THEORETICAL STRUCTURES FOR PROTONATED METHANE AND PROTONATED ETHANE

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Protonated methane (CH_5^+) and protonated ethane ($C_2H_7^+$) are of interest as simple models for electrophilic attack on alkanes. We wish to report theoretical structures for these species using $\underline{ab}$ $\underline{initio}$ molecular orbital theory with a minimal basis set of Slater-type atomic orbitals.

The actual basis functions are linear combinations of three gaussian functions which are fitted to Slater orbitals by least-squares methods (STO-3G).[1] Standard molecular exponents (ζ-values) were used throughout. All geometrical parameters were varied (subject only to certain symmetry constraints) until the calculated total energy was minimized.

For CH_5^+, we considered a trigonal bipyramid (D_{3h}), a square pyramid (C_{4v}) and the less symmetric (C_s) structure shown in the figure (I). The optimum energies were found to be ordered $E(D_{3h}) > E(C_{4v}) > E(C_s)$. For the C_s structure, the geometrical parameters are

$$r_1 = 1.098 \text{ Å} \qquad r_2 = 1.106 \text{ Å}$$
$$r_3 = 1.370 \text{ Å} \qquad r_4 = 1.367 \text{ Å}$$
$$\alpha = 140.0° \qquad \beta = 83.8°$$
$$\theta = 37.2° \qquad \zeta = 117.7°$$

This structure corresponds to a rather loose complex between a CH_3^+ ion and a hydrogen molecule. The energy of the C_{4v} structure is about 2 kcal/mole higher. This is an activation energy for hydrogen rearrangement within the ion. These conclusions parallel those of other workers.[2,3]

For $C_2H_7^+$, there is a previous semi-empirical study by Olah, Klopman and Schlosberg,[4] but without full geometrical variation. We have made a careful study of the two structures illustrated in the figures (II and III). Structuré II (symmetry C_{2v}) corresponds to a protonated C-C bond. Structure III is analogous to the lowest energy form of CH_5^+ and can be considered as a complex between an ethyl cation and a hydrogen molecule (protons 6 and 7). III corresponds to protonation of a C-H bond.

The calculations show that the protonated C-C structure II has the lowest energy (11 kcal/mole below the lowest energy for III). The geometrical parameters for II are

$$r_1 = 2.362 \text{ Å} \qquad\qquad r_2 = 1.251 \text{ Å}$$
$$r_3 = 1.097 \text{ Å} \qquad\qquad r_4 = 1.094 \text{ Å}$$
$$\alpha = 52.7° \qquad\qquad \beta = 89.5°$$
$$\theta = 115.6°$$

The bridging proton H_7 is at the vertex of a very flat isosceles triangle with a long C-C distance. This suggests that protonation of alkanes can easily lead to carbon-carbon cleavage.
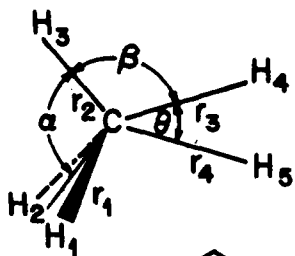
The optimum structure for III is a very loose $C_2H_5^+-H_2$ complex, the distance r_5 being 2.746 Å. It appears, therefore, that $C_2H_5^+$ has a smaller hydrogen molecule affinity than CH_3^+, presumably because the additional methyl group donates electrons into the vacant orbital on the carbonium center, making it less available for the electrons of an approaching hydrogen molecule. A number of other structures including methylated versions of the D_{3h} form of CH_5^+ were tested, but not refined. These all led to higher energies. Thus, although the complete potential surface has not been explored, these studies do indicate that the C-C bridged form II is the lowest energy configuration of $C_2H_7^+$.
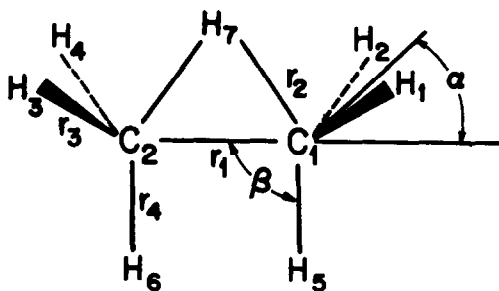
References

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2. W. Th. A. M. Van der Lugt and P. Ros, Chem.Phys.Ltrs. 4, 389 (1969).

3. H. Kollmar and H.·O. Smith, Chem.Phys.Ltrs. 5, 7 (1970).

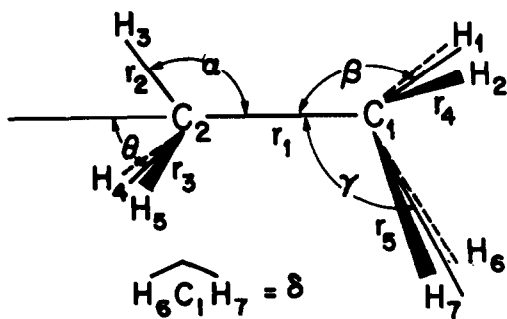4. G. A. Olah, G. Klopman and R. H. Schlosberg, J.Am.Chem.Soc. 91, 3261 (1969).

$$\widehat{H_1CH_2} = \zeta$$

I

$$\widehat{H_1C_1H_2} = \widehat{H_3C_2H_4} = \theta$$

II

$$\widehat{H_6C_1H_7} = \delta$$

$$\widehat{H_4C_2H_5} = \zeta$$

$$\widehat{H_1C_1H_2} = \eta$$

III