Ab initio investigation of electrophilic addition of chlorine to norbornadiene

Rza Abbasoğlu
Department of Chemistry, Karadeniz Technical University, 61080 - Trabzon, Turkey
Email: rabbas@ktu.edu.tr

Received 1 May 2004; accepted (revised) 8 February 2005

Full geometry optimization of norbornadiene (NB) has been done by ab initio HF/3-21G*, HF/3-21G**, HF/6-31G*, HF/6-311G* and HF/6-311G* methods and the structure of the molecule is investigated. The double bonds of molecule are endo pyramidalized. The electron densities (q0,BoN0) on endo and exo faces of the double bonds are not equal and it is bigger on the exo face. The NB-Cl system is investigated by HF/3-21G* method and the stable configurations are determined. The stable configurations of the NB-Cl system correspond to NB...Cl (exo) and NB...Cl (endo) molecular complexes that are formed by the exo and endo orientation of Cl molecule to the double bond of NB, respectively. The exo-molecular complex has been found to be relatively more stable than the endo-complex. The cationic intermediates of the reaction have been studied by ab initio methods. The exo-chlorocarbonation is found to be more stable than endo-chlorocarbonation. The exo-facial selectivity should be observed in the addition reaction to NB of chlorine. The results obtained indicate that a multicenter nonclassical chlorocarbonation cation formed by the rearrangement of exo-chlorocarbonation ion is the most stable ion among the cationic intermediates. It is likely that the ionic addition reaction proceeds via the nonclassical chlorocarbonation ion and results in the formation of the rearranged products. The mechanism of the addition reaction is also discussed.

Keywords: Electrophilic addition, norbornadiene, chlorocarbonium

IPC: Int.Cl.7 C 07 C

The reactions between halogens and olefins have been extensively studied both theoretically and experimentally over a long period of time. Factors such as reaction medium, solvent, temperature, structure of the olefin, polarity of the electrophile are the factors that affect the kinetics and stereochemistry of these reactions considerably. Recent studies have shown that an important role is played by the halogen-olefin molecular complexes, the existence of which has been proved. In order that the role of the complexes may be correctly understood, structural information is required that is difficult to obtain by experimental means because of the fast reactions occurring in the systems. Quantum chemical methods can furnish data on the structures and stabilities of the complexes without recourse to experimental measurements. Such calculations are also important to understand the stabilities and structures of the cationic intermediates that are formed through the reactions. Since these reactions proceed in the pseudostationary conditions, it is difficult to obtain information about the reaction intermediates by experimental routes. Quantum-chemical calculations provide a reliable source of information about the intermediates.

We have been interested for some time in the regiochemistry and stereochemistry of the additions of halogens to unsaturated strained molecules. In continuation of our interest in the quantum-chemical studies related to the addition of halogens to rigid and unsaturated strained molecules, we wish to report herein the results obtained from the investigation of addition of chlorine to norbornadiene (NB). This work describes a theoretical investigation of the NB...Cl2 molecular complexes and cationic intermediates. Stereoselectivity of this reaction depends on the electron distribution of the double bonds to a large extent. For a detailed analysis of the formation mechanism and the stereochemistry of the product, a quantum-chemical investigation of the structures and the stabilities of the reaction intermediates are important.

Methods of calculation
The geometry and the electronic structure of NB were investigated by ab initio SCF method in 3-21G*, 3-21G**, 6-31G* and 6-311G** basis. The theoretical investigation of NB...Cl2 molecular complexes was performed by ab initio HF/3-21G*
method. The cationic intermediates predicted in the reaction were searched by *ab initio* SCF method in 3-21G*, 3-21G**, 6-31G* and 6-311G* basis. Full geometry optimization was carried out employing the Polak-Ribiére (conjugate gradient) algorithm (convergence of 0.00001 kcal mol⁻¹) and RMS gradient at 0.0001 kcal/Å mol. All the calculations were performed on an IBM PC PENTIUM IV using HyperChem 6 program.

**Results and Discussion**

Full geometry optimization of NB was done by HF/3-21G*, HF/3-21G**, HF/6-31G*, HF/6-311G* and HF/6-311G** methods and the structure of the molecule was investigated in detail. The pyramidalization parameters were determined with the aim of determining the structural deformation of the double bond. The calculated double bond pyramidalization angle (θ) and the out-of-plane bending angle (ϕ) are given in Table 1. Accordingly, the double bonds are *endo* pyramidalized and the two faces of the double bond are no longer equivalent. The electron density in *exo* direction is bigger than in *endo* direction. This geometrical feature causes a noticeable π-facial stereoselectivity in addition reactions of the double bond. Thus, the addition reaction of chlorine to NB should show *exo*-selectivity. In general, the facial selectivity of attack on a pyramidalized olefin parallels the pyramidalization. When the degree of pyramidalization of the double bond increases, the chemical reactivity also increases.

