# The Electronic Structures of Ethyl Cation and Protonated Ethylene; a Non-empirical LCAO–MO–SCF Investigation

By D. T. CLARK* and D. M. J. LILLEY

*(Department of Chemistry, The University, Durham)*

*Summary* *Ab initio* calculations have been performed on ethyl cation and protonated ethylene and it is shown that there is no activation barrier to transformation of the "bridged" to classical ion.

THE electronic structures of ethyl cation and protonated ethylene, and the role of these species as prototypes for intermediates in electrophilic addition to olefins are of considerable importance. There are basically two points; the energy difference between the two species and the activation barrier to transformation between them.

Dewar and his co-workers[1] have shown that semi-empirical all-valence-electron SCF–MO treatments, in the NDDO and less complete schemes, considerably over-estimate the stability of the bridged ion. An *ab initio* study[1] of the two species yielded an energy difference of 9·0 kcal/mole, with ethyl cation being the lower in energy; however this result rests to some extent on a presumed geometry for protonated ethylene. We report here preliminary results of non-empirical LCAO–MO–SCF calculations on ethyl cation and protonated ethylene and an idealized reaction co-ordinate transforming one into the other.

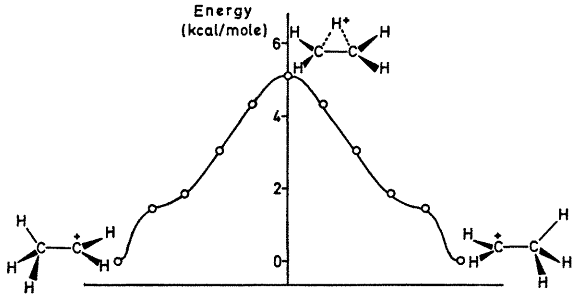
The calculations have been carried out using the IBMOL IV[2] computer program using a contracted gaussian basis set[3] (7,3,3/3,1,1). For the final geometries of ethyl cation and protonated ethylene, polarization functions ($2p_z$, $2p_y$, $2p_x$) were added to the basis set for each hydrogen. For ethyl cation the energy was minimized with respect to C-1–C-2 bond lengths, whilst for protonated ethylene, the C–C bond length, distance of bridging hydrogen to the centre of the C–C bond, and out-of-plane bending of the ethylenic hydrogens were investigated. As C–H bond lengths tend to be nearly invariant within classes of compounds they were kept constant at 1·084 Å ($<$HCH 120°) for ethylene and the bonds to C-1 in ethyl cation, and 1·093 Å for the bonds to C-2 ($<$HCH 109·5°) in the latter.

The final geometries are given in the Table, together with those of ref. 1 for comparison.

|  | $r_{C-C}$(Å) | Ref. | Distance of bridging H to centre of C–C bond (Å) | Out-of-plane bending of hydrogens attached to ethylene fragment (Deg) | Rel. energy kcal/mole |
|---|---|---|---|---|---|
| Ethyl cation .. .. .. | 1·48 | [1] | — | — | (0·0) |
|  | 1·568 | This work | — | — | (0·0) |
| Protonated ethylene .. | 1·46[a] | [1] | 1·11[a] | — | 9·0 |
|  | 1·474 | This work | 1·339 | 0·0 | 5·16<br>3·39[b] |

[a] Presumed value. [b] Basis set including polarization functions on hydrogens.

The surprising feature is the considerable difference between the geometries, particularly the distance of the bridging hydrogen to the centre of the C–C bond in protonated ethylene. These geometry differences have important consequences as far as the relative energies of the two species are concerned. On the basis of the energy difference obtained in this work, 3·39 kcal/mole compared with 9·0 kcal/mole,[1] protonated ethylene becomes more probable as an intermediate in electrophilic addition to olefins.[4] However, as we have previously indicated, it is important to have some idea as to how easy it is to transform one species into the other.



FIGURE

We have therefore carried out calculations at points along an idealized reaction co-ordinate in which the bridging hydrogen in protonated ethylene slides along the bond such that the hydrogen moves in a straight line from its initial position to its final position in ethyl cation. This in fact corresponds to a continuous change in C-2–H bond lengths. The C–C and C-2–H bond lengths, and $<$HC(2)H bond angles were assumed to change continuously in going from protonated ethylene to ethyl cation. Calculations were carried out at intermediate points using the (7,3,3/3,1,1) basis set. The results are shown in the Figure. The interesting result emerges that it is possible to transform protonated ethylene to ethyl cation without an activation barrier. We therefore postulate that in the gas phase at any rate (and probably in solution also) rather than being an *intermediate*, protonated ethylene is the *transition state* for scrambling the hydrogens, as shown in the Figure. The calculated activation barrier for this process (3·39 kcal/mole), the energy difference between ethyl cation and protonated ethylene, would appear to be entirely reasonable (*cf.* refs 5, 6).

D.M.J.L. thanks S.R.C. for a research studentship.

(*Received, March 17th,* 1970; *Com.* 384.)

[1] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 5350.

[2] A. Veillard "IBMOL Version 4" Special IBM Technical Report, San Jose, California, 1968.

[3] D. R. Whitman and C. J. Hornback, *J. Chem. Phys.*, 1969, **51**, 398.

[4] *cf.* R. Breslow, "Organic Reaction Mechanism", Benjamin, New York, 1966, p. 114.; J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", Benjamin, New York, 1964, p. 179.

[5] B. Davis, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc.* (*B*), 1970, 81.

[6] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 1967 ,**89**, 4739.