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Dichlorocarbene Addition to C_{60} from the Trichloromethyl Anion: Carbene Mechanism or Bingel Mechanism?

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The reactions of C_{60} and trichloromethyl anion (CCl_3^-) via both the Bingel mechanism and the carbene mechanism were comparably studied by means of density functional theory (DFT) computations. The Bingel mechanism is highly competitive as compared with the carbene mechanism that leads to the formation of $C_{60}(CCl_2)$. Unlike the carbene mechanism with a weak regioselectivity and solvent sensitivity, the Bingel mechanism yields the [6,6]-$C_{60}(CCl_2)$ isomer as the exclusive product and favors highly polar solvents. The results receive strong experimental support and simultaneously rationalize these experimental findings.

Introduction

Several synthetic routes have been developed to attach a CCl_2 functional group to the framework of C_{60} (I_h) fullerene.[1−5] Among them, the most frequently used ones employ trichloromethyl anion (CCl_3^-) as a critical intermediate of dihalocarbene (CCl_2) precursor because of low cost and low toxicity.[1−5] Because CCl_3^- is unstable and rapidly equilibrates to CCl_2 and Cl^- in reaction media,[6] it can react as either CCl_2 or CCl_3^- itself.[6] Accordingly, similar to the reactions between CCl_3^- and alkenes,[6] there are two possible mechanisms for the CCl_2 to transfer from CCl_3^- to C_{60} (Figure 1), namely, carbene mechanism and Bingel mechanism. (The CCl_3^--addition/Cl^--elimination path resembles the Bingel reaction.[7,8])

According to accepted knowledge,[6] the reactions of CCl_3^- with alkenes strongly depend on the alkene substrates: the carbene mechanism dominates the reactions between CCl_3^- and electron-rich alkenes, affording stereospecific adducts, whereas the Bingel-like mechanism dominates the reactions with electron-deficient alkenes, affording nonstereospecific adducts. Because C_{60} readily reacts with both electrophiles and nucleophiles,[9] both paths may be rational for the reaction between CCl_3^- and C_{60}. However, it is impossible to study the competition of these two mechanisms by means of stereochemical investigations because no carbon−carbon bonds of C_{60} can rotate to yield stable stereoisomers, even in Bingel reactions, because of its rigidity. Theoretically, although the carbene mechanism for the reaction of CCl_3^- and C_{60} has been studied before,[10,11] the Bingel mechanism and its competition with the carbene mechanism has not yet been unraveled. Therefore, the mechanism of CCl_2 transfer from CCl_3^- to C_{60} is still ambiguous, and some experimental findings are waiting to be understood. For example, Zhu found that using highly polar solvents efficiently accelerates the $C_{60}(CCl_2)$ formation in the reaction between CCl_3^- and C_{60};[4] this result suggests the carbene mechanism that is known to be hardly affected by solvent polarities is not involved. Kiely et al.[2] used two carbene reagents, $PhHgCCl_2Br$ and sodium trichloroacetate, to synthesize $C_{70}(CCl_2)$, and different $C_{70}(CCl_2)$ isomers were obtained as the main products; this experiment suggested that two different mechanisms may be responsible for the two sets of reactions.

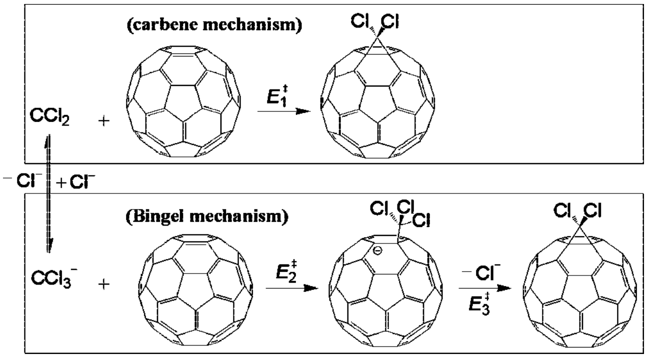

Figure 1. Possible mechanisms for the formation of $C_{60}(CCl_2)$ through the reaction of CCl_3^- and C_{60}.

