Journal of Catalysis 277 (2011) 173–195

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Mechanistic details of acid-catalyzed reactions and their role in the selective synthesis of triptane and isobutane from dimethyl ether

Dante A. Simonetti, John H. Ahn, Enrique Iglesia *

Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

ARTICLE INFO

Article history:
Received 14 August 2010
Revised 26 October 2010
Accepted 10 November 2010
Available online 18 December 2010

Keywords:
Carbenium ion
Dimethyl ether
Isomeric alkanes
Solid acid catalysis
Transportation fuels

ABSTRACT

We report here kinetic and isotopic evidence for the elementary steps involved in dimethyl ether (DME) homologation and for their role in the preferential synthesis of 2,2,3-trimethylbutane (triptane) and isobutane. Rates of methylation of alkenes and of hydrogen transfer, isomerization and β-scission reactions of the corresponding alkoxides formed along the homologation path to triptane were measured using mixtures of ^{13}C-labeled dimethyl ether (^{13}C-DME) and unlabeled alkenes on H-BEA. DME-derived C_1 species react with these alkenes to form linear butyls from propene, isopentyls from *n*-butenes, 2,3-dimethylbutyls from isopentenes, and triptyls from 2,3-dimethylbutenes; these kinetic preferences reflect the selective formation of the more highly substituted carbenium ions and the retention of a four-carbon backbone along the path to triptane. Hydrogen transfer reactions terminate chains as alkanes; chain termination probabilities are low for species along the preferred methylation path, but reach a maximum at triptyl species, because tertiary carbenium ions involved in hydrogen transfer are much more stable than those with primary character required for triptene methylation. Alkenes and alkanes act as hydrogen donors and form unsaturated species as precursors to hexamethylbenzene, which forms to provide the hydrogen required for the DME-to-alkanes stoichiometry. Weak allylic C–H bonds in isoalkenes are particularly effective hydrogen donors, as shown by the higher termination probabilities and ^{12}C content in hexamethylbenzene as ^{12}C-2-methyl-2-butene and ^{12}C-2,3-dimethyl-2-butene pressures increased in mixtures with ^{13}C-DME. The resulting dienes and trienes can then undergo Diels–Alder cyclizations to form arenes as stable by-products. Isomerization and β-scission reactions of the alkoxides preferentially formed in methylation of alkenes are much slower than hydrogen transfer or methylation rates, thus preventing molecular disruptions along the path to triptane. Methylation at less preferred positions leads to species with lower termination probabilities, which tend to grow to C_{8+} molecules; these larger alkoxides undergo facile β-scission to form *tert*-butoxides that desorb preferentially as isobutane via hydrogen transfer; such pathways resolve methylation "missteps" by recycling the carbon atoms in such chains to the early stages of the homologation chain and account for the prevalence of isobutane among DME homologation products. These findings were motivated by an inquiry into the products formed via C_1 homologation, but they provide rigorous insights about how the structure and stability of carbenium ions specifically influence the rates of methylation, hydrogen transfer, β-scission, and isomerization reactions catalyzed by solid acids.

1. Introduction

The conversion of CH_3OH and dimethyl ether (DME) to hydrocarbons provides a potential route to transportation fuels from C_1 intermediates produced from synthesis gas derived from diverse natural gas, coal, or biomass sources [1,2]. 2,2,3-Trimethylbutane (triptane; 112 research octane number) forms with high selectivity from methanol at modest temperatures (~450 K) via carbenium ion transition states using Zn or In iodide in aqueous batch systems [3–7]. These systems are strongly inhibited by the water formed in dehydration and homologation reactions and appear to catalyze only a few methanol turnovers [3–5]. Acid zeolites also convert DME and methanol selectively to isobutane and triptane at modest temperatures (400–500 K) and pressures (60–250 kPa) in continuous gas-phase flow systems with moderate deactivation and a significant number of catalytic turnovers (>10 mol of C per Al after 20 ks on stream) [8,9]. H-BEA was chosen for this study because it showed the highest productivity (740 μmol (s mol Al)$^{-1}$), triptane selectivity (21% selectivity to C_7 species and 72% selectivity to triptyls within C_7), and stability (0.04 ks^{-1} first-order deactivation rate constant) among the large-pore zeolites studied (H-MOR, H-USY, H-BEA) [9]; zeolites with smaller 8-MR and 10-MR

* Corresponding author. Fax: +1 510 642 4778.
E-mail address: iglesia@berkeley.edu (E. Iglesia).

0021-9517/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2010.11.004

structures (H-FER, H-MFI) gave lower rates [9], apparently as a result of steric constraints on diffusion rates or transition states. DME preferentially formed C_4 and C_7 hydrocarbons (each with ~30% selectivity); isobutyl species (isobutene and isobutane, 90%; –tyl suffix is used here and elsewhere to denote alkanes and alkenes with a given backbone structure) and triptyl species (triptene and triptane; 80%) were the predominant isomers within the C_4 and C_7 fractions, respectively [9], in spite of the strong thermodynamic preference for other isomers [10]. The most abundant isomers within C_5 (isopentane and isopentenes) and C_6 (2,3-dimethylbutane and 2,3-dimethylbutenes) products also contain the linear four-carbon backbone structure characteristic of triptane [9].

Here, we provide kinetic and isotopic evidence for chain growth and termination pathways that selectively form triptane and isobutane from DME reactants. We use competitive reactions between ^{13}C-labeled dimethyl ether (^{13}C-DME) and unlabeled alkenes of varying size and shape to measure individual rates of methylation, hydrogen transfer, isomerization, and β-scission reactions and develop a quantitative description of the mechanistic details of chain growth during DME homologation to triptane on solid acid catalysts. The remarkable specificity for triptane and isobutane reflects (i) a preference for methylation at positions that preserve a four-carbon backbone, (ii) slow isomerization and β-scission reactions of these four-carbon backbones, which would divert chains from the path to triptane, (iii) fast isomerization and β-scission of chains that grow beyond triptane to form isobutane and isobutene, thus returning part of these longer chains to the homologation reaction manifold, and (iv) the high hydrogen transfer rates to *tert*-butoxide and 2,3,3-trimethyl *sec*-butoxide compared with methylation of isobutene and triptene because of the more stable carbenium ion transition states for hydrogen transfer relative to methylation. These mechanistic features are shown to reflect pathways mediated by ion-pairs at late transition states ubiquitous in acid catalysis instead of any specific spatial constraints imposed by the zeolite BEA structure; indeed, the preferential formation of C_4 and C_7 products, and of isobutane and triptane as their respective preferred isomers are observed on all large-pore zeolites examined [9] and also on mesoporous heteropolyacids and silica–alumina [11]. Thus, the conclusions presented here, derived from an inquiry into the unique selectivity to isobutane and triptane from acid-catalyzed conversion of C_1 species, provide guidance about the effects of molecular structure and of carbenium ion stability on acid catalysis in general.

2. Experimental methods

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

The acid form of BEA zeolite was prepared by heating NH_4-BEA (Si/Al = 12.5, Zeolyst [8]) to 773 K (at 0.02 K s^{-1}) and holding for 10 h in flowing, dry air (1.7 cm^3 s^{-1} g^{-1}, zero grade, Praxair). Reactant mixtures consisted of $^{13}CH_3O^{13}CH_3$ (99%, ISOTEC; denoted as ^{13}C-DME) and unlabeled alkenes (^{12}C-alkenes). These alkenes included propene (99%, Sigma Aldrich), 1-butene (99%, Scott Specialty Gases), trans-2-butene (99%, Sigma Aldrich), isobutene (99%, Matheson), 2-methyl-2-butene (99%, Sigma Aldrich), 2-pentenes (mixture of cis and trans isomers, 98%, Sigma Aldrich), 2,3-dimethyl-2-butene (98%, Acros Organics), 2-methyl-2-pentene (98%, Fluka), 2,3,3-trimethyl-1-butene (triptene; 98%, Sigma Aldrich), 2,4-trimethyl-2-pentene (99%, ChemSampCo), and 3,4,4-trimethyl-2-pentene (99%, ChemSampCo). Reactant streams consisting of ^{13}C-DME (75–84 kPa) with small concentrations (0.5–3.7 kPa) of one of these alkenes were mixed with He (99.999%, Praxair) and introduced into a stainless steel tubular reactor (6.4 mm outer diameter) containing the H-BEA catalyst (5–40 mg; 180–250 μm particles) held in place by a fritted VCR gasket and quartz wool.

Temperatures were measured with a type-K thermocouple placed at the external reactor wall and held constant using a Watlow controller (Series 96) and a resistive heater. All samples were heated to reaction temperature (at 0.8 K s^{-1}) in flowing He (0.083 cm^3 s^{-1}) before introducing reactant mixtures. The chemical and isotopic composition of the reactor effluent was determined by gas chromatography using flame ionization and mass selective detectors (HP 5890/HP 5972), each connected to a capillary column (HP-1, methyl silicone, 50 m × 0.32 mm × 1.05 μm film). Isotopologue distributions were determined from mass fragmentation patterns using deconvolution methods reported previously [8,12].

2.2. Determination of individual rates of methylation, hydrogen transfer, isomerization, and β-scission from isotopic tracer studies

The rate of hydrogen transfer for homologation intermediates of a given size (n) and structure ($R_{HT,n}$) was determined from the rate of formation of the unlabeled alkane corresponding to the added unlabeled alkene. These rates were determined from:

$$R_{HT,n} = \frac{R_{C_n} \times j}{n} \quad (1)$$

in which R_{C_n} is the total rate (on a carbon basis) of formation of alkanes of the same size and structure as the co-fed alkene, j is the fraction of these alkanes that are unlabeled, and n is the number of carbons in the co-fed alkene. The rates of β-scission ($R_{bs,n}$) of DME homologation intermediates were determined from the rates of formation of unlabeled products (alkenes and alkanes) of β-scission of co-fed unlabeled alkenes. Skeletal backbone rearrangement rates ($R_{Is,n}$) were determined from the rate of appearance of unlabeled isomers (alkene and alkane) with shorter and longer backbones than the co-fed alkene. These rates were calculated using Eqs. (2) and (3), in which j and n are defined as in Eq. (1), $R_{C_{m<n}}$ is the total rate of formation (on a carbon basis) of species from β-scission of the co-fed alkene, and R_{C_n-Is} is the total rate of formation (on a carbon basis) of skeletal alkane and alkene isomers of the co-fed alkene:

$$R_{bs,n} = \frac{R_{C_{m<n}} \times j}{n} \quad (2)$$

$$R_{Is,n} = \frac{R_{C_n-Is} \times j}{n} \quad (3)$$

The rates of methyl shift ($R_{MS,n}$) isomerization (without concomitant changes in backbone chain length) were determined using the same method as for $R_{Is,n}$, except that the rate of unlabeled isomers (alkene and alkane) with methyl groups located at different positions along the backbone than the co-fed alkene was used in place of R_{C_n-Is}.

Methylation of ^{12}C-alkene with ^{13}C-DME forms molecules containing ^{12}C- and ^{13}C-atoms, but hydrogen transfer, isomerization, and β-scission of the alkoxides derived from ^{12}C-alkenes form only unlabeled molecules; the rate of formation of such unlabeled molecules represents the combined rates of these three reactions. The position and rate of methylation ($R_{Me,n}$) of each added alkene can be determined from the rate of formation of all molecules containing at least one ^{12}C-atom, except for those containing only ^{12}C-atoms:

$$R_{Me,n} = \frac{(\sum_i R_i \times X)}{n} - R_{HT,n} - R_{Is,n} - R_{MS,n} - R_{bs,n}. \quad (4)$$

In this equation, R_i is the total rate (on a carbon basis) of formation of molecules with i-carbons, X is the ^{12}C-atomic fraction in each molecule (determined from isotopologue distributions), and n is the number of carbons in the co-fed alkene.

Chain termination probabilities (β):

$$\beta = \frac{R_{HT,n}}{R_{Me,n} + R_{HT,n}} \quad (5)$$

are defined as the ratio of the rate of hydrogen transfer to the sum of the rates of methylation and hydrogen transfer (the less reversible termination step). The probabilities of skeletal isomerization (γ_{Sk}), β-scission (γ_C), and methyl shift (γ_{MS}) are defined by analogy with Eq. (5), with the rates of chain lengthening or shortening ($R_{Is,n}$), β-scission ($R_{bs,n}$), or methyl shift ($R_{MS,n}$) in the numerator (Eqs. (6)–(8)):

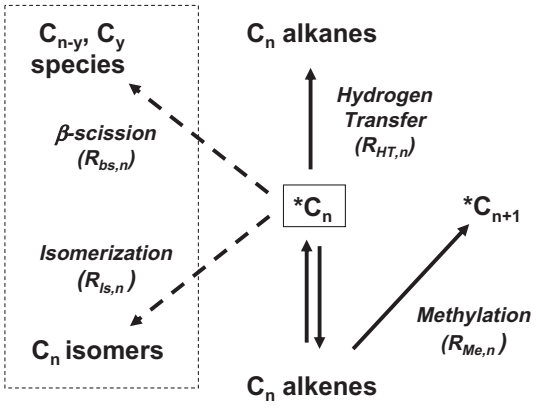
$$\gamma_{Sk} = \frac{R_{Is,n}}{R_{Me,n} + R_{HT,n}} \quad (6)$$

$$\gamma_C = \frac{R_{bs,n}}{R_{Me,n} + R_{HT,n}} \quad (7)$$

$$\gamma_{MS} = \frac{R_{MS,n}}{R_{Me,n} + R_{HT,n}} \quad (8)$$

3. Results and discussion

^{12}C-alkenes co-fed with ^{13}C-DME are methylated to larger species [3,4,9,13–24] or protonated to alkoxides [25–28], which can undergo hydrogen transfer [4,9,29–35], isomerization [30,36–39], or β-scission [40–44] via the pathways shown in Scheme 1. Thus, ^{13}C-DME reactions with ^{12}C-alkene isomers of varying size along the chain growth path to triptane were used to probe the rate and position of methylation of alkenes, as well as the rates of hydrogen transfer, isomerization, and β-scission of alkoxides formed in DME homologation reactions. These experiments were conducted at 473 K, because such conditions lead to significant rates of triptane formation (3.8 μmol (s mol Al)$^{-1}$) and high selectivities to triptane and isobutane (21% selectivity to C_7 hydrocarbons with 72% selectivity to triptyls in C_7 and 42% selectivity to C_4 hydrocarbons with 94% selectivity to isobutyls in C_4) [9]. Unlabeled $^{12}C_5$–$^{12}C_7$ alkenes lacking the four-carbon backbone in triptane, and thus not involved as precursors to triptane, were used to show how deviations from the four-carbon backbone lead to chain growth beyond C_7 molecules and to fast β-scission of the products of these reactions. The facile β-scission paths of C_8 molecules and their selective formation of isobutyl species were confirmed by ^{13}C-DME co-homologation with ^{12}C-3,4,4-trimethyl-2-pentene, the isomeric octene preferentially formed by methylation of triptene [9].



Scheme 1. Reaction pathways for alkenes and alkoxides formed as intermediates along dimethyl ether homologation pathways. Reactions denoted with solid lines occur faster than those denoted with dashed lines.

These experiments show how molecular structures and carbenium ion stabilities dictate the rates of chain growth and termination during the homologation of C_1 species derived from equilibrated methanol-DME reactants [8] via the chain growth pathways shown in Scheme 2. These experiments also show more generally how molecular structures determine the rates of the carbenium-ion-mediated pathways ubiquitously involved in acid catalysis [45].

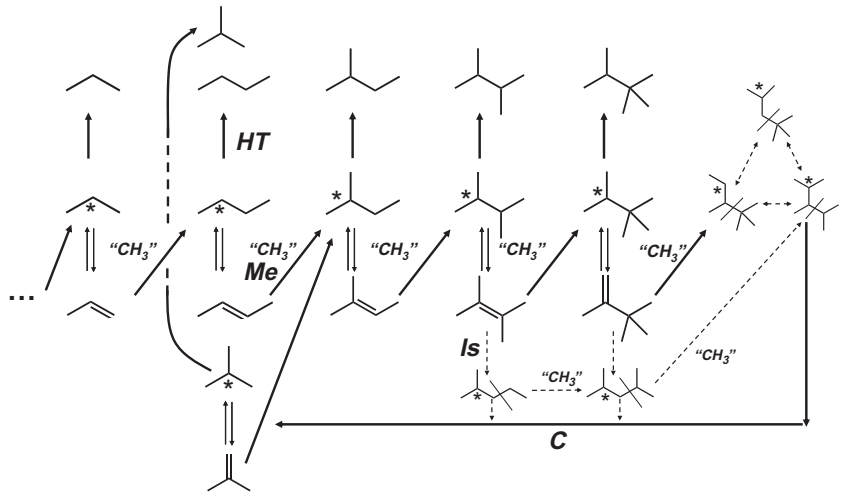
3.1. Selective methylation of propene to form linear C_4 species

Propene can be methylated at the terminal carbon atom to form linear C_4 species or at the central carbon atom to form isobutyl species. Co-reactions of ^{13}C-DME (84 kPa) and ^{12}C-propene (2 kPa) were used to probe the preferential methylation position in propene and whether propene methylation accounts for the high isobutane selectivites prevalent in DME homologation catalysis on acid zeolites [8,9].

The selectivity to linear C_4 chains (*n*-butane and *n*-butenes) and to singly labeled C_4 isotopologues formed by a single methylation with ^{13}C-DME/^{12}C-propene mixtures decreased with increasing reactor residence time (Fig. 1), indicating that these molecules form as primary products via deprotonation or hydrogen transfer of *sec*-butoxide species derived from ^{12}C-propene reactions with ^{13}C-DME. The trans-2-butene isotopologues consisted predominantly of singly labeled species, with a minority binomial component containing more highly labeled isotopologues (dashed curve; Fig. 2a). We chose trans-2-butene as the representative linear C_4 alkene, because it shows the same isotopic distribution as *n*-butane, but is present at higher concentrations than *n*-butane and the other *n*-butene isomers. At all residence times, singly labeled trans-2-butene molecules are ~10 times more abundant than 2-butenes with two or more ^{13}C-atoms (Fig. 2a), indicating that linear C_4 species predominantly form via a single methylation of propene with ^{13}C-DME. In contrast, selectivities to isobutyl species (and to their singly labeled isotopologues) increased with increasing residence time (Fig. 1); thus, we conclude that isobutane and isobutene form via secondary β-scission of larger chains. Indeed, isobutane molecules show a binomial isotopologue distribution (Fig. 2b), also consistent with β-scission reactions of larger isomeric chains containing C-atoms from both DME and propene as the predominant route to isobutane products.

The prevalence of singly labeled isotopologues in *n*-butyl (but not isobutyl) species and their higher selectivity at shorter residence times show that methylation of propene occurs preferentially at the terminal carbon to form linear instead of branched butoxides that desorb via deprotonation or hydrogen transfer as linear butenes or butane, respectively. Preferential methylation at the terminal carbon in propene reflects the higher stability of their secondary butyl carbenium ion transition state in *sec*-butoxide formation compared with the primary cations involved in the transition state for the formation of *tert*-butoxides via methylation at the internal carbons in propene (as shown in Scheme 3). We conclude that isobutane (and isobutene) does not form via propene methylation, which forms linear C_4 species instead. The predominant formation of binomial isobutane isotopologues (Fig. 2b) shows that isobutane predominantly forms via secondary β-scission of larger chains, after extensive skeletal rearrangements that scrambled ^{13}C-atoms along the backbone of these larger chains.

