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Catalytic Co-Homologation of Alkanes and Dimethyl Ether and Promotion by Adamantane as a Hydride Transfer Co-Catalyst

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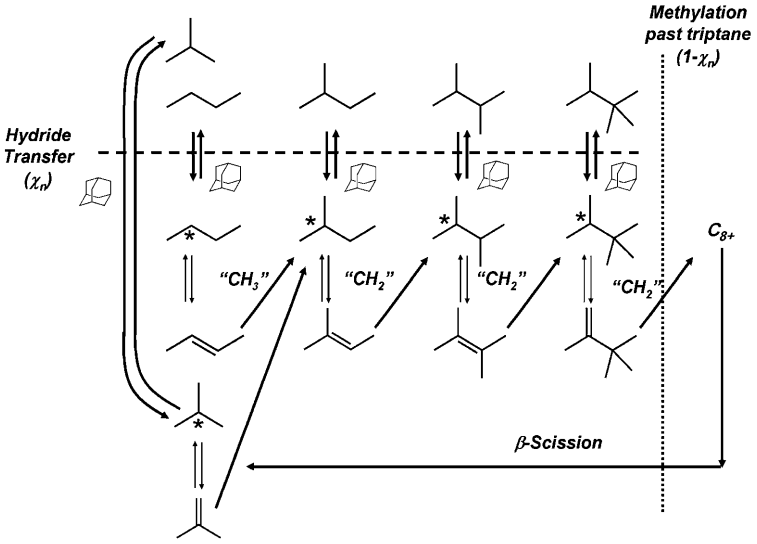
We provide kinetic and isotopic evidence for the co-homologation of linear and branched alkanes with dimethyl ether (DME) to form larger branched alkanes and isobutane on H-BEA zeolites, and for the role of adamantane as a hydride transfer co-catalyst that allows the activation of C–H bonds in alkanes at low temperatures (< 500 K) on Brønsted acid sites. Branched alkanes (isobutane, isopentane, and 2,3-dimethylbutane) present in equimolar mixtures with DME form the corresponding alkenes via hydride transfer to bound alkoxides (formed in DME homologation steps) and subsequent deprotonation; these alkenes, derived from the added alkanes, are then methylated to lengthen their chain by using DME-derived C_1 species, as shown by the isotopologues formed in reactions of ^{13}C-DME with ^{12}C-alkanes. Linear alkanes are much less reactive than branched alkanes, because of their stronger C–H bonds and larger carbenium ion formation energies, which determines hydride-transfer rates to a given acceptor molecule. Adamantane increased the hydride-transfer rates to bound alkoxides from branched alkanes, and even from unreactive linear alkanes, while also increasing their extent of incorporation into DME homologation pathways; adamantane acts as a reversible hydrogen donor that mediates dehydrogenation of alkanes at low temperatures on acid sites. The co-homologation of alkanes with DME avoids the need for carbon rejection in the form of arenes to satisfy the hydrogen balance in the DME conversion to alkanes, provides a robust strategy for increasing the chain length and extent of branching in light alkanes through the selective addition of C_1 species, and mitigates the formation of unsaturated by-products ubiquitous in the homologation of DME or methanol on Brønsted acids.

1. Introduction

Competitive reactions between ^{13}C-labeled dimethyl ether (^{13}C-DME) and unlabeled alkenes have been used to examine the mechanistic details of chain growth and termination pathways leading to the selective formation of triptane and isobutane by means of the homologation of DME or methanol (Scheme 1).[1] These studies have also provided specific and quantitative evidence for the ubiquitous role of carbenium-ion stability on the relative rates of competing reactions catalyzed by solid acids.

Homologation of C_1 reactants occurs at modest temperatures (400–500 K) through Brønsted acid catalyzed pathways mediated by carbenium ion transition states in homogeneous ZnI_2 and InI_3[2–6] liquid-phase systems and on acidic zeolites (ZSM-5, USY, BEA),[1,7] amorphous SiO_2–Al_2O_3, and supported Keggin heteropolyacids (5 wt% $H_3PW_{12}O_{40}/SiO_2$).[8] The remarkable selectivity to isobutane and triptane reflects a preference for methylation at positions that preserve hydrocarbon chains with four-carbon backbones; the resulting alkoxides do not readily restructure via skeletal isomerization or β-scission, but terminate reversibly by means of deprotonation to form alkenes and also through essentially irreversible hydride-transfer reactions to form alkanes.

Alkoxides can desorb as alkenes, which can undergo subsequent methylation by DME-derived intermediates, isomeriza-



Scheme 1. The chain growth sequence for co-homologation of dimethyl ether and alkanes with adamantane co-catalyst. The asterisk indicates the position of alkoxide attachment to the surface. "CH_3" represents surface methylating species derived from dimethyl ether. Adamantane is shown as a dehydrogenation-hydrogenation co-catalyst.

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tion, or β-scission at rates that depend strongly on the degree of substitution at carbon atoms along the backbone.[1,3,6] Desorption as alkanes through hydride transfer is essentially irreversible, because the strong alkane C–H bonds formed are relatively unreactive at the temperatures required for DME homologation.[9,10] The reversal of the chain termination steps that form alkanes becomes more facile for molecules with higher degrees of backbone substitution, which undergo hydride transfer with surface alkoxides in steps with lower activation barriers that reflect weaker tertiary C–H bonds. Chains that grow beyond triptyl species undergo facile isomerization and β-scission reactions, which form fragments that ultimately desorb as isobutene or isobutane.[1,6,7] These mechanistic features reflect a preference for elementary steps involving cationic transition states with lower free energies, because of either enthalpic or entropic stabilization (as shown previously[9,11–13]); consequently, the conclusions reached apply in general to reactions catalyzed by Brønsted acids that are mediated by charged transition states.

Chain termination by means of hydride transfer from prevalent gas phase hydrocarbons (alkanes and alkenes) occurs at rates that reflect the stability of the carbenium ions derived from the alkoxide hydrogen acceptor and the energy required to cleave the C–H bond in the H-donor molecule.[2–6,14,15] Therefore, tertiary alkoxides that form tertiary carbenium-ion transition states undergo hydride transfer much faster than secondary or primary alkoxides. Alkenes with tertiary allylic C–H bonds (the weakest among the prevalent hydrocarbons[16,17]) are the most reactive H-donors and form highly unsaturated alkenyl species upon hydride transfer. These alkenyl species desorb as conjugated dienes with even weaker C–H bonds, which can undergo subsequent hydride transfer and dehydrogenation to form trienes. Trienes then convert to arenes, such as hexamethyl benzene (HMB) by means of Diels–Alder reactions to provide the carbon-rejection mechanism required to satisfy the stoichiometry of DME conversion to alkanes[1,3,6,7] [Eq. (1)]:

$$[3n+12]CH_3OCH_3 \rightarrow 6\,C_nH_{2n+2} + 2\,C_6(CH_3)_6(HMB) + [3n+12]H_2O \quad (1)$$

Alkanes can also re-enter chain growth pathways by acting as H-donors; the rates of these reactions increase in the presence of a hydride transfer co-catalyst (e.g., adamantane), as shown previously for co-homologation of DME and alkanes in liquid ZnI_2 systems[5] and for acid-catalyzed alkane isomerization and alkylation reactions.[18–24] Thus, co-homologation of alkanes and DME forms larger alkanes via routes that satisfy stoichiometry without the need for carbon rejection as arenes [Eq. (2)]:

$$\left[\frac{m-n}{2}\right]CH_3OCH_3 + C_nH_{2n+2} \rightarrow C_mH_{2m+2} + \left[\frac{m-n}{2}\right]H_2O; \quad m > n \quad (2)$$

We explore in this study the introduction of alkanes into DME chain growth pathways through the reverse of hydride-transfer steps prevalent in acid-catalyzed C_1 homologation reactions, as well as the effects of adamantane on the rate and selectivity of alkane-DME co-homologation. This study provides experimental evidence for the role of alkanes as H-donors and for the reactivity of the resulting alkenes in chain growth. Furthermore, this study provides mechanistic insights into the high reactivity of tertiary alkanes in hydride-transfer reactions and the effects of adamantane on chain termination via hydride transfer to bound alkoxides and on its microscopic reverse, the incorporation of alkanes into DME homologation pathways. This study also demonstrates a route for upgrading light alkanes to higher value alkanes with specific isomeric structures and molecular weight distributions via addition of DME-derived C_1 species using adamantane to control hydride-transfer rates.

2. Results and Discussion

Co-reaction of DME (40 kPa) individually with each of several alkanes (40 kPa; *n*-butane, isobutane, isopentane, or 2,3-dimethylbutane) were used to probe the effects of added alkanes and adamantane on homologation selectivities. The competitive reactions of ^{13}C-DME and these unlabeled alkanes, in the presence and absence of small amounts of adamantane (1 kPa), were used to probe the mechanism of alkane incorporation into the DME homologation paths. Additionally, the effects of adamantane as a hydride transfer co-catalyst were examined for DME/alkane co-homologation. We address first the effects of adamantane on DME homologation rates and selectivities in the absence of added alkanes and then examine its effects on homologation of alkane-DME co-reactants.

2.1. Effect of adamantane on chain termination during DME homologation

The addition of adamantane (1 kPa) in reactions of DME (70 kPa) with propene (2 kPa to eliminate induction periods[3,7]) decreased selectivities to C_4 and C_7 hydrocarbons (Figure 1 a), increased those to C_5 and C_6 hydrocarbons (Figure 1 a), and decreased alkene-to-alkane ratios (by about 3 and >10 for the C_4 and C_5-C_6 fractions, respectively; Table 1). Inlet and outlet adamantane mole fractions were similar ($\approx$0.01), indicating that adamantane was not consumed during DME homologation on H-BEA.

The selectivities to 2,3-dimethylbutyl isomers (2,3-dimethylbutane and 2,3-dimethylbutenes; -tyl suffix is used here and elsewhere to denote alkanes and alkenes with a given backbone structure) within C_6 hydrocarbons (Table 1) decreased slightly (39 to 36%), whereas the methyl-pentyl isomer selectivity concurrently increased (56 to 60%). Upon addition of adamantane to DME reactants the triptyl selectivities within C_7 decreased (71 to 54%), whereas dimethyl-pentyl and isoheptyl selectivities concurrently increased (24 to 39%). These increases in selectivity to the C_6 and C_7 isomers, which do not lie along the path to triptane (with adamantane addition to DME), indicate that adamantane causes these chains to desorb as alkanes (through hydride transfer) before they are selective-

