HYDROGEN ABSTRACTION FROM HYDROCARBONS: MODELING OF ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS


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HYDROCARBON RADICAL CHEMISTRY

Accurate reactor simulation

- Kinetic data
- Hydrogen abstraction reactions most common reactions in radical reaction network
- Experimental data: scarce
- Reliability and fast rate prediction required
- Current models for H abstraction limited to certain radicals (H, CH3, ...)
- Develop group additive model based on ab initio kinetics, that is generally applicable

GROUP ADDITIVE METHOD

Benson group
- Central atom C
- Together with all of its ligands X1...X6
- C-D(X1)(X2)(X3)(X4)(X5)(X6)
- Group additivity for kinetics
- Based on Benson group additivity for the ΔH° and ΔS° of the transition state
- Resonance model
- Correction for every type of cross-interaction between resonance and hyperconjugative elements

Example: x-x resonance interaction

CH3 + CH4 → CH2 + CH4

ΔG°(298 K) = -71.9 kJ mol⁻¹

π conjugation

Additional stabilization due to cross-π conjugation

Resonance model

Correction for every type of cross-interaction between resonance and hyperconjugative elements

Example

1. π→π
2. σ→π, σ→π
3. π→σ+π

Model predictions

Ea / kJ mol⁻¹ 52.1 52.4
logA / s⁻¹ 4.551 4.547
k / m³ mol⁻¹ sec⁻¹ 38.8 29.6

CONCLUSIONS

- Significant resonance and hyperconjugative stabilization of the transition state through cross-conjugation interaction
- Temperature-independent ΔG° and corrections
- Accurate rate prediction within factor of 3