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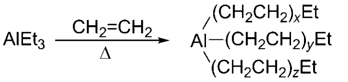
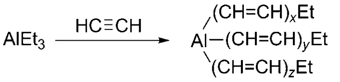
Revisiting the Aufbau Reaction with Acetylene: Growth at Aluminium Producing a Unique Oligomer Distribution

Samuel Karpiniec,[a] David McGuinness,*[a] Jim Patel,[b] and Noel Davies[c]

The pyrolysis of natural gas can be employed to produce acetylene and hydrogen, therefore acetylene conversion reactions are of interest as a means of upgrading abundant gas reserves.[1,2] The direct oligomerization of acetylene to liquid hydrocarbons is attractive and, unlike existing gas-to-liquid processes, is potentially very carbon efficient. As such, a selective process for the oligomerization of acetylene to fuel-length oligomers is currently of interest.[3] Although the cyclo-oligomerization of acetylene has been known since the work of Reppe,[4] linear oligomerization is much less common.[5] Heterogeneous nickel catalysts have been studied for acetylene oligomerization,[3] as have early transition metal, lanthanide and actinide complexes for oligomerization of substituted alkynes.[6–8] As part of our studies in this area, we became interested in the possibility of using aluminium alkyls for acetylene oligomerization. The stepwise growth of aluminium alkyls through ethylene insertion, termed the Aufbau reaction, was reported by Ziegler in the early 1950s [Eq. (1)].[9] For over half a century this reaction has formed the basis of large scale industrial production of ethylene oligomers, with the advantage that a relatively narrow and controllable Poisson distribution of chain lengths results.[10] The analogous Aufbau reaction with acetylene [Eq. (2)] is unknown, although this reaction was apparently attempted by Ziegler. More detailed studies followed from Wilke, who showed that acetylene ceases to react after one insertion, leading to $\mathrm{Et_2Al(CH{=}CHEt)}$.[11] Herein we show that under appropriate conditions further growth at aluminium does indeed occur, but does so through an unprecedented mode of addition quite different from the Aufbau reaction of ethylene.



$$\mathrm{AlEt_3} \xrightarrow[\Delta]{\mathrm{CH_2{=}CH_2}} \mathrm{Al}\begin{array}{l}\diagup\mathrm{(CH_2CH_2)_{\mathit{x}}Et}\\ -\mathrm{(CH_2CH_2)_{\mathit{y}}Et}\\ \diagdown\mathrm{(CH_2CH_2)_{\mathit{z}}Et}\end{array} \tag{1}$$



$$\mathrm{AlEt_3} \xrightarrow{\mathrm{HC{\equiv}CH}} \mathrm{Al}\begin{array}{l}\diagup\mathrm{(CH{=}CH)_{\mathit{x}}Et}\\ -\mathrm{(CH{=}CH)_{\mathit{y}}Et}\\ \diagdown\mathrm{(CH{=}CH)_{\mathit{z}}Et}\end{array} \tag{2}$$

We began our investigations by exposing toluene solutions of $\mathrm{AlEt_3}$ ([Al] = 300 mM) to acetylene at a pressure of 1 bar gauge (2 bar absolute pressure). From room temperature up to 60 °C the only growth products (after quenching the solution) are 1-butene (95-98 %) along with some 1,3-hexadiene (2-5 %), indicating that $\mathrm{Et_2Al(CH{=}CHEt)}$ is the major product and broadly consistent with the results of Wilke.[11] Evidently some double insertion occurred resulting in Al-hexadienyl groups, prompting us to try under more forcing conditions. At 100 °C the solution darkens considerably after two hours and, following quenching, a broad range of higher oligomers was detected by GC (Figure 1). The most striking feature was the near absence of any C_8 oligomers, followed by much larger C_{10} peaks. This pattern is repeated in the higher oligomers for which the C_{14} and C_{18} oligomers are more concentrated than the C_{12} and C_{16} products (Figure 2). This gives the appearance that the oligomers higher than C_6 are preferentially growing by four carbons at a time, and clearly a non-standard mode of growth is occurring. We were intrigued to study this further, and have undertaken a number of detailed experiments in an attempt to understand the origin of this effect.

