

Alkanal-Alkene Prins Condensation Reactions on Brønsted Solid Acids

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Abstract: Isobutanal-isobutene Prins condensation to 2,5-dimethyl-hexadienes catalyzed by Brønsted acids provides a renewable route for the formation of *p*-xylene. Experiment and theory are combined here to assess and interpret effects of acid strength and of confinement on Prins condensation rates and selectivities in porous aluminosilicates. Prins condensation and parallel isobutene oligomerization both involve kinetically-relevant cationic C-C coupling transition states (TS). Their TS charges depend differently on the acid strength, leading to higher 2,5-dimethyl-hexadiene selectivities on weaker acids. Prins condensation and oligomerization prefer aluminosilicate voids of intermediate sizes, reflecting the compensation between dispersive host-guest interactions and structural distortions required for such interactions.

Keywords: Acid catalysis, C-C coupling, Reaction mechanism.

1. Introduction

Prins condensations form C-C bonds between carbonyl C-atoms in alkanals and terminal C-atoms of C=C bonds in alkenes, thus rendering two carbon chains linked via their terminal C-atoms, a specificity unattainable in other C-C coupling reactions (e.g. alkene oligomerization and aldol condensation of carbonyl compounds) [1]. Isobutanal-isobutene Prins condensations selectively form 2,5-dimethyl-hexadiene regioisomers (2,5-DMH) that act as convenient precursors to *p*-xylene. Both isobutene and isobutanal reactants can be formed from biomass-derived isobutanol, which enables an alternate route to produce *p*-xylene from renewable resources [2]. Isobutanal-isobutene condensation occurs on solid acids, in parallel with isobutene oligomerization and secondary isomerization, cyclization, and β -scission of the 2,5-DMH products. Experiment and theory are used here to show that these reactions are mediated by cationic transition states (TS) that differ in charge or size, leading to strong effects of acid strength and of confinement within aluminosilicate voids of molecular dimensions on rates and selectivities [3,4].

2. Experimental and theoretical

Turnover rates and selectivities on SiO₂-supported Keggin heteropolyacids, niobic acid, and microporous (TON, MFI, BEA, FAU), mesoporous (Al-MCM-41) and amorphous aluminosilicates were measured in a packed-bed reactor (453-633 K, 0.1-20 kPa for isobutanal and isobutene). Protons were counted using titrations with 2,6-di-*tert*-butylpyridine during catalysis or thermal decomposition of NH₄⁺-exchanged forms of solid acids. Density functional theory methods implemented in the VASP program were used to determine free energies and charge distributions for all reactant, product, and TS structures.

3. Results and discussion

Rates of isobutanal-isobutene Prins condensation and isobutene oligomerization on all solid acids were fully suppressed by non-coordinating 2,6-di-*tert*-butylpyridine titrants, reflecting these reactions occur exclusively on Brønsted acid sites. Turnover rates (per proton) for Prins condensation (r_{prins}) and oligomerization (r_{oligo}) both increased as the acid strength of solid acid increases (Fig. 1a), but the $r_{\text{prins}}/r_{\text{oligo}}$ ratios were significantly larger on the weaker acids (Fig. 1a). Kinetic and theoretical assessments indicate that Prins condensation and oligomerization are limited by kinetically-relevant C-C bond formation steps, in which gaseous isobutene reacts with protonated isobutanal and isobutene-derived *tert*-butyl carbenium ions, respectively. Measured second-order rate constants for Prins condensation (k_{prins}) and oligomerization (k_{oligo}) were both lower on Al-MCM-41 than on H₃PW₁₂O₄₀, while $k_{\text{prins}}/k_{\text{oligo}}$ ratios were much larger on Al-MCM-

41 than on $\text{H}_3\text{PW}_{12}\text{O}_{40}$; these data are consistent with theoretical estimates based on aluminosilicate slabs and Keggin $\text{H}_3\text{PW}_{12}\text{O}_{40}$ cluster models; they confirm the less reactive (for both reactions) but more selective (for Prins condensation) nature of weaker acids. Theory also showed that C-C coupling transition states in Prins condensation (TS_{prins}) and oligomerization (TS_{oligo}) are cationic. TS_{prins} structures become full ion-pairs only on stronger acids, while TS_{oligo} structures exist as an ion-pair on all acids. The values of k_{prins} and k_{oligo} therefore both increase with acid strength, but TS_{oligo} preferentially benefits from the greater stability of the conjugate anions in the stronger acids, leading to higher 2,5-DMH selectivities on the weaker acids.