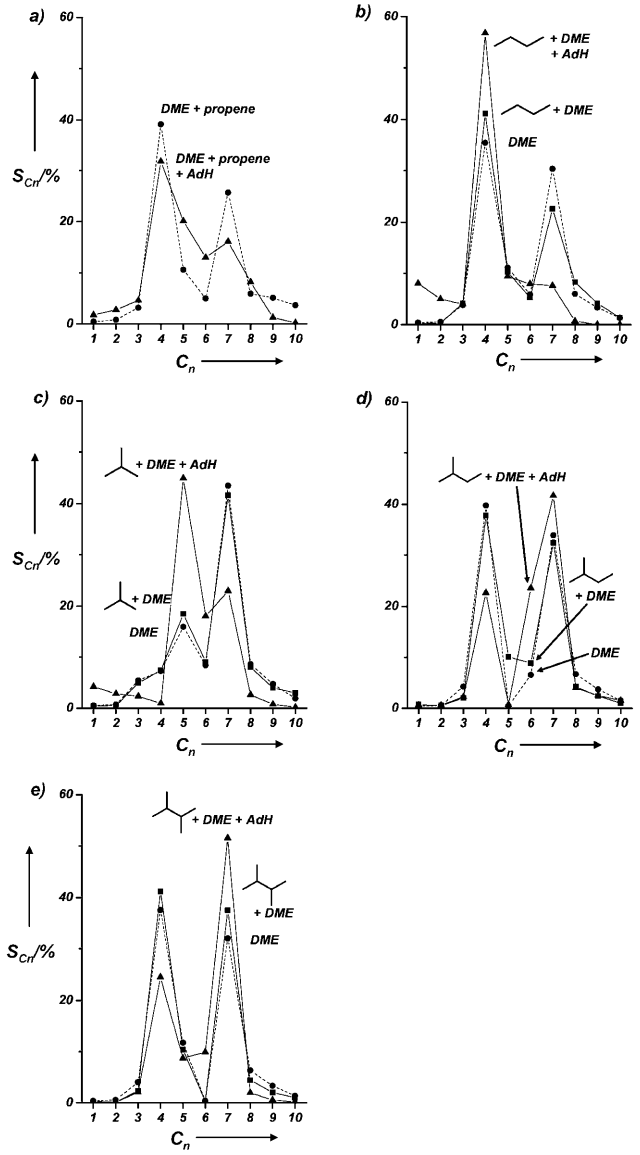


Figure 1. Carbon selectivities (S_{Cn}) for the homologation of dimethyl ether (●; 40 kPa), dimethyl ether/alkane (■; 40 kPa each), and dimethyl ether/alkane/adamantane (▲; 40 kPa DME, 40 kPa alkane, 1 kPa adamantane) reactant mixtures. Co-reactants used were a) propene (2 kPa with 70 kPa DME), b) *n*-butane, c) isobutane, d) isopentane, and e) 2,3-dimethylbutane. The selectivities for dimethyl ether homologation in panels b)–e) are for *n*-butane, isobutane, isopentane, and 2,3-dimethylbutane free bases, respectively. Data were collected at 473 K, 101 kPa total pressure (29 kPa Ar), a space velocity of 0.04 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.12 cm^3 s^{-1} total inlet gas flow rate, 0.14 g H-BEA with Si:Al = 12.5:1), and total carbon conversions of less than 5%. The data in panel d) are from co-reaction of ^{13}C-DME and ^{12}C-isopentane.

ly removed from the chain growth pool as isobutane by growing past C_7 and β-scission.[1,3,7] Thus these chains appear as backbone structures that do not resemble that found in triptane, and these effects reflect faster rates of hydride transfer to surface alkoxides catalyzed by adamantane. Isobutyl selectivities within C_4 species increased (73 to 86%) upon addition of adamantane to DME/propene reactants as opposed to an expected decrease in isobutyl species as a result of faster chain termination. The prevalence of isobutyl species within C_4, and the concurrent decrease in selectivity to C_7 species and triptyl isomers, reflects the re-incorporation of triptane molecules into chain-growth pathways through adamantane catalyzed dehydrogenation, leading to their methylation to C_{8+} chains, and subsequent β-scission to isobutane. The increase in isobutyl selectivity within C_4 species when adamantane is present also reflects the higher rates of the hydride-transfer reactions of the branched alkanes relative to the hydrogenation of linear butoxides, as discussed in the context of the effects of molecular structure on hydride-transfer rates later (Section 2.2). We conclude from these data that adamantane decreases C_7 selectivities during DME homologation by prematurely terminating chains and also decreases the preference for triptane isomers within C_7 by allowing triptane molecules to return to homologation pathways as triptene formed via adamantane-mediated dehydrogenation steps.

In Sections 2.2 and 2.3, we describe co-homologation studies of ^{13}C-DME with ^{12}C-alkanes, with and without adamantane as a co-catalyst, to examine the catalytic consequences of adamantane-mediated hydride-transfer reactions, which lead to chain termination and to the incorporation of the co-fed alkanes during DME homologation. First, we use these ^{13}C-DME/^{12}C-alkane reactions to show the effects of adamantane on termination probabilities (β; defined in Section 4.3) that form isopentyl, 2,3-dimethylbutyl, and triptyl products (determined from competitive reactions between ^{13}C-DME and ^{12}C-isobutane, ^{12}C-isopentane, and ^{12}C-2,3-dimethylbutane). The β values for isopentyl, 2,3-dimethylbutyl, and triptyl species increased from 0.28 to 0.55, 0.07 to 0.12, and 0.35 to 0.59, respectively, with adamantane addition to ^{13}C-DME/^{12}C-alkane reactants (Figure 2), indicating that adamantane preferentially increases hydride-transfer rates over methylation rates. These increases in β are consistent with the effects of adamantane on product selectivities discussed in the previous paragraph and confirm

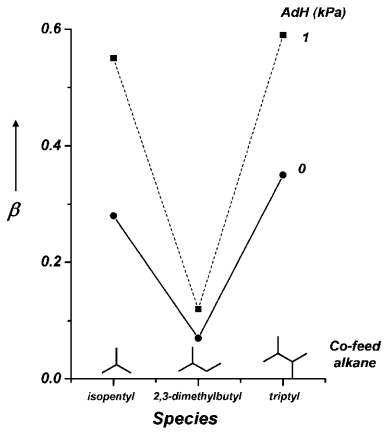


Figure 2. Effect of adamantane on the termination probability (β; ratio of the rate of hydride transfer to the sum of the rates of methylation and hydride transfer[1]) of isopentyl, 2,3-dimethylbutyl, and triptyl species produced during co-homologation of dimethyl ether and alkanes. Data collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5).

the role of adamantane as a co-catalyst for hydride transfer between alkanes and adsorbed alkoxides.

Adamantane promotes chain termination during DME homologation by donating tertiary H-atoms to bound alkoxides (R′H*) to form the alkane ($R'H_2$) and adamantyl cations (Ad^+) [Eq. (3)]:[22–25]

$$AdH + R'H^* \rightarrow Ad^+ + R'H_2 \quad (3)$$

Adamantyl cations can then abstract a hydride from an alkane (RH_2) to form a new alkoxide (RH*) and then desorb adamantane [Eq. (4)],

$$Ad^+ + RH_2 \rightarrow AdH + RH^* \quad (4)$$

The resulting alkoxide then desorbs as an alkene [R; Eq. (5)] that methylates further.

$$RH^* \rightarrow R + H^* \quad (5)$$

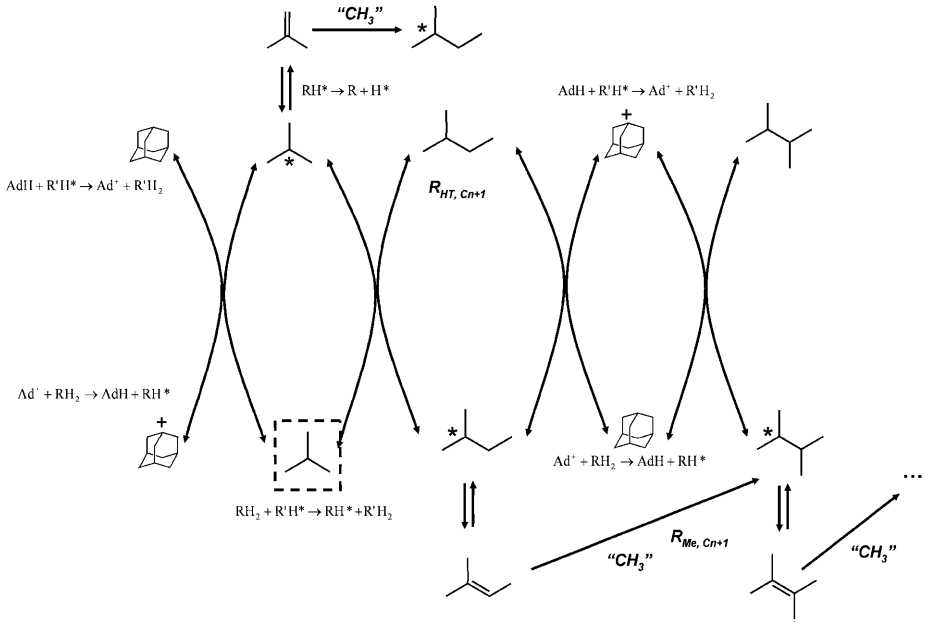
As a result, adamantane mediates the introduction of alkanes into DME homologation paths via dehydrogenation,[5,18] while concurrently increasing the termination of chains by means of hydride transfer (as depicted in Scheme 2).

Next, we investigated the effects of added alkanes and adamantane on homologation rates and selectivities from reactions of equimolar mixtures of DME and alkanes (40 kPa each) with and without adamantane (≈1 kPa) present. We also probed the mechanism of adamantane-catalyzed alkane incorporation for the co-reaction of ^{12}C-alkanes (^{12}C-*n*-butane, ^{12}C-isobutane, ^{12}C-isopentane, and ^{12}C-2,3-dimethylbutane; 40 kPa) co-fed individually with ^{13}C-DME (40 kPa).

Table 1. Effect of adamantane on isomer selectivities and alkene to alkane ratios for homologation of dimethyl ether (70 kPa) with propene (2 kPa). Data collected at 473 K, 101 kPa total pressure (21 kPa Ar), 1.0% total carbon conversion, and a space velocity of 0.04 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.12 cm^3 s^{-1} total inlet gas flow rate, 0.14 g H-BEA with Si:Al = 12.5:1).

		Adamantane [kPa]	
		0	1
alkene/alkane molar ratio	C_4	0.33	0.10
	C_5	0.39	0.02
	C_6	0.13	0.00[a]
isomer selectivity within C_n [%]	isobutyl in C_4	73	86
	triptyl in C_7	71	54
	dimethyl-pentyl and iso-hexyl[b] in C_7	24	39
	2,3-dimethylbutyl in C_6	39	36
	Methyl-pentyl[c] in C_6	56	60

[a] Total rate of C_6 alkene formation below detection limit of GC (10^{-3} μmol(C) mol(Al)$^{-1}$ s^{-1}); [b] 2,3-dimethylpentyl, 2,4-dimethylpentyl, 2-methylhexyl, 3-methylhexyl isomers within C_7 products; [c] 2-methylpentyl and 3-methylpentyl isomers within C_6 products



Scheme 2. The catalytic cycle for hydride transfer between alkanes and surface alkoxides and adamantane-catalyzed hydride transfer between alkanes and surface alkoxides. Isobutane is used as a representative co-fed alkane. AdH and Ad^+ represent adamantane molecules and adamantyl cations, respectively. "CH_3" represents surface methylating species derived from dimethyl ether. R_{HT} and R_{Me} indicate reactions used to measure termination probabilities.

2.2. Effects of added alkanes on DME homologation without adamantane co-catalyst

The addition of *n*-butane to DME (without adamantane) did not lead to increases in the C_5-C_7 selectivities (Figure 1b), suggesting that the introduction of *n*-butane into DME co-homologation through H-transfer step is slow compared with chain growth. The alkene to alkane ratios in C_5 and C_6 products were similar to those without added *n*-butane (Table 2), reflecting the unreactive nature of *n*-butane in hydride transfer to surface alkoxides. ^{13}C-DME/^{12}C-*n*-butane mixtures formed products with very small ^{12}C fractions (0.12, 0.06, and 0.05 in isopentane, 2,3-dimethylbutane, and triptane, respectively, Figure 3a–c) and a low ^{12}C/^{13}C ratio among all products (0.09; Table 3). The ratios of product isotopologues derived from *n*-butane methylation (^{12}C-rich binomial; Figure 3a–c) to those derived from ^{13}C-DME (^{13}C-rich binomial; Figure 3a–c) are small (0.14, 0.06, and 0.08 for isopentane, 2,3-dimethylbutane, and triptane, re-

Table 2. Effect of adamantane on isomer selectivities and alkene to alkane ratios for homologation of dimethyl ether (40 kPa) with *n*-butane, isobutane, isopentane, and 2,3-dimethylbutane (40 kPa). Data collected at 473 K, 101 kPa total pressure (21 kPa Ar), 1.0% total carbon conversion, and a space velocity of 0.04 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.12 cm^3 s^{-1} total inlet gas flow rate, 0.14 g H-BEA with Si:Al = 12.5:1).

