CATALYTIC DIMERIZATION OF OLEFINS BY NICKEL COMPLEXES IN ORGANOCHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

Organochloroaluminate molten salts based on aluminum trichloride or aluminum ethyl dichloride and 1-methyl 3-butylimidazolium chloride, 1-butylpyridinium chloride or tetrabutylphosphonium chloride can be used as solvents for the catalytic dimerization of propylene to isohexenes by nickel complexes; the structure of the new molten salts has been determined by Raman and 1H n.m.r. spectroscopies.

INTRODUCTION

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 of the insolubility of the reaction products of the catalytic reaction in these solvents. That is what we have tried to do by dissolving, in organochloroaluminates (3), nickel complexes already known to catalyze the dimerization of olefins 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 still remaining liquid below ambient temperature. If the mole fraction of A1X3 in the melt is higher than 0.5, the medium is acidic; if lower, the medium is basic. Complexes such as \( \eta^3 \)-allylnickel bromide are soluble (and stable) in, e.g., 1-methyl 3-butylimidazolium chloride (MBIC)/AlCl3, whereas olefins are not.

Figure 1 illustrates the mechanism generally assumed for e.g. the dimerization of propylene by nickel complexes. The formation of dimers results from a series of insertions into the Ni-H and Ni-C bonds, thus affording various structures: n-hexenes, methyl pentenes, dimethylbutenes. The presence of basic trialkylphosphines can modify the repartition of dimers by increasing the dimethylbutene content.
EXPERIMENTAL PART

All experiments were performed under nitrogen or argon atmosphere by standard Schlenk techniques or in drybox. MIBC/AlCl₃ molten salt was prepared as described previously (5). **AlEtCl₂ based molten salts:** the calculated volume of freshly distilled AlEtCl₂ was transferred to the solid quaternary salt at room temperature.

**Dimerization of propylene.** In a typical experiment NiCl₂.2PiPr₃ (0.009g; 0.02 mmol) was placed in a 60 ml double-walled glass reactor with a magnetic bar. The reactor was purged from air and moisture, connected to a propylene supply and cooled at -15°C. Then 3ml heptane and 2 ml 0.7 M AlEtCl₂/MBIC molten salt were successively added and stirred. When the reactor was nearly full of liquid, the hydrocarbon phase was decanted and withdrawn by syringe through a septum without releasing the pressure. The product was weighted and analyzed by conventional VPC techniques. The yellow molten salt, containing the catalyst, can be used several times.

RESULTS

Selected results obtained for the oligomerization of propylene are given in Table 1. As commonly observed in two-phase systems, the reaction rate (hence the yield) strongly depends on the stirring efficiency, so the figures herein in no way represent a chemical limitation. In the absence of any nickel complex acidic melts catalyze the formation of oligomers, the molecular weight of which is characteristic of a cationic reaction (entry 1). This can be probably ascribed to the presence of traces of protons. In 0.45 M melts, η₃-methallyl nickel bromide is not active (entry 3), whereas in the 0.60 M melt, nickel complexes catalyse the formation of dimers and trimers in mixture with cationic oligomers (entry 2).

To overcome the drawback of cationic side reactions, we have developed new salts based on aluminum ethyl dichloride (AlEtCl₂ was already known as a proton scavenger in organochloroaluminates (6)) 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 these of the corresponding AlCl₃ based melts, permitting to obtain liquid compositions for several other quaternary salts, e.g. tetrabutylphosphonium chloride. Not only cationic side reactions were suppressed (entry 4), but catalytic activity could also be extended to nickel complexes not containing a metal-carbon bond, such as Ni(acac)₂ (entry 5) or NiCl₂.2PiPr₃ (entries 6,7,8,9). In these latter experiments the 2,3-dimethylbutene
content in the dimer fraction is high, thus demonstrating the effectiveness of the "phosphine effect" (4) in molten salts (there is no displacement of trialkylphosphine bonded to nickel by any anionic species present in the medium).

Although we were, up to now, unable to characterize the active species during the reaction, it is likely to be cationic nickel complexes as in chlorinated solvents (4).

