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ORIGINAL PAPERS**Semi-quantitative Analysis of
Fragmentation Processes of Ethylene Ion
by Modified Extended Hückel Method**

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For the theoretical study of fragmentation processes to produce acetylene ion, a modified extended Hückel method was presented, where the explicit inclusion of repulsive potential was intended between the two nuclei. The potential curves were calculated for possible fragmentation processes, direct detachment of a hydrogen molecule and detachment of the molecule after scrambling of hydrogen atoms, in order to obtain the required barrier energies. The results showed that the scrambling process through the asymmetric structure required the lowest energy, that is, the most probable process is the scrambling. This is compatible with the experimental results reported previously.

1. Introduction

Many experimental studies on the fragmentations of ethylene have widely been performed by impacts of photon, electron and ion beams, and the obtained results showed that the exchanges among the hydrogen atoms (scrambling) take place very frequently before the formation of acetylene ion.^{1,2)} However, a few theoretical approaches have been made on this problem so far because of the difficulties of the computational analysis on the molecular energies during the dissociation processes.

A. J. Lorquet and J. C. Lorquet tried to calculate potential energy surfaces of the neutral C_2H_4 molecule and its positive ion by the SCF CNDO/2 method^{3,4)}. They reported that the ground $C_2H_4^+$ ion is twisted in equilibrium and that the two methylene groups in the ion can twist each other nearly freely and further that the scrambling in the ion takes place through the asymmetrical configuration CH_3-CH^+ . Their result on the scrambling is derived by comparing the energy differences among only four possible structures, the bridged

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structure $\text{HC} \overset{\text{H}^+}{\text{H}} \text{CH}$, doubly bridged structure $\text{C} \overset{\text{H}^+}{\text{H}} \text{C}$, asymmetrical structure $\text{H}_3\text{C}^+ - \text{CH}$ and asymmetrical bridged structure $\text{HC} \overset{\text{HH}^+}{\text{H}} \text{CH}$. However, this comparison of the energy differences cannot give sufficient proof for the scrambling. It is necessary to examine the molecular energies along the entire path of the scrambling process. If we try to calculate those energies with the SCF method, a lot of time is necessary in computation. More simplified and practical method is useful for semi-quantitative understanding.

In the present study, a modified extended Hückel method has been proposed in order to calculate the potential surfaces for the dissociation processes to produce acetylene ion from ethylene ion. The potential curve of the twisting motion was calculated first for comparison with that of the CNDO/2 method. The potential energy surfaces were calculated for possible dissociation processes and the obtained barrier energies were compared with the experimental results.

2. Method of calculation

It is well known that the extended Hückel theory (EHT) is rather a crude approximation but is very effective in predicting the electronic structures of organic molecules, and also the band structures of solid materials³⁻⁹⁾. The theory, however, would not be so effective for discussion of the dissociation phenomena because it does not include nuclear repulsion and electron correlation terms explicitly. We, therefore,

have attempted to add the repulsion terms to the framework of the EHT method. The total energy was calculated with changing the inter-nuclear distance between the two H atoms for the simplest case of H_2 molecule within the framework of the EHT. The result of the calculation is given in Fig. 1. No minimum can be

Fig. 1. Potential energies of hydrogen molecule as a function of the inter-nuclear distance. (without inter-nuclear repulsion).
(a) Extended Hückel method
(b) Heitler-London method (Ref. 9)
(c) Observed (Ref. 10)

found in the total energy. Simple addition of the nuclear repulsive term was intended to improve the situation. The total energy of H_2 is assumed to be presented by the energy of $\text{EHT} + \text{const.} \times \frac{1}{r}$. The value of the constant (const.) is determined so as to give the experimental dissociation energy -4.7 eV at the equilibrium distance 0.74 Å ¹¹⁾, and the value was found to be $3.02 [\text{eV} \cdot \text{Å}]$. Using this value, the total

energy was calculated over a wide range of the nuclear distance and the result is given in Fig. 2. The calculated curve

Fig. 2. Potential energies of hydrogen molecule as a function of the inter-nuclear distance, (including inter-nuclear repulsion)
(a) Extended Hückel method + modified repulsive potential
(b) Heitler-London method (Ref. 9)
(c) Exact calculation (Ref. 12)

shows a minimum and is very close to the result of the exact calculation¹². The same procedure was applied to CH radical to find the corresponding value for CH bond, and $0.952 [\text{eV} \cdot \text{\AA}]$ was obtained for the const. value. These two values were applied to the discussion of the fragmentation processes of ethylene ion. In treating the ethylene molecule, the atomic orbitals used were $1s$ of hydrogen and $2s$, $2p_x$, $2p_y$, and $2p_z$ of carbon, and the Slater-type orbitals were adopted. For the K value, the original Hoffmann's value 1.75 was used^{6,13}. According to this modified EHT method, the potential curves of possible paths through which C_2H_4^+ dissociates into C_2H_2^+ were calculated.

