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NOTE

Oligomerization of *n*-Butenes Catalyzed by Nickel Complexes Dissolved in Organochloroaluminate Ionic Liquids

The industrial synthesis of higher olefins is generally performed via oligomerization of lower olefins by transition metal complexes or acidic catalysts. The broad variety of olefins that are nowadays produced by these reactions are used as polyethylene co-monomers or as intermediates in the synthesis of detergents, surface active compounds, lubricating oils, and plasticizers (1). Thus, in the Dimersol® process (2, 3), butenes are dimerized into C_8 olefins which are usually further hydroformylated giving C_9 alcohols used in the manufacture of plasticizers. In spite of important research efforts devoted to these homogeneous phase oligomerization reactions (4–7), activity and conversion still need to be improved. In a more general sense, the separation of the products from the catalyst and the solvent is a major drawback, which leads to increased operational costs and environmental impact.

Organochloroaluminate ionic liquids (8, 9) have been envisioned as solvents of nickel catalysts in oligomerization reactions to overcome this technical limitation (10–12). The solubility of nickel complexes and the poor solubility of olefins in polar and non-coordinating ionic liquids make possible the separation of the reaction products by simple decantation, with low costs and absence of by-products. In the present article, we report the use of 1-butyl-3-methylimidazolium chloro-ethyl-aluminate (**1**) ionic liquids as solvents in butene oligomerization catalyzed by nickel complexes in a two-phase system.

All reactions were performed under argon using standard Schlenk techniques. Solids were dried under reduced pressure and liquids were distilled over appropriate desiccant agents immediately prior to use (13, 14). Ethylaluminum dichloride (EADC) was purchased from Witco and used as supplied. Tributylphosphine (Aldrich) was distilled and triphenylphosphine (Aldrich) was recrystallized before use. Tricyclohexylphosphine-carbondisulphide adduct (PCy_3CS_2) was supplied by Alpha and used without further purification. Tricyclohexylphosphine has been obtained from this adduct by cracking in ethanol. IR spectra of the complexes were determined from nujol mulls using KBr plates on a Perkin Elmer 1430 spectrometer. UV-visible spectra were recorded on a Shimadzu 160-A spectrometer. Microanalyses (C, H, N) were determined on Perkin Elmer 2400 equipment.

Ionic liquids (**1**) were prepared by mixing 226 mmol of doubly sublimed $AlCl_3$, 185 mmol of 1-butyl-3-methylimidazolium chloride and 19 mmol of EADC, obtaining a 57 aluminium mol% liquid mixture, as previously described (8).

$[Ni(MeCN)_6][BF_4]$ (**2**) was prepared as described by Hathaway *et al.* (15). In a 100 mL Schlenk tube, 18 mmol of metallic nickel, 20 mL of acetonitrile and 22 mmol of nitrosyltetrafluoroborate were mixed. Immediate evolution of gaseous NO was observed and the solution became progressively blue. After 5 h, the suspension was filtered and the volume was reduced under vacuum until precipitation of the complex. The raw product was recrystallized from acetonitrile-ethyl acetate, giving 8.9 mmol of **2** in 81% yield. IR: ν(CN): 2325 cm^{-1} (w) and 2275 cm^{-1} (w), ν(BF): 1070 cm^{-1} (vs). UV-Vis (ε in $L \cdot mol^{-1} \cdot cm^{-1}$): 362 nm (14.3), 591 nm (6.8), 718 nm (7.0). Elemental analysis (%) found: C, 27.1; H, 3.7; N, 15.4; theor.: C, 26.4; H, 3.7; N, 15.4.

$NiCl_2(PBu_3)_2$ (**3**) was synthesized as previously described (12). Catalytic reactions were conducted as follows, butenes (Alphagaz) being oligomerized either batchwise or in a semi-continuous way.

Batch experiments were carried out in a 500 mL Fischer–Porter flask containing a magnetic stirring bar and the flask was immersed in a cooling bath. In a typical experiment, the flask containing 0.1 mmol of nickel complex was purged with gaseous butene, then 7 mL of heptane, 3 mL of ionic liquid and 50 mL of liquid butene, containing butane as internal standard, were injected. The temperature was maintained at 10°C. Conversions were determined by analyzing aliquots of the gaseous phase.

Semi-continuous experiments were carried out as described for propene dimerization (12) in a 150 mL double-walled glass reactor containing a magnetic stirring bar with constant supply of neat gaseous butene at atmospheric pressure. In a typical experiment, the reactor containing 0.1 mmol of nickel complex was purged with gaseous butene, then 7 mL of heptane and 3 mL of ionic liquid were injected at 10°C. Consumption of butene was determined by measuring the weight loss of the supply tank.

