Catalytic Dimerization of Alkenes by Nickel Complexes in Organochloroaluminate Molten Salts

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Organochloroaluminate molten salts based on aluminium trichloride or ethylaluminium dichloride and 1-methyl-3-butylimidazolium chloride, 1-butylpyridinium chloride or tetrabutylphosphonium chloride can be used as solvents for the catalytic dimerization of propene to hexenes isomers by nickel complexes.

Molten salts have already been used in organic synthesis either as solvents or acidic catalysts.[1,2] However it seems that no attempt has been made to take advantage of the solubility of an organometallic catalyst and the insolubility of the reaction products of the catalytic reaction in these solvents. This is what we have tried to do by dissolving, in organochloroaluminates, *i.e.* $AlCl_3$–R^+Cl^- mixtures,[3] nickel complexes already known to catalyse the dimerization of alkenes when used in aromatic or chlorinated hydrocarbons.[4] From this point of view chloroaluminate molten salts are all the more interesting in that it is possible to make their Lewis acidity vary within a wide range, while they still remain liquid below ambient temperature. If the mole fraction of AlX_3 (N_A) in the melt is higher than 0.5, the medium is acidic; if it is lower, the medium is basic. Complexes such as η^3-allylnickel bromide are soluble in, *e.g.* 1-methyl 3-butylimidazolium chloride $AlCl_3$, whereas alkenes are not. So, the separation of alkenes from the catalyst is quite easy, thus overcoming the main drawback of homogeneous catalysis.

Dimerization reactions were conducted in well-dried glass

Table 1. Dimerization of propene by nickel complexes in molten salts[a]

	Molten salt		Ni complex[h]				Dimer			
								Composition(%)		
Entry	Composition	Al molar fraction	Type	Conc./ mmol dm^{-3}	T/°C	P/MPa	Yield, g/g Ni	DMB[b]	M2P[b]	nH[b]
1	$AlCl_3MBI$[c]	0.60	None		−15	0.1	0[d]			
2	$AlCl_3$–MBI	0.60	$[Ni_2Br_2L_2]$	67	−15	0.1	1500[e]	1	67	32
3	$AlCl_3$–MBI	0.45	$[Ni_2Br_2L_2]$	42	−15	0.1	0			
4	$AlEtCl_2$–MBI	0.70	$[Ni_2Br_2L_2]$	34	−15	0.1	6600	6	76	18
5	$AlEtCl_2$–MBI	0.70	$[Ni(acac)_2]$	61	−15	0.1	1400	16	46	38
6	$AlEtCl_2$–MBI	0.70	$[NiCl_2(PPr^{i}{}_3)_2]$	12	−15	0.1	3300	76	21	3
7	$AlEtCl_2$–BP[f]	0.70	$[NiCl_2(PPr^{i}{}_3)_2]$	10	0	0.1	5300	69	28	3
8	$AlEtCl_2$–MBI	0.70	$[NiCl_2(PPr^{i}{}_3)_2]$	07	−10	0.3	4900	40	48	12
9	$AlEtCl_2$–TBP[g]	0.65	$[NiCl_2(PPr^{i}{}_3)_2]$	82	50	0.6	900	44	48	8

[a] Preparation of molten salts: to the quaternary chloride maintained below 0 °C was added the calculated amount of aluminium compound; the upper phase was then eliminated. [b] DMB: 2,3-dimethylbutenes; M2P: 2-methylpentenes; nH: n-hexenes. [c] MBI: 1-methyl-3-butylimidazolium chloride. [d] 6.55 g of viscous cationic type oligomers were obtained. [e] 5.2 g of viscous oligomers were also obtained. [f] BP: 1-butylpyridinium chloride. [g] TBP: tetrabutylphosphonium chloride. [h] L = 2-methylallyl; Hacac = pentane-2,4-dione.

or stainless-steel double-walled reactors. Molten salts (2 ml) containing the nickel complex and heptane (3 ml) were stirred for 2 h in an atmosphere of propene which was fed as a gas. As the reaction proceeded, the size of the liquid hydrocarbon phase increased until the reactor was filled. The upper phase was then removed and analysed by conventional gas chromatography. The reaction can then be carried out again several times.

Selected results are given in Table 1. As commonly observed in two-phase systems, the reaction rate (hence the yield) is strongly dependent on the stirring efficiency, so the figures herein do not represent a chemical limitation. In the absence of any nickel complex acidic melts catalyse the formation of oligomers, the molecular weight of which is characteristic of a cationic reaction (entry 1). This can be possibly ascribed to the presence of traces of protons. In basic melts (molar fraction of Al 0.45), η^3-methallylnickel bromide is not active (entry 3), whereas in the acidic ones (0.60), nickel complexes catalyse the formation of dimers and trimers in mixtures with oligomers originating from a cationic side reaction (entry 2).

To overcome the drawback of cationic side reactions, we have developed new salts based on ethylaluminium dichloride ($AlEtCl_2$ is already known as a proton scavenger in organochloroaluminates)[5] and conventional quaternary salts such as pyridinium and imidazolium chloride. These mixtures proved to be liquid at low temperature. Their eutectic points are lower than those of the corresponding $AlCl_3$ based melts, which enables the liquid compositions to be extended to some other quaternary salts, *e.g.* tetrabutylphosphonium chloride. In these molten salts, even for a mole fraction up to 0.6, no $AlEtCl_2$ was found in the hydrocarbon upper phase, despite its well known solubility in organic media. Not only were cationic side reactions suppressed (entry 4), but catalytic activity could also be observed with nickel complexes not containing a metal–carbon bond, such as $[Ni(acac)_2]$ (entry 5) or $[NiCl_2(Pr^{i}{}_3P_2)_2]$ (entries 6–9). In these latter systems the 2,3-dimethylbutene content, which is well known to increase with increasing steric effect, is high, thus demonstrating the effectiveness of the 'phosphine effect'[4] in molten salts (there is no displacement of the trialkylphosphine bonded to nickel by any anionic species potentially present in the medium).

Although so far we have been unable to characterize the active species during the reaction, it is likely to involve cationic nickel complexes as in chlorinated solvents.[4]

Contrary to what was observed in acidic melts, no catalytic activity was observed in basic melts (molar fraction of Al 0.45) and Cl^- anions displaced most of the ligands coordinated on nickel forming $NiCl_4{}^{2-}$ or $NiCl_3L^-$ anionic species (UV spectroscopy, absorption bands at 705 and 655 nm), without any alkylation of nickel by the ethyl group of $AlEtCl_2$.

The structure of $AlEtCl_2$ based molten salts was shown by Raman spectroscopy to consist of $AlEtCl_3{}^-$ and $Al_2Et_2Cl_5{}^-$ anions[6] associated with 1-methyl-3-butylimidazolium cations.

Up to now, it seems there has not been any accurate method for determining the charge on the metal atom in chloroaluminate molten salts. Owing to the presence of an aluminium–carbon bond in 1-methyl-3-butylimidazolium chloride–$AlRCl_2$ salts, ^1H NMR spectroscopy could be a valuable method. In order to simplify the spectrum we determined the ^1H NMR shift of the Al–Me protons of a methylbutylimidazolium chloride–$AlMeCl_2$ melt. The downfield shift is greater for higher molar fractions of aluminium (less negatively charged): molar fraction 0.45 (shift −0.240 ppm); 0.55 (−0.145); 0.65 (+0.034). This opens up a way for the quantitative determination of the charge on the aluminium atom in such liquids.

This research is an extension of useful two-phase systems (*viz.* phase-transfer catalysis) to noncoordinating and nonproton-active solvents.

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