistent with experiments and expectation for a normal Cl atom chlorination reaction in an inert solvent. The reaction of the S═C═S⋯Cl complex toward DMB exhibited noticeably different behavior with the primary abstraction becoming endothermic by ∼5.9 kcal/mol and the tertiary abstraction reaction being still exothermic by ∼1.3 kcal/mol at the UB3LYP/6-311G** level of theory. This predicts that the primary abstraction reaction with DMB will be noticeably slower than the tertiary abstraction and is consistent with experimental observations. The inhibition of the primary abstraction reaction in the S═C═S⋯Cl complex

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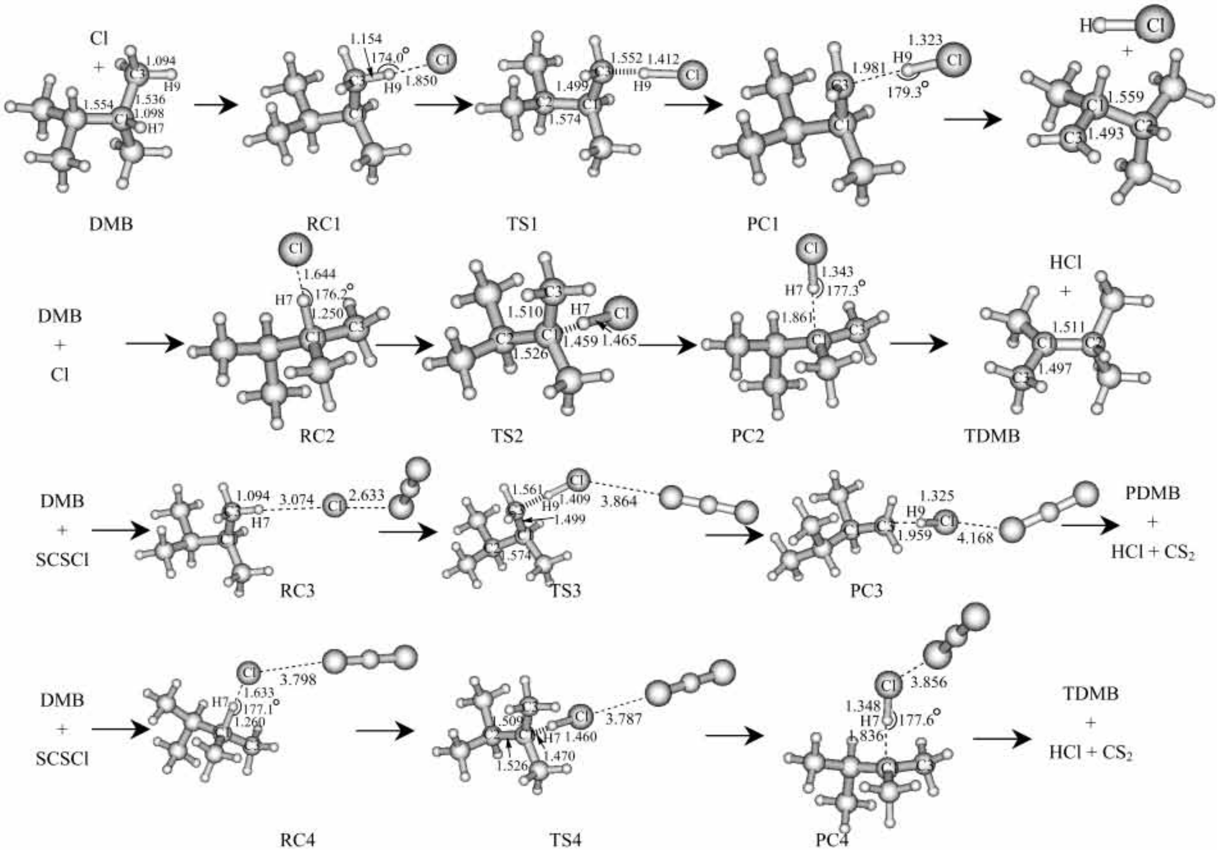