In this article, the Bingel mechanism for the reaction of CCl_3^- and C_{60} was theoretically studied for the first time and compared with the carbene mechanism by using the B3LYP method in conjunction with basis sets up to 6-31+G(d). Our results suggest that the Bingel mechanism is highly competitive, with the carbene mechanism leading to the formation of $C_{60}(CCl_2)$. Unlike the carbene mechanism, the Bingel mechanism has a strong regioselectivity and solvent sensitivity. The present study answered the long-pending mechanistic question and provided valuable indications to future experiments.

Computational Methods

All stationary points were optimized using the B3LYP method[12−14] in conjunction with two basis sets, 6-31G(d) and 6-31+G(d),[15,16] respectively. Zero-point energies (ZPEs) were obtained by frequency analyses at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. All minima were characterized to have zero imaginary frequency, and all transition states have only one imaginary frequency. The energy profile for the $C_{60}(CCl_3)^-$ intermediate formation was simulated by a series of geometry optimizations at the B3LYP/6-31+G(d) level with the distance between CCl_3^- and C_{60} moiety constrained (d is

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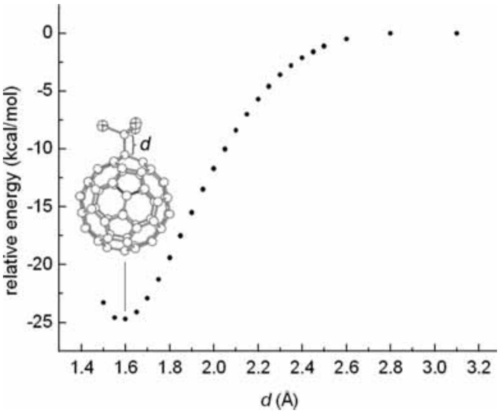

Figure 2. Energy profile for the reaction of C_{60} and CCl_3^- that affords $C_{60}(CCl_3)^-$ intermediate. Geometry optimizations were performed in the gas phase with *d* fixed at the B3LYP/6-31+G(d) level of theory; single-point energies were calculated in THF as solvent at the same level.

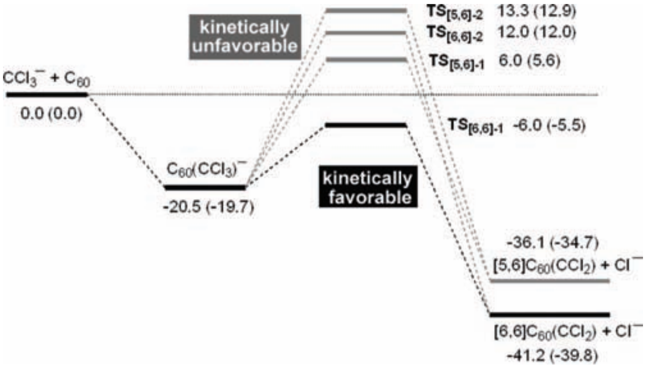

Figure 3. Schematic energy profiles (kcal/mol) for the reaction of C_{60} and CCl_3^- via the Bingel mechanism. Geometry optimization was performed in gas phase at the B3LYP/6-31+G(d) level, and single-point energies were computed in THF at the same level. ZPE (unscaled) corrected data are given in parentheses.

constrained; for the definition of *d*, see Figure 2): relaxing the geometry with *d* fixed and then changing the value of *d* for another round of geometry relaxation. In our calculations, *d* was stepped from 1.5 to 3.2 Å. Solvent effects were studied by single-point energy calculations using the PCM model[17] with the B3LYP/6-31+G(d) method on the basis of the geometries optimized at the same level of theory (B3LYP/6-31+G(d)//B3LYP/6-31+G(d)). All calculations were performed with the Gaussian03 package.[18]

Results and Discussion

Bingel Mechanism. Our calculations suggested that the addition of CCl_3^- to C_{60} is an exothermic, barrierless process ($E_2^{\ddagger} = 0$), affording $C_{60}(CCl_3)^-$ as the exclusive intermediate (Figures 2 and 3). This is consistent with the experimentally observed high electron affinity of C_{60}[19] and also with the theoretical depiction that C_{60} has triply degenerate, low-lying LUMOs (lowest unoccupied molecular orbitals)[20] capable of accommodating as many as six electrons.