The total amount of oligomers formed in a given run is always approximately the same as the amount of $\mathrm{AlEt_3}$ present. Thus insertion initiates at only one ethyl group per Al centre, as found by Wilke, and further growth also seems to follow this behaviour. GC-MS confirms that the molecular weights of the major products are consistent with the addi-

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[a] S. Karpiniec, Dr. D. McGuinness
School of Chemistry, University of Tasmania
Private bag 75, Hobart 7001 (Australia)
Fax: (+61)362262783
E-mail: david.mcguinness@utas.edu.au

[b] Dr. J. Patel
CSIRO Petroleum Resources
Private Bag 10, Clayton South 3169 (Australia)

[c] Dr. N. Davies
Central Science Laboratory, University of Tasmania
Private Bag 74, Hobart 7001 (Australia)

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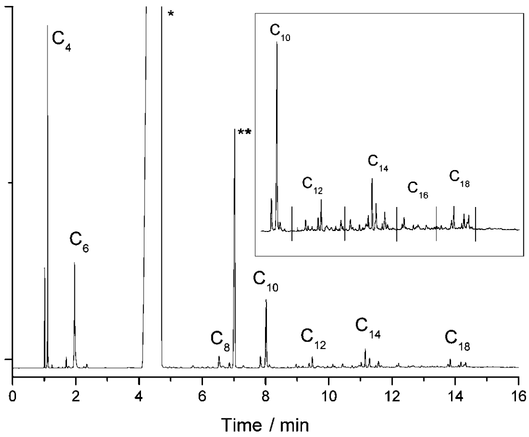


Figure 1. GC-FID trace of post-quench products from acetylene oligomerization with $AlEt_3$ (inset: expansion of C_{10}–C_{18} fractions). *Toluene (solvent), **Nonane (internal standard).

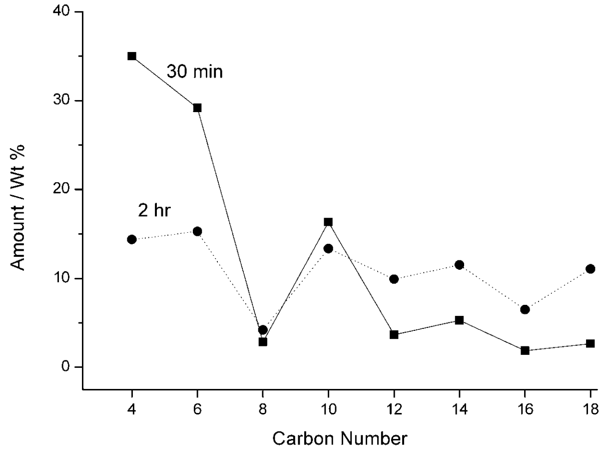
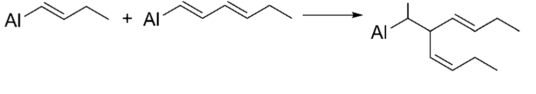


Figure 2. Product distribution (wt %) for acetylene oligomerization with $AlEt_3$ after 30 min and 2 h (Toluene, $T=100\,°C$, $[Al]=300$ mM, 1 barg acetylene).

tion of acetylene units to one ethyl group, leading to H-$(HC{=}CH)_n$-Et (C_xH_{x+4}). Chain termination does not occur to any great extent. This was demonstrated by quenching the reaction with D_2O which produced [D_1]oligomers, and showed that the growing chain remained at Al until it was quenched off.[12]

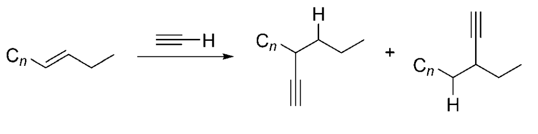
Our initial thought was that the observed product distribution could arise from addition of the Al-butenyl group across any double-bond unsaturation present in the oligomers, for example the reaction in Equation (3). The major species present in solution, $Et_2Al(CH{=}CHEt)$, could explain the apparent favoured growth by four carbons at a time. Additionally, a similar reaction was observed by Wilke.[11] However, the experimental findings are all inconsistent with such a process. Firstly, the molecular weights of the oligomers were lower than would result from growth by addition of butenyl groups. Secondly, [D_1]oligomers resulting from the D_2O quench suggest only one point of attachment to Al. Finally, heating a solution of the lower Al-oligomers in the absence of acetylene led to only minor formation of higher oligomers; significant further growth occurred only in the presence of acetylene.