Figure 1. Simple schematic diagrams of the UB3LYP/6-311G** optimized geometry found for the reactants (DMB, Cl, and S═C═S⋯Cl), reactant complexes (RC1−RC4), transition states (TS1−TS4), product complexes (PC1−PC4) and products (PDMB, TDMB, HCl, and CS_2) for reactions 1−4. Selected structural parameters are given as Å for bond lengths or degrees for bond angles.

toward DMB compared to the tertiary abstraction reaction can help explain the experimentally observed tertiary selectivity for photochlorination reactions done in CS_2 solvent. We discuss the reaction mechanism and the properties of the S═C═S⋯Cl complex. We briefly discuss potential implications for tertiary selectivity in related photochlorination reactions.

Results and Discussion

The chemical reactions of the S═C═S⋯Cl complex species and the Cl atom toward DMB were compared for both primary and tertiary hydrogen abstraction. The general model of radical reactions[33] shown below as Scheme 1 was used to explore these reactions

Scheme 1

$$\mathrm{R} \rightarrow \mathrm{RC} \rightarrow \mathrm{TS} \rightarrow \mathrm{PC} \rightarrow \mathrm{P}$$

where R represents the reactants, RC is the reactant complex, TS is the transition state, PC is the product complex, and P represents the products. Following this scheme, one would expect the formation of a weak complex between the DMB substrate and the Cl atom or S═C═S⋯Cl complex species. This would be followed by partial formation of an H−Cl bond and partial C−H bond cleavage in the transition state with subsequent completion of the C−H bond cleavage to give a product complex that then proceeds to give the product. The products would be the primary-2,3-dimethyl butyl radical (denoted as PDMB) or the tertiary-2,3-dimethylbutyl radical (denoted as TDMB) and either HCl or CS_2 + HCl. The following specific reactions were investigated using B3LYP/6-311G** and MP2/6-31G* calculations:

$$\mathrm{DMB} + \mathrm{Cl} \rightarrow \mathrm{RC1} \rightarrow \mathrm{TS1} \rightarrow \mathrm{PC1} \rightarrow \mathrm{PDMB} + \mathrm{HCl} \quad (1)$$

$$\mathrm{DMB} + \mathrm{Cl} \rightarrow \mathrm{RC2} \rightarrow \mathrm{TS2} \rightarrow \mathrm{PC2} \rightarrow \mathrm{TDMB} + \mathrm{HCl} \quad (2)$$

$$\mathrm{DMB} + \mathrm{S{=}C{=}S\cdots Cl} \rightarrow \mathrm{RC3} \rightarrow \mathrm{TS3} \rightarrow \mathrm{PC3} \rightarrow \mathrm{PDMB} + \mathrm{CS_2} + \mathrm{HCl} \quad (3)$$

$$\mathrm{DMB} + \mathrm{S{=}C{=}S\cdots Cl} \rightarrow \mathrm{RC4} \rightarrow \mathrm{TS4} \rightarrow \mathrm{PC4} \rightarrow \mathrm{TDMB} + \mathrm{CS_2} + \mathrm{HCl} \quad (4)$$

The PDMB and TDMB radicals produced from reactions 1−4 can then easily undergo further very facile reaction with Cl_2 to produce the chlorinated DMB product and another Cl atom. The tertiary selectivity in photochlorination reactions with alkanes is thought to be due to differences in the production of the PDMB and TDMB radicals, so we focus our study on reactions 1−4. Figure 1 displays simple schematic diagrams of the UB3LYP/6-311G** optimized geometry found for the reactants (DMB, Cl, S═C═S⋯Cl), reactant complexes (RC1−RC4), transition states (TS1−TS4), product complexes (PC1−PC4), and products (PDMB, TDMB, HCl, and CS_2) shown in reactions 1−4. The corresponding schematic diagrams from the MP2 calculations are shown in the Supporting Information (Figure S1). Selected structural parameters are given as Å for bond lengths or degrees for bond angles in Figure 1 and Figure S1. The Cartesian coordinates, total energies, and zero-point energies for the species shown in Figure 1 and Figure S1 are listed in the Supporting Information. Figure 2 and Figure S2 present a simple energy profile (in kcal/mol) for the reactions 1−4