	Co-feed alkane	None	*n*-Butane		Isobutane		2,3-dimethylbutane	
	Adamantane pressure [kPa]	0	0	1	0	1	0	1
alkene/alkane molar ratio	C_4	0.57	–	–	–	–	0.23	0.052
	C_5	0.76	0.60	0.02	0.13	0.003	0.42	0.035
	C_6	0.24	0.21	0.00[a]	0.03	0.00[a]	–	–
isomer selectivity within C_n [%]	isobutyl within C_4	90	–	–	–	–	94	94
	triptyl in C_7	74	74	48	73	57	72	72
	dimethyl-pentyl and iso-hexyl[b] in C_7	20	23	50	25	40	21	21
	2,3-dimethylbutyl in C_6	46	44	38	58	44	–	–
	methyl-pentyl[c] in C_6	47	50	55	40	50	–	–

[a] Total rate of C_6 alkene formation below detection limit of GC (10^{-3} μmol(C) mol(Al)$^{-1}$ s^{-1}); [b] 2,3-dimethylpentyl, 2,4-dimethylpentyl, 2-methylhexyl, 3-methylhexyl isomers within C_7 products; [c] 2-methylpentyl and 3-methylpentyl isomers within C_6 products.

Table 3. Effect of adamantane on the ratio of the total rate appearance of ^{12}C-atoms to ^{13}C-atoms in all products, the rates of ^{13}C-appearance and ^{12}C-appearance in all products, the ratio of the total rate of appearance of C in alkanes to hexamethyl benzene, and the ratio of ^{12}C-atoms to ^{13}C-atoms in *n*-butane, isobutane, isopentane, 2,3-dimethylbutane, triptane, and hexamethyl benzene molecules produced from reactions between ^{13}C-labeled dimethyl ether (40 kPa) and unlabeled isobutane, isopentane, 2,3-dimethylbutane, and *n*-butane (40 kPa). Data collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5).

	Co-feed alkane	*n*-Butane		Isobutane		Isopentane		2,3-dimethylbutane	
	adamantane pressure [kPa]	0	1	0	1	0	1	0	1
^{12}C/^{13}C within	trans-2-butene	–	–	–	–	0.7	3.0	1.2	3.9
	isobutane	–	–	–	–	0.6	1.0	0.8	4.1
	isopentane	0.12	1.2	1.5	3.3	–	–	0.7	2.2
	2,3-dimethylbutane	0.06	1.0	1.0	1.9	1.4	4.8	–	–
	triptane	0.05	0.6	0.6	1.2	1.0	2.1	1.5	4.5
	hexamethylbenzene	0.11	1.0	0.8	1.3	0.2	1.0	0.07	0.9
	all products[a]	0.09	1.2	0.9	1.8	0.8	1.9	1.1	4.1
	total rate ^{12}C-appearance [mol(C) mol(Al)$^{-1}$ s^{-1}]	0.034	0.043	0.07	0.23	0.67	1.8	0.64	2.7
	total rate ^{13}C-appearance [mol(C) mol(Al)$^{-1}$ s^{-1}]	0.36	0.04	0.10	0.12	0.83	0.90	0.60	0.66
	$C_{alkanes}/C_{hexamethyl\ benzene}$[b]	23	35	4.5	20	52	55	61	63

[a] Ratio of total rate of ^{12}C appearance in all products to total rate of ^{13}C appearance in all products; [b] ratio of total rate of C appearance in all alkanes to total rate of C appearance in hexamethyl benzene.

spectively), also showing that products of ^{13}C-DME/^{12}C-*n*-butane mixtures predominantly formed from the ^{13}C-DME component.

In contrast with these *n*-butane data, the addition of equimolar isobutane amounts to DME (without adamantane) increased the selectivity to C_5 hydrocarbons (Figure 1c). Similarly, the selectivities to C_6 and C_7 species increased when isopentane (Figure 1d) or 2,3-dimethylbutane (Figure 1e) were respectively added to DME, consistent with a concomitant increase in the concentration of alkenes derived from the co-fed alkane through hydride transfer and dehydrogenation reactions. Alkene-to-alkane ratios within C_4-C_6 products also decreased (greater than two-fold; Table 3) if isobutane or 2,3-dimethylbutane were added to DME reactants. These changes in product selectivities and alkene-to-alkane ratios reflect an increase in the rates of chain termination as alkanes ($R'H_2$) through hydride transfer from co-fed alkanes (RH_2) to surface alkoxides (R′H*) [Eq. (6)]:

$$RH_2 + R'H^* \rightarrow RH^* + R'H_2 \quad (6)$$

These steps form a new alkane-derived alkoxide (RH*) that deprotonates to form alkenes (R) [Eq. (5)] that grow by methylation with DME-derived C_1 species.[1,3,7] We conclude from these data that branched alkanes can be incorporated into growing chains by the reverse of their desorption by means of hydride transfer (as shown in Scheme 2) if such alkanes are present together with DME in equimolar concentrations. The presence of weak C–H bonds in tertiary carbon atoms in branched alkanes leads to much higher incorporation rates than for *n*-alkanes in co-homologation reactions. Carbon atoms from alkanes are incorporated into products to a similar extent as those from DME even at these low temperatures, making such co-homologation reactions an attractive route for the upgrading of light alkanes into larger isomers with minimal formation of arene by-products.

The isotopic composition of the products formed in reactions of ^{13}C-DME (40 kPa) with a given unlabeled alkane

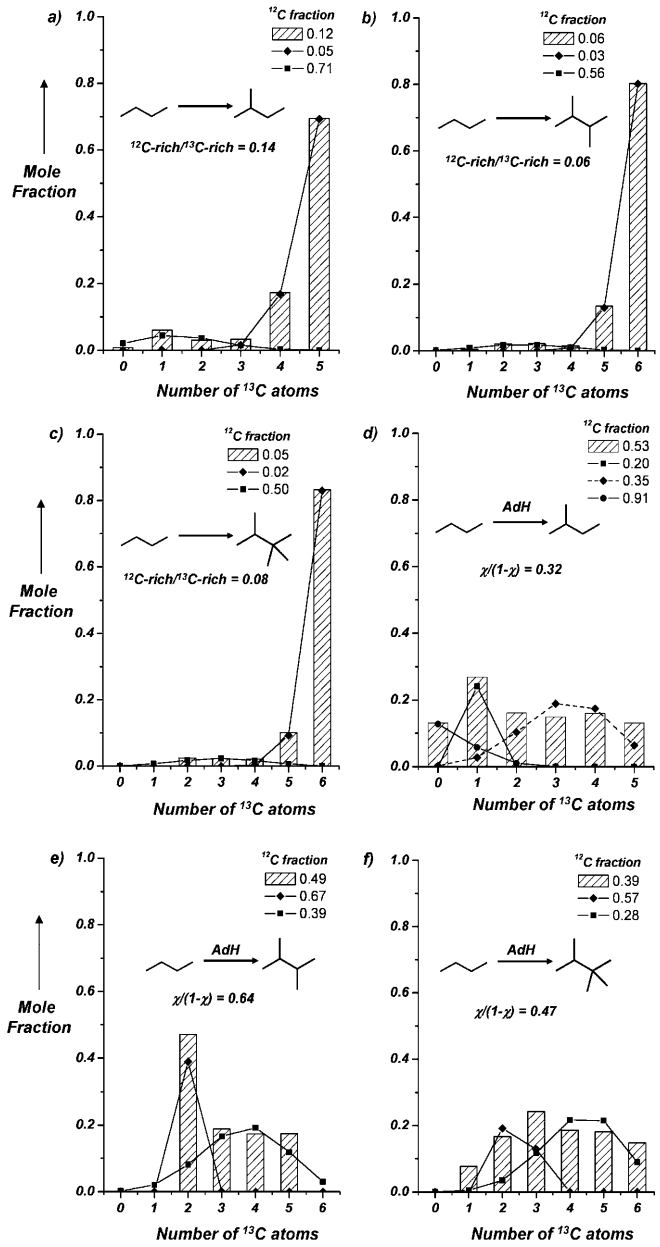


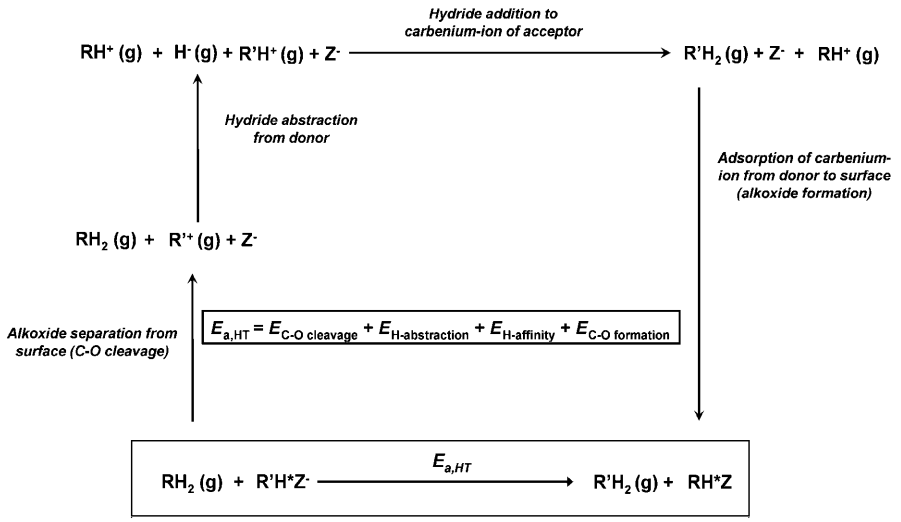
Figure 3. Effect of adamantane on the isotopologue distributions of isopentane (a, d), 2,3-dimethylbutane (b, e), and triptane (c, f) molecules from reactions between ^{13}C-labeled dimethyl ether (40 kPa) and ^{12}C-*n*-butane (40 kPa). Panels a)–c) are for reactions without adamantane, and panels d)–f) are for reactions using 1 kPa adamantane. Data were collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5). Square and circle markers represent binomial components of the total distribution, and diamond markers represent unimodal components of the total distribution. The 85 amu fragment of triptane appeared in higher concentrations in the mass spectrometer than the parent ion. Therefore, we use this fragment as a surrogate for the parent ion. Triply-labeled triptane molecules fragment into doubly-labeled and triply-labeled 85 amu fragments, resulting in peaks at 2 and 3 ^{13}C atoms in the isotopologue distribution of the 85 amu fragment of triptane.