The selective formation of *n*-butyl species in the methylation of propene is consistent with cluster calculations of reactions of co-adsorbed propene with methanol [21,46], which show smaller barriers for methylation at terminal than internal C-atoms in propene. These studies suggest that the stability imparted upon methylation transition states by the formation of the most substituted carbenium ions dictates that methylation occurs preferentially at the



Scheme 2. Chain growth sequence for dimethyl ether homologation (starting with propene for simplicity). The asterisk indicates the position of alkoxide attachment to the surface. HT, Me, Is, and C labels represent hydrogen transfer, methylation, isomerization, and cracking reactions, respectively. "CH_3" represents surface methylating species derived from dimethyl ether.

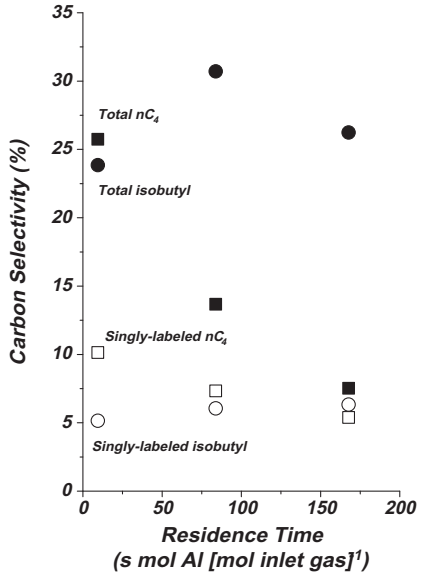


Fig. 1. Selectivity (% carbon basis) to linear C_4 species and isobutyl species as a function of reactor residence time (s mol Al [mol inlet gas]$^{-1}$) for reactions between ^{13}C-labeled dimethyl ether (84 kPa) and unlabeled propene (2 kPa) at 473 K on H-BEA (Si/Al = 12.5). Total carbon conversions were less than 5%.

less substituted C-atom in C=C bonds of alkenes [21,46]. Methylation transition states, however, distribute the positive charge between the two C-atoms in the alkene C=C bond; as a result, methylation activation barriers decrease as the combined number of alkyl substituents on the two C-atoms in C=C bond increases [21,46]. In later sections, we show that the rate and position of methylation for alkenes are indeed consistent with this qualitative guidance.

^{13}C-DME (78 kPa) and ^{12}C-propene (0.5 kPa) reactions were used to measure the rates of methylation of propene (to form linear C_4 species) and hydrogen transfer to propoxide species formed by protonation of propene (to form propane). The termination probability (Eq. (5)) for C_3 species ($\beta = 0.013$; Table 1) indicates that propene undergoes methylation much faster than propoxide formation and irreversible termination by hydrogen transfer. Theoretical studies using DFT methods have shown that hydrogen transfer between a gas-phase hydride donor and an alkoxide form transition states that resemble the carbenium ion formed by detachment of alkoxide through cleavage of C–O bond with the zeolite framework [30,33]. Therefore, the low termination probability for C_3 species reflects the greater stability of the butyl carbenium ion transition state formed in methylation of propene (with its positive charge stabilized over two secondary C-atoms) compared with the propyl carbenium ion transition state formed by breaking the C–O bond in *sec*-propoxide during hydrogen transfer [30] (Scheme 3). As in the case of the methylation and hydrogen transfer steps examined in the next sections, the stability of the cationic transition states involved dictates the preferred routes along the path to triptane. In this case, such considerations favor the selective methylation of propene at its terminal carbon to form linear C_4 species over methylation to form isobutyl species or irreversible termination by hydrogen transfer to *sec*-propoxide to form propane.

3.2. Methylation, termination, isomerization, and β-scission of C_4 species derived from butenes

The rates of methylation, hydrogen transfer, isomerization, and β-scission of linear and branched C_4 molecules were measured from individual experiments in which unlabeled isobutene, 1-butene, or trans-2-butene were introduced as reactants with ^{13}C-DME (Table 1a). The isotopologue distributions of isopentane and isobutane molecules formed from these reactants are shown in Fig. 3. These alkenes can undergo methylation to form C_5 alkoxides that ultimately desorb via deprotonation as C_5 alkenes (and methylate again) or as C_5 alkanes via hydrogen transfer. Butoxides can also undergo β-scission or isomerization before methylation or hydrogen transfer; the rates of formation of unlabeled skeletal C_4 isomers and of unlabeled C_1–C_3 species from ^{13}C-DME/$^{12}C_4$ alkene reactants reflect the respective rates of isomerization and β-scission of butoxides derived from C_4 alkenes. These rates were used to determine the termination, β-scission, and isomerization probabilities (listed in Table 1b and defined in Eqs. (5)–(7)).

Co-reactions of ^{13}C-DME (78 kPa) with ^{12}C-1-butene or ^{12}C-trans-2-butene (0.5 kPa) were used to measure the rates of acid-catalyzed intramolecular hydride shifts, which move the alkoxide linkage to the surface and the location of the double bond within the alkene as it deprotonates. The trans and cis isomers of 2-butene were formed in equilibrium ratios (2.0–2.4 vs. 2.0 equilibrium

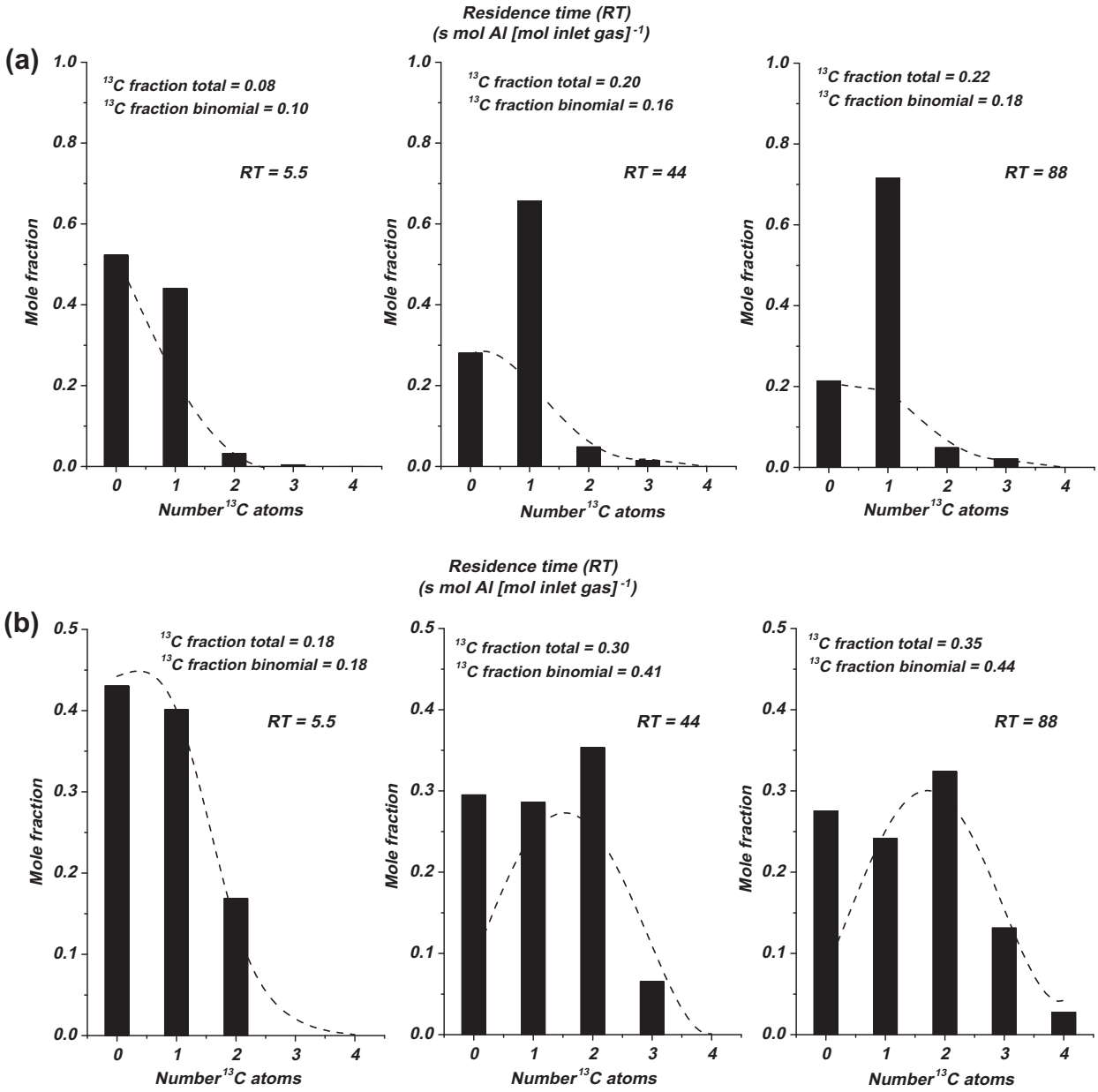
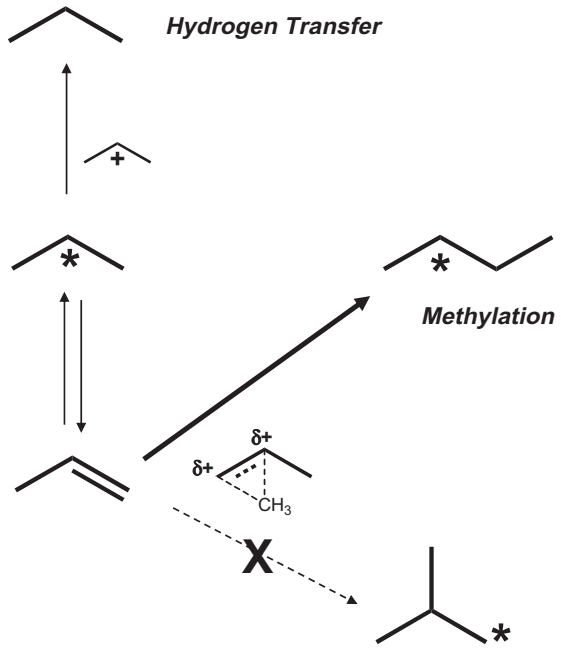


Fig. 2. Isotopologue distributions and ^{13}C-atomic fractions of (a) trans-2-butene and (b) isobutane molecules produced from reactions between ^{13}C-labeled dimethyl ether (84 kPa) and ^{12}C-propene (2 kPa) at 473 K on H-BEA at residence times of 5.5 (left), 44 (middle), and 88 (right) s mol Al [mol inlet gas]$^{-1}$ and propene conversions of 13% (left), 63% (middle), and 73% (right). Total carbon conversions (DME and propene) were less than 5%. The dashed markers indicate the binomial distribution expected for the ^{13}C-fraction in the binomial portion present in each particular chemical species [8].

value at 473 K [10]; Table 1) and termination (β), skeletal isomerization (γ_{Sk}), and β-scission (γ_C) probabilities were similar for ^{12}C-1-butene ($\beta = 0.08$, $\gamma_{Sk} = 0.02$, $\gamma_C = 0.05$) and ^{12}C-trans-2-butene ($\beta = 0.10$, $\gamma_{Sk} = 0.02$, $\gamma_C = 0.04$) reactions with ^{13}C-DME (Table 1), as expected from the fast equilibration of their double-bond position. These data indicate that linear C_4 species (*sec*-butoxide and *1*-butoxide) exist at equilibrium on acid sites and the gas-phase thermodynamics are ultimately established by subsequent readsorption and hydride shift during reactions of ^{13}C-DME and ^{12}C-linear butenes. We conclude that protonation–deprotonation events and intervening hydride shift isomerization occur much faster than methylation, hydrogen transfer, isomerization, and β-scission steps during DME homologation on acid sites even at the low temperatures of these reactions.

Methylation of linear butenes, and subsequent deprotonation or hydrogen transfer, can occur at internal C-atoms of 2-butenes or at the terminal C-atom of 1-butene to form branched or linear C_5 species, respectively. Co-reactions of ^{13}C-DME with all ^{12}C-linear butenes at 473 K gave much higher rates of formation of isopentyl species (isopentane and isopentenes; 18–21 μmol [mol Al s]$^{-1}$; Table 1) than of linear pentyl species (*n*-pentane and *n*-pentenes; 0.76–0.91 μmol [mol Al s]$^{-1}$; Table 1), indicating that methylation occurs preferentially at internal C-atoms of 2-butenes instead of the terminal C-atom in 1-butene (Scheme 4). The isopentane and isopentene molecules are mostly singly labeled (Fig. 3a), indicating that branched C_5 products predominantly form via methylation of linear butenes at methylene positions. Previous studies have proposed that transition states for methylation of 2-butene and 1-butene resemble *tert*-pentyl and *n*-pentyl carbenium ions, respectively, with charge delocalized over both of the C-atoms in the alkene double bond [21,46]. These studies also indicate that methylation at the internal C-atom in 1-butene does not occur,



Scheme 3. Reaction pathways for C_3 species (propene and propoxide) in acid-catalyzed dimethyl ether homologation pathways. Methylation of propene occurs faster than hydrogen transfer to propoxide. Methylation of propene to isobutane does not occur because of the formation of a primary carbenium ion.

Table 1
(a) Rates (μmol [mol Al s]$^{-1}$) of methylation, hydrogen transfer, skeletal isomerization, β-scission, and formation of isopentyl ($R_{iso\text{-}C5}$) and normal pentyl ($R_{normal\text{-}C5}$) species and (b) trans/cis-2-butene ratios, termination (β), skeletal isomerization (γ_{Sk}), and β-scission (γ_C) probabilities for reactions of ^{13}C-labeled dimethyl ether (78 kPa) and unlabeled propene, trans-2-butene, 1-butene, or isobutene (0.5 kPa) at 473 K on H-BEA (Si/Al = 12.5). Reactions conducted at a space velocity of 0.024 mol inlet gas [mol Al s]$^{-1}$. Total carbon conversions (DME and alkene) were less than 5%, and alkene conversions were 97% of propene, 97% of isobutene, 85% of 1-butene, and 34% of trans-2-butene.

	Co-feed alkene			
	Propene	trans-2-Butene	1-Butene	Isobutene
(a)				
Methylation	37	53	68	33
Hydrogen transfer	0.5	5.8	5.9	38
Skeletal isomerization	–	1.4	0.9	0.4
β-scission	–	2.2	3.5	3.5
$R_{iso\text{-}C5}$	–	18	21	9.5
$R_{normal\text{-}C5}$	–	0.91	0.76	–[a]
(b)				
trans/cis-2-Butene ratio	–	2.4	2.0	2.3
β	0.01	0.10	0.08	0.54
γ_{Sk}	–	0.02	0.02	0.006
γ_C	–	0.04	0.05	0.05

[a] Rate of neopentane formation below detection limit of gas-chromatograph (1.4×10^{-3} μmol [mol Al s]$^{-1}$).

consistent with the required involvement of *tert*-pentyl carbenium ions with primary character [21]. The selective formation of isopentyl species confirms the preference for transition states that can delocalize charge over tertiary and secondary C-atoms (Scheme 4). This preference for isopentyl cations also leads to the smaller barriers of methylation of 2-butenes than 1-butenes derived from theoretical treatments [21]. Kinetic preferences based on double-bond location become undetectable by experiment because of the rapid interconversion among linear butene isomers in the time scale of methylation turnovers.

Eq. (4) (Section 2.2) is used to determine the total methylation rate of linear butenes by ^{13}C-DME, which includes the C_5 species that methylate further to form longer chains with more ^{13}C-atoms that can undergo β-scission after intramolecular rearrangements. Linear C_4 species can undergo hydrogen transfer, skeletal isomerization, and β-scission before the corresponding butenes methylate to branched C_5 products. The rates of these reactions are determined here from the rates of formation of unlabeled *n*-butane, unlabeled isobutyl species, and unlabeled C_1–C_3 species, respectively, from ^{13}C-DME/^{12}C-linear butene reactants. The corresponding termination, isomerization, and β-scission probabilities for linear C_4 species are then calculated, in turn, from these rates (Eqs. (5)–(7)).

The data obtained from ^{13}C-DME/^{12}C-linear butene reactants data showed that methylation of linear C_4 alkenes (with ^{13}C-DME-derived C_1 species) occurs faster than steps involving hydrogen transfer (β = 0.08–0.10; Table 1), isomerization (γ_{Sk} = 0.02; Table 1), or β-scission (γ_C = 0.04–0.05; Table 1) of butoxide species. These low probabilities of termination (β), isomerization (γ_{Sk}), and β-scission (γ_C) allow the preferential growth of linear C_4 species to isopentane and isopentene, instead of terminating chains as *n*-butane or altering their linear C_4 backbone via isomerization or β-scission. The observed preference for methylation of linear butenes over hydrogen transfer, skeletal isomerization, or β-scission of butoxides reflects the greater stability of the *tert*-pentyl carbenium ions involved in methylation at central carbons in 2-butene (with charge delocalized over secondary and tertiary C-atoms) relative to the transition states with only secondary carbenium ions required to cleave C–O bonds in hydrogen transfer to adsorbed linear butoxides [4,9,29–35] or the carbenium ions with primary character required for their skeletal isomerization [30,36–39] or β-scission [40–44] (Scheme 4).

The small measured skeletal isomerization probabilities (γ_{Sk}; Table 1) also show that the high observed isobutane selectivities (observed previously [9] and in the ^{13}C-DME/^{12}C-alkene studies presented herein [8]) must reflect β-scission of larger chains instead of *n*-butoxide skeletal isomerization, which occurs infrequently before sequential chain growth of linear butenes. The binomial isobutane isotopologue distributions formed from ^{13}C-DME/^{12}C-linear butene mixtures (Fig. 3b) contain small contributions from unlabeled molecules (0.05) and ^{13}C contents higher than in isopentane (0.49 vs. 0.25), consistent with their formation via β-scission of larger chains formed by subsequent methylation with ^{13}C-DME after extensive intramolecular carbon scrambling. Isobutane does not form by isomerization or hydrogen transfer to butoxide species derived from protonation of ^{12}C-linear butenes (γ_{Sk} = 0.02) or via isopentane cracking (γ_C = 0.002; Table 2; discussed in Section 3.3.5).

