



Acid strength and solvation effects on methylation, hydride transfer, and isomerization rates during catalytic homologation of C₁ species

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ABSTRACT

Dimethyl ether (DME) homologation forms isobutane and triptane (2,2,3-trimethylbutane) with supra-equilibrium selectivities within C₄ and C₇ hydrocarbons on both mesoporous solid acids (SiO₂–Al₂O₃, H₃PW₁₂O₄₀/SiO₂) and the acid forms of various zeolites (BEA, FAU, MFI) via methylation and hydride transfer steps that favor isobutane and triptane formation because of the relative stabilities of ion-pairs at transition states for chains along the preferred growth path. The stabilities of ion-pair transition states increase as acid sites become stronger and energies for charge separation decrease and as van der Waals interactions within pores become stronger, which respectively lead to higher rates on H₃PW₁₂O₄₀/SiO₂ and aluminosilicate zeolites than on amorphous SiO₂–Al₂O₃. Solid acids with different strengths and abilities to solvate ion-pairs by confinement differ in selectivity because strength and solvation influence transition states for the hydride transfer, methylation, and isomerization steps to different extents. Stronger acid sites on H₃PW₁₂O₄₀/SiO₂ favor isomerization and hydride transfer over methylation; they lead to higher selectivities to *n*-butane and non-triptane C₇ isomers than the weaker acid sites on BEA, FAU, and mesoporous SiO₂–Al₂O₃. This preference for hydride transfer and isomerization on stronger acids reflects transition states with more diffuse cationic charge, which interact less effectively with conjugate anions than more localized cations at methylation transition states. The latter recover a larger fraction of the energy required to form the ion-pair, and their stabilities are less sensitive to acid strength than for diffuse cations. Large-pore zeolites (BEA, FAU) form triptane with higher selectivity than SiO₂–Al₂O₃ because confinement within large pores preferentially solvates the larger transition states for hydride transfer and methylation, which preserve the four-carbon backbone in triptane, over smaller transition states for alkoxide isomerization steps, which disrupt this backbone and cause growth beyond C₇ chains and subsequent facile β-scission to form isobutane. MFI forms isobutane and triptane with much lower selectivity than mesoporous acids or large-pore zeolites, because smaller pores restrict the formation of bimolecular methylation and hydride transfer transition states required for chain growth and termination steps to a greater extent than those for monomolecular alkoxide isomerization. These data and their mechanistic interpretations show that the selective formation of isobutane and triptane from C₁ precursors like DME is favored on all acids as a result of the relative stability of methylation, hydride transfer, and isomerization transition states, but to a lesser extent when small confining voids and stronger acid sites preferentially stabilize monomolecular isomerization transition states. The observed effects of acid strength and confinement on rates and selectivities reflect the more effective stabilization of all ion-pairs on stronger acids and within solvating environments, but a preference for transition states with more diffuse charge on stronger acids and for ion-pairs with the appropriate solvation within voids of molecular dimensions.

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1. Introduction

Recent studies have demonstrated the selective synthesis of triptyl species (2,2,3-trimethylbutane and 2,3,3-trimethyl-1-butene; -tyl

used here and throughout to define alkenes and alkanes with a given backbone structure) and isobutyl species from methanol or dimethyl ether (DME) via Brønsted acid-catalyzed pathways mediated by carbenium ion transition states. This reaction occurs at modest temperatures (400–500 K) in liquid-phase metal–halogen systems [1–5] and on zeolites in their acid forms (H-FER, H-MOR, H-MFI, H-FAU, H-BEA) [6]. Competitive reactions between ¹³C-labeled dimethyl ether (¹³C-DME) and unlabeled alkenes on BEA,

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the zeolite that showed the highest triptane selectivity (21% C₇ species; 72% triptyls within C₇) [7], led to the detailed reaction network shown in Scheme 1.

Chain growth occurs via methylation events that avoid primary carbocationic transition states such that C₁ species add to alkenes at positions that retain a four-carbon backbone. Chains terminate via hydride transfer reactions at rates dictated by the strength of the C–H bonds in the hydride donor molecules and by the stability of the carbenium ions formed as transition states during hydride transfer to alkoxide acceptors [7–10]. Methylation is fast relative to hydride transfer for chains along the preferred methylation path, but hydride transfer to 2,3,3-trimethyl *sec*-butoxide (the alkoxide precursor to triptane) is faster than triptene methylation. Chains terminate preferentially as triptane or isobutane because the tertiary carbenium ion transition states involved in hydride transfer to their alkoxides are more stable than those with primary character required for methylation of triptene or isobutene. The formation of alkanes requires that arenes be concurrently formed to satisfy the hydrogen stoichiometry of methanol and DME homologation to these saturated products [2,6,7,11]. Slow isomerization and β -scission of the alkoxide isomers preferentially formed along the chain growth path to triptane prevent backbone rearrangement or cleavage during chain growth. Methylation at less preferred positions forms species that rapidly grow to chains larger than C₇ (C₈₊), which undergo facile β -scission to form isobutene and isobutane. These mechanistic features of C₁ homologation and the resulting isomer and chain size distributions reflect the selective formation of the most highly substituted carbenium ions at transition states of elementary steps (i.e. methylation, termination, isomerization, and β -scission) involved in chain growth pathways [2,5–7].