(40 kPa) provides a quantitative measure of the extent to which each alkane incorporates into DME homologation pathways via sequential dehydrogenation and methylation. The mean $^{12}C/^{13}C$ ratios (Table 3) are nearly in unity among all products of ^{13}C-DME/^{12}C-isobutane (0.9), ^{13}C-DME/^{12}C-isopentane (0.8), and ^{13}C-DME/^{12}C-2,3-dimethylbutane (1.1) reactant mixtures, indicating that these alkanes are incorporated into homologation products to a similar extent. The significant incorporation of these alkanes into C_1 chain growth pathways, even in the absence of hydride transfer co-catalysts, reflects their ability to desorb alkoxides through hydride transfer [Eq. (6)] and is also consistent with the increase in C_{n+1} selectivities upon alkane addition to DME (Figure 1c–e). We conclude that alkanes with weak tertiary C–H bonds are dehydrogenated to their respective alkenes through hydride-transfer reactions with surface alkoxides in the absence of metals or cations in H-BEA at modest temperatures ($<$ 500 K), and that the strength of the C–H bonds in the hydride donor and the stability of the carbenium ions formed from bound alkoxides control hydride-transfer rates.[1,3,7,15,26,27]

The total rate of appearance of ^{12}C atoms in products (Table 3) was higher for isopentane (0.67 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) and 2,3-dimethylbutane (0.64 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) co-reactants than for isobutane (0.07 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) and *n*-butane (0.034 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}), because isopentene and 2,3-dimethylbutene methylate faster than C_4 alkenes.[1] The $^{12}C/^{13}C$ ratios in products formed from co-reaction of ^{13}C-DME with branched alkanes are similar (Table 3), however, because this faster methylation of isopentene and 2,3-dimethylbutene (compared to isobutene) also leads to higher rates of ^{13}C-appearance in co-homologation products from isopentane (0.83 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) and 2,3-dimethylbutane (0.60 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) co-reactants than from isobutane (0.10 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}).

The higher rates of ^{12}C-appearance in the products formed if branched ^{12}C-alkanes instead of ^{12}C-*n*-butane are co-reacted with ^{13}C-DME (Table 3) show that alkanes with weak tertiary C–H bonds are more effective H-donors than alkanes with stronger primary or secondary C–H bonds; which are essentially unreactive in the absence of hydride transfer co-catalysts at the conditions required for DME homologation. The enthalpy of formation of gas phase *sec*-butyl cations from *n*-butane (247 kcal mol^{-1}) is larger than for the tertiary cations formed from isobutane (230 kcal mol^{-1}), isopentane (228 kcal mol^{-1}), or 2,3-dimethylbutane (226 kcal mol^{-1}).[28] Thus, weaker C–H bonds lead to concomitantly higher rates of H-abstraction in the elementary step that ultimately leads to the formation of alkenes (via subsequent deprotonation), which ultimately methylate by means of reactions with DME-derived C_1 species. These trends in reactivity among alkane hydrogen donor are consistent with the expected consequences of their heterolytic C–H bond-dissociation energies, which reflect the enthalpy required to form a carbenium ion and a hydride, on hydride-transfer rates to a given bound alkoxide.

Hydride transfer between alkanes and alkoxides [Eq. (6)] can be rigorously described by the thermochemical cycle in Scheme 3, in which the corresponding activation barrier consists of four terms: i) alkoxide separation from the surface, ii) hydride abstraction from the alkane donor, iii) reaction of H^- with the alkoxide-derived carbenium ion, and iv) adsorption of



Scheme 3. Thermochemical cycle for hydride transfer between a gas phase hydrocarbon donor and a surface alkoxide

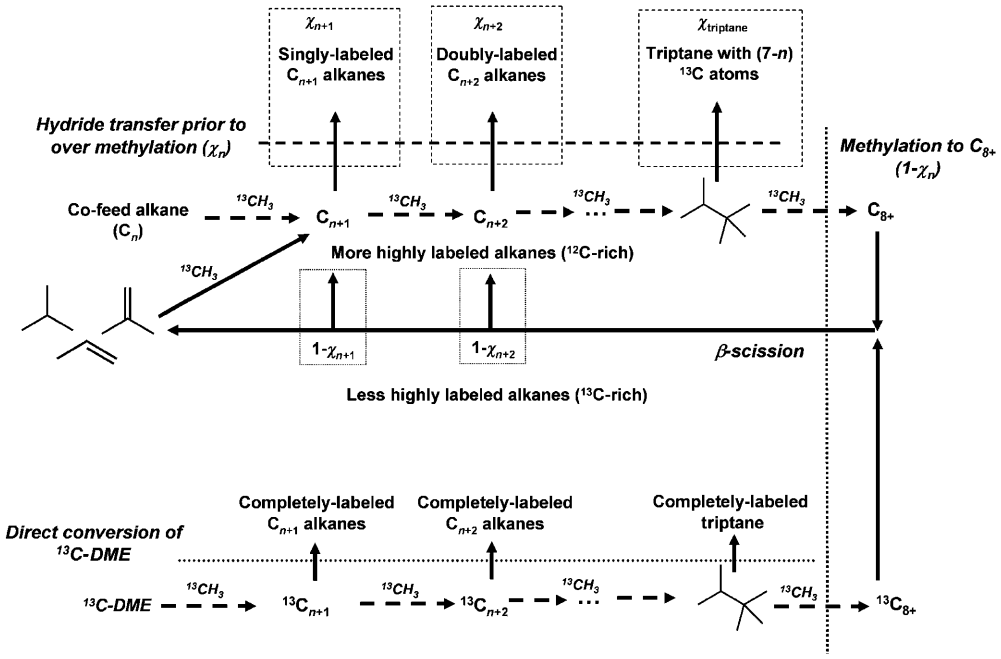
the alkane-derived carbenium ion to form the new alkoxide. The heterolytic C–O bond-dissociation energy in the alkoxide ($E_{C-O,\ cleavage}$) accounts for alkoxide detachment as a carbenium ion and separation from the anionic zeolite oxygen to non-interacting distances. $E_{H-abstraction}$ is the energy required to dissociate the alkane into a hydride and an alkyl carbenium ion. $E_{H-affinity}$ is the hydride affinity of the alkoxide-derived cationic acceptor (step 3) and $E_{C-O,\ formation}$ is the energy associated with the return of the donor-derived alkyl carbenium ion to the anionic framework oxygen to form the new alkoxide. DFT studies have suggested that that hydride transfer involves a transition state that resembles the donor molecule and a carbenium ion formed from desorption of the acceptor alkoxide.[14,26] Interaction between the donor molecule and carbenium ion leads an intermediate carbonium ion in which H^- is shared between these species, and this intermediate decomposes into the donor-derived alkoxide and the acceptor-derived alkane with the concerted or subsequent desorption of the former.[14,26] This decomposition step involves a transition state that resembles the carbenium ion from the donor molecule and the alkane from the acceptor alkoxide. Therefore, the reaction energies associated with the thermochemical cycle in Scheme 3 are properties of the molecules and the carbenium ions formed as transition states during detachment of acceptor alkoxide and H-abstraction from the donor molecule. The activation barrier for hydride transfer ($E_{a,HT}$) is related to these properties by Equation (7):

$$E_{a,HT} = E_{C-O\ cleavage} + E_{H\text{-}abstraction} - E_{H\text{-}affinity} - E_{C-O\ formation} \quad (7)$$

Gas-phase donor alkanes differ predominantly in their respective H-abstraction energies; branched alkanes have smaller hydride abstraction enthalpies (230, 228, and 226 kcal mol^{-1} for, isobutane, isopentane, and 2,3-dimethylbutane) than linear alkanes (247 kcal mol^{-1} for *sec*-butyl formation and 265 kcal mol^{-1} for 1-butyl),[28] because the resulting conjugated carbenium ions are more stable. Also, the tertiary alkoxides derived from branched alkane donors, which also desorb via carbenium ion transition states, are more likely to deprotonate to form the corresponding alkenes compared with secondary and primary alkoxides derived from *n*-alkanes (discussed in greater detail in Section 2.3). Alkenes with tertiary allylic C–H bonds are even more reactive hydride donors than branched alkanes because of their more effective delocalization of the positive charge, which leads, in turn, to more stable carbenium ions than those formed from alkanes (224 kcal mol^{-1} to form tertiary allylic carbenium ions from 3-methyl-1-butene or 2,3-dimethyl-1-butene[28]). The high reactivity of alkenes in hydride-transfer reactions leading to an increase in chain-termination probabilities with increasing alkene concentrations in reactants during homologation of DME on H-BEA has been demonstrated recently.[1]

We conclude from these data that branched alkanes participate in C_1 homologation paths at modest temperatures ($\approx$500 K) by pathways that essentially consist of stepwise dehydrogenation routes involving bimolecular hydrogen-transfer reactions. These reactions do not require hydride transfer cocatalysts if the alkanes are branched, because their tertiary C–H bonds readily undergo hydride transfer to bound alkoxides. The alkenes that formed undergo subsequent methylation and chain growth by using DME-derived C_1 species to form larger alkanes, which contain carbon atoms from both DME and alkane co-reactants. Such processes allow the growth of alkanes to longer chains and the potential upgrading of low-value small alkanes, derived from natural gas or petroleum processing, into larger hydrocarbons.

The significant participation of alkanes in DME homologation and the various routes leading to each product are also evident in the distribution of ^{13}C-isotopologues formed from ^{13}C-DME/^{12}C-alkane reactants. The homologation pathways leading to the products formed are depicted in Schemes 1 and 4. Methylation of the alkane-derived alkenes leads to chains that can desorb as larger alkanes before growth past C_7; these processes preserve the predominant isotopologue in each larger chain, which appears as molecules with *m*-^{13}C-atoms in the C_{n+m} products of ^{13}C-DME/$^{12}C_n$ alkane mixtures. The fraction of this component in the isotopologue distribution for each product is denoted as χ (measured as described in Section 4.2). Methylation can also form C_{8+} chains that undergo rapid β-scission to form isobutane and smaller alkenes, the latter of which rapidly re-enter the ^{13}C-DME homologation pathways.[1] Methylation events that form C_{8+} molecules lead to a nearly binomial component in the isotopologue distribu-



Scheme 4. Product formation pathways that occur during co-homologation of ^{13}C-labeled dimethyl ether and ^{12}C-alkanes. The molecules that form through methylation of the co-feed alkane and terminate prior to methylation past triptane, form unimodal components of the experimental isotopologue distributions (χ). Molecules that form by means of methylation of fragments from the β-scission of C_{8+} chains, form binomial components of the experimental isotopologue distribution ($1-\chi$). Molecules that consist exclusively of ^{13}C atoms are from the direct homologation of ^{13}C-DME.

tion (with a fraction denoted as $1-\chi$), because skeletal isomerization of larger chains occurs before β-scission and subsequent methylation. Direct homologation of ^{13}C-DME without ^{12}C-alkane participation forms fully-labeled products in alternate routes that contribute only a small fraction (less than 0.15; Figures 4–6) to measured isotopologue distributions in ^{13}C-DME/^{12}C-branched alkane reactions because of the low rates of initial C–C bond formation from C_1 species relative to the methylation of larger chains.[29–33] If the co-fed alkanes only participate to a small extent in homologation (e.g., *n*-butane; $^{12}C/^{13}C$ ratio of 0.09 in all products), the products of ^{13}C-DME/^{12}C-alkane mixtures consist of higher fractions of fully-labeled species (>0.75; Figure 3a–c) from the direct homologation of ^{13}C-DME

