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A mechanistic explanation for selectivity in the conversion of methanol to 2,2,3-trimethylbutane (triptane): Moderate acidity allows kinetic control to operate

Nilay Hazari, Jay A. Labinger *, Valerie J. Scott

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125, USA

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ABSTRACT

Methanol is converted to hydrocarbons by reaction with ZnI_2 or InI_3 at 200 °C, with surprisingly high selectivity (yields on the order of 20%) to a single highly branched alkane, 2,2,3-trimethylbutane (triptane). Mechanistic studies demonstrate that the previously proposed mechanism, which proceeds via a carbocation-based route that involves methylation of olefins and hydride transfer to carbocations, can account quantitatively for the selectivity. Differences in product distribution between the Zn- and In-based systems represent quantitative, not qualitative, differences in behavior, and can be attributed to the slightly higher effective acidity of the latter.

1. Introduction

The ongoing depletion of oil reserves and the rising cost of oil have led to increased interest in methanol as both a direct energy source and a petrochemical feedstock [1,2]. One common approach involves acid-catalyzed dehydrative condensation of methanol into hydrocarbons [3]; different classes of hydrocarbons can be obtained depending on the nature of the catalyst and the temperature (typically 200–450 °C). The most familiar examples are the methanol-to-gasoline (MTG) and methanol-to-olefins (MTO) processes, which operate at temperatures above 300 °C over zeolitic and aluminophosphate catalysts [4–6].

In 1978, the reaction of methanol with ZnI_2 at 200 °C was reported to give quite different results: the hydrocarbon product mixture consisted primarily of highly branched alkanes and highly methylated benzenes, with striking selectivity for one particular alkane, 2,2,3-trimethylbutane (triptane), which was obtained in overall yields of up to 20% (based on moles of carbon), corresponding to as much as half of the gasoline-range fraction (Eq. (1)) [7]. Besides the obvious practical advantages that would result from development of a convenient synthetic route to a potentially highly valuable fuel (triptane's research octane number is 112), there is a fundamental question of considerable interest: how can we account for the unusual selectivity in mechanistic terms?

The chemistry here appears to be significantly different from that of the MTG and MTO reactions, which take place at considerably higher temperatures and give very different product distributions. Their mechanism(s) have inspired lengthy debate, but consensus seems to be coalescing about a "hydrocarbon pool" route, which involves polymethylbenzenes as the key intermediates. These undergo rearrangements and fragmentations to split off small (C_{2-4}) olefins, generating less-substituted benzenes which are remethylated by methanol. For MTG the main products are C_{2-4} paraffins, obtained via hydrogen transfer processes, and C_{7-10} methylbenzenes; the shape-selective properties of the catalyst ensure that larger arenes are unable to exit the cages [8]. In the case of MTO *no* arenes can get out, and the products consist of C_{2-4} olefins; selectivity among those may be controlled by speciation preferences in the hydrocarbon pool (which in turn is presumably governed by the catalyst's shape selectivity) [9]. It seems most unlikely that any analogous mechanism could explain the ZnI_2 catalyzed conversion.

Our initial studies implicated a carbocation-based mechanism, involving homologation via successive olefin methylation and deprotonation (Scheme 1). Formation of the first reactive C=C bonded species is catalyzed heterogeneously: it does not take place if the ZnI_2 is fully dissolved in methanol prior to heating. (The growth stage, in contrast, is homogeneous, proceeding equally well whether or not any solid is present.) This initiation can be completely bypassed by the addition of a suitable promoter, either an unsaturated compound (olefin or arene) or a higher alcohol; the latter presumably functions as a facile precursor to an olefin [10].

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* Corresponding author. Fax: +1 626 449 4159.
E-mail addresses: nhazari@caltech.edu (N. Hazari), jal@caltech.edu (J.A. Labinger), val@caltech.edu (V.J. Scott).

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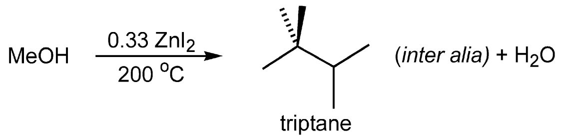
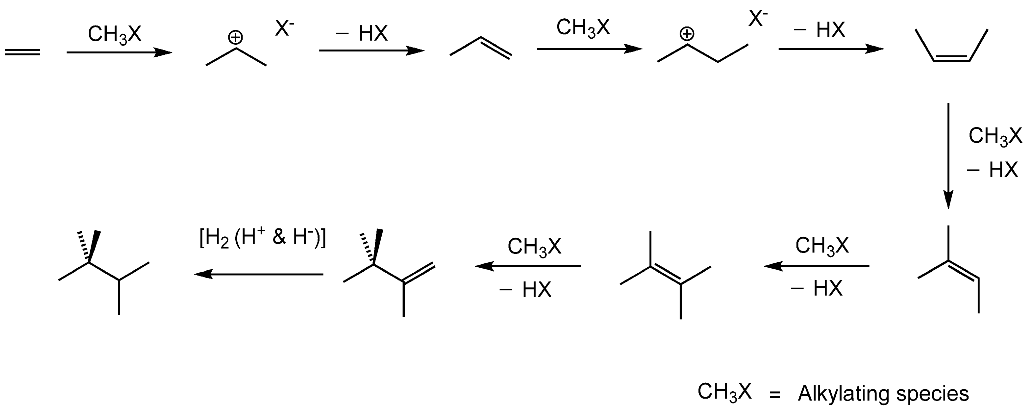
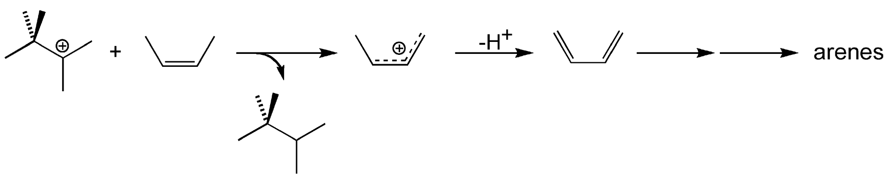


(**1**)

Equation 1.



Scheme 1.



Scheme 2.

Table 1

PIANO analysis [10,12] results for conversion of methanol over metal iodides.[a]

Compound or class	Yield with ZnI_2[b]	Yield with InI_3[b]
n-Paraffins	1.3	0.6
Isoparaffins	45.0	58.7
i-Butane	2.6	2.8
2-Methylbutane	2.9	9.1
2-Methylpentane	0.4	2.3
3-Methylpentane	0.3	1.6
2,3-Dimethylbutane	1.8	5.3
Total C_6 isoparaffins	2.5	9.1
2,3-Dimethylpentane	0.7	2.4
2,4-Dimethylpentane	0.4	1.5
Triptane	24.9	26.6
Total C_7 isoparaffins	26.2	30.7
Total C_8 isoparaffins	3.8	4.3
Olefins	14.2	0.4
Triptene	5.6	–
Arenes	10.7	23.3
1,2,3,5-Tetramethylbenzene	0.5	1.7
1,2,4,5-Tetramethylbenzene	0.3	1.2
Pentamethylbenzene	0.6	13.1
Hexamethylbenzene	3.4	5.5
Naphthenes	5.2	4.6

[a] For 2 h reactions at 200 °C.

