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Mechanism of olefin polymerization by a soluble zirconium catalyst [1]

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Abstract

A mechanistic study has been carried out on the homogeneous olefin polymerization/oligomerization catalyst formed from Cp_2ZrMe_2 and methylaluminoxane, $(MeAlO)_x$, in toluene. Formal transfer of CH_3 from Zr to Al yields low concentrations of Cp_2ZrMe^+ solvated by $[(Me_2AlO)_y(MeAlO)_{x-y}]_y$. The cationic Zr species initiates ethylene oligomerization by olefin coordination followed by insertion into the $Zr–CH_3$ bond. Chain transfer occurs by one of two competing pathways. The predominant one involves exchange of $Cp_2Zr–P^+$ (P = growing ethylene oligomer) with $Al–CH_3$ to produce another Cp_2ZrMe^+ initiator plus an Al-bound oligomer. Terminal Al–C bonds in the latter are ultimately cleaved on hydrolytic workup to produce materials with saturated end groups. Concomitant chain transfer occurs by sigma bond metathesis of $Cp_2Zr–P^+$ with ethylene. Metathesis results in cleavage of the Zr–C bond of the growing oligomer to produce materials also having saturated end groups; and a new initiating species, $Cp_2Zr–CH=CH_2^+$. The two chain transfer pathways afford structurally different oligomers distinguishable by carbon number and end group structure. Oligomers derived from the Cp_2ZrMe^+ channel are C_n (n = odd) alkanes; those derived from $Cp_2Zr–CH=CH_2^+$ are terminally mono-unsaturated C_n (n = even) alkenes. Chain transfer by beta hydride elimination is detectable but relatively insignificant under the conditions employed. Propylene and 1-hexene react similarly but beta hydride elimination is the predominant chain transfer step. The initial Zr-alkyl species produces a Cp_2ZrH^+ complex that is the principle chain initiator. Chain transfer is fast relative to propagation and the products are low molecular weight oligomers. © 1998 Elsevier Science B.V.

1. Introduction

In 1980, Kaminsky [1–12] reported the synthesis from dimethylzirconocene, Cp_2ZrMe_2 ($Cp = \eta^5$-C_5H_5) and methylaluminoxane, $(MeAlO)_x$, of a soluble olefin polymerization catalyst. This longlived, high activity catalyst is capable of producing polyethylene having narrow polydispersity. That discovery has stimulated intense interest in Group IV-olefin poly-

merization chemistry. The initiating site is thought, but not proven, to be a cationic zirconium species and much effort has been put into the synthesis and characterization of cationic organometallic model compounds containing Zr [13–20] (titanium-based model systems have also been studied [21]) Th and U [22–25], Co [26–28], Cr [29] and Ti [30–33] as well as neutral materials containing Sc [34,35], Lu [36–38] and the lanthanides La, Nd and Sm [39–42]. That work has led to new synthetic routes to cationic organometallic compounds based on silver [17,18] and ferrocenium [19] tetraarylborates and carborane ligands $B_9C_2H_{11}$ and

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[1] Dedicated to Prof. Roy M. Adams, Geneva College, Beaver Falls, PA, USA, on the occasion of his 71st birthday.

$(B_9C_2H_{11})_2M$ (M = Fe, Co, Ni) [39–42] and these in turn have yielded new advances in C–H and C=C bond activation chemistry. Much effort too has been devoted to understanding the original Kaminsky catalyst [43–46] but there remain some unanswered fundamental questions. We have studied this catalyst system in detail and have addressed the following issues: (1) what is methylaluminoxane?; (2) how does it interact with Cp_2ZrMe_2 and what initiating species is produced?; and (3) what are the mechanism(s) of chain initiation and transfer? Our results go beyond the particulars of the Kaminsky catalyst and bear more generally on the area of olefin activation by soluble metal catalysts.

2. The nature of methylaluminoxane

Controlled hydrolysis of trimethylaluminum can be achieved in a two-phase system (Me_6Al_2 and a hydrocarbon solvent) containing an additional, insoluble reagent, such as $MgCl_2 \cdot 6H_2O$, that slowly releases water. After filtration and evaporation of solvent and unreacted Me_6Al_2, there remains $(MeAlO)_x$. Even today, methylaluminoxane is an enigma. It is not yet established whether this noncrystalline material is a single species (one suspects that it is not), or whether it is cyclic and contains only MeAlO subunits; or is linear with Me_2AlO end groups. The two possibilities are not mutually exclusive. The ^{13}C-NMR spectrum of a toluene-d_8 solution comprises a broad, non-Lorentzian singlet at -6.7 ppm (cf. Me_6Al_2, -7.2 ppm) and a portion of this signal may be due to residual trimethylaluminum which is difficult to remove completely from $(CH_3AlO)_x$. The ^{17}O-NMR spectrum (of a ^{17}O enriched sample) displays a broad ($w/2$ 1500 Hz) resonance centered at $+73$ ppm relative to external H_2O that is invariant between 25 and 90°C. These data provide scant evidence of molecular level homogeneity. The ^{27}Al-NMR spectrum at 25° exhibits a broad resonance centered at 154 ppm, cf. Fig. 1. This is assigned to four-coordinate Al, i.e., aluminum complexed either inter- or intramolecularly to an additional oxygen atom or involved in Al–CH_3–Al bridge bonding (and possible Me_6Al_2, vice supra). A feature near 50 ppm in Fig. 1 is due to background Al in the spectrometer probe. However, at 90°, an additional, broad peak at 100 ppm is observed. This we attribute to three-coordinate aluminum. Although one would expect to find aluminum having a lower coordination number at lower rather than higher field, this assignment is substantiated by the fact that the model compound $MeAl(BHT)_2$ (BHT = 2,6-di-t-butyl-4-
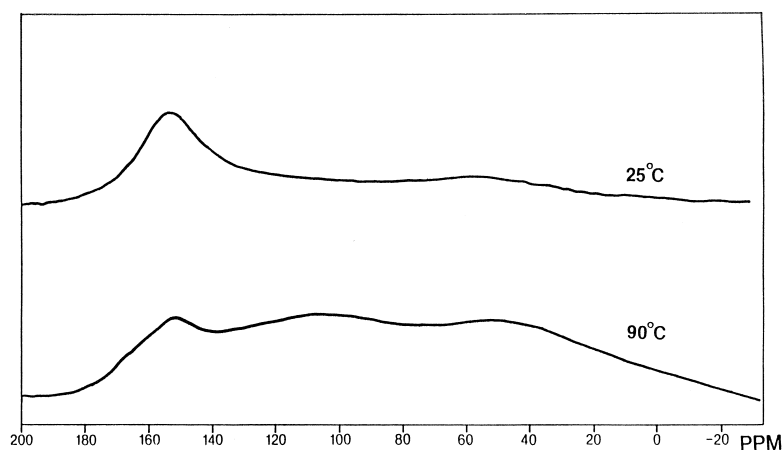

