



Mechanistic interpretation of the effects of acid strength on alkane isomerization turnover rates and selectivity



William Knaeble, Robert T. Carr, Enrique Iglesia *

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States

ARTICLE INFO

Article history:

Received 7 July 2014

Revised 20 August 2014

Accepted 6 September 2014

Available online 10 October 2014

Keywords:

Keggin polyoxometalates

Heteropolyacids

Skeletal isomerization

Bifunctional catalysis

Acid strength

Deprotonation energy

Ion-pair transition state theory

ABSTRACT

Acid strength effects on alkane isomerization turnover rates and selectivities are probed using hexene isomers as reactants on bifunctional catalysts containing tungsten Keggin polyoxometalates (POM) with different central atoms and exhibiting well-defined structures amenable to reliable estimates of deprotonation energies (DPE) as rigorous descriptors of acid strength. Titrations of protons with hindered bases during catalysis and mechanistic interpretations of rate data on POM acids in terms of a common sequence of elementary steps give isomerization rate constants that decrease exponentially with increasing DPE. The sensitivity to acid strength is the same for all interconversions among isomeric hexenes because their respective transition states are similar in the amount and localized character of their cationic charges, which determine, in turn, the extent to which the ionic and covalent interactions that determine DPE are recovered upon formation of ion pairs at transition states. The ratios of rate constants for such interconversions, and thus selectivities, are independent of acid strength and their magnitude merely reflects the stability of the gaseous analogs of their respective transition states on all acids.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Catalysis by solid Brønsted acids is ubiquitous in the synthesis and upgrading of fuels and petrochemicals [1]. Rigorous connections between the structure and strength of acid sites and their specific consequences for reactivity and selectivity remain imprecise and often contradictory. Prevailing uncertainties about the number, location, and structure of acid sites during catalysis, the challenges inherent in the unambiguous experimental assessment of acid strength, and measured rates and selectivities that are seldom interpreted in terms of chemical mechanisms have contributed to the pervasive controversies about the strength of acids and about the consequences of acid strength for rates and selectivities of specific reactions and for catalysis in general.

Deprotonation energies (DPE) reflect the ionic and covalent interactions between a proton (H^+) and its conjugate base. These interactions must be overcome to transfer this proton to the intermediates and transition states that mediate transformations catalyzed by acids. DPE values represent a rigorous and probe-independent measure of acid strength; it is accessible to density functional theory (DFT) treatments for well-defined solid acids, such as Keggin polyoxometalate (POM) clusters ($1087\text{--}1143\text{ kJ mol}^{-1}$ for

$H_{8-n}X^{n+}W_{12}O_{40}$; $X = P, Si, Al$, or Co in order of increasing DPE) [2, 3] and zeolites with different frameworks [4] and heteroatoms [5].

The effects of DPE, and consequently of acid strength, on alkanol dehydration [3,6,7] and *n*-hexene isomerization [8] rate constants (per accessible H^+) on Keggin POM clusters ($H_{8-n}X^{n+}W_{12}O_{40}$; $X = P, Si, Al$, or Co) indicate that the ion-pair transition states (TS) that mediate the kinetically-relevant elementary steps are lower in energy with respect to fully protonated clusters on stronger acids, in part, because of their more stable conjugate anions. Differences in the amount and localization of cationic charge at kinetically-relevant TS relative to those properties for the most abundant surface intermediates (MASI) determine the sensitivity of measured rate constants to acid strength [7,8]. Cations that are small and contain a highly localized charge resemble H^+ and interact most effectively with the conjugate anion [9]; as a result, proton-like TS structures attenuate the effects of acid strength on reactivity most effectively, by recovering most of the energy required to separate the proton. These studies have shown that the effects of acid strength on reactivity reflect differences in interaction energies between the TS and the conjugate anion and those between the MASI species and the conjugate anion.

Here, we assess the effects of acid strength on isomerization turnover rates of hexane and hexene isomers with different backbone structures on bifunctional catalyst mixtures consisting of well-defined Brønsted acids (*W*-based Keggin POM clusters) and

* Corresponding author. Fax: +1 510 642 4778.