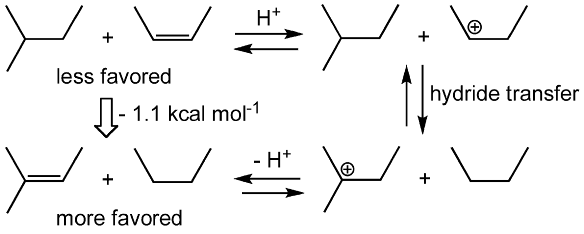
[b] Stated as the weight percent of the corresponding compound or class of compounds in the organic layer, after separation of the aqueous layer.

Since homologation products are obtained in large (molar) excess over the amount of added promoter, there must be a "feedback" mechanism that regenerates light olefin building blocks; possible candidates will be discussed later.

Although stoichiometrically the dehydrative condensation of methanol would lead to alkenes, C_nH_{2n}, the actual product distribution consists primarily of alkanes and arenes, with only small amounts of alkenes. Alkane formation is accomplished via hydride transfer from an unsaturated hydrocarbon to a carbocation, which effects the net transfer of H_2 from one olefinic hydrocarbon to another. This results in an alkane and a multiply unsaturated species which eventually ends up as an arene, as illustrated in Scheme 2 [10].

Because conversion is limited by water formation, reactions are carried out with relatively high catalyst loadings: methanol:metal iodide molar ratios are typically around 3. However, we have previously shown that much higher turnover numbers, which would clearly be needed in a practical process, can be achieved by operating in batch mode with periodic removal of volatiles (including water) [10].

In subsequent work we established that P–H bonded species (phosphorous and hypophosphorous acids) can serve as alternate hydride sources and thus increase triptane yields by reducing the fraction of feed sacrificed to arene formation [11]; that InI_3 also functions as a catalyst for this transformation [12]; and that InI_3 is further able to catalyze the homologation of branched alkanes with methanol to produce heavier and more highly branched alkanes [13]. Table 1 shows typical product slates for ZnI_2 and InI_3 catalyzed reactions (run for 2 h at 200 °C with a 3:1 ratio of methanol:catalyst), obtained from standard refinery "PIANO" analysis [10,12] (these will not be precise because of volatility of lighter hydrocarbons and incomplete identification of GC peaks for heavier ones); the results are generally similar except for the virtual absence of any olefins, and a corresponding increase in isoparaffins and arenes, for the In case. The strong preference for generating the most substituted possible carbocation at each methylation step in Scheme 1 can account for the general selectivity to branched products (with the exception of C_4 which will be discussed in a later section), and a mixture of alkanes plus arenes will be pre-



Scheme 3.

ferred over alkenes on thermodynamic grounds. However, these points do not account for the high selectivity to triptane, which has nothing to do with thermodynamics [10]. In contrast, methanol condensation induced by polyphosphoric acid (reported approximately contemporaneously with the first ZnI_2 publication) takes place at similar temperatures and likewise gives primarily alkanes and arenes, but there is no comparable selectivity: a broad distribution of alkanes (in terms of both molecular weight and isomerism) is obtained [14].

Our tentative explanation for these results centered on the fact that there will effectively be a competition between methylation and hydrogenation for each of the growing olefins in Scheme 1 and that the relative rates of those two processes will depend strongly on the degree of substitution of the olefin. As previously discussed [10], the increased electron richness of more substituted olefins will make methylation faster, although a counterbalancing steric retardation probably sets in at some point. On the other side of the balance, hydrogenation is thermodynamically more favorable for *less* substituted olefins, as exemplified in Scheme 3. Of course, reactions of the sort shown cannot be fully equilibrated under reaction conditions, since that would lead to a thermodynamic product distribution; but the relative values of the individual rate constants for the various steps must reflect these preferences to some degree, whether or not the transformations are reversible. (At the time we suggested that there *was* some degree of reversibility – *i.e.*, that alkanes, once formed, could still be further transformed – but had no definitive evidence one way or the other [10].)

Taken together, these two trends might provide an explanation for triptane selectivity: they predict that the relative preference for hydrogenation over growth by methylation will be significantly greater for less-substituted olefins. Since triptene is a *di*substituted olefin – the first olefin along the growth sequence that is *less* substituted than its precursor – that argument implies that growth should be increasingly efficient *up to but not beyond* C_7. However, this explanation must be considered tentative: several obvious issues remained unresolved. Would it be possible to demonstrate the postulated trends experimentally? If so, are the magnitudes of the changes in relative reactivity with hydrocarbon size *quantitatively* consistent with the observed selectivities? Can this mechanistic framework account for the similarities and differences between ZnI_2 and InI_3 catalyzed reactions, as well as the non-selective polyphosphoric acid system? We report here on work aimed at answering these (and other) questions, and thereby establishing our mechanistic explanation of triptane selectivity on firmer footings.

2. Experimental

2.1. General

InI_3 (purchased from Alfa Aesar), ZnI_2 (purchased from Sigma-Aldrich), methanol and other organic compounds were reagent-grade commercial samples used without further purification. GC analyses were performed on an HP model 6890N chromatograph equipped with a 10 m × 0.10 mm × 0.40 μm DB-1 column. GC/MS analyses were performed on an HP model 6890N chromatograph equipped with a 30 m × 25 mm × 0.40 μm HP5-1 column and equipped with an HP 5973 mass selective EI detector. ^1H and ^{13}C NMR spectra were obtained on a Varian 300 MHz instrument.

2.2. Standard reaction protocols

All reactions were performed in thick-walled pressure tubes equipped with Teflon stopcocks (Kontes valves), rated up to 10 bar. The procedure for standard reactions is based on the procedure reported earlier for methanol to hydrocarbon conversions using ZnI_2 and InI_3 [10,12]. In a typical experiment, the tube was equipped with a stir bar and charged with ZnI_2 (2.4 g, 7.52 mmol), methanol (1.0 mL, 24.8 mmol) and ^iPrOH (0.050 mL, 0.65 mmol), if an initiator was required. (If InI_3 was used as the catalyst it was weighed out in a glove box due to its hygroscopic nature; however the reactions were carried out under an atmosphere of air.) If another organic compound was utilized as an additive, it was added at this stage. Unless otherwise noted, the catalyst was fully dissolved prior to heating. For reactions of HMB and triptene in the absence of a methylating reagent, the catalyst was dissolved in 3 equivalents of water followed by the addition of the desired reagent. The pressure tube was then placed in a pre-heated oil bath behind a blast shield and stirred at the appropriate temperature for the desired period of time. After heating, the tube was removed from the bath and allowed to cool to room temperature and then placed in an ice bath. The stopcock was removed and chloroform (1.0 mL), containing a known amount of cyclohexane as an internal standard, was pipetted into the reaction mixture followed by water (0.5 mL). The stopcock was replaced, the mixture was shaken vigorously and the organic layer separated. A small aliquot was diluted with acetone or decane for GC analysis.