Fig. 1. ^{27}Al-NMR spectra of $(MeAlO)_x$.

methylphenoxy) has the same ^{27}Al chemical shift. X-ray crystallographic studies have shown that, owing to steric factors, this model compound is forced to remain monomeric; it thus contains three-coordinate aluminum bonded to two oxygen atoms and one methyl group [71], the same ligand environment expected of an isolated –O–Al(Me)–O group. There is no observable hysteresis in the ^{27}Al-NMR spectrum of $(MeAlO)_x$ and on re-cooling, the original ^{27}Al spectrum is restored. For nuclei such as ^{27}Al ($I = 5/2$), the quadrupolar spin lattice relaxation time varies inversely with temperature and, thus, the resonances become more narrow on heating [47,48]. The 100 ppm signal, unobservably broad at room temperature, has become sufficiently narrow at 90° to be detected. Gel permeation chromatography experiments indicate that heating $(MeAlO)_x$ at 60°C for 6 h (vs. approx. 0.5 h in our NMR experiment) leads to increased amounts of higher molecular weight oligomers [49]. We believe that, because of the large linewidths and small chemical shift dispersion, ^{27}Al-NMR is relatively insensitive to degree of aggregation in $(MeAlO)_x$ and is best used to ascertain gross chemical features such as aluminum coordination number.
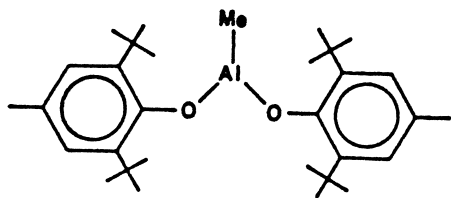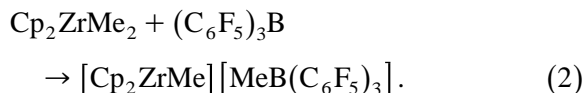

That $(MeAlO)_x$ contains three-coordinate aluminum is chemically reasonable. Except for a cubane-like tetramer ($x = 4$), it appears difficult if not impossible to arrange Al–O–Al or Al–CH$_3$–Al inter- or intramolecular interactions so that all aluminum atoms attain the preferred coordination number of four. A similar situation arises in trimeric $[(Et_2Al)_2O]_3$ [50] in which all the aluminum atoms cannot simultaneously be coordinatively saturated. This

compound too displays only a broad ^{27}Al resonance at 160 ppm at 25° but at 90°, an additional signal appears (reversibly) at 110 ppm.

There is chemical evidence as well that $(MeAlO)_x$ contains three coordinate aluminum. We have shown that this compound undergoes facile ($\Delta G^{\ddagger} = 13.9$ kcal mol^{-1} at 22° in dichloromethane) methyl exchange with $Cp_2Zr(^{13}CH_3)_2$ as do also Me_6Al_2 and $MeAl(BHT)_2$ [51]. The presence of ion pairs in this system has been previously proposed by Besconi et al. [52]. Empirically, it appears that the availability of three-coordinate aluminum is necessary for the exchange process to occur. We surmise that it proceeds via an ionic mechanism, Eq. (1).

$$Cp_2Zr(^{13}CH_3)_2 + R_1R_2R_3Al$$
$$\rightarrow [Cp_2ZrCH_3^+][R_1R_2R_3Al\text{-}^{13}CH_3]. \qquad (1)$$
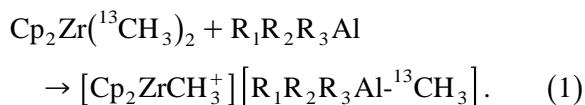
In this scenario, Cp_2ZrMe_2 acts as a methyl donor and (three coordinate) aluminum as a methyl acceptor. Thus, no alkyl exchange is observed with compounds such as $(Et_2AlOEt)_2$ in which aluminum is constrained by the strong Al–O bridge bonds to remain four-coordinate. Precedent for the intermediacy of ionic species in the methyl exchange reaction shown above comes from related experiments in which $(C_6F_5)_3B$ acts as a formal Me$^-$ acceptor towards dimethylzirconocene, Eq. (2) [53]

$$Cp_2ZrMe_2 + (C_6F_5)_3B$$
$$\rightarrow [Cp_2ZrMe][MeB(C_6F_5)_3]. \qquad (2)$$

We believe that the presence of three-coordinate aluminum in $(MeAlO)_x$ is crucial to its role as a co-catalyst in the Kaminsky system.

2.1. Reaction of methylaluminoxane and dimethylzirconocene

When $Cp_2Zr(^{13}CH_3)_2$ and $(^{12}CH_3AlO)_x$ are combined in toluene ($[Zr] = 0.21$, $[Al] = 1.97$, $[Al]/[Zr] = 9.4$), a yellow, homogeneous solution results. ^{13}C-NMR analysis indicates that the

$^{13}CH_3$ groups become statistically distributed between the $Zr–CH_3$ and $Al–CH_3$ sites within minutes. After ca. 0.5 h, an orange oil begins to separate as a denser phase. After phase separation is complete, the upper layer contains only unreacted Cp_2ZrMe_2. Importantly, we and others [54] find that this denser phase, after isolation, is capable of catalytically polymerizing olefins. Addition of CD_2Cl_2 dissolves the isolated lower phase. Its ^{13}C-NMR spectrum in this solvent contains major peaks at 116.7 and 38.9 ppm along with weaker Cp signals at 114.7 and 113.4 ppm. The ^{91}Zr-NMR spectrum shows two broad resonances at $+100$ and -100 ppm. These results can be interpreted as follows.

We suggest that there is rapid equilibrium transfer of, formally, CH_3^- from Zr to the three-coordinate aluminum acceptor sites in $(MeAlO)_x$. This accounts for the rapid $^{13}CH_3$ scrambling. The reaction may be represented by Eq. (3).

$$yCp_2ZrMe_2 + (MeAlO)_x \rightarrow (Cp_2ZrMe)_y$$

$$+ \left[(Me_2AlO)_y(MeAlO)_{x-y}\right]^{y-}. \quad (3)$$
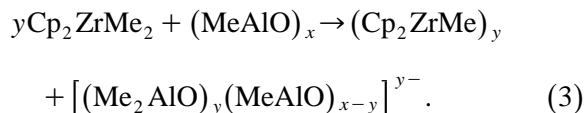
As the reaction progresses, y increases and, as it does the product takes on the properties of a polyelectrolyte and exhibits decreasing volubility in toluene with phase separation eventually occurring.

