# *Ab Initio* MO Study on the 1,2-Hydrogen Migration from the Twisted Propene

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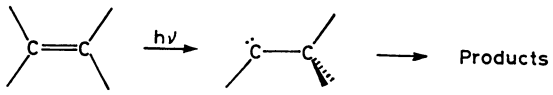
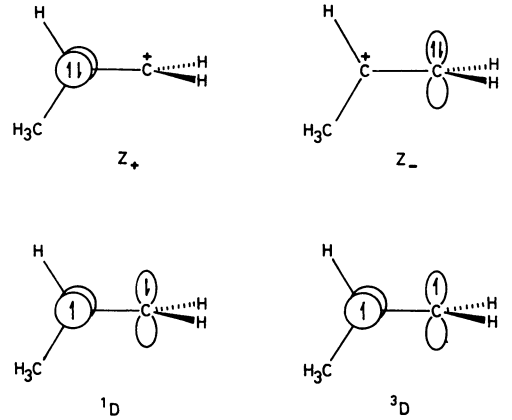
**Synopsis.** The 1,2-hydrogen migration from the 90°-twisted propene to the corresponding carbenes was examined on the basis of *ab initio* MO CI calculations. It was predicted that, in the polarized zwitterionic states of the twisted propene, the 1,2-hydrogen migration occurs from the negatively-charged carbon atom to the positively-charged one.

There is experimental evidence[1] that photochemical reactions of olefins involve the carbene intermediates.

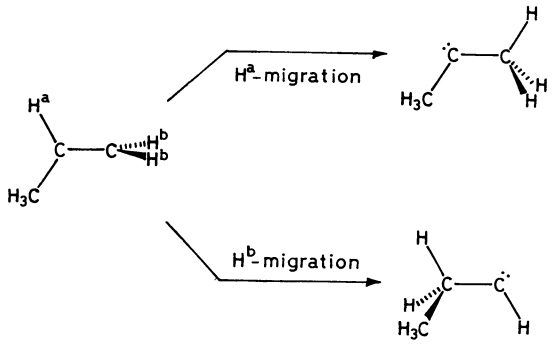



Also, it is well known that the excited state of an olefin is stabilized by a double-bond rotation which gives the twisted structure.[2] Thus a working hypothesis is used that the intermediate carbene is formed by the 1,2-hydrogen migration from the twisted structure.[3] Evleth and Sevin[4] have investigated theoretically the photodecomposition processes of ethylene and have shown that the 1,2-hydrogen migration occurs from the zwitterionic state of the 90°-twisted ethylene.




In the case of the 90°-twisted propene, there are two lower-lying zwitterionic states, $Z_+$ and $Z_-$, which have different polarizations. In each zwitterionic state, two different 1,2-hydrogen migrations are possible: the $H^a$-migration to form isopropylidene and the $H^b$-migration to form propylidene. This note intends to compare these two reaction paths on the basis of *ab initio* MO CI calculations and to predict the reactivity of the twisted unsymmetric olefins.

First, the 1,2-hydrogen migration of the twisted ethylene is described. The energy diagrams for the twisted ethylene, ethylidene, and the half-reacted species are shown in Fig. 1. Each energy level in Fig. 1 was calculated by means of the closed-shell or restricted open-shell SCF method with the 4-31G basis set[5] by using the molecular structure which was optimized with the STO-3G basis set.[6] The overall shape of Fig. 1




is similar to that observed in the energy variations reported by Evleth and Sevin.[3]

In the calculation of the propene system, the molecular structures of the twisted propene, propylidene, isopropylidene, and the half-reacted species were obtained by introducing a methyl group into the optimized structure of the $^1D$ state of the ethylene–ethylidene system. Moreover, the intermediate structures were estimated by interpolation. The MO basis set used in the CI calculation[7] was the open-shell SCF solution for the $^1D$ state. In the CI calculation, 41 singly- and doubly-excited configurations were selected. The potential energy curves obtained with the 4-31G basis set are shown in Fig. 2.

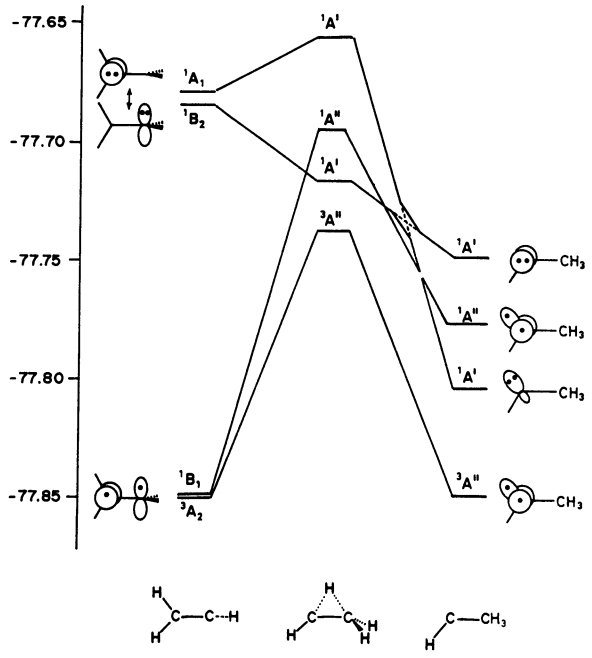



Fig. 1. Energy diagrams for the twisted ($D_{2h}$) ethylene, the half-reacted species, and ethylidene. The electronic structures of the twisted ethylene and ethylidene are shown schematically on both sides of the diagrams. The energies are in a.u.