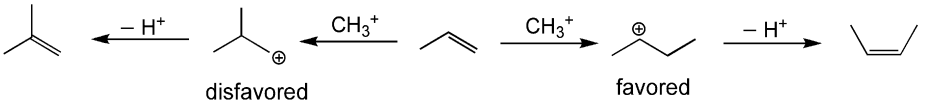
3. Results and discussion

3.1. Evidence for cracking in feedback and formation of isobutane

As noted above, in promoted reactions the molar quantity of products vastly exceeds the amount of promoter added, requiring that the lighter building blocks can be regenerated by some feedback mechanism. Two candidates appear reasonable: cracking of heavier aliphatic carbocations, and/or the "paring" mechanism, whereby small olefins are split off from methylated benzene rings as suggested for MTO [5]. It is quite possible that *both* of these are operating. Analysis of arene speciation as a function of reaction time and catalyst composition shows that hexamethylbenzene and pentamethylbenzene can be partially demethylated as the reaction proceeds [12], which could be a consequence of a paring process generating ethylene, propene, and isobutene [5], although simple methyl transfer is also possible. Attempts to establish the role of paring by means of isotopic labeling studies have so far proven inconclusive.

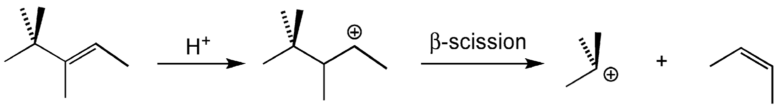
An indication that cracking of higher aliphatics *does* play a role may be found in the product distributions shown in Table 1: very little *n*-butane is present, but a significant quantity of isobutane is observed. Since reaction of propene with Me^+ should preferentially lead to the more stable secondary *s*-butyl rather than the primary *i*-butyl carbocation, we would not expect the main growth sequence to lead to much *i*-C_4 product (Eq. (2)).

An alternative possibility is that *i*-C_4 species arise via cracking of higher carbocations, particularly through β-scission. In order to test this hypothesis a number of C_7 and C_8 olefins were added to standard ZnI_2 catalyzed reactions. The results are summarized in Table 2. Addition of the C_8 olefin 3,4,4-trimethyl-2-pentene results in increased yield of $C_{4–6}$ alkanes as well as "triptyls" (combined triptane plus triptene yield), strongly suggesting that some fragmentation is occurring; β-scission of a secondary carbocation obtained from protonation of this olefin would lead to the *t*-butyl



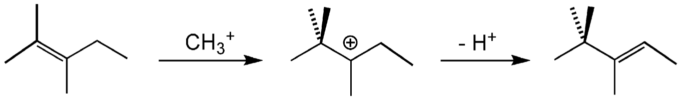
(2)

Equation 2.



(3)

Equation 3.



(4)

Equation 4.

Table 2
Yields of selected alkanes from the ZnI_2 catalyzed conversion of methanol to hydrocarbons in the presence of certain C_7 and C_8 olefins.[a] Unless otherwise stated all quantities are in milligrams.

Olefin	Amount of olefin added	Isobutane	Isopentane	DMB[b]	Triptyls[c]
None[d]	0	18	11	5	63
Triptene	71	20	11	5	87
2,4-Dimethyl-2-pentene	73	17	10	5	73
2,3-Dimethyl-2-pentene	73	22	14	6	71
3,4,4-Trimethyl-2-pentene	74	23	14	6	71
3,4,4-Trimethyl-2-pentene	128	23	14	6	73

[a] All reactions were heated at 200 °C for 3 h and contained 7.52 mmol of ZnI_2, 24.8 mmol of methanol and the specified amount of olefin.

[b] DMB is 2,3-dimethylbutane.

[c] Triptyls is combined yield of triptane and triptene.

[d] 50 µl of $^{i}PrOH$ was used as an initiator in this reaction.

cation (Eq. (3)). The latter in turn would undergo hydride transfer to give isobutane, in competition with proton loss to give isobutene followed by methylation to C_{5+} products. It seems at first surprising that increasing the amount of 3,4,4-trimethyl-2-pentene does not result in a significant increase in the yields of triptyls and light alkanes, but this is probably the result of increased olefin oligomerization at the higher concentration; the GC traces from these reactions show the presence of substantially more higher molecular weight species.

As for the three C_7 olefins examined, it can readily be seen that none of the possible secondary or tertiary carbocations that can be derived from either protonation or methylation of any of these olefins can undergo a β-scission process which will produce a stable tertiary carbocation; however, methylation of 2,3-dimethyl-2-pentene (but *not* the other two) *can* lead to 3,4,4-trimethyl-2-pentene (Eq. (4)) which would undergo cracking as above. Coupled with the fact that this C_7 tetrasubstituted olefin is most reactive toward methylation (see below), this may explain why only 2,3-dimethyl-2-pentene of the three C_7 olefins tested leads to an increase in light alkanes. Taken together, these results strongly suggest that cracking of C_8 (and, perhaps, higher) olefins accounts for the formation of at least part and probably most of the isobutane observed in the final product distribution, as well as for the feedback mechanism regenerating building blocks for hydrocarbon growth.

3.2. Is alkane formation reversible?

As noted above, the argument for less-substituted olefins being relatively more prone to hydrogenation does not necessarily depend on whether or not alkanes and olefins interconvert as the reaction proceeds; but it is a significant issue with regard to the overall mechanistic interpretation. Several experiments were performed to determine whether alkanes are at least partially reactive under the standard reaction conditions of ZnI_2 catalyzed methanol conversion.

Table 3
Recovered yields (by gas chromatography) of added alkanes after 2 h at 200 °C in a solution containing methanol, ZnI_2 and alkane.[a]

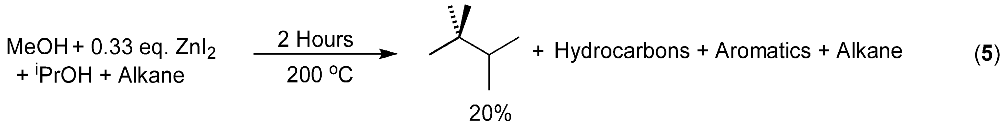
Alkane	Recovered yield %
2,3-Dimethylbutane	98
3-Methylpentane	93
2,3-Dimethylpentane	99
2,4-Dimethylpentane	93
2,2,4-Trimethylpentane (iso-octane)	100

[a] Reactions contained 24.8 mmol methanol, 7.52 mmol ZnI_2 and 0.6 mmol of the alkane and were heated for 2 h at 200 °C. ZnI_2 was predissolved in the methanol/alkane mixture prior to heating.

When 0.33 equivalents of ZnI_2 were pre-dissolved in methanol in the presence of the branched alkanes 2,3-dimethylpentane, 2,4-dimethylpentane, 3-methylpentane, 2,3-dimethylbutane (DMB) and iso-octane (2,2,4-trimethylpentane), no new hydrocarbon formation was observed under the standard reaction conditions. Table 3 shows the recovered yields of the alkanes and demonstrates that within experimental error (approximately 5–10%) the alkanes are recovered quantitatively.

Since no hydrocarbons were produced in the above experiments; it is conceivable that the results might be different under reaction conditions where triptane synthesis is taking place. Another set of experiments were performed using methanol, ZnI_2 and the same alkanes used previously, but in this case isopropanol ($^{i}PrOH$) was used to initiate hydrocarbon formation (Eq. (5)). Table 4 shows the recovered yields of the alkanes, corrected for the amounts expected from a typical triptane-forming reaction. It should be noted that in all cases the triptane yield ($\sim$20%) and the product distributions (apart from the added alkane) are very similar to those in reactions with no added alkane. Hence within experimental error the addition of alkanes does not perturb the triptane-forming reaction at all; the alkane is simply recovered, again virtually quantitatively.