The calculations were made by using HITAC-8000 of the University of Tokyo. The computational time was only one second in the calculation of the total energy

for a nuclear configuration, much shorter than those by the usual CNDO/2 procedures.

3. Results

Two potential curves for the fragmentation processes from the planar structure of C_2H_4^+ to C_2H_2^+ were first calculated; one is the case for detachment of the two hydrogen atoms, forming a hydrogen molecule, from the same carbon atom and the other is that from the different carbon atoms. In Figs. 3 and 4, these calculated potential curves are given. In the latter case, the calculations were made in such a way that in detachment of the two hydrogen atoms from the carbon atoms the remaining C_2H_2^+ forms the acetylene ion

Fig. 3. Potential curve of the dissociation process from the planar structure; detachment of two hydrogen atoms from the same carbon atom to form a hydrogen molecule. It is shown as a function of the distance R between a carbon atom and a detaching hydrogen atom. The energy barrier of this process is 2.47 eV.

$\text{H}-\text{C}-\text{C}-\text{H}^+$ in linear structure. Many calculations for these processes were made with varying the distance from the $\text{C}-\text{C}$

Fig. 4. Potential curve of the dissociation process from the planar structure; detachment of two hydrogen atoms from the different carbon atoms to form a hydrogen molecule. It is shown as a function of the distance R between a carbon atom and a detaching hydrogen atom. The energy barrier of this process is 2.23 eV.

axis to the position where H_2 molecule is formed. It was found that the potential barrier appears for every case. Only the curves that have the lowest energy barriers are shown for the two types of the dissociation in the figures. The energy barriers of these processes are found to be about 2.47 eV and 2.23 eV, respectively.

In the next stage, non-planar structure cases were examined. Calculations for the twisting motion for both ionic and neutral ethylenes were made, and the results are given in Fig. 5. The ground state of ethylene ion is twisted by 40° in equilibrium and the ion can twist over wide angle more freely than the neutral molecule. This result is in good agreement with that of CNDO/2 method by Lorquet and Lorquet¹⁹. On the basis of the obtained

Fig. 5. Potential curves of twisting motion of two methylene groups as a function of the twist angle θ .
(a) Ethylene ion
(b) Neutral ethylene

results of the calculations, the process toward the asymmetric structure was the examined on paths as shown schematically in Fig. 6. The hydrogen atoms H^1 and H^2 turn around C^1 with keeping the relative positions among C^1 , H^1 and H^2 in the same structure as the ground state. (Angle α changes from 60° to 90° .) Then, the H^2 moves toward the opposite methylene group in parallel with the X-axis. Throughout these motions $C^2H^3H^4$ was fixed and the distances between C^1 and H^1 and between C^1 and C^2 were kept constant. The results are given in Fig. 7 for several fixed twist

Fig. 6. Scheme of rearrangement process toward an asymmetric structure. θ is the twist angle between the two methylene groups, α is the angle between the C^1H^2 and the C^1-C^2 axis. The rearrangement proceeds from (a) to (e).

angles ($\theta = 40^\circ, 50^\circ, 60^\circ, 70^\circ, 80^\circ$ and 90°). The most probable process is that the H^2 atom rotates by 90° of α in the twist angle of 40° and with changing the position of the H^2 atom on the X-axis, the twist angle increases and reaches 90° when the position of H^2 becomes about $-0.5 \text{ \AA}$ in the X-coordinate. After the process, the hydrogen atom moves toward the $H^3H^4C^2$ group at the twist angle of 90° . In moving to the $H^3H^4C^2$ group, the H^2 atom can pass through a path at a distance from the C-C axis, and the $H^3H^4C^2$ group and H^2 can change their configuration into methyl group structure $-C \begin{smallmatrix} H^2 \\ H^3 \\ H^4 \end{smallmatrix}$. Many calculations with

changing the Z-coordinates of H^2 were made in order to find the minimum energy path to the final asymmetric structure as shown in Fig. 6(e). Figure 8 shows the minimum energy path as a function of the X-coordi-

Fig. 7. Potential curves of rearrangement processes. At a fixed angle θ , H^1 and H^2 rotate in the plane of $H^1C^1H^2$ with keeping the angle of $H^1C^1H^2$ at 120° , and after the α value becomes 90° ($\angle H^2C^1C^2 = 90^\circ$), H^2 moves toward the opposite methylene group in parallel with the X axis. These curves are shown as a function of α and X-coordinate of H^2 .

