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# Carbonium ion formation in zeolite catalysis

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Based on data of *n*-butane conversion over HZSM5, different transition states are proposed for the Brønsted acid catalyzed reactions of alkanes involving carbonium ions as intermediates. Hydrogen–deuterium exchange, dehydrogenation and cracking are proposed to proceed via pentacoordinated carbonium ions that are stabilized by the zeolite lattice.

**Keywords:** *n*-alkane conversion; carbonium ions; cracking; dehydrogenation; alkane

## 1. Introduction

Currently, there is significant increase in the understanding of the reaction mechanisms of *n*-alkane conversions over zeolites. One of the reasons for this is the availability of well defined and well characterized zeolites and the knowledge of how to control the reaction mechanism by adjusting the reaction conditions [1]. Secondly, quantum chemical studies provide us with increasingly refined means to understand these reactions on a molecular level [2].

The two major mechanistic routes proposed for alkane conversions over acidic zeolites involve activation of the molecules by (i) hydride abstraction from the reacting alkane by the adsorbed carbenium ion (bimolecular reaction route) [3] and (ii) addition of a proton to the alkane (monomolecular reaction route [4]), respec-

tively. Carbenium ions are the intermediates for the bimolecular reaction route [3], while pentacoordinated carbocations (carbonium ions) are the commonly accepted intermediates for monomolecular conversions of alkanes [4,5].

In this short communication, we address the nature and stability of carbonium ions involved in the acid catalyzed monomolecular reactions of alkanes that can be postulated as intermediates. The reactions of *n*-butane over HZSM5 will be used to exemplify the variations in the transition states for the different reaction channels of light alkanes. Experimental data and computational results will serve to formulate the different transition state structures and their implications on the reaction mechanisms.

## 2. Results

Only those experimental data that are relevant for the formulation of the reaction mechanisms outlined below are highlighted. A detailed description of the reactions of light alkanes is given in ref. [6].

*n*-butane conversion over HZSM5 (Si/Al 35, provided by Mobil) was studied under reaction conditions which exclude all bimolecular reactions, i.e., at conversions below 5%, temperatures between 735 and 825 K and a typical *n*-butane partial pressure of 20 mbar. Three types of monomolecular reactions were observed: cracking, dehydrogenation and hydrogen/deuterium exchange between deuterated *n*-butane and the hydroxyl groups of the zeolite. All three reactions were found to be of perfect first order with respect to the partial pressure of *n*-butane (and also linearly dependent upon the concentration of the acid sites in the zeolite). The apparent rate constants and the apparent energies of activation for the three pathways are compiled in table 1. The apparent energies of activation decrease in the order of 140, 105 and 85 kJ mol<sup>-1</sup> for cracking, dehydrogenation and H/D exchange, respectively. Because the heat of adsorption of *n*-butane on HZSM5 was found to be approximately 60 kJ mol<sup>-1</sup>, the true energies of activation with respect to the adsorbed state would be 60 kJ mol<sup>-1</sup> higher (for details see ref. [6]). By protolytic cracking, equimolar amounts of methane and propene (55% selectivity) as well as of ethane and ethene (45% selectivity) were formed. The selectivity did not depend upon the temperature. The overall selectivity to cracked products was 64% at 773 K.

Table 1

Apparent first order rate constant of *n*-butane conversion (rate normalized to the catalyst weight and the partial pressure) and apparent energies of activation for H/D exchange, dehydrogenation and cracking over HZSM5 at 773 K

	H/D exchange	Dehydrogenation	Cracking
$k$ (mol/s g mbar)	$1.7 \times 10^{-7}$	$4.8 \times 10^{-9}$	$1.1 \times 10^{-8}$
$E_{\text{App}}$ (kJ/mol)	85	105	140

### 3. Discussion

#### 3.1. CURRENT MECHANISTIC CONCEPTS ON PROTONATION

The first theoretical study of the protonation of an olefin by Kazanskii et al. [7] demonstrated that ethene can be adsorbed at the SiOHAl site as hydrogen bonded ethene ( $\pi$ -bonding) and as  $\sigma$ -bonded ethyl group. The conversion from the  $\pi$ -bonded to the  $\sigma$ -bonded state proceeds via a geometric rearrangement such that the charge separation between the organic complex and the zeolite is compensated by a short distance between the positively charged carbon atom of the methylcarbonium ion ( $\text{CH}_3\text{CH}_2^+$ ) and the negatively charged oxygen atom of the zeolite lattice. The  $\sigma$ -bonded ethyl group can be considered as a stabilized carbenium ion intermediate.