Further tests were carried out to determine whether there might be any exchange between protons or methyl groups of the added alkane and other molecules in the reaction mixture without any net change in the amount of alkane present. Reactions were performed between ^{13}C-labeled methanol, $^{i}PrOH$, ZnI_2 and unlabeled alkane, either DMB or 2,2,4-trimethylpentane (Eq. (6)).



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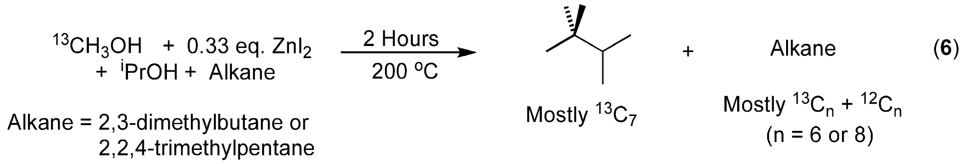

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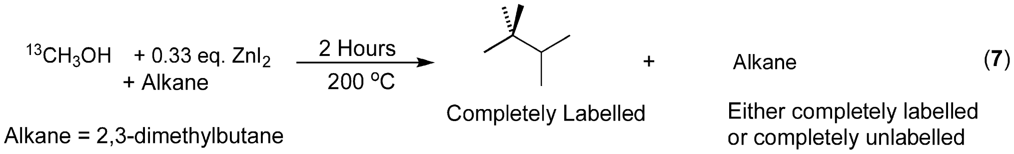

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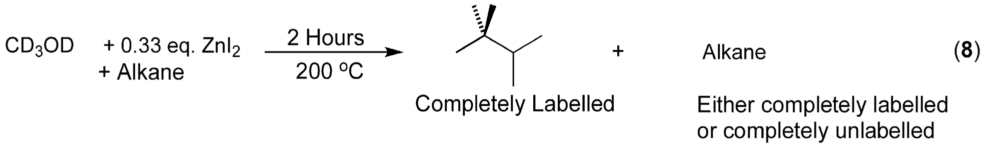


Equation 8.

Table 4

Recovered yields (by gas chromatography) of added alkane after 2 h at 200 °C in a solution containing methanol, ZnI_2, ^{i}PrOH and alkane.[a]

Alkane	Recovered yield %	Amount formed in typical reaction (mg)[b]	Adjusted yield %[c]
2,3-Dimethylbutane	113	6.0	96
3-Methylpentane	95	1.2	92
2,4-Dimethylpentane	92	3.2	85
2,3-Dimethylpentane	95	2.5	90
2,2,4-Trimethylpentane	101	1.2	98

[a] Reactions contained 24.8 mmol methanol, 7.52 mmol ZnI_2, 0.6 mmol of the alkane and 0.6 mmol of ^{i}PrOH and were heated for 2 h at 200 °C. ZnI_2 was predissolved in the methanol/alkane/^{i}PrOH mixture prior to heating.

[b] 2,3-Dimethylbutane, 2,3-dimethylpentane, 2,4-dimethylpentane and 3-methylpentane are all produced when triptane is formed. The amount formed in a typical reaction is used to calculate the adjusted yield.

[c] Adjusted yield subtracts the amount of alkane formed in a typical reaction from the recovered yield of the alkane.

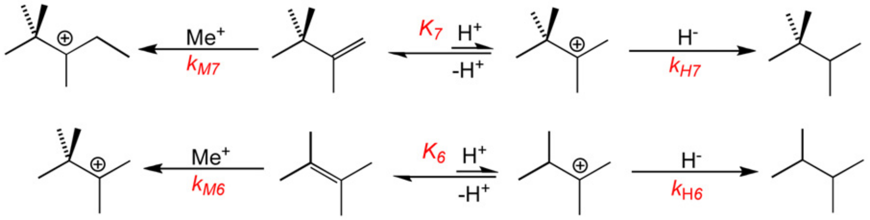
A control experiment without added alkane was also run. Product mixtures were analyzed by GC/MS (see supporting information for further details).

The MS patterns corresponding to the added alkane (for either DMB or 2,2,4-trimethylpentane) showed the presence of fully ^{13}C-labeled as well as completely unlabeled molecules, which would be expected for species formed entirely from ^{13}C-labeled methanol and unreacted added alkane respectively, but only marginally detectable signals corresponding to any *partially* labeled species. Similarly, the labeling and fragmentation pattern and relative intensities of the triptane and triptene peaks in the MS were identical regardless of whether an alkane additive was present, with nearly all the carbon atoms being ^{13}C-labeled. The presence of partially labeled species in the MS patterns is attributed to incorporation only from the (unlabeled) ^{i}PrOH initiator, not from the alkane. To verify this conclusion, an experiment was carried out in which ^{13}C-labeled methanol and DMB but no initiator were added to ZnI_2; the solution was not predissolved or stirred so that the presence of solid provided initiation (Eq. (7)). In this case, GC/MS unequivocally showed that *all* of the triptane and triptene generated in the reaction was labeled in all positions, and only completely unlabeled or completely labeled DMB was present. A similar experiment was performed using methanol-d_4 (Eq. (8)); here ^{1}H and ^{13}C NMR spectroscopy indicated that there had been no incorporation of deuterium into DMB, and GC/MS analysis indicated that all the triptane and triptene present was deuterated in all positions. Taken together, these results demonstrate that under standard conditions for ZnI_2 catalyzed methanol conversion (200 °C, 2 h reaction time), once alkanes are formed they are essentially completely inert to further reaction, and undergo neither transformation to other products nor exchange of carbon or hydrogen atoms with other species present in the reaction mixture.

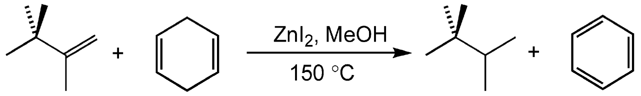
3.3. Structural dependence of relative methylation:hydrogenation rates

The key parameters controlling selectivity in our model are shown, for the examples of triptene and 2,3-dimethyl-2-butene, in Scheme 4. For each C_x olefin, k_{Mx} represents the rate of methylation, K_x is the equilibrium constant for protonation to the carbocation, and k_{Hx} represents the rate of hydride transfer to that carbocation. Our mechanistic proposal (see above) entails that the ratio of the rate of methylation of triptene to form a C_8 carbocation to the rate of hydrogenation to triptane is lower than the corresponding ratios for C_7 and lighter olefins. Since hydrogenation is effected by (reversible) protonation to form a carbocation followed by (irreversible, according to the results of the preceding section) abstraction of a hydride from another unsaturated species, the ratio for a C_x olefin would be given by the expression $k_{Mx}/k_{Hx} \cdot K_x$.

To test this theory, olefins were allowed to react with one equivalent of 1,4-cyclohexadiene (CHD), which is expected to be a particularly good hydride donor, in the presence of ZnI_2 and

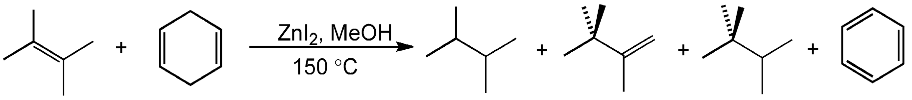


Scheme 4.



(**9**)

Equation 9.



(**10**)

Equation 10.

