

Research Note

Entropy considerations in monomolecular cracking of alkanes on acidic zeolites

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Abstract

Compensation between adsorption entropies and enthalpies results in less than a two-fold variation in adsorption equilibrium constants for C₃–C₆ alkanes at temperatures relevant for monomolecular cracking; the size-independent activation energy for C–C bond activation in C₃–C₆ alkanes indicates that the marked increase in monomolecular cracking turnover rates observed with alkane chain size reflects a concurrent increase in activation entropies. Thermodynamic treatments for non-ideal systems rigorously describe confinement effects within zeolite channels and show that pre-exponential factors depend on solvation effects of the zeolite-host environment through variations in the thermodynamic activity of the zeolitic proton. Observed differences in rates and selectivities of monomolecular alkane activation with zeolite structure, after normalization to intrazeolitic concentrations, reflect differences in intrinsic rate constants.

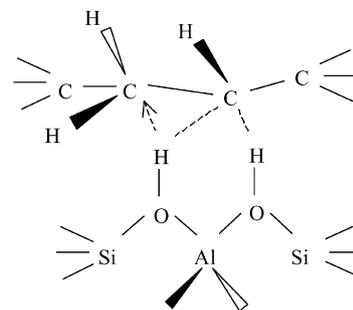
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Keywords: Entropy; Enthalpy; Compensation effect; Confinement effects; Intrazeolitic concentration; Monomolecular alkane activation

1. Results and discussion

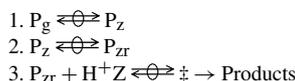
Monomolecular cracking of alkanes via the Haag–Dessau mechanism prevalent at high temperature and low conversions (<1%) is purported to occur via cationic transition states with three-center/two-electron bonds that include both carbon atoms in the C–C bond being cleaved and a proton acting as a Brønsted acid (Scheme 1; Ref. [3]) [1–4]. In cracking of *n*-alkanes, Haag et al. [5], Narbeshuber et al. [6], Kotrel et al. [2], Babbitz et al. [7], and Ramachandran et al. [8] attributed differences in turnover rates (per H⁺) among acidic zeolites with different structures and among alkanes of varying size to differences in the prevalent concentration of physisorbed alkanes within zeolite channels. These authors concluded that no residual effects of Brønsted acid strength or of zeolite topology were required to account for variations in cracking rates with alkane size or zeolite structure.

We comment here about how a ubiquitous compensation between alkane adsorption enthalpies (ΔH_{ads}) and entropies (ΔS_{ads}) leads to differences in adsorption constants that cannot possibly account for the strong effects of alkane size and zeolite structure on monomolecular cracking turnover rates at typical reaction conditions (773 K, 0.1–10 kPa alkane). We propose instead that intrinsic cracking rate constants vary with zeolite topology and carbon number. In the specific case when C–C bond activation barriers do not change with carbon number, the



Scheme 1. Monomolecular cracking of alkanes on H⁺ sites in zeolites proposed based on computational studies [3,19,20].

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Scheme 2. Plausible reaction sequence for monomolecular paraffin cracking in zeolite channels.

strong increase in cracking rates (per H^+) with carbon number reflects correspondingly higher activation entropies. Our analysis focuses on monomolecular cracking of C_3 – C_6 alkanes; these pathways differ in concept and detail from bimolecular pathways prevalent for larger alkanes, which involve cyclopropyl carbenium-ion-like transition states and β -scission pathways mediated by hydride transfer [9–11].

Zeolites can ‘solvate’ molecules by confining them within channels of molecular dimensions. These channels provide a thermodynamically non-ideal environment and lead to concentrating effects mediated by equilibrium between intrachannel and external fluid phases. Transition state treatments for chemical reactions in thermodynamically non-ideal media rigorously describe the effects of solvation and intrachannel concentrations on rates of reactions catalyzed by zeolites [12]. In monomolecular cracking, alkanes adsorb onto channels (P_z) from the contacting fluid phase (P_g) in quasi-equilibrated steps and acquire the requisite conformation for reaction with Brønsted acid sites to form a precursor state (P_{zr}) in subsequent quasi-equilibrated steps. Alkanes in this precursor state then react with Brønsted sites via transition states that form cracking products (Scheme 2). These transition state treatments lead to cracking rates given by

$$r = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^{\circ\dagger}}{R_g T}\right) \times \frac{\gamma_{H+Z} C_{H+Z} \gamma_{P_{zr}} C_{P_{zr}}}{\gamma^\ddagger} \quad (1)$$

