Bull. Chem. Soc. Jpn., *59*, *1249—1250 (1986)*

Ab Initio MO Theoretical Studies on Direct Fragmentation of Organic Ions Produced by Electron-Bombardment

Hiroshi Ichikawa* and Atsushi Shigihara
Hoshi College of Pharmacy, Shinagawa, Tokyo 142
(Received November 8, 1985)

Synopsis. The possibility of bond-scission within a single vibration (direct fragmentation) in a molecular ion produced by electron-bombardment has been studied. MP2/6-31G* calculations have shown that a direct fragmentation in the ground-state ion is possible for the C–H bonds of hydrocarbons.

So far, fragmentations which are caused by vibrational excitations have been well-studied from both theoretical and experimental standpoints. Much knowledge about such fragmentations has been accumulated and it is recognized that most fragmentations take place in the ground electronic state, consuming a lot of time (more than 10^{-13} s).[1] However, we do not have any information on fragmentation within a single vibration, termed direct fragmentation. It is uncertain whether direct fragmentation actually occurs. However, an apparent difference in the mass spectra between lower and higher ionization energies suggests the existence of direct fragmentations. Such a difference is not a proof.

The electron-impact (EI) ionization takes place by a resonance between the wave of an electron in a molecule and that of an impinging electron; those electrons are indistinguishable. Therefore, any kind of excited state can possibly take place during electron-bombardment. Two types of direct fragmentation are possible according to the Franck-Condon principle: A direct fragmentation at the ground electronic state and that due to antibonding states (Fig. 1). We examined the former case using the second order Mφller-Plesset perturbation method[2] based on the 6-31G* basis set[3] (MP2/6-31G*).[4]

Previous work on intramolecular rearrangements in smaller systems has indicated that relative energies (including up to third order of Mφller-Plesset perturbation (MP3)) are in good agreement (less than 5 kJ mol^{-1}) with the results of a full coupled-cluster calculation.[5] We estimate a similar error for a MP2/6-31G* calculation, since it is shown that the difference of the effect of electron correlation between MP2 and MP3 are almost the same.[6]

The investigation method for the ground-state process is rather straightforward since it is sufficient to consider the potential energies referring to the potential energy curves of the molecule and the ions in the ground state, whatever the process is (see Fig. 1).

Most molecules are in the ν_0 state (the ground vibrational state) while maintaining a near-equilibrium distance (r_0). Vertical ionization reaches the point p_0 of the ground-state potential-energy curve of the molecular ions. If the potential energy at $p_0(V_0)$ is higher than that after dissociation (V_∞), i.e. ΔV ($=V_0-V_\infty$) is positive, ions can possibly undergo ground state direct fragmentation; if ΔV is negative, direct fragmentation can not take place. However, the latter case does not always mean that direct fragmentation never occurs. Although it is a small possibility, there is a chance that a molecule can be ionized at a shorter distance. If the potential energy at p_- (V_-) is higher than V_∞, direct fragmentation can occur.

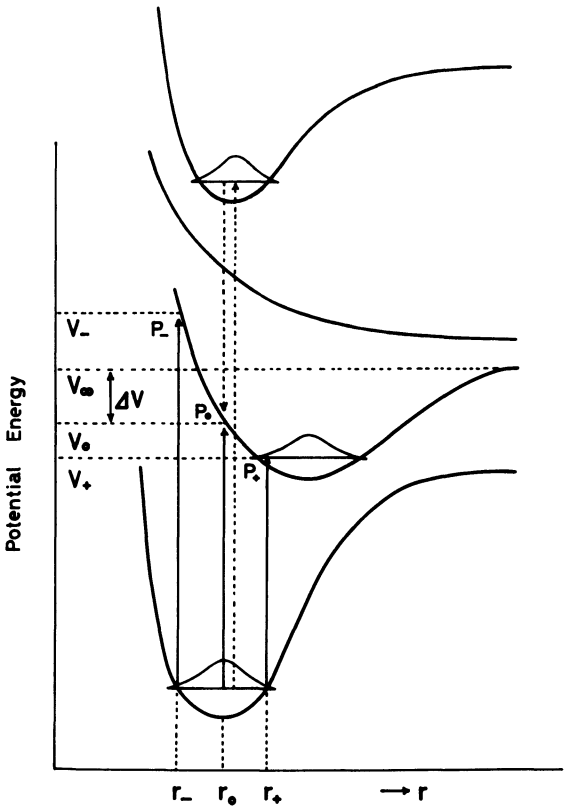

Fig. 1. The Franck-Condon principle of vertical ionization of molecule.

Figure 2 shows the results for hydrogen fluoride. The equilibrium distance of the ground-state ion is increased by about 0.1 Å from that of the molecular state. The vertical ionization at the equilibrium distance reaches a PE of −99.610387 au; this is lower than the energy after dissociation (−99.487271 au). Therefore, it may be concluded that ground-state direct fragmentation does not take place.

