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Density functional theory investigation of electrophilic addition reaction of chlorine to tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene

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Potential energy surface (PES) of the tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (TCDD)-Cl_2 system was studied by B3LYP/6-311+G(d,p) method and the configurations [reactants, molecular charge-transfer (CT) complex, transition states (TS1 and TS2), intermediate (INT), and product (P)] corresponding to the stationary points (minima or saddle points) were determined. Initially, a molecular CT-complex forms between Cl_2 and TCDD. With a barrier of 22.362 kcal mol^{-1} the CT-complex can be activated to an intermediate (INT) with energy 14.682 kcal mol^{-1} higher than that of the CT-complex. The intermediate (INT) then transforms easily (barrier 5.102 kcal mol^{-1}) into the final, N-type product. Accompanying the breaking of the Cl-Cl bond, C1-Cl, C5-Cl and C2-C6 bonds are formed, and C1=C2 and C5=C6 double bonds transform into single bonds. The direction of the reaction is determined by the direction of the intramolecular skeletal rearrangement that is realized by the formation of the C2-C6 bond.

Key Words: DFT calculations, intrinsic reaction coordinates, transannular reactions, tricyclo [4.2.2.2^{2,5}]dodeca-1,5-diene.

Introduction

Attack of an electrophile on an unsaturated strained molecule having 2 isolated double bonds in spatial proximity usually leads to transannular bridge formation, for which 2 formal possibilities, cross (N-type) and parallel (U-type), exist.[1−4] Experimental results on this type of reaction have been confusing. In some cases only the cross or the parallel bridged product is isolated, while in other cases both products are formed simultaneously.[5−20]

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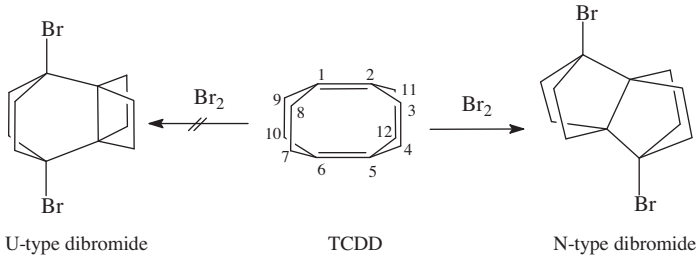
In order to learn the details of the structure and energy changes that occur during the course of the reactions in question, it is crucial to evaluate the potential energy surface (PES) of the reaction. Hence, this allows the inner mechanism and dynamic stereochemistry of the reaction to be understood in detail. What's more, the determination of the structures and energies of the configurations (molecular charge-transfer complexes, transition states, intermediates and products) corresponding to the stationary points (minima or saddle points) by studying the PES of the reaction, is important in order to understand the inner mechanism and dynamic stereochemistry of the reaction.

The addition reactions of halogens to unsaturated strained molecules and the reaction intermediates have been quantum chemically investigated.[21−36] Moreover, theoretical investigations of the addition of bromine and chlorine to olefins with rigid structures have recently been reported by us.[37−45] In continuance of our interest in quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we wish to report here the results obtained from the investigation of the mechanism and stereochemistry of the addition reaction of chlorine tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (TCDD). Bromination of the TCDD molecule gives only the adduct of N-type(1,5-addition product)[9−12]. However, the formation of U-type (1,6-addition product) adduct cannot be observed (Scheme).

In the present study, the potential energy surface (PES) of the TCDD-Cl_2 system was investigated by DFT method and hence the structure and energies of the configurations (TCDD+Cl_2, molecular charge-transfer complex (TCDD...Cl_2), transition states (TS1 and TS2), intermediate, and product) corresponding to the stationary points (minima or saddle points) were determined and the mechanism of the addition reaction was discussed.



Scheme

Methodology

The configurations (reactants, molecular charge-transfer complex, transition states, intermediate, and product) corresponding to the stationary points (minima or saddle points) of the potential energy surface of the addition reaction of chlorine tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene have been investigated using the B3LYP/6-311+G(d,p)[46−49] method. The reactants, molecular charge-transfer complex, and intermediate were characterized by all the real frequencies. The transition state has only one imaginary frequency. Connections of the transition states between 2 local minima have been confirmed by intrinsic reaction coordinate (IRC)[50−52] calculations at the B3LYP/6-311+G(d,p) level. The intrinsic reaction coordinates were followed to verify the energy profiles connecting each transition state to the correct local minima. The calculations were performed with the Gaussian 03 program on an IBM PC Pentium IV computer.