2,3-Dimethylbutane (Figure 4a) and triptane (Figure 4b) molecules formed from ^{13}C-DME/^{12}C-isopentane mixtures show unimodal distributions of singly-labeled and doubly-labeled species, respectively, as a result of one and two methyl additions to ^{12}C-isopentane. Each molecule also contains a binomial component with a ^{12}C fraction (0.24 and 0.21 in 2,3-dimethylbutane (Figure 4a) and triptane (Figure 4b), respectively), which is smaller than in the unimodal component (0.83 and 0.73 in 2,3-dimethylbutane and triptane, respectively), and also smaller than the mean ^{12}C fraction in each of these products (0.58 and 0.51 in 2,3-dimethylbutane and triptane). Triptane molecules formed from ^{13}C-DME/^{12}C-2,3-dimethylbutane mixtures (Figure 5a) also consist of a unimodal component of singly-labeled isotopologues (from a single methylation) and a binomial component with a smaller mean ^{12}C-fraction (0.32 versus 0.60). The more highly-labeled molecules (than singly-labeled 2,3-dimethylbutane in Figure 4a and doubly- and singly-labeled triptane in Figures 4b and 5a, respectively) reflect multiple methylation by $^{13}C_1$ species and contain ^{12}C fragments smaller than the ^{12}C-alkane; therefore, they must reflect β-scission reactions of C_{8+} chains (which occur at much higher rates than for smaller C_4-C_7 chains[1,3,7]), as also shown previously from the binomial isobutane isotopologues formed from ^{13}C-DME/^{12}C-alkene mixtures.[1] The ratio of unimodal to binomial components ($\chi/(1-\chi)$) is 1.3 for both 2,3-dimethylbutane and triptane (from ^{13}C-DME/^{12}C-isopentane), suggesting that methylation of the co-fed alkane and methylation of fragments from β-scission of larger chains contribute at similar rates to the formation of products from ^{13}C-DME/^{12}C-alkane reactants. The ratio of unimodal to binomial components in triptane molecules from ^{13}C-DME/^{12}C-2,3-dimethylbutane mixtures ($\chi/(1-\chi)=1.1$) is smaller than for triptane formed from ^{13}C-DME/^{12}C-isopentane (1.3). These data indicate that chains initiated by 2,3-dimethylbutane-derived alkenes are more likely to methylate past triptane compared with those initiated by isopentane-derived alkenes, simply because fewer methylation events are required to form C_{8+} chains from 2,3-dimethylbutane than from isopentane.

The *trans*-2-butene and isobutane molecules formed from ^{13}C-DME/^{12}C-isopentane mixtures (Figure 4c–d) and ^{13}C-DME/^{12}C-2,3-dimethylbutane mixtures (Figure 5b–c) show binomial isotopologue distributions with smaller mean ^{12}C fractions (0.36 in isobutane, 0.41 in trans-2-butene from ^{12}C-isopentane and 0.55 in trans-2-butene, 0.46 in isobutane from ^{12}C-2,3-dimethylbutane) than in the 2,3-dimethylbutane and triptane molecules formed from these mixtures. These data are consistent with the formation of chains smaller than the co-fed alkanes via β-scission of C_{8+} chains after their significant intra-molecular scrambling. The $\chi/(1-\chi)$ values close to unity (Figures 4a–b and 5a) indicate that the rate to form products by single (or double) methylation of the co-feed alkane followed by termination is similar to the total rate of products formed by methylation of fragments formed via β-scission of C_{8+} chains. Therefore, we conclude that methylation of alkenes derived from added ^{12}C-alkanes and the termination of these chains via hydride transfer before C_{8+} chains form, occurs concurrently with the methylation of β-scission fragments, which represents the preferential route for the formation of products smaller than the co-fed alkane (binomial distributions in Figures 4c–d and 5b–c).

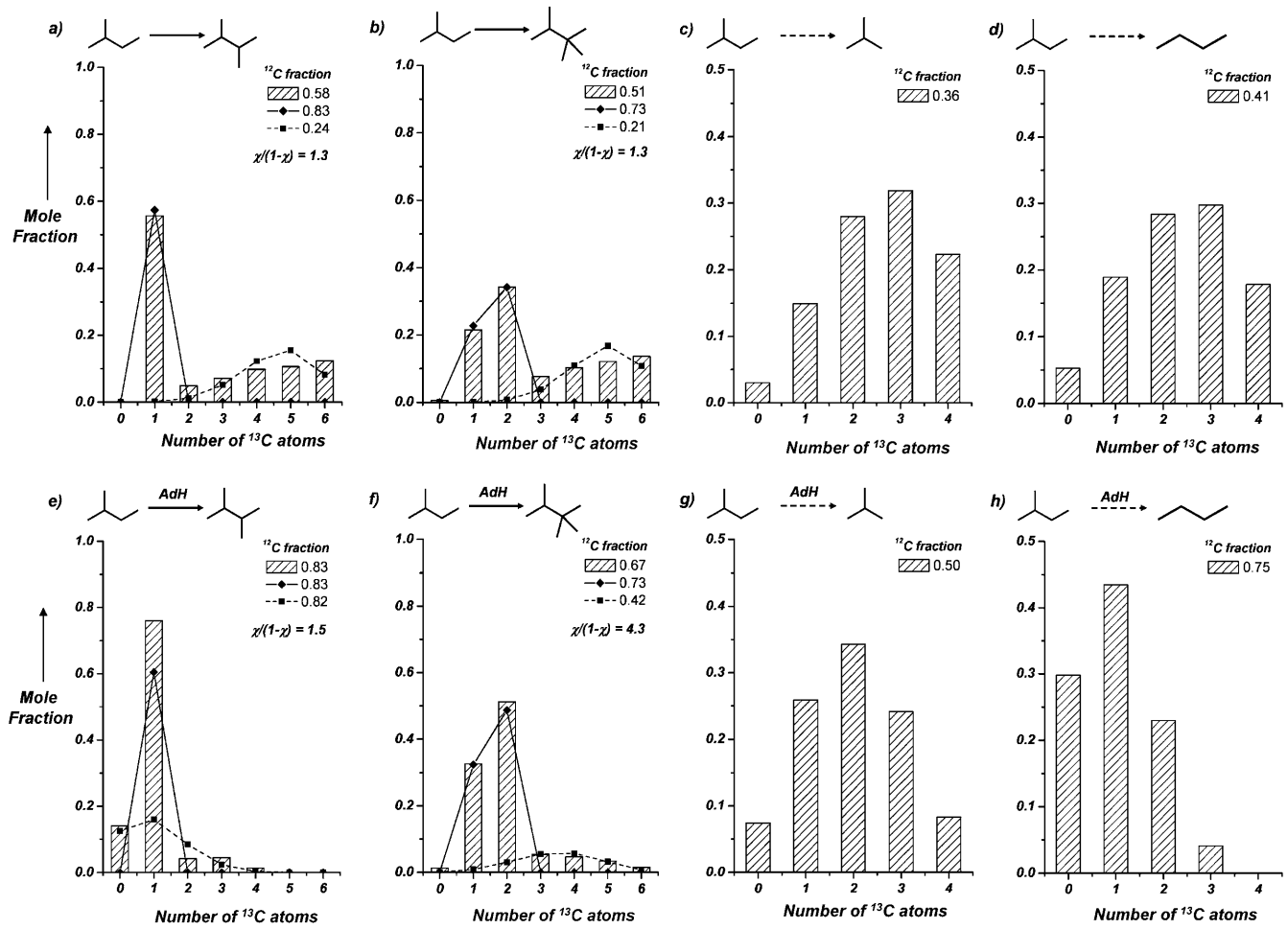


Figure 4. Effect of adamantane on the isotopologue distributions of 2,3-dimethylbutane (a, e), triptane (b, f), isobutane (c, g), and trans-2-butene (d, h) molecules from reactions between ^{13}C-labeled dimethyl ether (40 kPa) and ^{12}C-isopentane (40 kPa). Panels a-d are for reactions without adamantane, and panels e-h are for reactions using 1 kPa adamantane. Data were collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5). The square markers represent binomial components of the total distribution, and the diamond markers represent unimodal components of the total distribution. The 85 amu fragment of triptane appeared in higher concentrations in the mass spectrometer than the parent ion. Therefore, we use this fragment as a surrogate for the parent ion. Doubly-labeled triptane molecules fragment into doubly-labeled and singly-labeled 85 amu fragments, resulting in peaks at 1 and 2 ^{13}C atoms in the isotopologue distribution of the 85 amu fragment of triptane.

Isopentane, 2,3-dimethylbutane, and triptane molecules formed from ^{13}C-DME/^{12}C-isobutane mixtures (Figure 6a–c) also consist of unimodal and binomial isotopologue components, corresponding to isobutene methylation and β-scission of C_{8+} chains, respectively. The $\chi/(1-\chi)$ values for isopentane (1.0), 2,3-dimethylbutane (1.2), and triptane (0.82) molecules formed from isobutane are smaller than for 2,3-dimethylbutane molecules formed from isopentane (1.3) or triptane molecules formed from isopentane (1.3) and 2,3-dimethylbutane (1.1), indicating that more chains grow past C_{8+} and undergo β-scission for isobutane than for isopentane or 2,3-dimethylbutane co-reactants. These smaller $\chi/(1-\chi)$ values reflect lower rates of hydride transfer from isobutane than from isopentane or 2,3-dimethylbutane (consistent with the rates of ^{12}C appearance in Table 3), which cause, in turn, lower termination rates for all growing chains. As a result, singly-labeled isopentane, doubly-labeled 2,3-dimethylbutane, and triply-labeled triptane products from ^{13}C-DME/^{12}C-isobutane reactants form at lower concentrations than other isotopologues of each respective product.

The formation of molecules containing both ^{12}C and ^{13}C atoms from ^{13}C-DME/^{12}C-alkane reactants in the absence of adamantane (Table 3 and Figures 4–6) indicates that these alkanes are incorporated into homologation paths through dehydrogenation and subsequent methylation by DME-derived C_1 species. Dehydrogenation occurs if a prevalent gas-phase alkane donates a hydride to a surface alkoxide to desorb it as an alkane and form a new alkoxide, which subsequently desorbs as an alkene via deprotonation. The smaller extent of incorporation of *n*-butane compared with isobutane, isopentane, and 2,3-dimethylbutane reflects the preeminent role of heterolytic C–H bond dissociation energies in determining hydride donor reactivity. C–H bonds at tertiary carbons in branched alkanes act as more reactive hydride donors than alkanes with only secondary and primary carbons, which are essentially unreactive in the absence of hydride transfer co-catalysts. Similar

