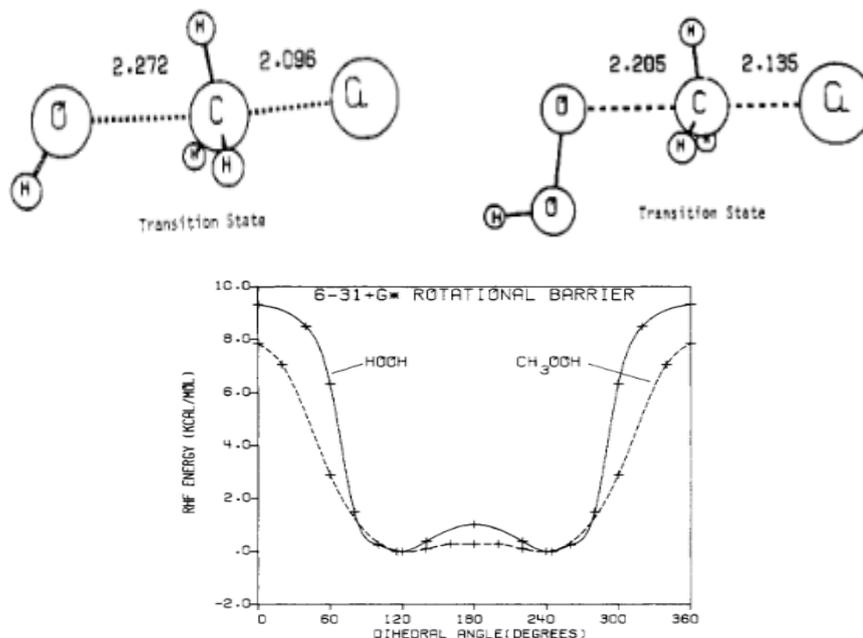
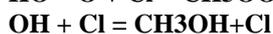


- Extent of stabilization will be proportionate to contribution of diradicaloid character:
- Substrates with high electron affinity (lower LUMO) are more likely to undergo an ET event.
- Explains observation of smaller α -effects in Sn2 reactions relative to addition to unsaturated compounds.
- Large β -values associated with ET reactions.
- Dependence of magnitude of α -effect on β agrees with Hudson's work.

Solvent effects

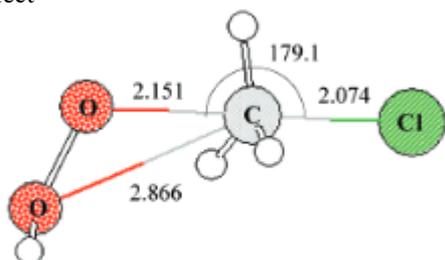
- The magnitude of the α -effect is dependent on β .
- Prior reactions have low selectivity.
- Evident by 20kcal/mol difference in proton affinities.
- It is likely that β approaches 0, so we would expect to observe no α -effect.
- "Determination of β_{nuc} is essential in order to obtain a meaningful conclusion.

Solvent effect – theoretical study



The magnitude of alpha effect

- More electronegative α -atoms lead to larger α -effects (FO- vs ClO-)
- Electron withdrawing groups diminish the alpha effect
- Higher electron density at the α -atom and greater positive charge at the electrophile lead to a greater α -effect



CONCLUSION

Although the α -effect is heavily modulated by solvent, theoretical and experimental results that the α -effect is an intrinsic property and α -nucleophiles. The physical origin of the α -effect is related to similarities in the electronic structure of the products and the transition state. However, the precise origin of these similarities is still inconclusive.

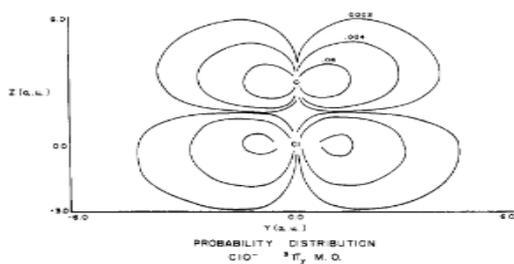


Figure 1.

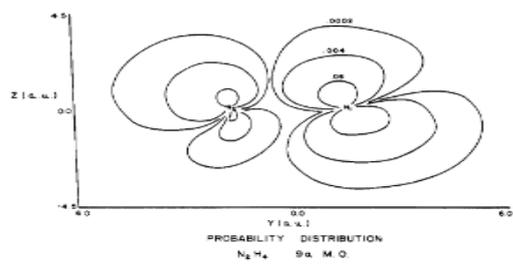


Figure 3.

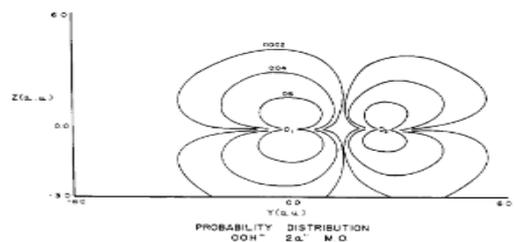


Figure 2.

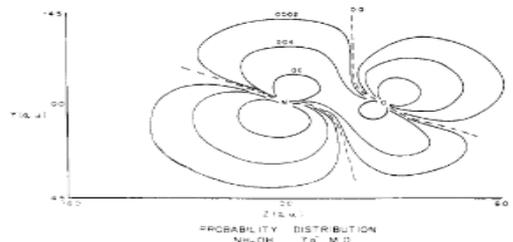


Figure 4.

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