The Electronic Structure of Bridge-protonated Fluoroethylene and the Interconversion of 1- and 2-Fluoroethyl Cations

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Summary Nonempirical LCAO–MO–SCF calculations have been performed on an idealized reaction co-ordinate relating 1- and 2-fluoroethyl cations through bridge-protonated fluoroethylene.

IN a previous study[1] we have discussed the electronic structures of 1- and 2-fluoroethyl cations. We present here preliminary results on an idealized reaction co-ordinate relating the two ions through bridge-protonated fluoroethylene.

The calculations have been carried out with a basis set of contracted gaussian functions as previously described.[1,2] The equilibrium geometry for the bridged ion was taken to be that previously optimized for protonated ethylene,[2] with a hydrogen atom being replaced by fluorine, the C–F bond length being taken as 1·33 Å. Starting from the energetically-preferred eclipsed conformation of 2-fluoroethyl cation, the transformation to the bridged ion involves moving H(3)[H(4)] in a straight line from its initial position to its final position in bridge-protonated fluoroethylene, whilst rotating H(4)[H(3)] into the F–C(2)–C(1) plane. This, in fact corresponds to a continuous change in the C(2)–H(3)[H(4)] bond length. The C–C and C(2)–H(4) [H(3)] bond lengths and the F–C–H(4)[H(3)] bond angles were assumed to change continuously throughout the transformation.

The results are shown in Figure 1. The interesting feature emerges that it is possible to transform 2-fluoroethyl cation into the 1-fluoroethyl cation without activation barrier through bridge-protonated fluoroethylene. The bridge ion is calculated to be 12·10 kcals/mole more stable than the classical 2-fluoroethyl cation. However, this does not imply a discrete existence for the ion since the transformation to the energetically-preferred 1-fluoroethyl cation involves no activation barrier. Some measure of the electronic effect of replacing hydrogen by fluorine in the bridged ion can be obtained by comparing the relative energies for formation of the bridged ions from the corresponding ethanes. Taking protonated ethylene as standard, the relative energy for production of protonated fluoroethylene is calculated to be —7·8 kcal/mole. This stabilizing effect of fluorine is reflected in the gross atomic population on fluorine (9·15). This may be compared with the larger stabilizing effect in 1-fluoroethyl cation, and destabilizing effect in 2-fluoroethyl cation where the populations on fluorine are 9·10 and 9·22, respectively.[1]

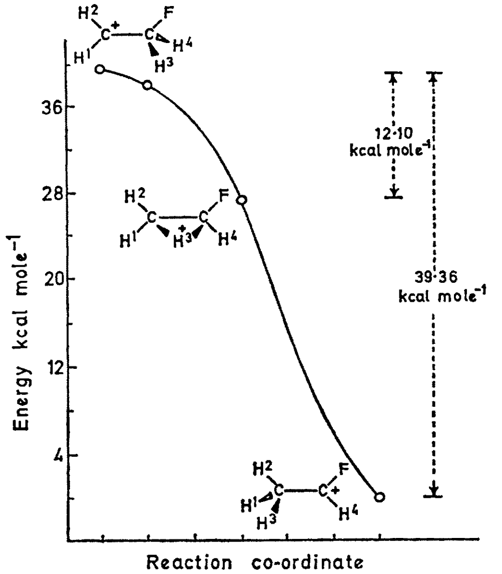

FIGURE 1. *Energy diagram for the interconversion of* 1- *and* 2-*fluoroethyl cations.*

On the basis of the results displayed in Figure 1, the following conclusions may be drawn. The activation barrier for the transformation of the 1- into the 2-fluoroethyl cation is large, whilst that for the reverse reaction is negligible, (the transition state must approximate to the 2-fluoroethyl cation very closely). This means that starting from, say, CH_2F–CD_2^+ only CH^+F–CD_2H should be produced with no scrambling at C(2), and we are currently investigating this experimentally. This contrasts with the scrambling in ethyl cation discussed previously.[2] A further point of difference is that the bridged ion is no longer the transition state for the transformation as for the ethyl cation rearrangement.

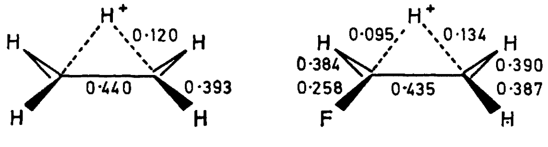

FIGURE 2. *Bond-overlap populations for bridge-protonated ethylene and fluoroethylene.*

Figure 2 shows the bond overlap population for the bridged ions. The interesting feature is that for the bridge-protonated fluoroethylene, although the bridging hydrogen is symmetrically placed along the C–C axis, the C–H bond overlap populations are unequal. This inequality is biased in favour of the formation of 1-fluoroethyl cation and provides a simple pictorial interpretation for the driving force for the transformation.

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[1] D. T. Clark and D. M. J. Lilley, *Chem. Comm.*, 1970, 603.
[2] D. T. Clark and D. M. J. Lilley, *Chem. Comm.*, 1970, 549.