^{91}Zr-NMR provides an incisive characterization of the zirconium species formed in the $Cp_2ZrMe_2–(MeAlO)_x$ system (but is subject to the limitation that linewidths for some unsymmetrical species may be so large as to preclude their observation) [55]. This is due to the considerable dispersion of ^{91}Zr chemical shifts as shown in Fig. 2. Species having $\delta^{91}Zr$ near $+100$ ppm contain the fragment $Cp_2Zr(Me)X$, where X is a strongly electron withdrawing group. Of the available model compounds, that which most closely matches the $+100$ ppm peak in the phase-separated Kaminsky catalyst is a cationic methyl zirconocene compound containing coordinated THF, first synthesized by

Jordan [14], $[Cp_2ZrMe(THF)][BPh_4]$, ^{91}Zr 115. Another possibility, $Cp_2Zr(Me)Cl$, is discounted because its 32.4 ppm $Zr–CH_3$ resonance is not observed. We consider that this ^{91}Zr-NMR experiment comprises strong evidence for the presence in the Kaminsky catalyst system of a (solvated) cationic Cp_2ZrMe^+ species. This conclusion is supported by comparison of the 38.9 ppm ^{13}C-NMR signal, assigned to $Zr–CH_3$ in a metallocenium ion, with that of 40.9 ppm in $[Cp_2ZrMe][MeB(C_6F_5)_3]$ [53]. It is improbable that Cp_2ZrMe^+ exists as such in this system and more likely that zirconium in it is coordinated to the weakly nucleophilic oxygen atoms connected to two aluminum atoms. In this regard, methylaluminoxane bears a resemblance to a crown ether [56]. The equilibrium in Eq. (3) that produces a patently ionic (or, more probably, polarized $Zr–CH_3$ species) lies far to the left and, if phase separation did not supervene, formation of new products would be very difficult to detect experimentally. Our results are in agreement with recent CPMAS–NMR studies of the material obtained from reaction of Cp_2ZrMe_2 and $(MeAlO)_x$ (in toluene followed by evaporation of solvent) that reveal the formation of Cp_2ZrMe^+ [57]. Evidence that the metallocenium ion Cp_2ZrMe^+ is involved in olefin polymerization is given below.

The other zirconium species, with $\delta^{91}Zr$-100, lies in a chemical shift region uniquely occupied (to date) by compounds of the type $Cp_2Zr(Me)(OR)$ (R = OMe, $OSiMe_2$-t-Bu). We suggest that this resonance is due to a $Cp_2Zr(Me)–OAl$ species formed by cleavage of AlO–Al bonds on methylaluminoxane. Also, the ^{13}C-NMR peak at 18 ppm (vide supra) agrees with this assignment and matches closely $Cp_2Zr(Me)(OMe)$, $\delta^{13}C$ 19 [51,52]. Kaminsky [58] has recently proposed that such a process occurs and we have reported an analogous cleavage of BO bonds, Eq. (4) [51,52].

$$Cp_2ZrMe_2 + 2Et_2BOMe \rightarrow Cp_2Zr(OMe)_2$$

$$+ 2Et_2BMe. \quad (4)$$
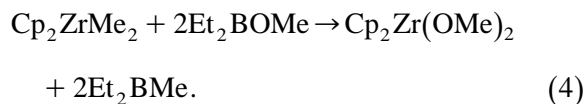
Zr-91 NMR CHEMICAL SHIFTS
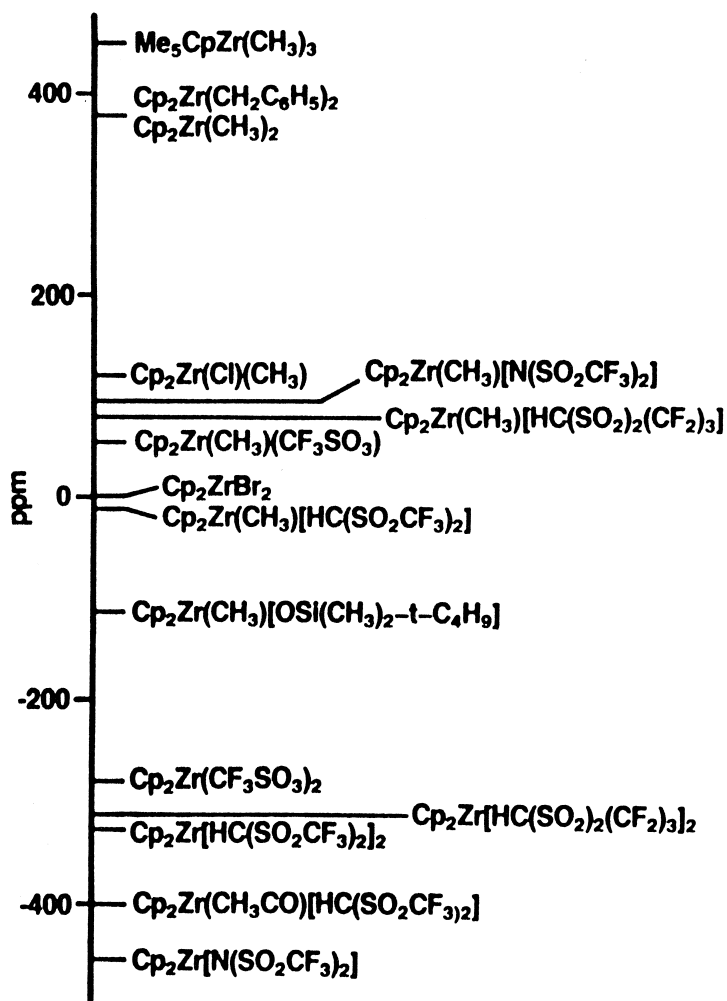
Fig. 2. ^{91}Zr-NMR chemical shift scale.

2.2. Mechanisms of ethylene polymerization

The details of the mechanism of olefin polymerization by the Kaminsky catalyst depend, inter alia, on the structure of the olefin. Ethylene is singular and has been studied in most detail. Results for the substituted ethylenes, propylene and 1-hexene, will be given later. We find that the most detailed mechanistic picture can be inferred from a careful analysis of the organic products. It emerges that partitioning among several mechanistic pathways is a func-

tion of experimental conditions, particularly olefin concentration, a factor that must be borne in mind in assessing net mechanisms.