The assumption of equilibrium between P_{zr} and P_z ,

$$K_r = \frac{a_{P_{zr}}}{a_{P_z}} = \frac{\gamma_{P_{zr}} C_{P_{zr}}}{\gamma_{P_z} C_{P_z}} \quad (2)$$

allows Eq. (1) to be recast as

$$r = \frac{k_B T}{h} K_r \frac{\gamma_{H+Z} \gamma_{P_z}}{\gamma^\ddagger} C_{H+Z} \exp\left(\frac{\Delta S^{\circ\dagger}}{R_g}\right) \times \exp\left(\frac{-\Delta H^{\circ\dagger}}{R_g T}\right) C_{P_z}, \quad (3)$$

in which $\Delta S^{\circ\dagger}$ and $\Delta H^{\circ\dagger}$ are the entropy and enthalpy of activation, respectively. This expression contains pre-exponential (A) and activation energy terms ($\Delta H^{\circ\dagger}$)

$$r = A \exp\left(\frac{-\Delta H^{\circ\dagger}}{R_g T}\right) C_{P_z}. \quad (4)$$

The parameter A contains the equilibrium constant (K_r) and the ratio of activity coefficients $\gamma_{H+Z} \gamma_{P_z} / \gamma^\ddagger$; both depend on the properties of the zeolite channels and of the acid sites within them. When the precursor and the transition state are solvated to the same extent by the intrachannel environment, as is likely to occur in monomolecular cracking because of the chemical resemblance between precursors and transition states, their respective activity coefficients fortuitously cancel. Then, only the

activity coefficient for the Brønsted acid sites remains in the rate equation. This activity coefficient, together with K_r , reflects the role of the chemical properties of acid sites and of the channel structure on pre-exponential factors. We note that this fortuitous cancellation renders rates rigorously proportional to the concentration of adsorbed alkanes within zeolite channels:

$$r = \frac{k_B T}{h} K_r \gamma_{H+Z} C_{H+Z} \exp\left(\frac{\Delta S^{\circ\dagger}}{R_g}\right) \times \exp\left(\frac{-\Delta H^{\circ\dagger}}{R_g T}\right) C_{P_z} = k C_{P_z} \quad (5)$$

in agreement with experiments [1–6].

Narbeshuber et al. [6] noted that cracking rates for C_3 – C_6 alkanes on H-MFI increased markedly with size, while apparent activation energies concurrently decreased (Figs. S1 and S2; supplemental information). The reaction conditions used led to predominantly unoccupied H^+ sites in H-MFI, in which case C_{P_z} is proportional to alkane pressure (P):

$$r = k \cdot K \cdot P. \quad (6)$$

In Eq. (6), k is the cracking rate constant for alkane-derived intermediates and K is the adsorption equilibrium constant for a given alkane. K values measured from adsorption isotherms predominantly reflect interactions of alkanes via van der Waals interactions with framework oxygen atoms, because of the weak nature of the specific induced-dipole interactions of alkanes with protons [13–15]. The temperature dependences of K and k are given by:

$$K = e^{(-\Delta G_{\text{ads}}/RT)} = e^{(-\Delta H_{\text{ads}}/RT)} e^{(\Delta S_{\text{ads}}/R)}, \quad (7)$$

$$k = A e^{(-E/RT)}. \quad (8)$$

Combining (6), (7) and (8), we obtain the apparent rate constants (k_{app}), activation energies (E_{app}), and pre-exponential factors (A_{app}) in terms of the thermodynamic properties of adsorbed reactants and transition states:

$$k_{\text{app}} = k \cdot K, \quad (9)$$

$$E_{\text{app}} = E_{\text{act}} + \Delta H_{\text{ads}}, \quad (10)$$

$$\ln(A_{\text{app}}) = \ln(A_{\text{act}}) + (\Delta S_{\text{ads}}/R). \quad (11)$$

Eder and Lercher [13–15] used calorimetry and infrared spectroscopy to show that non-specific van der Waals interactions of alkanes with framework oxygens led to more negative adsorption enthalpies with increasing chain size. Narbeshuber et al. [6] noted that the lower apparent activation energies (Eq. (10); Fig. S2 in supplemental information) measured for larger alkanes predominantly reflect their more exothermic adsorption, and consequently that intrinsic activation barriers for monomolecular cracking from adsorbed reactants are very similar for C_3 – C_6 alkanes ($E_{\text{int}} = 194$ – 198 kJ mol^{-1} ; 7% standard deviation). The selectivity for cleaving the various C–C bonds in n - C_5H_{12} was insensitive to temperature, indicating that activation energies were similar for all C–C bonds in each alkane. These findings are in marked contrast with the strong effects of alkane size and the high specificity for activation of C–C bonds β to tertiary carbons for the case of larger alkanes reacting via

Table 1

ΔH_{ads} and ΔS_{ads} for C₃–C₆ alkanes on H-MFI taken from Eder et al. [14,15]. K calculated from Eq. (7) by assuming ΔH_{ads} and ΔS_{ads} to be independent of temperature

Carbon number	ΔH_{ads} (kJ mol ⁻¹)	ΔS_{ads} (J mol ⁻¹ K ⁻¹)	K (373 K)	K (/10 ⁻⁴) (773 K)
3	-45	-102	10	55
4	-58	-119	78	51
5	-69	-135	494	46
6	-83	-152	4410	46

cyclopropyl carbocationic transition states [9–11]. The higher monomolecular cracking reactivity of larger alkanes (*n*-C₆H₁₄ is ~120 times more reactive than C₃H₈ at 773 K) has been ascribed to the relative adsorption constants for *n*-alkane reactants [6].

