

Assessing the molecular basis of the fuel octane scale: A detailed investigation on the rate controlling steps of the autoignition of heptane and isooctane

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Abstract: N-heptane and isooctane are the primary reference fuels and key species in the modelling of ignition of hydrocarbon based fuel formulations. The octane rating scale is defined as the fraction of isooctane in a mixture of isooctane and n-heptane. It is employed to access the quality of different fuels used in spark-ignition engines. Isooctane is knock-resistant while n-heptane is a very knock-prone hydrocarbon. In the low-temperature mechanism of autoignition, the parent alkane molecule is converted to an alkyl radical, which can subsequently react with O₂ forming an alkylperoxy (ROO•) intermediate. The ROO• can internally transfer a hydrogen atom to form a hydroalkylperoxy (•QOOH) or decompose directly to an olefin and HO₂. [1] The •QOOH species are directly related to chain-branching in the low-temperature autoignition chemistry. It has been suggested that interconversion of alkylperoxy and hydroalkylperoxy species via hydrogen-transfer isomerization reaction is the key step to understand the different knocking behavior of alkanes. [2] In this work, the kinetics of unimolecular hydrogen-transfer and HO₂ elimination reactions of n-heptylperoxy and isooctylperoxy are determined using canonical variational transition state theory (CVT) and multidimensional small curvature tunneling (SCT). [3] The rate coefficients are calculated in the temperature range 300–900K, relevant to low-temperature autoignition. The relations between the rate constants and tunneling corrections to the geometrical parameters of the species involved are discussed. The concerted HO₂ elimination is an important reaction that competes with some H-transfer and is associated with chain termination, since the lowly reactive HO₂ radical is formed. The branching ratio between elimination and isomerization channels constitutes an important parameter to understand the knock propensity. Variational and multidimensional tunneling effects on the reaction coordinate cannot be neglected for the H-transfer reaction. In particular, in the small curvature approximation the ‘corner cutting’ effect may considerably enhance the reaction rate. The SCT and ZCT (zero curvature tunneling) transmission coefficients are compared to the Wigner and Eckart models. For the HO₂ elimination, we show that it is the endothermicity of the reaction and not the higher mass that is responsible for its low tunneling probability. Internal rotations of reactants and saddle points are taken explicitly into account in the molecular partition function.[4] At the transition state of the H-transfer isomerization reaction, several internal rotations of the reactant are hindered. Thus, the entropy of activation and hence the rate constant are strongly affected by changes in the vibrational partition



XIX SBQT

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function. In particular, the constraints of alkyl rotations are found to be particularly effective in decreasing reactant entropy. The segmented reference Pitzer-Gwin method (SRPG) [5] is used to calculate the hindered rotor partition functions. A recently proposed generalized Arrhenius function is used to study the temperature dependence of the rate constants. [6] The activation energy calculated using this model function has the correct asymptotic behavior at absolute zero. In addition, this model is found to yield a lower fitting error as compared to the widely used model: $k = AT^n \exp(-E/RT)$. The H-transfer pre-exponential and activation energy vary strongly with temperature. This is a direct consequence of the increase tunneling transmission at temperatures below 500 K. Based on our results, a consistent model for the reasons for different knock behavior observed for n-heptane and isooctane is proposed.[7]

Key-words: Octane Rating, Autoignition, Transition-State Theory, Peroxy-radicals, Tunneling, conformation analysis, unimolecular reactions

Support: CENPES-Petrobrás

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