The catalytic reaction products were analyzed by GC on a Delsi DI200 instrument, with a 50 m PONA capillary column (HP, cross-linked methylsilicone gum,

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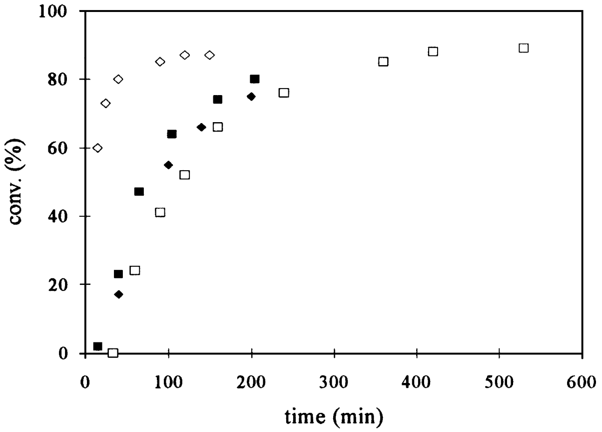

FIG. 1. Batchwise experiments. Conversion of 2-butene versus time using complex **2** (0.1 mmol) dissolved in **1** ionic liquid (3.0 mL) at 10°C: □, without additive; ◆, one eq. of PPh_3 added; ■, one eq. of PBu_3 added; ◇, one eq. of PCy_3CS_2 added.

I.D. 0.2 mm, 0.5 μm film thickness). Temperature programming was 30 min at 20°C and then 10°C min^{-1} up to 250°C. The selectivities in C_8 olefins were obtained from these data and expressed as weight percentages without correction factors. The composition of the C_8 fraction was determined after hydrogenation over Pd on carbon (Aldrich). The resulting products, *n*-octane (*n*C8), 3-methylheptane (MeC7) and 3,4-dimethylhexane (dMeC6), identified by comparison with authentic samples, enabled the determination of the branching index (BI). The branching index was defined (16, 17) as $BI = 2 \cdot$ [dMeC6 molar fraction] + [MeC7 molar fraction].

Batch experiments. In Fig. 1 are given the conversions of 2-butene versus time using complex **2** in the presence of various additives. As a general feature, one can observe the presence of an induction period before butene conversion. In Table 1 are given first-order rate constants and selectivities. Addition of one equivalent of phosphorous(III) ligand (PPh_3, PBu_3, or PCy_3) does not modify the rate constants which are in the range 1.0 ± 0.3 (mol $Ni^{-1} \cdot s^{-1}$) (entries 1–5). Higher rate constants, up to 9 (mol $Ni^{-1} \cdot s^{-1}$) can be observed using PCy_3CS_2 as an additive (entries 6 and 7). This effect cannot be ascribed to the presence of carbon disulfide solely (entry 8). Whatever the catalytic system used, selectivities in dimers are in the range of 92 to 98%.

Semicontinuous experiments. These experiments were carried out in order to obtain information on the stability of the catalytic species versus time. Results are given in Table 2. The presence of a phosphine ligand has a non-negligible effect on the turnover frequency (TOF) (entries 10–11 and 17). This is in contrast to what was observed in the batch experiments (Table 1) for which the rate constants were not significantly altered by the addition of phosphine. This suggests that the first-order rate constants conceal a complex phenomenon. Addition of PCy_3CS_2 enhances the TOF. Values up to 1.9 s^{-1} were obtained which corresponds to a productivity of 6 kg of products $(g_{Ni})^{-1} \cdot h^{-1}$. These activities are higher than those usually obtained using homogeneous catalytic systems (18–22). The addition of PBu_3CS_2 does not show such an important effect.

Quite similar results (TOF and branching index (BI); see below) were obtained starting either from 1- or 2-butene (compare entries 10 and 15). Using 1-butene feed, entry 15, the residual substrate contained 3% of 1-butene, 68% *trans*-2-butene and 29% *cis*-2-butene. When feed was 97%

TABLE 1

Batchwise Experiments

Entry	Ni^{+2} (mmol)	Additive[a]	Feed[b] (10^3)	k[c] ($Ni^{-1} \cdot s^{-1}$)	Selectivity[d] (%)	
					C_8	C_{12}
1	0.13	—	4.2	1.10	93	7
2	0.11	—	7.1	0.92	92	8
3	0.13	PBu_3	6.5	1.03	98	2
4	0.10	PPh_3	5.4	1.23	97	3
5	0.11	PCy_3	4.1	1.23	95	5
6	0.09	PCy_3CS_2	5.9[e]	8.65	95	5
7	0.19	PCy_3CS_2	4.2	9.17	96	4
8	0.13	CS_2	5.4	0.88	93	7
9	0.06[f]	—	9.9	1.21	92	8

Note. 2-Butene dimerization batch experiments using **2** as catalyst precursor dissolved in **1** ionic liquid (3.0 mL) at 10°C.

[a] One equivalent per nickel atom.

[b] Butene feed, mol per mol Ni.

[c] First-order rate constant, $(\text{mol Ni})^{-1} \cdot s^{-1}$.

[d] Weight fraction in dimers (C_8) and trimers (C_{12}).

[e] Three successive butene introductions with a total feed of 1.48×10^4 mol butene per mol nickel.

[f] Run performed with complex **3**.