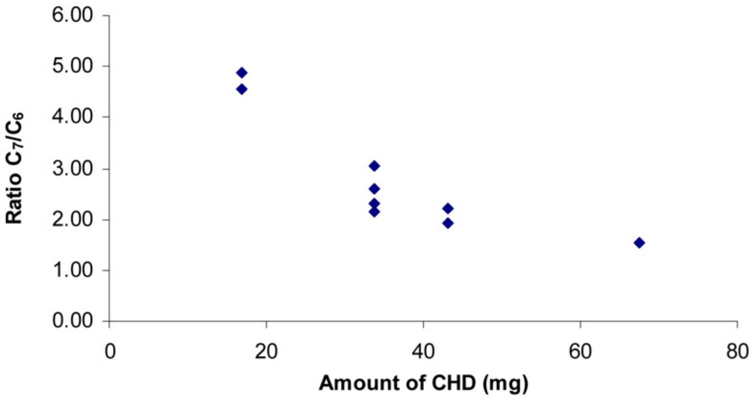


Fig. 1. Ratio of C_7 to C_6 products versus amount of CHD.

methanol, at a temperature low enough (150 °C) to prevent initiation of any direct conversion of methanol to triptane [10]. With triptene, this resulted in the formation of triptane and benzene only (Eq. (9)); no C_8 products which would arise from the methylation of triptene were observed. Hence for this particular combination of reagents and reaction conditions, the value of $k_{M7}/k_{H7}\cdot K_7$ is effectively negligibly small. In contrast, when the same reaction was performed using 2,3-dimethyl-2-butene, the C_7 products triptene and triptane were observed along with the reduction product DMB (Eq. (10)); unlike the C_7 case, here the rates of methylation and hydrogenation are much more comparable. As the concentration of 1,4-cyclohexadiene decreased (along with that of 2,3-dimethyl-2-butene, as these were added in a 1:1 ratio) the ratio of C_7/C_6 products increased (Fig. 1), as would be expected, because the relative concentration of the active methylating species to hydride donor is increasing.

Similar experiments were performed using 2-methyl-2-butene and isobutylene. In the case of 2-methyl-2-butene C_7 products (triptane and triptene), C_6 products (DMB and 2,3-dimethyl-2-butene) and C_5 product (2-methylbutane) were all observed, along with a range of other products. As above, the ratio of $(C_6 + C_7)/C_5$ products varied inversely with the concentration of CHD (Fig. 2).

For all these experiments mass balance is well below 100%, indicating that side reactions, such as isomerization, dimerization, etc., divert some material to products other than those analyzed. Since alkanes are completely inert (see above) while olefins are not, this factor will tend to exaggerate the apparent extent of hydrogenation; that is, the deduced value of each $k_{Mx}/k_{Hx}\cdot K_x$ will be lower than its true value. Furthermore, the mass balances for the reactions involving 2,3-dimethyl-2-butene and 2-methyl-2-butene were progressively worse than that for triptene, presumably because there are more branching points that can lead to side products before reaching unreactive end products such as triptane or DMB. For isobutylene, competing reactions leading to isobutylene dimers and trimers perturbed the product distribution to such an extent that reliable determination of relative methylation and hydrogenation rates was not feasible. Nonetheless, the trend is clear: the relative rate of methylation compared to hydrogen transfer is slowest for the disubstituted olefin triptene, intermediate for trisubstituted 2-methyl-2-butene, and fastest for tetrasubstituted 2,3-dimethyl-2-butene.

To further investigate the effect of olefin substitution on relative rates, similar studies compared the behaviors of 2,3-dimethyl-2-pentene, 2,4-dimethyl-2-pentene, 2,4-dimethyl-1-pentene and triptene – compounds that all contain seven carbon atoms and have roughly similar steric properties, but differing degrees of substitution at the double bond. Solutions of olefin, ZnI_2 and methanol were heated for two hours at 150 °C with either *no* or one equivalent of added CHD. In the former case the source for hydride transfer must be the olefin itself, presumably a less efficient hydride donor than CHD. The ratios of C_8 products to C_7 alkane were

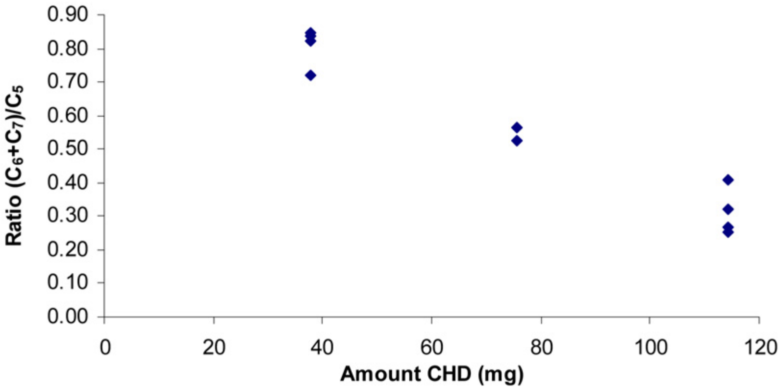


Fig. 2. Ratio of $(C_6 + C_7)$ products to C_5 versus amount of CHD.

Table 5
Ratio of C_8 products to reduced C_7 alkane for a number of different C_7 olefins.[a]

Olefin	Ratio of C_8 products:C_7 alkane without CHD	Ratio of C_8 products:C_7 alkane with CHD
2,3-Dimethyl-2-pentene	16.2:1	0.8:1
2,4-Dimethyl-2-pentene	6.2:1	0.3:1
2,4-Dimethyl-1-pentene	6.4:1	0.2 : 1
Triptene	3:1	<0.05:1
Triptene	0.3:1[b]	<0.05:1

[a] All reactions contained 24.8 mmol methanol, 7.52 mmol ZnI_2 and 0.7 mmol of the olefin; those in the last column also contained 0.7 mmol CHD; all were heated for 2 h at 150 °C.

[b] Also contained 0.7 mmol 2-methyl-2-butene.

determined for each olefin using GC (^{13}C NMR spectroscopy was used to differentiate between triptane and triptene). The results for the two sets of experiments are summarized in Table 5.

Two trends are clearly evident in Table 5. First, the relative amount of C_8 products is dramatically reduced by the addition of CHD in all cases, consistent with the substantially greater hydride donating ability of the latter reagent. For the first three entries, the ratios of C_8:C_7 alkane decrease by a fairly constant factor (19–29), implying that hydrogen transfer from CHD is about 20 times faster than from the acyclic monoolefins (and also that the latter are roughly similar as hydrogen donors). The corresponding decrease for triptene is substantially greater, >60 fold; most probably this reflects the fact that triptene cannot be readily dehydrogenated to a diene, and hence is probably a considerably poorer source of hydrogen. To compensate for that, an additional experiment was run with triptene and one equivalent of 2-methyl-2-pentene, which should provide hydrogen at a rate comparable to the other olefins while, as a C_5 olefin, not generating enough C_7 and C_8 co-products to significantly perturb the triptene-derived products. That lowers the C_8:C_7 alkane ratio by tenfold, to >6 times the value found with CHD, more consistent (allowing for the fact that we have only an upper limit for the ratio with CHD) with the rest of the data.