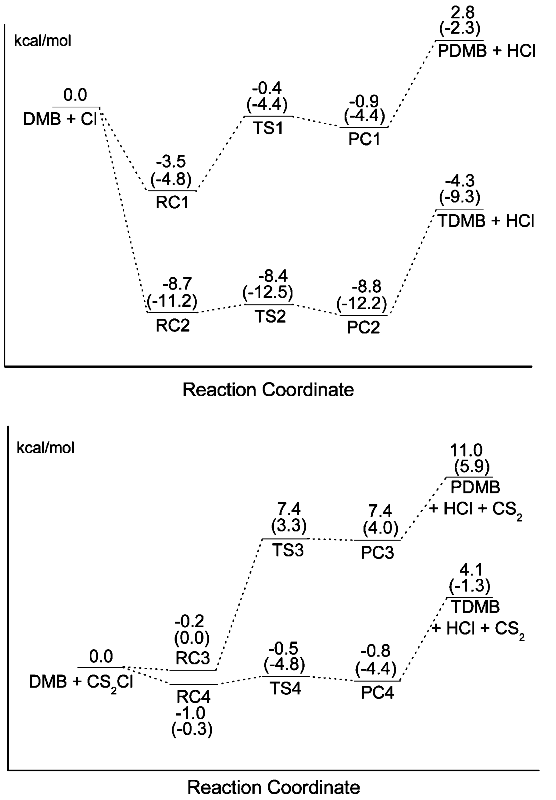

Figure 2. Energy profile (in kcal/mol) for the reactions 1−4 obtained from the UB3LYP/6-311G** calculations. The values in parentheses include the zero-point energies.

obtained from the UB3LYP/6-311G** and UMP2/6-31G* calculations, respectively. The potential energy surfaces are somewhat flat between the reactant complex and product complex for most of the reactions. Vibrational analysis was used to confirm the transition states connected the corresponding reactant and product species. Inspection of Figure 2 shows both reaction pathways are overall exothermic when the zero-point energy is included with the PDMB pathway exothermic by 2.3 kcal/mol and the TDMB pathway exothermic by 9.3 kcal/mol. The results for Cl atom reaction with DMB are consistent with both formation of PDMB and TDMB being facile and leading to little tertiary selectivity for chlorination as observed for photochlorination experiments done for DMB in inert solvents (where the selectivity of tertiary to primary hydrogens is 4.2 for DMB on a per hydrogen basis).[34] The tertiary DMB radical is significantly more stable than the primary DMB radical. This leads the transition state for formation of the tertiary radical to stay at lower energies because the partial C−H bond cleavage results in changes of the valence orbital hybridization of C and give more σ(C−H)−p(C) conjugation for TS2 compared to TS1. However, the highly reactive Cl atom does not allow this difference between the tertiary and primary radicals to be exploited.