Results and discussion

The optimized structures at the B3LYP/6-311+G (d,p) level for the TCDD molecule and all stationary points [TCDD...Cl_2 molecular CT-complex, transition states (TS1 and TS2) intermediate (INT), and product(P)] are given in Figure 1. The total energies (E_{tot}) and relative energies (E_r) at B3LYP/6-311+G(d,p) level for all the involved stationary points are summarized in Table 1. Selected structural parameters (bond lengths) are listed in Table 2.

Table 1. Total energies E_{tot} and relative energies E_r of various species involved in the reaction of Cl_2 with TCDD using B3LYP/6-311+G(d,p) level of theory.

Species	E_{tot} (hartree)	E_r (kcal mol^{-1})
TCDD+Cl_2	-1387.321064	0.0
TCDD...Cl_2	-1387.337008	-10.006
TS1	-1387.301373	12.356
INT	-1387.313612	4.676
TS2	-1387.305482	9.778
Product (P)	-1387.442876	-76.440

Table 2. Selected structural parameters of the TCDD-Cl_2 stationary points[a].

Geometry	TCDD+Cl_2	TCDD...Cl_2	TS1	INT	TS2	Product(P)
C1=C2	1.351	1.382	1.482	1.528	1.531	1.534
C5=C6	1.351	1.351	1.352	1.384	1.404	1.534
Cl-Cl	2.053	2.259	3.535	5.833	7.534	6.786
C1-Cl	-	2.501	1.921	1.820	1.818	1.817
C5-Cl	-	-	-	4.078	3.661	1.817
C2-C6	2.764	2.753	2.704	2.224	1.923	1.558
∠C1C2C6	60.238	60.733	62.765	77.459	83.709	92.986

[a] Bond lengths are in Å and angles are in degrees. The numbers of the C atoms are shown in the Scheme.

The potential energy surface (PES) for the TCDD+Cl_2 electrophilic addition reaction is illustrated in Figure 2.

As known, olefin-halogen molecular CT-complexes are formed in the first step of electrophilic addition of halogens to olefins.[23–25,27–29,31,33,34] The addition reaction of chlorine to TCDD starts with the exothermic formation of reactive, essential 1:1 TCDD...Cl_2 complex, which is lower in energy than the reagents. The TCDD...Cl_2 molecular CT-complex formed by the approach of a Cl_2 molecule to the double bond in the axial position (Scheme). The molecular CT-complex (TCDD...Cl_2) is of $\mathbf{C}_{2V}$ symmetry. The stabilization energy of the complex is 10.006 kcal mol^{-1} (Figure 2) and the equilibrium distance R_{X-Cl}(X is the midpoint of the C=C bond of TCDD) is 2.404 Å (Scheme). The bond length of the chlorine atoms (R_{Cl-Cl} = 2.259 Å) in the molecular complex is longer than that of the isolated Cl_2 molecule (2.053 Å). The chlorine molecule in the

TCDD...Cl_2 complex is partially polarized. The chlorine atom near the double bond has a partial positive charge (+0.015 e) and the other one has a partial negative charge (-0.183 e). The results obtained for the stability and geometric parameters of the TCDD...Cl_2 complex show that the π interaction between Cl_2 and the highly pyramidalized double bond of the TCDD molecule is strong.