Because C_{60} has two symmetrically unique carbon−carbon bonds, that is, [6,6]-bond and [5,6]-bond (Figure 4a), there are two possible isomers for the $C_{60}(CCl_2)$ adduct, that is, [6,6]-$C_{60}(CCl_2)$ and [5,6]-$C_{60}(CCl_2)$, corresponding to structures where the CCl_2 addend bridges either one of the two symmetry unique bonds, respectively. The reaction paths for the subsequent cyclizations of $C_{60}(CCl_3)^-$ that yield both $C_{60}(CCl_2)$ isomers are illustrated in Figure 3. For the formation of either isomer, two reaction paths were located: the cyclization via $TS_{[6,6]-1}$ or $TS_{[6,6]-2}$ gives [6,6]-$C_{60}(CCl_2)$ as a product, whereas that via $TS_{[5,6]-1}$ or $TS_{[5,6]-2}$ gives [5,6]-$C_{60}(CCl_2)$ as a product (Figure 3). Comparing the barrier heights of these paths (Figure 3), the formation of the more thermally stable [6,6]-$C_{60}(CCl_2)$ isomer via transition structure $TS_{[6,6]-1}$ is the most competitive one, with the cyclization barrier of 14.2 kcal/mol. The energy of $TS_{[6,6]-1}$ is lower than that of the reactants by 5.5 kcal/mol; this means that the reverse reaction changing the $C_{60}(CCl_3)^-$ intermediate back to the reactants is uncompetitive compared with the forward reaction (Figure 3). The other three paths (via $TS_{[6,6]-1}$, $TS_{[6,6]-2}$, and $TS_{[5,6]-2}$, respectively) are kinetically unfavorable because they each have a higher energy barrier than that of the reverse reaction (Figure 3). Therefore, the Bingel mechanism has a significant selectivity, yielding [6,6]-$C_{60}(CCl_2)$ isomer as the exclusive product. The structures of the $C_{60}(CCl_3)^-$ intermediate and four transition states are shown in Figure 4. For each transition state, the orientations toward which the CCl_2 cyclizes and the Cl^- eliminates in the forward reaction were labeled (Figure 4c−f). The result shows that Cl^- leaving away from the direction of cyclization is kinetically favored.

Carbene Mechanism. To compare the Bingel mechanism with the carbene mechanism at the same level of theory, the addition of free CCl_2 to C_{60} (i.e., carbene mechanism) was reinvestigated here. Similar to the results by Bettinger at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory,[10] our calculations at the B3LYP/6-31+G(d) level found two reaction paths: the one-step, concerted formation of [6,6]-$C_{60}CCl_2$ via transition state $TS_{[6,6]}$ and the one-step, concerted formation of [5,6]-$C_{60}CCl_2$ via transition state $TS_{[5,6]}$. (For the structures of $TS_{[6,6]}$ and $TS_{[5,6]}$, see ref 10.) The activation energy barriers in the gas phase (with ZPE correction) that we obtained for the two paths were 2.2 and 4.6 kcal/mol, respectively, which were also comparable to those reported by Bettinger (1.8 and 4.1 kcal/mol, respectively).[10] After considering the solvent effect of tetrahydrofuran (THF), these two barriers slightly increased to 3.2 and 5.5 kcal/mol, respectively. These values suggest that via the carbene mechanism the formation of [6,6]-$C_{60}CCl_2$ is only slightly favored over the formation of [5,6]-$C_{60}CCl_2$, which is sharply different from the strong regioselectivity of the Bingel mechanism.