The analysis of frontier orbital (HOMO) of NB showed that this orbital is principally localized in the double bonds. As seen in Figure 1, *exo* and *endo* faces of *endo*-pyramidalized double bonds of the molecule are not equal. The electron density on the *exo*-face of double bonds is higher than the electron density on the *endo* face. Therefore, the chlorination reaction of NB should be stereoselective and the addition must be realized from the *exo* direction.

<table>
<thead>
<tr>
<th>Method</th>
<th>θ (HOMO)</th>
<th>ϕ (HOMO)</th>
<th>θ (C-C)</th>
<th>ϕ (C-C)</th>
<th>θ (C-Cl)</th>
<th>ϕ (C-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/3-21G*</td>
<td>-8.723</td>
<td>4.287</td>
<td>1.320</td>
<td>2.111</td>
<td>2.273</td>
<td></td>
</tr>
<tr>
<td>HF/3-21G**</td>
<td>-8.707</td>
<td>4.281</td>
<td>1.320</td>
<td>2.059</td>
<td>2.254</td>
<td></td>
</tr>
<tr>
<td>HF/6-31G*</td>
<td>-8.603</td>
<td>4.249</td>
<td>1.319</td>
<td>2.586</td>
<td>2.753</td>
<td></td>
</tr>
<tr>
<td>HF/6-311G*</td>
<td>-8.723</td>
<td>3.877</td>
<td>1.318</td>
<td>2.794</td>
<td>3.010</td>
<td></td>
</tr>
<tr>
<td>HF/6-311G**</td>
<td>-8.734</td>
<td>3.852</td>
<td>1.318</td>
<td>2.801</td>
<td>3.030</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1** — Electron density distribution (HOMO) of the norbornadiene molecule (HF/6-31G*).

To find out the possible direction of approach and to determine the center of attack by Cl₂, the NB-Cl₂ system was investigated in detail at the HF/3-21G* level. As known, olefin-halogen molecular complex is formed in the first step of electrophilic addition of halogens to olefins. According to the thermodynamic stability of the molecular complexes, it is possible to determine from what direction the halogen attacks the double bond. The attack of bromine to the double bond of NB is possible either from *exo* or *endo* side. Moreover, a chlorine molecule may approach the carbon-carbon double bond in a manner that the Cₓ axis of chlorine is either perpendicular or parallel to the double bond plane. Taking these possibilities into consideration, full geometry optimization of various configurations of NB-Cl₂ system was carried out and the stable configurations corresponding to the minimum energy levels were searched. Two configurations were found. One configuration corresponds to *exo* NB...Cl₂ complex and the other configuration corresponds to *endo* NB...Cl₂ complex, each having σ₁Cl-Cl₁ perpendicular to the olefinic bond (Figure 2).

The stabilization energies, ΔE = (Eₛₛ + E_(12)) - Eₙᵢ₋ₐ₆, of the *exo* and *endo* molecular complexes, the distance between the carbon-carbon double bond and the nearer chlorine atom (called as equilibrium distance R) for each complex and the other properties
of the complexes were calculated and are given in Table I. The exo complex is 1.62 kJ/mol more stable than the endo complex. The results indicate that an exo selectivity must be considered in the electrophilic addition of chlorine to norbornadiene. The \( \pi \)-facial selectivity observed in the [2,2,1] systems parallels the double bond pyramidalization. The electron density (\( q_{\text{HOMO}} \)) on the exo face of the endoparamidalized double bond of NB is higher than the electron density on the endo face (Figure 1).

That is, HOMO_{\text{HCl}}-LUMO_{\text{HCl}} interaction realized from the exo face of the double bond in the formation of the exo molecular complex is more effective than the endo face and should be optimal. According to the Frontier Molecular Orbital theory, HOMO_{\text{of}}-LUMO_{\text{halogen}} interaction is the decisive factor in the formation of olefin-halogen complex.\(^{23}\) The formation of olefin-halogen molecular complex is realized with the pyramidalization of the double bond.\(^{13}\) The stability of complex increases by increasing the pyramidalization of the olefinic bond. HF/3-21G* calculations showed that the value of the out-of-plane bending angle \( \chi \) of the double bond in exo-NB...Cl\(_2\) complex is higher than that in endo-NB...Cl\(_2\) complex (Table II). Hence, facial selectivity in the addition of chlorine to NB is caused by the electronic effect in the important degree.

The chlorine molecule is partly polarized in both the molecular complexes. The bond length between the chlorine atoms in the molecular complexes is relatively longer than that of the neutral chlorine molecule (Table II). The results obtained indicate that the molecular complexes play an important role in the heterolytic splitting of chlorine molecule leading to an ionic addition.

