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Feature Article

Structurally uniform 1-hexene, 1-octene, and 1-decene oligomers: Zirconocene/MAO-catalyzed preparation, characterization, and prospects of their use as low-viscosity low-temperature oil base stocks

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ABSTRACT

An original approach to α-olefin oligomerization as well as novel thermally stable zirconocene catalysts for use in such reactions has been elaborated. The method reported allows the achievement of fractions of lightweight α-olefin oligomers up to 90% yields without considerable formation of byproducts like internal alkenes, alkanes, and higher oligomers. Trimers, tetramers, and pentamers of 1-hexene, 1-octene, and 1-decene were isolated as individual compounds and were hydrogenated. Viscosity characteristics of the isolated saturated and unsaturated hydrocarbons have been studied at various temperatures. The isolated saturated oligomers of 1-octene and 1-decene outperform the traditional electrophilic oligomerization products in terms of viscosity indexes, pour points, and low-temperature viscosity.

1. Introduction

Saturated high-boiling hydrocarbons are traditionally used as base stocks of engine oils and lubricants. Hydrocarbon-based oils can be divided into four groups of products [1]. Group I represents the dewaxed and deasphalted crude oil fractions, whose catalytic hydrogenation leads to Group II oils. Group III represents *semi-synthetic* oils produced by the catalytic hydrocracking of higher crude oil distillates. This process is accompanied by partial transformation of linear paraffins into branched saturated hydrocarbons. Group IV represents *fully synthetic* oils, which comprise the hydrogenated α-olefin oligomers. Compounds that belong to this group are generally called poly-alpha-olefin (PAO) oils or PAOs. High-quality engine oil should have moderate viscosity at low temperatures, which is necessary for a safe "cold start" of the engine. The reliability of engine oil at low temperatures is characterized in terms of the pour point (PP) and kinematic viscosity at -40 °C (KV^{-40}). At the same time, engine oil should remain viscous at working engine temperatures to minimize friction and engine aging. A commonly accepted quantitative characteristic that describes the dependence of oil viscosity on the temperature is the viscosity index (VI), which is determined by a standard method, ASTM D-2270, in which the values of kinematic viscosity of an oil at 40 °C (KV^{40}) and 100 °C (KV^{100}) are compared against the viscosities of two reference oils.

It was found that the PP and VI values of oils depend strongly on the architecture of the constituent hydrocarbons [2–5]. Long, linear hydrocarbons, petroleum waxes (Fig. 1A), present in high quantities in Group I and II oils, are characterized by high PPs. It is for this reason that Group I and II oils cannot be used at low temperatures. Group III oil base hydrocarbons, which contain compounds with short branches (Fig. 1B) and cycloalkanes (Fig. 1C), also have relatively high PP and KV^{-40} values. On the other hand, long-chain branched hydrocarbons (Fig. 1D) are characterized by low PPs and high VIs. Oligomerization of α-olefins followed by hydrogenation is the only way to obtain hydrocarbons with the structure type D [3]. An important aspect of PAO use is their biodegradability, which is also dependent from the hydrocarbon molecular structure. It has been determined [6] that the presence of quaternary carbon atoms blocks the oxidative breakdown of hydrocarbons in surrounding media. It has been reported [7] that PAOs based on 1-decene are characterized by satisfactory biodegradability, surpassing that of Group III oils. Therefore, structural type D offers prospects in minimizing the environmental impact of the use of PAOs.

Compounds of the structural type D are targeted for Group IV base stock synthesis *via* α-olefin oligomerization. However, bulk scale production of low-viscosity PAOs utilizes electrophilic catalysis with

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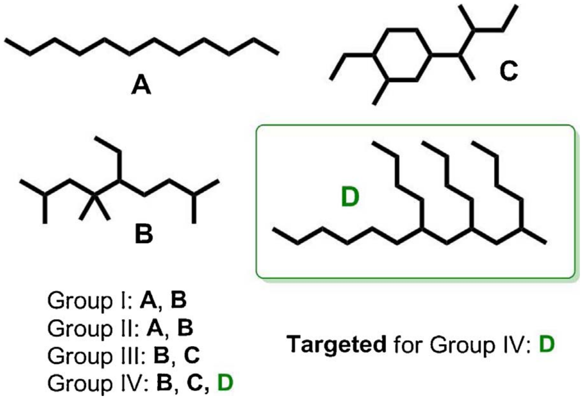


Fig. 1. Main structural types of hydrocarbons – components of oils.

significant skeletal isomerization (Scheme 1a). In particular, many methyl groups are generated at random positions along the carbon chain with formation of type B structures [4,5,8]. In some cases, alicyclic type C products are formed [9–11]. These skeletal isomerizations lead to complex hydrocarbon mixtures containing spillover components having lower viscosity indexes than those of targeted type D hydrocarbons. An alternative approach to olefin oligomer synthesis is based on coordination polymerization. Various catalytic systems using this process have been studied. It has been determined that coordination oligomerization in the presence of heterogeneous titanium–aluminum [12,13] and chromium [14] Ziegler–Natta catalysts is also accompanied by skeletal rearrangements. Isomerization of the skeleton has been observed even for oligomerization catalyzed by dimethylzirconocenes, activated by perfluoroborates [15], and post-metallocene catalysts [16–18].

