Tetrahedron Letters No. 22, pp 1859 - 1862, 1977. Pergamon Press. Printed in Great Britain.

QUALITATIVE MO INTERPRETATIONS OF AB INITIO CALCULATIONS

B. M. Gimarc[1]
Department of Chemistry
Princeton University
Princeton, New Jersey 08540

(Received in USA 4 February 1977; received in UK for publication 19 April 1977)

Elsewhere I have used qualitative MO arguments to predict that molecules and ions of the general formula AH_4 with 6 valence electrons should be square planar rather than tetrahedral in shape.[2] Recently Schleyer, Pople, and co-workers[3] have published results of ab initio MO calculations on the 6 electron series BeH_4, BH_4^+, and CH_4^{2+}. They report that indeed these species do have lower energy in the square planar geometry. However, their studies went beyond angular geometry variations. They found square planar BeH_4 to be unstable with respect to BeH_2 and H_2 and that CH_4^{2+} dissociates into the lower energy products CH_3^+ and H^+. For BH_4^+ they found stable structures of C_{2v} symmetry that correspond to a slightly bent BH_2^+ unit loosely associated with H_2. These $H_2B^+\cdots H_2$ structures were of nearly equal energy and only a couple of kcal/mole below the energy of separated BH_2^+ and H_2. This seemingly bewildering variety of results for rather similar systems can be understood with the aid of qualitative MO ideas plus simple electrostatic arguments.

Walsh's rules[2,4] say that 6 electron AH_4 molecules should be square planar and 4 electron AH_2 molecules should be linear. Figure 1 is the correlation diagram for the dissociation of square planar AH_4 into linear AH_2 and H_2. Assuming that the dissociation follows C_{2v} symmetry, the process is symmetry allowed.[5] Electrons flow smoothly from reactant energy levels to fill the appropriate energy levels of the correct products. From qualitative MO assumptions, the σ_u orbital of linear AH_2 has exactly the same energy as the e_u pair of square planar AH_4. The nodeless σ_g MO of AH_2 should be slightly higher but otherwise comparable in energy to the nodeless a_{1g} MO of AH_4. Whether the dissociation $AH_4 \rightarrow AH_2 + H_2$ is exothermic or endothermic depends on the relative energies of $\sigma_g(H_2)$ and $\sigma_u(AH_2)$. The energy of $\sigma_g(H_2)$ will be the same whether the reactant is BeH_4, BH_4^+, or CH_4^{2+}. The energy of $\sigma_u(AH_2)$ depends on the energy of the 2p AO's of the central atom A. For Be, with low electronegativity and high energy 2p AO's, the energy of $\sigma_u(AH_2)$ is higher than that of $\sigma_g(H_2)$ and the dissociation of BeH_4 into BeH_2 and H_2 would be exothermic as computed by Schleyer, Pople, and co-workers and as implied by the order of product energy levels in Figure 1. Boron and carbon have progressively larger electronegativities and lower energy 2p AO's and these move the $\sigma_u(AH_2)$-$e_u(AH_4)$ level to lower energies. For BH_4^+, the energies of $\sigma_g(H_2)$ and $\sigma_u(AH_2)$ must be about the same to account for the

