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Fluoride-Induced Elimination of Ethyl Fluoride. The Importance of High-Level Optimizations in ab Initio and DFT Studies

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In recent years, *ab initio* calculations have emerged as a powerful tool for investigating organic reaction mechanisms, and they are ideally suited for studying the complicated potential energy surfaces found in E2 eliminations.[1] For the sake of simplicity, some workers have used the reactions of F^- with alkyl fluorides as models;[1d,e,2] however, these systems suffer from two major complications: (1) the elimination is endothermic unless a leaving group complex is formed,[3] and (2) it is difficult to characterize the high charge density of the fluoride ion. In a recent paper, Bickelhaupt *et al.* (BBNZ) have used a density functional theory (DFT) approach to study the reaction of F^- with ethyl fluoride ($F^- + CH_3CH_2F$), and on the basis of their results, they have questioned the ability of conventional *ab initio* calculations to characterize the potential energy surface (PES).[2] If true, this assertion would have broad implications in modern computational chemistry. In the present paper, we report high-level *ab initio* and DFT calculations on the $F^- + CH_3CH_2F$ system which resolve this conflict but raise serious concerns about the latter method's ability to adequately describe species with diffuse electron distributions, e.g., transition structures (TS).

With its combination of large basis sets (up to 6-311+G-[3df,2p]) and extensive correlation corrections (up to QCISD(T)), the G2+ method is well suited for accurately characterizing reaction pathways.[4] Application of the G2+ approach to the reaction of F^- with CH_3CH_2F leads to the reaction profile shown in Figure 1.[5,6] It can be seen that the G2+ structures (MP2/6-31+G(d,p) optimizations) are in sharp contrast to those found by Bickelhaupt *et al.* (Xα/DZP optimizations).[2] In the ion−dipole complex, we find a long F−H distance (~2 Å) and only a slight elongation of the C_β−H bond (<1%) whereas the DFT approach predicts that the H−F bond (1.2 Å) is nearly formed and that there is a 25% elongation of the C_β−H bond. In the E2(anti) transition state, BBNZ found a long C_β−H distance and an interaction between the HF fragment and the α-carbon; however, no such interaction was found in the G2+ study. Surprisingly, the geometric differences in the E2(syn) transition state are more modest. In terms of energies, the DFT method underestimates the stability of the complex by 5.9 kcal/mol relative to the G2+ value. More importantly, it underestimates the E2 barriers (with respect to the reactants) by 6.3 (anti) and 4.7 (syn) kcal/mol. In fact, BBNZ predict that relative to the complex, there is almost no barrier (1.2 kcal/mol) to the E2(anti) reaction.

The differences between the G2+ and DFT results can easily be explained. In their optimizations, BBNZ grossly underestimated the stability of fluoride because they used a very modest level of theory (Xα)[7] and did not include functions to describe the diffuse character of F^-. Clear evidence of this inadequacy is found in the fact that the Xα/DZP calculations overestimate the stability of FHF^- (relative to HF + F^-) by ~36 kcal/mol and predict that the ion−dipole complex is 44 kcal/mol more stable than the reactants—an unrealistically large complexation energy.[8] At their level of theory, F^- appears to be exceptionally basic (PA = ~419 kcal/mol)[9] and therefore forms a complex where the β-proton is almost equally shared by carbon and fluorine. This effect also leads to a very late transition state for the E2(anti) elimination and hence the unconventional geometry—the elimination is already complete at the transition state. Because BBNZ used these poorly optimized geometries for their higher-level calculations, significant errors resulted. In going from Xα/DZP to their highest level (LDA/NL/TZPP), the relative energies of the complex and E2(anti) and E2-(syn) transition states vary by 33, 11, and 29 kcal/mol, respectively. These large changes suggest that the optimization level provides a poor description of the system. In contrast, the G2+ energies vary by 2.3, 1.8, and 2.1 kcal/mol, respectively, from the optimization level (MP2/6-31+G(d,p)). *When single-point energies differ significantly from those found at the optimization level, one must question the validity of the optimized geometries.* We do not question the DFT approach, but are the current methods capable of describing base-induced eliminations?

In order to address the above question, a series of DFT calculations were carried out in which the basis set and density functional were varied with a basis set (6-31G-(d,p))[10] comparable to the one employed by Bickelhaupt *et al.*, the Xα,[7] Becke88,[11] and Becke88-VWN(V)[12] func-

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[1] (a) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 652. (b) Gronert, S. *J. Am. Chem. Soc.* **1992**, *114*, 2349. (c) Gronert, S. *J. Am. Chem. Soc.* **1991**, *113*, 6041. (d) Minato, T.; Yamabe, S. *J. Am. Chem. Soc.* **1988**, *110*, 4586. (e) Minato, T.; Yamabe, S. *J. Am. Chem. Soc.* **1985**, *107*, 4621. (f) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 187. (g) Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845.