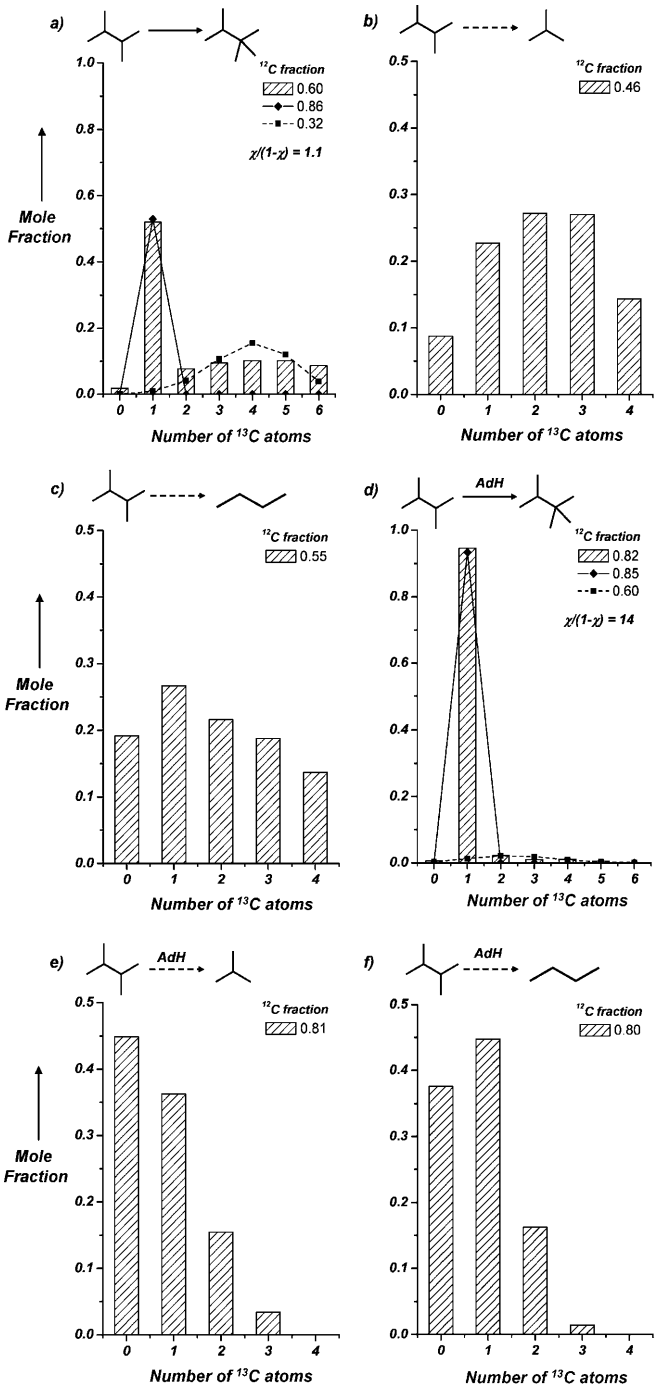


Figure 5. Effect of adamantane on the isotopologue distributions of triptane molecules (85 amu fragment; a, d), isobutane (b, e), and trans-2-butene (c, f) from reactions between ^{13}C-labeled dimethyl ether (40 kPa) and ^{12}C-2,3-dimethylbutane (40 kPa). Panels a)–c) are for reactions without adamantane, and panels d)–f) are for reactions using 1 kPa adamantane. The square markers represent binomial components of the total distribution, and the diamond markers represent unimodal components of the total distribution. Data were collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5). The 85 amu fragment of triptane appeared in higher concentrations in the mass spectrometer than the parent ion. Therefore, we use this fragment as a surrogate for the parent ion.

to alkane hydride donors, alkoxides with tertiary carbon atoms are more reactive hydride acceptors than secondary and primary alkoxides, as shown in previous studies of DME homologation on BEA.[1]

2.3. Effects of adamantane addition on co-homologation of DME and alkanes

Hydride transfer co-catalysts, such as adamantane, have been shown to increase rates of H-abstraction from alkanes.[5,18–21] In this section, we examine the ability of adamantyl species to catalyze alkane activation by means of H-abstraction and subsequent desorption of the resulting alkoxide as an alkene (Eqs. (4)–(5) and Scheme 2) by comparing alkane incorporation from ^{13}C-DME/^{12}C-alkane mixtures with and without adamantane. In doing so, we explore whether such hydride transfer co-catalysts can render linear alkanes reactive as co-reactants and branched alkanes even more effective as hydrogen donors.

The addition of adamantane (1 kPa) to ^{13}C-DME/^{12}C-*n*-butane mixtures led to a marked increase in the ^{12}C/^{13}C ratio within isopentane (0.12 to 1.2), 2,3-dimethylbutane (0.06 to 1.0), and triptane (0.05 to 0.6), as well as in the mean ^{12}C/^{13}C ratio among all products formed (0.09 to 1.2) (Table 3). The significant ^{12}C-content in the products formed when adamantane is present (Figure 3 d–f) shows that even n-alkanes can be introduced into homologation paths via adamantyl-mediated dehydrogenation pathways. Isopentane isotopologues formed from ^{13}C-DME/^{12}C-*n*-butane/adamantane mixtures consist of two binomial components and one singly-labeled unimodal component (from methylation of ^{12}C-*n*-butane). The binomial component with the smaller ^{12}C fraction (0.35) consists of species formed by the methylation of β-scission fragments, some of which can methylate again to C_{8+} chains (containing more than four ^{13}C-atoms) and subsequently undergo β-scission to form fragments with low ^{12}C content. The binomial component with the higher ^{12}C content (0.91) consists of species that form through *n*-butene oligomerization-β-scission reactions. The ratios of molecules in the unimodal and combined binomial components ($\chi/(1-\chi)$) for isopentanes (0.32; Figure 3 d) and in the single binomial component in 2,3-dimethylbutane (0.64; Figure 3 e) and triptane (0.47; Figure 3 f) indicate that adamantane activates even the strong secondary C–H bonds in *n*-butane to form *n*-butenes that methylate to form larger chains. Hydride transfer from *n*-butane to adamantyl cations occurs even for secondary C–H bonds in *n*-butane, apparently because adamantane replaces the acceptor alkoxides formed in C_1-homologation paths, and in doing so, becomes the hydride acceptor itself, providing an intermediate species with C–H bond energies intermediate between those in strong secondary C–H bonds in *n*-alkanes and weaker tertiary C–H bonds in branched alkanes. Thus, adamantane separates the single H-transfer step between a donor and an acceptor [Equation (6)] into two separate steps [Equations (3) and (4)], each with an apparently smaller activation barrier. Another possibility is that adamantane can stabilize transition states for H-transfer between a given donor and an acceptor by solvating the

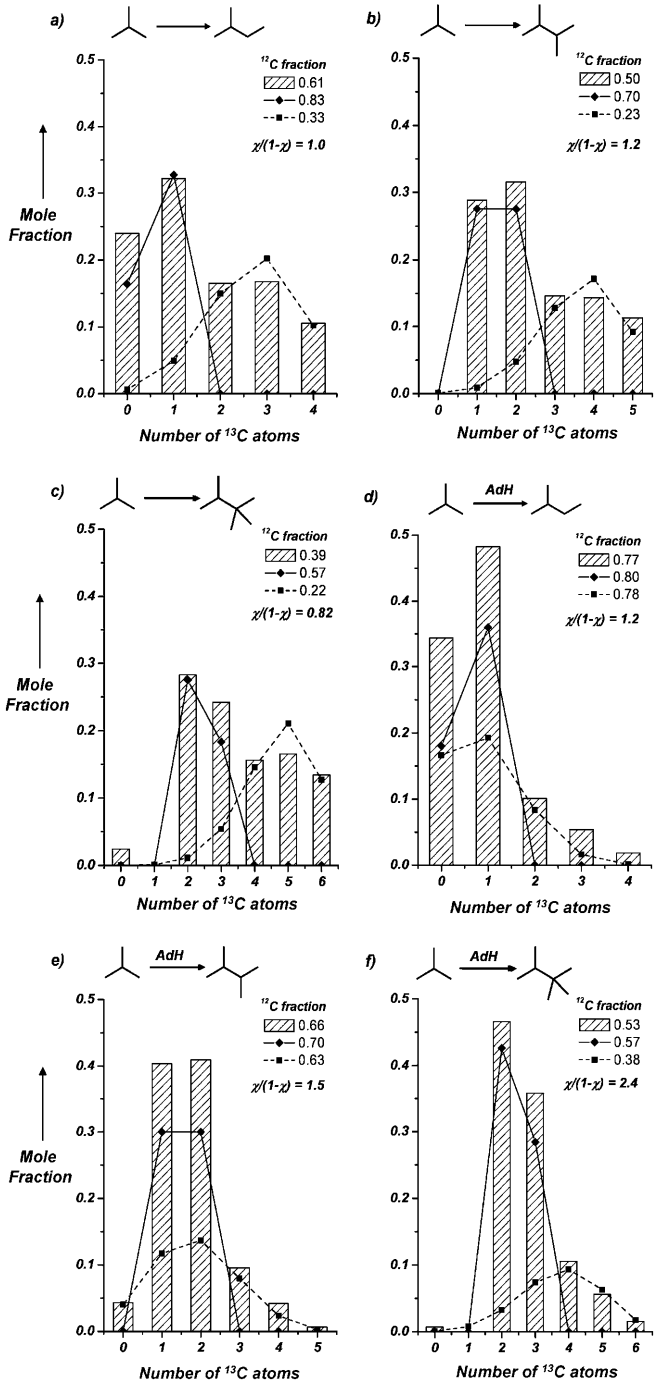


Figure 6. Effect of adamantane on the isotopologue distributions of isopentane (a, d; 57 amu fragment), 2,3-dimethylbutane (b, e; 71 amu fragment), and triptane (c, f; 85 amu fragment) molecules from reactions between ^{13}C-labeled dimethyl ether (40 kPa) and ^{12}C-isobutane (40 kPa). Panels a)–c) are for reactions without adamantane, and panels d)–f) are for reactions using 1 kPa adamantane. Data were collected at 473 K, less than 2.0% total carbon conversion, and a space velocity of 0.05 mol(inlet gas) mol(Al)$^{-1}$ s^{-1} (0.023 cm^3 s^{-1} total inlet gas flow rate; 0.020 g H-BEA with Si/Al = 12.5). The square markers represent binomial components of the total distribution, and the diamond markers represent unimodal components of the total distribution. The 85 amu fragment of triptane, 71 amu fragment of 2,3-dimethylbutane, and 57 amu fragment of isopentane appeared in higher concentrations in the mass spectrometer than their respective parent ions during co-reaction of ^{13}C-DME with ^{12}C-isobutane. Therefore, we use these fragments as surrogates for their respective parent ions. Singly-labeled isopentane molecules fragment into unlabeled and singly-labeled 57 amu fragments, resulting in peaks at 0 and 1 ^{13}C atoms in the isotopologue distribution of the 57 amu fragment of isopentane. Doubly-labeled 2,3-dimethylbutane molecules fragment into singly-labeled and doubly-labeled 71 amu fragments, resulting in peaks at 1 and 2 ^{13}C atoms in the isotopologue distribution of the 71 amu fragment of 2,3-dimethylbutane. Triply-labeled triptane molecules fragment into doubly-labeled and triply-labeled 85 amu fragments, resulting in peaks at 2 and 3 ^{13}C atoms in the isotopologue distribution of the 85 amu fragment of triptane.

cationic charge without the formation of adamantyl cations. Finally, it seems plausible that adamantyl cations formed via hydride transfer from adamantane to surface alkoxides [Equation (3)] can react with alkenes to form species that form more stable carbenium ions with smaller barriers than those involved in H-transfer to alkoxides bound directly to framework oxygen atoms in zeolites. Discriminating among these possibilities requires theoretical treatments that rigorously describe van der Waals stabilization within spatially constrained zeolite structures; such studies are outside the scope of this manuscript and will be addressed as theoretical methods are developed in future studies.