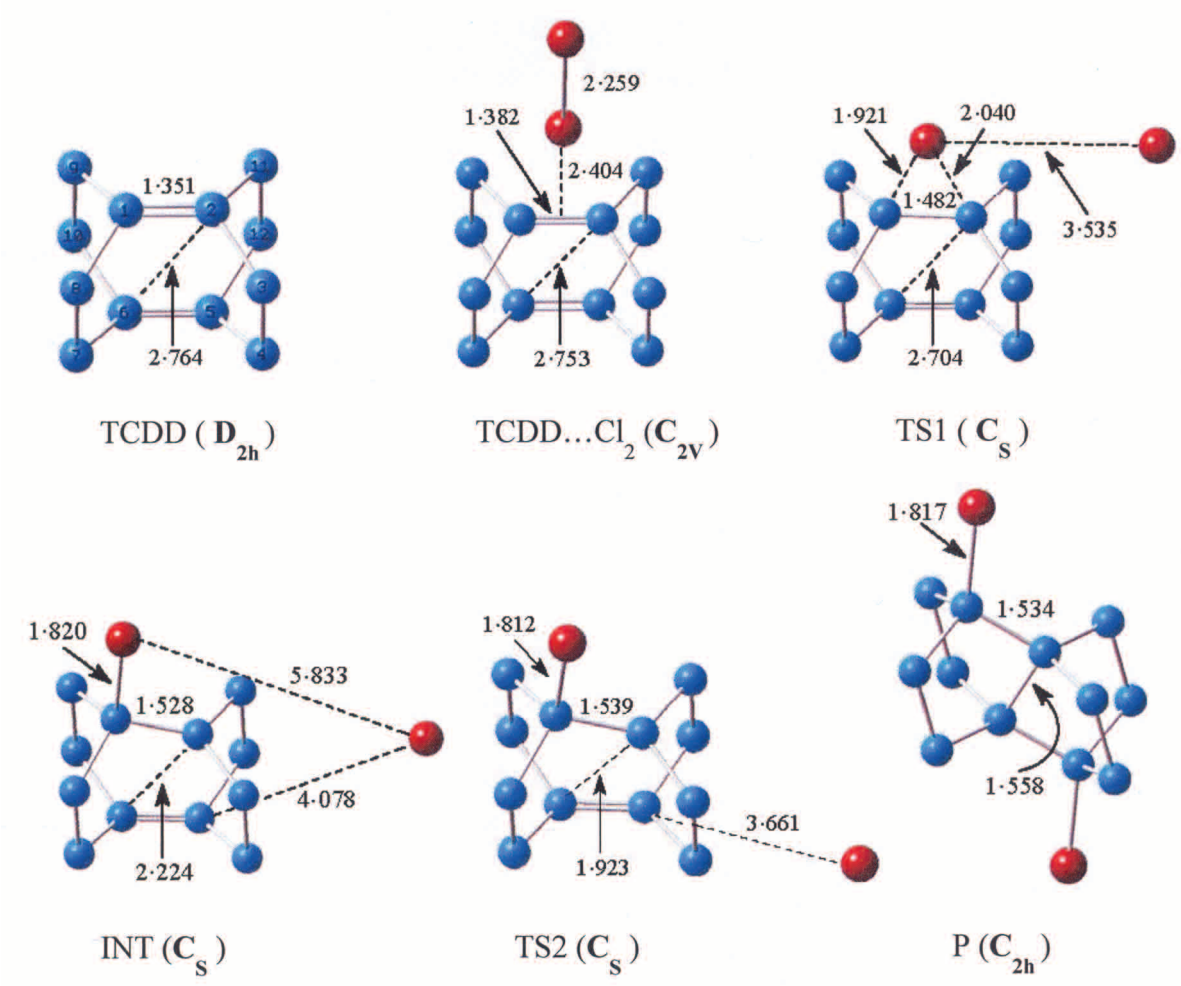


Figure 1. Optimized geometries of reactant (TCDD), charge-transfer complex (TCDD...Cl_2), transition states (TS1 and TS2), intermediate (INT), and product (P) at B3LYP/6-311+G(d,p) level. Bond lengths are in Å. Point group in parentheses.

The second step of the reaction takes place over the transformation of CT-complex (TCDD...Cl_2) into intermediate (INT) over TS1. According to the calculation of the IRC of TS1 and the further optimization calculation of the IRC results, TS1 connects CT-complex (TCDD...Cl_2) and intermediate (INT). In this step, the C1-Cl bond forms, the Cl-Cl bond breaks, the C2-C6 distance shortens, and C1=C2 double bond transforms into single bond. As the system is activated to transition states TS1, considerable structural change occurs. First, when the chlorine approaches the double bond, R_{C1-Cl} is shortened from 2.501 to 1.921 Å, where R_{Cl-Cl} is lengthened from 2.259 to 3.535 Å, indicating that the partial C1-Cl bond formation and Cl-Cl bond breaking

happen in a concerted way. For TS1, the chlorine atom in the 3-membered ring has a positive charge (+0.140 e) and the other chlorine atom has a negative charge (-0.852 e). Second, the C2-C6 distance is shortened from 2.753 to 2.704 Å and the C1-C2 bond distance is lengthened from 1.382 to 1.482 Å, indicating that the C1-C2 bond partly transforms from a double bond to a single bond. These results imply that, at the same time, the interaction in the system transforms from π character into σ character. It should be emphasized that the structure of TS1 is similar to the structure of the bridged chloronium cation.