Co-reactions of ^{13}C-DME (78 kPa) and ^{12}C-isobutene (0.5 kPa) were used to probe reaction pathways of isobutene, whether formed directly from DME or via β-scission of larger chains during homologation reactions and to contrast the reactivity of branched and linear butenes. Isobutene can be methylated by DME at its terminal C-atom to form isopentyl molecules or at its tertiary C-atom to form neopentane after hydrogen transfer. Isopentyl species form at much higher rates (9.5 μmol [mol Al s]$^{-1}$; Table 1) than neopentane (below the detection limit of 10^{-3} μmol [mol Al s]$^{-1}$) from ^{13}C-DME/^{12}C-isobutene mixtures, consistent with the exclusive methylation at the terminal carbon in isobutene (Scheme 4). The isopentane isotopologues formed from ^{13}C-DME/^{12}C-isobutene reactants (Fig. 3c) consisted mostly of singly labeled species (0.63 mole fraction), consistent with their predominant formation via single ^{13}C-DME methylation events. The selective methylation at isobutene terminal carbons reflects the greater stability of its *tert*-pentyl carbenium ion transition state compared with the primary carbenium ion and terminal alkoxides involved in the

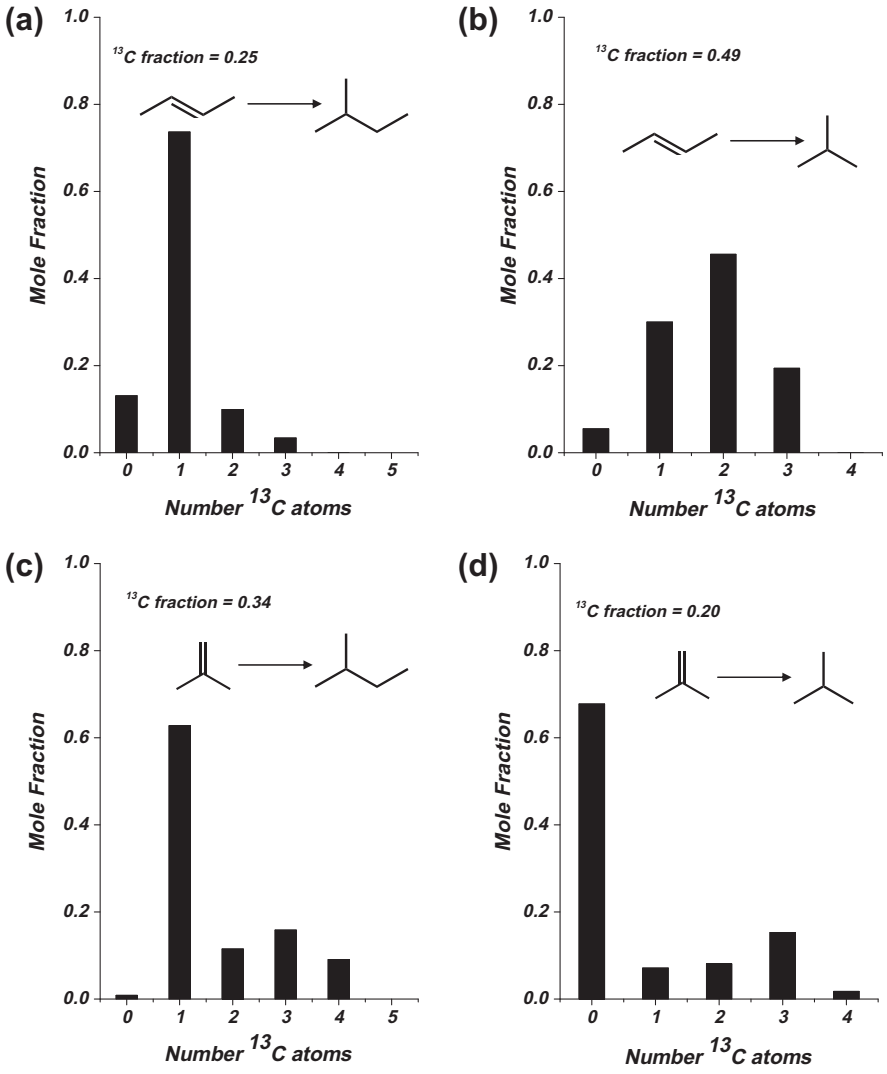
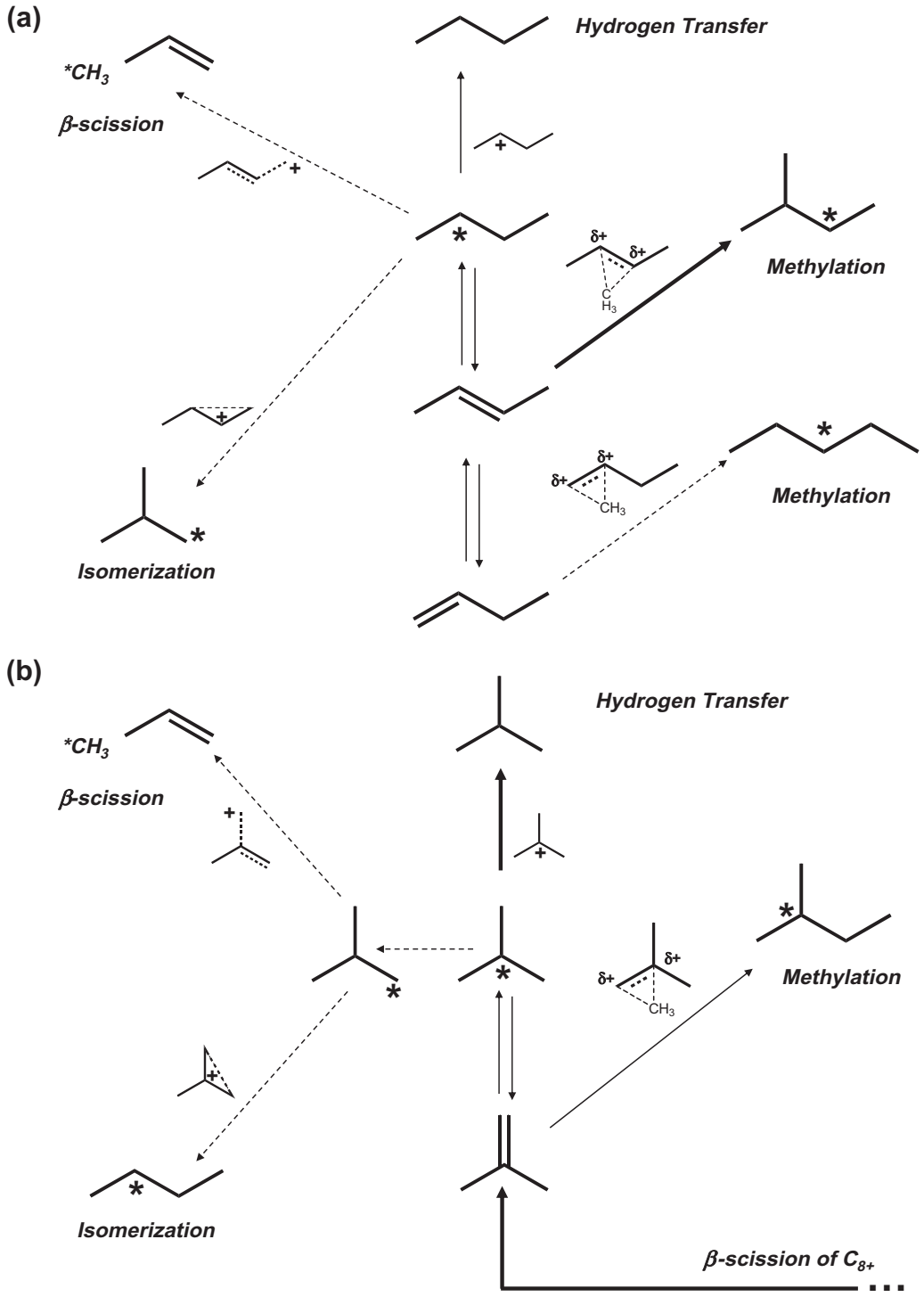


Fig. 3. Isotopologue distributions and ^{13}C-atomic fractions for (a) isopentane and (b) isobutane molecules produced from co-reaction of ^{13}C-labeled dimethyl ether (78 kPa) with ^{12}C-linear butene (0.5 kPa) and (c) isopentane and (d) isobutane molecules produced from co-reaction of ^{13}C-labeled dimethyl ether (78 kPa) with ^{12}C-isobutene (0.5 kPa). Reactions conducted at 473 K on H-BEA (Si/Al = 12.5) at space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

formation of the neopentyl precursors to neopentane, consistent with theoretical estimates, indicating that the methyl group is preferentially placed at the less substituted C-atom in the C=C bond of an alkene [21]. The presence of isotopologues other than singly labeled isopentane (Fig. 3a and c) indicates that some isopentane molecules are produced from growing chains that undergo β-scission reactions, thus returning the alkenes formed to the methylation pathways leading to isopentane and larger alkanes.

Comparison of the rates of methylation of butene isomers and hydrogen transfer to their respective alkoxides (and their respective β values) allows consideration of how the structure of these molecules and the stability of the respective carbenium ion transition states lead to a preference for chain growth for butyl species and for termination in the case of isobutyl species. Unlabeled isobutane is the predominant isotopologue formed from ^{13}C-DME/^{12}C-isobutene mixtures (0.68 mole fraction; Fig. 3d), indicating that *tert*-butoxide species formed via protonation of isobutene undergo rapid hydrogen transfer to form isobutane. The similar rates of hydrogen transfer to *tert*-butoxide (38 μmol [mol Al s]$^{-1}$; Table 1) and methylation of isobutene (33 μmol [mol Al s]$^{-1}$; Table 1) reflect the similar stabilities of *tert*-butyl and *tert*-pentyl carbenium ion transition states required for hydrogen transfer to *tert*-butoxide [30,33] and for methylation of isobutene [21] (Scheme 4), respectively. In contrast to isobutyl species, *sec*-butoxides undergo hydrogen transfer at much lower rates than *n*-butenes methylate (5.8 vs. 53–68 μmol [mol Al s]$^{-1}$; Table 1) because hydrogen transfer involves secondary *n*-butyl carbenium ions in transition states, while methylation proceeds via more stable *tert*-pentyl carbenium ions with tertiary character. These rates of methylation and hydrogen transfer for C_4 species result in higher termination probabilities (β) in reactions of isobutene than linear butenes (0.54 vs. 0.08–0.10; Table 2), which reflect the more stable transition state for hydrogen transfer to *tert*-butoxides than to *sec*-butoxides as a result of the tertiary carbenium ions involved in hydrogen transfer to branched alkoxides [30,33] (Scheme 4). These β values also suggest that methylation of primary–tertiary C=C bonds in isobutene would involve a less stable transition state than methylation of secondary–secondary C=C bonds in 2-butene, because the former bonds retain some positive charge at a primary C-atom in its transition state [21,24] (Scheme 4).

We conclude from these β values that linear C_4 species preferentially grow to form branched C_5 chains (via *n*-butene methylation),



Scheme 4. Reaction pathways for (a) *n*-butyl species (*n*-butenes and *sec*-butoxide) and (b) isobutyl species (isobutene and *tert*-butoxide) in acid-catalyzed dimethyl ether homologation pathways. Methylation of *n*-butene to isopentyl species occurs faster than hydrogen transfer to *sec*-butoxide. Methylation of isobutene to isopentyl species occurs slower than hydrogen transfer to *tert*-butoxide. Isomerization and β-scission of both *sec*-butoxide and *tert*-butoxide occur much more slowly than hydrogen transfer to these alkoxides and methylation of their alkenes.

while isobutyl species predominantly terminate as isobutane (via hydrogen transfer to *tert*-butoxide). We also find that branched species give higher termination probabilities than their linear isomers, because their tertiary C-atoms form more stable cationic transition states for hydrogen transfer. These β values also show that the preferential formation of linear butenes from propene avoids premature chain termination during methylation reactions via the facile hydrogen transfer to *tert*-butoxides that would prevail from the alternate methylation of propene at its internal carbon atom.

Schemes 3 and 4 show the reaction pathways for C_3 and C_4 species during homologation of DME (or methanol) on Brønsted acid sites. The formation of stable cationic transition states dictates the selective methylation at the terminal C-atom in propene to

Table 2
(a) Rates (μmol [mol Al s]$^{-1}$) of methylation, hydrogen transfer, skeletal isomerization, β-scission, and methylation at internal C-atoms ($R_{\text{internal C-atoms}}$) and terminal C-atoms ($R_{\text{terminal C-atoms}}$) and (b) 2-/1-alkene ratios and termination (β), skeletal isomerization (γ_{Sk}), methyl shift isomerization (γ_{MS}), and β-scission (γ_C) probabilities for reactions of ^{13}C-labeled dimethyl ether (78 kPa) and 0.5 kPa of unlabeled 2-methyl-2-butene (2M2B), 2-pentene (2P), 2,3-dimethyl-2-butene (23DM2B), 2-methyl-2-pentene (2M2P), triptene, 2,4-dimethyl-2-pentene (24DM2P), or 3,4,4-trimethyl-2-pentene (344TM2P) at 473 K on H-BEA (Si/Al = 12.5). Reactions conducted at space velocity of 0.024 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

	Co-feed alkene						
	2M2B	2P	23DM2B	2M2P	Triptene	24DM2P	344TM2P
(a)							
Methylation	56	59	70	66	33	91	25
Hydrogen Transfer	21	3.9	7.4	13	48	17	0.02
Skeletal Isomerization	0.16	0.25	0.73	0.2	0.91	2.0	–
β-scission Cracking	0.22	0.66	1.0	0.8	0.77	1.9	46
$R_{\text{internal C-atoms}}$	30[a]	13[d]	45[b]	18[e]	–	5.0[c]	0.02[c]
$R_{\text{terminal C-atoms}}$	8.0[d]	–	5.0[e]	–	0.19[c]	–	–
(b)							
2-/1-Alkene ratio	3.4[f]	–	1.3[g]	–	–	–	–
β	0.27	0.06	0.10	0.16	0.59	0.17	0.001
γ_{Sk}	0.002	0.004	0.009	0.002	0.011	0.018	–
γ_C	0.003	0.005	0.013	0.010	0.009	0.018	1.3
γ_{MS}	–	–	–	0.03	–	0.04	–

[a] 2,3-Dimethylbutyl species.
[b] Triptyl species.
[c] Total rate of formation of trimethylpentyl isomers.
[d] Methylpentyl species and 2,2-dimethylbutyl species.
[e] Dimethyl-pentyl species.
[f] Ratio of 2-methyl-2-butene to the sum of 2-methyl-1-butene and 3-methyl-1-butene.
[g] Ratio of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene.

form linear butyl chains (Fig. 2a) and internal C-atoms in linear butenes to form isopentyl species (Fig. 3a). These methylation trends preserve the four-carbon backbone also present in triptane (Scheme 2) and account for the early steps in its preferential formation in DME and methanol homologation. We conclude that the relative stabilities of ion-pairs at methylation transition states lead to the selective formation of *n*-butyl species from propene and isopentyl species from *n*-butenes at rates faster than those of the intervening isomerization, β-scission, or hydrogen transfer of the respective alkoxides (as shown by the termination, isomerization, and β-scission probabilities in Table 1). The relative transition state stabilities for hydrogen transfer to *tert*-butoxide and methylation of isobutene leads to the preferential termination of isobutyl species as isobutane (β = 0.54; Table 1) after they form via β-scission of larger chains, but a fraction of these isobutyl species are incorporated into the chain growth path and ultimately appear as triptane via selective methylation of isobutene to isopentyl species (as shown in Fig. 3c and Scheme 4).

3.3. Propagation, termination, isomerization, and β-scission of C_5–C_7 species

Next, we examine the isotopologue distributions of C_{n+1} (Fig. 4) and C_4 (Fig. 5) products formed from ^{13}C-DME reactions with $^{12}C_n$-alkenes and the chain termination, isomerization, and β-scission probabilities (Table 2) of C_5–C_7 molecules involved as intermediates

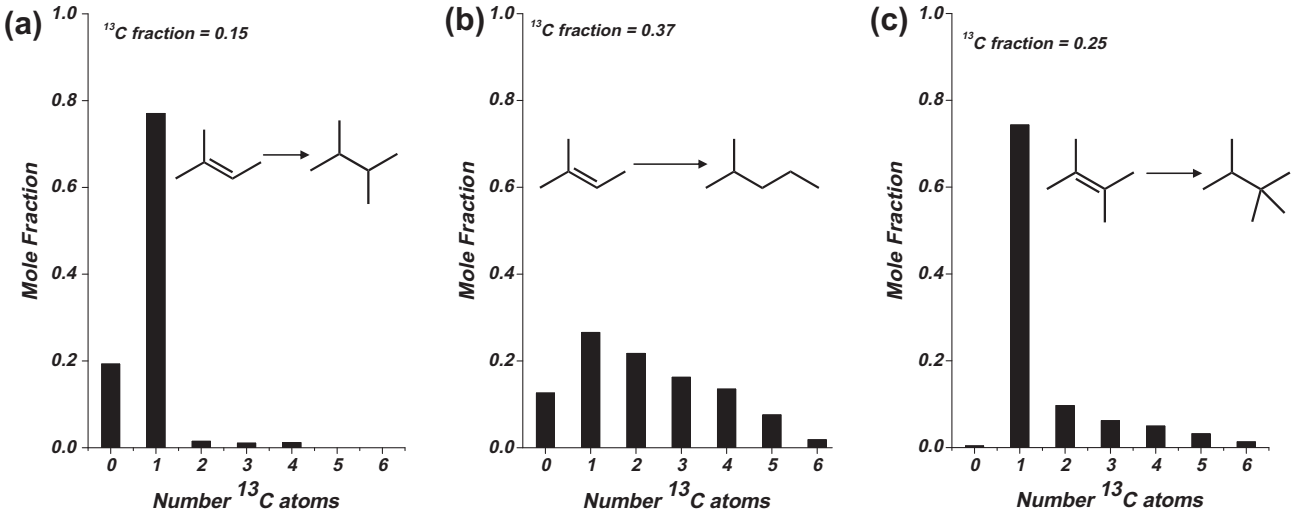


Fig. 4. Isotopologue distributions and ^{13}C-atomic fractions of (a) 2,3-dimethylbutane molecules and (b) 2-methylpentane molecules produced from co-reaction of ^{13}C-labeled dimethyl ether (78 kPa) with ^{12}C-2-methyl-2-butene (0.5 kPa) and (c) triptane molecules produced from co-reaction of ^{13}C-labeled dimethyl ether (78 kPa) with ^{12}C-2,3-dimethyl-2-butene (0.5 kPa). We use the 85 amu fragment of triptane as a surrogate for the parent ion, because the former appears in much higher concentrations in the mass spectrometer than the latter. Reactions conducted at 473 K on H-BEA (Si/Al = 12.5) at space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

