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A Theoretical Study on Bromochlorination

Shinichi Yamabe* and Tsutomu Minato†,††
Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630
†Yuge Mercantile Marine College, Yuge-cho, Ochi-gun, Ehime 794-25
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Synopsis. The bromochlorination to ethylene is studied by ab initio MO calculations. The presence of the bridge ion is verified by a transition state (TS) search. The TS geometry is represented as an ion pair. Two mechanistic questions, orientation of Br-Cl and the anti Cl^- addition, are discussed in terms of the frontier-orbital theory.

Additions of bromine chloride (BrCl) in CCl_4 or CH_2Cl_2 have been investigated extensively.[1,2] The regioselectivity of the bromochlorination may be explained by the AD_E (electrophilic addition) mechanism, where a bridged bromonium ion intermediate is attacked by a chloride ion.[1] This scheme is based on the product analysis of 1-hexene in a nonpolar solvent (CCl_4) and a protic solvent (methanol).

n-BuCH=CH$_2$ + BrCl → n-BuCHCl-CH$_2$Br + Others (in CCl_4)

n-BuCH=CH$_2$ + BrCl → n-BuCH(OMe)-CH$_2$Br + Others (in MeOH)

Two mechanistic questions emerge.

(1) Why is no chloronium ion intermediate formed in the electrophilic attack of BrCl on a double bond?

(2) What is the driving force for anti addition of a nucleophile to a bridged bromonium ion in Fig. 1? In a cyclic intermediate, the cationic nature is retained in the bromine atom, and two carbon atoms are somewhat anionic (see Fig. 4).

To solve these problems, ab initio MO calculations were made with 3-21G and 3-21G(*) basis sets,[3] using the GAUSSIAN 82 program.[4]

MO Calculations of the BrCl Addition to Ethylene

In Fig. 2, two TS structures are shown. The two geometries are found to be similar. Bromide and chloride ions are remote from the cyclic chloronium and bromonium ions, respectively. It is noteworthy that bridged halonium ions are almost formed at TS. The ion-pair formation is more complete in TS *b* ($Br^{+0.370}$ vs. $Cl^{-0.881}$) than in TS *a* ($Cl^{+0.201}$ vs. $Br^{-0.793}$). Also, there is a noticeable difference in the bonding nature between the C···Br bonds and the C···Cl bonds. While the C···Br bonds have large bonding populations ($\underline{+0.216}$ and $\underline{+0.147}$), one of the C···Cl bonds has a small bonding population ($\underline{+0.004}$). These results of the electron population indicate that TS *b* is more favorable for the formation of a bridged intermediate plus an anion than TS *a*. In fact, the activation energy of TS *b* [=44.6 kcal mol^{-1} (1 cal mol^{-1}=4.184 J mol^{-1}), 3-21G(*)//3-21G relative to the energy of the C_{2v} π complex, C_2H_4···BrCl] is much smaller than that of TS *a* [=71.9 kcal mol^{-1}]. Thus, the present calculation

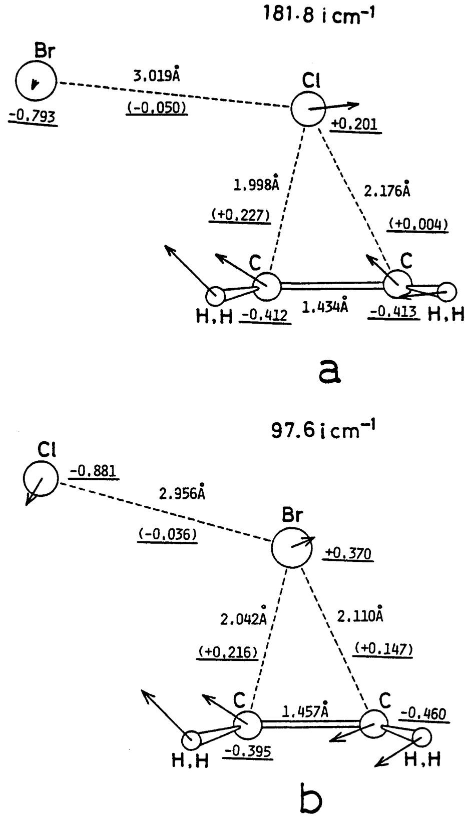

Fig. 2. Transition-state geometries of the bromochlorination to ethylene obtained with the 3-21G optimization. The imaginary-frequency vibrational mode showing the reaction path is sketched with arrows. The 3-21G(*)//3-21G total energies are −3095.12477 a.u. (a) and −3095.17221 a.u. (b). 1 a.u.=627.566 kcal mol^{-1}=2625.736 kJ mol^{-1}.
The underlined numbers denote the 3-21G(*) atomic net charges (negative, anionic) and those in parentheses are atom–atom bond populations.