The structure of AlEtCl$_2$ based molten salts was elucidated by Raman spectroscopy. Raman spectra of the pure compounds, MBIC and AlEtCl$_2$ are given Figure 2. No strong vibration appears in the frequencies range 100-800 cm$^{-1}$. Thus, the strong band at 367 cm$^{-1}$ observed in basic and neutral melts (Figure 3.) can be assigned to an aluminum ionic species. When the acidity of the melt increases (N>0.5) the intensity of the 367 cm$^{-1}$ band decreases with parallel appearance of two new strong bands at 349 and 420 cm$^{-1}$ (Figure 4.), the intensity ratio of which is nearly constant ($I_{349}/I_{421} = 1.20$) (Table 2.), thus proving that these two bands are characteristic of a single species. These band positions may be compared to the assignments which have been made for AlCl$_4^-$ (351 cm$^{-1}$) and for Al$_2$Cl$_7^-$ (315 and 434 cm$^{-1}$) in AlCl$_3$ based molten salts (7). Assuming that the mole fractions of the ionic species are proportional, approximately, to the intensity of the strongest bands for each species we have compared the intensity ratio for the peaks at 349 and 367 cm$^{-1}$ for different compositions with the ratio of the concentrations of the species calculated by supposing the existence of the quantitative reaction:

$$\text{AlEtCl}_3^- + \text{AlEtCl}_2 \rightarrow \text{Al}_2\text{Et}_2\text{Cl}_5^-$$

The straight-line confirms this assumption (Figure 5)

Table 3 summarizes the Raman vibrational frequencies (cm$^{-1}$) of AlEtCl$_3^-$ and Al$_2$Et$_2$Cl$_5^-$. In Figure 6 are given spectra obtained for a very acidic melt (0.7 N) before and after removal of contributions of other species. Three characteristic bands at 272, 337 and 404 cm$^{-1}$ may be assigned to a third species that we tentatively formulate as Al$_3$Et$_3$Cl$_7^-$ and which compares with Al$_3$Cl$_{10}^-$ (8).

Up to now, there has not been any accurate method for the determination of the charge on the metal atom in chloroaluminate molten salts. Due to the presence of an aluminum-carbon bond in MBIC/AlMeCl$_2$ we were able to determine the $^1$H n.m.r. shift of the Al-Me protons. The downfield shift is all the greater as the molar fraction of aluminum is high (less negatively charged): 0.45 M (-0.240); 0.55 M (-0.145); 0.65 M (+0.034). The use of ethyl aluminum dichloride based melt would allow to calculate the electronegativity of the aluminum atom.

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by the Dailey-Shoolery equation:

\[ \chi = 0.62 \Delta + 2.07 \]

This relationship between the electronegativity of a central metal atom of a compound CH\textsubscript{3}-CH\textsubscript{2}M and its internal chemical shift \( \Delta_{CH_{2}-CH_{3}} \), a difference in proton chemical shifts of CH\textsubscript{2} and CH\textsubscript{3}, has been previously applied to ethylaluminum halides and their complexes (9,10). This opens up a way to the quantitative determination of the charge on the aluminum atom in such liquids.

**CONCLUSION**

Chloroaluminate molten salts seem to be useful solvents for coordination catalysts, mainly for the dimerization of olefins. With such a solvent the separation between the reaction products and the catalyst becomes easy.

The new molten salts containing AlEtCl\textsubscript{2} prove to be all the more interesting as:
- they are liquid within a wide range of composition and temperature;
- they can remove protons impurities and thus suppress the cationic side reactions;
- they allow to use nickel complexes not containing metal carbon-bonds.

From a fundamental point of view, the main feature of these new molten salts is the possible determination of the charge of the aluminum atom by \textsuperscript{1}H NMR.