The widely accepted mechanism for ethylene polymerization in the Kaminsky and related systems involves coordination to Cp_2ZrMe^+ by the olefin. Subsequent insertion of C_2H_4 into the Zr–CH_3 bond in $Cp_2ZrMe(C_2H_4)$ produces $Cp_2Zr(C_3H_7)^+$. This species can continue along the olefin coordination–insertion pathway or, alternatively, can undergo beta elimination to produce C_3H_6 and Cp_2ZrH^+. This zirconium

hydride species can add to ethylene to form $Cp_2ZrC_2H_5^+$ which too can continue to coordinate and then add olefin. This scheme is satisfactory for monosubstituted olefins (vide infra) but not for ethylene itself. We begin to unravel the ethylene chemistry by looking for mechanisms of chain initiation and do this primarily by examining the organic products. To do this, we have carried out not polymerizations but rather oligomerizations of ethylene by using low pressures of the olefin. In this way, low molecular weight materials (C_n with $n < 30$) are produced that are amenable to gas chromatographic and gas chromatographic/mass spectroscopic analysis. It must be borne in mind that the chemistry which transpires under much higher ethylene partial pressures, such as encountered in commercial processes, may differ in detail. In particular, it is not clear that complexation with (excess) olefin cannot compete with agnostic M–H–C interactions.

Ethylene–$^{12}C_2$ was polymerized in a closed system using $Cp_2Zr(^{13}CH_3)_2$–$(MeAlO)_x$ in toluene ([Zr] = 0.16 M, [Al] = 1.72 M, [Al]/[Zr] = 10.8, $T = 25°C$ and initial $p(C_2H_4)$ = 100 mm). At the conclusion of the reaction, indicated by cessation of pressure drop, any unreacted ethylene and some of the toluene were pumped away. CD_2Cl_2 was added to give a homogeneous solution that was then analyzed by NMR spectroscopy. The ^{1}H-NMR spectrum shows an 8:1 ratio of CH_2 to CH_3 groups and so, on average, four C_2H_4 units have been incorporated into the oligomer. Examination of the ^{13}C satellites flanking the CH_3 signal indicates that the terminal methyl groups are about 10% ^{13}C enriched. An enrichment of 16% is expected based on statistical scrambling of the Zr–CH_3 and Al–CH_3 groups. This means that, under the specified experimental conditions, about 60% of the oligomer methyl end groups were originally attached to Zr. This is consistent with chain initiation by Cp_2ZrMe^+ or a species like it. The other 40% are $^{12}CH_3$ end groups whose origin will be discussed below. The important conclusions so far are that the Kaminsky catalyst system contains an ionic Cp_2ZrMe^+ species; and that ethylene oligomerization is initiated in part by a Zr–CH_3 species. There is no definitive proof that the former and latter species are one and the same but we believe that they are.

An extensive series of ethylene oligomerizations was conducted using dimethylzirconocene and a commercially available toluene solution that was 0.9 M each in $(MeAlO)_x$ and Me_3Al. Under these conditions [Zr] = 0.04, [Al] = 0.72, [Al]/[Zr] = 18 and [MeAl]/[Zr] = 36. The initial ethylene pressure in the closed reactor was 250 mm. At the conclusion of the reaction (indicated by cessation of pressure drop), the reaction mixture was hydrolyzed with CH_3OH then aqueous HCl. GC and GC/MS analysis of the ethylene oligomers revealed some critical facts about the products.

(1) Hydrocarbons containing an odd number of carbon atoms are more abundant with $C_{odd}/C_{even} = 2.6$.

Scheme 1. Alkene structures and ^{13}C chemical shifts.

(2) The odd-numbered hydrocarbons are predominantly (96%) saturated.

(3) The even-numbered hydrocarbons are predominantly (92%) mono-unsaturated.

(4) When the reaction mixture was quenched with CH_3OD–DCl–D_2O, the odd numbered hydrocarbons were about 62% monodeuterated and the C_{even} hydrocarbons were about 60% monodeuterated, the balance being nondeuterated.

(5) The C_{odd} hydrocarbons are predominantly linear alkanes.

(6) The C_{even} fraction contains a small amount of these linear alkanes but the majority alkenes are structurally quite varied. Scheme 1 shows the structures of these alkenes as deduced by ^{13}C-NMR spectroscopy in an experiment in which [13]C_2H_4 was oligomerized at 100 mm initial pressure, owing to the scarcity of the labeled monomer (vide infra). This is shown more vividly by the numerous GC peaks for the C_{even} fractions, Fig. 3.

These results can be accommodated by the mechanism shown in Scheme 2. In it, oligomerization (polymerization) is initiated by coordination of ethylene to solvated Cp_2ZrMe^+ followed by olefin insertion into the Zr–CH_3 bond. Repetition of this sequence leads to a linear C_{odd} hydrocarbon chain attached to zirconium. Exchange of alkyl groups with $(MeAlO)_x$ (or Me_3Al) represents a chain transfer step that leads eventually to a new Cp_2ZrMe^+ initiation site and to Al-bound oligomers. The latter, on hydrolysis with CH_3OD–DCl–D_2O, leads to the observed monodeuterated C_{odd} hydrocarbons.

The notable feature of Scheme 2 is a new chain-initiating species, $Cp_2Zr(CH{=}CH_2)^+$ (which, like Cp_2ZrMe^+, may be solvated by methylaluminoxane). We propose that it arises via a sigma bond metathesis reaction of Cp_2Zr–$alkyl^+$ with ethylene. Precedent for such a process comes from the recent work of Bercaw on isoelectronic scandium systems [59]. In this reaction, ethylene behaves operationally as a protic acid and cleavage by it of the Zr–C bond [38] in Cp_2Zr–$alkyl^+$ leads to the observed non-deuterated C_{odd} hydrocarbons. The C_{odd} d_0 and d_1 have in common initiation by a Zr–CH_3 species. The former are proposed to arise from sigma bond metathesis and the latter from deuterolysis.