(3)

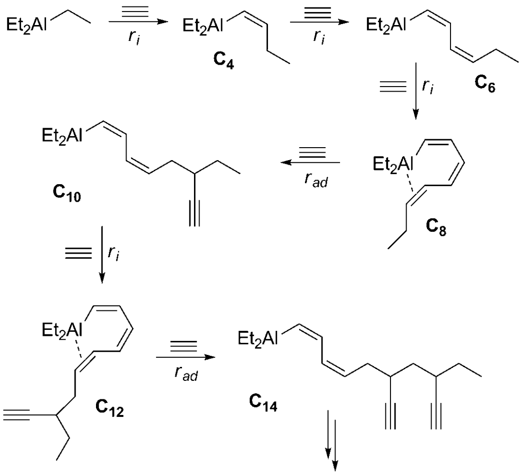
Although the lower oligomers, 1-butene and 1,3-hexadiene, were easily identified, the C_{10+} fractions contained increasing numbers of products and the mass spectra indicated branching. To better identify the skeletal structures, the sample was hydrogenated which allowed identification of three out of four of the $C_{10}H_{22}$ paraffins formed. The major product post-hydrogenation is 3-ethyloctane (≈90 %), followed by more minor amounts of 4-ethyloctane (≈5 %) and *n*-decane (≈4 %). The major C_8H_{18} paraffin present was *n*-octane. It therefore appears that linear oligomerization produces the small amount of C_8 oligomer, but that this is extended to the linear C_{10} oligomer to only a small extent. Another process is taking place to produce ethyl branching in the hydrogenated C_{10+} oligomers. The most obvious explanation for ethyl branching was addition of Al–Et across the unsaturated oligomers, but again the molecular weights of the oligomers prior to hydrogenation were too low and show that addition of acetylene must be responsible for the branching. An experiment with $AlMe_3$ supports this. When $AlMe_3$ was exposed to acetylene under the same conditions (100 °C, 1 barg acetylene), the dominant oligomer distribution was made up of C_3 (propene), C_5 (1,3-pentadiene), C_9, C_{13}, and C_{17} products. The major C_9 product (90 %) following hydrogenation was 3-ethylheptane and mass spectrometry of the higher oligomers also indicated ethyl branching. Thus, the branching arises from acetylene addition and not addition of the Al-alkyl group. This experiment further confirmed that the major products do not arise from condensation of lower Al-oligomers, as addition of these would not lead to the distribution observed. Just as with $AlEt_3$, it seems two insertions of acetylene occur before an apparent jump of two further acetylene additions take place, at the same time branching is introduced.

After oligomerization with $AlEt_3$, removal of the volatiles under vacuum left the higher C_{10+} fractions as a yellow liquid. ^1H NMR spectroscopy of these oligomers provided further clues as to the process occurring. One end group of the oligomers is represented by a multiplet at 5.0 ppm corresponding to two terminal olefinic protons. The remaining olefinic resonances from 5.2–6.5 ppm are consistent with internal olefin protons, including conjugation (>6 ppm). The methylene protons of the other end group, the initiating ethyl group, are fully accounted for by a peak at 1.60 ppm. This shift is inconsistent with a methylene group hydrogen α to the double bond, and reveals that unsaturation adjacent to the ethyl end group has been removed in the C_{10+} oligomers. A broad peak centred at 2.0 ppm is consistent with terminal-alkyne unsaturation, and functional-group tests confirm this.[13] Finally, a series of multiplets between 2.4–3.0 ppm are consistent with a methine proton α to the alkyne. These observations suggest that the major C_{10+} oligomers are formed according to Equation (4). Additionally, this process is consistent with the identity of the branched C_{10} products, 3- and 4-ethyloctane following hydrogenation.