The addition of adamantane (1 kPa) to DME/*n*-butane did not influence C_5 or C_6 selectivities (Figure 1b). The combined selectivity to C_1-C_4 species, however, increased (from 46 to 74%; Figure 1b) with concurrent decreases in C_7 selectivities (from 23 to 7.6%, Figure 1b) and the selectivity to triptyls within C_7 molecules (from 74 to 48%, Table 3). C_1-C_4 products formed at the expense of C_7 products as adamantane also mediates the re-introduction of larger alkanes into chain growth pathways, causing their growth past triptane and their rapid β-scission to form smaller molecules (discussed in Section 2.1).[1,3,7] These data are consistent with the low values of $\chi/(1-\chi)$ (<1) for isopentane, 2,3-dimethylbutane, and triptane molecules formed from DME/*n*-butane mixtures (Figure 3d–f), which also reflect adamantane mediated re-incorporation of alkanes larger than the co-fed *n*-butane. Alkene-to-alkane ratios in C_5 and C_6 products decreased (Table 2), reflecting the concomitant increase in hydrogenation rates of surface alkoxides to alkanes by means of hydride transfer catalyzed by adamantane. The increase in selectivity to C_1-C_4 species (at the expense of C_5-C_7 hydrocarbons and triptane isomers) with adamantane addition to DME/*n*-butane reactants show that adamantane catalyzes *n*-butane dehydrogenation (^{12}C/^{13}C ratios in Table 3), but at lower rates than the hydrogenation of alkoxides (decrease in alkene-to-alkane ratios; Table 2) and the dehydrogenation of alkanes larger than *n*-butane, which contain tertiary C–H bonds (e.g., isopentane, 2,3-dimethylbutane, and triptane), as discussed in greater detail in Section 2.2.

In contrast with the effects of adamantane addition for DME/*n*-butane, adamantane led to an increase in the combined selectivity to C_{5-6} products formed from DME/isobutane mixtures (from 26 to 53%; Figure 1c) and to a concomitant decrease in the selectivity to C_7 products (from 43 to 23%) and to triptyl isomers within C_7 species (from 73 to 57%; Table 3). Adamantane led also to an increase in C_7 selectivities from DME/2,3-dimethylbutane mixtures (from 38 to 56%; Figure 1e). The observed increase in C_{5-6} (Figure 1c) and C_7 selectivities

(Figure 1e) reflects the higher prevalent concentrations of isobutene and 2,3-dimethylbutene resulting from adamantane-mediated alkane dehydrogenation; the decrease in C_7 selectivity from DME/isobutane reflects the premature termination of growing chains through adamantane-mediated hydride transfer to alkoxides. The concurrent decrease in C_4 selectivity (from 41 to 24%) and increase in C_7 selectivity (from 38 to 56%) for DME/2,3-dimethylbutane mixtures also indicates that adamantane causes chains to terminate before forming C_{8+} chains that undergo rapid β-scission to form isobutane. The selectivity to isobutyl species within C_4 products remains high (94% for DME/2,3-dimethylbutane mixtures with and without adamantane; Table 3), however, even though chain termination rates increased markedly if adamantane was added. The prevalence of isobutyl species within C_4 products reflects rates of methylation of triptene (followed by β-scission of the resulting C_{8+} chains) larger than of hydride transfer to *sec*-butoxide (to form *n*-butane), as a result of the high concentration of the immediate precursor to triptyls (i.e., 2,3-dimethylbutenes that methylate to 2,3,3-trimethyl *sec*-butoxide). The alkene-to-alkane ratios within C_5 and C_6 chains from DME/isobutane reactants and within C_4 and C_5 chains from DME/2,3-dimethylbutane (Table 2) also decreased with adamantane addition, because of the concomitant increase in the rate of hydride transfer to bound alkoxides and their preferential desorption as alkanes instead of more reactive alkenes. Therefore, we conclude that adamantane increases the rate of hydride transfer events, which incorporate added alkanes by means of dehydrogenation to alkenes and terminate chains formed in methylation via alkoxide desorption as alkanes instead of alkenes.

The mean $^{12}C/^{13}C$ ratio among all products (Table 3) increased upon adamantane addition to mixtures of ^{13}C-DME with ^{12}C-isopentane (0.9 to 1.8), ^{12}C-2,3-dimethylbutane (1.1 to 4.1), or ^{12}C-isobutane (0.8 to 1.9), consistent with adamantane-mediated alkane activation. The presence of adamantane in ^{13}C-DME/^{12}C-alkane reactant streams increased $\chi/(1-\chi)$ values for 2,3-dimethylbutane (from 1.3 to 1.5; Figure 4a,e) and triptane (from 1.3 to 4.3; Figure 4b,f) molecules formed from ^{13}C-DME/^{12}C-isopentane reactants and also for triptane molecules formed from ^{13}C-DME/^{12}C-2,3-dimethylbutane reactants (from 1.1 to 14; Figure 5a,d). The addition of adamantane also increased $\chi/(1-\chi)$ values (Figure 6) for all the products formed from ^{13}C-DME/^{12}C-isobutane reactants. These larger $\chi/(1-\chi)$ values reflect an increase in the rate of hydride transfer to surface alkoxides, which inhibits their growth to C_{8+} chains that ultimately undergo facile β-scission. The isotopologue distributions for isobutane and trans-2-butene molecules formed from ^{13}C-DME/^{12}C-isopentane (Figure 4 g–h) and ^{13}C-DME/^{12}C-2,3-dimethylbutane (Figure 5 e–f) mixtures in the presence of adamantane are binomial and contain larger mean ^{12}C contents than without adamantane, reflecting their formation from β-scission of C_{8+} chains that contain fragments of the co-fed alkane.

The stronger effects of adamantane on the incorporation of *n*-butane compared with that of isobutane, isopentane, or 2,3-dimethylbutane (as shown by the $^{12}C/^{13}C$ ratios in Table 3) reflect the faster rates of dehydrogenation of branched alkanes. Adamantane increased the total rate of *n*-butane incorporation from 0.034 to 0.043 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1} (Table 3), however, it also decreased ^{13}C-DME consumption rates (from 0.36 to 0.04 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}) because *sec*-butoxides displaced $^{13}C_1$ species on Brønsted acid sites. Adamantane caused larger increases in rates of co-fed alkane incorporation (^{12}C-appearance rates in all products; Table 3) in the cases of branched alkanes than *n*-butane (isobutane: 0.07 to 0.23; isopentane: 0.67 to 1.8; 2,3-dimethylbutane: 0.64 to 2.7; 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}), but rates of ^{13}C-DME consumption from DME/branched-alkane mixtures in the presence of adamantane remain similar to those without added adamantane (isobutane: 0.10 to 0.12; isopentane: 0.83 to 0.90; 2,3-dimethylbutane: 0.60 to 0.66; 10^{-3} mol(C) mol(Al)$^{-1}$ s^{-1}). The alkoxides derived from these branched alkanes also displace $^{13}C_1$ species on acid sites, but undergo faster deprotonation and subsequent methylation than *sec*-butoxides because they form stable tertiary carbenium ion transition states, leading to shorter effective surface residence times and lower surface concentrations for these species than for *sec*-butoxides. Therefore, the observed increase in the rates of branched alkane dehydrogenation with adamantane addition to DME/alkane mixtures do not cause a decrease in the surface concentration of $^{13}C_1$ species (and rates of ^{13}C-DME consumption) observed with *n*-butane co-reactants.

The incorporation of these added alkanes into DME homologation can mitigate the formation of unsaturated arenes (e.g., HMB) as by-products by supplying the hydrogen atoms required by the stoichiometry of DME conversion to alkanes [Eqs. (1)–(2)]. Therefore, the ratio of formation rates (on a carbon basis) of alkane products to HMB increases as products form by way of Equation (2) instead of Equation (1). These ratios (Table 3) indeed increased with adamantane addition to ^{13}C-DME/^{12}C-*n*-butane (from 23 to 35) and ^{13}C-DME/^{12}C-isobutane (from 4.5 to 20) mixtures, confirming that carbon rejection as unsaturated arenes becomes less prevalent when chains can be initiated by the added alkanes. These ratios, however, are similar for ^{13}C-DME/^{12}C-isopentane (52 versus 55) and ^{13}C-DME/^{12}C-2,3-dimethylbutane (61 versus 63) mixtures with and without adamantane, indicating that the isopentene and 2,3-dimethylbutene derived from these co-fed alkanes participate in subsequent hydride-transfer reactions (as H-donors) at similar rates as they are methylated by ^{13}C-DME.

Alkenes (derived from co-fed ^{12}C-alkanes) that donate hydrogen to bound alkoxides instead of undergoing methylation reactions will preferentially form unsaturated precursor molecules that ultimately form arenes via cyclization reactions,[1,3,7,34–36] causing their ^{12}C-atoms to appear within HMB molecules as opposed to alkanes formed from ^{13}C-DME/^{12}C-alkane reactants. $^{12}C/^{13}C$ ratios within HMB molecules (Table 3) from isopentane and 2,3-dimethylbutane co-reactants increased (with adamantane addition) to a greater extent (from 0.2 to 1.0 for isopentane and 0.07 to 0.9 for 2,3-dimethylbutane) than $^{12}C/^{13}C$ ratios within all alkane products from these co-feed alkanes (from 0.8 to 1.9 for isopentane and 1.1 to 4.1 for 2,3-dimethylbutane). These changes in $^{12}C/^{13}C$ ratios within HMB indicate that increasing the concentration of isopentenes

and 2,3-dimethylbutenes, via adamantane-catalyzed dehydrogenation of their respective alkanes, increases their rates of subsequent hydride transfer more strongly than their respective methylation rates. The increase in the $^{12}C/^{13}C$ ratios in HMB from ^{13}C-DME/^{12}C-*n*-butane and ^{13}C-DME/^{12}C-isobutane mixtures are smaller (from 0.11 to 1.0 for *n*-butane and 0.8 to 1.3 for isobutane) than the increases in $^{12}C/^{13}C$ ratios within all alkane products from these reactants (from 0.09 to 1.2 for *n*-butane and 0.9 to 1.8 for isobutane), reflecting that isobutene and *n*-butenes do not participate in subsequent hydride transfer before methylation. This behavior reflects the lower H-abstraction energies of tertiary allylic C–H bonds in isopentenes and 2,3-dimethylbutenes than of primary and secondary allylic C–H bonds in *n*-butenes in isobutene,[34–36] which lead to lower activation barriers for hydride transfer (as discussed previously).

These effects of adamantane on $\chi/(1-\chi)$ values and $^{12}C/^{13}C$ ratios of products from ^{13}C-DME/^{12}C-alkane reactants reflect the known ability of adamantane as a hydride transfer co-catalyst.[18–24] The addition of adamantane to ^{13}C-DME/^{12}C-alkane mixtures increases the rate of dehydrogenation of the alkane co-reactants and leads to a concomitant increase in $\chi/(1-\chi)$ ratios and ^{12}C content in all chains that result from the subsequent methylation of these alkenes. The increase in ^{12}C content of products with adamantane addition to ^{13}C-DME/^{12}C-alkane reactants reflects higher rates of alkane incorporation into homologation chains, and the concurrent increase in alkane to hexamethylbenzene formation rates indicates that these co-feed alkanes supply, in part, the necessary H-atoms for alkane formation from DME. Increases in $^{12}C/^{13}C$ ratios within HMB, however, reflect that alkane-derived alkenes containing tertiary allylic C–H bonds donate H-atoms before they methylate by ^{13}C-DME. The higher values of $\chi/(1-\chi)$ ratios, which reflect the ratio of chains formed via methylation of the added alkane to those from methylation of β-scission fragments, also indicate that adamantane catalyzes the termination of chains along the homologation path.

We have shown here that adamantane serves as a hydride transfer co-catalyst during Brønsted acid-catalyzed DME homologation. Adamantane facilitates incorporation of co-fed alkanes into homologation pathways, leading to a chain growth route from DME-derived C_1 species that occurs with less rejection of carbon as arene by-products because the alkane co-reactant supplies a portion of the stoichiometric H-atoms. Furthermore, adamantane influences the molecular weight distribution of homologation products by increasing chain termination rates via hydride transfer to bound alkoxides. These effects of adamantane on DME homologation extend analogously to other acid-catalyzed hydrocarbon conversion processes (such as alkylation) which involve hydride transfer steps that prodeed through carbenium ion transition states.