The sigma bond metathesis process produces concomitantly a vinylzirconocene species $Cp_2Zr(CH{=}CH_2)^+$. It too can undergo the eth-
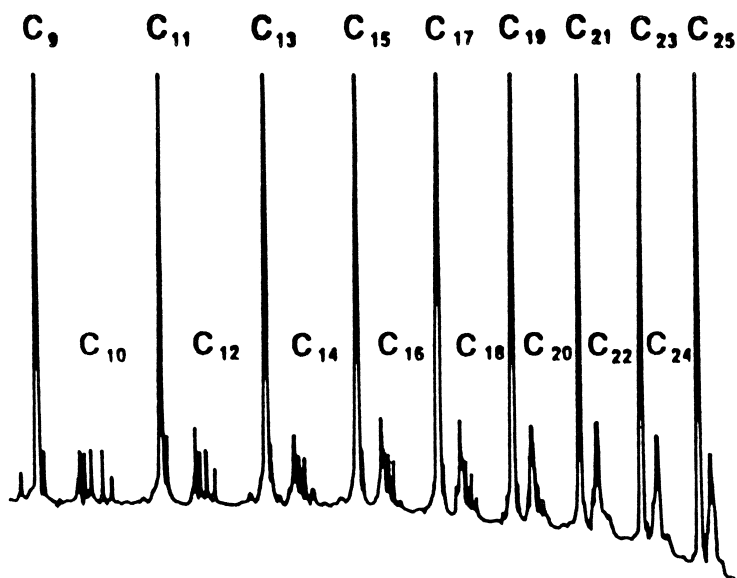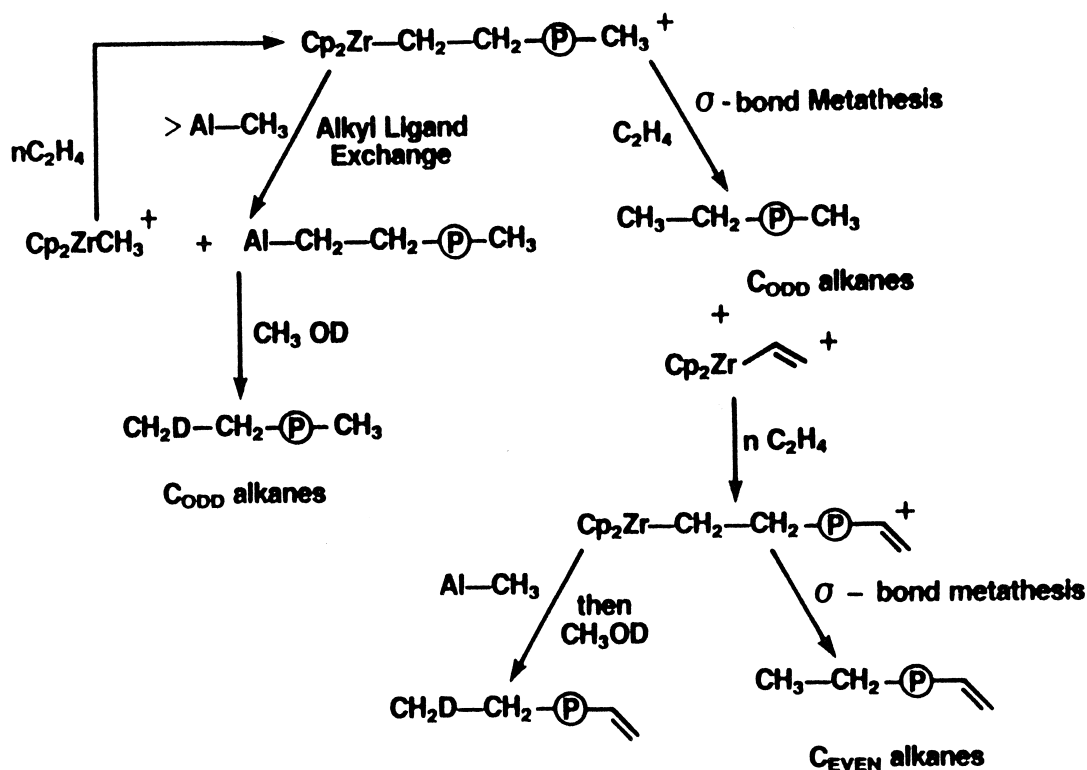

Fig. 3. Gas chromatogram of ethylene oligomerization products.

Scheme 2. Proposed mechanism for ethylene polymerization.

ylene coordination and then insertion steps to yield a growing oligomer chain but this chain is always vinyl-terminated. The chain can be cleaved on deuterolysis to yield monodeuterated C_{even} alkenes. Or, it too, can undergo subsequent sigma bond metathesis with C_2H_4 to form undeuterated C_{even} alkenes. The charms of the sigma bond metathesis component of the Kaminsky ethylene oligomerization reactions are that it accounts for the observations that (1) the C_{even} products are predominantly alkenes — as they must be for they arise from a vinyl — Zr initiation site; (2) it accounts for the quantity of $^{12}CH_3$ end groups observed when $Cp_2Zr(^{13}CH_3)_2$ is used; and (3) both d_0 and d_1 alkenes are formed on deuterolysis. Exchange of Zr–R and Al–CH_3 as well as sigma bond metathesis could involve (formally) cationic Cp_2ZrR^+ or neutral $CpZrR^1R^2$. The two possibilities are not distinguishable by our results.

Metathetic reactions of Cp_2ZrR^+ with strongly coordinating ligands such as pyridine are well described in Ref. [60] and references therein.

Our mechanism predicts that, after deuterolysis, the Kaminsky ethylene oligomerization should produce a mixture of d_0 and d_1 alkanes and alkenes. That such is the case is demonstrated by Fig. 4. This figure displays the $C_{15,16}$ portion of a gas chromatogram of products obtained after deuterolysis. Atomic emission detection (AED) was used [61–65]. In AED, the separated analyses are swept by the helium carrier gas into a microwave cavity. There, a 2.4 GHz microwave source ionizes the helium and converts it into a plasma having a temperature of 8000–10 000 K. This plasma, in turn, literally atomizes the hydrocarbons in the helium stream. The constituent atoms in the analyte produce line spectra that are analyzed with a multiwavelength spectrograph. In this way, iso-
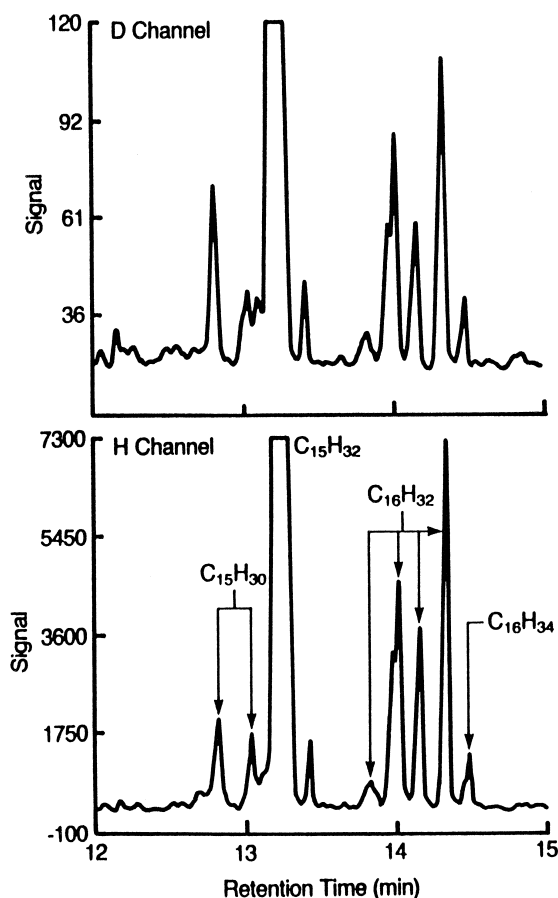
Fig. 4. Gas chromatogram ($C_{14,16}$ region), using atomic emission detection, of hydrocarbons isolated from C_2H_4 oligomerization after deuterolysis.