[2] Bickelhaupt, F. M.; Baerends, E. J.; Nibbering, N. M. M.; Ziegler, T. *J. Am. Chem. Soc.* **1993**, *115*, 9160.

[3] For F^- + ethyl fluoride, the reaction to give $CH_2{=}CH_2$, HF, and F^- is endothermic by 10.4 kcal/mol. For experimental data, see: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. The slightly updated form is available on a personal computer, *NIST Negative Ion Energetics Database* (Version 3.00, 1993), NIST Standard Reference Database 19B.

[4] Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

[5] It may be improper to refer to the energies of transition states as G2+ since the application of the high level correction might be inappropriate; the barriers, however, still correspond approximately to QCISD(T)/6-311+G(3df,2p) energies. In addition, the counterpoise approach used in the original study of F^- (ref 4) was omitted in this work to maintain consistency with the DFT calculations.

[6] All of the reported calculations, unless otherwise noted, were carried out using Gaussian 92, Revision G.2: Frisch M. J.; Trucks G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B. ; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1993.

[7] Slater, J. C. *The Self-Consistent Field for Molecules and Solids* (*Quantum Theory of Molecules and Solids*); McGraw-Hill: New York, 1974; Vol. 4.

[8] For example, see: Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1984**, *23*, 2029.

[9] The proton affinity of fluoride is 421.5 and 417.2 kcal/mol at the Xα/6-31G(d,p) and Xα/cc-pVDZ levels, respectively. These basis sets are very similar to the one employed by Bickelhaupt et al.

[10] (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[11] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