The stronger adsorption of larger alkanes within a channel (or of each alkane as channels become smaller) also leads to more constrained adsorbed species and to more negative adsorption entropies. These compensation effects between ΔH_{ads} and ΔS_{ads} for adsorption of alkanes on zeolites (Fig. S3 in supplemental information), shown by Eder and Lercher [14,15], lead, in turn, to much weaker effects of molecular size on K values than expected from measured adsorption enthalpies. The data of Eder and Lercher [14,15] on H-MFI (with the reasonable approximation that ΔH_{ads} and ΔS_{ads} are insensitive to temperature; see supplemental information) give the K values in Table 1 for alkanes of varying size. We note that differences in K , which are evident at 373 K, become much smaller at temperatures relevant for monomolecular cracking (~773 K). Configurational-bias Monte Carlo simulations also concluded that compensation between entropy and enthalpy terms leads to intrazeolitic concentrations that vary by a factor of ~2 for C₃–C₆ alkanes adsorbed on MFI at 775 K [16]. Larger differences in intrazeolitic concentrations may prevail for larger alkanes (C₈–C₂₀) because of their larger heats of adsorption and of the lower temperatures at which they crack via monomolecular pathways [17]. At high temperatures (945 K), however, very similar intrazeolitic concentrations of C₂–C₂₀ alkanes in MFI primarily resulting from adsorption enthalpy-entropy compensation were computed by Maesen et al. [16]. As a result, differences in K among alkanes cannot account for the large differences in cracking rates measured for propane and *n*-hexane (>100-fold in rate with K values differing by less than a factor of 2). Yet, adsorption enthalpies indeed account fully for the measured differences in apparent activation energies for the cracking of these two molecules (Eq. (10)) [6]. Differences of 30 kJ mol⁻¹ in the true activation barriers for the monomolecular cracking of adsorbed alkanes would be required to account for the measured 100-fold cracking rate differences between C₃H₈ and *n*-C₆H₁₄ in contradiction with the constant values measured (194–198 ± 14 kJ mol⁻¹ for C₃–C₆ alkanes) [6].

Hence, differences in cracking rates (Eq. (6)) and rate constants (Eq. (9)) among C₃–C₆ alkanes at ~773 K must reflect a significant increase in pre-exponential factors (Eq. (8)) and activation entropies (Eq. (11)) with alkane chain size. Table 2 shows pre-exponential factors and activation entropies calcu-

Table 2

Pre-exponential factor (A), entropy of activation (ΔS_{act}) and the fraction of entropy ($\Delta S_{\text{act}}/|\Delta S_{\text{ads}}|$) regained at the transition state for C₃–C₆ alkane cracking on H-MFI calculated using data from Narbeshuber et al. [6] and Eder et al. [14,15] and Eq. (6). Turnover frequencies reported at 773 K

Carbon number	TOF (/10 ⁻³) (mol (mol H ⁺) ⁻¹ s ⁻¹ bar ⁻¹)	A (/10 ¹³) (s ⁻¹)	ΔS_{act} (J mol ⁻¹ K ⁻¹)	$\Delta S_{\text{act}}/ \Delta S_{\text{ads}} $
3	1.31	0.57	-8.6	-0.08
4	5.80	2.3	3.0	0.03
5	22.3	6.2	11	0.08
6	60.0	27	23	0.15

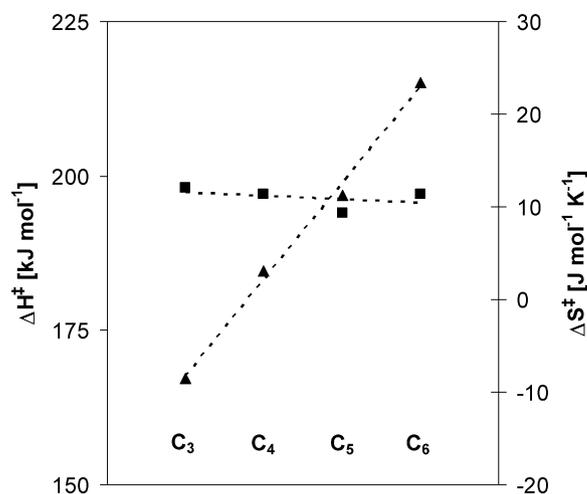


Fig. 1. Activation enthalpy (■) and entropy (▲) for C₃–C₆ alkane cracking in H-MFI from data reported in Narbeshuber et al. [6].

