Mendeleev Commun., 2004, 14(2), 59–60

Metathesis of hex-1-ene in ionic liquids

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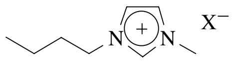
10.1070/MC2004v014n02ABEH001870

The WCl_6 + $BMIMBF_4$ and $NaReO_4$ + BMIMCl–$AlCl_3$ (BMIM is 1-butyl-3-methylimidazolium) systems are effective catalysts for the metathesis of hex-1-ene to form oct-4-ene.

Olefin metathesis is the disproportionation of unsaturated hydrocarbons based on the exchange of alkylidene groups between two olefin molecules.[1] The well-known catalysts for the process are either Re-, Mo- and W-containing heterogeneous compounds[2] or organometallic comlpexes of metals such as Ru, W and Mo.[3,4] The metathesis of olefins is accompanied by side reactions such as double bond shift, polymerization and solvent alkylation reactions.

Ionic liquids are unique systems, which are considered as an alternative to traditional solvents or homogeneous catalysts. For example, the metathesis of non-conjugated dienes for the synthesis of alicyclic compounds was studied.[5–8] The carbenium complexes of Ru (so-called Grubbs catalysts) were used as the catalysts, and neutral ionic liquids ($BMIMBF_4$, $BMIMPF_6$ and BMIMOTf, where BMIM is 1-butyl-3-methylimidazolium) were taken as reaction media.



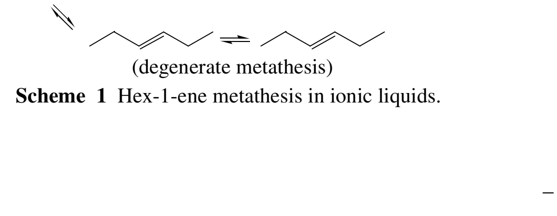
X = BF_4, PF_6, OTf

The metathesis of pent-2-ene in the presence of tungsten-containing compounds promoted by organoaluminium compounds was described.[9] The reaction was performed in an ionic liquid characterised by high Lewis acidity (BMIMCl–$AlCl_3$, 1:1.1 mol).

We studied the metathesis of hex-1-ene in the presence of catalysts dissolved in ionic liquids as reaction media. Both neutral ($BMIMBF_4$) and acidic (BMIMCl–$AlCl_3$) ionic liquids were used. The effect of Lewis acidity on the catalyst activity was studied using the BMIMCl–$AlCl_3$ ionic liquid with component ratios of 1:2 and ~1:1. These compositions correspond to the $AlCl_4^-$ and $Al_2Cl_7^-$ anions, as found by spectroscopic methods.[10] The catalysts were WCl_6, $NaReO_4$ and palladium and rhodium chlorides. It was of interest to test these compounds, which form organometallic complexes that are presumably active in hex-1-ene metathesis.

Hex-1-ene and the ionic liquids are practically immiscible and form two-phase reaction mixtures. WCl_6 and $NaReO_4$ were found to exhibit catalytic activity in the metathesis reaction. Note that the main reaction product was oct-4-ene rather than dec-5-ene, which is the expected product of hex-1-ene disproportionation (Scheme 1).

Thus, the first step of the reaction is the double bond isomerisation of hex-1-ene into hex-2-ene, and the rate of the double bond shift reaction is higher than that of the metathesis reaction. Therefore, the starting olefin to be converted in the metathesis reaction is mainly hex-2-ene. The equilibrium concentrations of hex-1-ene, hex-2-ene and hex-3-ene in the reaction mixture at 20 °C are equal to 1, 66 and 33%,[11] respectively. It is anticipated that hex-3-ene also takes part in the metathesis reaction (as the next product of bond shift in hex-2-ene). However, in this case, hex-3-ene must be the main reaction product because of degenerate metathesis.



Scheme 1 Hex-1-ene metathesis in ionic liquids.