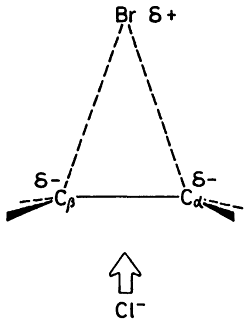

Fig. 1. Schematic presentation of the anti attack of Cl^- to the cyclic bromonium ion.

[††] Present address: Institute for Natural Science, Nara University, 1500 Misasagi-cho, Nara 631.

shows that a bromonium ion intermediate is formed in the bromochlorination.[1]

The ease of the cyclic bromonium ion formation in the BrCl addition is explicable by the shape of the lowest unoccupied MO (LUMO) of Br-Cl. The ionization potential of the chlorine atom (=12. 976 eV) is larger than that of the bromine atom (=11.814 eV). The difference leads to the asymmetric orbital extension. The energy of the LUMO of BrCl is close to that of the Br atomic orbital, and the LUMO has a bromine $4p_\sigma$ character. Therefore. the electrophilicity is larger at the bromine site, and the charge transfer (CT) from the ethylene π MO to the LUMO is effective in $C_2H_4 \rightarrow BrCl$ coordination as is shown in Fig. 3. Thus, the first question of the bromonium ion selectivity has been answered by the frontier orbital theory. [5]

The Origin of the Anti Nucleophilic Addition

After the cyclic bromonium ion is formed, how is the anti addition of the chloride ion brought about? In Fig. 4, the optimized structure of the cyclic bromonium ion is shown. It is realized that the geometry is close to that at TS *b* in Fig. 2. The b_2 in-plane antisymmetric vibrational mode is also shown in Fig. 4 and it has the lowest value among the 15 (=3×7 atoms−6) harmonic frequencies. This mode indicates that the "b_2 spring" is the most fragile (C⋯Br bond cleaved) against the external fluctuation (i.e., the Cl^- attack). When the C_{2v} geometry is deformed along the b_2 vibration, two low-lying vacant MO's mix with each other. The mixing leads to the lowering of the energy level of the LUMO and consequently to higher reactivity against the nucleophilic attack. The mixing also causes a change in the shape of the MO's as is shown in Fig. 5. The α carbon atom has the larger lobe of the LUMO and is ready to catch Cl^- in syn and anti directions (two bold empty arrows). The syn direction is apparently more favorable than the anti one, because there is a larger lobe of the LUMO along the C⋯Br bond. However, a crucial factor of making the syn attack unfavorable is the nodal property of the LUMO. Although the magnitude of the spatial extension of the LUMO is larger at the syn site than the anti site, the presence of the distinct node prohibits the effective CT from the chloride ion. The anti attack is not prohibited by the nodal property of the LUMO and may cause the larger CT. Thus, the second question is answered. The anti attack shown by the lower arrow is initiated by the geometric distortion along the lowest-frequency vibration and the resultant MO mixing. The Cl^- orientation is determined not by the electrostatic force but by the shape of the frontier orbital, the LUMO. To prove this prediction, the partial geometric optimizations for syn and anti attacks were made with the $Cl^- \cdots C_\alpha$ distance fixed to 2.3 Å. The

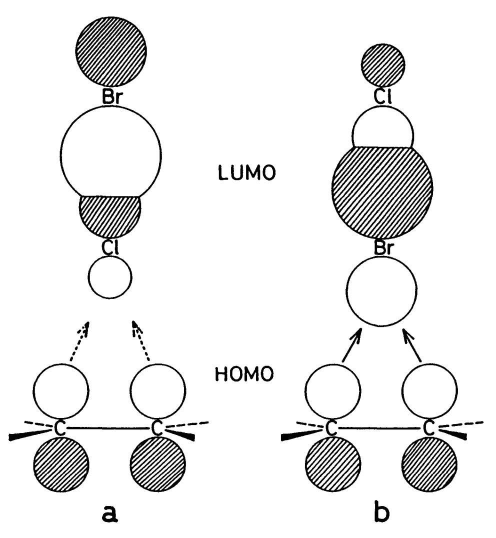

Fig. 3. $C_2H_4 \rightarrow ClBr$(a) and $C_2H_4 \rightarrow BrCl$(b) charge-transfer interactions.