Second, as before, the ratio of C_8 products to the reduced C_7 alkane is highest for the tetrasubstituted olefin, 2,3-dimethyl-2-pentene, decreasing markedly for (trisubstituted) 2,4-dimethyl-2-pentene and again for (disubstituted) triptene. The results for disubstituted olefin 2,4-dimethyl-1-pentene resemble those for 2,4-dimethyl-2-pentene rather than triptene, which at first seems inconsistent. However, under the reaction conditions we observe substantial isomerization of 2,4-dimethyl-1-pentene to (thermodynamically preferred) 2,4-dimethyl-2-pentene, and it is probable that most or all of the C_8 products obtained starting with 2,4-dimethyl-1-pentene actually arise via the isomerized internal olefin, since the detailed C_8 product distributions from reactions starting with 2,4-dimethyl-2-pentene and 2,4-dimethyl-1-pentene are almost identical.

The results of all the above experiments involving competitive methylation versus hydrogen transfer are thus at least *qualitatively* consistent with our mechanistic explanation of C_7 selectivity; we address the question of whether the explanation may be *quantitatively* adequate in the following section. The fact that triptene is the first olefin in the growth sequence which is *less* substituted than its predecessors appears to be crucial, as it slows down the rate of growth by methylation and/or increases the rate of trapping as triptane by hydride transfer. As discussed above, we believe that both of those factors are operating, but there is no way to assess their relative importance – *i.e.*, the relative magnitude of dependence of the k_{Mx} and $k_{Hx} \cdot K_x$ terms on the degree of olefin substitution – from these data.

3.4. Modeling methanol conversion

While the results of the preceding section support the hypothesized trends in relative reactivity, and even give some estimate of their magnitude, it is not yet obvious whether they are sufficient to account for the high selectivity for triptyls displayed in Table 1. A kinetic model could assess how the values of the relative rates influence the outcome. Given our limited knowledge of many details, including the initiation and feedback mechanisms and any precise quantitation of the lighter and heavier products, attempting to capture all or even most of the complexity of the reaction network does not seem feasible at this time. Accordingly, we have constructed a highly simplified model with the following main features (a more detailed description, including the component reactions and resulting differential equations, and the BASIC program used to solve them, may be found in the supporting information):

- Initiation is represented by direct formation of olefin from methanol, at a rate first-order in [methanol] (which is assumed to be proportional to the concentration of the methylating species). For simplicity we ignore the lightest olefins (which we have not been able to measure reliably in any case) and allow initiation to lead directly to n-C_4; i-C_4 is assumed to arise only via cracking of heavier species (see above).
- Each C_{4-7} olefin undergoes competing reactions:
    (i) With the methylating species to give the next higher olefin, with the rate expression k_{Mx}[olefin][methanol]. Only one isomer (the most branched) of each C_{5-7} olefin is formed. C_8 products undergo no further growth.
    (ii) With an olefin capable of undergoing dehydrogenation (n-C_4, C_5, C_6), to give the corresponding alkane. Following the implications of the preceding section, we assume that the rates of these steps depend only on the identity of olefin$_x$, the one to which hydrogen is transferred, and that all the

Table 6
Comparison of "experimental" and modeled product distributions for conversion of methanol over ZnI_2.

Compound or class	"Experimental"[a]	Model[b]
Total C_{4-7} isoparaffins	45%	57%
n-Butane	–	1%
i-Butane	3%	15%
2-Methylbutane	3%	3%
2,3-Dimethylbutane	1%	1%
Triptane	38%	36%
Total C_{4-7} olefins	20%	2%
Triptene	14%	0.3%
Total C_{8+}	22%	23%
Total arenes	10%	18%

[a] Based on data from experimental PIANO analysis, using only those species accounted for in the model and normalizing to make those add up to 100%.

[b] See text for procedure used to assign parameter values, and supporting information for details.

sources (the olefin$_y$'s) provide hydrogen to a given olefin$_x$ at the same rate. Further, we assume that dienes and other multiply unsaturated species (short of arenes) are even more reactive for hydrogen transfer, and hence never accumulate. To maintain overall mass balance, this situation is represented by the following stoichiometry:

$$3\ \text{olefin}_x + \text{olefin}_y = 3\ \text{alkane}_x + \text{arene}_y$$

and the rate expression $k_{Hx}[\text{olefin}_x][\text{olefin}_y]$ (where k_{Hx} here stands for the entire composite term defined earlier).

- Cracking is represented by a single process, the reaction of C_8 with methylating species to give *i*-C_4 + C_5.

The resulting model is still far too complex to optimize by trial-and-error variation of all (twelve) individual rate constants – a process that would have questionable significance in any case, since with that many independent parameters it should be possible to reproduce almost any set of data. Instead, we took the values for k_{Mx}/k_{Hx} implied by the experiments on C_7 olefins in the preceding section (Table 5): 16, 6 and 0.3 for the tetra-, tri- and disubstituted cases respectively. We then made two additional assumptions: (i) those values apply to *any* olefin of the same substitution pattern; and (ii) the overall reactivity ($k_{Mx} + k_{Hx}$) is the same for each olefin. Neither of these is likely to be very accurate – among other flaws, they neglect any steric contribution to relative reactivity – but at least they should give us a reasonable starting point. That leaves only the rates of initiation (by formation of *n*-C_4 olefins) and cracking undetermined.

Since many processes in the real system are not captured by this model, particularly the formation of non-maximally branched isomers at each growth stage, we constructed a hypothetical "experimental" product distribution by renormalizing the analytical data to reflect only species that are part of the model (see supporting information for further details). We then ran the model using the k_{Mx} and k_{Hx} values determined as discussed above, *with no adjustments whatsoever*, only varying the initiation and cracking rates to match the "observed" C_8 yield. The results are compared in Table 6. Given the constraints placed upon the rate constants, the agreement is striking. In particular, the high selectivity for triptane compared to lighter branched alkanes and heavier products is almost perfectly reproduced.

The major discrepancy is the serious underprediction of olefins, including triptene. That implies that the hydrogen transfer rate has been overestimated; as a consequence *i*-C_4 (because too much of the cracking product is trapped as the alkane) and arenes (produced via hydrogen transfer) both come out too high. As discussed in the previous section, the k_{Mx}/k_{Hx} values probably *do* overestimate k_{Hx}, since a portion of the methylation products undergo isomerization and other side reactions that take them out of the accounting. It would surely be possible to get much better overall agreement by varying the individual rate constants to reflect that point, as well as relaxing the highly restrictive assumptions used to define them; and perhaps such an exercise would shed further light on mechanistic detail. However, for the present purposes, the level of agreement achieved is enough to validate the basic postulate: that the dependence of methylation and hydrogen transfer rates on olefin structure is both qualitatively and quantitatively sufficient to account for the observed selectivity.

3.5. Investigating the differences between ZnI_2 and InI_3 catalyzed reactions

As mentioned earlier, InI_3 can also catalyze the transformation of methanol to triptane; although the general features are quite similar to the ZnI_2 system and the same chain growth mechanism was postulated, there are some obvious differences between the two systems. In InI_3 catalyzed methanol conversion, no olefins are observed in the final product distribution; this is accompanied by higher quantities of aromatics, implying more efficient hydride transfer as compared with the ZnI_2 system. Methylation of arenes is also much faster with In than with Zn. Finally, at 200 °C, where (as shown above) alkanes appear completely inert to the ZnI_2 system, InI_3 is able to activate (some) alkanes: reaction of InI_3 with neat alkanes results in isomerization and cracking, methanol conversion can be initiated by alkanes, and alkanes can be directly homologated with methanol [12,13].