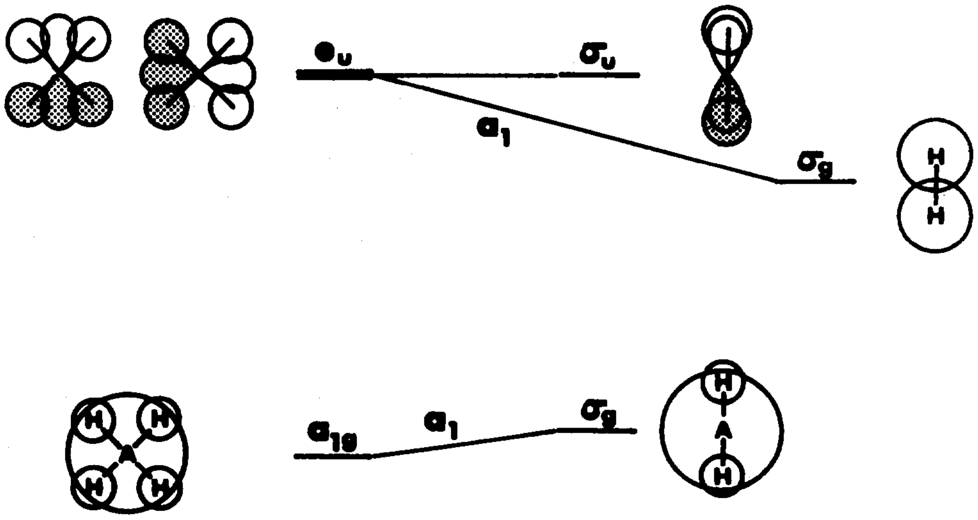

Figure 1. $AH_4(D_{4h}) \xrightarrow{C_{2v}} AH_2(D_{\infty h}) + H_2$

loosely bound $H_2B^+\cdots H_2$ complex. For CH_4^{2+}, $\sigma_u(AH_2)$ must be lower than $\sigma_g(H_2)$, making the reaction $CH_4^{2+} \rightarrow CH_2^{2+} + H_2$ endothermic, blocking the dissociation. Instead CH_4^{2+} breaks up into CH_3^+ and H^+. But why does CH_4^{2+} give up H^+ while BeH_4 and BH_4^+ do not? Figure 2 is the correlation diagram for the dissociation of square planar AH_4 into planar triangular AH_3 and H. Again, assume a process of C_{2v} symmetry. The hydrogen atom nonbonding 1s AO should be far above the energies of the bonding MO's of AH_4 and AH_3. All 6 electrons of AH_4 flow into the AH_3 product orbitals, leaving the hydrogen 1s AO empty and producing H^+. Hydrogen 1s and A atom 2p AO overlap differences between $e_u(AH_4)$ and $e'(AH_3)$ clearly show that the e' levels of product are above the energy of the related e_u levels of reactant, making the dissociation endothermic for any A and blocking the process. This conclusion is correct for BeH_4 and BH_4^+ but the dissociation of CH_4^{2+} occurs anyway. Why?

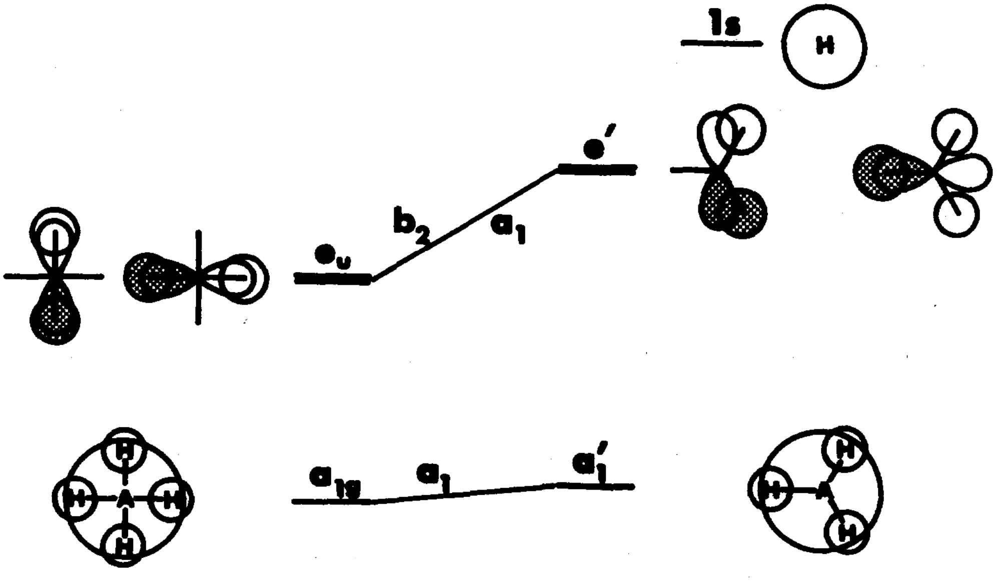

Figure 2. $AH_4(D_{4h}) \xrightarrow{C_{2v}} AH_3(D_{3h}) + H$

The qualitative MO model and the extended Hückel method on which the qualitative model is based fail to account properly for large changes in electrostatic potential.[6,7] Internal electrostatic repulsions clearly increase through the series BeH_4, BH_4^+, and CH_4^{2+}. The dissociation of BeH_4 into BeH_3^- and H^+ would separate opposite charges. Both MO and electrostatic energetics oppose this process. The dissociation of BH_4^+ into BH_3 and H^+ would produce no new ions but it would lower internal electrostatic repulsions in BH_4^+. Electrostatic repulsions in CH_4^{2+} could be substantially reduced by dissociation into two ions: CH_3^+ and H^+. This electrostatic driving force for dissociation of H^+, reversed in direction in BeH_4 and small or zero in BH_4^+, is large in CH_4^{2+} where it apparently outweighs the qualitative MO energetics. Similar considerations are not appropriate for the processes summarized in Figure 1 because the product projected in each case is neutral H_2.

This research was sponsored by a grant from the National Science Foundation.

References and Notes

1. On leave from Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.
2. B. M. Gimarc, Accounts Chem. Res., 7, 384 (1974).
3. J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, J. Am. Chem. Soc., 98, 3436 (1976).
4. A. D. Walsh, J. Chem. Soc., 2260 (1975), and papers immediately following.
5. R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1, 17 (1968).
6. R. Hoffmann, J. Chem. Phys., 40, 2480 (1964).
7. L. C. Allen, "Why Three Dimensional Hückel Theory Works and Where it Breaks Down," in Sigma Molecular Orbital Theory, O. Sinanoğlu and K. Wiberg, Eds., Yale University Press, 1970, p. 227.