Competition between Bingel Mechanism and Carbene Mechanism. Figure 5 illustrates the competition between the carbene mechanism and the Bingel mechanism, where the preferable paths of both mechanisms are comparably shown. The energy of CCl_3^- is lower than that the sum of energies of CCl_2 and Cl^- by 8.0 kcal/mol; this indicates that in the reaction system the concentration of CCl_3^- is higher than that of CCl_2 at equilibrium. Because the formation of $C_{60}(CCl_3)^-$ is a barrierless, hardly reversible process, as has been discussed above, the generation of CCl_2 and thereby the carbene mechanism will be suspended. It is noteworthy that C_{60} can accept as many as six electrons,[9,19,20] and one C_{60} molecule may readily capture more than one CCl_3^- in the meantime. Therefore, the generation of CCl_2 and thereby the carbene mechanism could be suppressed under conditions where the amount of C_{60} exceeds that of CCl_3^-. The $C_{60}(CCl_3)^-$ intermediate exists in the Bingel path; however, its experimental lifetime depends on how fast the solvent carries away the reaction energy in the step of its formation. On the basis of these results, we can deduce that the Bingel mechanism is highly competitive compared with the carbene mechanism and that it may dominate the reaction when the amount of CCl_3^- in the reaction system is relatively small.

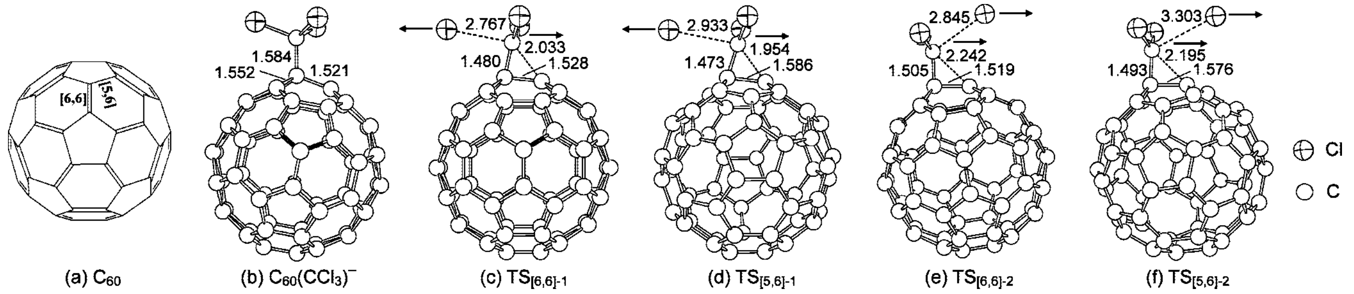

Figure 4. Structures of (a) C_{60}, (b) $C_{60}(CCl_3)^-$ intermediate, and (c−f) transition states at the B3LYP/6-31+G(d) level of theory. Bond lengths are given in angstroms. The arrows of c−f designate the orientations toward which the CCl_2 cyclizes or the Cl^- leaves in the forward reactions that form $C_{60}(CCl_2)$.

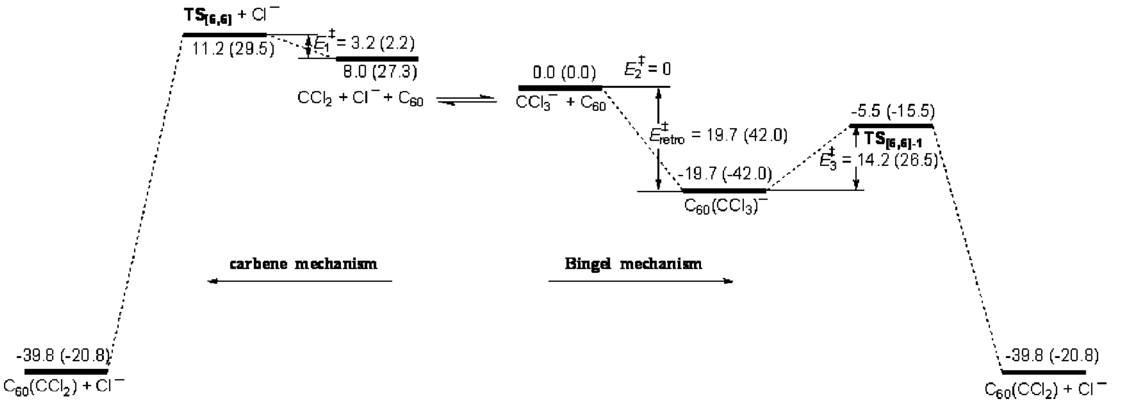

Figure 5. Energy profiles (in kcal/mol) reflecting the competition between the carbene and Bingel mechanisms for the reaction of CCl_3^- and C_{60}. Geometry optimization was performed in the gas phase at the B3LYP/6-31+G(d) level, and single-point energies were computed in THF at the same level. The gas phase energies are given in parentheses. ZPEs (unscaled) were included.

