Resonance stabilization during the group additive modeling of the kinetics of hydrogen abstraction from hydrocarbons

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1. Introduction

Hydrogen abstraction reactions play an important role in many free-radical processes such as polymerization, combustion, pyrolysis and steam cracking of hydrocarbons. Accurate kinetic modeling of these complex processes requires a detailed reaction network that can contain hundreds of elementary hydrogen abstraction reactions. For every elementary reaction, kinetic parameters are required. The determination of all these kinetic parameters is one of the largest challenges in kinetic modeling. There are however only a limited number of experimentally determined kinetic parameters for hydrogen abstraction available in literature. Also, despite the increasing accuracy and computational performance, ab initio methods are still too demanding to determine accurate kinetic data for all hundreds of hydrogen abstractions in reaction networks, particularly for larger species. Therefore, parameterized methods such as group additivity based methods are often applied to predict the kinetics in large reaction networks.[1,2]

2. Computational procedures

2.1. Ab initio methods

Rate coefficients are calculated according to the methodology described by Vandeputte et al.[3] This ab initio computational approach yields a mean factor of deviation between experimental and calculated rate coefficients of 6 in the temperature range of 300-1000K.[3] Following this procedure rate coefficients are calculated using the transition state theory (TST) in the high pressure limit, with the activation barrier at 0 K determined with the CBS-QB3 complete basis set method of Montgomery et al.[4] All ab initio calculations have been performed using the *Gaussian 03* computational package.[5] Partition functions q are calculated using statistical thermodynamics based on a B3LYP/6-311G(2d,d,p) frequency calculation using a default scale factor of 0.99. The partition functions are evaluated using the rigid rotor and harmonic oscillator approximation assuming separability of translational, rotational, rovibrational and electronic contributions.

The influence of most of the internal rotations upon the rate coefficient is limited, as the contributions of internal rotations present in both the reactants and the transition state largely cancel out in the rate equation. For all reactions, internal rotation about the axis formed by the breaking and forming C−H−C bond in the transition state was treated as a 1D-hindered rotation (HR) using the methodology described by Van Speybroeck et al.[6-9]   The potential energy profiles for internal rotation were
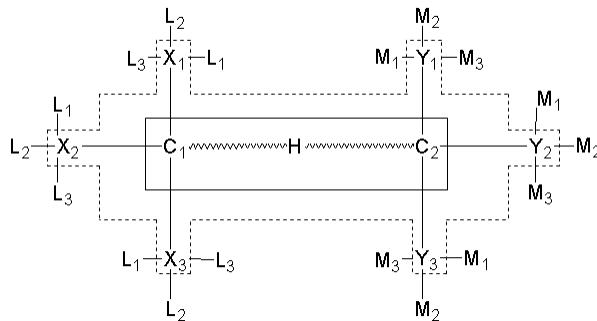
Figure 1: Schematic representation of a H abstraction transition state. The full line indicates the central atoms of the primary contributions of Eqs. 2 and 3. The dotted line indicates which groups will contribute to the reaction kinetics if non-nearest-neighbor effects are neglected.

determined using a relaxed scan at the B3LYP/6-31G(d) level to which a third-order Fourier series is fitted.

Zero curvature tunneling coefficients $\kappa(T)$ were calculated using the Eckart tunneling[10] scheme. All rate calculations were performed using in-house developed programs.

2.2. Group additivity

In the group additive model, the rate coefficient is expressed as

$$k = \kappa n_e k_{\mathrm{GA}} = \kappa n_e \tilde{A} \exp(-\frac{E_a}{RT}) \tag{1}$$

with κ the tunneling coefficient, n_e the number of single events, $\tilde{A}$ the single-event pre-exponential factor and E_a the activation energy. The Arrhenius parameters can be modeled using the group additivity method as described in detail in previous work:[11,12]

$$E_a(T) = E_{a,\mathrm{ref}}(T) + \sum_{i=1}^{2} \Delta GAV_{E_a}^{o}(C_i) + \Delta E_{\mathrm{Ea,resonance}}^{o} \tag{2}$$

$$\log \tilde{A}(T) = \log \tilde{A}_{\mathrm{ref}}(T) + \sum_{i=1}^{2} \Delta GAV_{\log \tilde{A}}^{o}(C_i) + \Delta \log \tilde{A}_{\mathrm{resonance}} \tag{3}$$

with $E_{a,ref}$ and $\log A_{\mathrm{ref}}$ the activation energy and pre-exponential factor of the reference reaction, i.e., the H abstraction by methyl from methane for this reaction family. The group additive values ΔGAV° express the contributions from the Benson groups in the reactive moiety relative to the reference reaction (see Figure 1). The formulation with respect to a reference reaction yields the group additive values temperature-independent. The resonance corrections account for resonance and hyperconjugative effects in the transition state of hydrogen transfer reactions between allylic, propargylic and alkylic hydrocarbons.

3. Results

Group additive values for 50 groups are derived from rate coefficients determined using the high level CBS-QB3 ab initio method, corrected for tunnelling and the hindered internal rotation around the transitional bond.

Cross-resonance and hyperconjugative effects between the reactive fragments, caused by redistribution of the spin density (e.g. Figure 2) stabilize the transition state relative to the group additive prediction. The presence of cross-resonance and hyperconjugative stabilization of the transition state is accounted for by introducing 4
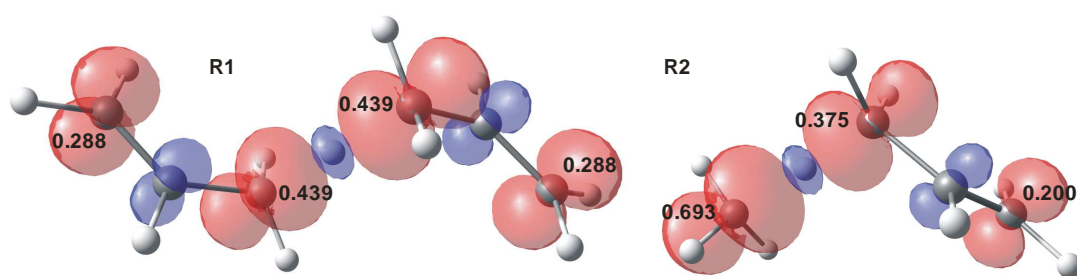
Figure 2: Spin density plots illustrating the resonance stabilization of the transition state for reactions of allylic radicals, with indication of the most important Mulliken atomic spin densities. (R1: allyl+propene, R2:allyl+methane, B3LYP/6-311G(d,p), 0.006 isosurfaces).

corrections based on the transition state topology. The corrections, determined on a set of 28 reactions, are temperature independent and reduce the mean absolute deviation to 0.7 kJ mol^{-1} on E_a and to 0.04 for log$A$.

Final validation for 16 reactions yields a mean factor of deviation between group additive prediction and ab initio calculation of 2.4 at 300 K, and 1.8 at 1000 K. In a comparison with 6 experimental rate coefficients (600-719 K), the mean factor of deviation is less than 3.

4. Conclusion

The group additive model described in this work allows an accurate prediction of rate coefficients for bimolecular hydrogen abstraction reactions for a broad range of hydrocarbons and hydrocarbon radicals in the temperature range 300-1300 K.

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