TABLE 2

Semi-continuous 2-Butene Dimerization Catalyzed by Nickel(II) Complexes Dissolved in 1 Ionic Liquids (3 mL) at 10°C and under Atmospheric Pressure

Entry	Complex	$[Ni^{+2}]$ (mmol)	TOF[a] (s^{-1})	Selectivity[c] (%)		Observations
				C_8	C_{12}	
10	**2**	0.20	0.6	93	7	—
11	**2**	0.11	1.1	92	8	2 eq. of PCy_3
12	**2**	0.07	1.9	98	2	1 eq. of PCy_3CS_2
13	**2**	0.20	1.9	97	3	1 eq. of PCy_3CS_2
14	**2**	0.17	1.2	95	5	1 eq. of PBu_3CS_2
15	**2**	0.11	1.0	96	4	1-butene feed
16	**2**	0.11	0.4	93	7	EADC molten salt[b]
17	**3**	0.15	1.2	92	8	—

[a] Turnover frequency (TOF) in mol of butene converted per mol of nickel per second.

[b] Ionic liquid obtained from BMIC and EADC.

[c] The C_8 fraction BI of the reactions 10–17 were 1.32 ± 0.05, independent of the composition of the system.

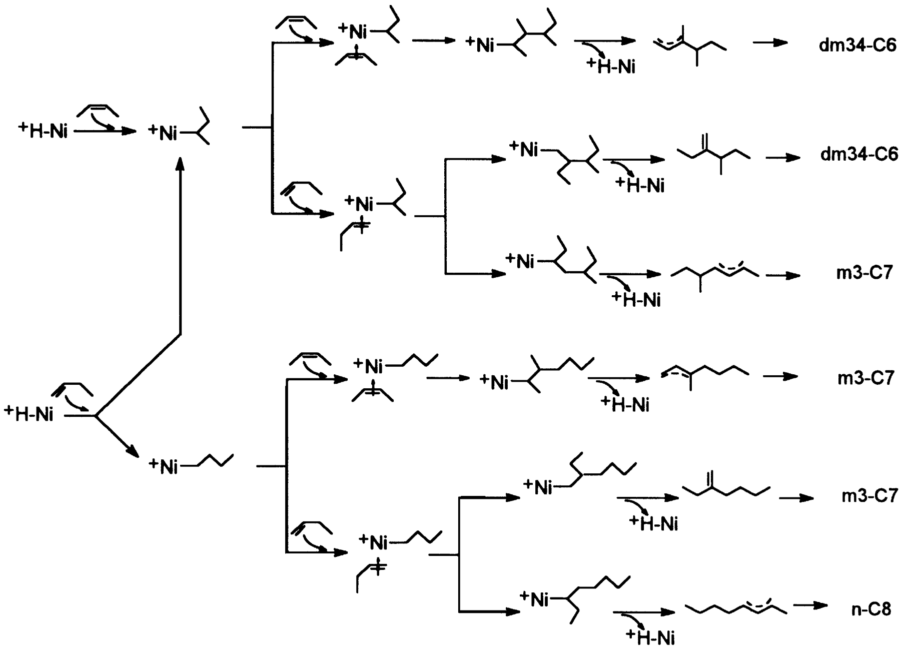

FIG. 2. Reaction pathway for the formation of isomeric octenes from butenes.

2-butene (3% of 1-butene, entry 10) the residual olefin contained 4% of 1-butene. This demonstrates that isomerization (double bond shift) is not a limiting step.

Using ionic liquids not containing $AlCl_3$ gives a lower TOF (entry 16). As already discussed in the case of propene dimerization (12), this demonstrates the strong effect of the anion associated with the cationic active species on the activity. Surprisingly, contrary to what was observed in propene dimers, the structure of the butene dimers does not depend on the phosphine ligands. The addition of PCy_3CS_2 (entries 12, 13) gives high dimer selectivities but does not affect the structure of the C_8 species. After hydrogenation, the C_8 products obtained in all reactions consist of a mixture of dMeC6 ($39 \pm 1\%$), MeC7 ($56 \pm 2\%$), and *n*-C8 ($6 \pm 1\%$) corresponding to a BI of 1.32. This distribution is similar to that obtained with the homogeneous system (Dimersol® process) and is technologically attractive compared to that obtained by acidic catalysis (higher BI). The absence of other different branched C_8 isomers suggests that there are no side reactions involving carbocationic intermediates.

The active species is probably a cationic nickel hydride complex as indicated by the coexistence of activity in carbon–carbon bond formation (oligomerization) and carbon–carbon double bond shift (isomerization). The formation of the nickel active species may result from the alkylation of nickel (II) complex by the alkylaluminum derivative present in the **1** ionic liquid. Its ionic nature is confirmed by the fact that it remains in the ionic phase and can be used several times, thus improving considerably the productivity of the catalyst. The important effect of PCy_3CS_2 can be ascribed to the formation of a mixed Ni-CS_2-PR_3 complex. Such compounds are already known to be characterized with difficulty (23, 24).

The reaction pathway for the formation of isomeric octanes is given in Fig. 2. The regioselectivity is determined by Ni-C_1 and Ni-C_2 reactivities and by the insertion mode of the second butene molecule. It shows that the C_8 distribution observed involves butene isomerization as a nonlimiting step.

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