

## Ab initio Structures of Transition States in Electrophilic Addition Reactions of Molecular Halogens with Ethene

Shinichi Yamabe,<sup>\*a</sup> Tsutomu Minato,<sup>b</sup> and Satoshi Inagaki<sup>c</sup>

<sup>a</sup> Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630, Japan

<sup>b</sup> Yuge Mercantile Marine College, Yuge, Ochi, Ehime 794-25, Japan

<sup>c</sup> Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

The fluorination of ethene occurs *via* a four-centred transition state, while chlorination and bromination give zwitterionic three-centred transition states.

The electrophilic *anti* addition of bromine (or chlorine) to ethene is known to proceed *via* a cyclic three-membered bromonium (or chloronium) ion intermediate.<sup>1</sup> The fluorination was recently reported to occur in a stereoselective *syn* manner.<sup>2</sup> Thus, the *syn-anti* selectivity is of mechanistic interest, and the explicit determination of the structure of the transition state (TS) may help to explain the difference.

*Ab initio* M.O. calculations were carried out with the 3-21G basis set<sup>3</sup> to determine the three TS geometries, using the GAUSSIAN 82 program.<sup>4</sup>

The TS structure for the fluorination of ethene (Figure 1a) is four-centred, indicating concerted *syn* addition. The atom-atom bond populations show that the incipient bonds between C and F are formed at both reacting sites. The vibrational mode for the sole imaginary frequency shows an in-plane motion, and the vector is consistent with the concertedness.

The TS geometry for chlorination, shown in Figure 1b, is entirely different from that for fluorination. The structure can be regarded as a cyclic chloronium ion plus a chloride ion. The heterolytic fission of the Cl<sub>2</sub> molecule is almost complete at the TS giving rise to the ion pair (charges on Cl +0.324 vs. -0.833). It is noteworthy that the heterolysis occurs intrinsically, without any assistance from polar solvents.

The TS geometry for bromination (Figure 1c) is similar to that for chlorination. The charge separation in Br-Br (+0.517 vs. -0.850) is greater than that in Cl-Cl, which suggests that bromination proceeds more heterolytically than chlorination.

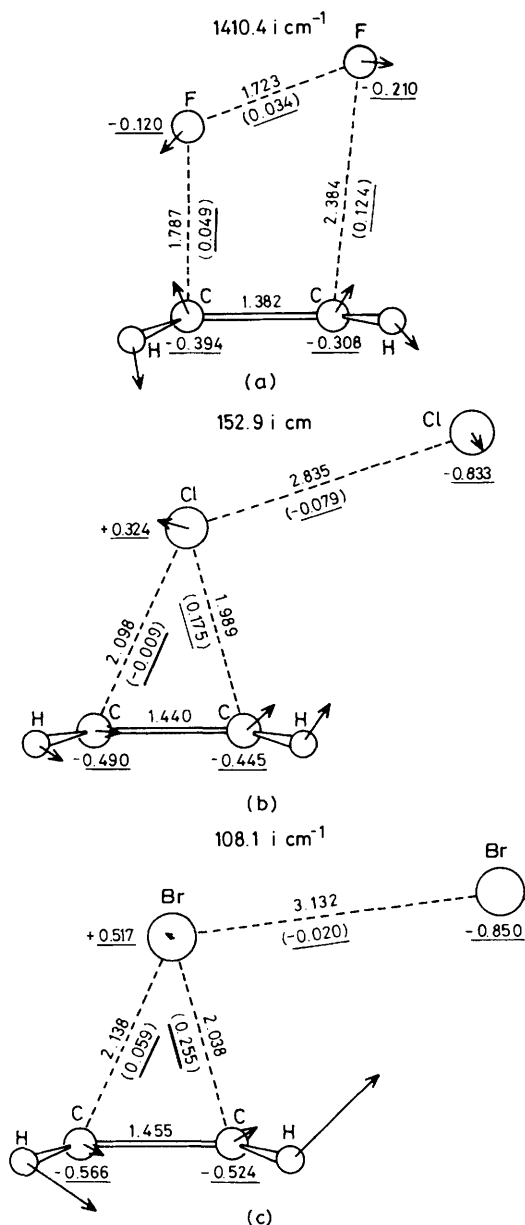
The TS structures can account for the observed *syn-anti* stereoselectivities. Chlorination and bromination proceed *via* three-centred geometries very like those of the cyclic halonium intermediates. These are necessary for *anti* addition. Fluorination does not proceed *via* the three-centred TS, but passes into a four-centred TS. Considerable polarization of the X-X bond is required for the three-centred geometry. The polarizability of F<sub>2</sub> is low, which may explain the four-centred TS which is consistent with the observed *syn* stereoselectivity.<sup>2</sup> Substituents attached to the olefinic site would affect the TS structure appreciably (much more than the solvent). Such a Markovnikov-type analysis and the intervention of the  $\pi$  complex are the subject of further study.

We thank the Institute for Molecular Science for use of a HITAC S-810 computer.

Received, 15th December 1987; Com. 1805

### References

- 1 F. Freeman, *Chem. Rev.*, 1975, **75**, 439.
- 2 S. Rozen and M. Brand, *J. Org. Chem.*, 1986, **51**, 3607.
- 3 M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.*, 1982, **104**, 2797; K. D. Dobbs and W. J. Hehre, *J. Compt. Chem.*, 1986, **7**, 359.
- 4 J. S. Binkley, M. J. Frish, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, and J. A. Pople, Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, 1984.



**Figure 1.** The 3-21G transition state geometries for three electrophilic addition reactions,  $X_2 + C_2H_4 \rightarrow C_2H_4X_2$  [ $X =$  (a) F, (b) Cl, and (c) Br]. The imaginary frequency vibrational mode is sketched. The underlined numbers denote the atomic net charges (positive, cationic), and those in parentheses are the atom-atom bond populations. Lengths in Å. The MP3/3-21G//RHF/3-21G total energies are (a) -275.60893, (b) -992.37291, and (c) -5197.87398 Hartree (1 Hartree =  $4.359814 \times 10^{-18}$  J). These energies correspond to the activation energies: (a) 212.5, (b) 212.1, and (c) 256.9 kJ mol<sup>-1</sup>. In the  $C_{2v}$  symmetry bridged ions,  $C_2H_4Cl^+$  and  $C_2H_4Br^+$ , the  $C \cdots Cl$  and the  $C \cdots Br$  distances are 2.071 and 2.160 Å, respectively.