

The Rate-Limiting Step for Alkane Dehydrogenation in Zeolite H-ZSM-5

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Introduction: We have carried out a computational study of protolytic cracking, dehydrogenation, and H/D exchange of ethane, propane, and butane using a cluster model of H-ZSM-5. Our previous work has demonstrated that quantum-chemical techniques can give quantitatively accurate activation energies for alkane cracking in zeolites [1]. Experimental kinetic studies have shown that the apparent activation energies for cracking and H/D exchange *decrease* with n-alkane chain length, while for dehydrogenation the energies *increase* [2,3]. Our goal is to study the dependence of the activation energy on the alkane chain length in these reactions and to understand why the dehydrogenation reaction behaves so differently.

Theoretical Methods: We optimized the geometries of each structure using the HF/6-31G(d) method and the B3LYP/6-31G(d) level of density functional theory. Our transition state structures have only one imaginary vibrational frequency, corresponding to the reaction coordinate. Our cluster model for the zeolite framework, denoted 5T, has five tetrahedral atoms and is terminated by H atoms at its periphery. To determine the activation barriers, we calculated corrections for (i) scaled zero-point energies and thermal corrections for the experimental reaction temperature of 773 K; (ii) an extended basis set, calculated at the B3LYP/6-311+G(3df,2p) level; and (iii) the long-range electrostatic effects of the zeolite framework. The electrostatic correction was determined by performing a partial optimization of each transition state in a much larger zeolite cluster model constructed from the experimental geometry of H-ZSM-5.

Results and Discussion: A schematic potential energy surface for protolytic dehydrogenation of propane is shown in Fig. 1. Starting from an adsorbed complex ($ZOH \cdots C_3H_8$), the acidic proton attacks a terminal C-H bond. Via an ionic transition state ($ZO^- \cdots C_3H_9^+$) this forms H_2 and a surface-bound propoxy species (ZOC_3H_7). In order to close the catalytic cycle, a proton is abstracted from the propoxy species by a nearby framework oxygen atom. This proceeds through another transition state ($ZO^- \cdots H^+ \cdots C_3H_6$) to form a new Bronsted acid site with an adsorbed propene molecule ($ZOH \cdots C_3H_6$). The final step is propene desorption. Previous experimental and computational studies suggest that the rate-limiting step for protolytic cracking of n-alkanes by acidic zeolites is the initial protonation of the adsorbed alkane molecule. Narbeshuber et al. [2] concurred but provided evidence from kinetic isotope effect studies that the initial protonation is *not* the rate-limiting step for dehydrogenation of alkanes. Instead, they suggested that the desorption of the product alkene is rate-limiting, and that this might explain the observed *increase* of activation energy with alkane chain length.

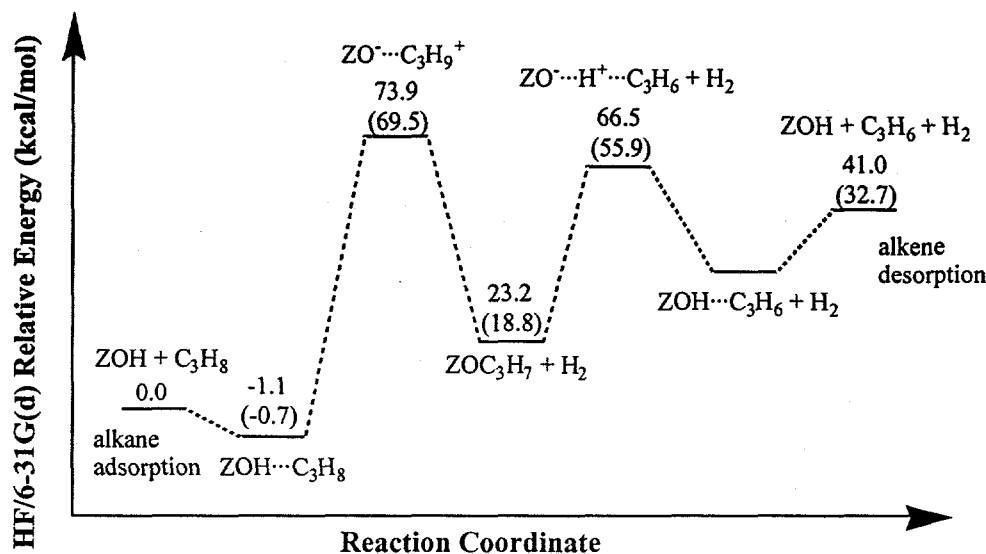


Fig. 1. Schematic potential energy surface for dehydrogenation of propane. Energies in parentheses include zero-point corrections.

However, this proposed explanation does not agree with available thermochemical data for the relative stability of *n*-alkanes (i.e., C₃H₈) with respect to their corresponding dehydrogenation products (C₃H₆ + H₂). If the desorption of the product alkene were rate-limiting, the apparent barrier for dehydrogenation would simply be the enthalpy difference between the alkane and its corresponding alkene + H₂. To explain the observed *increase* of activation energy with alkane chain length, this enthalpy difference would be expected to increase as chain length increases. However, experimental thermochemical data indicate that this enthalpy difference is very nearly constant, having a value of about 30 kcal/mol for propane. This fact is very difficult to reconcile with the apparent barriers of 23 and 16 kcal/mol measured by Narbeshuber et al. for propane dehydrogenation in H-ZSM-5 and H-Y zeolites, respectively [2].

Our preliminary results indicate that the apparent barriers for both cracking and dehydrogenation reactions *decrease* as the alkane chain length increases, and that the initial protonation step in both reactions is rate-limiting. Possible reasons for this discrepancy between computational and experimental results will be discussed.

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