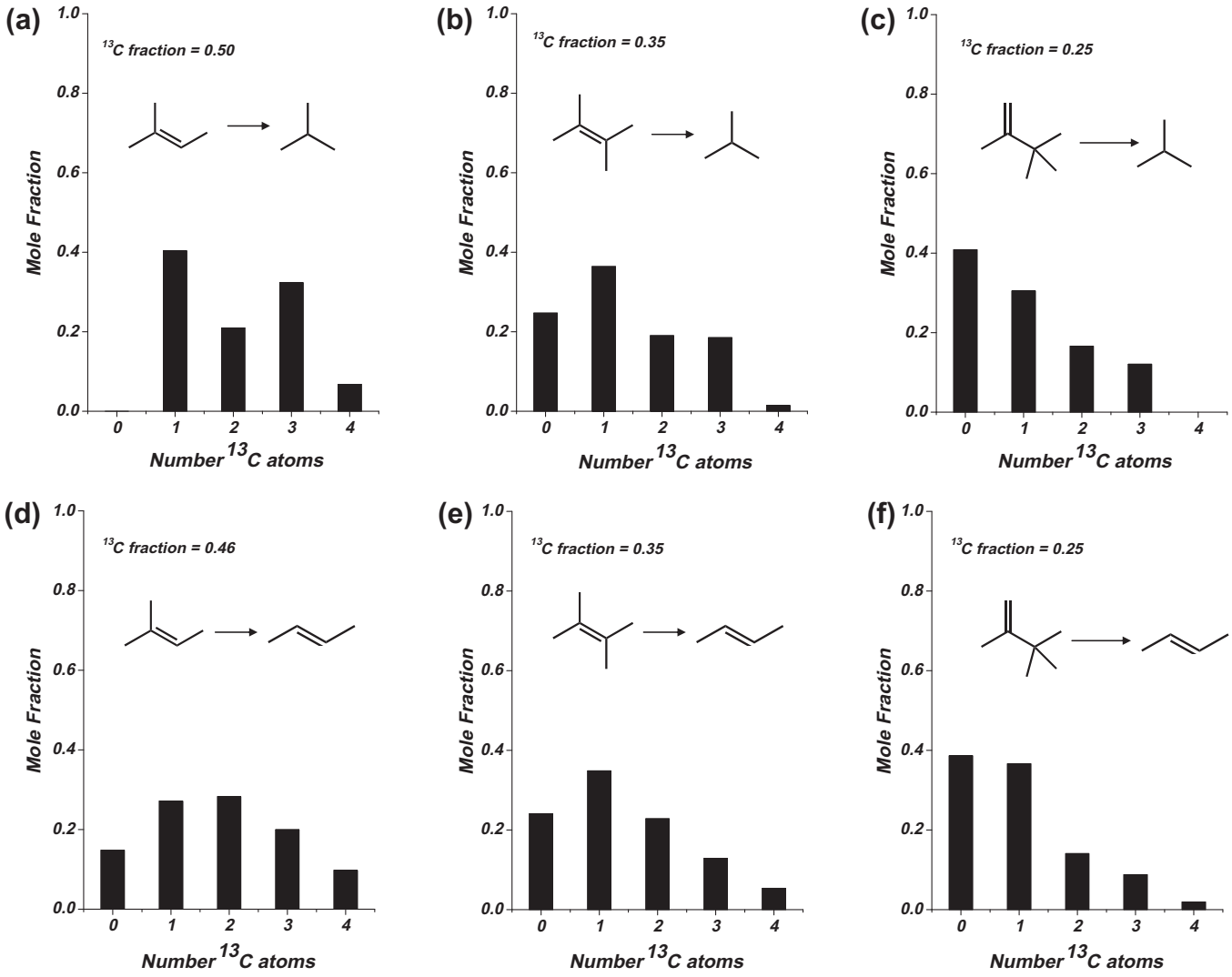


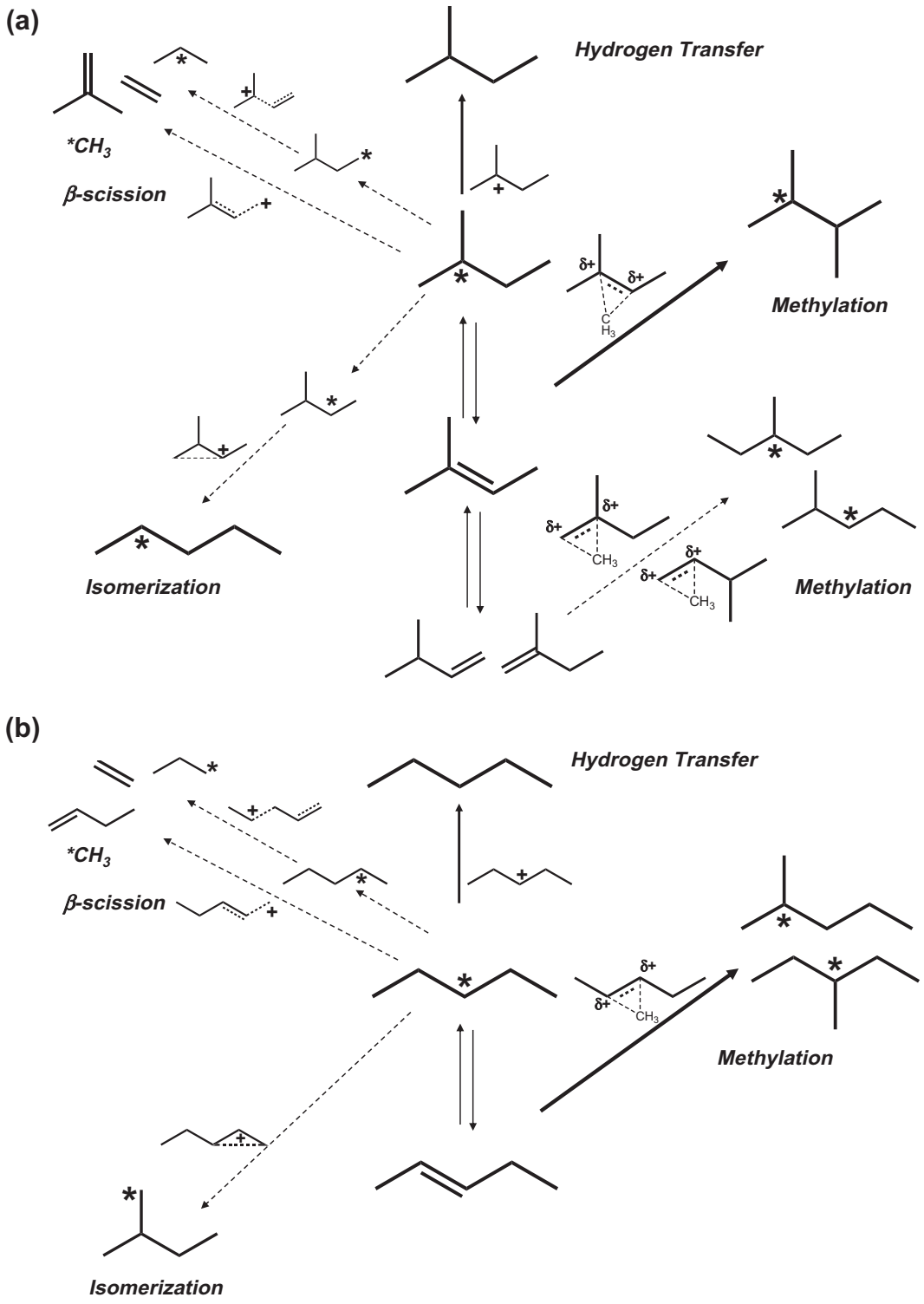
Fig. 5. Isotopologue distributions and ^{13}C-atomic fractions of isobutane (a–c) and trans-2-butene (d–f) molecules produced from co-reaction of ^{13}C-labeled dimethyl ether (78 kPa) with 0.5 kPa of ^{12}C-2-methyl-2-butene (panels a and d), ^{12}C-2,3-dimethyl-2-butene (panels b and e), and ^{12}C-triptene (panels c and f). Reactions conducted at 473 K on H-BEA (Si/Al = 12.5) and at a space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

along the chain growth path to triptane. Specifically, ^{13}C-DME (78 kPa) reactions with unlabeled 2-methyl-2-butene, 2,3-dimethyl-2-butene, or triptene (0.5 kPa) were used to probe how the stability of carbenium ion transition states in methylation reactions tends to preserve a linear four-carbon backbone along the chain growth path and ultimately form 2,3,3-trimethyl *sec*-butoxide; such species desorb via fast hydrogen transfer to form triptane before significant methylation of its triptene desorption products to form C_{8+} chains. We also examine rates of methylation, termination, isomerization, and β-scission (Table 2) for molecules that do not form along the methylation route to triptane (from ^{13}C-DME (78 kPa) reactions with 2-pentene, 2-methyl-2-pentene, and 2,4-dimethyl-2-pentene) to probe the reactivity of alkene molecules lacking the four-carbon backbone present in triptane.

3.3.1. Methylation of isopentenes, linear pentenes, 2,3-dimethylbutenes, methylpentenes, triptene, and dimethyl-pentenes

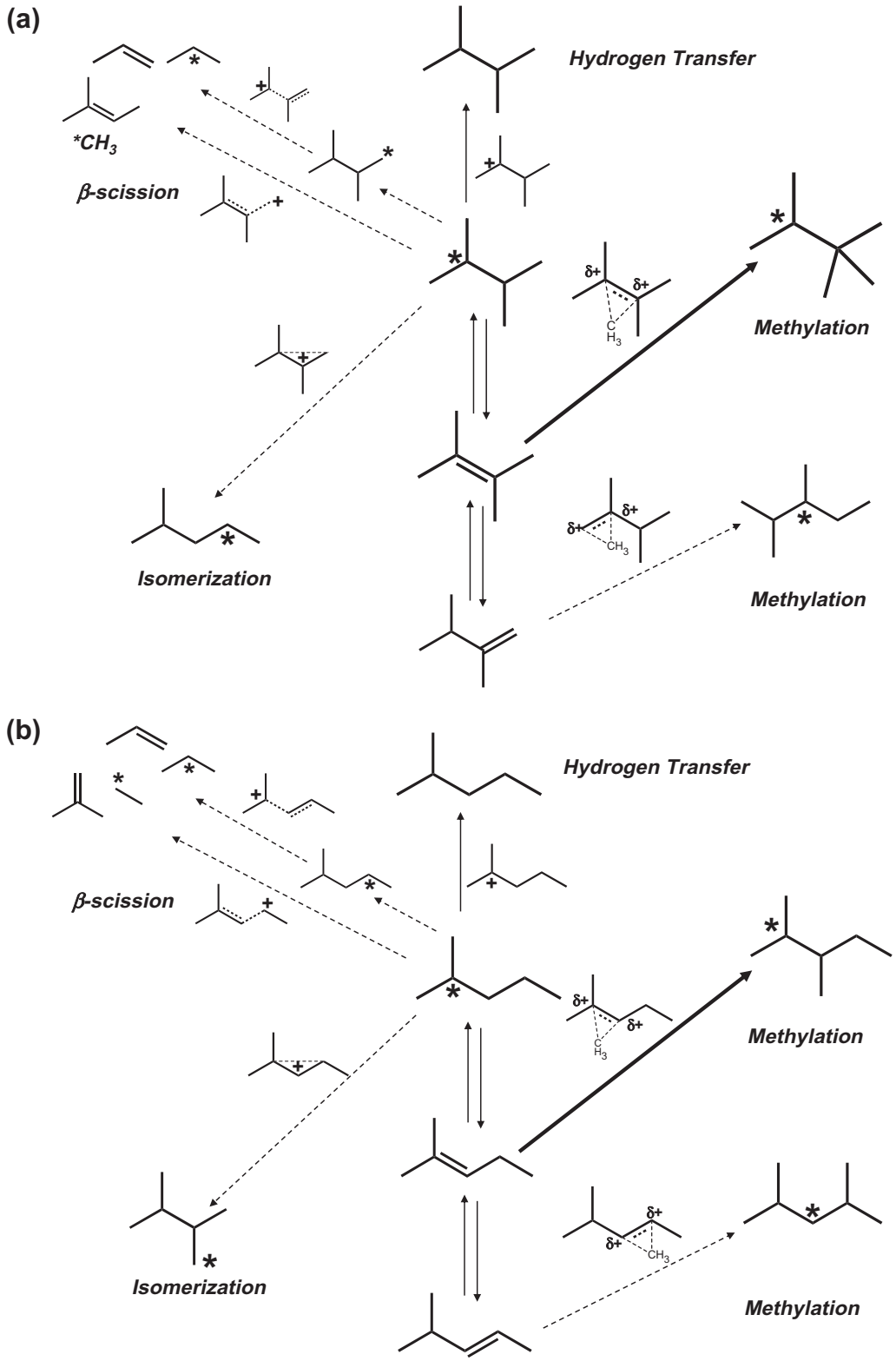
Reactions of ^{13}C-DME with ^{12}C-2-methyl-2-butene give the rates and position of methylation of isopentene intermediates shown in the previous section to form preferentially in methylation reactions of *n*-butenes and isobutene. The ratio of 2-methyl-2-butene to the sum of the 2-methyl-1-butene and 3-methyl-1-butene isomers was similar to that expected at equilibrium (3.4 vs. 3.6 [10]; Table 2) as a result of fast intramolecular hydride shift reactions. This equilibrated mixture of isopentenes can undergo methylation by ^{13}C-DME and subsequent deprotonation or hydrogen transfer (Scheme 5) at the secondary C-atom of 2-methyl-2-butene to form 2,3-dimethylbutyl species (2,3-dimethylbutane and 2,3-dimethylbutenes), at terminal C-atoms of 2-methyl-1-butene and 3-methyl-1-butene to form methyl-pentyl isomers (2-methylpentane, 3-methylpentane, 2-methylpentenes, 3-methylpentenes, and 4-methylpentenes), and at the tertiary C-atom of 2-methyl-2-butene to form 2,2-dimethylbutyl isomers (2,2-dimethylbutane and 4,4-dimethyl-1-butene).

The rate of formation of 2,3-dimethylbutyl species from mixtures of ^{13}C-DME with ^{12}C-2-methyl-2-butene (4.9 μmol [mol Al s]$^{-1}$; Table 2) is significantly larger than the combined rates of formation of methyl-pentyl and 2,2-dimethylbutyl species (0.9 μmol [mol Al s]$^{-1}$; Table 2), indicating that methylation occurs preferentially at the secondary C-atom in 2-methyl-2-butene instead of at the terminal or the tertiary C-atom of the other isopentene isomers (Scheme 5). Isotopologues of 2,3-dimethylbutane (and all 2,3-dimethylbutenes) predominantly consist of singly labeled species (0.77 mole fraction; Fig. 4a), indicating that



Scheme 5. Reaction pathways for (a) isopentyl species (isopentenes and 2-methyl *sec*-butoxide) and (b) *n*-pentyl species (*n*-pentenes and *sec*-pentoxide) in acid-catalyzed dimethyl ether homologation pathways. Methylation of isopentene to 2,3-dimethylbutyl species occurs faster than hydrogen transfer to 2-methyl *sec*-butoxide. Methylation of *n*-pentenes to methyl-pentyl species occurs faster than hydrogen transfer to *sec*-pentoxide. Isomerization and β-scission of both *sec*-pentoxide and 2-methyl *sec*-butoxide occur much more slowly than hydrogen transfer to these alkoxides and methylation of their alkenes.

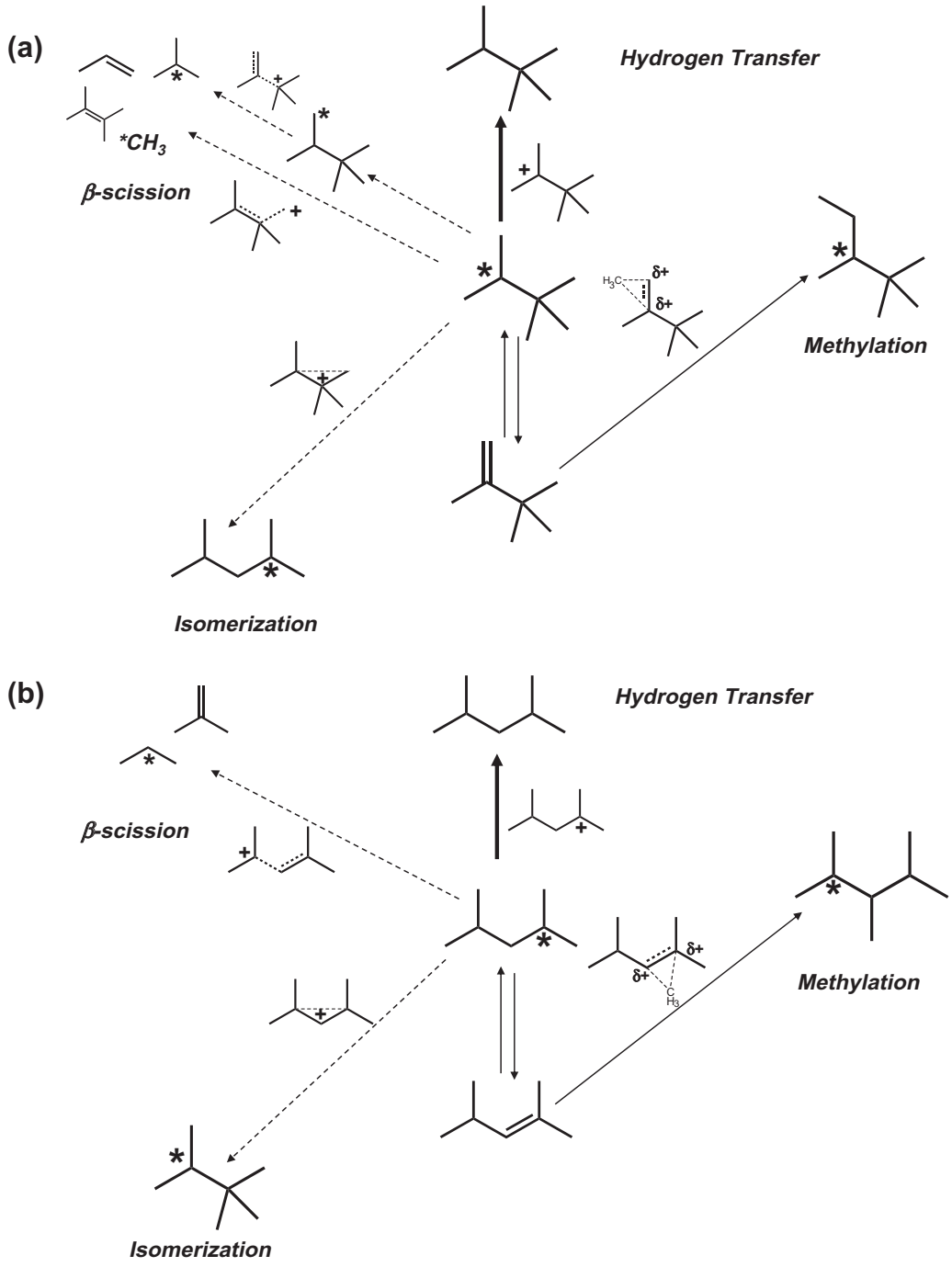
most of them form via a single methylation of 2-methyl-2-butene at its secondary carbon. In contrast, isotopologues of 2-methylpentane (and of all methyl-pentyl species) formed from ^{13}C-DME/^{12}C-2-methyl-2-butene mixtures show a much broader distribution (Fig. 4b) and a much larger ^{13}C content than 2,3-dimethylbutane (0.37 vs. 0.15). These data indicate that methylpentanes (and methyl-pentenes) form only after significant intramolecular rearrangements of larger chains that then undergo β-scission and subsequent methylation events. The preference for methylation of the tertiary–secondary C=C bond of 2-methyl-2-butene to form 2,3-dimethyl *sec*-butoxide reflects the greater stability of carbenium ion transition states with their charge at



Scheme 6. Reaction pathways for (a) 2,3-dimethylbutyl species (2,3-dimethylbutenes and 2,3-dimethyl *sec*-butoxide) and (b) methyl-pentyl species (methyl-pentenes and 2-methyl *sec*-pentoxide) in acid-catalyzed dimethyl ether homologation pathways. Methylation of 2,3-dimethylbutenes to triptyl species occurs faster than hydrogen transfer to 2,3-dimethyl *sec*-butoxide. Methylation of methyl-pentenes to dimethyl-pentyl species occurs faster than hydrogen transfer to 2-methyl *sec*-pentoxide. Isomerization and β-scission of both 2,3-dimethyl *sec*-butoxide and 2-methyl *sec*-pentoxide occur much more slowly than hydrogen transfer to these alkoxides and methylation of their alkenes.