lated from measured rates (after correcting for the number of C–C bonds in each molecule) and activation energies [6]. Table 2 also shows the fraction of the adsorption entropy loss that is ultimately recovered as adsorbed alkanes reach the transition state for monomolecular cracking. The size-independent barrier for this transition [6] suggests that the extent of charge separation and the C–H–C bond configuration in transition states, relative to those in adsorbed alkanes, is essentially independent of chain size. The larger entropy loss upon adsorption of larger alkanes ultimately leads to a larger entropy gain as they form higher energy complexes along the reaction coordinate towards the transition states required for C–C bond activation, as shown by the linear trend of ΔS_{act} with carbon number in Fig. 1.

Monomolecular cracking reactions lead to substantial entropy gains as six internal modes are incipiently converted into three translational and rotational degrees of freedom in the transition state [18]. A part of this entropy gain arises from rocking vibrations of the two fragments, which become hindered rotations as C–C bonds are elongated in the transition state, a process inferred from *ab initio* and density functional calculations [19,20]. This process decreases the directionality and restoring forces for the movement of one fragment relative to the other. We surmise that the entropy gains that favor reactions of larger alkanes arise from an increase in the number of accessible configurations from the adsorbed state to the transition state and from the mass of the two fragments involved in these hindered rotations [18].

Table 3
Intrinsic rate constant for propane cracking, k_{int} on H-MFI (Si/Al = 39), H-MOR (Si/Al = 9.9), H-BEA (Si/Al = 10.5) calculated using rates and activation energies from Xu et al. [21] and adsorption parameters from Eder et al. [14,15]. Turnover frequencies are reported as apparent turnover frequencies at 823 K

Zeolite	TOF ($/10^{-3}$) ($\text{mol}(\text{mol H}^+)^{-1} \text{s}^{-1} \text{bar}^{-1}$)	ΔH_{ads} (kJ mol^{-1})	ΔS_{ads} ($\text{J mol}^{-1} \text{K}^{-1}$)	K ($/10^{-3}$) (823 K)	E_{app} (kJ mol^{-1})	k_{int} ($\text{mol}(\text{mol H}^+)^{-1} \text{s}^{-1}$)
H-MFI	23.6	-45.3	-101.9	3.55	147	6.6
H-MOR	22.2	-41.3	-84.6	15.9	145	1.4
H-BEA	6.9	-41.3 ^a	-84.6 ^a	15.9	157	0.4

^a ΔH_{ads} and ΔS_{ads} for H-BEA considered to be similar to those for H-MOR.

The effects of zeolite structure on monomolecular cracking rates have also been ascribed to intrazeolitic concentration effects based on adsorption enthalpies for propane [21] and *n*-hexane [22], suggesting that activation barriers are unaffected by structure. We note, however, that these effects on measured rates (per H^+) cannot be accurately described by mere differences in intrachannel reactant concentrations stabilized by the zeolite solvent. Xu et al. [21] measured propane cracking and dehydrogenation rates (per H^+ ; 823 K, <5% conversion) on H-MFI, H-MOR, and H-BEA. Table 3 shows these rate data together with ΔH_{ads} and ΔS_{ads} for propane adsorption (Fig. S3, supplemental information) from Eder and Lercher [14,15]. Equilibrium constants (assuming H-BEA and H-MOR to have similar adsorption thermodynamics), apparent activation energies, and intrinsic rate constants are also shown for these zeolites in Table 3. Rate constants for monomolecular cracking of propane are clearly influenced by the structure and solvating properties of zeolite channels. These effects of environment on rate parameters reflect the thermodynamic activity of zeolitic protons (Eqs. (3), (4) and (5)) through pre-exponential factors, but also possibly because of effects on activation energies. The systematic changes in intrinsic activation barriers reported with changes in channel structure have not been measured with the precision required to discern whether structural effects on rates arise solely from activation entropies or from combined entropy and energy changes induced by channel geometry.

The predominant effects of activation entropy in monomolecular cracking rates of light alkanes have not been clearly recognized in previous studies. These effects account for the marked effects of chain size on cracking rates and to a large extent for the varying reactivity of various zeolite structures. Residual contributions from channel constraints on activation barriers cannot be discerned from available data and require more precise measurements of the effects of geometry on monomolecular cracking rates. The approach and concepts discussed here are applicable to other acid-catalyzed reactions for which the effects of molecular and channel structure on the entropy and energy of activation remain unresolved and controversial.

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Supplemental information

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