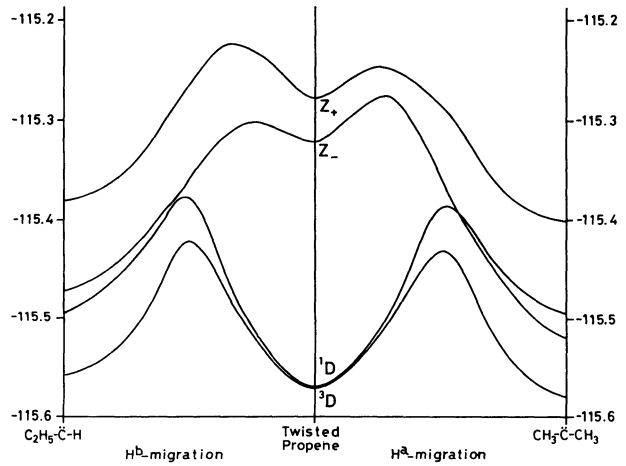
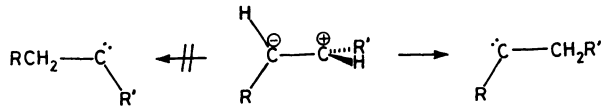



Fig. 2. Potential energy (in a.u.) curves along the hydrogen migrations from the twisted propene. The electron configurations of the twisted propene are shown in the text. The electron configurations at the carbene centers in four electronic states of propylidene and isopropylidene are same as those of ethylidene which are shown in Fig. 1.

The $Z_+$ and $Z_-$ zwitterionic states of propene are largely polarized. In the $Z_-$ state, for example, the negative charge on the $C^-$ atom was calculated to be $-1.04$ and the positive charge on the $C^+$ atom to be $+0.69$. The $Z_-$ state was found to be lower in energy than the $Z_+$ state. This may be understood simply from the electron-donating character of the methyl group.

Figure 2 indicates the preferable path for the hydrogen migration from the zwitterionic states. From the $Z_-$ state, the $H^b$-migration is expected to occur easily more than the $H^a$-migration, while the $H^a$-migration is expected to occur from the $Z_+$ state. These two different results give a common conclusion that the 1,2-hydrogen migration from the zwitterionic states of the twisted non-symmetric olefins occurs from the negatively-charged carbon atom to the positively-charged carbon atom. Figure 2 also indicates that the singlet diradical ($^1D$) and the triplet diradical ($^3D$) of twisted olefins might not undergo the 1,2-hydrogen




migration, since the activation energy is very large.

The preferential migration, which occurs to the positive center, involves 2 electrons (4N+2) in the C···H···C bond of the transition state, while the migration to the negative center involves 4 electrons (4N) in it. This is quite parallel to the ground state 1,2-migrations in carbonium ions and carbanions: the 1,2-migration occurs very easily in carbonium ions (2 electron transition state), while it is absent in carbanions (4 electron transition state).[8] Although the present study treats the excited states, the conclusion obtained is equivalent to the ground state reactivity which is widely accepted.

## References

1) P. J. Kropp, *Pure Appl. Chem.*, **24**, 585 (1970); S. S. Hixson, *J. Am. Chem. Soc.*, **97**, 1981 (1975); Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1635; R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 4602 (1978); P. J. Kropp and F. P. Tise, *ibid.*, **103**, 7293 (1981).

2) The electronic structure of twisted olefins has been discussed in connection with the sudden polarization phenomenon: L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979); J.-P. Malrieu, *Theoret. Chim. Acta*, **59**, 251 (1981); I. Nebot-Gil and J. P. Malrieu, *J. Am. Chem. Soc.*, **104**, 3320 (1982).

3) Another model to address the 1,2-migration is the reaction from the Rydberg state of the planar olefin: P. J. Kropp, *J. Org. Photochem.*, **4**, 1 (1979).

4) E. M. Evleth and A. Savin, *J. Am. Chem. Soc.*, **103**, 7414 (1981).

5) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

6) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

7) Since the symmetry property of the system is not preserved during the $H^b$-migration and the excited singlet state can not be obtained by usual SCF calculations, the CI method was used for the propene system.

8) H. E. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).