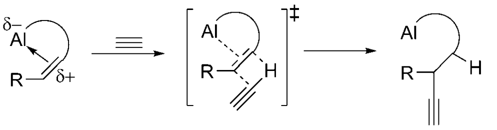


(4)

At this stage direct evidence for any particular mechanism is limited, but in the interest of stimulating discussion, herein we have suggested one possibility. Clearly normal migratory insertion of acetylene cannot produce the branching suggested above, and as such, a second mode of acetylene addition must be considered. A mechanism which fits the experimental data is shown in Scheme 1. According to this mechanism, conventional migratory insertion sequentially produces butenyl-Al, hexadienyl-Al and octatrienyl-Al. Once the octatriene moiety forms, the chain can back-bite such that a double bond can interact with the fourth coordination site of monomeric trialkyaluminium. This is not possible with the shorter chains, whereas simple models show that two *cis* double bonds closest to the Al would leave the third in an ideal position to interact with a vacant coordination site of Al.[14] This interaction could activate the double bond, facilitating acetylene addition across it and producing the branched C_{10} oligomers. Once the third double bond is removed, the next acetylene unit must insert to give Al-C_{12}, before another addition across the double bond can occur. The distribution of oligomers observed can be explained by a model whereby the rate of addition across the double bond, r_{ad}, is significantly greater than that for insertion, r_i. This would lead to a situation whereby oligomeric chains with a favourable double bond interaction with Al (Al-C_8, Al-C_{12}…) would rapidly react, resulting in the observed depletion of these chain lengths. A possible intermediate for acetylene addition across the double bond is shown in Equation (5), which could be facilitated by interaction of the acetylene and alkene π orbitals. We are unaware of any precedent for such a reaction, although it does seem feasible given the known low bond strength of the acetylene C–H bond. Other possibilities can also be envisaged, such as interaction of the unsaturated chain with a coordinated (C–H activated) acetylene molecule, which is perhaps just as likely. These alternatives are shown in the Supporting Information. Further studies are required to ascertain the likelihood of such processes.



Scheme 1. Proposed possible mechanism of acetylene chain growth at $AlEt_3$.



(5)

In summary, it is worth pointing out that our results are not inconsistent with the work of Ziegler and Wilke. Even after two hours the major Al species present (on a molar basis) is still $Et_2Al(CH{=}CHEt)$. Given the complexity and range of higher oligomers formed, and lacking modern capillary GC in addition to MS, it is little wonder that these growth products were not observed. We have however shown here that further growth does indeed occur, but that the reaction is more complex than the Aufbau reaction with ethylene. Further mechanistic studies are required to fully understand this process. In addition, keeping in mind our aim of an efficient acetylene oligomerization process, further work will look at promoting chain transfer reactions, such that the process can be rendered catalytic.

Experimental Section

Acetylene oligomerization was conducted in a LabCrest glass reactor immersed in an oil bath for temperature control. Toluene (50 mL) and $AlEt_3$ (15 mmol) were introduced under an argon atmosphere and the reactor heated to the required temperature. Argon was removed by brief evacuation and acetylene added to a constant pressure of 1 bar gauge. After the required run time, the reactor was cooled in ice, vented and quenched with dilute HCl. The organic phase was analyzed by GC-FID and GC-MS following addition of an internal standard. Further details of the analysis are given in the Supporting Information.

Acknowledgements

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Keywords: acetylene • aluminum • aufbau reaction • insertion • oligomerization

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[12] The possibility of the products arising by means of trace transition metal catalysis was suggested by a referee, but this can be ruled out based upon a wider study of acetylene oligomerization with a variety of metal catalysts (to be published). A range of early transition metal complexes trialled had no effect on the growth reaction, whereas later transition metals, which were active, gave a different range of products. In addition, catalysis was conducted in a glass autoclave, thereby eliminating the usual source of metal contamination.

[13] See the Supporting Information for details.

[14] Insertion of acetylene proceeds in a *cis* fashion, although the barrier to *cis*/*trans* isomerism in the growing chain is low, see: I. Hyla-Kryspin, R. Gleiter, *J. Mol. Catal. A* **2000**, *160*, 115–124.

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