E-mail address: iglesia@berkeley.edu (E. Iglesia).

metal sites (Pt/Al₂O₃). In such mixtures, Pt sites equilibrate alkanes and alkenes with a given backbone structure via fast hydrogenation–dehydrogenation reactions when such sites are present in sufficient amounts; in such cases, reactant alkenes are present throughout the catalyst mixture at low and constant concentrations; such low concentrations cannot be detected but are known from thermodynamic data at each given temperature and H₂ and alkane pressures. These alkenes undergo skeletal isomerization on acid sites and the alkene isomers formed rapidly equilibrate with the respective alkanes upon contact with Pt sites [10–12].

Isomerization rate constants (per H⁺) were measured for the conversion of 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and n-hexane reactants through mechanistic interpretations of rate data and measurements of the number of accessible protons by titrations with organic bases during catalysis. These rate constants reflect TS energies relative to unoccupied Brønsted acid sites and gaseous alkene reactants. Selectivities to isomerization products formed from reactant-derived alkenes after only a single sojourn at an acid site cannot be estimated directly from measured selectivities, because secondary interconversions of alkene products and hydrogenation reactions occur at comparable rates; hydrogenation occurs, either locally within acid domains via hydrogen transfer from alkane reactants or via reactions with H₂ after diffusion of alkene isomer products through such acid domains to reach Pt sites. Such selectivities to 3-methylpentene isomer products from 2-methylpentane derived alkenes, which reflect the stability of methyl shift TS relative to those for TS that vary backbone length, were determined—without the use of measured selectivities—from the measured isomerization rate constants for the conversion of each hexane isomer through mechanistic interpretations of rate data. We find that acid strength influences the isomerization rates and selectivities of all skeletal isomers to a similar extent, suggesting that charge distributions are also similar among the ion pairs that mediate each of these reactions. We conclude that the preferential formation of certain isomers reflects the different proton affinities among the gaseous analogs of their respective transition states; these differences and the extent to which deprotonation energies are recovered by interactions of such TS structures with the conjugate anion are not affected, however, by the stability of the conjugate anion and thus do not depend on the strength of the solid acid catalyst.

2. Experimental methods

2.1. Catalyst synthesis and characterization

H₃PW₁₂O₄₀ (Sigma–Aldrich; reagent grade; CAS #12501-23-4), H₄SiW₁₂O₄₀ (Aldrich; >99.9%; CAS #12027-43-9), H₅AlW₁₂O₄₀ (as prepared in [13]), and H₆CoW₁₂O₄₀ (prepared as in [14,15]) were supported on amorphous SiO₂ (Cab-O-Sil HS-5; 310 m² g⁻¹; 1.5 cm³ g⁻¹ pore volume) by incipient wetness impregnation with ethanol as the solvent. SiO₂ was washed three times with 1 M HNO₃ and treated in flowing dry air (UHP Praxair; 0.5 cm³ g⁻¹ s⁻¹) at 573 K for 5 h before impregnation. Ethanolic POM solutions (ethanol, Sigma–Aldrich; >99.5%; anhydrous) were added to pre-treated SiO₂ (1.5 cm³ solution [g dry SiO₂]⁻¹) and impregnated samples were stored in closed vials for >24 h before treatment in flowing dry air (UHP Praxair; 0.5 cm³ g⁻¹ s⁻¹) by heating from ambient temperature to 323 K at 0.033 K s⁻¹ and holding for 24 h. SiO₂-supported POM clusters are denoted as “H_nXW/SiO₂”, where *n* is the stoichiometric number of protons per cluster and X is the central atom. POM concentrations in the impregnation solutions were set to give a surface density of 0.04 POM [nm-SiO₂]⁻² (~5.0 wt%) for all central atoms, unless noted otherwise. ³¹P-MAS-NMR spectra of H₃PW/SiO₂ (Fig. S.1. in Supporting Informa-

tion) confirmed that the procedures used to disperse POM clusters on SiO₂ did not alter their Keggin structures. Transmission electron micrographs (Fig. S.2. in Supporting Information) showed that, prior to their exposure to reaction conditions, POM clusters were present as isolated clusters or small two-dimensional oligomers on SiO₂ at the surface densities used in this study.