Inspection of Figure 2 shows the reactions of the S=C=S$\cdots$Cl complex with DMB are significantly different than those for the Cl atom with DMB. The S=C=S$\cdots$Cl complex first reacts with DMB to produce weakly bound reactant complexes RC3 and RC4 that are very weakly endothermic or exothermic (about 0.0 and −0.3 kcal/mol with the zero-point energy included). This contrasts with the Cl atom reactions with DMB that lead to more strongly bound and exothermic reactant complexes RC1 and RC2 (−4.8 and −11.2 kcal/mol, respectively, with the zero-point energy included). The key steps going from the reactant complexes RC3 and RC4 to form product complexes PC3 and PC4 via TS3 and TS4, respectively, takes about 4.0 kcal/mol of energy to get the primary DMB product complex PC3. However, this is an exothermic process (by about 4.4 kcal/mol with zero-point energy) with little or no barrier to produce the tertiary DMB complex PC4. This indicates it is much easier to make the tertiary DMB product complex PC4 than the primary DMB product complex PC3. The decomposition of the product complexes PC3 and PC4 into the corresponding products requires about the same amount of energy (1.9 and 3.1 kcal/mol, respectively, with the zero-point energy included). The overall reaction to produce the primary DMB radical (PDMB), HCl, and CS$_2$ products is endothermic by about 5.9 kcal/mol, whereas the reaction to make the tertiary DMB radical (TDMB), HCl, and CS$_2$ products is exothermic by −1.3 kcal/mol. This suggests that some of the energy released as the tertiary reaction complex RC4 goes on to form the product complex PC4 could be used to help climb the last barrier to form the product molecules. However, this is not available for the primary reaction pathway to make PDMB, HCl, and CS$_2$. Our results indicate that the reaction of S=C=S$\cdots$Cl complex with DMB to produce primary DMB radical product becomes substantially more difficult compared to the reaction to make tertiary DMB radical product. This indicates a stronger preference for formation of tertiary DMB chlorination products compared to primary DMB chlorination products and is consistent with experimental observations that photochlorination of DMB in CS$_2$ solvent results in a large enhancement of tertiary selectivity.[2,18,26] Comparison of the Cl atom reactions and the S=C=S$\cdots$Cl reactions with DMB in Figure 2 reveals that the main role of the S=C=S$\cdots$Cl species is to make the Cl atom less reactive as well as to modify the hydrogen abstraction reaction pathways.

TABLE 1: Relative Energies (without Zero-Point Energy) for the Key Reaction Step to Go from Reactant Complexes to Product Complexes in Reactions 1−4 Calculated from the UB3LYP/6-311G, the UCCSD(T)/6-31G* at the UB3LYP/6-311G**Optimized Geometry, and the UMP2/6-31G* Calculations[a]**

reaction	UB3LYP/6-311G**	UCCSD(T)/6-31G*	UMP2/6-31G*
(1)	3.1	7.3	12.2
(2)	0.3	1.2	3.6
(3)	7.6	11.2	11.9
(4)	0.5	1.4	2.8

[a] The relative energies are given in kcal/mol.