The activation of alkanes has been shown to proceed via pentacoordinated carbocations, i.e., carbonium ions. Recently, the formation of carbonium ions has also been experimentally studied for the activation of methane [8]. The work addressed the proton/deuterium exchange between deuterated methane and the strongly acidic hydroxyl groups of the zeolite. A high activation energy was found and the geometry of the transition state of the reaction was close to that for the pentacoordinated carbonium ions proposed by Haag and others [4,5]. The calculations indicate that the carbonium ion is a transition state stabilized by nearly covalent interactions of two of its protons with two negatively charged oxygens in the vicinity of the aluminum atom. The reaction coordinate can be identified from a vibrational frequency analysis and, at the maximum energy, corresponds to the imaginary frequency of one of the eigen modes of the transition state.

The transition states for ethene and methane protonation have in common that the energy for the charge separation is provided by compensating interactions between the evolving positive charge on the substrate atom involved in the reaction and a negatively charged oxygen atom of the zeolite around the site of sorption. We will use this principle (with *n*-butane conversion as example) to discuss and propose different transition states for three *n*-alkane reactions having carbonium ion intermediates.

#### 3.2. MODELS OF POSSIBLE TRANSITION STATES

Because all reactions discussed here are concluded to be catalyzed primarily by the strongly acidic SiOHAl groups of HZSM5, the observation of three different energies of activation for H/D exchange, dehydrogenation and cracking requires the existence of three different transition states. We start with proposing the analog to the transition of hydrogen/deuterium exchange of methane [8] for the hydrogen–deuterium exchange of *n*-butane (see fig. 1a). In this transition state, two hydrogens bonded to the pentacoordinated carbon atom have a coordination with two oxygen atoms around the tetrahedrally coordinated aluminum of the zeolite

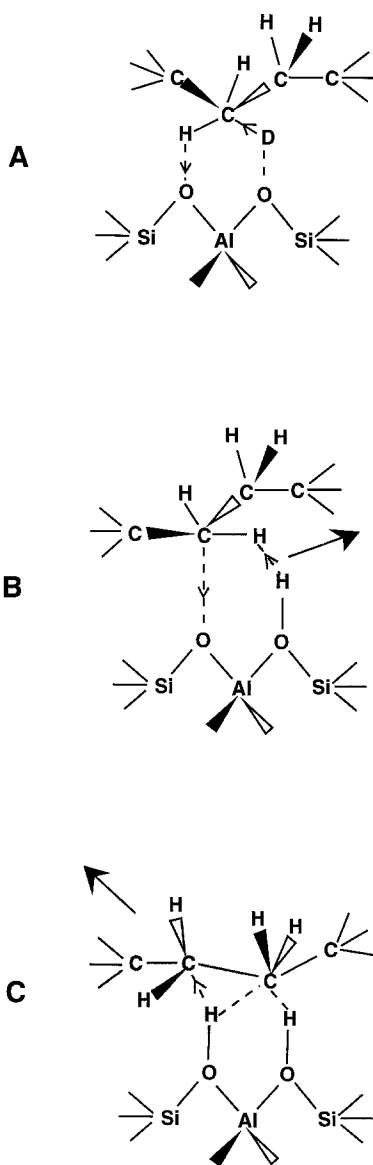


Fig. 1. Schematic representation of the proposed transition states for (A) H/D exchange, (B) butane dehydrogenation (note that the CH bond stretches and H<sub>2</sub> and a  $\sigma$ -bonded carbenium ion are generated) and (C) cracking (note that the carbon-carbon bond stretches, ethane and a  $\sigma$ -bonded carbenium ion are generated). The arrows indicate the atomic motion.

lattice. One expects the protonation of the secondary carbon atoms in *n*-butane to be more favorable than protonation of the primary. Therefore, also the corresponding activation energy for protonation of *n*-butane should be lower than that for methane. Of the two different structures of carbon pentacoordinated intermedi-

ates conceivable (i.e., protonation of the butane molecule end on or protonation of the butane molecule on a secondary carbon atom) the latter seems, thus, to be more plausible at present.