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Figure 1. Mechanism of the Dimerization of Propylene by Nickel Complexes.
| Entry | Molten salts | Ni complexes | Temp. | Pressure | Dimer % | Composition % |
|-------|--------------|--------------|-------|----------|---------|---------------|
|       | Composition | Al molar fraction | Type | mol dm<sup>-3</sup> | °C | MPa | g/g Ni | DMB | M2P | n-Hexes |
| 1     | AlCl<sub>3</sub>/MBIC | 0.50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2     | AlCl<sub>3</sub>/MBIC | 0.50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3     | AlCl<sub>3</sub>/MBIC | 0.45 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4     | Al<sub>3</sub>C<sub>3</sub>/MBIC | 0.70 | 0.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5     | Al<sub>3</sub>C<sub>3</sub>/MBIC | 0.70 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6     | Al<sub>3</sub>C<sub>3</sub>/MBIC | 0.70 | 0.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7     | Al<sub>3</sub>C<sub>3</sub>/BPC | 0.70 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8     | Al<sub>3</sub>C<sub>3</sub>/BPC | 0.70 | 0.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 9     | Al<sub>3</sub>C<sub>3</sub>/TBPC | 0.65 | 0.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

* Preparation of molten salts: to a suspension of quaternary chloride in heptane maintained below 0°C was added the calculated amount of aluminum compound; the upper phase was then eliminated. Propylene dimerization: in a well dried double-walled reactor were added: the nickel derivative, 3 ml heptane, 2 ml molten salt; a propylene pressure was kept constant with good stirring for two h.

<sup>4</sup> DMB: 2,3-dimethylbutene, M2P: 2-methylpentene, n-Hexes: n-hexenes.
<sup>5</sup> MBIC: 1-methyl 3-butylimidazolinium chloride.
<sup>6</sup> 6.55 g of viscous oligomers were obtained.
<sup>7</sup> DPC: 1-butylpyridinium chloride.
<sup>8</sup> TBPC: tetrabutylphosphonium chloride.

Table 1. Dimerization of Propylene by Nickel Complexes in Molten Salts
Figure 2. Raman Spectra of Pure Compounds:
- upper: Ethyl Aluminum Dichloride
- lower: 1-Methyl 3-Butyl Imidazolium Chloride Molten
Figure 3. Raman Spectra: - upper: AlEtCl₂-MBIC 0.50 N
- lower: MBIC Molten

Figure 4.
Raman Spectra of AlEtCl₂-MBIC
Composition:
  a) 0.50 N
  b) 0.54 N
  c) 0.60 N
  d) 0.64 N
| N    | I$_{349}$ | I$_{421}$ | I$_{349}$/I$_{421}$ |
|------|-----------|-----------|-------------------|
| 0.541| 184       | 150       | 1.23              |
| 0.556| 226       | 181       | 1.25              |
| 0.574| 587       | 490       | 1.20              |
| 0.598| 854       | 709       | 1.20              |
| 0.625| 1057      | 919       | 1.15              |
| 0.641| 1535      | 1246      | 1.23              |

Table 2. Intensity Ratio of the Vibrations at 349 and 421 cm$^{-1}$

![Graph showing the variation of the intensities ratio of vibrations of AlEtCl$_3^-$ (367 cm$^{-1}$) and of Al$_2$Et$_2$Cl$_5^-$ (349 cm$^{-1}$).]

Figure 5. Variation of the Intensities Ratio of Vibrations of AlEtCl$_3^-$ (367 cm$^{-1}$) and of Al$_2$Et$_2$Cl$_5^-$ (349 cm$^{-1}$)
Figure 6. Raman Spectra: - upper AlEtCl₂-MBIC 0.70 N
- lower AlEtCl₂-MBIC 0.70 N
after removal of contributions of Al₂Et₂Cl₅⁻

| AlEtCl₃⁻  | Al₂Et₂Cl₅⁻  |
|-----------|-------------|
| 150 (m, dp) | 166 (m, dp) |
| 182 (m, dp) | 178 (m, dp) |
| 273 (m, dp) | 253 (m, p)  |
| 349 (sh, p) | 349 (s, p)  |
| 367 (st, p) | 367 (st, p) |
| 450 (w, dp) | 450 (w, dp) |
| 621 (m, p)  | 621 (m, p)  |

st = strong, br = broad, m = medium, sh = shoulder, s = small, w = weak
dp = depolarized, p = polarized

Table 3. Raman Frequencies (cm⁻¹) of AlEtCl₃⁻ and of Al₂Et₂Cl₅⁻