To help assess the accuracy of the UB3LYP/6-311G** calculated results, we performed more accurate UCCSD(T)/6-31G* single-point energy calculations at the UB3LYP/6-311G** optimized geometry for the reactions of the S=C=S$\cdots$Cl complex with DMB. Table 1 lists the relative energies (without zero-point energy) for the key reaction step to go from reactant complexes to product complexes in reactions 1−4 calculated from the UB3LYP/6-311G**, UCCSD(T)/6-31G* at the UB3LYP/6-311G**optimized geometry, and the UMP2/6-31G* calculations. The barriers for the key reaction step to form product complexes PC1, PC2, PC3, and PC4 from reactant complexes RC1, RC2, RC3, and RC4 via TS1, TS2, TS3, and TS4 were found to be about 7.3, 1.2, 11.2, and 1.4 kcal/mol, respectively, without zero-point energy corrections from the UCCSD(T) computations. These values are reasonably close to the 3.1, 0.3, 7.6, and +0.5 kcal/mol without zero-point energy computed from the UB3LYP/6-311G** calculations. Both the UCCSD(T)/6-31G* and UB3LYP/6-311G** calculations indicate that it is significantly more difficult to abstract the primary hydrogen atom from DMB using the S=C=S$\cdots$Cl complex than it is to abstract the tertiary hydrogen atom from DMB. This difference results in a decrease in the primary abstraction reaction rates relative to the tertiary reactions and the increased tertiary selectivity observed experimentally in CS_2 solvent.[2,18,26] The barrier of the primary abstraction reaction for the S═C═S···Cl complex increases by about 3.9 kcal/mol for the UCCSD(T) and about 4.5 kcal/mol for the UB3LYP calculations respectively compared to the free Cl reaction. The UCCSD(T) results also suggest that the UB3LYP/6-311G** calculations may underestimate the barriers to reaction by a couple of kcal/mol but exhibit the same basic reaction behavior and agreement with the experimental observation of increased tertiary selectivity of the photochlorination reactions done in CS_2 solvent.[2,18,26] This provides us with some confidence that the UB3LYP/6-311G** computations give a reasonably accurate description of reactions 1−4 suitable for semiquantitative elucidation of the role of the S═C═S···Cl complex in the enhanced tertiary selectively observed for alkane photochlorination reactions occurring in CS_2 solvent. In contrast, the UMP2/6-31G* calculations predict almost no difference in the tertiary selectivity between the S═C═S···Cl complex reactions compared to the free Cl reactions. The UMP2/6-31G* barriers for the key step in reactions 1 and 2 are about the same as those for reactions 3 and 4, respectively, in Table 1. This occurs because the UMP2 calculations predict a much weaker interaction between the Cl atom and CS_2 for the S═C═S···Cl complex and this leads to the Cl atom reactivity being almost the same as the free Cl atom. The UMP2 results are not in agreement with the experimental observation of increased tertiary selectivity of photochlorination reactions done in CS_2 solvent.[2,18,26] UMP2 calculations have also previously been noted to be inadequate to reasonably describe the two isomers of the CS_2/Cl complex (the C and S isomers), and the reader is referred to refs 30 and 32 for more details. Comparison of the UMP2 results to those found from the UB3LYP and UCCSD(T) results illustrates the importance of the strength of the interaction of the Cl atom with the solvent to form a solvent−Cl complex. This is consistent with the experimental observations of greater tertiary selectivity for the photochlorination reactions done in pyridine (where relatively strong σ-bonded pyridine/Cl complexes are formed) compared to reactions done in benzene (where relatively weak π-bonded benzene/Cl complexes are formed).

Comparison of the structures and properties of the transition states and intermediates for the Cl atom and S═C═S···Cl complex reactions with DMB reveal some interesting changes in chemical reactivity. The computed potential energy surface shown in Figure 2 indicates that the Cl atom reaction with DMB leads first to more stable reactant complexes RC1 and RC2 which are about 3.5 and 8.7 kcal/mol more stable than their separated species. However, the S═C═S···Cl complex first reacts to form noticeably weaker reactant complexes RC3 and RC4 that are only a little more stable (by 0.2 and 1.0 kcal/mol, respectively) than their separated species. This indicates the more reactive Cl atom first forms a more stable charge complex species with DMB, whereas the CS_2 moiety of the S═C═S···Cl complex reduces the charge-transfer character and reactivity of the Cl atom when it reacts with DMB. The reactant complex H−Cl distances are about 1.850, 1.644, 3.074, and 1.633 Å for RC1, RC2, RC3, and RC4, respectively. For the primary abstraction reaction, the RC3 complex has a very weak H−Cl interaction compared to RC1 consistent with a weakly bound RC3 species with not much charge-transfer character. However, the RC4 species has a somewhat larger H−Cl interaction than found for RC2, and this suggests it still has a noticeable amount of charge transfer character. However, it is also a weakly bound species only a little more stable than its separated parts. This is due to some of the energy being used to weaken the S−Cl bond which becomes 3.798 Å in RC4 compared to about 2.636 Å in the S═C═S···Cl complex. The S−Cl bond in RC3 (2.633 Å) is almost the same as that in the S═C═S···Cl complex. This suggests that the S═C═S···Cl complex reduces the Cl atom reactivity more for the primary reactant complex RC3 (which has little H−Cl interaction and little charge-transfer character) compared to the tertiary reactant complex RC4 (which still has a strong H−Cl interaction and noticeable charge transfer character). The potential energy surfaces are fairly flat for the RC3 complex, but both UB3LYP and UMP2 calculations predict a weak H−Cl interaction with distances of 3.074 and 2.941 Å, respectively.