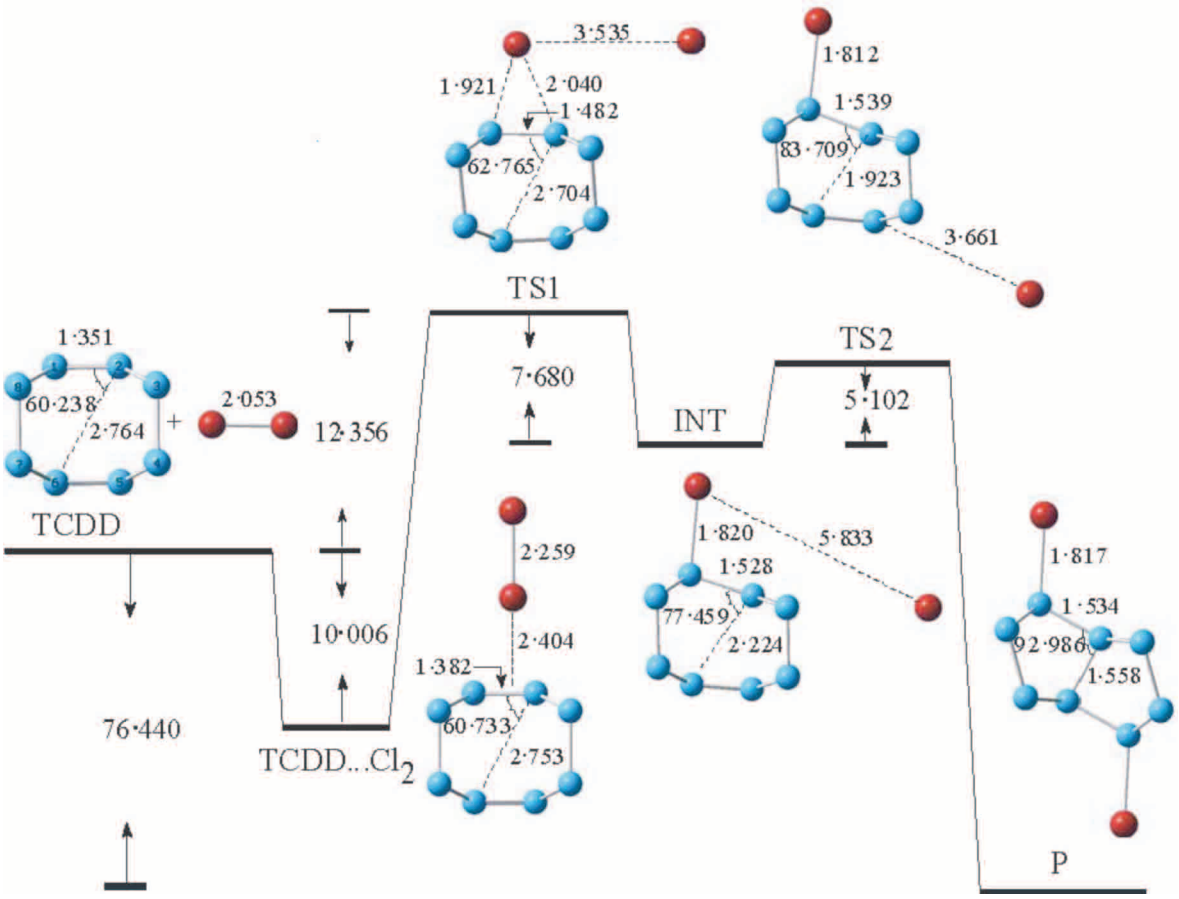


Figure 2. Potential energy profile along the minimal energy pathway for the stepwise mechanisms of the electrophilic transannular addition reaction of chlorine to TCDD. The energy values are given in kcal mol^{-1} at B3LYP/6-311+G(d,p) level. Bond lengths are in Å and angles are in degrees.

To activate CT-complex to TS1, 22.362 kcal mol^{-1} is required. Over this barrier, the system goes to the intermediate (INT). The energy of INT is 14.682 kcal mol^{-1} relative to CT- complex. The transformation of the TS1 to INT involves the shortening of the C2-C6 distance from 2.704 to 2.224 Å, the increase in C1-C2 bond length from 1.482 to 1.528 Å, and the lengthening of the Cl-Cl distance from 3.535 to 5.833 Å. For INT, the C1-C2 bond is single and the positive charge (+0.142 e) is localized over the C2 atom. As the transannular interaction between the C2 cation center and C5=C6 double bond increases, for INT, C2-C6 distance shortens. The distance between the chloride ion (Cl^-), which is formed as a result of the lengthening of Cl-Cl distance

to 5.833 Å, and the C5 atom is 4.078 Å.