The TS_{prins} and TS_{oligo} structures on aluminosilicates are of similar sizes (van der Waals volume 0.153 vs. 0.144 nm^3) and are stabilized to similar extents by van der Waals contacts with voids; these similar TS sizes and the similar strength of acid sites in all aluminosilicates, lead to similar $k_{\text{prins}}/k_{\text{oligo}}$ ratios (15-20, 473 K) on all mesoporous and microporous aluminosilicates. These TS_{prins} and TS_{oligo} structures, however, are much larger than their respective precursors, H-bonded isobutanal and *tert*-butoxide, respectively; as a result, r_{prins} and r_{oligo} both sense the size or shape of the confining voids. Measured first-order Prins condensation rate constants ($k_{\text{prins}}/K_{\text{al}}$; K_{al} , isobutanal adsorption constant) reflect the Gibbs free energy of TS_{prins} relative to a H-bonded isobutanal and a gaseous isobutene molecule. These $k_{\text{prins}}/K_{\text{al}}$ values increase with increasing void size (TON < BEA < FAU, Fig. 1b) as a result of the enthalpic and entropic penalties brought forth by host-guest distortions in the smaller voids, but then decrease with further increases in void size (Al-MCM-41) because of the less effective van der Waals contacts within mesoporous voids. Protons at MFI channel intersections gave slightly larger $k_{\text{prins}}/K_{\text{al}}$ values (about two-fold) than in cylindrical BEA channels (Fig. 1b), in spite of their similar diameters, indicating that the quasi-spherical nature of MFI intersections favors contacts with the TS structures. These effects of the size and shape of aluminosilicate voids on $k_{\text{prins}}/K_{\text{al}}$ were consistent with theoretical treatments that rigorously account for van der Waals interactions and for the entropy losses and host-guest distortions required for confinement within confining voids.

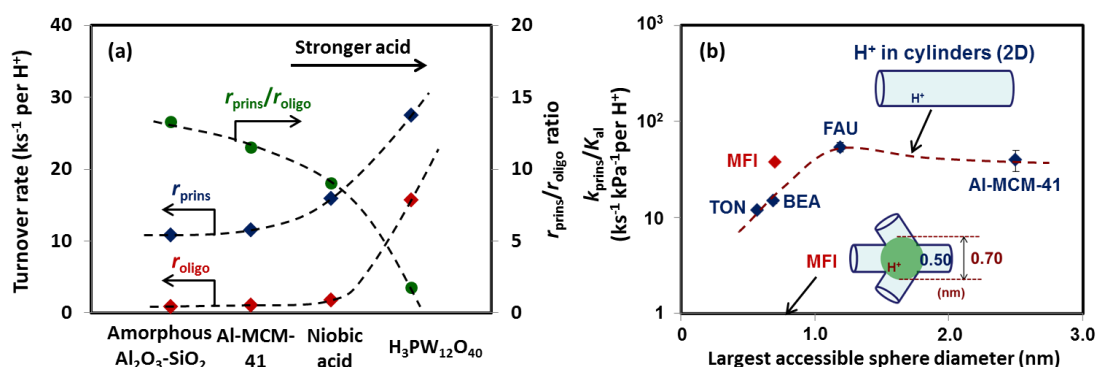


Figure 1. (a) Turnover rates of Prins condensation and isobutene oligomerization and their rate ratios on solid acids (473 K, 2.0 kPa isobutanal, 1.0 isobutene); (b) measured $k_{\text{prins}}/K_{\text{al}}$ values as a function of the largest accessible sphere diameter of aluminosilicate voids (473 K).

4. Conclusions

Isobutanal-isobutene Prins condensation and parallel isobutene oligomerization occurred on Brønsted acid sites are both mediated by cationic C-C coupling transition states (TS). The stability of these TS structures increases with increasing acid strength of the Brønsted acid sites, but their sensitivity to such effects becomes weaker as the TS charge decreases. The difference in size between these TS structures and their respective bound precursors also leads to confinement effects on reactivity, because these guest species are stabilized by the confining voids via van der Waals contacts to different extents.

References

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