tope-specific analysis (here H and D) of each GC peak is possible. The two portions of Fig. 4 display the output of the H- and D-detector channels as the $C_{15,16}$ portion of the gas chromatogram is scanned. It can be seen that the two traces are virtually congruent, indicating that, in accordance with our mechanism, all of the hydrocarbon products are deuterated and to approximately the same degree.

Further substantiation of our mechanism is provided by the the finding that the C_{odd}/C_{even} ratio (2.6), the d_1/d_0 ratio (1.6) and the alkane/alkene ratio (1.9) are all approximately equal. This occurs because, for every alkyl-ligand exchange step, both an oligomer-d_1 and an initiator of C_n (n = odd) alkane chains (i.e.,

$Zr–CH_3$) are produced. Likewise, for every sigma bond metathesis event, an oligomer-d_0 and a C_n (n = even) alkene chain initiator ($Zr–CH=CH_2$) are formed. Thus, these different ratios all reflect the average relative rates of the two competing chain transfer processes, viz. alkyl-ligand exchange and sigma bond metathesis.

In other words these ratios correspond to the branching ratio, that is, the ratio of the number of chains initiated by a $Cp_2Zr–CH_3^+$ species to the number initiated by $Cp_2Zr–CH=CH_2^+$. Our data do not lead to a unique value for this branching ratio but rather to an average value. This is because the concentration of the two initiators are functions of Al–CH_3 and ethylene concentrations respectively. $[C_2H_4]$ decreases during the oligomerization experiment and Al–CH_3 is used in large excess. The three independent measurements of the average branching ratio (vide supra) give a range of 1.6–2.6.

In another attempt to measure the branching ratio, $^{13}C_2H_4$ was oligomerized using $Cp_2Zr(^{12}CH_3)_2–(^{12}CH_3AlO)_x$ but without hydrolytic workup. In the ^{13}C-NMR spectrum, one can observe 34 Hz doublets and triplets (due to C–C coupling) at 23.3 ppm that are due to the beta ^{13}C nucleus in $–^{13}CH_2–^{13}CH_2–^{12}CH_3$ and $–^{13}CH_2–^{13}CH_2–^{13}CH_3$ end groups respectively. The ratio of these two features is 5:2. Recalling that the sigma bond metathesis step produces a free alkane with two methyl end groups and that the only source of $^{12}CH_3$ end groups is insertion of the labeled olefin into a $Zr–^{12}CH_3$ bond, then the branching ratio is calculated from this experiment to be 1.5. In addition, the NMR results provides additional confirmation that some of the ethylene oligomer chains are initiated by $Zr–CH_3$.

The [Al]/[Zr] ratio in these studies is lower than that usually employed in $Cp_2ZrMe_2–$ $(MeAlO)_x$ catalyst systems. In an additional experiment, the [Al]/[Zr] ratio was increased to 270 by using less Cp_2ZrMe_2, but GC and GC-MS analysis showed that the product distribution is not greatly different. Thus, C_{odd} hydro-

carbons are 94% saturated, C_{even} hydrocarbons 20% saturated. The C_{odd}/C_{even} ratio is less, 0.8, and the alkane/alkene ratio is 1.1.

We do not claim that beta-hydride elimination chemistry does not occur in this catalyst system — only that it is not an important determinant of the relative abundances of the various organic products obtained from ethylene. It is probable that beta-elimination is responsible for the small amounts of C_{odd} alkenes (4% using Cp_2ZrMe_2 as the organometallic) and C_{even} alkanes. The effect of variations in the nature of the organometallic component of the catalyst system on the product composition is shown in Table 1. Notable is $(Me_3SiC_5H_4)_2ZrCl_2$ (zirconocene halides are considered to be methylated by the excess $(MeAlO)_x$ and/or Me_3Al present). Empirically, this organometallic produces significantly more unsaturated C_{odd} hydrocarbons. If our mechanism is correct, one expects to be able to find an additional class of organic products, alpha,omega dienes. These would arise by beta-hydride elimination from a vinyl-terminated oligomer chain. In the $(Me_3SiC_5H_4)_2ZrCl_2–(MeAlO)_x–Me_3Al$ catalyst system, $C_{14,16}$ compounds are the most abundant C_{even} hydrocarbons and so these were further examined by GC with CH_4 chemical ionization mass spectrometric detection to see if dienes were formed. The CI-MS spectra of dienes show peaks with m/z corresponding to $P − 1^+$ ions (P is the mass of

the parent molecular ion). Characteristic m/z 193 and 221 ions were indeed found and these we attribute to the $P − 1^+$ ions derived from the dienes $C_{14}H_{26}$ and $C_{16}H_{30}$. This result is consistent with our mechanism although the mass spectrometric analysis does not establish the positions of the double bonds in the dienes.

An issue that needs to be considered is why sigma bond metathesis occurs with ethylene but not with toluene, which, as solvent, is present in much greater concentration. Benzene is known to undergo such a reaction with Sc–CH$_3$ bonds [59]. One would assume that aromatic hydrocarbons should react similarly with $Zr–CH_3^+$ compounds although the thermodynamic data base does not permit a conclusion to be drawn about the relative strengths of $Zr–CH=CH_2$ and $Zr–C_6H_5$ bonds [66–68]. We surmise that toluene is unable to coordinate effectively to the $Cp_2Zr–alkyl^+$ site and, therefore, does not participate in sigma-bond metathesis at a significant rate relative to ethylene. This could possibly be due to steric effects for the metal site in $Cp_2ZrCH_3^+$ associated with the bulky methylaluminoxane-derived counter ion could be less accessible than in $(Me_5C_5)_2ScCH_3$. In any event, we have no evidence that the toluene solvent is incorporated to a significant degree into the ethylene oligomerization products.