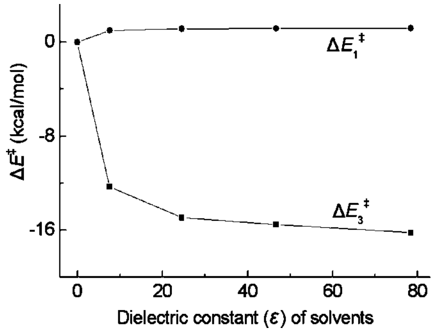

Figure 6. Changes of $E_1^‡$ and $E_3^‡$ in THF ($\varepsilon = 7.6$), ethanol ($\varepsilon = 24.6$), DMSO ($\varepsilon = 46.7$), and water ($\varepsilon = 78.4$) with respect to the barriers in the gas phase ($\varepsilon = 1.0$). $\Delta E^‡ = E_{\text{solvent}}^‡ - E_{\text{gas}}^‡$.

Experimental Supports to Bingel Mechanism. The operation of the Bingel mechanism in the reaction of CCl_3^- and C_{60} receives strong experimental support[2,4] and simultaneously rationalizes these experimental findings. Recently, Zhu synthesized [6,6]-$C_{60}(CCl_2)$ through the reaction of CCl_3^- using several solvents and found that using highly polar ionic liquid $[BMIM]^+[BF_4]^-$ enhances the formation rate by 5.5 times as compared with the organic solvent THF.[4] Because barriers $E_1^‡$ and $E_3^‡$ are responsible for the reaction rates of carbene and the Bingel mechanism, respectively (Figure 5), we calculated the solvent effects on these two barriers. In the gas phase, the ZPE-corrected values of $E_1^‡$ and $E_3^‡$ are 2.2 and 26.5 kcal/mol, respectively. As Figure 6 shows, $E_3^‡$ greatly decreases as the dielectric constant (polarity) of solvents increases, whereas $E_1^‡$ is little changed. This is because charged species are strongly dependent on solvent dielectric constants. Therefore, the solvent effects are responsible for lowering the energy of $TS_{[6,6]\text{-}1}$ with respect to the $C_{60}(CCl_3)^-$ intermediate. As a result, the Bingel mechanism is consistent with Zhu's experiment. To synthesize $C_{70}(CCl_2)$, Kiely et al.[2] have used two different carbene reagents, $PhHgCCl_2Br$ as the precursor for the generation of CCl_2 without CCl_3^-[21] and sodium trichloroacetate as the precursor for CCl_3^-. They obtained completely different product ratios.[2] The carbene mechanism is certainly responsible for the reactions of the former reagent, whereas our present finding that the Bingel mechanism operates for the latter case is in accord with their experimental results.

Conclusions

The Bingel mechanism is highly competitive compared with the carbene mechanism for the reaction between CCl_3^- and C_{60}; in reaction systems where the amount of C_{60} is abundant, the Bingel mechanism dominates the reactions in accordance with our calculations. This finding receives support from experiments and simultaneously rationalizes some formerly unexplained experimental results. According to the Bingel mechanism, the addition of CCl_3^- to C_{60} leads to a $C_{60}(CCl_3)^-$ intermediate that subsequently cyclizes to $C_{60}(CCl_2)$ by losing Cl^-. Unlike the carbene mechanism that slightly prefers [6,6]-$C_{60}(CCl_2)$ to [5,6]-$C_{60}(CCl_2)$, the Bingel mechanism affords [6,6]-$C_{60}(CCl_2)$ as the exclusive product. Highly polar solvents effectively enhance the rate via Bingel mechanism; therefore, using polar solvent is recommended to take advantage of this regioselectivity fully.

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Supporting Information Available: Cartesian coordinates of all reported stationary points optimized at the B3LYP/6-31+G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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