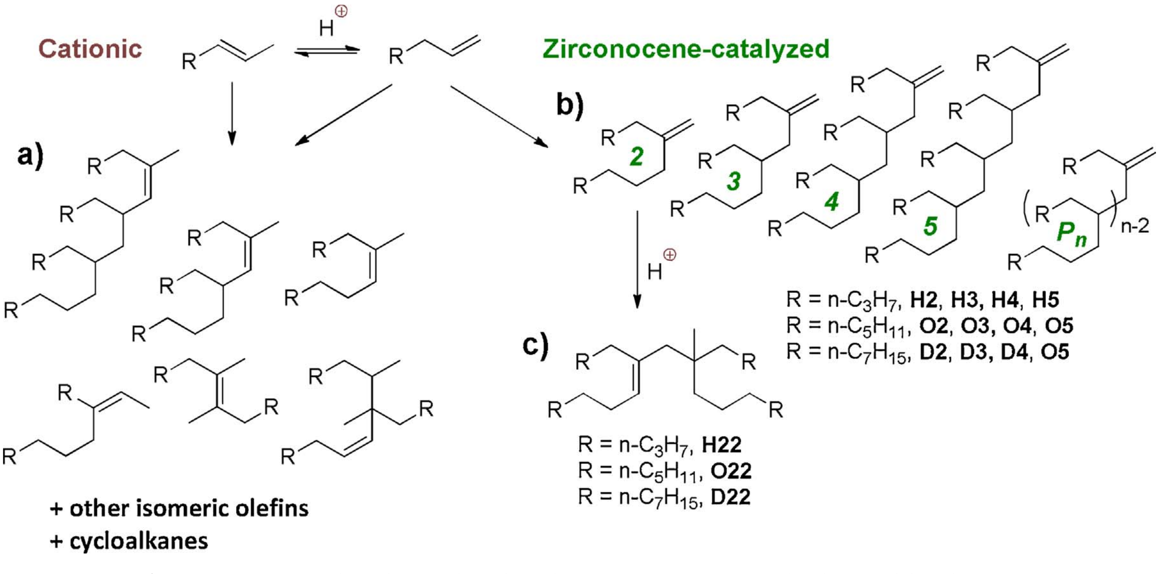
It was found that undesirable side reactions are minimal for oligomerization of α-olefins when the process is catalyzed by zirconocene dichlorides ($LZrCl_2$) activated by methylalumoxane (MÀO) [19–22]. In this case, chain growth occurs only by 1,2-insertions and the chain terminates by β-hydride elimination or β-hydride transfer. As a result, the products of this process characterized by Flory-Shultz distribution are vinylidene-type α-olefin oligomers with uniform molecular structures (Scheme 1b). Vinylidene dimers of α-olefins are not suitable for use as oil base stocks because of their low VI and high PP. However, they can be transformed into hydrocarbons structurally similar to type D species by electrophilic dimerization (Scheme 1c) [23].

To date, vinylidene dimers of 1-hexene, 1-octene, and 1-decene have been isolated and characterized [23–26]. Higher α-olefin oligomers prepared by single-site catalysis have been usually isolated in the form of mixtures with a large P_n range [26–32]. Thus, the characteristics of individual oligomers and hydrogenated oligomers of 1-hexene, 1-octene, and 1-decene as a components of PAO base stocks are currently unknown. The determination of these characteristic remains a fundamental issue.

The main practical issue of zirconocene catalysis of α-olefin oligomerization to obtain type D hydrocarbons lies in reaching the maximum isolated yield of dimers and lower oligomers, corresponding to a degree of oligomerization $P_n = 2$ and 3–5, respectively. The problem in the selective synthesis of α-olefin *dimers* ($P_n = 2$) has been successfully solved by using low Al_{MAO}/Zr ratios (1–10 by mol) and zirconocene catalysts of specific structural types. It was reported that zirconocene dichloride $(\eta^5\text{-}C_5H_5)ZrCl_2$ (**1**) [24–27], ring monosubstituted zirconocenes [29], and *ansa*-complexes $Z(C_5H_4)_2ZrCl_2$ [33] selectively dimerize α-olefins in the presence of a minimal excess of MAO activator to produce dimers of the vinylidene structure (Scheme 1). It has been found that an increase in the Al_{MAO}/Zr ratio for reactions of **1**, $(\eta^5\text{-}C_5H_4R)ZrCl_2$, and certain ring disubstituted zirconocenes leads to the growth of the proportion between the contents of lower oligomers and dimers, which can reach ~1:1 [26,29,31,34,35]. Basing on GC data, Kissn and Schwab [23,36] reported that **1** and $(n\text{-}BuC_5H_4)_2ZrCl_2$ (**2**) are very effective in 1-hexene and 1-decene oligomerization at $Al_{MAO}/Zr = 200$.

At first glance, the effectiveness of the α-olefin oligomerization process can be qualified only by the distribution of lightweight α-olefin oligomers, since the mass fraction of higher oligomers usually does not exceed several mass percent. However, real yields of oligomers are also affected by some side processes. One such process is the isomerization of initial α-olefins. In our recent work [37], we showed that internal alkenes can comprise as much as 25% of the yield during zirconocene-catalyzed oligomerization. Another such side reaction is the reduction of starting α-olefins and the formation of *n*-alkanes through hydroalumination. This reaction is stimulated on increasing the Al_{MAO}/Zr ratios and has not been studied yet.

In this paper, we report our study of α-olefin oligomerization catalyzed by a series of catalysts derived from zirconocenes **1–14** (Scheme 2), at medium (200) and low (10) Al_{MAO}/Zr ratios. We found that the catalyst prepared from the heterocyclic zirconocene **14** demonstrated the best performance. As far as α-olefin oligomerization in the presence of zirconocene **14** at low Al_{MAO}/Zr ratios went without any



Scheme 1. Cationic (a) and coordination (b) α-olefin oligomerization. Dimerization of α-olefin vinylidene dimers (c).