Fig. 8. Potential curves of rearrangement processes. The dashed curve corresponds to the lowest potential curve in Fig. 7. The solid curve shows the lowest potential energies minimized with readjustment of the distance between X-axis and H^2 of the structure of $H^2H^3H^4$.

nate of the H^2 atom. The results show that no other energy is required for going into the asymmetric structure $[CH-CH_3]^+$, once after the ion turns into the structure shown in Fig. 6(d). The total required energy for the hydrogen rearrangement in $C_2H_4^+$ is estimated to be about 1.02 eV from Fig. 8. An asymmetric structure ion with 0.38 eV internal energy can return to the symmetric structure through the reverse process of this rearrangement. This reverse process takes place more frequently than the dissociation from the asymmetric structure because the latter process needs another energy for the dissociation (see below). This suggests that hydrogen atoms can exchange their positions before the dissociation.

Next process to produce $C_2H_2^+$ from

this asymmetric structure is to remove the two hydrogen atoms and form a hydrogen molecule. The potential curves of the dissociation process from the asymmetric structure $CH-CH_3^+$ were calculated for a variety of distances of the hydrogen molecule formation. The curve which has the lowest energy barrier is shown in Fig. 9. The energy required for this dissociation process is 0.92 eV.

The required energies for the three dissociation processes mentioned above are summarized in Fig. 10. For the scrambling process this energy is totally 1.56 eV as illustrated in lower part of the figure. By comparing the energies, it can be noticed that the most probable process for the dissociation is the scrambling through the path mentioned above. This is compatible

Fig. 9. Potential curve of dissociation process from the asymmetric structure, as a function of the distance R between a carbon atom and a detaching hydrogen atom. The energy barrier of this process is 0.92 eV.

Fig. 10. Diagram for the three fragmentation processes.

with the experimental results reported in the previous papers^{1,2}.

4. Discussion

In the extended Hückel theory the res-

onance integral H_{ij} is estimated empirically from the following relation by use of the ionization potentials I_i and I_j and the overlap integral S_{ij} between the orbitals i and j .

$$H_{ij} = \frac{1}{2} (I_i + I_j) K S_{ij}, \quad (1)$$

where K is an arbitrary parameter. Hoffmann determined the K value appropriately for all bonds between H and C atoms by using experimental results for many organic compounds⁶. His determination, however, was based on the results on fixed inter-nuclear distances in the compounds, and the Hoffmann's K value is not appropriate to discuss the fragmentation processes of molecules. It was pointed out that for diatomic molecules the EHT does not give the minimum in the potential energy curves⁷. We also obtained the results as shown in Fig. 1 for H_2 by changing the inter-nuclear distance R within the framework of Hoffmann's procedure: the K value was kept constant. The result can be compared with other results for H_2 molecule, as shown in Fig. 1 (b) and (c). The latter curves, based on the Heitler and London's procedure and experimental results, include only the electron energy terms but do not include the nuclear repulsion term between the two protons. The three curves are quite similar to each other. This result means that the EHT does not give effectively the repulsive energy term between the two nuclei.

Inclusion of the repulsive term for the Heitler and London's curve gives us an adequate potential energy curve, as is well known, and the result is given in Fig 2.

This means that inappropriate character by the EHT method may be compensated by inclusion of the repulsive term between the two nuclei.

Some improvements for the framework by Hoffmann have been presented. J. C. Leclerc and J. C. Lorquet estimated the resonance integral by following relation⁷⁾.

$$H_{ij} = \frac{1}{2} (I_i + I_j) K S_{ij} (1 - |S_{ij}|), \quad (2)$$

where K value is determined to reproduce the dissociation energy for each pair of the concerning atoms. This gave certainly good results in predicting the bond dissociation scheme, although the physical meaning of the formula (2) is not necessarily clear.