The DFT computed structures for the transition states show that the Cl atom abstracts one hydrogen from either a primary or tertiary C near a linear path with the $A_{\mathrm{C-H-Cl}}$ angle in the range of 175 to 180°. The interaction between C and H is weakened and that of H and Cl is strengthened as the reaction proceeds to the transition states. This leads to the C−H and H−Cl bond lengths changing to 1.552 and 1.412 Å in TS1, 1.459 and 1.465 Å in TS2, 1.561 and 1.409 Å in TS3, and 1.470 and 1.460 Å in TS4. There is not a great amount of difference between the C−H and H−Cl bond lengths, and the hydrogen atom appears to be shared by both the C and Cl atoms (like C···H···Cl bonding).[35,36] The distance between C and Cl in TS1−TS4 is noticeably shorter than in traditional C−H···Cl or C···H−Cl bonding, and the proton is shared between the C and Cl atoms. This C···H···Cl bonding is also characterized by low electron density on the proton. The transition states TS1−TS4 appear to be stabilized by the proton-shared bonding. In the S═C═S···Cl complex reactions with DMB, the charge located on the shared proton increases by +0.003 and +0.030 for TS3 and TS4, respectively. This suggest that TS3 and TS4 are stabilized less than TS1 and TS2, and this is consistent with TS3 and TS4 being at higher energies relative to their reactant complexes (see Figure 2).

The proton shared nature of the C···H···Cl bonding in TS1-TS4 leads to relatively low vibrational "stretching" frequencies for the reaction coordinate as has been found in previous studies for proton-shared hydrogen bonds.[35,36] The reaction vectors are $0.882\ R_{\mathrm{C3-H9}} - 0.345\ R_{\mathrm{H9-Cl}} - 0.107\ A_{\mathrm{H9-C3-H10}}$ for the 278i cm^{-1} mode of TS1 and $0.827\ R_{\mathrm{C1-H7}} - 0.449\ R_{\mathrm{H7-C1}}$ for the 357i cm^{-1} mode of TS2. The $A_{\mathrm{H9-C3-H10}}$ component found for the reaction vector for TS1 suggests that the interaction between H and Cl may be somewhat more important for the tertiary abstraction compared to the primary abstraction associated with TS1. The reaction vectors found for the S═C═S···Cl complex reactions with DMB were found to be $0.884\ R_{\mathrm{C3-H9}} - 0.338\ R_{\mathrm{H9-Cl}} - 0.106\ A_{\mathrm{H9-C3-H10}}$ for the 247i cm^{-1} mode of TS3 and $0.826\ R_{\mathrm{C1-H7}} - 0.458\ R_{\mathrm{H7-Cl}}$ for the 297i cm^{-1} mode of TS4. The presence of CS_2 in the S═C═S···Cl complex leads to a little smaller H9−Cl contribution to the reaction vector for the primary H abstraction reaction associated with TS3 and to a greater H7−Cl contribution to the reaction vector for the tertiary H abstraction reaction associated with TS4. This suggests that the CS_2 moiety in the S═C═S···Cl complex perturbs TS3 to be more reactant-like to give a higher transition state energy, whereas it perturbs TS4 to be more product-like to give a lower transition energy. This is consistent with greater tertiary to primary H abstraction from DMB when the Cl atom is complexed with CS_2 solvent.