Table 1 Hex-1-ene metathesis in various catalytic systems (20 °C; 1 h; hex-1-ene:ionic liquid:catalyst molar ratio of 1:0.8:0.08; 500–600 rpm).[a]

Catalytic system	Hex-1-ene conversion (%)	Yield (mol%)		Other products
		oct-4-ene	dec-5-ene	
$NaReO_4$ + $BMIMBF_4$	0.5	0.2	—	—
$NaReO_4$ + BMIM–$AlCl_3$ 1:2	100.0	—	—	Polymers
$NaReO_4$ + BMIMCl–$AlCl_3$ 1:1.05	5.4	4.9	0.1	—
WCl_6 + $BMIMBF_4$	12.8	8.4	4.2	—
WCl_6 + BMIMCl–$AlCl_3$, 1:1.05	100.0	—	—	Polymers

[a] But-2-ene and ethylene were also formed in accordance with the reaction stoichiometry.

The results obtained[†] in the metathesis of hex-1-ene in both neutral ($BMIMBF_4$) and acidic (BMIMCl–$AlCl_3$) ionic liquids with various catalysts are given in Table 1.

$NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05) and WCl_6 + $BMIMBF_4$ are the most active systems in the metathesis reaction. At the same time, $PdCl_2$ and $RhCl_3$ dispersed in BMIMCl–$AlCl_3$ and $BMIMBF_4$ ionic liquids are inactive in the reaction.

$NaReO_4$ dissolved in an ionic liquid with a high concentration of $AlCl_3$ gave no metathesis products, and oligomers and polymers were the main products of the reaction. This fact is consistent with published data on the activity of acidic ionic liquids in olefin oligomerisation.[12] The above reactions took place in the WCl_6 + BMIMCl–$AlCl_3$ system (1:1.05), and in the pure ionic liquid BMIMCl–$AlCl_3$ (1:1.05). These results suggest that

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[†] *Synthesis of ionic liquids.* BMIMCl. A mixture of 0.3 mol of *N*-methylimidazole and 0.3 mol of butyl chloride was refluxed for 20 h in an argon atmosphere. The reaction product BMIMCl was formed as a separate phase. The salt was washed with dry acetone (3×100 ml). A white solid (0.26 mol) was obtained. Yield 86%.

$BMIMBF_4$. 0.25 mol of ammonium tetrafluoroborate (NH_4BF_4) was added to 0.25 mol of BMIMCl in 120 ml of dry acetone in an Ar atmosphere. The reaction mixture was vigorously stirred at 20 °C for 72 h. The precipitate (NH_4Cl) was filtered off, and the solution of $BMIMBF_4$ in acetone was evaporated in a vacuum. The ionic liquid (0.21 mol) was obtained. Yield 84%.

BMIMCl–$AlCl_3$. 0.114 mol [in the case of BMIMCl–$AlCl_3$ (1:2)] or 0.06 mol [in the case of BMIMCl–$AlCl_3$ (1:1.05)] of $AlCl_3$ was gradually added to 0.057 mol of BMIMCl for 2–3 h at 20 °C. Ionic liquids (0.057 mol) were obtained. Yield 100%.

Hex-1-ene metathesis. The experiments were carried out in a cylindrical 15 cm^3 vessel after purging dry nitrogen for 0.5 h. In the course of purging, the components (hex-1-ene, ionic liquids and catalysts in a molar ratio of 1:0.11:0.125, in some runs, Bu_4Sn) were placed in the vessel. The vessel was sealed and the reaction mixture was vigorously stirred (20 °C; 500–600 rpm). After the experiments (standard time of 1 h), the vessel was cooled to 0 °C, and the reaction mixture was analysed by GLC.

Analysis of reaction products. The metathesis products were analysed by GLC on a packed column (3 m×3 mm) with SE-30 on Chromosorb; an SE-30 capillary column (30 m) and a Carbowax 20M capillary column (40 m) using the method of internal standards.

Table 2 Formation of hex-1-ene (and hex-2-ene) metathesis products in WCl_6 + $BMIMBF_4$ (20 °C; hex-1-ene, ionic liquids and catalysts in a molar ratio of 1:0.8:0.08; 500–600 rpm).[a]

Time/h	Hex-1-ene conversion (%)	Yield (mol%)		
		oct-4-ene	dec-5-ene	Total
1.0	12.8	8.4	4.2	12.5
2.5	22.9	17.7	4.8	22.5
5.0	27.4	22.2	5.0	27.2

[a] But-2-ene and ethylene were also formed in accordance with the reaction stoichiometry.