Yoneda formulated a seven-term polynomial including overlap integrals for the K value and gave satisfactory agreement between the calculated bond energy from the total energies and the observed bond energy for H_2 molecule¹⁰⁾.

We, however, rather preferred simpler method; the explicit introduction of the modified repulsive potential. We only changed the effective nuclear charges of the two protons so as to make the calculated energy difference of the total energies between infinity and the observed equilibrium distance of the H_2 molecule equal to the observed bond energy. The effective nuclear charge was estimated and the calculated total energy curve was already shown in Fig. 2. The curve has a minimum and is close to that of the exact calculation. The same procedure was applied to CH bond. The present approximation was used in the calculation of the frag-

mentation processes. The computational time of this method is very short, and this method is advantageous in the calculations of the potential curves for the fragmentation processes for which direct application of the SCF method is difficult.

The present method is empirical one and may leave some results undecided. In the cases of detachment of H_2 from $C_2H_4^+$, the potential curves show a tendency of going down into lower energy value than that of initial structure of $C_2H_4^+$ as the inter-nuclear distances increase. This also appeared in the results by the EHT without the repulsive term. It has been pointed out that empirical LCAO method could give rise to incorrect results when it is applied to the cases of large inter-nuclear distances, because it does not include electron correlation effects explicitly^{3,15,16)}. The present modified potential is still inadequate to compensate for the demerit of the EHT method completely when the inter-nuclear distances become large. The modified potential is also applied for the radical CH in the present study, although no appropriate potential curve exists in the references. The bond energy and the equilibrium distance calculated by the present method are both slightly smaller than those of the experiment.

In spite of these situations, energy maxima were obtained in the total energies for all cases of the bond dissociations, and the present method predicts that the scrambling process through the asymmetric structure has the lowest maximum (lowest energy barrier). These results are compatible with the experimental results of the fragmentation processes of ethylene

ions^{1,2)}. The present method also gives good results of the structures of methylcarbene (CHCH_3) and its ion. Rearrangements of methylcarbene were discussed by Altmann et al. by using the rigorous ab initio basis¹⁷⁾, and both results obtained by the two methods were in fairly good agreement with each other.

Lorquet calculated the energy differences among several isomers of C_2H_4^+ with doublet and quartet multiplicities and found out that the energies of the doublets for several specific geometries were around 12 ~ 16 eV, whereas those for the quartet states around 19 ~ 21 eV, about 5 ~ 6 eV higher than those of the doublet states⁴⁾. As far as the discussion is limited to the energy range around the appearance potential of C_2H_4^+ , the effects of the quartet states can be ruled out.

In general, the method presently proposed is capable of giving qualitatively reliable guide for the fragmentation process of the molecular ion and is useful in understanding of the experimental results by electron, ion and photon impacts.

References

- 1) I. H. Suzuki and K. Maeda, *Int. J. Mass Spectrom. Ion Phys.*, **15**, 281 (1974).
- 2) S. M. Gordon and G. J. Krige, *Int. J. Mass Spectrom. Ion Phys.*, **14**, 109 (1974).
- 3) A. J. Lorquet and J. C. Lorquet, *J. Chem. Phys.*, **49**, 4955 (1968).
- 4) A. J. Lorquet, *J. Phys. Chem.*, **74**, 895 (1970).
- 5) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).
- 6) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
- 7) J. C. Leclerc and J. C. Lorquet, *J. Phys. Chem.*, **71**, 787 (1967).
- 8) C. C. Wan and S. T. Tong, *Surface Sci.*, **34**, 739 (1973).
- 9) W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).
- 10) J. C. Slater, *Quantum Theory of Matter*, 2nd Ed. McGraw-Hill, New York (1968), p. 424.
- 11) G. Herzberg, *Commentarii Pontificia Academia Scientiarum*, **2**, No. 49, 1 (1972).
- 12) W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **49**, 404 (1968).
- 13) O. Kikuchi, *BUNSHI-KIDOHIO*, Kodansha, in Japanese (1971).
- 14) Y. Yoneda, *Bull. Chem. Soc. Japan*, **51**, 2472 (1978).
- 15) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965).
- 16) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S 136 (1965).
- 17) J. A. Altmann, I. G. Csizmadia and K. Yates, *J. Amer. Chem. Soc.*, **96**, 4196 (1974).

Keywords

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