Starting from INT, the system can be easily activated to the second transition state (TS2), which leads to the final product. According to the calculation of the IRC of TS2 and the further optimization calculation of the IRC results, TS2 connects the intermediate (INT) and the product (P). The energy barrier of the third step is 5.102 kcal mol^{-1}. It is obvious that from CT-complex across TS1 to INT, the second step along the reaction path, is rate limiting. The structure of INT is similar to that of TS2, with R_{C2-C6} further shortened (Scheme). During the transition of the system from INT to TS2, the decrease from 2.224 to 1.923 Å in the C2-C6 distance proves that for TS2 the transannular interaction increases. One of the remarkable changes during the transition is the increase in the interaction between the C5 atom and the bromide ion (Cl^-) and the decrease in the C5-Cl distance (R_{C5-Cl} = 3.661 Å). With the reaction going, the distances C2-C6 (INT: 2.224 Å, TS2: 1.923 Å, P: 1.558 Å) and C5-Cl (INT: 4.078 Å, TS2: 3.661 Å, P: 1.817 Å) gradually shorten, the angle C1C2C6 (INT: 77.459°, TS2: 83.709°, P: 92.986°) gradually increases and the C5-C6 bond (INT: 1.384 Å, TS2: 1.404 Å, P: 1.534 Å) gradually elongates, where finally the INT transforms into the product (P) via the transition state (TS2), with a low barrier of 5.102 kcal mol^{-1}. Thus, the intramolecular skeletal isomerization of the INT into product (P) over TS2 is realized through the formation of the C2-C6 bond over transannular cross-mechanism. In this step, the C5-Cl bond is also formed and the C5=C6 double bond transforms into single bond. Since serious geometric changes occur in the system in this step of the reaction, a remarkable energy change is realized (Figure 2).

Hence, the reaction takes place through the formation of 3 bonds (C1-Cl, C2-Cl, and C2-C6), the splitting of 1 bond (Cl-Cl), and the transformation of 2 double bonds (C1=C2 and C5=C6) into single bonds. The C1-Cl bond is formed from TCDD... Cl_2 to INT, the Cl-Cl bond breaks, and the C1=C2 bond transforms into a single bond and from INT to product (P) C2-C6 and C2-Cl bonds are formed and the C5=C6 bond transforms into a single bond.

The energy of the product (P) is -76.440 kcal mol^{-1} relative to the initial reactants (TCDD+Cl_2), the chlorination is thermodynamically favored (Figure 2). The N-type product was 18.595 kcal mol^{-1} [B3LYP/6-311+G(d,p)] more stable than the U-type product. The reaction is realized through the transannular cross (N-type) bonding of the double bonds (formation of C2-C6 bond) and formation of a more stable skeletal structure. Therefore, the direction of the reaction is determined by the direction of the intramolecular skeletal isomerization. The reaction progress is accompanied by shortening of C2-C6 distance along the reaction pathway, eventually resulting in bond formation and [from TCDD+Cl_2 to product (P)] C1C2C6 angle gradually increases (Figure 2).

Conclusions

The chlorination of tricyclo[4.2.2.$2^{2,5}$]dodeca-1,5-diene is a typical electrophilic transannular addition reaction. The present reaction pathway can be divided into 3 steps: first, the exothermic formation of reactive, essential 1:1 TCDD... Cl_2 molecular CT-complex, for which the stabilization energy is 10.006 kcal mol^{-1}; second, the prereactive CT-complex is activated to an intermediate (INT) 14.682 kcal mol^{-1} higher in energy (the barrier of the rate limiting step is 22.362 kcal mol^{-1}); third, the intermediate (INT) transforms into the final product

(P) with a barrier of 5.102 kcal mol^{-1}. Accompanying the C1-Cl bond formation, the Cl-Cl bond splits and the C1=C2 bond transforms into C1-C2 in the second step, and C2-C6 and C2-Cl bonds are formed and the C5=C6 bond transforms into a C5-C6 bond in the third step. The direction of the reaction pathway is determined by the direction of the intramolecular skeletal isomerization. The reaction is realized so as to follow the direction where transannular cross (N-type) bonding of double bonds (formation of C2-C6 bond) occurs and a more stable skeletal structure (N-type product) is obtained.

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