The structures of the alkene products deserves further comment. The presence of internal olefins cannot be accommodated by our

Table 1
Hydrocarbons produced using different organometallic catalysts

Cocatalyst	C_{odd} (%) SATD	C_{even} (%) SATD	C_{odd}/C_{even}	Alkanes/Alkenes
Cp_2ZrMe_2	92	9	2.6	1.9
Cp_2ZrCl_2	96	20	7.7	6.9
Cp_2ZrMe_2	93	54	10.3	8.2
$(TMS\,Cp)_2ZrCl_2$	79	52	1.7	2.2
Cp^*ZrCl_3	98	30	7.1	8.9
$CpZrCl_3$	69	33	3.6	1.6
Cp_2HfMe_2	90	10	5.2	5.9
$CpZrI_2$	100	0	7.8	7.8
Cp_2TiCl_2	97	0	3.8	3.3
Cp^*HfMe_3	95	14	2.2	2.3
$(IND)_2ZrMe_2$	92	42	1.5	2.6

mechanism and we propose that they arise by isomerization of terminal olefins. This could occur by reversible addition and elimination of a $Cp_2Zr–H$ species to an olefin but when 1-hexene is oligomerized by the Kaminsky catalyst, virtually no isomerization of unreacted hexene is observed after 30 h (during which 80% conversion to oligomers occurs). Thus, other isomerization mechanisms need to be considered. One of these is due to Turner and Hlatky [69]. It involves rearrangement of a zirconium-coordinated 1-butenyl unit to a $Zr(H)–\eta^4$-butadiene$^+$ fragment via beta-hydrogen elimination. Readdition of the Zr–H hydride to the terminal carbon atom produces a Zr–(1-methallyl)$^+$ fragment which then collapses to a Zr-coordinated 2-butenyl moiety. Subsequent ethylene insertion would then produce the observed internal olefins.

The structural variety of oligomers observed in the oligomerization of $^{13}C_2H_4$ (vice supra) is in accord with our proposed mechanism. It should be recalled that the oligomerization was done in a closed system with a low (ca. 100 mm) initial ethylene pressure so that the concentration of product olefins increases while that of ethylene-$^{13}C_2$ falls. Eventually, these unsaturated products compete with ethylene in further insertion chemistry; they also bear alkyl substituents which tend to favor beta hydrogen elimination. The $CH_2=C(CH_3)R^2$ can arise from addition of $Cp_2ZrCH_3^+$ or Cp_2ZrR^+ to such olefins followed by beta hydrogen elimination. Relative to a commercial ethylene polymerization process operating at much higher pressure, these compounds may be viewed as artifacts observable only at much lower monomer pressures.

The same may be said of sigma bond metathesis for, in our experiments, when the ethylene pressure was increased from 250 to 600 mm, the yield of oligomers decreased (relative to insoluble polymer) and, in the those oligomers, the relative amounts of C_{even} alkenes were significantly less. In a related study of the kinetics of 1-hexene polymerization by Kamin-

sky's catalyst system, we found that the order in olefin concentration depended on [hexene] but was always > 1 [70]. If we make the reasonable extrapolation that the kinetic order in $[C_2H_4]$ is also greater than unity, then increasing ethylene pressure should favor the insertion and alkyl ligand exchange steps in our mechanism. Of course, if the reaction were conducted for long periods, sigma bond metathesis products should begin to accumulate (as they do). However, longer reaction times at the higher ethylene pressure are not practical from a mechanistic standpoint because the reaction mixture solidifies due to formation of insoluble polyethylene.

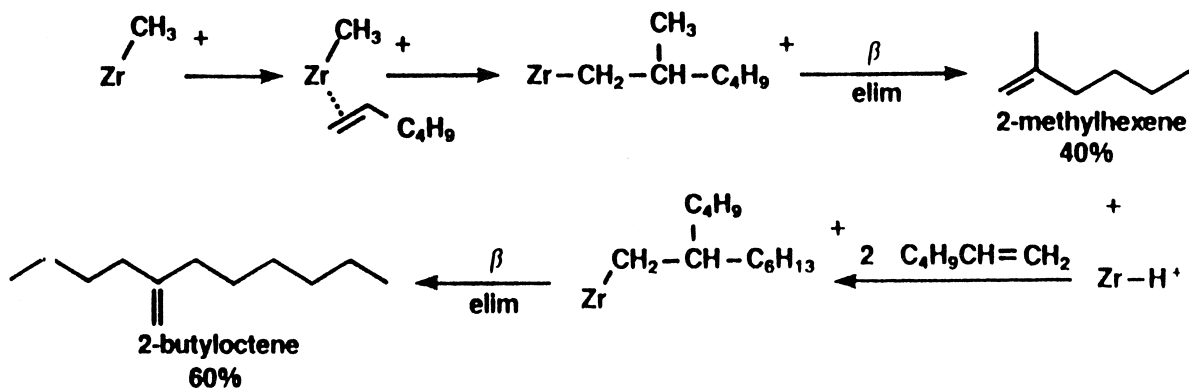## 2.3. Mechanism of propylene and 1-hexene oligomerization