Comparison of the Cl atom and S═C═S···Cl complex reactions with DMB suggests that the tertiary selectivity of the photochlorination reactions would show some correlation with the strength of the solvent−Cl bond and this is consistent with a range of experimental observations. The benzene−Cl π complex is expected to have a small bond enthalpy. For UB3LYP/Aug-cc-PVTZ calculations, the solvent−Cl bond enthalpies were found to be 10.5 kcal/mol for the S═C═S⋯Cl complex[32] and 14.5 kcal/mol for the pyridine-Cl complex.[32] These solvent−Cl bond strengths exhibit a strong correlation with both the experimentally observed equilibrium constants for these complexes and the tertiary/primary selectivity for the chlorination of DMB: $K = 200$, 1900, and 123 000 M^{-1}, respectively, for the benzene−Cl, S═C═S⋯Cl, and pyridine−Cl complexes; tertiary/primary selectivity = 50/1, 100/1, and 200/1 respectively for the benzene−Cl, S═C═S⋯Cl, and pyridine−Cl complexes.[7,11,17,18,26] The benzene−Cl complex is thought to be a π complex[7,17,18] although there have been suggestions for a 6-chlorocyclohexadienyl radical or σ complex.[5,6,8] The S═C═S⋯Cl complex has both σ and π bonding interactions between the Cl atom and the CS_2 moiety similar to three-electron-two center bonding (see ref 32 for a more complete description of this complex species). Breslow and coworkers[11] demonstrated that the pyridine−Cl species is a σ complex with three-electron-two center N−Cl bonding. The Cl atom is a highly reactive reagent with high electronegativity and an unpaired electron in the p orbital and therefore can readily interact with solvent molecules by p−σ or p−π conjugation. As the solvent−Cl bonding becomes stronger in these moderately bound molecular complexes, the reactivity of the Cl atom is reduced so that the natural difference between the primary and tertiary H atom abstraction reactions can be exploited to give reasonably high tertiary selectivity in the alkane chlorination reactions.

Free radical chlorination of alkanes in several halogenated solvents were recently investigated, and these experiments found tertiary selectivity to be enhanced in these solvents similar to reactions in aromatic and CS_2 solvents.[19] The observed tertiary selectivity in the halogenated solvents decreased with increasing Cl atoms in the solvent which varies with the ionization potential of the solvent.[19] It was suggested that Cl forms complexes with the halogenated solvents, and these complexes have higher selectivity in hydrogen abstraction reactions than Cl atoms. The selectivity decreases with increasing Cl atoms of the halogenated solvent and correlates with the ionization potential of the solvent. This and the higher selectivity in bromoalkane solvents compared to chloroalkane solvents suggest the halogenated solvent−Cl complexes are donor/acceptor complexes. We note that halogenated solvent−halogen atom complexes have been experimentally observed in a number of transient absorption studies following laser flash photolysis and/or pulse radiolysis in room-temperature solutions on the microsecond timescale.[37−44] These types of complexes exhibited strong broad transient absorption bands in the near-ultraviolet and visible regions[37−44] similar to transient absorption bands observed for isopolyhalomethanes that have similar halogen atom−halogen atom chromophores.[45−47] The transient absorption bands observed after ultraviolet photolysis of a number of polyhalomethanes (like CH_2I_2, CH_2Br_2, and CH_2BrI) were directly probed using time-resolved resonance Raman experiments and shown to be mainly due to isopolyhalomethane species (CH_2X−X or CH_2X−Y) on the picosecond to nanosecond time scales.[48−53] We recently used the transient resonance Raman spectra and density functional theory calculations to characterize the CH_3I⋯I and CH_2I_2⋯I molecular complexes[54,55] and found they had a weak I−I bond similar to that found in the isodiiodomethane species (CH_2I−I) but a noticeably different structure relative to the C−I bond. The CH_3I−I and CH_2I_2⋯I molecular complexes showed little perturbation of the C−I bond when the loosely bound I−I bond is formed,[54,55] and this is similar to the small perturbation of the C═S bonds in the S═C═S⋯Cl complex as the loosely bound S−Cl bond is formed. This suggests that the halogenated solvent−Cl complexes have similar structures as the CH_3I⋯I and CH_2I_2⋯I molecular complexes[54,55] and the S═C═S⋯Cl complex. Thus, it seems likely that the halogenated solvent−Cl complexes have similar properties for lowering the reactivity of the Cl atom as the S═C═S⋯Cl complex, and this is consistent with the observation of increased selectivity in the photochlorination reactions done in halogenated solvents.[19,44]