Pt/Al₂O₃ (1.5 wt%), used as a cocatalyst in physical mixtures with POM/SiO₂ Brønsted acids, was prepared by incipient wetness impregnation of γ -Al₂O₃ (Sasol SBA-200; 193 m² g⁻¹, 0.57 cm³ g⁻¹ pore volume) with aqueous H₂PtCl₆ (Aldrich; CAS #16941-12-1; 0.57 cm³ g⁻¹ dried Al₂O₃) solution. The γ -Al₂O₃ was treated in dry air (UHP Praxair; 0.5 cm³ g⁻¹ s⁻¹) at 923 K for 5 h prior to impregnation. The impregnated sample was treated in dry air (Praxair UHP, 0.7 cm³ g⁻¹ s⁻¹) at 383 K for 10 h before heating to 823 K at 0.033 K s⁻¹ and holding for 3 h in flowing dry air (Praxair UHP, 0.7 cm³ g⁻¹ s⁻¹). This sample was then treated in H₂ (Praxair 99.999%; 0.2 cm³ g⁻¹ s⁻¹) by heating to 723 K at 0.083 K s⁻¹ and holding for 2 h. After cooling to 303 K in He (UHP Praxair; 0.7 cm³ g⁻¹ s⁻¹), the Pt/Al₂O₃ was treated in a dry air/He mixture (2.1% mol O₂, 7.9% mol N₂, 90% mol He, 0.7 cm³ g⁻¹ s⁻¹ total flow) for 2 h.

The Pt dispersion in Pt/Al₂O₃ (0.92; defined as the fraction of Pt-atoms located at the surfaces of Pt particles) was determined by H₂ uptakes at 298 K using a volumetric chemisorption unit and a 1:1 H-atom:Pt₅ adsorption stoichiometry (Pt₅, surface Pt-atom). Pt/Al₂O₃ was treated in H₂ (99.999% Praxair) at 598 K for 1 h and then held under vacuum at 598 K for 0.5 h before chemisorption measurements. A H₂ adsorption isotherm (99.999% Praxair) was measured at 298 K from 0.1 to 50 kPa H₂. The cell was then evacuated for 0.25 h at 298 K and a second isotherm was measured under the same conditions. The amount of chemisorbed H₂ was calculated from the difference between the first and second isotherms after their respective extrapolations to zero pressure. The Pt dispersion was also determined by CO chemisorption at 298 K using similar pretreatments, a single CO (99.5% Praxair) adsorption isotherm extrapolated to zero pressure, and by assuming a 1:1 CO:Pt₅ adsorption stoichiometry (0.78 Pt₅/Pt_{total}). Their average (0.85) was used to calculate (Pt₅/H⁺) ratios of acid–metal mixtures.

Pt/Al₂O₃ samples were mixed with POM/SiO₂ (P, Si, Al, and Co central atoms) in a mortar and pestle (<100 μ m Al₂O₃ and SiO₂ particles) and then pressed into wafers, crushed, and sieved to retain 125–180 μ m aggregates. The compositions of these mixtures are reported here as the ratio of Pt₅ (from the average dispersion from H₂ and CO chemisorption) to accessible H⁺ (measured by titration during catalysis; Section 3.1.1); this ratio (Pt₅/H⁺) was varied between 6.2 and 22.9 to determine the ratios required to achieve reactant alkane–alkene equilibrium during isomerization catalysis (Section 3.1.2).

2.2. Alkane isomerization rate measurements and titrations with 2,6-di-*tert*-butylpyridine

2-Methylpentane (2MP), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB), and n-hexane (nH) isomerization rates were measured on catalyst mixtures (0.01–0.3 g) held within a quartz tubular flow reactor (1.0 cm I.D.) using a porous quartz disk and maintained at 473 K by resistive heating (Watlow Series 982 controller). Temperatures were measured using a K-type thermocouple (Omega; \pm 0.2 K) held within an indentation at the reactor wall. Mixtures of POM/SiO₂ and Pt/Al₂O₃ were heated to 473 K at 0.083 K s⁻¹ in flowing He (UHP Praxair; 0.83 cm³ s⁻¹) and held for 1 h before catalytic measurements

Liquid 2-methylpentane (Fluka; >99.5% analytical standard), 3-methylpentane (Fluka; >99.5% analytical standard), 2,3-dimethylbutane (Fluka; >99.5% analytical standard), and n-hexane (Fluka; >99.0% GC standard) reactants were evaporated into a flowing He (UHP Praxair) and H₂ (99.999% Praxair) stream using a syringe

Download English Version:

<https://daneshyari.com/en/article/61018>

Download Persian Version:

<https://daneshyari.com/article/61018>

[Daneshyari.com](https://daneshyari.com)