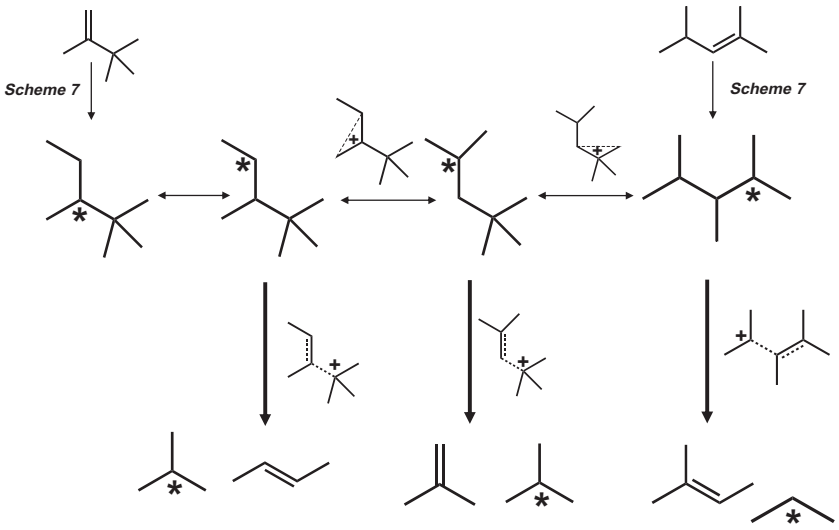
tertiary and secondary C-atoms [21], compared with those required for methylation of the primary–tertiary or primary–secondary C=C bonds in 2-methyl-1-butene or 3-methyl-1-butene, respectively, which retain some charge at a primary C-atom (Scheme 5).

Reactions of ^{13}C-DME with ^{12}C-2,3-dimethyl-2-butene allow estimates of the rate and position of methylation of the 2,3-dimethylbutenes that preferentially form by methylation of isopentenes. Fast intramolecular hydride shifts lead to ratios of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene at near equilibrium values (1.3



Scheme 7. Reaction pathways for (a) triptyl species (triptene and 2,3,3-trimethyl *sec*-butoxide) and (b) dimethyl-pentyl species (dimethyl-pentenes and 2,4-dimethyl *sec*-pentoxide) in acid-catalyzed dimethyl ether homologation pathways. Methylation of triptene to 3,4,4-trimethyl *sec*-pentoxide occurs much more slowly than hydrogen transfer to 2,3,3-trimethyl *sec*-butoxide. Methylation of methyl-pentenes to 2,3,4-trimethyl *sec*-pentoxide occurs faster than hydrogen transfer to 2,4-dimethyl *sec*-pentoxide. Isomerization and β-scission of both 2,3,3-trimethyl *sec*-butoxide and 2,4-dimethyl *sec*-pentoxide occur much more slowly than hydrogen transfer to these alkoxides and methylation of their alkenes.

vs. 1.5 [10]; Table 2). This equilibrated mixture of 2,3-dimethylbutenes can grow via methylation at internal tertiary carbons to form triptyls (triptane and triptene) or at terminal carbon atoms to form 2,3-dimethyl-pentyls (2,3-dimethylpentane, 2,3-dimethylpentenes, and 3,4-dimethylpentenes). Triptyls form from ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene reactants much faster (49 μmol [mol Al s]$^{-1}$; Table 2) than 2,3-dimethyl-pentyls (1.5 μmol [mol Al s]$^{-1}$; Table 2), indicating that methylation occurs preferentially at internal C-atoms in 2,3-dimethyl-2-butene instead of terminal C-atoms in 2,3-dimethyl-1-butene (Scheme 6). The predominant triptane isotopologues are singly labeled (Fig. 4c), consistent with their formation via a single methylation of 2,3-dimethylbutenes. This methylation position again preserves the four-carbon backbone, as in the case of the preferential methylation routes for *n*-butenes and isopentenes (Schemes 4 and 5). These data show that chain growth in acid-catalyzed homologation reactions involves the step-wise addition of C_1 species (derived from methanol and DME) to alkene intermediates at positions that selectively form



Scheme 8. β-Scission pathways for trimethylpentoxides that form from methylation of triptene and 2,4-dimethyl-2-pentene. β-Scission of 3,4,4-trimethyl *sec*-pentoxide and 2,4,4-trimethyl *sec*-pentoxide occurs more rapid than β-scission of 2,3,4-trimethyl *sec*-pentoxide.

the four-carbon backbone and then preserve it along the path to triptane shown in Scheme 2. This selective C_1 addition occurs because methylation of alkenes occurs at positions for which the required transition state involves the most stable carbenium ion. Such pathways lead to the formation of highly branched products, which involve transition states with more highly substituted carbenium ions than those involved in the formation of less branched isomers.

^{13}C-DME reactions with unlabeled 2-pentenes (mixture of cis and trans isomers) or 2-methyl-2-pentene were used to examine the rate and position of methylation for C_5–C_6 molecules that do not preferentially form along the DME homologation route to triptane. The rate of formation of methyl-pentyl species (2-methylpentane, 3-methylpentane, 2-methylpentenes, 3-methylpentenes, and 4-methylpentenes) is higher for 2-pentene than for 2-methyl-2-butene (13 vs. 8.0 μmol [mol Al s]$^{-1}$), and the rate of formation of dimethyl-pentyl species (2,3-dimethylpentane, 2,3-dimethylpentenes, and 3,4-dimethylpentenes) from 2-methyl-2-pentene was also larger than from 2,3-dimethyl-2-butene (18 vs. 5.0 μmol [mol Al s]$^{-1}$). These data show that methylation of C_5 and C_6 alkenes without the four-carbon backbone leading to triptane occurs selectively at internal C-atoms (or internal alkenes) to form larger homologs that also lack the required four-carbon backbone (Schemes 5b and 6b). We show below (Section 3.3.3) that hydrogen transfer to these alkoxides is slower than methylation of the corresponding alkenes, causing them to grow beyond C_7 chains.

^{13}C-DME reactions with ^{12}C-triptene or ^{12}C-2,4-dimethyl-2-pentene were used to examine the rate and position of methylation of these two C_7 alkene isomers to form C_8 molecules. 2,2,3-Trimethylpentane (formed via methylation of triptene at its terminal C-atom; Scheme 7) and 2,2,4-trimethylpentane (formed via methylation of triptene followed by methyl shifts; Scheme 8) were not detected in ^{13}C-DME reactions with ^{12}C-triptene (<10^{-3} μmol [mol Al s]$^{-1}$). The combined rates of formation of 2,3,4-trimethylpentane and 2,3,3-trimethylpentane (the other isomers formed by methyl shifts along the 2,2,3-trimethylpentane backbone) from ^{13}C-DME reactions with ^{12}C-triptene (0.19 μmol [mol Al s]$^{-1}$; Table 2) account for ~20% of all C_8 products (0.92 μmol [mol Al s]$^{-1}$). These low trimethylpentane formation rates suggest that trimethyl-pentoxides undergo rapid isomerization and β-scission prior to hydrogen transfer.

2,2,3- and 2,2,4-Trimethylpentane isomers were also undetected among the products formed from ^{13}C-DME/^{12}C-2,4-dimethyl-2-pentene reactants. The combined rates of formation of 2,3,4-trimethylpentane and 2,3,3-trimethylpentane in this case (5.7 μmol [mol Al s]$^{-1}$; Table 3) accounted for ~30% of the total C_8 formation rate (20 μmol [mol Al s]$^{-1}$). The higher 2,3,4-trimethylpentane selectivity within C_8 species from ^{13}C-DME/^{12}C-2,4-dimethyl-2-pentene (relative to ^{13}C-DME/^{12}C-triptene reactants) indicates that dimethyl-pentenes are methylated at internal C-atoms (or internal alkenes) to form 2,3,4-trimethylpentyl isomers that undergo slower β-scission reactions than 2,2,3- and 2,2,4-trimethylpentyl isomers (Schemes 7 and 8).

These data indicate that triptene is methylated to C_8 isomers that undergo rapid β-scission before hydrogen transfer, reflecting the formation of stable tertiary transition states in β-scission reactions of 2,2,3- and 2,4,4-trimethyl *sec*-pentoxides [40–44] formed via triptene methylation and subsequent methyl shifts (Schemes 7 and 8). 2,3,4- and 2,3,3-Trimethylpentanes are much more abundant among octane isomers than 2,2,4- and 2,2,3-trimethylpentanes, because the latter give more favorable β-scission transition states and are rapidly depleted via such reactions [40,41,44]. This rapid β-scission of C_8 species and its role in returning the fragments of larger molecules to the chain growth path and in the formation of isobutane are discussed in detail in Section 3.4.

Table 3
Termination probabilities (β) and ^{13}C-fractions within hexamethyl benzene (^{13}C-HMB) and C_{n+1} alkane ($^{13}C_{n+1}$) molecules for reactions between ^{13}C-labeled dimethyl ether (78 kPa) and unlabeled 2-methyl-2-butene (2M2B) or 2,3-dimetyl-2-butene (23DM2B) at 473 K on H-BEA. Reactions carried out between 2% and 7% total carbon conversions (DME and alkene) with >90% conversion of alkenes.

	Co-feed alkene			
	2M2B[a]	2M2B[b]	23DM2B[a]	23DM2B[b]
β	0.27	0.48	0.10	0.27
$^{13}C_{n+1}$	0.15[c]	0.14[c]	0.26[d]	0.20[d]
^{13}C-HMB	0.75	0.52	0.72	0.44

[a] 0.5 kPa alkene and at space velocity of 0.024 mol inlet gas [mol Al s]$^{-1}$.
[b] 3.7 kPa alkene and at a space velocity of 0.006 mol inlet gas [mol Al s]$^{-1}$.
[c] ^{13}C-fraction within 2,3-dimethylbutane molecules.
[d] ^{13}C-fraction within triptane molecules.

These ^{13}C-DME/^{12}C-alkene reaction data also allow accurate estimates of the total rates of methylation for each of the C_3–C_7 alkenes used (Tables 1 and 2); such methylation events include molecules that formed via multiple methylation events and even possible subsequent or intervening β-scission (Eq. (4)). The methylation rates for alkenes that contain only terminal C=C bond isomers, such as propene (37 μmol [mol Al s]$^{-1}$), isobutene (33 μmol [mol Al s]$^{-1}$), and triptene (34 μmol [mol Al s]$^{-1}$) are smaller than for alkenes that can form internal C=C bonds, such as *n*-butenes (53–68 μmol [mol Al s]$^{-1}$), isopentenes (56 μmol [mol Al s]$^{-1}$), and 2,3-dimethylbutenes (70 μmol [mol Al s]$^{-1}$). These trends reflect the greater stability of the more highly substituted methylation transition states of internal alkenes that avoid the involvement of terminal carbons, which form carbenium ions with primary character [21,46].

In general, the rates and selectivities (shown in the supporting information) derived from ^{13}C-DME/^{12}C-alkene experiments are consistent with two general features of methylation of alkenes by C_1 species derived from methanol or DME: (i) C_1 species add at the less substituted C-atom in the alkene C=C bond so as to preserve the more highly substituted C center (and the more stable carbenium ion at the transition state) and (ii) methylation is faster for molecules that can form internal alkenes (*n*-butenes, isopentenes, and 2,3-dimethylbutenes) than for molecules that can form only terminal alkanes (propene, isobutene, and triptene), because internal alkenes preclude the need to form carbenium ions with primary character in methylation transition states. As a result, high triptyl selectivities in acid-catalyzed DME homologation merely reflect the stability of ion-pairs at methylation transition states, which favor methylation positions that form molecules with four-carbon backbones and the higher methylation rates for triptyl precursors (*n*-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene) than for triptene. It also reflects the high termination probabilities via hydrogen transfer to alkoxides with tertiary carbon atoms, as we discuss next.

3.3.2. Hydrogen transfer to alkoxides derived from C_5–C_7 alkenes

In this section, we address the effect of co-fed alkene size on hydrogen transfer rates (Table 2a) to provide evidence for the role of alkoxide structure on hydrogen transfer rates and its consequences for chain termination probabilities and for selective triptane formation. We also show how the relative magnitude of methylation and hydride transfer rates (reflected in termination probabilities shown in Table 2b) of highly branched species combine to lead to their selective formation during C_1 homologation reactions involving methylation of alkenes and hydrogen transfer to the resulting alkoxides to form the respective alkanes.

Alkenes introduced with ^{13}C-DME protonate to form alkoxides that desorb either via deprotonation or hydrogen transfer in reactions concurrent with the methylation of such alkenes via reactions with adsorbed DME-derived C_1 species. The relative rates of methylation of alkenes and of hydrogen transfer to their respective alkoxides determine the probability that these growth pathways will be interrupted by the formation of less reactive alkanes. The rates of formation of the unlabeled alkane corresponding to the co-fed alkene gives accurate estimate rates of hydrogen transfer and termination probabilities (β; Eq. (5)) for C_5–C_7 species formed during DME and methanol homologation on solid acids.

Hydrogen transfer rates to alkoxides derived from C_5–C_7 alkenes along the chain growth path to triptane (21, 7.4, and 49 μmol [mol Al s]$^{-1}$ for 2-methyl *sec*-butoxide, 2,3-dimethyl *sec*-butoxide, and 2,3,3-trimethyl *sec*-butoxide, respectively; Table 2) are much larger than for propoxide (0.5 μmol [mol Al s]$^{-1}$, Table 1) and *n*-butoxide (5.8 μmol [mol Al s]$^{-1}$; Table 1). The higher hydrogen transfer rates to branched alkoxides relative to the corresponding linear alkoxide is also reflected in the higher rates of hydrogen transfer to *tert*-butoxide and 2-methyl *sec*-butoxide compared with *sec*-butoxide and *sec*-pentoxide (33 vs. 5.8 and 21 vs. 3.9 μmol [mol Al s]$^{-1}$; Tables 1 and 2). These hydrogen transfer rates and trends indicate that alkoxides with tertiary carbon centers form more stable tertiary carbenium ions upon cleavage of their C–O bonds than linear alkoxides with similar carbon number.

We note, however, that hydrogen transfer rates for 2,3-dimethyl *sec*-butoxide are not much larger than for *sec*-butoxide (7.4 vs. 5.8 μmol [mol Al s]$^{-1}$) and actually smaller than for 2-methyl *sec*-pentoxide (13 μmol [mol Al s]$^{-1}$; Table 2) in spite of the tertiary character in the hydrogen transfer transition state for 2,3-dimethyl *sec*-butoxide. This appears to reflect the high rates of 2,3-dimethyl-2-butene methylation (Table 2), which deplete it along the catalyst bed, with a consequent decrease in 2,3-dimethyl *sec*-butoxide concentrations available for hydrogen transfer. We also note that the rates of hydrogen transfer of *tert*-butoxide (33 μmol [mol Al s]$^{-1}$; Table 1) and 2,3,3-trimethyl *sec*-butoxide (38 μmol [mol Al s]$^{-1}$; Table 2) are larger than for 2-methyl *sec*-butoxide, 2,3-dimethyl *sec*-butoxide, and 2,4-dimethyl *sec*-pentoxide (21, 7.4, and 17 μmol [mol Al s]$^{-1}$; Table 2), in spite of the presence of tertiary carbenium ions in all of their hydrogen transfer transition states. These trends suggest that low methylation rates of isobutene and triptene (compared with isopentenes, 2,3-dimethylbutenes, and 2,4-dimethylpentenes; Tables 1 and 2) lead to large intracrystalline concentrations and thus higher surface concentrations of the corresponding alkoxides and higher rates of hydrogen transfer compared to other alkoxides that also form tertiary carbenium ion transition states in hydrogen transfer. Intracrystalline alkene gradients and their high reactivity and conversions make accurate estimates of hydrogen transfer rates difficult. In what follows, we circumvent such difficulties by comparing termination probabilities (β), which contain ratios of methylation and hydrogen transfer rates, which are both proportional to alkene concentrations and thus unaffected by alkene gradients that depend on the size and reactivity of individual alkenes.

Table 2 shows β values for molecules formed in DME homologation reactions. Triptyl (β = 0.59; Table 2) and isobutyl (β = 0.54; Table 2) species exhibit much higher termination probabilities compared with C_3–C_6 species that form along the chain growth path to triptane (0.01, 0.10, 0.27, and 0.10 for propyl, *n*-butyl, isopentyl, and 2,3-dimethylbutyl species, respectively; Tables 1 and 2). The high β values for isobutyl and triptyl species reflect the fast hydrogen transfer to their respective alkoxides, which involve tertiary carbenium ion transition states (Schemes 4b and 7a). The corresponding low rates of methylation of isobutene and triptene, which involve species with significant charge at primary carbons, also contribute to the high β values for isobutyl and triptyl species (Schemes 4b and 7a) and to the predominance of triptane and isobutane as DME homologation products (Fig. 1 in [9] and Figs. S1–S2 in the supporting information).

Low β values for propyl, *n*-butyl, isopentyl, and 2,3-dimethylbutyl species indicate that methylation of their alkenes is much faster than hydrogen transfer to their respective alkoxides. Preferential chain growth can arise from low hydrogen transfer rates (hydrogen transfer to propoxide; Table 1), high methylation rates (methylation of 2,3-dimethylbutenes; Table 2), or both (hydrogen transfer to *sec*-butoxide and methylation of *n*-butenes; Table 1). Propene methylation is slow (relative to larger alkenes) because, as in the case of isobutene and triptene, it contains only terminal C=C bonds; however, C_3 species preferentially methylate because hydrogen transfer to *sec*-propoxides (requiring secondary carbenium ions) is slower than methylation of propene (and also slower than hydrogen transfer to larger alkoxides) (Section 3.1; Scheme 3). In contrast, 2,3-dimethyl *sec*-butoxides form tertiary carbenium ions during hydrogen transfer, but the fast methylation of 2,3-dimethyl-2-butene (a tetra-substituted alkene) leads to low chain

termination probabilities (Scheme 6). *n*-Butyl species show low β values because the internal C=C bonds of *n*-butenes undergo rapid methylation (via *tert*-pentyl carbenium ions), while *sec*-butoxides undergo slow hydrogen transfer (via secondary carbenium ions) as shown in Scheme 4a. High β values reflect fast hydrogen transfer (tertiary alkoxides) and slow methylation (terminal alkene); conversely, low termination probabilities reflect stable transition states for methylation of alkenes with alkyl substituents at both C-atoms in the C=C bond (*n*-butenes, 2-methyl-2-butene, and 2,3-dimethyl-2-butene) and/or secondary carbenium ions in hydrogen transfer steps (*sec*-propoxide and *sec*-butoxide). High triptane selectivities (Fig. S1 in the supporting information) result, in turn, from chain growth intermediates (propyl, *n*-butyl, isopentyl, and 2,3-dimethylbutyl species) with low termination probabilities and with a sharp increase in termination probability at triptyls.

