Condensed Phase Effects on the Structural Properties of Freidel-Craft Intermediates: RF′—BF_3

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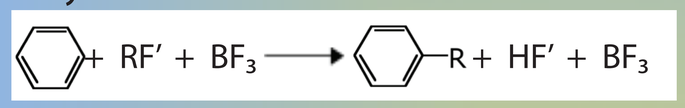
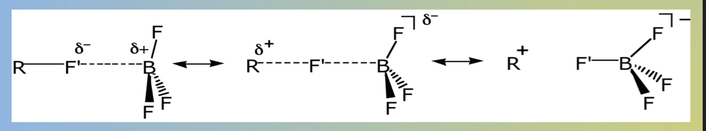
Context

Ackylation of Benzene:

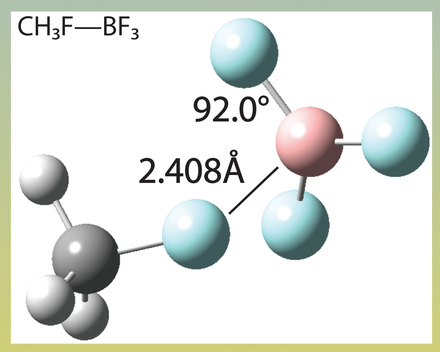


Intermediates:

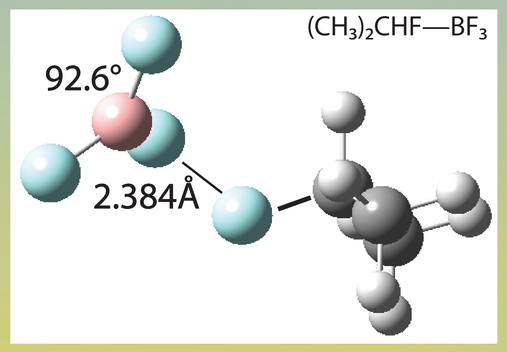


• We want to assess the role of solvent effects on the structures of these intermediates in the context of the overall reaction mechanism.

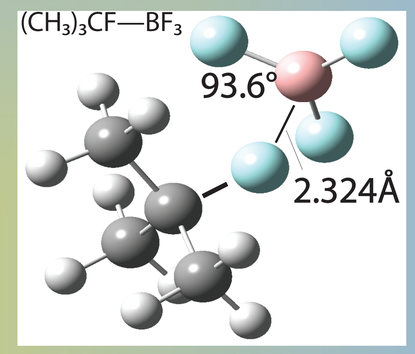
Structures (X3LYP/aug-cc-pVTZ) and Binding Energies (MP2/aug-cc-pVTZ)



ΔE = -5.4 kcal/mol



ΔE = -6.5 kcal/mol

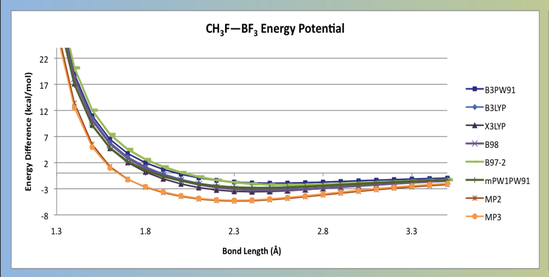


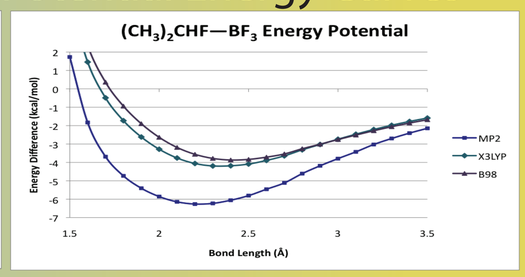
ΔE = -6.7 kcal/mol

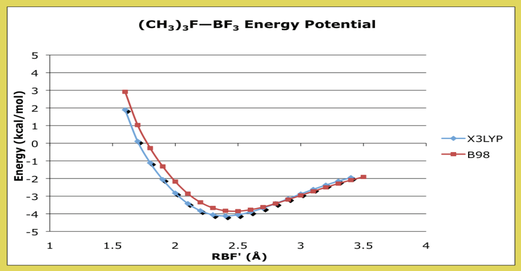
• B—F bonds are long (Colvalent radii are 1.46Å[1])
• The B—F bond compresses slightly with larger R groups.