It is known that an olefin-halogen molecular complex is more stable in a solvent than in gas phase and the stabilization energy of the complex becomes higher as the solvent polarity increases.\(^{27}\) As a result, in the first step of addition of chlorine to NB, the exo-NB...Cl\(_2\) molecular complex must essentially be formed either in a gas or a solvent medium. The polarization of chlorine and subsequently the heterolytic splitting of exo-NB...Cl\(_2\) molecular

<table>
<thead>
<tr>
<th>Molecular complex</th>
<th>Stabilization energy (kcal mol(^{-1}))</th>
<th>Equilibrium distance, ( R(A) )</th>
<th>( r_{\text{Cl-Cl}} ) (( A ))</th>
<th>Transferred change from NB to Cl(_2) (degree)</th>
<th>( \chi ) (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>exo</td>
<td>2.378</td>
<td>3.164</td>
<td>2.017</td>
<td>0.032</td>
<td>3.718</td>
</tr>
<tr>
<td>endo</td>
<td>1.991</td>
<td>3.281</td>
<td>2.014</td>
<td>0.031</td>
<td>0.953</td>
</tr>
</tbody>
</table>

*Figure II* — The optimized geometries of the NB...Cl\(_2\) (exo) and NB...Cl\(_2\) (endo) molecular complexes (HF/3-21G*).
complex results in the formation of a cation. This cation and its isomers are the possible intermediates of the addition reactions of chlorine to NB in gas phase and solvent medium (Scheme I). In order to determine the structures and the relative stabilities of the predicted cationic intermediates, their full geometry optimization was performed using ab initio HF/3-21G*, HF/3-21G**, HF/6-31G* and HF/6-311G* methods and the total energies ($E_{\text{tot}}$) were calculated (Table III).

The exo-chloronium cation I is relatively more stable than the endo-chloronium cation II. In other words, exo-bridged cation formed by the splitting of the exo-molecular complex is more stable than the endo-bridged cation. This reveals that an absolute exo-selectivity must be considered in the mechanism of electrophilic addition of Cl₂ to NB. As shown in Table III, the most stable cationic intermediate is the rearranged nonclassical chlorocarbonium ion IV among the possible cationic intermediates I-V. These results are consistent with those calculated for the 2-norbornyl, 2-exo-bromo-3-benzonorbornenyl and 6-tricyclo[3.2.1.0²⁷]octyl cations using various quantum chemical methods. 

Table III — The calculated total energies of cations

<table>
<thead>
<tr>
<th>Cations</th>
<th>$E_{\text{tot}}$ (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-725.191</td>
</tr>
<tr>
<td>II</td>
<td>-725.181</td>
</tr>
<tr>
<td>III</td>
<td>-725.209</td>
</tr>
<tr>
<td>IV</td>
<td>-725.218</td>
</tr>
<tr>
<td>V</td>
<td>-725.216</td>
</tr>
</tbody>
</table>

The exo-chloronium cation I is predicted to rearrange in order to form the more stable multicenter cation IV. It is reasonable to consider that the ionic addition of chlorine to NB proceeds via the formation of the nonclassical chlorocarbonium ion IV due to its high stability.

The rearranged cation IV possesses two effective cationic centers as C-4 and C-6. Because of the interaction between the C-4 cationic center and the $\pi$-electron clouds of the double bond, the electrophilic attack of the chloride ion to this center occurs from the opposite side of the double bond, and so, 2-exo-7-anti-dichloronorborn-5-ene 1 (Scheme II) is formed as a Wagner-Meerwein rearrangement product. In the ionic addition of Cl₂ to NB, the formation of 2-endo-7-anti-dichloronorborn-5-ene 2 is not possible due to the electronic interaction. On the other hand, the C-6 cationic center of carboxonium ion IV has a nearly planar structure. For this reason, the attack of a bromide ion to this center is geometrically possible either from exo or endo, so exo, exo-dichloronortricyclane 3 and exo, endo-dichloronortricyclane 4 (Scheme II) are formed.

The positive charge density for C-6 center of chlorocarbonium ion IV is higher than that of C-4 center according to each ab initio method. Hence, the nucleophilic attack of chloride ion is predicted to occur easily and more effectively on C-6 as compared to C-4. Since the ionic addition proceeds via cation IV, the formation of a trans product must not be expected.

Consequently, the investigations of chlorine addition to norbornadiene by ab initio methods give
some important results as mentioned below. The double bonds of NB molecule are endo-pyramidalized. The electron density ($q_1$) on endo faces of the double bonds are not equal and it is bigger on the exo face. The exo-NB...I$_2$ complex is more stable than the endo-NB...I$_2$ complex and an essentially endo complex is formed throughout the reaction. The molecular complex plays an important role in heterolytic splitting of chlorine. The bridged exo-chloronium cation I is relatively more stable than the endo-chloronium cation II. exo-Facial selectivity should be observed in the addition of chlorine to NB. Facial selectivity in the addition reaction by chlorine to NB molecule is caused by electronic effect in the important degree. The most stable cationic intermediates is the rearranged nonclassical delocalized chlorocarbenium IV and the ionic addition occurs via this cation.

References