The guiding principles responsible for acid-catalyzed synthesis of triptane via C_1 homologation and relating molecular properties, carbenium ion transition state stabilities, and chain termination probabilities also apply to other molecules, such as those lacking the four-carbon backbone of triptane. ^{13}C-DME reactions with ^{12}C-2-pentenes, ^{12}C-2-methyl-2-pentene, and ^{12}C-2,4-dimethyl-2-pentene were carried out to determine β values for these species and contrast them with their more highly branched isomers and to confirm the effects of backbone structure on chain termination probabilities. The rate of hydrogen transfer to *sec*-pentoxide is ~5 five times smaller than for 2-methyl *sec*-pentoxide (3.9 vs. 21 μmol [mol Al s]$^{-1}$; Table 2), because the transition state for hydrogen transfer to latter (tertiary carbenium ion; Scheme 5a) is more stable than that of the former (secondary carbenium ion; Scheme 5b). The rate of methylation of *n*-pentenes, however, resembles that for isopentenes (59 vs. 56 μmol [mol Al s]$^{-1}$; Table 2), in spite of the difference in substitution along the backbone. As a result, β values are much smaller for *n*-pentyl than for isopentyl species (0.06 vs 0.27; Table 2), predominantly because of the effects of substitution on hydrogen transfer rates. We find that β values for species of a given carbon number are higher for the branched isomer compared to the linear isomer, because the effect of branching on transition state stability is greater for hydrogen transfer to their alkoxides than for methylation of the corresponding alkene.

The small β value for *n*-pentyl species indicates that their methylation to isohexyl species (Section 3.3.1; Scheme 6b) is faster than termination of *sec*-pentoxides to *n*-pentane causing them to preferentially grow, albeit not along the path to triptane. In what follows, we show that methy-pentyl species also rapidly methylate to dimethyl-pentyl species and then onto C_8 chains, which undergo subsequent isomerization and β-scission reactions to form isobutyl species that rapidly terminate as isobutane via hydrogen transfer to *tert*-butoxide. We conclude that the formation of *n*-pentyl species (and other molecules without the four-carbon backbone) do not decrease the triptane fraction within C_7 products, because they grow beyond C_7 and return some of their carbon atoms to chain growth pathways via β-scission reactions.

^{13}C-DME reactions with ^{12}C-2-methyl-2-pentene are used next to extend these conclusions about the effects of structure on β values to reactions of C_6 species. Both methyl-pentenes and 2,3-dimethylbutenes form highly substituted alkenes and, as a result, methylate at similar rates (66 and 70 μmol [mol Al s]$^{-1}$; Table 2). 2-Methyl *sec*-pentoxide and 2,3-dimethyl *sec*-butoxide also show similar hydrogen transfer rates (13 vs. 7.4 μmol [mol Al s]$^{-1}$; Table 2), consistent with the involvement of tertiary carbenium ions at hydrogen transfer transition states for the respective alkoxides. As a result, methyl-pentyl and 2,3-dimethylbutyl species have similar termination probabilities (0.16 vs. 0.10; Table 2) reflecting their similar structure and their respective ability to form highly substituted alkenes and tertiary alkoxides (Scheme 6). In contrast with methyl-pentyl and 2,3-dimethylbutyl species, isopentyl and triptyl species (discussed in previous and latter paragraphs, respectively) do not share these properties with their less branched isomers (*n*-pentyls and dimethyl-pentyls) and consequently exhibit higher β values.

The reactions of ^{13}C-DME with ^{12}C-2,4-dimethyl-2-pentene were used to explore backbone structure effects on β values for C_7 species. The ability of dimethyl-pentenes to form internal alkenes compared with triptene (which can only form a terminal alkene) leads to their higher rates of methylation (91 vs. 33 μmol [mol Al s]$^{-1}$; Table 2), which leads in turn to lower hydrogen transfer rates because of rapid depletion of dimethyl-pentenes and the corresponding alkoxide along the catalyst bed. As a result, dimethyl-pentyl species exhibit smaller rates of hydrogen transfer than triptyls (17 vs. 48 μmol [mol Al s]$^{-1}$; Table 2), even though both 2,3,3-trimethyl *sec*-pentoxide and 2,4-dimethyl *sec*-pentoxide form tertiary carbenium ions at their hydrogen transfer transition states (Scheme 7). These rates give, in turn, smaller β values for dimethyl-pentyl (0.17; Table 2) than triptyl (0.59; Table 2) species. We conclude that high triptyl selectivities among C_7 products reflect not only their favored formation via alkene methylation events (Section 3.3.1), but also their higher termination probabilities compared with less highly branched C_7 isomers.

The reaction pathways depicted in Scheme 2 and the termination probabilities for all species and intermediates involved (Tables 1 and 2) account for the remarkable isobutane and tiptane selectivities found in DME homologation on Brønsted acid sites. Triptyl and isobutyl species are preferentially detected among products because of their slow methylation (only terminal C=C bonds) and the fast hydrogen transfer to their tertiary alkoxides. Methylation positions dictated by the stability of the cationic transition states involved lead to the retention of the four-carbon backbone in triptane, but these species (*n*-butyl, isopentyl, and 2,3-dimethylbutyl) contain internal C=C bonds and methylate rapidly via highly substituted carbenium ions that cause them to terminate infrequently until they form triptane. Isobutane does not form via primary DME homologation pathways, but appears as a predominant product because of its preferential formation via β-scission of C_{8+} chains and the fast hydrogen transfer rates of *tert*-butoxide species formed by isobutene protonation. Intermediates that form via methylation of alkenes at less preferred positions forms species that methylate beyond C_7 molecules, because they can form C=C bonds at non-terminal positions and/or lack the tertiary carbons required for fast hydrogen transfer to form less reactive alkanes.

Hydrogen transfer involves the removal of a hydride ion from gas-phase molecules (alkanes or alkenes) to bound alkoxides [4,9,29–35]. The reactivity of the gas-phase donor depends on its C–H bond strength; as a result, branched alkanes and alkenes (and in particular unsaturated species with allylic C–H bonds) are more effective than linear molecules with C–H bonds only at primary or secondary carbons. These donors transform into more unsaturated species upon hydrogen transfer and can subsequently cyclize to stable arenes, such as hexamethylbenzene (HMB) [47,48], which are required to satisfy the overall stoichiometry of DME or methanol conversion to alkanes (according to Eq. (9)) [4,9,17]:

$$\underset{\text{Dimethyl Ether}}{[3n+12]CH_3OCH_3} \rightarrow 6\underset{\text{Alkanes}}{C_nH_{2n+2}} + \underset{\text{Hexamethyl-benzene}}{2C_6(CH_3)_6} + \underset{\text{Water}}{[3n+12]H_2O}. \quad (9)$$

In the next section, we examine the effect of alkene concentration in ^{13}C-DME/^{12}C-alkene reactants on β values and ^{13}C-fractions in HMB (Table 3) to address the molecular properties required of hydrogen

donors and their role in the rejection of carbon via the formation of stable unsaturated HMB molecules.

3.3.3. Hydrogen transfer to C_5–C_7 alkoxides from prevalent gas-phase hydrocarbons

Alkanes, alkenes, and even more unsaturated species can act as hydrogen donors during DME homologation catalysis; their contributions depend on their relative abundance and their reactivity, which depends on their C–H bond strength and their ability to accommodate a positive charge as they transfer a hydride to adsorbed alkoxides and ultimately become the bound alkoxide themselves. The heterolytic dissociation energies of C–H bonds (to form an organic cation and a hydride) [49,50] indicate that tertiary allylic C–H bonds in alkenes are able to donate an H^- more effectively than primary allylic C–H bonds in alkenes or tertiary C–H bonds of alkanes, making such species the most effective molecules among the H-donor pool available during DME homologation and the likely precursors to polymethylated arenes that provide the carbon rejection route in DME homologation on solid acids.

Reactions of ^{13}C-DME with ^{12}C-2-methyl-2-butene and ^{12}C-2,3-dimethyl-2-butene at different inlet pressures (0.5 and 3.7 kPa) were conducted to probe the effects of alkenes on hydrogen transfer and the composition of HMB molecules formed as homologation by-products. The β values for isopentyl and 2,3-dimethylbutyl species increased from 0.27 to 0.48 and 0.10 to 0.27, respectively (Table 3), as the alkene pressure increased from 0.5 to 3.7 kPa. These effects of alkene pressure on β indicate that alkenes influence hydrogen transfer rates more strongly than methylation rates, even though both rates are expected to depend linearly on alkene pressures [24,30–33], suggesting that alkenes act as more effective H-donors than the pool of molecules that carry out such reactions during DME homologation without added alkenes. Hydrogen transfer from these alkenes to the prevalent alkoxides can lead to the formation of stable tertiary allylic cations and to conjugated dienes upon deprotonation of the unsaturated alkoxide analogs of these cations. Furthermore, the carbenium ion transition states involved in hydrogen transfer from 2,3-dimethylbutenes and isopentenes are likely to be more stable than those involved in hydrogen transfer from the prevalent tertiary alkanes (isobutane, triptane, isopentane, and 2,3-dimethylbutane). We conclude from the strong effects of 2,3-dimethyl-2-butene and 2-methyl-2-butene pressure on termination probabilities that alkenes with tertiary allylic H-atoms serve as preferred hydrogen donors because of their weak C–H bonds and stable carbenium ions; the unsaturated products of their hydrogen transfer reactions serve as intermediates in the formation of dienes and arenes required to balance the stoichiometry of DME conversion to alkanes.

The effects of alkene pressure on the ^{13}C-atomic fraction within HMB molecules formed in ^{13}C-DME reactions in the presence of ^{12}C-2-methyl-2-butene or ^{12}C-2,3-dimethyl-2-butene can be used to probe the probable precursors of polymethylated arenes. The ^{13}C-fraction in HMB molecules formed from ^{13}C-DME/^{12}C-2-methyl-2-butene and ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene reactants decreased from 0.75 to 0.52 and 0.72 to 0.44 (Table 3), respectively, as each alkene inlet pressure increased from 0.5 to 3.7 kPa. The ^{13}C-fraction in HMB decreased with increasing alkene pressure to a greater extent than in 2,3-dimethylbutane formed from ^{13}C-DME/^{12}C-2-methyl-2-butene (0.15–0.14; Table 3) or in triptane from ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene (0.26–0.20; Table 3). These data indicate that the co-fed alkene is more effectively converted to HMB via hydrogen transfer cyclization reactions than to larger alkanes via methylation reactions. We conclude from these data that alkenes are effective hydrogen donors involved in chain termination via hydrogen transfer. In doing so, these alkenes convert to more unsaturated species with even weaker allylic C–H bonds in diene and triene structures, which can then cyclize via homogeneous or acid-mediated Diels–Alder reactions to form arenes through intermolecular pathways that eliminate the need for intramolecular ring closure steps [47,48,51–59].

3.3.4. Isomerization of alkoxides derived from C_5–C_7 alkenes

C_5–C_7 alkoxides along the chain growth path to triptane (2-methyl *sec*-butoxide, 2,3-dimethyl *sec*-butoxide, and 2,3,3-trimethyl *sec*-butoxide) can undergo skeletal isomerization and, in doing so, disrupt their backbone structure before methylation occurs. In this section, we address the isomerization reactivity of alkoxides present as bound products of methylation steps along the chain growth path to triptane using measurements of the chemical and isotopic composition of products (Table 2) formed in ^{13}C-DME reactions with ^{12}C-alkenes.

2-Methyl *sec*-butoxide skeletal isomerization rates were measured from the formation rates of unlabeled *n*-pentane from ^{13}C-DME/^{12}C-2-methyl-2-butene mixtures. In the case of 2,3-dimethyl *sec*-butoxide and 2,3,3-trimethyl *sec*-butoxide isomerization, rates were measured from the formation rates of unlabeled 2-methylpentane and 3-methylpentane from ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene and of unlabeled 2,3-dimethylpentane and 2,4-dimethylpentane from ^{13}C-DME/^{12}C-triptene, respectively. The ratio of skeletal isomerization rates to combined rates of methylation and hydrogen transfer is reported here as the skeletal isomerization probability (γ_{sk}; Eq. (6)). Low values of γ_{sk} for isopentyl, 2,3-dimethylbutyl, and triptyl species (0.002–0.011; Table 2) indicate that the skeletal isomerization rates for these C_5–C_7 alkoxides are much smaller than the rates of hydrogen transfer to their respective alkoxides and methylation of their respective alkenes. The values of γ_{sk} are much smaller than unity for all relevant species, indicating that backbone rearrangements occur infrequently along chain growth to triptane, because the skeletal isomerization of the relevant alkoxides involve the formation of primary and secondary cyclopropyl carbenium ion transition states [30,36–39] that are much less stable than the tertiary cationic transition states involved in methylation of the respective alkenes and hydrogen transfer to the respective alkoxides (as shown in Schemes 5–7). The higher isomerization probabilities of 2,3-dimethylbutyl (0.009) and triptyl species (0.011) compared with isopentyl species (0.002) reflects the involvement of more stable secondary carbenium ions (Schemes 6 and 7); however, even for these alkoxides, isomerization remains a minority reaction path compared with methylation and hydrogen transfer. Therefore, molecules with four-carbon backbones are kinetically protected against deviations from their path to triptane because of the nature of their cationic transition states relative to those involved in the methylation and hydrogen transfer steps responsible for the growth and termination of chains.

Acid-catalyzed isomerization also occurs when methyl groups in alkoxides shift along their backbone; the detection of these pathways from ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene and ^{13}C-DME/^{12}C-trans-2-butene reactants requires that we identify the location of DME-derived ^{13}C-atoms within triptane and isopentane products formed via single methylation events of ^{12}C-2,3-dimethyl-2-butene and ^{12}C-trans-2-butene, respectively, because methyl shift isomerization in isopentyl and triptyl species does not change their molecular identity.

The ^{13}C-fractions within the *tert*-butyl and *iso*-propyl mass fragments of the triptane molecules formed from ^{13}C-DME/^{12}C-2,3-dimethyl-2-butene reactants were 0.199 and 0.203, respectively. These values are slightly higher than those expected for fast and equilibrated methyl shift along the backbone of singly labeled triptane molecules (0.15 and 0.13 for *tert*-butyl and *iso*-propyl, respectively) as a result of contributions from more highly labeled triptane molecules to these ^{13}C-fractions. The ratio (*tert*-butyl to *iso*-propyl) of these experimental fractions (0.98) is slightly smaller

than expected from ^{13}C-atoms located with equal probability at all methyl groups in *tert*-butyl and *iso*-propyl groups (1.13), but nevertheless consistent with fast methyl shifts along the 2,3,3-trimethyl *sec*-butoxide backbone. The absence of methyl shifts would have placed ^{13}C only at the *tert*-butyl end as a result of methylation of ^{12}C-2,3-dimethyl-2-butene with ^{13}C-DME. These data show that methyl shifts along the hydrocarbon backbone of 2,3,3-trimethyl *sec*-butoxide are fast relative to hydrogen transfer to this alkoxide and methylation of triptene, as for hydride shifts leading to double-bond isomerization but not for isomerizations that change the length of the hydrocarbon backbone. These marked differences in rate between methyl shift and skeletal isomerization reflect the more stable carbenium ion transition states required for shifting methyls along the backbone relative to steps that lengthen or shorten hydrocarbon backbones in alkoxides [38]. These fast methyl shifts along the backbone of triptane form the same molecule because the methyl shift occurs along the plane of symmetry in these molecules and therefore does not affect isomer selectivities within C_7 hydrocarbons.

The ^{13}C-fractions within the *iso*-propyl (0.33) and ethyl (0.47) mass fragments of singly labeled isopentane formed from ^{13}C-DME/^{12}C-trans-2-butene are larger than expected for equilibrated methyl shift along the alkoxide backbone (0.22 and 0.17 for *iso*-propyl and ethyl mass fragments respectively), and their ratio (*iso*-propyl to ethyl) of ^{13}C-fractions (0.70) is also smaller than expected for fast methyl shifts (1.3). The presence of ^{13}C-atoms in the ethyl fragment indicates that methyl shift does occur along 2-methyl *sec*-butoxide, because in the absence of such shifts, methylation of ^{12}C-trans-2-butene places ^{13}C-atoms exclusively on the *iso*-propyl end of isopentane. The slower methyl shifts in 2-methyl *sec*-butoxide compared with 2,3,3-trimethyl *sec*-butoxide may reflect the requirement for secondary alkoxides (3-methyl *sec*-butoxide) and carbenium ion transition states for isopentane instead of the tertiary alkoxides and transition states required for methyl shift in triptane.

Methyl shifts in 2,3-dimethylbutane are also slower than chain growth and termination reactions. 2,2-Dimethylbutane is the C_6 isomer favored by thermodynamics at 473 K (2.9 ratio of 2,2-dimethylbutane to 2,3-dimethylbutane [10]) and would preferentially form if methyl shifts were fast. The formation of 2,2-dimethylbutane from ^{13}C-DME/^{12}C-alkene reactants, however, is negligible (rates $<10^{-3}$ μmol [mol Al s]$^{-1}$; Section 3.3.1 and supporting information). Methyl shift isomerization of 2,3-dimethylbutane to 2,2-dimethylbutane requires the formation of a species with an unfavorable quaternary carbon atom and a secondary carbenium ion (2,2-dimethyl *sec*-butoxide), and thus, is unlikely to occur at rates comparable to methylation of 2,3-dimethylbutene and hydrogen transfer to 2,3-dimethyl *sec*-butoxide (which involve tertiary carbenium ion transition states). The methyl shift of triptyl intermediates, which also requires formation of quaternary carbon, occurs rapidly (in contrast to methyl shift along 2,3-dimethylbutyl backbones) apparently because both the initial and final states are tertiary alkoxides. This rapid methyl shift along the triptyl chains may also occur because triptane is the first species along the methylation path that can undergo simultaneous methyl shift (during methylation of 2,3-dimethyl-2-butene) via a cyclo-butyl carbenium ion that delocalizes charge more effectively than the cyclo-propyl cation envisioned as the 2,3-dimethyl-2-butene methylation transition state.