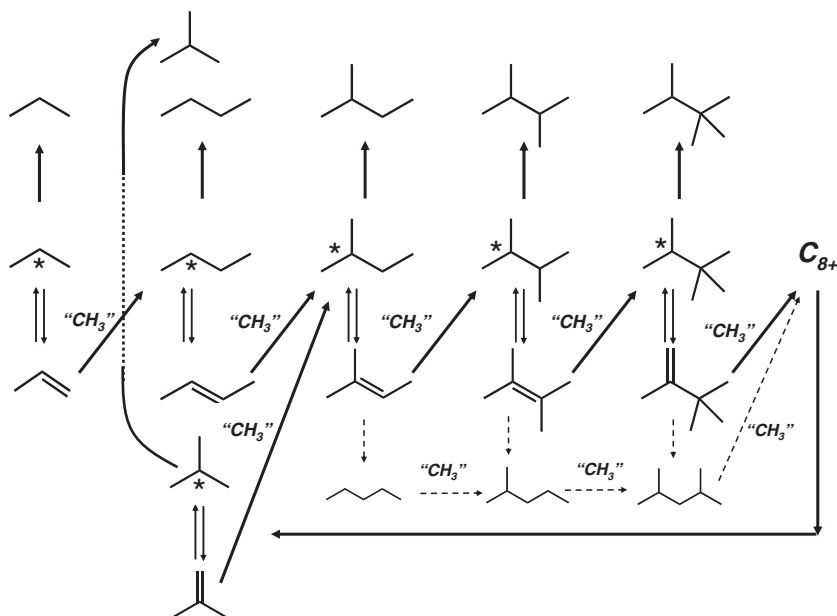
Here, we present data for DME homologation on acids with different spatial constraints but similar acid strength (mesoporous SiO₂–Al₂O₃ and zeolites BEA, FAU, and MFI), as well as on stronger acids on mesoporous supports (H₃PW₁₂O₄₀/SiO₂) to probe how spatial confinement and acid strength influence the rates of the various steps involved in acid-catalyzed homologation. These data and their mechanistic interpretation show that isomerization and hydride transfer rates are more sensitive to acid strength than methylation and that zeolites have higher rates of acid-catalyzed

reactions than mesoporous SiO₂–Al₂O₃, because transition states confined within zeolite channels are stabilized with respect to gas-phase reactants by van der Waals interactions. DME homologation on medium-pore zeolites leads to a broad distribution of hydrocarbon chain lengths instead of the bimodal distribution to C₄ and C₇ products observed on large-pore zeolites because smaller pores hinder the formation of monomolecular isomerization transition states to a lesser extent than those for methylation and hydride transfer steps. These data give insights into the respective roles of solvation and acid strength on methylation, hydride transfer, isomerization, and β -scission rates and rigorously assess these effects using stabilities of the carbenium ion transition states that mediate these reactions.

2. Experimental methods

2.1. Catalysts, reactants, and kinetic and isotopic tracer studies

The acid forms of zeolites BEA, MFI, and FAU were prepared by heating NH₄-BEA (Si/Al = 12.5, Zeolyst), NH₄-MFI (Si/Al = 15, Zeolyst), and NH₄-FAU (Si/Al = 3.2) to 773 K (at 0.02 K s⁻¹) for 10 h in flowing dry air (1.7 cm³ s⁻¹ g⁻¹, zero grade, Praxair). NH₄-FAU was prepared by treating NH₄-Y zeolite with ammonium hexafluorosilicate solutions, using procedures described previously [12,13]. H₃PW₁₂O₄₀/SiO₂ was prepared via incipient wetness impregnation of mesoporous SiO₂ (Cab-O-Sil HS-5; 310 m² g⁻¹; 1.5 cm³ g⁻¹ pore volume) with a solution of H₃PW₁₂O₄₀ (Sigma-Aldrich; reagent grade) in ethanol (Sigma-Aldrich; >99.5%; anhydrous) [14] to give samples with a 5% weight loading (5 wt.%). At this surface density, H₃PW₁₂O₄₀ species exist as isolated clusters or small two-dimensional aggregates on SiO₂ and have Keggin structure, as shown by MAS-³¹P NMR spectra and transmission electron micrographs [14]. Mesoporous SiO₂–Al₂O₃ (Si/Al = 5.7; Sigma-Aldrich) was used as received. DME homologation rates on each catalyst are normalized by the number of Brønsted acid sites (i.e., accessible protons) in each catalyst as measured from the number of 2,6-di-*tert*-butylpyridine molecules required to completely suppress methanol dehydration rates, assuming a 1:1 titrant:H⁺ adsorption stoichiometry [14].



Scheme 1. Chain growth sequence for dimethyl ether homologation (starting with propene for simplicity). The asterisk indicates the preferred position of alkoxide attachment to the surface. “CH₃” represents surface methylating species derived from dimethyl ether [1,6,7].

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