Figure 3 shows the case for methane. The PE curve for the ion is that of a C_{3v} adiabatic fragmentation, the lowest for a CH cleavage. It has a potential minimum at a very long distance (1.3280 Å).[7] Ionization at the equilibrium distance of the molecule gives a PE (−39.816667 au) which is higher than that after dissociation (−39.823607 au). Therefore, direct fragmentation is possible by ionization. It should be, however, stressed that this does not always mean that

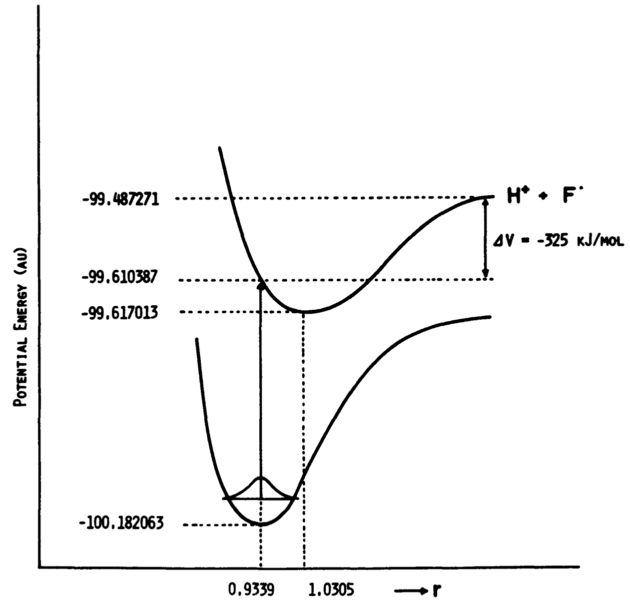

Fig. 2. Potential energy curves of the hydrogen fluoride ion and molecule by MP2/6-31G*.

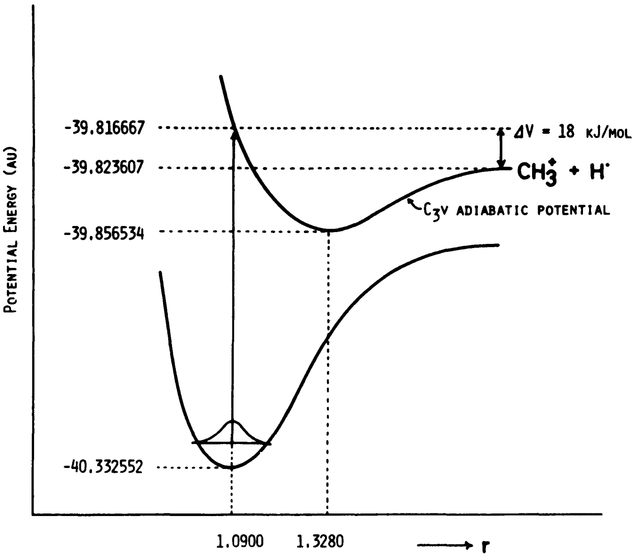

Fig. 3. Potential energy curves of the methane ion and molecule by MP2/6-31G*.

the appearance potential of a methyl cation is lower than that of a methane ion.[8)]

Table 1. The ΔV Values and Appearance Potentials by MP2/6-31G*

Compound	ΔV	$\mathrm{Ap}^{\mathrm{calcd\ a)}}$	$\mathrm{Ap}^{\mathrm{expl\ b)}}$
	kJ/mol	(eV)	(eV)
H-C_2H_5	73	12.1	12.7
CH_3-CH_3	−76	13.6	13.5
H-CH_2OH	−15	11.0	11.7
H-CH_2NH_2	−13	9.5	10.3
C_2H_5-NH_2	−254	11.7	13.5
CH_3-CH_2NH_2	−30	9.4	9.7

a)Zero-point energies are not corrected. b)Appearance potentials are taken from Ref. 9.

In a similar way, we obtained results for some other compounds (summarized in Table 1). As references, the calculated and experimental[9)] appearance potentials are listed in addition to the ΔV values. The positive ΔV values suggest a possible direct fragmentation. It is well known that the C–C bond in an ethylamine ion is easily broken under the EI condition; however, the present results show that such a cleavage is not a direct fragmentation. Consequently, it can be said that a direct fragmentation in the ground electronic state is possible in the CH bonds of hydrocarbons.

References

1) The works of Mass spectrometry have been periodically reviewed and recorded in "Mass Spectrometry," Vol. 1—7, The Chemical Society, London.

2) C. Mφller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).

3) P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta,* **28**, 213, (1973).

4) We have used the GAUSSIAN-80H program (Hitac version of GAUSSIAN-80 (QCPE 437, 1982)) at the Computation Center of the University of Tokyo. Geometry optimization has been carried out by the Fletcher-Powell procedure (R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963)). The thresholds of bond-length and angle are 0.0003 Hartree/Bohr or radian in terms of force.

5) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem.*, **14**, 545 (1978).

6) R. H. Nobes, W. R. Rodwell, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, **103**, 1913 (1981).

7) The bond length of the three equivalent C–H bonds is determined as 1.0965 Å.

8) The appearance potentials of CH_4^+ and CH_3^+ are observed at 12.7 eV and 14.3 eV, respectively.

9) H. M. Rosenstock, K. Draxl. B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data,* **6**, Suppl. 1 (1977).