The ratio of the rate of methyl shifts along the backbone to the combined rates of hydrogen transfer and methylation represents the methyl shift probability (γ_{MS}; Eq. (8)). These values were determined for C_6 and C_7 species that do not form along the preferred chain growth path to triptane and which, in contrast with triptyl species, form chemically distinct species upon methyl shifts, from the rate of formation of unlabeled 3-methylpentane from ^{13}C-DME/^{12}C-2-methyl-2-pentene mixtures and of unlabeled 2,3-dimethylpentane from ^{13}C-DME/^{12}C-2,4-dimethyl-2-pentene reactants. The rates of methyl shift along the methyl-pentyl and dimethyl-pentyl backbones are much slower than the rates of methylation of their respective alkenes and hydrogen transfer to their respective alkoxides (γ_{MS} = 0.03 and 0.04 for methyl-pentyl and dimethyl-pentyl species, respectively; Table 2). These low γ_{MS} values are consistent with the non-equilibrium ratios of 2-methylpentane to 3-methylpentane (greater than 3.0 vs. equilibrium value of 2.2 at 473 K [10]) and 2,4-dimethylpentane to 2,3-dimethylpentane (greater than 1.3 vs. equilibrium value of 0.24 at 473 K [10]) formed during DME homologation (see supporting information). These γ_{MS} values also reflect the less stable nature of the cyclopropyl carbenium ion transition states required for methyl shifts compared with the tertiary cationic transition states involved in both hydrogen transfer to their alkoxides and methylation of their alkenes. The γ_{MS} values for these methyl-pentyl and dimethyl-pentyl chains, however, are higher than their respective γ_{Sk} values (0.002 and 0.018 for methyl-pentyl and dimethyl-pentyl species, respectively), consistent with the more stable carbenium ion transition states required for shifting methyls along the backbone than those required for lengthening or shortening hydrocarbon backbones in alkoxides [38].

The lower rates of methyl shift along the backbones of these five-carbon backbone molecules relative to that along the backbone of triptyl chains reflects the requirement of secondary alkoxides and carbenium ion transition states for the former compared with tertiary species for the latter. These low rates of methyl shift also reflect the formation of chemically distinct species with different properties for methylation of their respective alkenes and hydrogen transfer to their respective alkoxides. These methyl shifts, however, are inconsequential to triptane selectivities within C_7 species, because the reactants and products in these isomerization steps tend to be selectively removed from the C_7 pool by fast chain growth (Sections 3.3.1–3.3.2) and subsequent β-scission (Sections 3.3.5 and 3.4) reactions.

3.3.5. β-Scission reactions of alkoxides derived from C_5–C_7 alkenes

β-Scission of C_5–C_7 alkoxides along the chain growth path to triptane can also disrupt their linear four-carbon backbones before methylation of the corresponding alkenes or hydrogen transfer steps that desorb these alkoxides as alkanes. We measure here β-scission rates of these alkoxides (Table 2a) and compare them to rates of hydrogen transfer to the corresponding alkoxides and methylation of alkenes formed by desorption of these alkoxides (Table 2b) to probe the effects of chain structures on these rates and the role β-scission reactions in the selectivity patterns observed in DME homologation reactions.

The rates of β-scission of 2-methyl *sec*-butoxide, 2,3-dimethyl *sec*-butoxide, and 2,3,3-trimethyl *sec*-butoxide (the C_5–C_7 alkoxides for alkenes on the methylation path to triptane) were determined from the respective rates of formation of unlabeled β-scission products in reactions of ^{13}C-DME with ^{12}C-2-methyl-2-butene, ^{12}C-2,3-dimethyl-2-butene, or ^{12}C-triptene. The ratio of the rates of β-scission of these alkoxides to the combined rates of hydrogen transfer to these alkoxides and methylation of their respective alkenes represents the β-scission probability (γ_C; Eq. (7)). The small values of γ_C for these C_5–C_7 species (0.003–0.013; Table 2) indicate that they undergo methylation and hydrogen transfer at much higher rates than for β-scission reactions. These low β-scission rates reflect the involvement of unstable primary carbenium ion transition states and alkoxides for β-scission pathways in molecules with the four-carbon backbone structure of triptane [40–44] (Schemes 5–7). Such molecules are kinetically protected against deviations from the path to triptane via β-scission, because the structure of the alkene-derived alkoxides leads

to less stable transition states for β-scission than for stable tertiary cationic transition states involved in alkene methylation or hydrogen transfer to the corresponding alkoxide.

The rates of β-scission of C_5–C_7 alkoxides that do not lie along the chain growth path to triptane (*sec*-pentoxide, 2-methyl *sec*-pentoxide, and 2,4-dimethyl *sec*-pentoxide) were measured from the respective rates of formation of unlabeled C_3–C_4 species from ^{13}C-DME mixtures with ^{12}C-1-pentene, ^{12}C-2-methyl-2-pentene, or ^{12}C-2,4-dimethyl-2-pentene; these rates were used to determine β-scission probabilities for these species. The small γ_C values (Table 2) measured for *n*-pentyl (0.005) and methyl-pentyl (0.010) species are similar to those for their more highly branched isomers (isopentyl (0.003) and 2,3-dimethylbutyl (0.013) species) and reflect the less stable primary carbenium ion transition states required for β-scission of *sec*-pentoxide and 2-methyl *sec*-pentoxide compared with the tertiary carbenium ions involved as transition states in hydrogen transfer to these alkoxides and methylation of the respective alkenes (Schemes 5b and 6b). The γ_C value for dimethyl-pentyl species (0.018) is slightly larger than for triptyl species (0.009), because of the greater stability of the secondary carbenium ion formed during β-scission pathways of C_7 alkoxides with five-carbon backbones compared with the primary carbenium ions and alkoxides required for β-scission in 2,3,3-trimethyl *sec*-butoxide (Scheme 7) [40]. This γ_C value for dimethyl-pentyl species, however, remains much smaller than unity, indicating that methylation of 2,4-dimethylpentenes and hydrogen transfer to 2,4-dimethyl *sec*-pentoxide occur much more frequently than β-scission of 2,4-dimethyl *sec*-pentoxide.

The small γ_{Sk} and γ_C values for C_5–C_7 molecules along the chain growth pathway to triptane preserve their four-carbon backbone, a structural feature that leads to much more stable carbenium ion transition states for methylation of their alkenes and hydrogen transfer to their alkoxides than for isomerization and β-scission of their alkoxides. C_5–C_7 molecules that lack the structure necessary for triptane also have low γ_{Sk} and γ_C values, but such molecules are removed from chain growth paths via alkene methylation to C_{8+} chains with facile β-scission paths. In the next section, we show how such β-scission pathways provide a kinetic "cleansing" mechanism that corrects deviations from the path to triptane.

3.4. Isobutane formation via β-scission of trimethylpentane isomers

The binomial isotopologue distributions of all isobutane molecules (Fig. 2b, Fig. 3b and d, and Fig. 5a–c) formed in reactions of ^{13}C-DME with ^{12}C-alkenes suggest that they form via β-scission of larger molecules that have undergone sequential methylation and intramolecular isomerization reactions. The low observed rates of formation of C_8 alkanes from ^{13}C-DME/$^{12}C_7$-alkene reactants (Section 3.3.1; Table 2) also indicate that methylation of triptene, which occurs infrequently in view of its high termination probability (Section 3.3.2), leads to C_8 chains that can undergo rapid β-scission and are therefore removed from the C_{8+} products. We return now to this specific issue and provide evidence for the selective formation of isobutyl species via facile β-scission of C_8 molecules, which form via the methylation of C_7 alkenes with DME-derived species. We report the rate of appearance of ^{12}C-atoms in C_4 products from ^{13}C-DME reactions with $^{12}C_n$-alkenes of varying size (n = 3–8; Fig. 6) and also examine the chemical and isotopic nature of the products (Figs. 7 and 8) formed from ^{13}C-DME reactions in the presence of ^{12}C-3,4,4-trimethyl-2-pentene, the isomer preferentially formed by methylation of triptene.

The contribution of the co-fed alkene to the products formed in ^{13}C-DME/^{12}C-alkene reactions can be determined from the rate of appearance of ^{12}C-atoms in each product molecule. Fig. 6 shows how the rates of incorporation of the alkene-derived ^{12}C-atoms into molecules that form along the chain growth path to triptane (as well as into isobutyl species) depend on the size of co-fed alkenes (involved in the preferred homologation path: propene, trans-2-butene, 2-methyl-2-butene, 2,3-dimetyl-2-butene, triptene, and 3,4,4-trimethyl-2-pentene). The alkene contributions to the rate of formation of triptane increased monotonically with increasing alkene size from propene (C_3) to 2,3-dimethyl-2-butene (C_6) (Fig. 6a), because the number of methylation events required to form 2,3,3-trimethyl *sec*-butoxide and desorb it as triptane via hydrogen transfer decreases with increasing alkene size. As for triptane products, the rate of ^{12}C appearance in isobutyl and *n*-butyl species (alkanes and alkenes) increases monotonically with alkene size, consistent with larger alkenes returning their carbon atoms more rapidly to C_4 products than smaller homologs. The

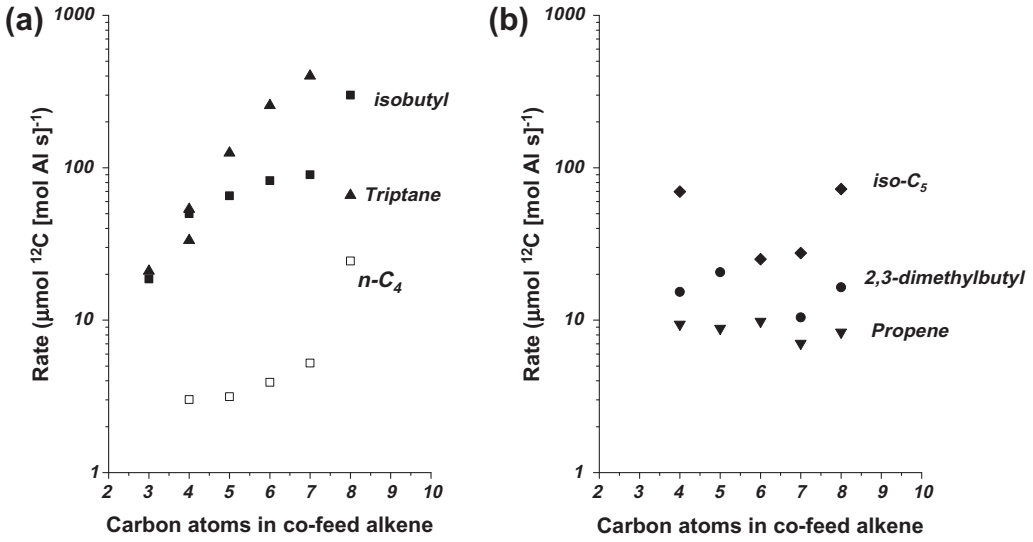


Fig. 6. Rate of formation (^{12}C-atomic basis) of (a) triptane (▲), isobutyl (■), and linear C_4 (□) species and (b) propene (▼), iso-C_5 (♦), and 2,3-dimethylbutyl (●) species for reactions between ^{13}C-labeled dimethyl ether (78 kPa) and 0.5 kPa unlabeled propene, trans-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, triptene, or 3,4,4-trimethyl-2-pentene at 473 K on H-BEA (Si/Al = 12.5). Reactions conducted at 473 K and space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

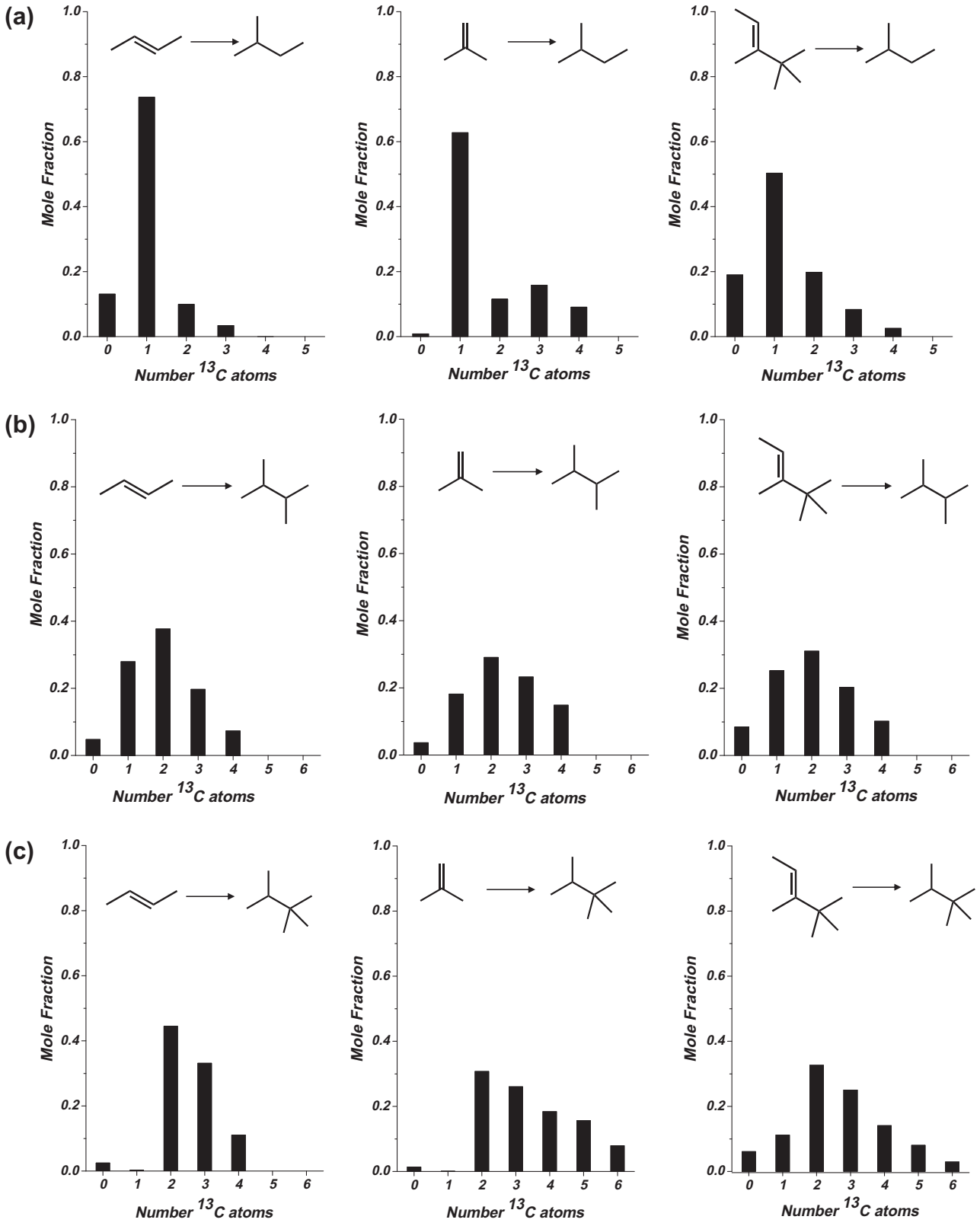


Fig. 7. Isotopologue distributions of (a) isopentane, (b) 2,3-dimethylbutane, and (c) triptane molecules produced from reactions between ^{13}C-labeled dimethyl ether (78 kPa) and 0.5 kPa unlabeled trans-2-butene (left), isobutene (middle), or 3,4,4-trimethyl-2-pentene (right) at 473 K on H-BEA (Si/Al = 12.5). We use the 85 amu fragment of triptane as a surrogate for the parent ion, because the former appears in much higher concentrations in the mass spectrometer than the latter. Reactions conducted at 473 K and space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

formation of unlabeled linear C_4 molecules reflects the β-scission of 3,3,4-trimethyl *sec*-pentoxide (the octane isomer formed via methylation of triptene as shown in Scheme 7), which forms *tert*-butoxide and *n*-butene (Scheme 8). These trends reflect the propensity for growth beyond triptane to form molecules of size and structure conducive to facile β-scission pathways.

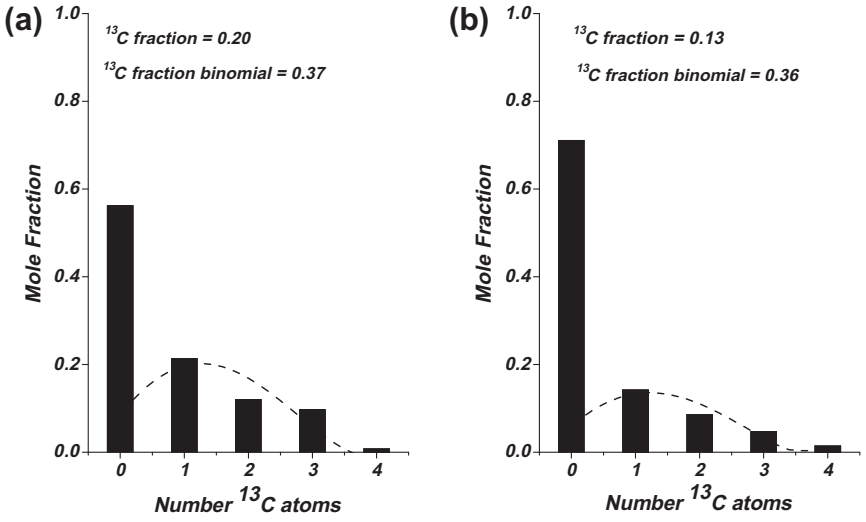


Fig. 8. Isotopologue distributions of (a) isobutane and (b) linear C_4 species produced from reactions between ^{13}C-labeled dimethyl ether (78 kPa) and ^{12}C-3,4,4-trimethyl-2-pentene (0.5 kPa) at 473 K on H-BEA (Si/Al = 12.5). Reactions conducted at 473 K and space velocity of 0.025 mol inlet gas [mol Al s]$^{-1}$ with >90% alkene conversion and less than 5% total carbon conversion (DME and alkene).

The rates of ^{12}C appearance in isobutyl and linear C_4 species increased sharply for the case of added 3,4,4-trimethyl-2-pentene relative to other added alkenes (Fig. 6a). In contrast to the rates of C_4 species, the rates of formation (^{12}C-atomic basis) of propene, isopentane, and 2,3-dimethylbutane are similar for co-feed alkenes of increasing size (less than a factor of 3 difference among rates; Fig. 6b). These similar rates show that the increases in the rates of formation (^{12}C-atomic basis) of C_4 species are a result of β-scission of C_8 molecules instead of an increase in the concentration of ^{12}C-atoms in the reactant inlet stream. In each ^{13}C-DME/^{12}C-alkene reaction, the rate of ^{12}C appearance in isobutane and isobutene was more than an order of magnitude higher than that in *n*-butane and *n*-butene (Fig. 6a), and the isobutene to isobutane ratio (less than 0.13) was much lower than the *n*-butene (1-butene, trans-2-butene, and cis-2-butene) to *n*-butane ratio (greater than 7.6). This preference for isobutane within C_4 hydrocarbons reflects the much lower rates of methylation of isobutene relative to hydrogen transfer to *tert*-butoxide ($\beta = 0.54$; Table 1) compared with the higher rates of *n*-butene methylation relative to hydrogen transfer to *sec*-butoxide ($\beta = 0.08$; Table 1). This higher β value explains the high selectivity to isobutane from β-scission of C_8 chains, even though β-scission of the octane isomers from triptene methylation also produces *n*-butyl species (Scheme 8).