Conclusion

The S═C═S⋯Cl complex main role appears to be to lower the reactivity of the Cl atom so that the different stability of the primary and tertiary DMB radicals can be used to enhance the selectivity of formation of the more stable tertiary radicals. The S═C═S⋯Cl complex also noticeably enhances the tertiary to primary DMB selectivity in two other ways. First, the formation of the reactant complexes is noticeably perturbed to reduce the H−Cl interaction in RC3, whereas the S−Cl bond is not perturbed very much from its value in the S═C═S⋯Cl complex. However, the formation of RC4 complex has some enhancement of the H−Cl interaction accompanied by a noticeable weakening of the S−Cl bond in the S═C═S⋯Cl moiety. Second, the transition state structures and reaction vectors indicate the S═C═S⋯Cl complex perturbs TS3 for the primary abstraction reaction to become more reactant-like, whereas TS4 for the tertiary reaction becomes more product-like. Both of these suggest that the properties and interactions of the solvent−Cl complex with DMB (or other alkane substrates) can also noticeably modify or enhance the tertiary to primary selectivity. It will be interesting to see how important these particular solvent−Cl interactions with the DMB (or other substrates) are in determining the overall observed tertiary selectivity compared to just lowering the basic reactivity of the Cl atom. Further work on a variety of solvent−Cl reactions with DMB and other alkanes will be needed to better assess this issue.

Computational Methods

All of the ab initio and density functional theory calculations reported here made use of the Gaussian 98W program suite.[56] UB3LYP density functional theory calculations were used to investigate the hydrogen abstraction reactions of the Cl atom and the CS_2/Cl complex with DMB. All of the stationary points were fully optimized using C_1 symmetry or as indicated in the text. Vibrational frequency calculations were done to verify the nature of each stationary point and to find the zero-point energy. The UB3LYP calculations made use of the 6-311G** basis set.[57−59] All of the first-order saddle points found were animated using the MOLDEN program[60] to verify that the transition states connected the relevant reactants and products. Their imaginary frequencies correspond to the antisymmetric motion of the bridging H along the C−H−Cl axis indicating the formation of a new H−Cl bond and cleavage of the old C−H bond for the hydrogen abstraction reactions. For the UB3LYP/6-311G** calculations, 26 basis functions were abstracted from 49 primitive Gaussians for Cl, 70 basis functions from 124 primitive Gaussians for CS_2, and 192 basis functions from 304 primitive Gaussians for 2,3-dimethylbutane (DMB). The unrestricted coupled-cluster theory with single and double excitations that includes a quasiperturbative treatment of triple-excitation terms,[61] referred to as UCCSD(T), has been demonstrated to provide good approximations to the transition state geometries and energies for radical-molecule reactions.[62] This method, in conjunction with the 6-31G* basis set, was used in the present work to carry out single point energy calculations on the basis of the B3LYP/6-311G** optimized structures.

We note that, for the flat parts of the reaction potential energy surface, small errors in the harmonic approximation used to estimate zero-point energies can cause the transition state to appear to lie a little below the reactant and/or product complexes when the zero-point energy is included.[35,63] This is only a limitation of using the harmonic approximation to estimate the zero-point energies and does not imply the transition states TS2-TS4 are actually below the energy of their respective reactant or product complexes.

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Supporting Information Available: Selected output from the density functional theory and ab initio calculations showing the Cartesian coordinates, total energies and vibrational zero-point energies for the $S{=}C{=}S\cdots Cl$ complex and DMB reactants, reactant complexes (RC1−RC4), transition states (TS1-TS4), product complexes (PC1−PC4), and PDMB, TDMB, HCl, and CS_2 products for the reactions 1−4. UCCSD(T) single-point calculations with the B3LYP optimized geometry are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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