oligomerisation and polymerisation reactions are catalysed by $AlCl_3$, but the latter processes do not take place in ionic liquids with the BMIMCl:$AlCl_3$ ratio of 1:1. The use of a 5% excess of $AlCl_3$ in the $NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05) system leads to the appearance of the catalytic activity in hex-1-ene metathesis. The main reason consists in the presence of strong acid sites related to $AlCl_3$, which can activate $NaReO_4$ (in the heterogeneous catalytic system Re_2O_7/Al_2O_3, the source of this acidity is the Al_2O_3 support).[13]

In the acidic system $NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05), the main product was oct-4-ene, as a product of hex-2-ene metathesis, with the oct-4-ene : dec-5-ene ratio of 50. On the contrary, in the neutral WCl_6–$BMIMBF_4$ system, both olefines were formed in comparable quantities, though oct-4-ene was the main product. Heptenes and nonenes (products of hexene isomer co-metathesis) were formed in these systems in 0.2 and 0.1% yields, respectively.

In order to evaluate the catalytic activity of the test ionic systems, we found the ratios between the highest possible yields of oct-4-ene and dec-5-ene and the yields obtained under the reaction conditions. The results obtained with the WCl_6 + + $BMIMBF_4$ system are given in Table 2.

The total possible yield of the metathesis products is about 27%. The WCl_6 + $BMIMBF_4$ system is more active than that based on $NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05). For the former system, the yield of oct-4-ene after 1 h of the reaction is 37% of the value obtained after 5 h, and the yield of dec-5-ene is 82%. For the latter systems, the yield of oct-4-ene under the same conditions is only about 18%.

The yield of dec-5-ene in the WCl_6 + $BMIMBF_4$ system remained unchanged after the first hour of the process; oct-4-ene was formed subsequently as the metathesis product.

The activity of metathesis catalysts is known to increase upon adding small amounts of tin-containing compounds. Therefore, experiments with the WCl_6 + $BMIMBF_4$ and $NaReO_4$ + + BMIMCl–$AlCl_3$ systems promoted by tetrabutyltin were performed. The results of the experiments are given in Table 3.

The addition of 10–30 mol% tetrabutyltin to the WCl_6 + + $BMIMBF_4$ system results in the yield of oct-4-ene about 2.5–3.0 times higher than that obtained in the standard experiment. At the same time, the yield of dec-5-ene significantly decreased (by a factor of about 10). This resulted in a considerable increase in selectivity for oct-4-ene. When tetrabutyltin was added to the $NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05) system, the yield of oct-4-ene was 2.5 times higher, whereas the selectivity of the process remained at a high level.

Table 3 Effect of Sn_4Bu on the catalyst activity in hex-1-ene metathesis (20 °C; 1 h; hex-1-ene, ionic liquids and catalysts, in a molar ratio of 1:0.8:0.08; 500–600 rpm).[a]

Catalytic system	Bu_4Sn/ mol%	Hex-1-ene conversion (%)	Yield (mol%)		Selectivity for oct-4-ene (%)
			oct-4-ene	dec-5-ene	
WCl_6 + $BMIMBF_4$	0	12.8	8.4	4.2	65.3
	10	21.7	21.2	0.4	97.7
	30	25.0	24.3	0.6	97.2
$NaReO_4$ + BMIMCl–$AlCl_3$ (1:1.05)	0	5.4	4.9	0.2	90.7
	10	12.1	11.6	0.1	95.9
	30	12.2	11.9	0.1	97.5

[a] But-2-ene and ethylene were also formed in accordance with the reaction stoichiometry.

Thus, we can conclude that the WCl_6 + $BMIMBF_4$ and $NaReO_4$ + BMIMCl–$AlCl_3$ systems exhibit high catalytic activity in the olefin metathesis reaction. Note that the initial step of the reaction is the double bond isomerisation of hex-1-ene into hex-2-ene, and the main product of the reaction is oct-4-ene. A considerable increase in the product yields can be achieved by adding small amounts of Bu_4Sn to the system. The oct-4-ene: dec-5-ene ratio can be increased by Bu_4Sn additives. When the reaction is carried out in the $NaReO_4$ + BMIMCl–$AlCl_3$ system, this ratio remains almost unchanged, and the selectivity of the process reaches an extremely high value (almost 97%).

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Received: 28th November 2003; Com. 03/2196