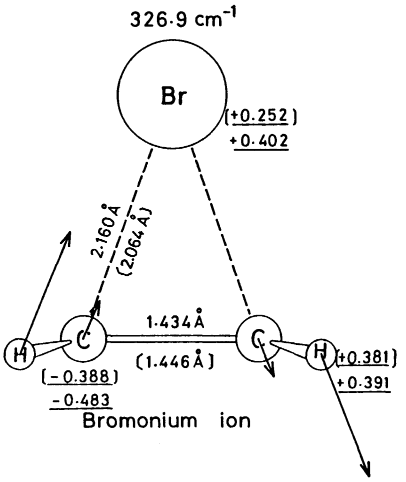

Fig. 4. The geometry of the bridged bromonium ion intermediate ($C_2H_4Br^+$) and the lowest-frequency vibrational mode. Numbers in brackets denote the 3-21G(*) optimized distances and the net charges. The C_{2v} geometry was also obtained by Poirier et al. with a somewhat different basis set.[6] The 3-21(*)//3-21G total energy is −2637.57871 a.u.

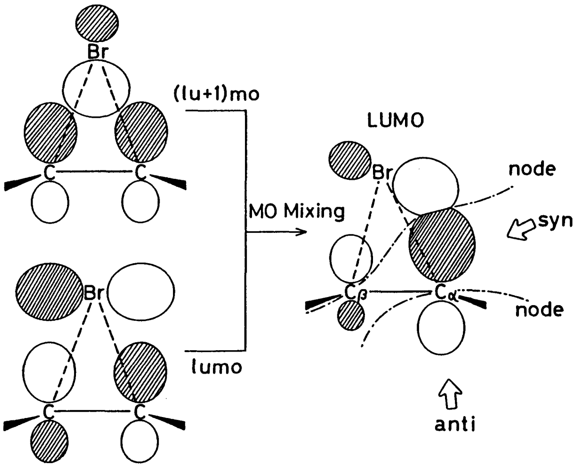

Fig. 5. The mixing of two low-lying vacant MO's, lumo and (lu+1)mo, to give LUMO through the geometric distortion along the harmonic vibration of the smallest frequency. LUMO and lumo are the lowest unoccupied MO's. The (lu+1)mo is the next lowest unoccupied one. Bold empty arrows indicate possible directions of the Cl^- attack.

distance is thought to correspond approximately to the transition state of the nucleophilic Cl^- addition. The anti attack is calculated to be 12.3 kcal mol^{-1} more stable (smaller activation-energy barrier) than the syn attack. This result supports the above prediction.

In Fig. 4, the 3-21G and 3-21G(*) bond distances are found to be similar. Therefore, the basis set dependence of the geometry seems not to be so significant as that of the electron distributions (underlined numbers), and the 3-21G(*)//3-21G calculation may be appropriate to the present discussion.

Concludig Remarks

In this work, an electrophilic addition of bromine chloride to ethylene is investigated theoretically. Two mechanistic questions are solved by the frontier orbital theory. The first is the orientation of Br–Cl toward the double bond of ethylene. The softer atom, bromine, gets the larger lobe in the LUMO and is directed to ethylene. Activation energies for two models of the BrCl approach are compared, and the predicted orientation is confirmed. Noteworthy is the TS geometry in Fig. 2(b), where the cyclic bromonium ion intermediate and the chloride ion are almost separated. The formation of the ion pair is found to be possible without the assistance of a polar solvent. The second question is concerned with the theoretical origin of the Cl^- anti addition. The nucleophilic attack becomes likely through the coupling of the fragle b_2 in-plane vibration and the MO mixing. In spite of the anionic nature of the ethylenic carbon atom, C_α, it accepts the Cl^- attack through the LUMO.

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