Fig. 6a also shows a decrease in the rate of ^{12}C appearance in triptane molecules for the case of added 3,4,4-trimethyl-2-pentene relative to other added alkenes. The rates of ^{12}C appearance in triptane (as well as isopentane and 2,3-dimethylbutane) would increase for the case of added 3,4,4-trimethyl-2-pentene (relative to other added alkenes, as they do for isobutane) if C_8 chains cracked to smaller species that then entered chain growth to triptane. The decrease in the rate of formation of triptane (on a ^{12}C-basis), however, indicates that once chains methylate to C_8 molecules, they undergo β-scission with the resulting species terminating as isobutane at much higher probabilities than methylating to triptane. We therefore conclude that high concentrations of isobutane from DME and methanol homologation results from facile β-scission of C_8 molecules that form via methylation of C_7 alkenes (Schemes 7 and 8).

Reactions of ^{13}C-DME (78 kPa) with ^{12}C-3,4,4-trimethyl-2-pentene (0.5 kPa) were used to measure rates of hydrogen transfer, methylation, and β-scission of C_8 molecules formed via methylation of triptene. The rate of hydrogen transfer to 3,4,4-trimethyl *sec*-pentoxide (0.02 μmol [mol Al s]$^{-1}$; Table 2) is more than an order of magnitude lower than those to C_3–C_7 alkoxides formed in DME homologation and suggests that C_8 chains undergo β-scission or methylation prior to terminating as C_8 alkanes. The total rate of formation of C_{9-10} species from ^{13}C-DME/^{12}C-3,4,4-trimethyl-2-pentene reactants (0.033 μmol [mol Al s]$^{-1}$) is also more than an order of magnitude lower than the rates of formation of C_{n+1} species (5.0–45 μmol [mol Al s]$^{-1}$; Table 2) from C_n-alkene co-feeds that are smaller than 3,4,4-trimethyl-2-pentene, suggesting that the C_{9-10} chains that form via C_8 methylation may also undergo rapid β-scission. Moreover, the β-scission probability of 3,4,4-trimethylpentyl species is >100 times larger than for all the smaller chains ($\gamma_C = 1.3$ vs. 0.003–0.013; Table 2). These data show that C_8 molecules formed via methylation of triptene undergo rapid β-scission well before significant methylation or hydrogen transfer can occur, apparently as the result of stable tertiary carbenium ion transition states for β-scission of these molecules, in contrast with the primary alkoxides or methyl carbenium ion transition states required for β-scission of triptane and its precursors (Schemes 4–7). These facile β-scission events of C_8 species lead to high concentrations of isobutane in DME homologation products (discussed in the previous paragraph).

The isopentane, 2,3-dimethylbutane, and triptane isotopologues formed from ^{13}C-DME/^{12}C-3,4,4-trimethyl-2-pentene, ^{13}C-DME/^{12}C-isobutene, and ^{13}C-DME/^{12}C-trans-2-butene reactants consist predominantly of singly labeled, doubly labeled, and triply labeled molecules, respectively (Fig. 7). The similarity among these distributions indicates that ^{12}C-3,4,4-trimethyl-2-pentene predominantly acts as source of C_4 species that methylate further to form the isotopologues of isopentane, 2,3-dimethylbutane, and triptane that are also formed when ^{12}C-butenes are added to ^{13}C-DME at the reactor inlet. Moreover, the isobutyl and linear C_4 species (Fig. 8) formed from ^{13}C-DME/^{12}C-3,4,4-trimethyl-2-pentene reactants contain a significant fraction of completely unlabeled molecules and binomial-like distributions of more highly labeled species (dashed markers in Fig. 8). The completely unlabeled components of these isotopologue distributions reflect the C_4 molecules produced from β-scission of C_8 species that are not methylated by ^{13}C-DME. The binomial portions of the distributions in Fig. 8 resemble the isotopologue distributions of isobutyl and *n*-butyl species from ^{13}C-DME/$^{12}C_{5-7}$ alkene reactions (Fig. 5), and thus, these molecules are likely the result of β-scission of

larger chains (derived from methylation by ^{13}C-DME of completely unlabeled C_4 species) that have undergone extensive intramolecular isomerization. We conclude from these data that isobutyl and *n*-butyl species are formed via β-scission of C_8 chains, although isobutane appears in much higher concentrations within homologation products than *n*-butane because of the higher termination probability of isobutyl species compared with *n*-butyl species. We also conclude that these C_4 species (particularly *n*-butenes because of their much higher methylation rates compared to hydrogen transfer of *sec*-butoxide) can re-enter chain growth pathways to triptane via methylation by DME. The isobutane molecules that form via β-scisson of C_8 chains may also be re-incorporated into growing chains using a hydrogen transfer co-catalyst such as adamantane [11,60].

Scheme 8 shows β-scission pathways for the C_8 molecules formed via methylation of triptene by DME (or methanol), which would preferentially form 3,3,4-trimethyl *sec*-pentoxide species based on the selective methylation position rules discussed in Sections 3.1–3.3.1. β-Scission of 3,3,4-trimethyl *sec*-pentoxide forms *n*-butene and *tert*-butoxide (which gives isobutene via deprotonation or isobutane via hydrogen transfer) in reactions that involve the formation of stable tertiary carbenium ions [40]. Methyl shift isomerization along the backbone of 3,3,4-trimethyl *sec*-pentoxide leads to 2,4,4-trimethyl *sec*-pentoxide, which forms isobutene and *tert*-butoxide in β-scission events that require tertiary carbenium ion transition states [40]. β-Scission of 2,3,4-trimethyl *sec*-pentoxide (a tertiary alkoxide formed from methyl shift along the backbone of 3,3,4-trimethyl *sec*-pentoxide and 2,4,4-trimethyl *sec*-pentoxide) produces isopentene and *sec*-propoxide [40] (a less stable secondary alkoxide that requires a secondary carbenium ion transition state). Higher concentrations of 2,3,4-trimethylpentane molecules compared to 2,2,3- and 2,2,4-trimentylpentane molecules within C_8 products from ^{13}C-DME/$^{12}C_7$-alkene reactants (Table 2) and higher rates of ^{12}C appearance in C_4 species (compared to isopentyl species) from ^{13}C-DME/^{12}C-3,4,4-trimethyl-2-pentene reactants indicate that β-scission of 2,3,4-trimethylpentyl species is slower than β-scission of 2,2,3-trimethylpentyl and 2,2,4-trimethylpentyl species, because the former requires the formation of less stable secondary carbenium ion transition states (Scheme 8). Thus, 2,3,4-trimethylpentyl species likely undergo methyl shift to 2,2,4-trimethylpentyl species followed by more facile β-scission events. This rapid β-scission of C_8 molecules (as well as C_7 isomers that lack the linear four-carbon backbone of triptane (Section 3.3.5)) provides a kinetic filtering mechanism that corrects for chain growth mistakes (albeit with some loss of carbon to isobutane) that would otherwise lead to a wider product distribution over a broader range of molecular weights.

3.5. Kinetic and isotopic probes of homologation pathways and their implications for selectivity in reactions mediated by carbenium ion transition states

The results presented here, although motivated by an inquiry into the unique selectivity to isobutane and triptane from C_1 species on acids, provide significant guidance about the effects of molecular structure and of carbenium ion stability on methylation, hydrogen transfer, β-scission, and isomerization reaction rates. The relative rates of these reactions, reported here with unprecedented numerical accuracy, can be rigorously interpreted in terms of the transition states envisioned (and suggested by theory) for methylation of alkenes, hydrogen transfer to adsorbed alkoxides, and rearrangements of the latter species to (i) cleave C–C bonds, (ii) change the position of surface attachment (hydride shift) or of methyls (methyl shifts), or (iii) change the backbone length. In doing so, methylation events, which can be monitored accurately from the formation of singly labeled C_{n+1} species from ^{13}C-DME/$^{12}C_n$-alkenes, provide a useful internal kinetic standard against which other rates can be accurately benchmarked at conditions that prevent fast secondary reactions that would otherwise preclude the rigorous mechanistic analysis of kinetic and isotopic data.

A confluence of kinetic preferences, at first glance seemingly fortuitous, leads to isobutane and triptane as predominant products of C_1 homologation. Methyls are added to incipient chains at positions that preserve a four-carbon backbone and the chain termination probability reaches a sharp maximum at triptyls, for which the relative stabilities of methylation and hydrogen transfer favor the latter. When methylation occurs at less preferred positions, the resulting chains do not terminate preferentially at C_7; instead, they form larger molecules, which undergo rapid β-scission to form isobutane and return carbon atoms to the incipient chain growth pathways. Isobutane becomes a preferred product, in spite of its infrequent formation via direct C_1 homologation pathways, because of this recycling of kinetic "mistakes"; *tert*-butoxides desorb as isobutane via hydrogen transfer before significant desorption as isobutene and methylation, because, as in the case of triptyls, they form much more stable transition states for hydrogen transfer than for methylation of isobutene. These rules, so clearly evident here from the specific and intricate details of intermediates and transitions states involved in homologation catalysis, apply with equal rigor and much more broader impact to acid catalysts in general.

4. Conclusions

Unprecedented measurement of reaction rates from competitive reactions between ^{13}C-DME and ^{12}C-alkenes led to quantitative description of the mechanistic details of chain growth during DME homologation to triptane on solid acid catalysts. The relative stabilities of carbenium ion transition states formed during methylation, hydrogen transfer, isomerization, and β-scission reactions preferentially form molecules with linear four-carbon backbone structures (isopentane, 2,3-dimethylbutane, and triptane). Methylation of alkenes occurs selectively to preserve the linear four-carbon backbones of molecules along the chain growth path to triptane. Termination probabilities are much higher for triptyl and isobutyl species, which terminate preferentially as alkanes via hydrogen transfer of 2,2,3-trimethyl *sec*-butoxide and *tert*-butoxide, than for C_3, linear C_4, isopentyl, and 2,3-dimethylbutyl species, which methylate preferentially along the chain growth path. Low rates of skeletal isomerization and β-scission of these molecules, relative to their rates of hydrogen transfer and methylation, prevent rearrangement of their linear four-carbon backbones. Molecules that deviate from the chain growth path to triptane, via isomerization away from the linear C_4 backbone structure of triptane and/or methylation to C_{8+} chains, are selectively removed from chain growth paths via rapid β-scission reactions.

These ^{13}C-DME/^{12}C-alkene studies show that DME homologation forms triptane because growing chains undergo slow isomerization or β-scission and terminate preferentially as triptane; rapid isomerization and β-scission forms isobutane when chain growth deviates from triptane. The remarkable isobutane and triptane selectivity during reactions of DME on H-BEA zeolite has also been measured on non-zeolite solid acids (5 wt.% $H_3PW_{12}O_{40}/SiO_2$ and SiO_2–Al_2O_3) [11] and reflects a chain growth mechanism characteristic of acid catalysis, in general, that is guided by the stability of carbenium ion transition states. The role of spatial constraints is to provide van der Waals stabilization of the required transition states and to alter their free energies via enthalpic or entropic effects.

Although relative rates will depend on spatial constraints as a result of transition states that differ in size and van der Waals contacts with the zeolite framework [61–64], the hierarchy of

reactivity imposed by carbenium ion stability remains pre-eminent even within confined environments. Indeed, the unique selectivities to C_4 and C_7 alkanes and to their isobutane and triptane isomers are also observed on other large-pore zeolites [9] and even in mesoporous solid acids [11].

Acknowledgments

We acknowledge with thanks the funding for this work by BP, p.l.c. as part of the Methane Conversion Cooperative Program at the University of California at Berkeley. We also acknowledge useful technical exchanges with Professor Matthew Neurock, Mr. Craig Plaisance, and Dr. Rado Raharintsalama (University of Virginia) and Professors Jay A. Labinger and John E. Bercaw (California Institute of Technology) regarding the mechanistic interpretation of the results reported in this manuscript.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.11.004.

References

[1] C.D. Chang, Catal. Rev.-Sci. Eng. 25 (1983) 1.
[2] Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas, United States Department of Energy, National Renewable Energy Laboratory, NREL/TP-510-34929, 2003.
[3] J.E. Bercaw, P.L. Diaconescu, R.H. Grubbs, N. Hazari, R.D. Kay, J.A. Labinger, P. Mehrkhodavandi, G.E. Morris, G.J. Sunley, P. Vagner, Inorg. Chem. 46 (2007) 11371.
[4] J.E. Bercaw, P.L. Diaconescu, R.H. Grubbs, R.D. Kay, S. Kitching, J.A. Labinger, X. Li, P. Mehrkhodavandi, G.E. Morris, G.J. Sunley, P. Vagner, J. Org. Chem. 71 (2006) 8907.
[5] J.E. Bercaw, R.H. Grubbs, N. Hazari, J.A. Labinger, X.W. Li, Chem. Commun. (2007) 2974.
[6] L. Kim, M.M. Wald, S.G. Brandenberger, J. Org. Chem. 43 (1978) 3432.
[7] S. Walspurger, G.K.S. Prakash, G.A. Olah, Appl. Catal. A 336 (2008) 48.
[8] See supporting information for further details.
[9] J.H. Ahn, B. Temel, E. Iglesia, Angew. Chem. Int. Ed. 48 (2009) 3814.
[10] D.R. Stull, E.F. Westrum, G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, John Wiley and Sons, New York, 1969.
[11] D. A. Simonetti, E. Iglesia, unpublished data.
[12] G.L. Price, E. Iglesia, Ind. Eng. Chem. Res. 28 (1989) 839.
[13] M. Bjorgen, U. Olsbye, D. Petersen, S. Kolboe, J. Catal. 221 (2004) 1.
[14] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[15] J.F. Haw, Phys. Chem. Chem. Phys. 4 (2002) 5431.
[16] J.F. Haw, W.G. Song, D.M. Marcus, J.B. Nicholas, Acc. Chem. Res. 36 (2003) 317.
[17] N. Hazari, J.A. Labinger, V.J. Scott, J. Catal. 263 (2009) 266.
[18] V.B. Kazansky, Acc. Chem. Res. 24 (1991) 379.
[19] H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke, J. Am. Chem. Soc. 112 (1990) 4446.
[20] M. Stocker, Micropor. Mesopor. Mater. 29 (1999) 3.
[21] S. Svelle, B. Arstad, S. Kolboe, O. Swang, J. Phys. Chem. B 107 (2003) 9281.
[22] S. Svelle, S. Kolboe, O. Swang, U. Olsbye, J. Phys. Chem. B 109 (2005) 12874.
[23] S. Svelle, P.O. Ronning, U. Olsbye, S. Kolboe, J. Catal. 224 (2004).
[24] S. Svelle, P.O. Ronning, U. Olsbye, S. Kolboe, J. Catal. 234 (2005) 385.
[25] A. Bhan, Y.V. Joshi, W.N. Delgass, K.T. Thomson, J. Phys. Chem. B 107 (2003) 10476.
[26] M. Boronat, C.M. Zicovich-Wilson, P. Viruela, A. Corma, J. Phys. Chem. B 105 (2001) 11169.
[27] E.M. Evleth, E. Kassab, H. Jessri, M. Allavena, L. Montero, L.R. Sierra, J. Phys. Chem. 100 (1996) 11368.
[28] A.M. Rigby, M.V. Frash, J. Mol. Catal. A – Chem. 126 (1997) 61.
[29] M. Bjorgen, U. Olsbye, S. Kolboe, J. Catal. 215 (2003) 30.
[30] M. Boronat, P. Viruela, A. Corma, J. Phys. Chem. A 102 (1998) 9863.
[31] M. Boronat, P. Viruela, A. Corma, J. Phys. Chem. B 103 (1999) 7809.
[32] M. Boronat, P. Viruela, A. Corma, Phys. Chem. Chem. Phys. 2 (2000) 3327.
[33] M.J. Janik, R.J. Davis, M. Neurock, J. Catal. 244 (2006) 65.
[34] V.B. Kazansky, M.V. Frash, R.A. van Santen, Catal. Lett. 48 (1997) 61.
[35] V.B. Kazansky, M.V. Frash, R.A. van Santen, Prog. Zeolite Micropor. Mater. 105 (1997) 2283.
[36] T. Demuth, X. Rozanska, L. Benco, J. Hafner, R.A. van-Santen, H. Taulhoat, J. Catal. 214 (2003) 68.
[37] E. Iglesia, S.L. Soled, G.M. Kramer, J. Catal. 144 (1993) 238.
[38] M.A. Natal-Santiago, R. Alcala, J.A. Dumesic, J. Catal. 181 (1999) 124.
[39] W.-Q. Xu, Y.-G. Yin, S.L. Suib, C.-L. O'Young, J. Catal. 150 (1994) 34.
[40] J.S. Buchanan, J.G. Santiesteban, W.O. Haag, J. Catal. 158 (1996) 279.
[41] B.S. Greensfelder, H.H. Voge, G.M. Good, Ind. Eng. Chem. 41 (1949) 2573.
[42] F.C. Jentoft, B.C. Gates, Top. Catal. 4 (1997) 1.
[43] C.L. Thomas, Ind. Eng. Chem. 41 (1949) 2564.
[44] J. Weitkamp, P.A. Jacobs, J.A. Martens, Appl. Catal. 8 (1983) 123.
[45] A. Corma, Chem. Rev. 95 (1995) 559.
[46] S. Svelle, C. Tuma, X. Rozanska, T. Kerber, J. Sauer, J. Am. Chem. Soc. 131 (2009) 816.
[47] E. Iglesia, J. Baumgartner, G.L. Price, K.D. Rose, J.L. Robbins, J. Catal. 125 (1990) 95.
[48] S.Y. Yu, G.J. Yu, W. Li, E. Iglesia, J. Phys. Chem. B 106 (2002) 4714.
[49] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, FL, 2003.
[50] Y.-R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, FL, 2007.
[51] A. Bhan, W.N. Delgass, Catal. Rev.-Sci. Eng. 50 (2008) 19.
[52] Y.I. Derbentsev, G.V. Isagulyants, Russ. Chem. Rev. 38 (1969) 714.
[53] E. Iglesia, J.E. Baumgartner, G.L. Price, J. Catal. 134 (1992) 549.
[54] Z. Paal, P. Tetenyi, Acta Chim. Acad. Sci. Hung. 54 (1967) 175.
[55] Z. Paal, P. Tetenyi, Acta Chim. Acad. Sci. Hung. 55 (1968) 273.
[56] Z. Paal, P. Tetenyi, Acta Chim. Acad. Sci. Hung. 58 (1968) 105.
[57] G.L. Price, G.R. Edegy, J. Catal. 84 (1983) 461.
[58] A.J. Silvestri, R.L. Smith, J. Catal. 29 (1973) 371.
[59] S.Y. Yu, J.A. Biscardi, E. Iglesia, J. Phys. Chem. B 106 (2002) 9642.
[60] J.E. Bercaw, N. Hazari, J.A. Labinger, V.J. Scott, G.J. Sunley, J. Am. Chem. Soc. 130 (2008) 11988.
[61] A. Bhan, R. Gounder, J. Macht, E. Iglesia, J. Catal. 253 (2008) 221.
[62] A. Bhan, E. Iglesia, Acc. Chem. Res. 41 (2008) 559.
[63] R. Gounder, E. Iglesia, J. Am. Chem. Soc. 131 (2009) 1958.
[64] R. Gounder, E. Iglesia, Angew. Chem. Int. Ed. 49 (2010) 808.