0022-3263/95/1960-0488$09.00/0

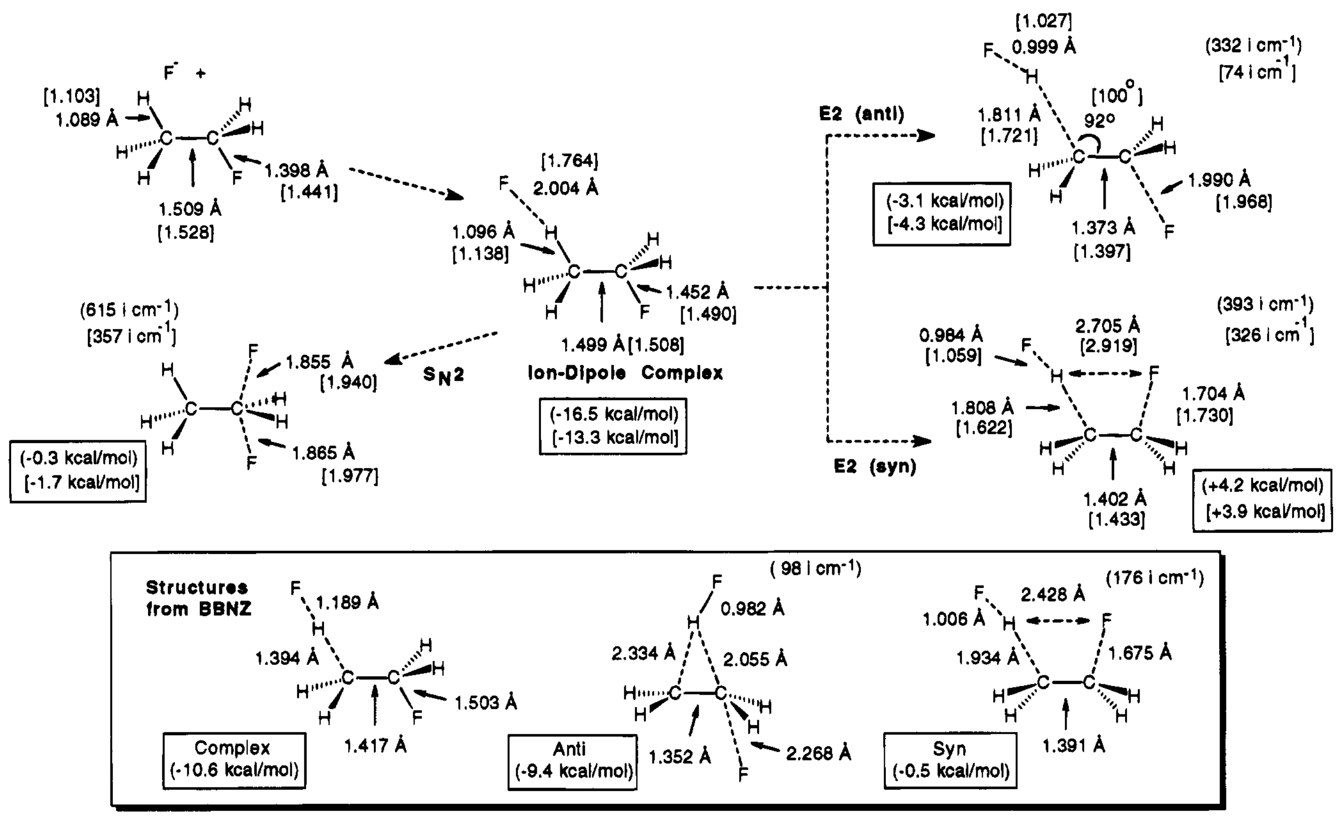

Figure 1. Reaction profile for F⁻ + ethyl fluoride at the G2+ and Becke88-VWN(V) levels. X(α) results from BBNZ; see ref 2. Values in square brackets correspond to the Becke88-VWN(V) results.

tionals were used to calculate the proton affinity (PA) of F^- (421.5, 426.8, and 426.6 kcal/mol, respectively) and the hydrogen-bond strength of FHF^- (77.9, 64.8, and 65.3 kcal/mol, respectively).[13,14] Addition of diffuse functions to the basis set, i.e., 6-31+G(d,p), leads to substantially improved values for the PA(F^-) (364.1, 366.4, and 372.4 kcal/mol) and the FHF^- binding energy (55.2, 40.7, and 43.5 kcal/mol) using Xα, Becke88, and Becke88-VWN(V), respectively. From this data it is apparent that diffuse functions (at least upon heavy atoms) are essential and a nonlocal correction to the exchange functional is needed.

On the basis of this conclusion, the reaction of F^- + CH_3CH_2F was reinvestigated at the Becke88-VWN(V)/aug-cc-pVDZ level of theory.[15] The optimized structures are given in Figure 1 and are similar to the MP2/6-31+G(d,p) *ab initio* results. The only appreciable differences are that the current-DFT elimination transition structures come a little earlier than the G2+ ones. Energetically, the two methods give the same ordering: E2(anti) < S_N2 < E2(syn) but the DFT activation energies are shifted 0.3 (E2(syn)) to 1.4 (S_N2) kcal/mol below the G2+ results. The energy differences between the TS's, however, are all reproduced to within <1 kcal/mol.

The basis set which was used to draw conclusions about several different functionals and the need for diffuse functions is not the same one that was employed for the F^- + CH_3CH_2F system. This is because we were unable to locate an E2(anti) TS using a split-valence basis set (6-31G(d,p) and 6-31+G(d,p)) despite numerous attempts. Moreover, a map of the PES obtained by fixing the C_β–H bond distance and optimizing the rest of the structure shows no indication of an energy maximum (i.e., saddle point). Only when a more complete basis set with diffuse functions (aug-cc-pVDZ) was employed could a TS be located, and it is a loose transition state with a small imaginary frequency (i = 74 cm^{-1}). This basis set sensitivity is troubling despite the fact that DFT is capable of reproducing results from high-level *ab initio* calculations and calls into question the former method's ability to elucidate complex reaction pathways.

In summary, S_N2 substitution or E2(anti) elimination are viable pathways but the latter should dominate because the barrier is smaller and the pathway is less entropically demanding. This is consistent with the experimental results of Ridge and Beauchamp on the F^- + CH_3CH_2F system.[16]

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Supplementary Material Available: Lists of total energies and geometrical parameters for the reactants and transition states (4 pages).

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(12) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(13) The proton and hydrogen fluoride affinities of F⁻ are 371.3 ± 2.1 and 45.8 ± 1.6 kcal/mol (for experimental data see ref 3 and Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.*, in press). The corresponding G2+ values at 298 K are 371.0 and 44.1 kcal/mol, respectively (373.0 and 46.1 kcal/mol without counterpoise, see ref 5).

(14) Gradient corrected functionals (LYP and P86) were also examined and were found to be less accurate than the local correlation functionals.

(15) For details about the aug-cc-pVDZ basis set see: Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. S. *J. Chem. Phys.* **1992**, *96*, 6796.

(16) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595.