The Selective Trimerization of Ethylene to Hex-1-ene

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A homogeneous three-component catalyst of chromium, hydrolysed alkylaluminium, and dimethoxyethane, trimerizes ethylene to hex-1-ene in 74% selectivity at a rate of 1.2 mol (mol Cr)$^{-1}$ s^{-1}.

Higher α-olefins (HAOs) represent an important family of industrial chemical products which find a variety of end uses.[1] Through hydroformylation, copolymerization, and arylation/sulphonation, they become components of plasticizers, solvents, plastics, and surfactants. HAOs can be obtained from ethylene through oligomerization technologies, such as those practiced by Shell (Shell Higher Olefins Process, nickel/phosphine catalyst), and Ethyl Corporation (alkylaluminium catalysts). These growth processes typically produce an 'envelope' of ethylene oligomers from which HAO fractions must be separated by distillation. In this paper we describe a selective, chromium-catalysed trimerization of ethylene to hex-1-ene, a particularly desirable HAO comonomer in low-pressure ethylene polymerization.

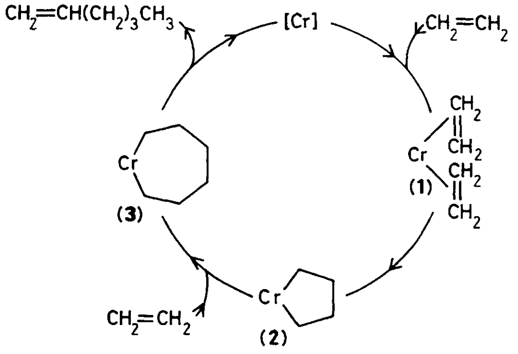
Union Carbide workers had previously shown[2] that a homogeneous ethylene polymerization catalyst, chromium(III) 2-ethylhexanoate and hydrolysed tri-isobutylaluminium, produced small quantities of hex-1-ene as the only significant oligomeric product in addition to the desired polyethylene. We have now developed this catalyst into one which produces hex-1-ene essentially as the sole HAO product in high selectivity.

As an example, a catalyst of chromium(III) 2-ethylhexanoate (0.20 mmol), hydrolysed tri-isobutylaluminium (6.0 mmol), and dimethoxyethane (glyme) (2.0 mmol) in heptane solvent at 95 °C and 400—500 psi ethylene pressure gives 74% hex-1-ene selectivity at a turnover frequency of 1.2 Cr^{-1} s^{-1}. The principal byproduct is polyethylene, although small amounts of butenes and octenes are also produced (totalling less that 2% of ethylene consumed). Of the C_6 products, 99.9% is hex-1-ene, with no detectable branched, and only small amounts of internal hexenes. Analysis of the byproduct polyethylene shows it to be of high molecular weight ($\approx 10^6$) with very few butyl side chains, indicating little or no incorporation of hex-1-ene into the polymer.

Variants on this catalyst system employing other ethers as replacements for dimethoxyethane can be used, although catalyst performance is generally inferior in these cases. Such replacements include di- and tri-glyme, tetrahydrofuran, and *o*-dimethoxybenzene.[3]

Few mechanistic details are available, but the operation of a growth mechanism involving insertion into a metal hydride seems unlikely in the light of the unique selectivity to hex-1-ene and lack of internal or branched products. Instead, we propose that the trimerization proceeds *via* metallacyclopentane and metallacycloheptane intermediates (Scheme 1).

Diolefin and metallacyclopentane complexes of the types proposed here [species (**1**) and (**2**)] have been suggested as intermediates in ethylene dimerization.[4] For a mechanism based on metallacyclic intermediates to lead to selective formation of hex-1-ene, insertion of ethylene into the metallacyclopentane (**2**) to yield a metallacycloheptane (**3**), must be faster than elimination of but-1-ene, and elimination of hexene from the metallacycloheptane must be faster than further insertions of ethylene to yield larger rings. Whitesides has shown that the thermal elimination of olefins from platinacycloheptanes is much more rapid than from smaller rings, and has suggested that this reflects the relative ability of the metallacycles to attain the required transition state for β-hydride elimination.[5] If this reasoning can be applied to chromacycles, then an appropriately fast insertion of ethylene into the chromacyclopentane could lead to the highly selective



Scheme 1. Proposed catalytic cycle for ethylene trimerization.

hexene synthesis observed with this catalyst. However, to our knowledge, there are no examples of olefin insertions into a simple metallacyclopentane in the literature.

The peaked product distribution observed with this catalyst is unique in ethylene oligomerization, and exemplifies the highly selective transformations that can be achieved in homogeneous catalysis. Further development of the chemistry responsible for this olefin trimerization is in progress.

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References

1 K. Weissermal and H.-J. Arpe, 'Industrial Organic Chemistry. Important Raw Materials and Intermediates,' Verlag Chemie, Weinheim, 1978.

2 (a) R. M. Manyik, W. E. Walker, T. P. Wilson, and G. F. Hurley, U.S. Pat. 3,231,550; 3,242,099; R. M. Manyik, W. E. Walker, and T. P. Wilson, U.S. Pat. 3,300,458; (b) R. M. Manyik, W. E. Walker, and T. P. Wilson, *J. Catal.*, 1977, **47**, 197.

3 John R. Briggs, U.S. Pat. 4,668.838, May 26, 1987.

4 See, 'Alkene and Alkyne Oligomerization, Co-oligomerization and Telemerization,' W. Keim, A. Behr, and M. Roper, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, Vol. 8, Pergamon, Oxford, 1982, p. 371, and references therein.

5 J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521; 1972, **95**, 4451.