All of these observations could be consistent with an assumption that the InI_3 solution exhibits higher effective acidity (Brønsted and/or Lewis) than ZnI_2; but is it simply a question of a quantitative factor, or is there a more fundamental qualitative difference? There could be pathways available to In but not Zn that might be responsible for some or all of the differences. For example, the activation of alkanes could conceivably involve a redox process, since reduction of In(III) to In(I) might be possible (although surely quite unfavorable) while the analogous reduction of Zn(II) to Zn(0) would not. If only quantitative factors are involved, then we might to be able to "turn on" some of the typical In behavior by carrying out Zn reactions at higher temperatures and/or for longer times; conversely, running In reactions at lower temperatures and shorter reaction times would give results that begin to look more like Zn. On the other hand, if the reagents *are* qualitatively different, we would not expect to see such changes. We have performed a number of experiments to distinguish between these two alternatives.

Table 7 shows results for several ZnI_2 catalyzed methanol conversion carried out at 230 °C. Most notably, in contrast to the behavior at 200 °C, DMB initiates reaction, resulting in approximately the same triptane yield as a reaction initiated with ^{i}PrOH (although this reaction was allowed to react longer, the results are comparable, because in each case MeOH/DME has been completely consumed, and we have shown that alkanes do not significantly react further). The average yield, 45 mg, is lower than that obtained for an otherwise similar reaction at 200 °C (60 mg) [10]. The yield of aromatics appears to drop significantly, but that is probably due to the longer reaction time, leading to formation of heavier compounds not observable in the GC analysis employed. Adamantane (AdH) also initiates reaction at 230 °C, and its presence significantly *improves* the triptane yield. Previous studies on InI_3 catalyzed alkane homologation (also see below) showed that AdH decreases the rate of the reaction but increases the selectivity by inhibiting side reactions that waste methanol [13]; slowing reaction should be much less of a problem at the higher temperatures of these studies.

A more extensive series of reactions containing ZnI_2, methanol, and ^{i}PrOH as an initiator was performed at different tempera-

Table 7
Yields of selected products from ZnI_2 catalyzed reactions at 230 °C.[a] Unless otherwise stated all quantities are in milligrams.

Time (h)	Added ^iPrOH	Added DMB	Added AdH	Recovered DMB	Recovered AdH	Isobutane	Isopentane	Triptane	PMB + HMB
3	39	0	0	8	–	29	20	42	42
6	39	0	50	8	26	38	23	62	39
6	0	0	50	8	32	29	19	55	47
16	0	33	0	32	–	42	25	45	17
16	0	33	0	29	–	31	23	48	11
16	0	33	0	32	–	33	25	44	16

[a] All reactions contained 7.52 mmol of ZnI_2 and 24.7 mmol of methanol.

Table 8
Effects of temperature and reaction time on ZnI_2 catalyzed methanol conversion.[a] Unless otherwise stated all quantities are in milligrams.

Temperature (°C)	Time (h)	Isobutane	Isopentane	2,3-Dimethyl-2-butene	DMB	Triptane	PMB	HMB
230	3	21	nd[b]	0	9	42	18	26
230	3	29	20	0	8	42	19	22
215	3	36	24	0	8	55	12	4
207	3	26	19	0.6	7	60	7	5
200	16	26	21	0	6	61	7	Trace
180	16	21	17	0	6	66	6	3
180	16	23	17	0	6	67	6	3

[a] Reactions were carried out using 7.52 mmol of ZnI_2, 24.7 mmol of methanol, and 0.65 mmol of ^iPrOH.
[b] Not determined.

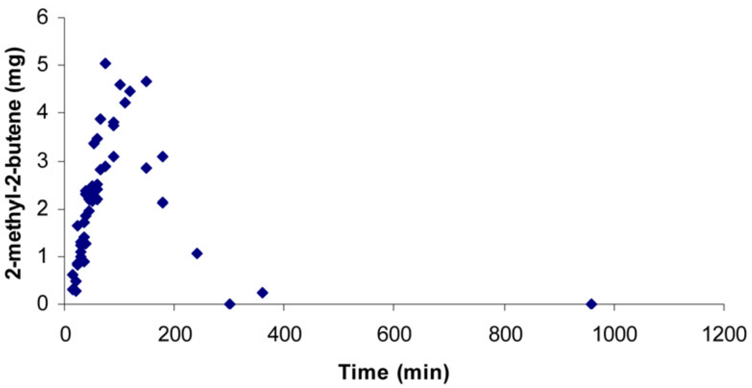


Fig. 3. Yield of 2-methyl-2-butene over time for ZnI_2-catalyzed methanol conversion at 200 °C.

tures and reaction times; results are shown in Table 8. Overall, the product distributions at higher temperatures or extended times resemble those of InI_3 catalyzed reactions: little or no olefins, more aromatics. Time-course experiments clearly show this trend. Fig. 3 shows the concentration of 2-methyl-2-butene (which is assumed to be representative of all olefins) over time for reactions carried out at 200 °C; complete absence of olefins is seen at longer times. Fig. 4 shows the analogous behavior for aromatics: there is an initial rise in the amount of hexamethylbenzene (HMB), followed by a slow decrease as pentamethylbenzene (PMB) and tetramethylbenzene (TMB) grow in. Consumption of HMB was further demonstrated by reacting ZnI_2 (7.52 mmol), 3 equivalents of water (22.6 mmol), and HMB (100 mg, 0.62 mmol) for 16 h at 200 °C; from the black reaction mixture, only 42.7 mg of HMB was recovered while 22.8 mg of PMB was formed. (The poor mass balance may be accounted for by the formation of heavier aromatic species that are not detected by GC.) A similar experiment containing triptene in place of HMB showed slower conversion of triptene, giving at the end a trace amount of triptane and slightly larger amounts of isobutane, isopentane, and C_6 and C_7 alkane isomers.

Since ZnI_2 can apparently activate alkanes to initiate triptane synthesis at 230 °C, can it also effect alkane homologation with methanol? The optimum conditions for InI_3 catalyzed homologation involve a 1:1 methanol:DMB ratio [13], but ZnI_2 is considerably less soluble in that composition; most remains undissolved, and the product distribution of such a reaction (Table 9, Entry 1) resembles that expected for direct conversion of methanol with no participation of DMB. However, at a ratio of approximately 3:1 methanol:DMB, the ZnI_2 catalyst can be completely dissolved, and (in the presence of AdH, which as noted above substantially improves yield and selectivity in the InI_3 system [13]) gives triptane yields much higher than can be accounted for by the methanol alone: the average yield (Entries 2–4 of Table 9) is about 68 mg, vs. 55 mg obtained for a comparable reaction using twice as much methanol, with AdH but without DMB (Table 7). The following labeling study was performed to demonstrate the incorporation of DMB into triptane: ZnI_2 (4.13 mmol) was predissolved in labeled methanol (12.4 mmol). Unlabeled DMB (3.84 mmol) and adamantane (0.367 mmol) were added and the reaction heated to 230 °C for 6 h. The largest triptane signal in the GC/MS spectrum appears at 86 m/z, corresponding to $(P\text{–}Me)^+$ for singly labeled triptane (there is also a strong signal at 91 m/z corresponding to fully labeled triptane resulting from direct methanol conversion). This finding is identical to that obtained for the analogous reaction over InI_3 at 200 °C [13], and confirms that DMB is homologated to triptane here as well.