These two olefins are much less reactive than ethylene and lead, under similar experimental conditions, to a mixture of low molecular weight oligomers containing predominantly dimers and trimers. The mechanisms proposed are shown in Schemes 3 and 4. We believe that, in both cases, oligomerization is initiated by solvated $Cp_2ZrCH_3^+$. However, with propylene and hexene, olefin coordination followed by $Zr–CH_3$ insertion leads to a beta-disubstituted Zr–alkyl species that is unstable and which eliminates butene (not observed in our experiments) or 2-methyl-1-hexene. It is known that β-alkyl substituents promote β-hydride elimination, possibly by stabilizing the incipient carbonium ion center in the transition state. Facile beta hydride elimination produces a (cationic) zirconium hydride species that initiates further oligomerization. Thus, propylene produces the C_6 dimers and C_9 trimers 2-methyl-1-pentene and 2,4-dimethyl-1-heptene which were identified by ^{13}C NMR and mass spectroscopy. Significant retention of the original $Zr–^{13}CH_3$ group in the products is not observed, in contrast to ethylene oligomers. Propylene oligomerization involves, within NMR detection limits, head-to-tail insertion into the Zr–R bond. Thus, when propylene-1-$^{13}CH_3$ is oligomerized with
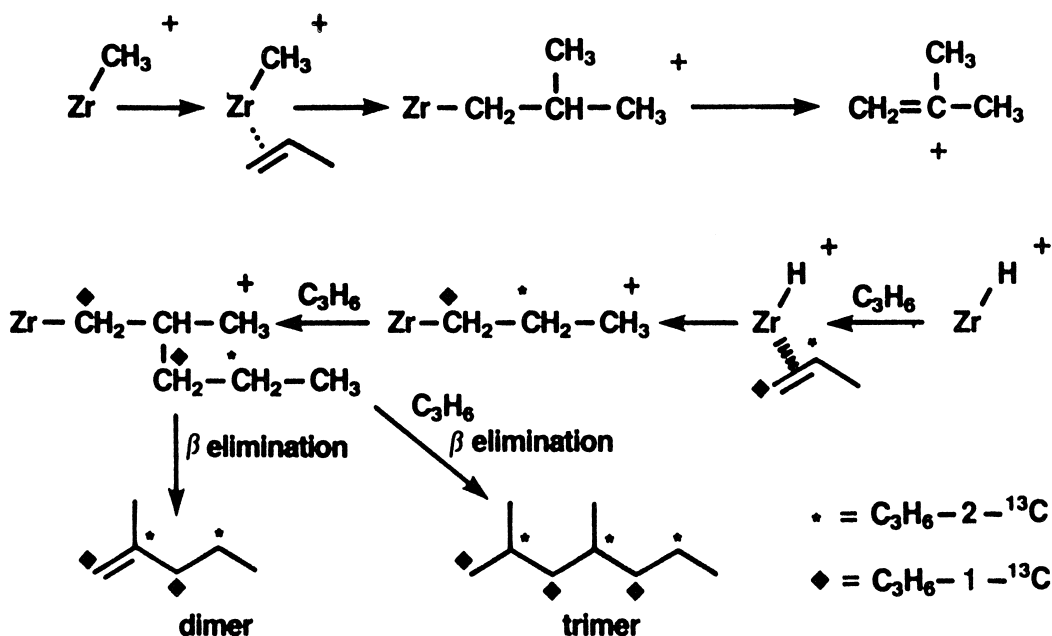
Scheme 3. Proposed mechanism for propylene polymerization.

the Cp_2ZrMe_2–$(MeAlO)_x$ catalyst system, the resulting 2-methylpentene contains the ^{13}C label only in the 1,3 positions. Similarly, this hydrocarbon is labeled only in the 2,4-positions when the precursor is propylene–2-^{13}C. These results do not rule out the possibility of less probable head-to-head or tail-to-tail olefin insertions that may be manifest only when a large number of unsymmetrical olefins are inserted into a Zr–R bond.

Oligomerization of 1-hexene under conditions comparable to those used for ethylene affords a mixture containing 2-methyl-1-hexene and 2-butyl-1-octene. The former olefin arises by insertion of a $ZrCH_3$ moiety into the 1-hexene skeleton followed by beta hydride elimination. The latter hydrocarbon is simply the dimer of 1-hexene formed at a Cp_2Zr–H^+ initiation site. Smaller amounts of higher oligomers are formed indicating that the relative rate of

Scheme 4. Proposed mechanism for 1-hexene olygomerization.

chain termination to chain transfer for 1-hexene is even higher than that of propylene in this catalyst system.

3. Experimental

Toluene and 1-hexene were dried by distillation from Na–K alloy. Ethylene and propylene were used as received from Matheson or, for ^{13}C isotopomers, from Merck. Methylaluminoxane was prepared as previously described [47,48]. A [17]O enriched sample was similarly synthesized using $MgCl_2$ that had been rehydrated with 20 atom% $H_2^{17}O$. A solution of $(MeAlO)_x$–Me_3Al in toluene was obtained from the Ethyl Corp.; it is stated to be ca. 0.9 M each in $(MeAlO)_x$ and Me_3Al. [13]C, ^{17}O, ^{27}Al and [91]Zr NMR spectra were obtained at 9.4T on a Varian XL-400 spectrometer whose ^{1}H operating frequency is 400 MHz. The external references Me_4Si, H_2O, $[Al(H_2O)_6][ClO_4]_3$ (1 M in D_2O) and Cp_2ZrBr_2 (1 M in THF) were used. Positive chemical shifts are downfield of these references.

Ethylene oligomerization reactions were carried out in a glass reactor of approx. 15 ml volume. This was charged in a nitrogen-filled drybox with 0.1 mmol of the zirconocene component of the catalyst, 1.0 ml of the methylaluminoxane solution and 1.5 ml toluene. The reactor was attached to a vacuum line and the contents freeze-pump-thaw degassed. While the catalyst system was still frozen, the reactor was connected to a small-volume manifold, pressurized to 250 mm with ethylene then isolated from the ethylene source. The pressure was measured by a capacitance manometer. After cessation of pressure drop, the reactor was taken back into the drybox and its contents transferred to a Schlenk tube fitted with a rubber septum and a nitrogen inlet (connected in turn to a bubbler). The reaction mixture was cooled to 0°C and methanol, 1.5 ml, was added via syringe followed by 5 ml 15% aqueous HCl. The organic layer was separated, dried over $CaCl_2$, then analyzed by GC and GC/MS.

GC/MS analyses were performed on a Hewlett-Packard HP 5995 instrument. The sample was injected splitless onto a 30 m (0.25 mm o.d.) DB-1 (0.1 micron film thickness) capillary column heated from 30 to 310°C at 10° min[−1]. A He flow rate of 2 ml min^{−1} was used. The GC to MS transfer line and mass spectrometer source were maintained at 280° and 150°, respectively. Full-scan, unit resolution mass spectra of the separated components were acquired from 29 to 500 amu in the electron impact mode (70 eV). In order to increase the intensity of high mass fragments, a second EI analysis was recorded in the 90–600 emu mass range. Chemical ionization mass spectra were obtained in a HP 5988 instrument using methane as the ionizing gas. Spectra were acquired with unit resolution in the 60–500 amu mass range.

Determination of the C–H/C–D ratio for alkanes was straightforward and done by comparison of the P^+ and $P+1^+$ parent ions after correction for ^{13}C in natural abundance. Intensities of molecular ions from alkenes are intrinsically low and made even lower by the fact that several C_{even} alkene peaks occur because of structural heterogeneity of the alkene products. Thus, C–H/C–D cannot be measured in this way. Instead, the intensities of the protonated molecular ion, $P+1^+$, and the $P+2^+$ deuterated analogue in the CI-MS were compared for the most abundant C_{14} and C_{16} alkenes.

Gas chromatographic separations with atomic emission detection were performed with a HP 5921A instrument interfaced with a HP 3354 data system.

Acknowledgements

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