The transition state for dehydrogenation is schematically illustrated in fig. 1b. It requires a CH bond to be stretched, the corresponding hydrogen atom to react with the zeolite hydroxyl group to form a hydrogen molecule and the positive charge on the nascent carbenium ion to be compensated by the short distance to the negatively charged lattice oxygen. For the methyl group this bond was characterized to be rather covalent [9]. Preliminary results of MNDO calculations [10] suggest that the transition state depicted in fig. 1a has a higher energy of activation than that depicted in fig. 1b. Again, the activation of the hydrogen atom attached to the primary or the secondary carbon atom is possible. In view of the 25 kcal mol<sup>-1</sup> difference in energy between the secondary and primary carbenium ions [11] formed by hydrogen abstraction, the activation of the hydrogen atom attached to the secondary carbon atom is expected to be preferred.

The proposed transition state for cracking is depicted in fig. 1c. In this case, protonation is expected to occur at the C–C bond yielding a shorter alkane and in sequence a lattice stabilized carbenium ion [12]. From *n*-butane, only primary carbenium ions will be formed in the cracking reaction. Hence, one expects the activation energy to be higher than that for dehydrogenation, where secondary carbenium ions can be formed. The equal energies of activation [6] found for the production of the different hydrocarbon fragments are in line with a transition state of a geometry that is close to that of the product state (i.e., the  $\sigma$ -bonded carbenium ion). Note that this is supported by the known absence of significant differences of stabilizing effects between methyl and ethyl groups on the primary carbenium ions [11].

The experimental data would also allow for a reaction model assuming the carbonium ion to exist as a stabilized intermediate rather than only in the transition state. This may become more of a possibility for larger hydrocarbons and hydrocarbons that contain tertiary carbon atoms. It should be emphasized that the difference between the reaction models would lie in the (somewhat) higher stabilization of the carbonium ion along the reaction coordinate in which then all computed frequencies would become real (see ref. [8]). The minimum values of the energies of activation for carbonium ion formation (assumed they were stable intermediates) are of the order of 145 kJ/mol for *n*-butane, i.e., the value of the sum of the apparent energy of activation for the H/D exchange and the negative heat of adsorption of *n*-butane. Nevertheless, the energy difference between the hydrogen bonded ground state and the hydrogen bonded carbonium ion would be substantially positive resulting in a very small equilibrium concentration of the carbocations.

Carbonium ions formed in the reaction of a proton with alkanes have been identified by mass spectrometry [13]. The major difference between carbonium ion formation in the gas phase and the formation of carbonium ions in zeolites is the need to generate protons by bond breaking of the zeolitic hydroxyl groups. The

energies involved in the heterolytic breaking of the OH bond of SiOHAl groups are typically in the order of 1300 kJ/mol [14,15]. A large fraction of this energy is provided by the formation of the carbonium ion and its hydrogen bonding to the zeolite lattice. The coexistence of the hydrogen bonded hydrocarbon in its ground state and the hydrogen bonded carbonium ion will depend upon the energy difference between these two forms and the shape of the OH...C and O...HC potential wells. The theoretical calculations available (e.g., ref. [8]) suggest that the strong interactions between the hydrocarbons and the zeolite walls (at the SiOHAl site) and the close distance between the *n*-alkane carbon atom and the zeolite oxygens do not allow for the stabilization of the carbonium ions. Hence at present, the carbonium ion in zeolites has to be viewed as transition state rather than a stable high energy intermediate.

## Acknowledgement

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