It thus appears that the differences between ZnI_2 and InI_3 catalyzed reactions largely disappear when the former is run at higher temperature and/or for longer times. That suggests that the converse observation – the presence of olefins in an InI_3 catalyzed re-

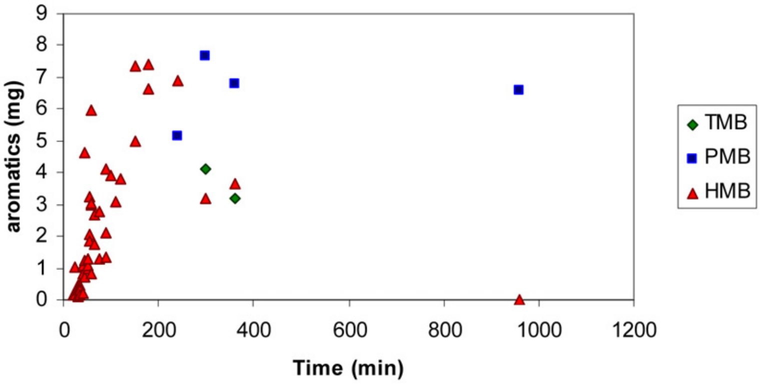


Fig. 4. Yield of aromatics over time for ZnI_2-catalyzed methanol conversion at 200 °C.

Table 9
ZnI_2 catalyzed homologation of DMB at 230 °C.[a] Unless otherwise stated all quantities are in milligrams.

Time (h)	Added MeOH	Added DMB	Recovered DMB	Recovered AdH	Isobutane	Isopentane	Triptyls	PMB + HMB
3	199 (6.2)[b]	533 (6.2)[b]	404	39	8	3	16	4
6	398 (12.4)[b]	330 (3.8)[b]	198	41	28	17	66	23
6	398 (12.4)[b]	330 (3.8)[b]	183	39	27	16	69	24
6	398 (12.4)[b]	330 (3.8)[b]	204	37	28	16	68	25

[a] All reactions contained 4.13 mmol of ZnI_2 and 0.367 mmol (49.9 mg) of AdH and were heated at 230 °C for 3 h.
[b] Number in parenthesis is the quantity in mmol.

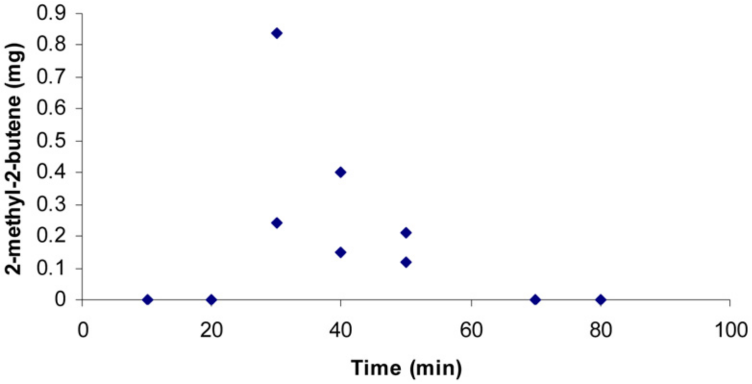


Fig. 5. Yield of 2-methyl-2-butene over time for InI_3-catalyzed methanol conversion at 170 °C.

action – should be possible at lower temperatures, and very short reaction times would probably be needed. Solutions containing InI_3 (4.13 mmol), methanol (12.4 mmol), and ^{i}PrOH (0.65 mmol) were heated at 170 °C for periods of time as short as 10 min; the yield of 2-methyl-2-butene (which is again taken as representative of all olefins) as a function of time is shown in Fig. 5. After an induction period, typical of triptane syntheses, the olefin grows quickly to low levels and then disappears; after about an hour none remains.

4. Conclusions

Our proposed mechanistic framework for the selective formation of triptane in the ZnI_2 and InI_3 catalyzed dehydrative condensation of methanol is based upon stepwise growth via cationic methylation of olefins competing with alkane formation via hydride transfer from olefins to carbocations (Scheme 1, above). The relative favorability of those competing steps is highly dependent upon the degree of olefin substitution at each stage of growth. Results presented here strongly validate this mechanistic picture as adequate to account for observed product distributions and trends, both qualitatively and quantitatively. The differences in behavior between the two catalysts can be largely accounted for by postulating somewhat higher effective acidity for the InI_3 system; there is no evidence for any fundamental, qualitative difference in chemical reactivity.

How do these catalytic reactions compare to other methanol-to-hydrocarbon conversions? Looking first at the Pearson system: that likewise gives a mixture of alkanes and arenes, but with little or no selectivity: the product distribution is much closer to what would be expected under thermodynamic control [14]. This presumably reflects the much higher acidity of the polyphosphoric acid catalyst. In contrast, both the ZnI_2 and InI_3 systems are under kinetic control. The higher acidity of the latter results in *some* alkane activation even at 200 °C, observed for the former at still higher temperatures; but these reactions are *much* slower than the main growth and alkane-forming processes, and do not even begin to approach full reversibility. It should be noted that the product distributions *within* the alkane fractions are not very different between Zn and In, even though the latter gives more total alkanes (and arenes) and essentially no olefins (suggesting hydrogen transfer is faster). This demonstrates that the same general pattern of dependence of relative reaction rates on olefin structure holds for both. Indeed, the model calculations, which were based on relative rates that probably overestimate the rate of hydrogen transfer for Zn (as discussed above), give pretty good agreement with the observed In behavior.

This argument would predict that the Zn and In catalysts would move in the direction of more thermodynamic product distributions at higher temperatures, while the polyphosphoric acid system should begin to show some signs of kinetic control at lower temperatures. We cannot go much higher in temperature with our systems before substantial decomposition to black material begins to dominate; but we have been able to show a small but significant increase in triptane selectivity by running the Pearson chemistry at lower temperatures (see supporting information). Clearly getting the acidity right – sufficient to bring about reaction at a convenient rate and reasonable temperature but not so high as to effect equilibration of products – is a crucial factor for a selective catalyst.

As for comparison to MTO/MTG, the product slates are obviously quite different from those observed here: why? The polymethylated benzenes that appear to be the key intermediates in the solid acid–catalyst systems are certainly present here as well, and the reactions leading to splitting off of light olefins may operate too, although we have no definite information on that issue; but the facile growth of those light olefins (however they are generated) to higher hydrocarbons, particularly triptane, is not observed in MTO/MTG. We attribute that to the effects of two major differences between the two cases. MTO/MTG is typically run in flow mode, whereas the homogeneous catalytic reactions are carried out in batch mode; also the temperature is considerably higher for the heterogeneous systems. At those high temperatures the residence time for the light olefins will probably be comparatively short, while the reactive hydrocarbon pool is held within the micropores; hence the methylating species derived from methanol will preferentially add to the latter, generating more of the precursors to light olefins, rather than homologating the former. In contrast, for the homogeneous system the olefins stay in solution (we have previously commented on the ability of concentrated aqueous ZnI_2 to dissolve organics, and InI_3 presumably behaves similarly) and compete much more effectively for the available methylating agents. Perhaps, if the reactions over the solid catalysts could be carried out at lower temperatures, the mechanistic considerations established here for the homogeneous case might be at least partially applicable there as well [15]?

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Supporting information

A more complete listing of experimental results and details of the kinetic model is available in the online version of this article.

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