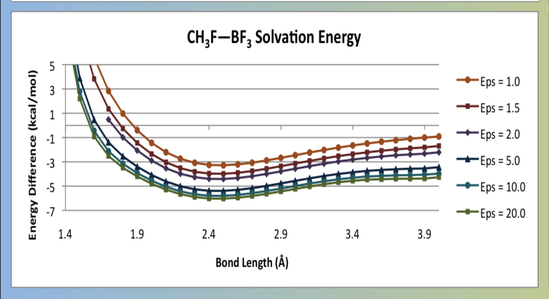
• Low binding energies indicate weak bonds.
• But $(CH_3)_3CF—BF_3$ and $(CH_3)_2CHF—BF_3$ complexes are ionic (R^+ and BF_4^-) in solution[2].

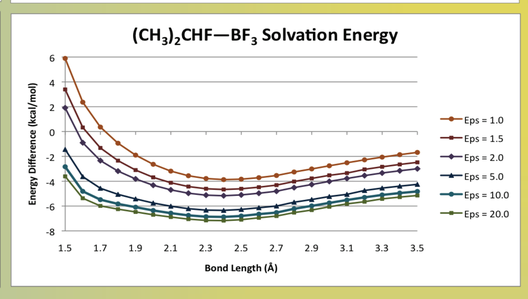
Potential Energy Curves

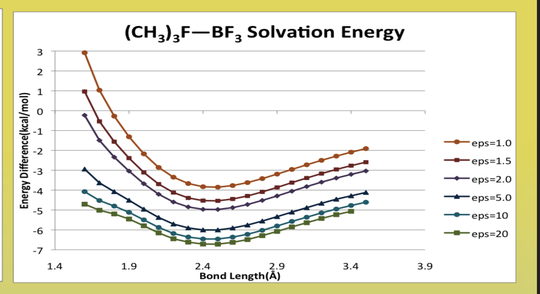








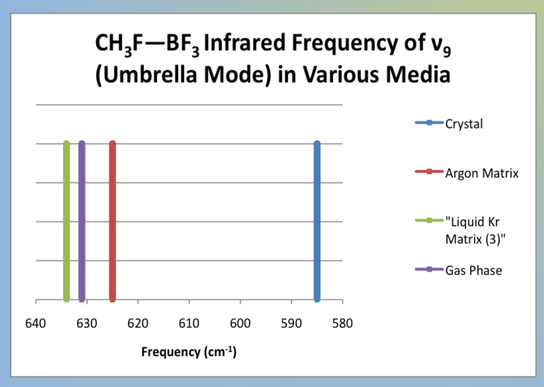


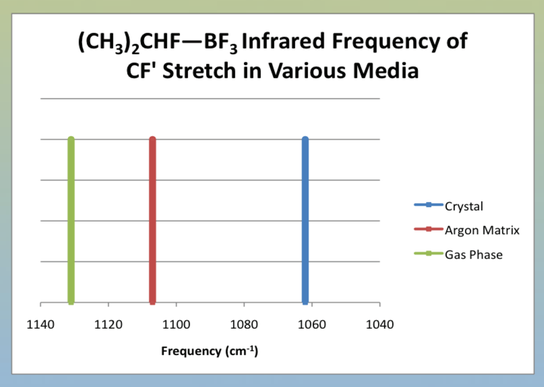


•Little evidence for condensed phase effects in $CH_3F—BF_3$

•Slight evidence for quasi-stable structures at short B—F′ distances for $(CH_3)_2CHF$ and $(CH_3)_3CF$ in dielectric media

Vibrational Frequencies





•For $CH_3F—BF_3$ there is evidence for significant structural change in the solid state, but little or no sturctural effects in inert media

•For $(CH_3)_2CHF—BF_3$ there is evidence for subtle condensed phase effects

Conclusions

· Calculated gas phase structures are clearly weaker than those in solution as implied via conductivity measurements[2].

· Our calculated curves indicate that dielectric media do partially stablilize shorter B—F structures - but are not minima on potential energy curves[2].

· This conflicts with older literature[2].

· The preliminary IR data is more consistent with our theory than the older literature.

Future Work

•Solidify assignments for other peaks in the infrared spectra.

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