3. Conclusions

Added alkanes (*n*-butane, isobutane, isopentane, and 2,3-dimethylbutane) and adamantane affect DME homologation rates and product selectivities by influencing rates of hydride-transfer reactions that desorb surface alkoxides as alkanes and activate alkanes for methylation via dehydrogenation to their respective alkenes. In the absence of added alkanes, adamantane decreased the selectivity to C_7 and to triptyl isomers by prematurely terminating surface alkoxides as alkanes by means of hydrogenation. Branched alkanes (isobutane, isopentane, 2,3-dimethylbutane) containing tertiary C–H bonds are dehydrogenated to alkenes and incorporated into homologation pathways, even in the absence of adamantane, through hydride-transfer reactions with surface alkoxides. *n*-Butane is essentially unreactive in the absence of adamantane, however, indicating that the strength of C–H bonds in alkane hydride donors predominantly controls rates of hydride transfer with surface alkoxides. The addition of adamantane to DME/alkane co-feeds increased the extent to which alkanes are incorporated into chain growth paths, especially linear isomers that are otherwise unreactive. Adamantane addition to DME/alkane co-reactants also led to a decrease in formation of hexamethyl benzene relative to alkane products, indicating the partial fulfillment, from the co-fed alkanes, of the stoichiometric hydrogen requirement to form alkanes from DME. These findings suggest that the presence of a hydride transfer co-catalyst (e.g., adamantane) during acid-catalyzed homologation can be used to produce higher value alkanes, with specific isomeric structures and molecular weight distributions, from the addition of DME- and methanol-derived C_1 intermediates to light alkanes with minimal formation of arene by-products.

4. Experimental Section

4.1. Catalyst, reactants, and kinetic and isotopic tracer studies: The acid form of zeolite BEA was prepared by heating NH_4-BEA (Si/Al = 12.5, Zeolyst) to 773 K (at 0.02 K s^{-1}) for 10 h in flowing dry air (1.7 $cm^3 s^{-1} g^{-1}$, zero grade, Praxair); its crystal structure was confirmed by using X-ray diffraction.[1] Rate data with unlabeled reactants were obtained using a quartz reactor (12.5 mm O.D.) with plug-flow hydrodynamics containing H-BEA (0.14-0.28 g; 180-250 μm particles) held onto a porous quartz disc. The sample was heated to 773 K (at 0.02 K s^{-1}) and held for 2 h in flowing, dry air (0.8 $cm^3 s^{-1}$) and cooled to 473 K. Temperatures were controlled electronically (Watlow, Series 989) and measured by using a type-K thermocouple held at the external reactor wall. Argon was used to remove residual air from the reactor (0.8 $cm^3 s^{-1}$, UHP, Praxair) before introducing reactants consisting of DME (0.04–0.08 $cm^3 s^{-1}$, 99.5%, Matheson) and Ar (0.02-0.04 $cm^3 s^{-1}$, 99.999%, Praxair) with isobutane (0.04-0.08 $cm^3 s^{-1}$, 99.99%, Praxair), *n*-butane (0.04-0.08 $cm^3 s^{-1}$, 99.99%, Praxair), or propene (0.63 $cm^3 s^{-1}$ of a 20% propene (99.999% purity), 5% Ar, 75% He mixture; Praxair). Gaseous reactants were metered with mass flow controllers (Porter, Model 201). Liquid 2,3-dimethylbutane (98%, Sigma Aldrich) was introduced into the reactor at 0.9 $cm^3 h^{-1}$ (as vapor 0.043 cm^3 (gas at STP) s^{-1}) using a 10 cm^3 syringe (Hamilton) and a syringe pump (KD Scientific 780100). Solid adamantane ($C_{10}H_{16}$, 99%, Fluka) was introduced by sublimation at 373 K into the gaseous reactants. The reactor effluent was transferred through heated lines (> 373 K) into a gas chromatograph (Agilent 6890) equipped with a methyl siloxane column (HP-1, 50 m × 0.32 mm × 1.05 μm) and a flame ionization detector for chemical composition analysis. Inlet and outlet mole fractions of adamantane were similar for all homologation ex-

periments as well as blank experiments in which the BEA catalyst was exposed to a feed consisting of adamantane (≈1 kPa) in Ar.

Rate data with ^{13}C-labeled DME (^{13}C-DME) and various unlabeled co-reactants were measured in a stainless steel reactor (6.35 mm O.D.) with plug-flow hydrodynamics containing H-BEA (0.02 g; 180–250 μm particles) samples held onto a fritted gasket by quartz wool. The catalyst was heated to reaction temperature (473 K at 0.08 K s^{-1}) in flowing He (0.08 cm^3 s^{-1}, UHP, Praxair). Reactant streams consisted of equimolar mixtures of ^{13}C-labeled DME (^{13}C-DME; 99%, ISOTEC) with various unlabeled alkanes (*n*-butane (99.99% Praxair), isobutane (99.99% Praxair), isopentane (98% Sigma–Aldrich), and 2,3-dimethylbutane (98% Sigma–Aldrich)). Adamantane was introduced into the reactor in small concentrations (≈1 kPa) by means of sublimation at 373 K into the flowing reactant mixture. The reactor effluent was transferred through heated lines (>373 K) into a gas chromatograph with flame ionization and mass selective detectors (HP 5890/HP 5972, Agilent 6890 A/Agilent 5973N, or Agilent 7890 A/Agilent 5975C) each connected to a capillary column (HP-1, methyl silicone, 50 m × 0.32 mm × 1.05 μm) to measure chemical and isotopic compositions. Isotopologue distributions were determined from mass fragmentation patterns using previously reported deconvolution methods.[37]

4.2. Calculation of binomial components of isotopologue distributions: The distributions of isotopologues formed in co-homologation of ^{13}C-DME and ^{12}C-alkanes typically contain superimposed binomial and unimodal components. The fraction of a given isotopologue with *n* carbon atoms and *i* ^{13}C atoms ($n^{13}C_i$) can be described in terms of its fractional content within the unimodal (χ) and binomial ($1-\chi$) components according to the following equation (in which $^{13}C_{binomial}$ is the ^{13}C fraction within isotopologues associated with the binomial component) [Eq. (8)]:

$$[n^{13}C_i] = [(\chi) + (1-\chi)(^{13}C_{binomial})^n(1-^{13}C_{binomial})^{(n-i)}] \quad (8)$$

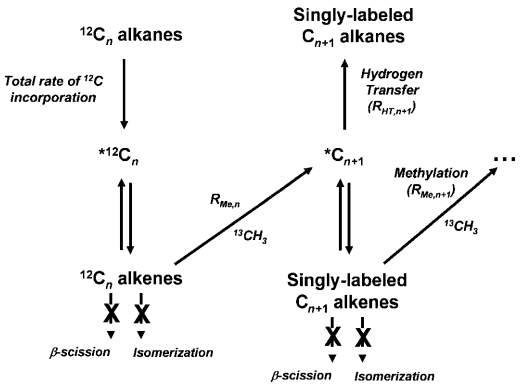
The values of χ and $^{13}C_{Binomial}$ were determined by minimizing the sum of the squares of the residuals between the experimental data and Equation (8).

In some cases, isotopologue distributions can consist of two superimposed binomial components. In this case, the unimodal component in Equation (8) is replaced with an additional binomial component [Eq. (9)] and the fractions of a particular isotopologue associated with the two binomials (χ and $1-\chi$) and the ^{13}C contents of these binomials ($^{13}C_\chi$ and $^{13}C_{1-\chi}$) were determined by minimizing the sum of the squares of the residuals between experimental data and Equation (9):

$$[n^{13}C_i] = [(\chi)(^{13}C_\chi)^i(1-^{13}C_\chi)^{(n-i)} + (1-\chi)(^{13}C_{1-\chi})^i(1-^{13}C_{1-\chi})^{(n-i)}] \quad (9)$$

These methods were used to determine the relative contributions of different hydrocarbon formation routes to experimental isotopologue distributions of products formed during co-homologation of ^{13}C-DME and ^{12}C-alkanes.

4.3. Measurements of termination probabilities from isotopic tracer data: ^{12}C-alkane isomers with *n* carbons enter chain-growth pathways through dehydrogenation to their respective alkenes and subsequent methylation by ^{13}C-DME to form singly-labeled C_{n+1} alkoxides (Scheme 5). These singly-labeled alkoxides can undergo hydride transfer to form singly-labeled C_{n+1} alkanes. The rates of these hydride transfer steps [$R_{HT,n+1}$; Eq. (10)] were estimated from the rate of formation of the singly-labeled isotopologue of the C_{n+1} alkane formed by means of a single methylation of co-fed C_n alkanes by ^{13}C-DME (singly-labeled isopentane, 2,3-dimethylbutane, and triptane from ^{13}C-DME/^{12}C-isobutane, ^{13}C-DME/^{12}C-isopentane, and ^{13}C-DME/^{12}C-2,3-dimethylbutane, respectively):



Scheme 5. Pathways for alkanes co-fed with ^{13}C-dimethyl ether during co-homologation reactions. The asterisk indicates alkoxide attachment to the surface. $^{13}CH_3$ represents surface methylating species derived from ^{13}C-dimethyl ether.

$$R_{HT,n+1} = \frac{R_{C_{n+1}} \times X_{^{13}C_1}}{n} \quad (10)$$

In this equation, $R_{C_{n+1}}$ is the total rate of formation of C_{n+1} alkanes (on a carbon basis) through methylation of the co-fed C_n alkane, $X_{^{13}C_1}$ is the fraction of these alkanes that are singly-labeled, and *n* is the size of the co-fed alkane. Alternatively, these singly-labeled C_{n+1} alkoxides can deprotonate to their alkenes and undergo further methylation to form molecules with two or more ^{13}C-atoms. The sum of the rates of hydride transfer and methylation of these singly-labeled species equals the rate of methylation of the $^{12}C_n$-alkenes derived from the co-fed alkane (as shown in Scheme 5), because rates of isomerization and β-scission are very slow relative to hydride transfer and methylation (as shown previously[1]). Thus, the rate of methylation [$R_{Me,n+1}$; Eq. (11)] of the singly-labeled alkenes can be determined by subtracting the rate of hydride transfer to their alkoxides [$R_{HT,n+1}$; Eq. (10)] from the total rate of introduction of ^{12}C-atoms into products of ^{13}C-DME/^{12}C-alkane reactants (because this rate of introduction reflects the rate of methylation of alkenes, $R_{Me,n}$, derived from $^{12}C_n$-alkanes)

$$R_{Me,n+1} = \frac{\left(\sum_i R_i \times X\right)}{n} - R_{HT,n+1} \quad (11)$$

In this equation, R_i is the total rate of formation (on a carbon basis) of molecules with *i* carbons and *X* is the ^{12}C-atomic fraction in each molecule (determined from isotopic data). These hydride transfer and methylation rates were used to determine termination probabilities for isopentyl, 2,3-dimethylbutyl, and triptyl species from competitive reactions between ^{13}C-DME and ^{12}C-isobutane, ^{12}C-isopentane, and ^{12}C-2,3-dimethylbutane, respectively, [β_{n+1}; Eq. (12), defined previously as the ratio of the rate of hydride transfer to the sum of the rates of methylation and hydride transfer[1]]

$$\beta_{n+1} = \frac{R_{HT,n+1}}{R_{Me,n+1} + R_{HT,n+1}} \quad (12)$$

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